Mr. Michael McCann
Project Manager
Voluntary Remediation Program
Office of Land Quality
Indiana Department of Environmental Management
100 North Senate Avenue IGCN, Room 1101
Indianapolis, Indiana 46204

Arcadis U.S., Inc.
150 W. Market Street
Suite 728
Indianapolis
Indiana 46204
Tel 317 231 6500
Fax 317 231 6514
www.arcadis.com

ENVIRONMENT

Subject:
Addendum to Revised Remediation Work Plan / Response to Revised Remediation Work Plan Comment Letter (June 11, 2020)
Former Indiana Creosoting Company
240 Country Club Road
Bloomington, Monroe County, Indiana 47403
VRP # 6970403

Date:
August 10, 2020

Contact:
Steve Sharp

Phone:
317-236-2829

Email:
steve.sharp@arcadis.com

Our ref:
30028139 Task 07

Dear Mr. McCann:

The Indiana Department of Environmental Management (IDEM) provided CSX Transportation (CSXT) with a comment letter **(Attachment 1)** based on your review of the *Revised Remediation Work Plan* (RRWP) for the Former Indiana Creosoting Company property (Site) located in Bloomington, Indiana (Site), submitted on April 23, 2020. The RRWP was prepared to document the extensive environmental-related investigations, assessments, sampling, characterizations, and remediation completed at the Former Indiana Creosoting Company (ICC) facility (Site) located 240 West Country Club Drive, Bloomington, Monroe County, Indiana (**Figure 1**).

Arcadis U.S., Inc. (Arcadis), on behalf of CSXT has responded to the IDEM comments below. Each IDEM comment is provided verbatim below, followed by a response.

COMMENTS / RESPONSE

IDEM Comment:

1. *The monitoring program is outlined in Section 7.2 of the RWP. A subset of 24 monitoring wells has been selected as a representative set to determine water quality for this project (Table 10, Figure 9). These monitoring wells will be sampled on a quarterly basis for a period of two years (eight quarters), or*

until sampling is deemed no longer necessary as agreed upon by the IDEM and CSXT / Arcadis. The monitoring system and duration are acceptable to IDEM.

Response:

CSX and Arcadis agree with IDEM's comment and will follow the monitoring program outlined in Section 7.2 of the RRWP.

IDEM Comment:

2. *Arcadis needs to confirm the operational status of the free product recovery system. To provide an accurate plume behavior analysis the recovery system cannot be in operation. A long-term plume behavior analysis can start once the aquifer has re-equilibrated (usually one year).*

Response:

The long-term plume behavior analysis has been monitored and evaluated for several years at this site through multiple lines of evidence supporting this conclusion. The Dense Non-Aqueous Phase Liquid (DNAPL) recovery system at this site is not a typical groundwater recovery system (i.e. pump and treat) which can significantly depress groundwater elevations in the vicinity of recovery wells. The DNAPL recovery system at this site was designed and implemented specifically to minimize groundwater extraction and does not appreciably affect groundwater elevations and flow patterns for the reasons described in the following sections.

Dense Non-Aqueous Phase Liquid (DNAPL Recovery)

The recovery of DNAPL at the site has been performed through manual recovery and not an automated system. The manual DNAPL recovery program was implemented at this site to recover as much DNAPL as possible without recovering large volumes of groundwater (although a minimal amount of groundwater is also recovered at the same time). DNAPL enters the wells and is collected in the well sumps without pumping of groundwater. Over the past several years the DNAPL/water recovery program has been limited to recovering approximately 20 gallons every two weeks from select recovery wells. Most of the 20 gallons is DNAPL not water. The recovery of 20 gallons of DNAPL/water every two weeks does not affect the karst groundwater flow system, and therefore does not require a waiting period for the aquifer to recover for monitoring of plume analysis. Additionally, because there is limited or no groundwater extraction from the recovery wells, there is no need to wait for the aquifer to recover before starting the quarterly groundwater sampling events. Furthermore, the DNAPL recovery system is generally paused for four (4) months during the winter as a health and safety precaution and no DNAPL/water is recovered during that period.

Transducer Water Elevation Study

As expected, the transducer water elevation study indicates there is no effect from the DNAPL/water recovery program, as Arcadis was recovering free product at the beginning of this study. The data shows the water elevations continue to remain stable during the recovery events and are only affected by rainfall events. The DNAPL recovery program has been halted and no additional recovery events are scheduled at this time. The details from the transducer study are presented in the next comment section.

Mann-Kendall Analysis

Plume stability has been performed on the groundwater system through Mann-Kendall analysis as documented in the Arcadis *Limited Risk Assessment Report* dated May 2015. The additional groundwater data collected after that May 2015 study continues to show the groundwater plume remains stable at the site. Arcadis will perform a final Mann-Kendall Analysis after the eight (8) consecutive quarters of groundwater sampling is competed to show final plume stability before closure.

Conclusion

Because the DNAPL recovery program does not rely on manipulating hydraulic gradients (extraction or injection of groundwater) to induce DNAPL to enter the collection wells, it does not materially affect groundwater flow conditions, ; therefore, there is no reason to wait for the aquifer to equilibrate before evaluating the plume behavior and beginning the quarterly groundwater sampling. Arcadis began the quarterly groundwater sampling program in December 2019 and expects to conclude the eight (8) quarters in September of 2021. One of those events will be the stormwater event which is discussed in more detail in the next section.

IDEM Comment:

3. *The plume behavior analysis needs to include samples collected shortly after (within 24 hours) a storm event. Arcadis requested clarification on IDEM's criteria used to identify a storm event. Rainfall is considered a storm event when at least 0.75 inch falls over a 24-hour period. Once a storm event occurs, sampling needs to take place within 24 hours.*

Response:

Arcadis agrees a stormwater sampling event should be included as part of the plume behavior analysis. The IDEM requested that one of the eight quarterly sampling events be conducted as a stormwater groundwater sampling event. The criteria IDEM provided to define a stormwater sampling event (at least 0.75 inch of rainfall over a 24-hour period) is reasonable; however, given their heterogeneity, predicting how an individual karst aquifer will respond to rainfall is difficult. For this reason, Arcadis conducted a water elevation study, as proposed in the RRWP, to provide site-specific data. These data were used to determine what size storm triggered a significant response in the aquifer, and how long it took for the aquifer to return to baseflow conditions. From these data, the site-specific size of a "threshold" storm event were determined, as well as the time interval following the event that was appropriate for conducting the storm-event sampling.

From March 18, 2020 through June 15, 2020, Arcadis deployed a series of transducers in nine (9) monitoring wells within three different geologic units (unconsolidated alluvium, Upper Ramp Creek, and Lower Ramp Creek) at the Site. Borden monitoring wells were not selected for this study as the Borden is an aquitard and is not hydraulically connected to the karst flow system. The monitoring wells for the study were selected based on their location (to provide good spatial coverage across the site), water quality, and the results of the dye-trace study conducted at the site (wells where dye was detected were given preference)..

The transducers were installed during this timeframe (springtime) when historically the most rainfall occurs in the Bloomington, Indiana area. The transducers were recovered periodically, and the data

downloaded to ensure proper operation and data quality. Arcadis utilized Van Essen Micro-Diver Pressure Sensor DI 601 transducers (10m/30ft length) which collected pressure readings as well as temperature. Data were collected every five (5) minutes by the transducers for the 90-day period. The data were plotted on graphs for evaluation purposes and the graphs are contained in **Appendix 2**. Given the large size of the data set (almost 25,000 lines or 200 pages for each transducer), the raw data are not included herein, but can be provided upon request.

Based on the data, Arcadis has determined that 0.75 inches of rain in a 24-hour period does constitute a valid threshold storm event for conducting the storm-event sampling round at the site, and that the samples should be collected within 48-hours of the storm event. All but two of the 9 wells monitored showed some response to large rainfall events based on changes in water levels. The two wells that show no response were screened in the Lower Ramp Creek formation, which is largely unkarstified.

Arcadis recommends all nine (9) wells that were evaluated as part of this study become the smaller subset of monitoring wells sampled during the future stormwater event. Once the subset of wells has been agreed upon, Arcadis will begin monitoring the weather for the minimal rainfall event for sampling purposes. Arcadis will utilize a real time monitoring system to alert Arcadis personnel of a rainfall event of more than 0.75 inches of precipitation within a 24-hour period. Arcadis will mobilize to the Site as soon as possible to collect groundwater samples from this predetermined subset of monitoring wells. Arcadis proposes to sample this subset of monitoring wells via bailer sampling methodology, which allows Arcadis to have the proper equipment ready and available to sample post storm flow event as soon as possible.

IDEM Comment:

4. *Appendix F included the Quality Assurance Project Plan (QAPP). The Tables E-1, E-2 and E-3 in Appendix F QAPP should be revised because the parameter list is missing some of the compounds (phenolics, phthalates, etc.) that are shown in Table 1 "Constituents of Concern". Also, the quality assurance and quality control acceptance limits were missing from the Appendix F QAPP and should be included. Section 8.2.2 indicated that the acceptance criteria and compounds used for the matrix spike and matrix spike duplicate analysis are identified in the SOP. However, copies of the SOPs for the constituents of concern were not included and should be added. If the QA/QC acceptance limits for each analysis will follow the EPA methods, then a statement to clarify this intent should be added to the QAPP.*

Response:

Arcadis has addressed the IDEM comments and has prepared a revised QAPP, which is provided in **Attachment 3**.

If you have any questions or comments regarding this submittal, please contact Steve Sharp (Arcadis) at 317-236-2829 or Daniel Dyer (CSXT) at 317-327-2242. Additionally, if IDEM would like to have a meeting to discuss this response, please contact us at your earliest convenience.

Sincerely,

Arcadis U.S., Inc.

Randall Woodruff
Geological Scientist

Steven C. Sharp, LPG (IN)
Senior Geologist / CPM-2

Copies:
Daniel Dyer, CSXT

Enclosures:

Figure 1: Quarterly Groundwater Sampling Locations

Attachment 1: IDEM Comment Letter dated June 11, 2020
Attachment 2: Transducer Water Elevation Graphs
Attachment 3: Revised QAPP

Figure

CITY: (KNOXVILLE) DIV/GROUP: (ENV/GIS) LD: (B.ALTOM) PIC: (-) PM: (S.SHARP) TM: (R.WOODRUFF) BY: TJSCOTT
PROJECT: IN000072 PATH: Z:\GISPROJECTS_ENV\CSX\IN_BLOOMINGTON\MAPDOCS\2020\F2 IN072_CC SITE 201601.MXD SAVED: 4/16/2020

LEGEND

- Property Boundary
- Former Site Features
- Wetlands
- Creek Liner (2007)
- Interceptor Trench
- Monitor Well
- Monitor Well (abandoned)
- Recovery Well
- Pilot Hole (abandoned)
- Stream Gauge
- Sump

NOTES:
1) Grayed out numbers indicate that wells have been abandoned.
2) SURVEY: Bledsoe Riggert & Guerrettaz, Inc. (November 2012).
3) PROJECTION: NAD83 State Plane Indiana West Feet.
4) AERIAL SOURCE: http://www.indiana.edu/~gisdata (2010).
5) CONTOURS: Monroe County GIS LiDAR (2010).
6) Highlighted wells denote quarterly monitoring well sampling locations.

MW-49A MW-49B MW-49C MW-9 MW-1D MW-1S MW-11S MW-11D MW-10 MW-P5 MW-P4 MW-P3 MW-2D MW-2S MW-40A MW-40B MW-40C MW-44A OW-1 OW-3 OW-2 MW-P2 MW-14D MW-14S MW-16S MW-16D MW-12D MW-12S MW-P6 MW-29B MW-29A MW-35A MW-35C MW-35B RW-1 MW-31C MW-31A MW-31B MW-15D MW-15S SG-4 BRIDGE MW-7D MW-7S MW-3S MW-3D MW-P1 MW-20S MW-20D MW-17S MW-17D MW-13 MW-25A RW-19 MW-18D MW-18S MW-21S MW-21D MW-8S MW-8D SG-3 MW-39A MW-39B MW-45A MW-45B MW-45C RW-3 MW-22D RW-16 RW-5 MW-42A MW-42B RW-7 MW-24A RW-2 RW-4 RW-6 RW-17 (MW-27A) MW-19S MW-19D PH-01 PH-09 MW-23D MW-4D MW-4S MW-26A MW-55A MW-55B MW-38B MW-38A MW-38C MW-38D MW-41A MW-36B MW-36A MW-36C RW-15 MW-53A MW-53B MW-30B MW-30A SG-2 MW-5D MW-5S PH-03 MW-48A MW-48B RW-18 MW-54A MW-54B RW-11 RW-10 MW-6D MW-6S PH-11 RW-12 RW-8 MW-51A MW-51B RW-14 MW-34A RW-9 RW-13 SG-1 MW-28A MW-28C MW-28B MW-43A MW-37A MW-37B MW-37C MW-46A MW-52A MW-32B MW-32C MW-32A MW-50A MW-50B MW-56A MW-56B MW-47A

CAMDEN DR.
W. CARPENTER DR.
S. MADISON ST.
ABANDONED TRACKS
WALL
CREEK
CLEAR
S. ROGERS ST.
COUNTRY CLUB DRIVE
CITY WALK BRIDGE
WESTERN COMPOUND
COMMERCIAL
EASTERN COMPOUND
LOT 1
LOT 2 (CVS)
LOT 3
LOT 4
Retention Pond
E. WALLS ST.
WALNUT STREET
ACCESS ROAD
LIMESTONE DR.
CHERRY ST.
BROOKSIDE DR.
GATE
HOOSIER ST.
E. SUNNY S
E. RIDGE
PINEWOOD DR.

0 250 500
SCALE IN FEET

CSX TRANSPORTATION, INC.
BLOOMINGTON, INDIANA

Quarterly Groundwater Sampling Locations

ARCADIS Design & Consultancy for natural and built assets

FIGURE
1

ATTACHMENT 1

IDEM Comment Letter dated June 11, 2020

INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT
We Protect Hoosiers and Our Environment.
100 N. Senate Avenue • Indianapolis, IN 46204
(800) 451-6027 • (317) 232-8603 • www.idem.IN.gov

Eric J. Holcomb
Governor

Bruno L. Pigott
Commissioner

June 11, 2020

Daniel Dyer
Manager of Environmental Remediation
CSX Transportation, Inc.
31 East Georgia Street
Indianapolis, IN 46204

Dear Mr. Dyer:

Re: Revised Remediation Work Plan
Former Indiana Creosoting Company
240 Country Club Road
Bloomington, IN 47403
VRP # 6970403

The Indiana Department of Environmental Management (IDEM) has reviewed the Revised Remediation Work Plan (Arcadis, dated April 23, 2020) for the Former Indiana Creosoting Company site located at 240 Country Club Road in Bloomington, Indiana.

The Revised Remediation Work Plan (RRWP) including appendices was uploaded to the IDEM Virtual File Cabinet (VFC) as documents # 82955186, 82970544, 82970546, 82970547, 82970548, and 82970549. Further site history can be found in the VFC located on the IDEM website www.idem.in.gov. This technical letter contains a brief background summary including comments generated during our review of the above mentioned response.

Background

The Site is bordered to the north and east by commercial/industrial properties; and to the southeast, south and west by predominantly residential properties, although there is some commercial/industrial property along these boundaries as well. The Site is a generally rectangular shaped parcel of land approximately 40 acres in size and is divided into two portions by Country Club Road. The first portion, approximately 14 acres in size, is located north of Country Club Road and is divided by Clear Creek, which flows from north to south through the portion. This entire portion of the site generally lies in or near the floodplain of Clear Creek.

The area west of Clear Creek (north of Country Club Road) is where the former creosoting operations were performed. Creosote storage tanks and various railroad spurs were also located here. The area to the east of Clear Creek is a marshy area of floodplain that was included among land that CSX purchased in 2006 and was not part of the former wood-treating operation. The second portion of the Site, which is also divided by Clear Creek, is located south of Country Club Road, and comprises approximately 26 acres. The area to the west of Clear Creek was historically used to store untreated railroad ties and was never developed. The area to the east of Clear Creek consists of floodplain land that was included in CSXT's 2006 purchase described in the preceding paragraph, as well as approximately 6 acres of commercial land located predominantly above the floodplain that CSXT purchased in 2010. This area (east of Clear Creek) has historically been undeveloped.

Wood-treating operations began circa 1914 by the American Creosoting Company and ceased in 1976. The Indiana Creosoting Company, a subsidiary of the Monon Railroad, purchased the property from the American Creosoting Company in 1961. The Monon Railroad merged with the Louisville and Nashville Railroad in 1971, which was the predecessor company to CSXT. All creosote storage, handling, and use appears to have occurred north of Country Club Road in the former operations area.

The Site was formally entered into the Indiana Department of Environmental Management (IDEM) Voluntary Remediation Program (VRP) May 13, 1997. The current remediation and clean-up objectives for soil and groundwater at the Site are 1996 VRP Tier II Default Non-residential (Industrial) Scenario for on-site impacts and residential for off-site impacts, unless an Environmental Restrictive Covenant (ERC) is agreed upon by the off-site property owners. CSXT expects the land-use of this property to remain industrial at this time. The Site's constituents of concern (COCs) are BTEX (benzene, toluene, ethylbenzene, and xylenes), poly aromatic hydrocarbons (PAHs), phenolic compounds, phthalates, arsenic, and lead. Components of a Remediation Work Plan (RWP) were submitted between 2011 and 2015.

Comments

1. The monitoring program is outlined in Section 7.2 of the RWP. A subset of 24 monitoring wells has been selected as a representative set to determine water quality for this project (Table 10, Figure 9). These monitoring wells will be sampled on a quarterly basis for a period of two years (eight quarters), or until quarterly sampling is deemed no longer necessary as agreed upon by the IDEM and CSXT/ Arcadis. The monitoring system and duration are acceptable to IDEM.

2. Arcadis needs to confirm the operational status of the free product recovery system. To provide an accurate plume behavior analysis the recovery system cannot be in operation. A long-term plume behavior analysis can start once the aquifer has re-equilibrated (usually one year).

3. The plume behavior analysis needs to include samples collected shortly after (within 24 hours) a storm event. Arcadis requested clarification on IDEM's criteria used to identify a storm event. Rainfall is considered a storm event when at least 0.75 inch falls over a 24-hour period. Once a storm event occurs, sampling needs to take place with 24 hours.

4. Appendix F included the Quality Assurance Project Plan (QAPP). The Tables E-1, E-2 and E-3 in Appendix F QAPP should be revised because the parameter list is missing some of the compounds (phenolics, phthalates, etc.) that are shown in the Table 1 "Constituents of Concern". Also, the quality assurance and quality control acceptance limits were missing from the Appendix F QAPP and should be included. Section 8.2.2 indicated that the acceptance criteria and compounds used for the matrix spike and matrix spike duplicate analysis are identified in the SOPs. However, copies of the SOPs for the constituents of concern were not included and should be added. If the QA/QC acceptance limits for each analysis will follow the EPA methods, then a statement to clarify this intent should be added to the QAPP.

Please respond within 30 days from the receipt of this letter with a plan or scope of work to address these comments. Once these comments have been addressed to IDEM's satisfaction, the RRWP can be technically approved and put out for public notice. It is not necessary to reprint the sections of the RRWP that these comments address; an addendum letter response is acceptable.

If you have any questions, please contact me at (317) 233-5298, (800) 451-6027, or at email mmccann@idem.in.gov.

Sincerely,

Michael R. McCann, Project Manager
Voluntary Remediation Program
Office of Land Quality

cc: Steve Sharp, Arcadis G&M, Inc., 150 West Market St, Suite 728, Indianapolis, IN 46204

It is the goal of IDEM to enable remediation sites to move forward in a timely manner. If an impasse has been reached over technical issues, a Technical Review Panel of non OLQ scientists is available to review and offer a non-binding opinion to help resolve technical disagreements with the VRP and State Cleanup Program project managers. The goal is to facilitate progress at your site. This review process is available immediately. If you would like to request a review by the Panel, please contact Bruce Oertel, Branch Chief, Remediation Services Branch, OLQ at (317) 232-4535 or boertel@idem.in.gov.

Any decision produced by the Technical Review Panel is not an agency action as defined in IC § 4-21.5-1-4 or an order as defined in IC §4-21.5-1-9. This decision is not subject to administrative review because it is not a determination of any legal rights, duties, privileges, immunities, or other legal interests, and because it is issued pursuant to an informal procedure for dispute resolution as allowed by IC 4-21.5-3-34 (a).

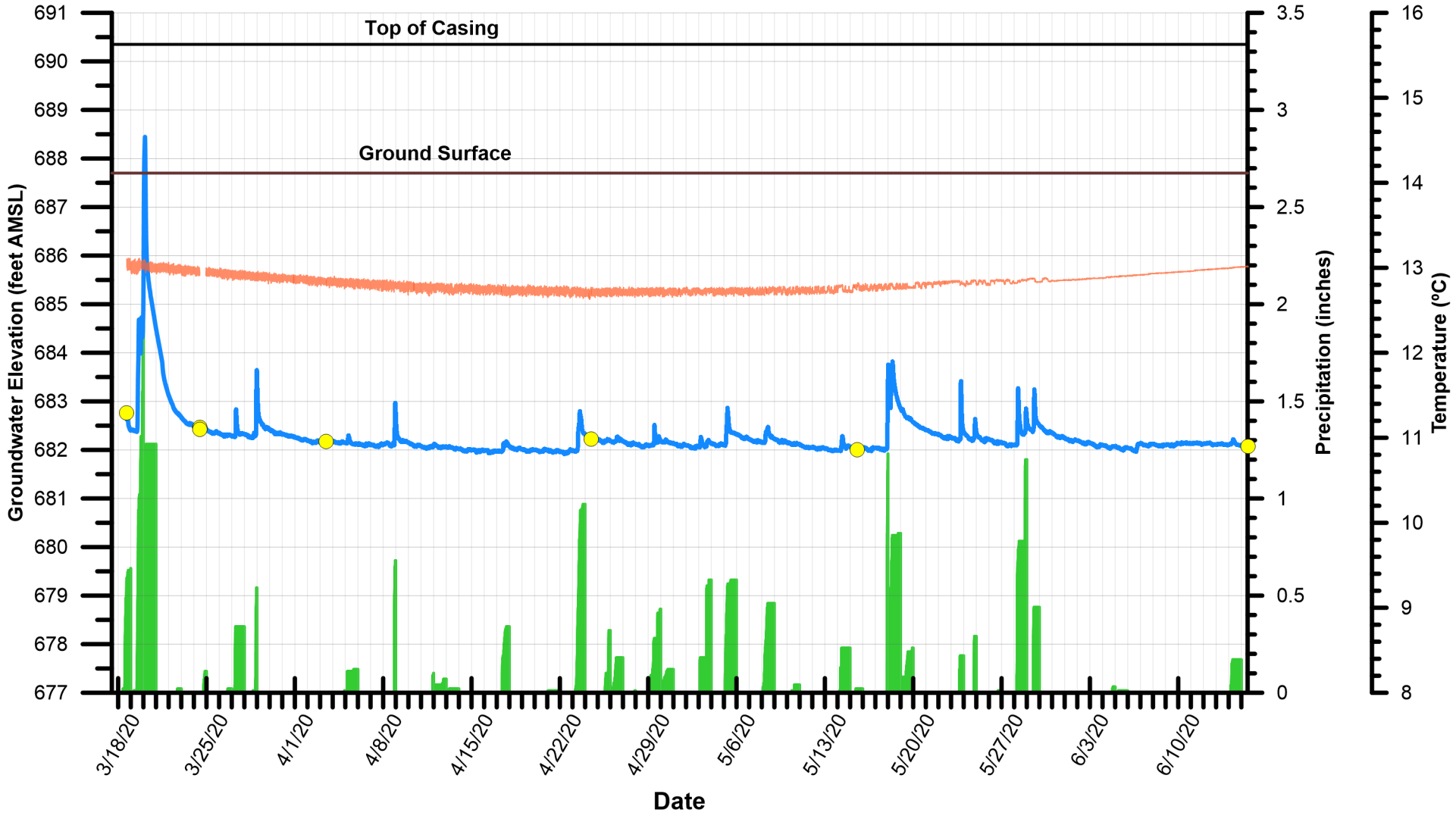
ATTACHMENT 2

Tranducer Water Elevation Graphs

CSX Bloomington
Bloomington, IN
Data Graph Prepared: 8/4/2020
Prepared by: CS, SO
Checked by: KW

ARCADIS Design & Consultancy for natural and built assets

MW-5D (URC) Hydrograph



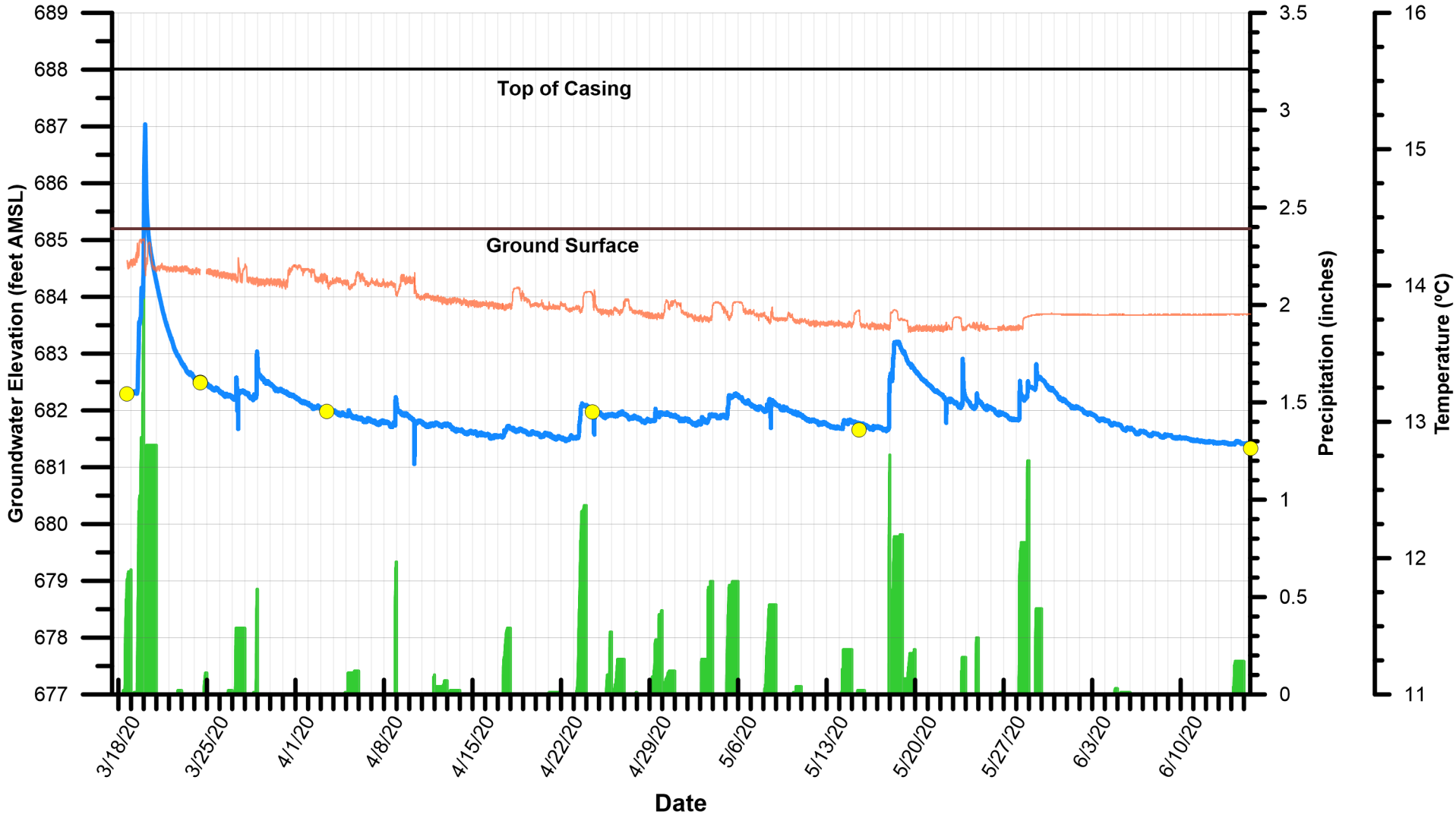
-All elevations are in feet in reference to North American Vertical Datum of 1988 (NAVD 88).
-Groundwater elevations are calibrated to manual measurements from surveyed measuring points.
-Precipitation collected from the Weather Underground KINBLOOM148 station located approximately 1.0 mile southwest of the site entrance at 240 W Country Club Dr, Bloomington, IN.
-AMSL = above mean sea level
-ºC = Celsius

MW-5D Groundwater Elevation (feet AMSL)
Manual Groundwater Measurements (feet AMSL)
Precipitation (inches)
Temperature (ºC)
Top of Casing (feet AMSL)
Ground Surface (feet AMSL)

CSX Bloomington
Bloomington, IN
Data Graph Prepared: 8/4/2020
Prepared by: CS, SO
Checked by: KW

ARCADIS Design & Consultancy for natural and built assets

MW-34A (URC) Hydrograph



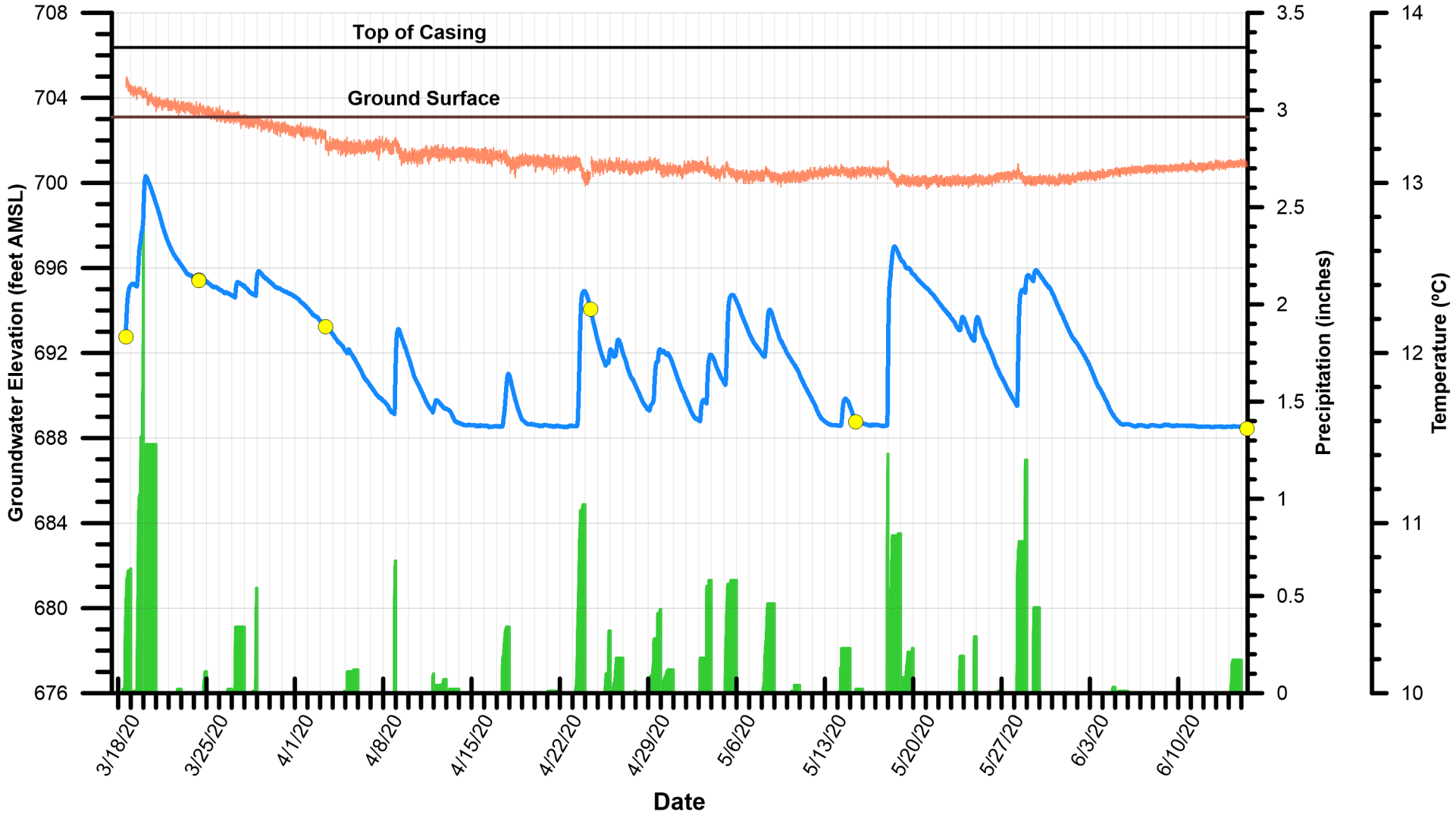
-All elevations are in feet in reference to North American Vertical Datum of 1988 (NAVD 88).
-Groundwater elevations are calibrated to manual measurements from surveyed measuring points.
-Precipitation collected from the Weather Underground KINBLOOM148 station located approximately 1.0 mile southwest of the site entrance at 240 W Country Club Dr, Bloomington, IN.
-AMSL = above mean sea level
-°C = Celsius

- MW-34A Groundwater Elevation (feet AMSL)
- Manual Groundwater Measurements (feet AMSL)
- Precipitation (inches)
- Temperature (°C)
- Top of Casing (feet AMSL)
- Ground Surface (feet AMSL)

CSX Bloomington
Bloomington, IN
Data Graph Prepared: 8/4/2020
Prepared by: CS, SO
Checked by: KW

ARCADIS Design & Consultancy for natural and built assets

MW-35B (URC) Hydrograph



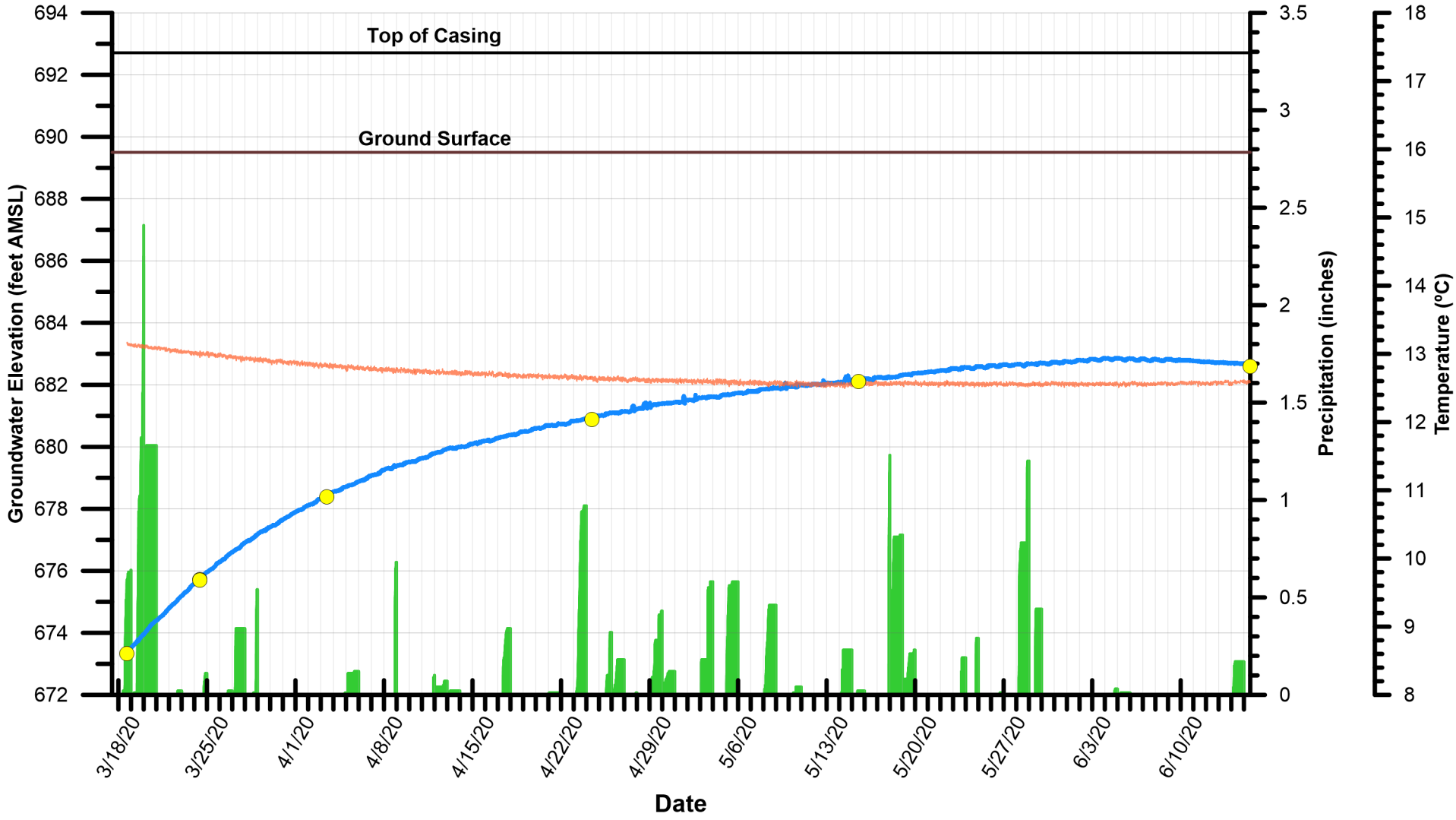
-All elevations are in feet in reference to North American Vertical Datum of 1988 (NAVD 88).
-Groundwater elevations are calibrated to manual measurements from surveyed measuring points.
-Precipitation collected from the Weather Underground KINBLOOM148 station located approximately 1.0 mile southwest of the site entrance at 240 W Country Club Dr, Bloomington, IN.
-AMSL = above mean sea level
-°C = Celsius

- MW-35B Groundwater Elevation (feet AMSL)
- Manual Groundwater Measurements (feet AMSL)
- Precipitation (inches)
- Temperature (°C)
- Top of Casing (feet AMSL)
- Ground Surface (feet AMSL)

CSX Bloomington
Bloomington, IN
Data Graph Prepared: 8/4/2020
Prepared by: CS, SO
Checked by: KW

ARCADIS Design & Consultancy for natural and built assets

MW-28C (LRC) Hydrograph



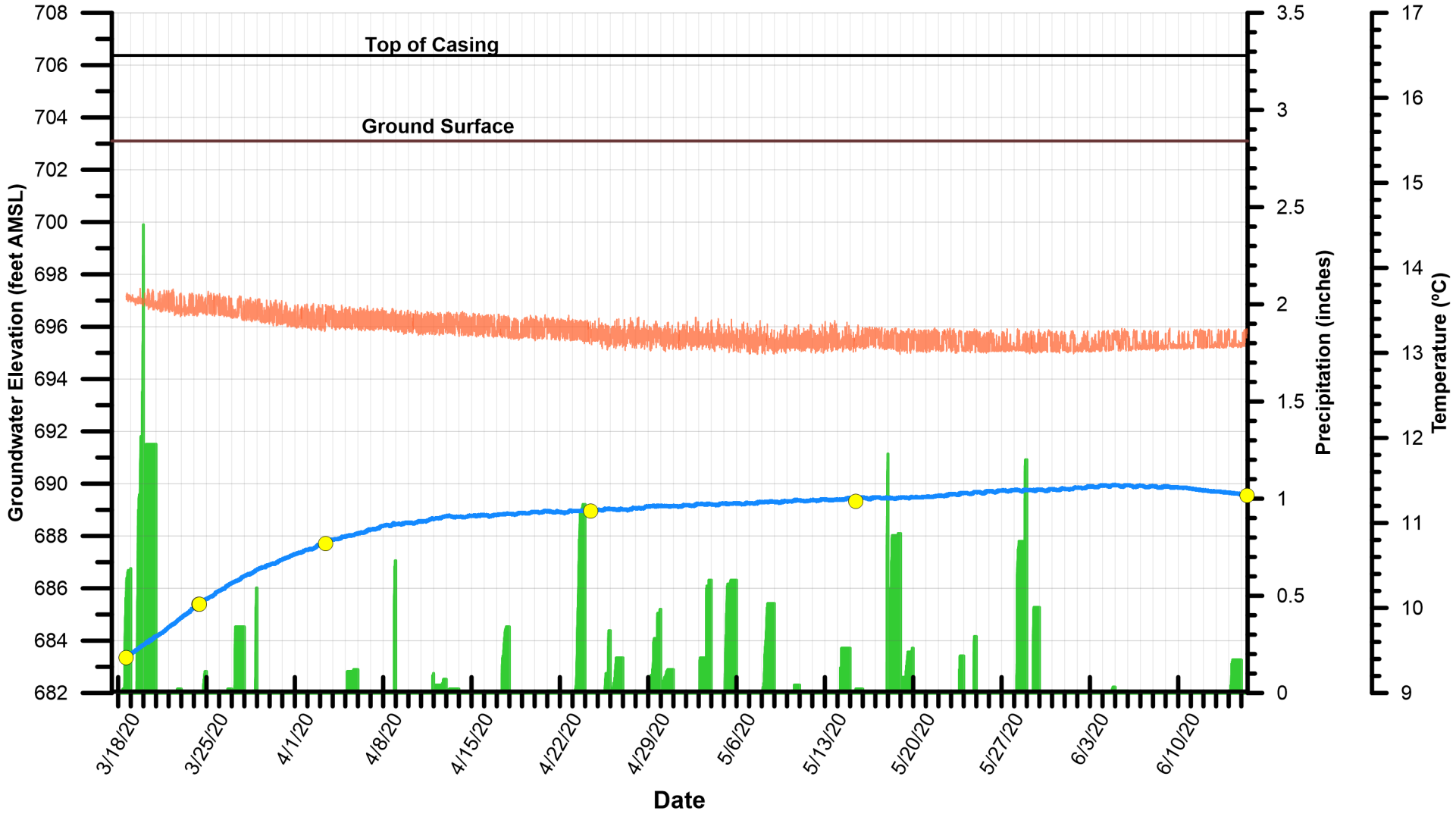
-All elevations are in feet in reference to North American Vertical Datum of 1988 (NAVD 88).
-Groundwater elevations are calibrated to manual measurements from surveyed measuring points.
-Precipitation collected from the Weather Underground KINBLOOM148 station located approximately 1.0 mile southwest of the site entrance at 240 W Country Club Dr, Bloomington, IN.
-AMSL = above mean sea level
-°C = Celsius

- MW-28C Groundwater Elevation (feet AMSL)
- Manual Groundwater Measurements (feet AMSL)
- Precipitation (inches)
- Temperature (°C)
- Top of Casing (feet AMSL)
- Ground Surface (feet AMSL)

CSX Bloomington
Bloomington, IN
Data Graph Prepared: 8/4/2020
Prepared by: CS, SO
Checked by: KW

ARCADIS Design & Consultancy for natural and built assets

MW-35C (LRC) Hydrograph



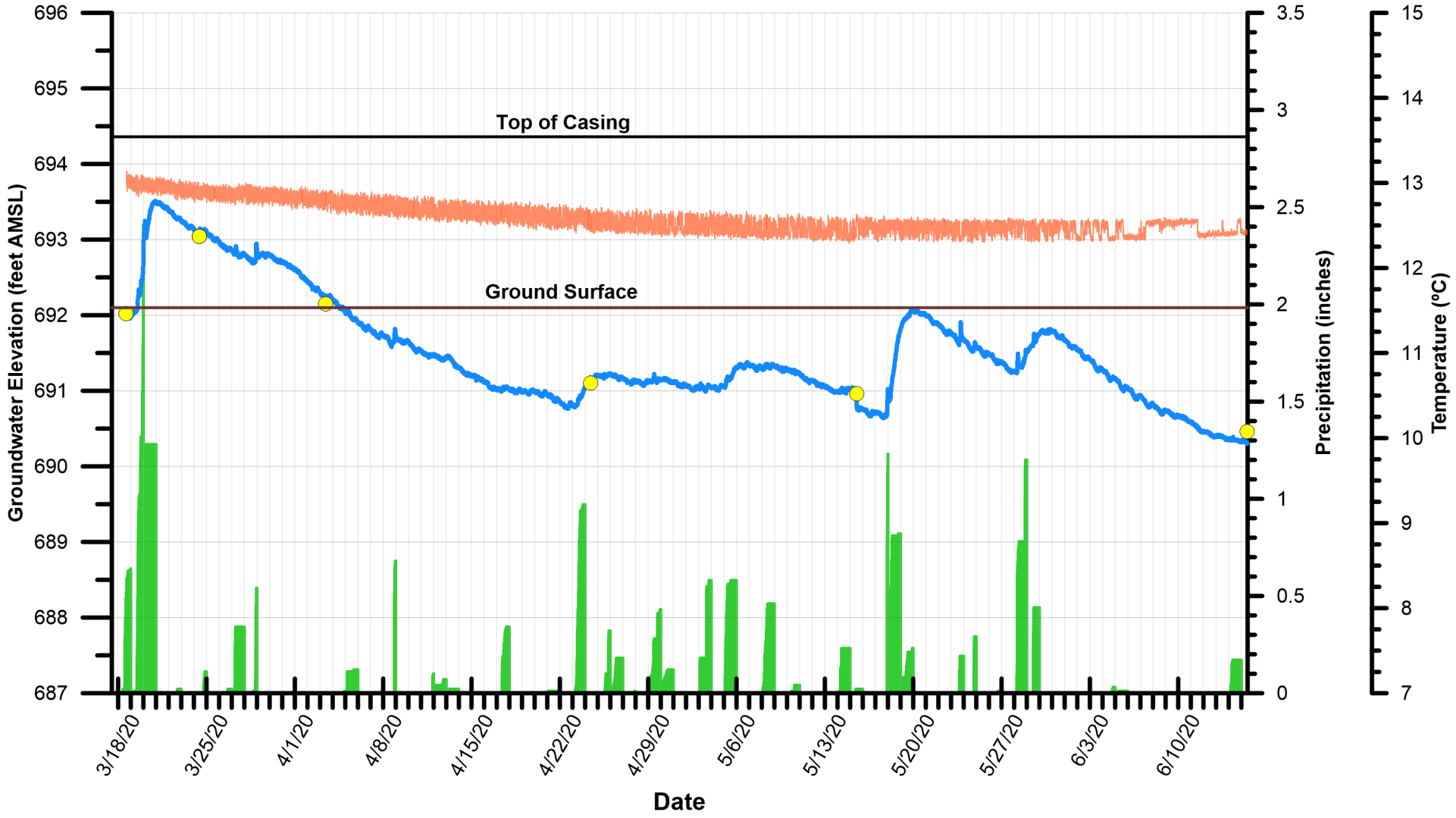
-All elevations are in feet in reference to North American Vertical Datum of 1988 (NAVD 88).
-Groundwater elevations are calibrated to manual measurements from surveyed measuring points.
-Precipitation collected from the Weather Underground KINBLOOM148 station located approximately 1.0 mile southwest of the site entrance at 240 W Country Club Dr, Bloomington, IN.
-AMSL = above mean sea level
-°C = Celsius

- MW-35C Groundwater Elevation (feet AMSL)
- Manual Groundwater Measurements (feet AMSL)
- Precipitation (inches)
- Temperature (°C)
- Top of Casing (feet AMSL)
- Ground Surface (feet AMSL)

CSX Bloomington
Bloomington, IN
Data Graph Prepared: 8/4/2020
Prepared by: CS, SO
Checked by: KW

ARCADIS Design & Consultancy for natural and built assets

MW-40A (LRC) Hydrograph



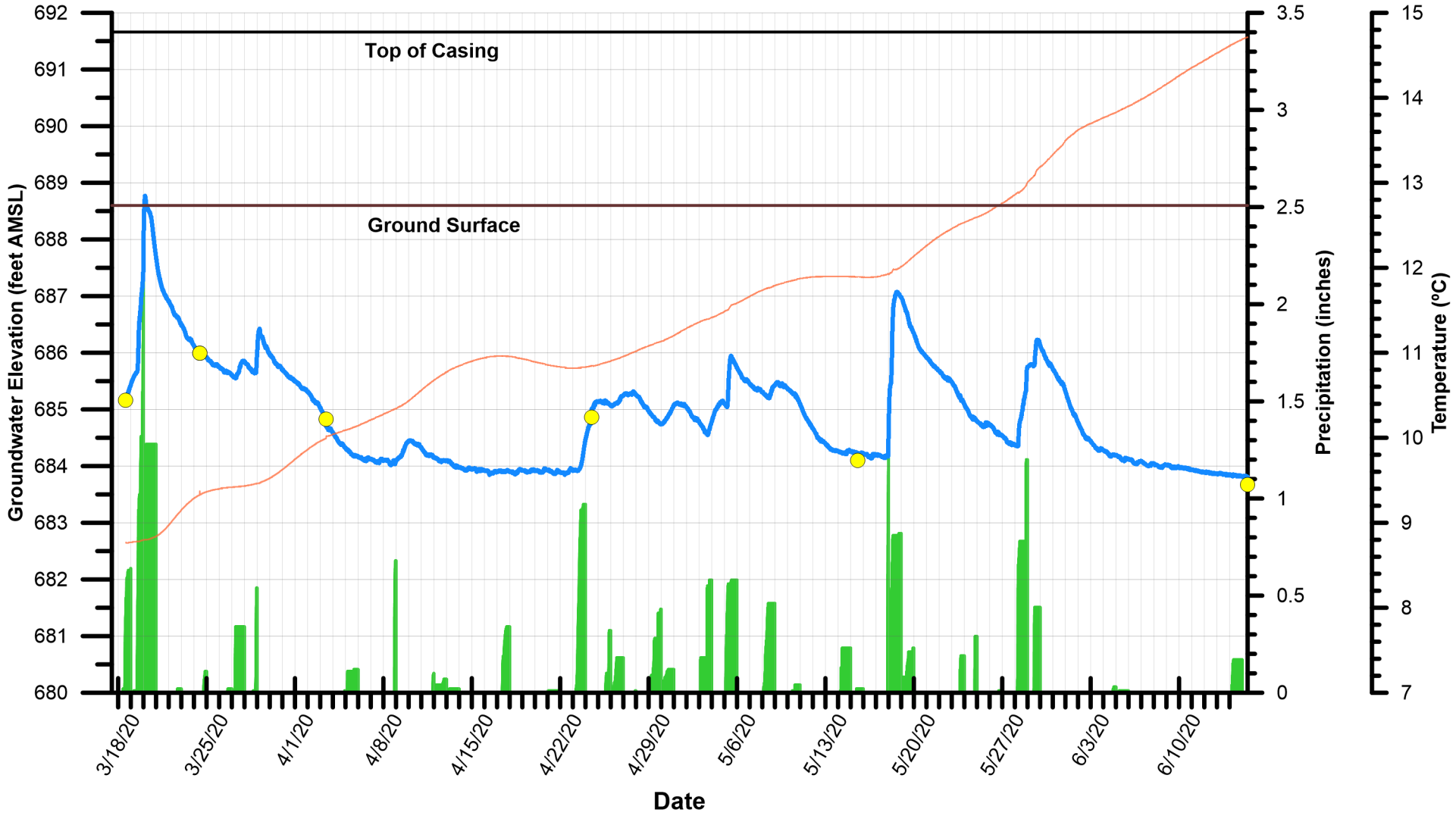
-All elevations are in feet in reference to North American Vertical Datum of 1988 (NAVD 88).
-Groundwater elevations are calibrated to manual measurements from surveyed measuring points.
-Precipitation collected from the Weather Underground KINBLOOM148 station located approximately 1.0 mile southwest of the site entrance at 240 W Country Club Dr, Bloomington, IN.
-AMSL = above mean sea level
-°C = Celsius

- MW-40A Groundwater Elevation (feet AMSL)
- Manual Groundwater Measurements (feet AMSL)
- Precipitation (inches)
- Temperature (°C)
- Top of Casing (feet AMSL)
- Ground Surface (feet AMSL)

CSX Bloomington
Bloomington, IN
Data Graph Prepared: 8/4/2020
Prepared by: CS, SO
Checked by: KW

ARCADIS Design & Consultancy for natural and built assets

MW-8S (Alluvium) Hydrograph



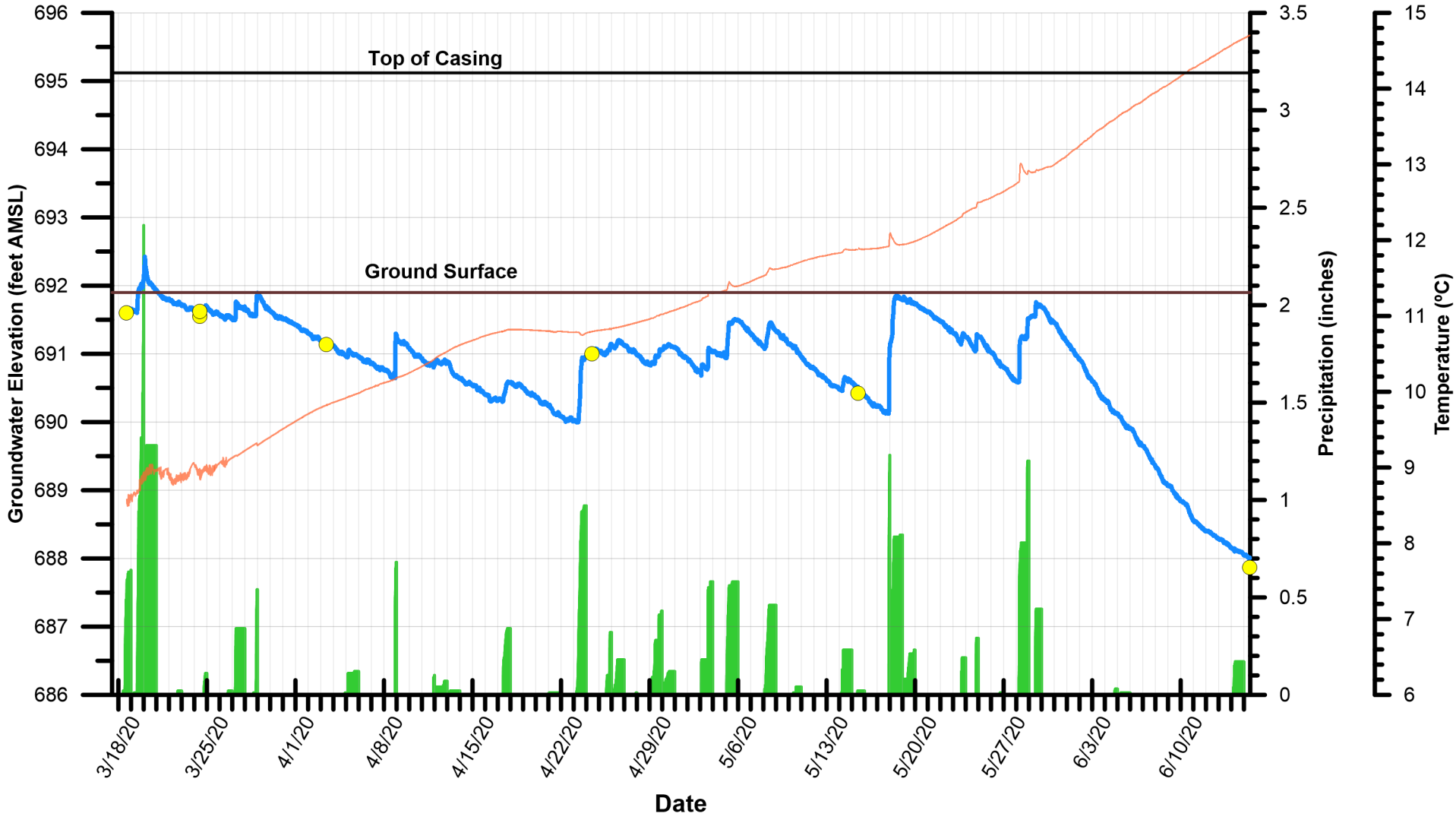
-All elevations are in feet in reference to North American Vertical Datum of 1988 (NAVD 88).
-Groundwater elevations are calibrated to manual measurements from surveyed measuring points.
-Precipitation collected from the Weather Underground KINBLOOM148 station located approximately 1.0 mile southwest of the site entrance at 240 W Country Club Dr, Bloomington, IN.
-AMSL = above mean sea level
-ºC = Celsius

MW-8S Groundwater Elevation (feet AMSL)
Manual Groundwater Measurements (feet AMSL)
Precipitation (inches)
Temperature (ºC)
Top of Casing (feet AMSL)
Ground Surface (feet AMSL)

CSX Bloomington
Bloomington, IN
Data Graph Prepared: 8/4/2020
Prepared by: CS, SO
Checked by: KW

ARCADIS Design & Consultancy for natural and built assets

MW-16S (Alluvium) Hydrograph



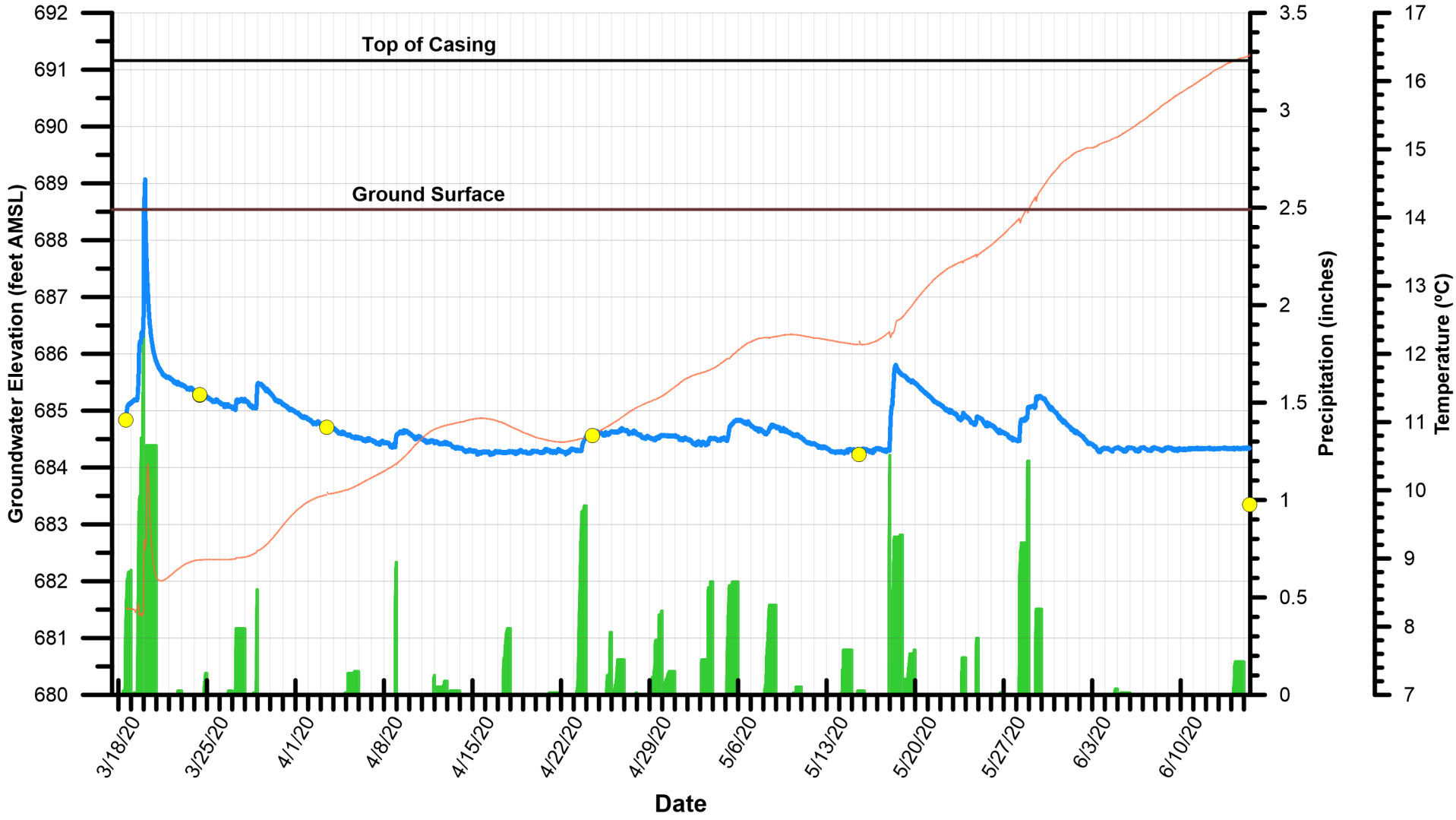
-All elevations are in feet in reference to North American Vertical Datum of 1988 (NAVD 88).
-Groundwater elevations are calibrated to manual measurements from surveyed measuring points.
-Precipitation collected from the Weather Underground KINBLOOM148 station located approximately 1.0 mile southwest of the site entrance at 240 W Country Club Dr, Bloomington, IN.
-AMSL = above mean sea level
-ºC = Celsius

MW-16S Groundwater Elevation (feet AMSL)
Manual Groundwater Measurements (feet AMSL)
Precipitation (inches)
Temperature (ºC)
Top of Casing (feet AMSL)
Ground Surface (feet AMSL)

CSX Bloomington
Bloomington, IN
Data Graph Prepared: 8/4/2020
Prepared by: CS, SO
Checked by: KW

ARCADIS Design & Consultancy for natural and built assets

MW-20S (Alluvium) Hydrograph



-All elevations are in feet in reference to North American Vertical Datum of 1988 (NAVD 88).
-Groundwater elevations are calibrated to manual measurements from surveyed measuring points.
-Precipitation collected from the Weather Underground KINBLOOM148 station located approximately 1.0 mile southwest of the site entrance at 240 W Country Club Dr, Bloomington, IN.
-AMSL = above mean sea level
-ºC = Celsius
-Transducer was hung at an elevation of approximately 684.4 feet AMSL. Disparities between the manual GW elevation measurements and transducer elevation measurements on 5/15/20 and 6/15/20 occur as a result of the water level falling below the transducer.

- MW-20S Groundwater Elevation (feet AMSL)
- Manual Groundwater Measurements (feet AMSL)
- Precipitation (inches)
- Temperature (ºC)
- Top of Casing (feet AMSL)
- Ground Surface (feet AMSL)

ATTACHMENT 3

Revised QAPP

ARCADIS Design & Consultancy for natural and built assets

CSX Transportation, Inc.

QUALITY ASSURANCE PROJECT PLAN (REVISION 1)

Former Indiana Creosoting Company Facility
240 Country Club Drive
Bloomington, Indiana
CSX Project #: 9415829

IDEM VRP Site #: 9970403

August 10, 2020

,

QUALITY ASSURANCE PROJECT PLAN

Former Indiana Creosoting Company Facility

240 Country Club Drive

Bloomington, Indiana

CSXT Project # 9415829

IDEM VRP # 6970403

Steven C. Sharp, LPG
Certified Project Manager 2 / Geologist
(Indiana LPG License #1682)

Randall Woodruff
Project Geological Scientist

Prepared for:

CSX Transportation, Inc

31 Georgia Street

Indianapolis, Indiana 46204

Prepared by:

Arcadis U.S., Inc.

150 W. Market Street

Suite 728

Indianapolis

Indiana 46204

Tel 317 231 6500

Fax 317 231 6514

Our Ref.:

30028139 Task 07

Date:

August 10, 2020

CONTENTS

TABLES

APPENDICES

1 INTRODUCTION

The Indiana Department of Environmental Management (IDEM) requires that all environmental monitoring and measurement efforts participate in a centrally managed quality assurance (QA) program.

Any party generating data under this program has the responsibility to implement minimum procedures to assure that the precision, accuracy, completeness, and representativeness of its data are known and documented. To ensure the responsibility is met uniformly, each party must prepare a written Quality Assurance Project Plan (QAPP) covering each project it is to perform.

This QAPP presents the organization, objectives, functional activities and specific QA and quality control (QC) activities associated with Initial Site Investigation (ISI) Work Plan/Report activities to be completed at the Former Indiana Creosoting Company facility located in Bloomington, Indiana. This QAPP also describes the specific protocols that will be followed for sampling, sample handling and storage, chain-of-custody, and laboratory and field analysis.

All QA/QC procedures will be in accordance with applicable professional technical standards, IDEM requirements, government regulations and guidelines, and specific project goals and requirements. This QAPP has been prepared on behalf of CSX Transportation, Inc. (CSX) by ARCADIS in accordance with all IDEM QAPP guidance documents and the model QAPP *Interim Guidelines and Specifications for Preparing Quality Project Plans (QAMS-005-08), and the Region V Model QAPP.*

2 PROJECT DESCRIPTION

2.1 Site Location and Description

The Former Indiana Creosoting Company site is located at 240 Country Club Drive, Bloomington, Monroe County, Indiana. The Site is located in Monroe County, Perry Township, and within the City limits of Bloomington, Indiana. The Site and the surrounding area are presented on Figures 1 and 2 of the Revised Remediation Work Plan (RRWP). A detailed Site Map is presented on Figure 2 of the RRWP.

The Site is bordered on the West by the Bloomington Rails to Trails, to the North by additional CSXT facilities, to the South by vacant land, and is bisected to the east by Clear Creek. Further to the East and North are commercial /industrial areas. Further to the South and West are residential areas.

The Site is a generally rectangular shaped parcel of land approximately forty (40) acres in size, divided into two portions. The first portion, approximately fifteen (15) acres, is located to the North of Country Club Road, and is the location of previous creosote storage areas, facility operations, railroad spurs, and previous excavations. The second portion of the Site, approximately twenty-five (25) acres, is located to the South of Country Club Road, and was used for untreated wood storage and a staging area.

The Site is relatively flat, sloping rapidly near clear creek. The Site is heavily covered with vegetation (brush and grasses) with a wooded area near Clear Creek. The Site is currently undeveloped; however, several concrete foundations remain. Two storage compounds, including one storage building, were erected on the south side in 2014. A Site Map depicting property lines, concrete foundation outlines, storage compounds, and other relevant features is presented as Figure 2.

2.2 Past Data Collection Activities

Several subsurface investigations have been completed at the Site dating back several years. Details of historical investigations are documented in the RRWP.

2.3 Project Scope and Objectives

The RRWP has been written in accordance with IDEM guidelines, by summarizing the investigative results completed to-date and outlining proposed geophysical assessment, subsurface investigation, and preferential pathways assessment activities to be completed at the Site.

Volatile organic compounds (VOCs), Polynuclear Aromatic Hydrocarbons (PAHs), and metals are the potential Site constituents of concern (COCs) and the proposed groundwater samples to be collected will be analyzed for VOCs – benzene, toluene, ethylbenzene, and xylenes (BTEX) only, PAHs, and total and dissolved metals (lead and arsenic only).

2.4 Sampling Network and Rationale

2.4.1 Soil Sampling and Analysis Program

As discussed in the RRWP, the horizontal and vertical characterization of soils have been fully assessed at the Site. Collection and analysis of soil samples at the Site are complete and will not take place during the RRWP activities.

2.4.2 Groundwater Sampling and Analysis Program

As discussed in the RRWP, quarterly groundwater sampling will be completed from select monitoring wells at the Site to assess current Site groundwater conditions. A summary of the proposed quarterly (8 total quarters) sampling plan is included in the ISI Work Plan and included in this QAPP (included as Tables E-1, E-2, and E-3).

2.4.2.1 Soil Sampling

Soil sampling activities will not be completed at the Site.

2.4.2.2 Groundwater Sampling

Quarterly (eight total quarters) groundwater sampling activities will be completed to assess current groundwater conditions at the Site, and to evaluate the migration of potential groundwater impacts.

Up to 24 monitoring well locations will be sampled per quarter (for the first 7 quarters, with all monitoring wells on site sampled during the eighth quarter) for laboratory analysis of VOCs (BTEX only) using United States Environmental Protection Agency (U.S. EPA) SW-846 Method 8260B, PAHs using U.S. EPA SW-846 Method 8270D Simultaneous Ion Monitoring (SIM), and total and dissolved metals U.S. EPA SW-846 Method 6010C (arsenic and metals only) (Table E-1).

VOC groundwater samples collected from each monitoring well will be placed into three, 40-milliliter vials preserved with hydrochloric acid (HCl). ARCADIS personnel will make sure sample vials do not contain any headspace that might allow volatilization of dissolved-phase VOCs. PAH groundwater samples collected from each monitoring well will be placed into two, unpreserved, 1-liter amber jars. Total metals groundwater samples collected from each monitoring well will be placed into one, 250-milliliter plastic jar preserved with nitric acid (HNO3). Dissolved metals groundwater samples collected from each monitoring well will be placed into one, unpreserved, 250-milliliter plastic jar; to be lab preserved and filters upon arrival. Samples will be properly labeled, placed in an ice-packed cooler and delivered for laboratory analysis using proper chain-of-custody procedures.

VAP groundwater sampling will be completed using Level IV QA/QC sample analysis. Therefore, ARCADIS will collect and submit blind duplicates, MS/MSDs, trip blanks at the frequency identified in this QAPP.

2.5 Parameters to be Tested and Frequency

Sample matrices, analytical parameters and frequencies of sample collection are presented in Table E-1.

2.6 Data Quality Objective (DQOs)

The overall quality assurance objective is to ensure that data of known and acceptable quality are produced. Proper execution of each task will yield consistent results that are representative of the media and conditions measured and are useful for meeting the intended project objectives. Data will be calculated and reported in units consistent with those of other agencies and organizations to allow comparability of databases.

DQOs are qualitative and quantitative statements that specify the quality of the data required to support decisions made during investigation and remediation activities and are based on the end uses of the data to be collected. The outputs from the DQO process are used to evaluate the remedial approach. As such, different data uses may require different levels of data quality. There are five levels of analytical support, which address various data uses, the QA/QC effort and analytical methods required to achieve the desired level of quality.

DQOs can be classified for the measurement data by defining the level of analytical support assigned to each type of data measurement.

The following defines the different levels of DQO analytical support:

Level I (Screening): This provides the lowest data quality but the most rapid results. It is often used for health and safety monitoring at a site, remediation performance evaluation, and for engineering screening of alternatives (bench scale tests). These types of data include those generated on-site through the use of a photoionization detector (PID), pH, conductivity, and other real-time monitoring equipment at the Site.

Level II (Field Analyses) - These data provide rapid results and better quality than in Level 1. This level may include mobile lab generated data depending on the level of quality control exercised.

Level III (Engineering) - This provides an intermediate level of data quality and is used for site characterization and periodic groundwater monitoring. Engineering analyses may include mobile lab generated data and some analytical lab methods (e.g., laboratory data with quick turnaround used for screening but without full quality control documentation);

Level IV (Confirmational) - This provides the highest level of data quality and is used for purposes of risk assessment, evaluation of remedial alternatives and verification that cleanup standards have been met. These analyses require full analytical and data validation procedures in accordance with EPA recognized protocols; and

Level V (Non-Standard) - This refers to analyses by non-standard protocols, for example, when exacting detection limits or analysis of an unusual chemical compound is required. These analyses often require method development or adaptation. The level of quality control is usually similar to DQO Level 4 data.

[NOTE: Level IV QA/QC has been selected for the CSX analytical data output.]

3 PROJECT ORGANIZATION AND RESPONSIBILITY

CSX has retained ARCADIS to complete all phases of proposed work at the project site and SGS Laboratories, Inc. of Orlando, Florida to perform laboratory analyses.

A summary of the responsibilities of key project personnel is presented below:

ARCADIS

Senior Project Manager

Steven C. Sharp

- Provide overall project management
- Overview of field activities
- Overview of laboratory activities
- Preparation and review of reports
- Technical representation of project activities

QA/QC Manager - Analytical Activities

Jennifer Singer

- Perform laboratory system audits
- Coordinate supply of performance evaluation samples
- Review laboratory QA/QC
- Data validation and assessment
- Advise on data corrective action procedures
- QA/QC representation of project activities

Task Manager(s)

Randall Woodruff

- Management of field activities and field QA/QC
- Data assessment
- Technical representation of field activities
- Preparation of reports
- Advise on field corrective action procedures
- Evidence file custodian

Staff (to be determined)

- Conduct field activities
- Assist in preparation of reports

SGS North America Inc., Orlando, Florida

Project Manager - Project Laboratory
Heather Wandrey

- Ensures all resources of the laboratory are available on an as-required basis
- Coordinate laboratory analyses
- Supervise in-house chain-of-custody
- Schedule sample analyses
- Oversee data review
- Oversee preparation of analytical reports
- Overview of final analytical reports

Laboratory QA Officer - Project Laboratory

- Overview laboratory quality assurance
- Overview QA/QC documentation
- Conduct detailed data review
- Decide laboratory corrective actions, if required
- Technical representation of laboratory QA procedures
- Preparation of laboratory Standard Operating Procedures (SOPs)
- Approve final analytical reports prior to submission to ARCADIS

Sample Custodian - Project Laboratory

- Receive and inspect the incoming sample containers
- Record the condition of the incoming sample containers
- Sign appropriate documents
- Verify chain-of-custody and its correctness
- Notify laboratory manager and laboratory supervisors of sample receipt and inspection.
- Assign a unique identification number and customer number and enter each into the sample receiving log.
- Initiate transfer of the samples to the appropriate laboratory departments with assistance provided by the laboratory supervisors.

- Control and monitor access/storage of samples and extracts.

3.1.1 IDEM Responsibilities

The IDEM Project Manager (PM) will be responsible for overview of this project. The PM will also be responsible for approving the QAPP. Michael McCann is the IDEM Voluntary Remediation Program (VRP) PM designated for this project.

4 QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

The overall QA objective is to develop and implement procedures for field sampling, chain-of-custody, laboratory analyses and reporting that will provide results that are scientifically valid, and the levels of which are sufficient to meet DQOs. Specific procedures for sampling, chain-of-custody, laboratory instruments calibration, laboratory analysis, reporting of data, internal quality control, audits, preventive maintenance of field equipment and corrective action are described in other sections of this QAPP. The purpose of this section is to state the specific, required QA objectives for accuracy, precision, completeness, and representativeness.

4.1 Quantitative/Qualitative QA Objective

4.1.1 *Quantitative QA Objectives*

Target compounds, analytical methods, and practical quantitation limits (PQLs) for each matrix are presented in Table E-2.

This section includes a discussion of the quantitative criteria accuracy, precision, and completeness.

4.1.1.1 Accuracy

Accuracy is the closeness of agreement between an observed value and an accepted reference value. The difference between the observed value and the referenced value includes components of both systematic error (bias) and random error. Sources of error include the sampling process, field contamination, preservation, handling, sample matrix, sample preparation, and analysis techniques. Laboratories assess the overall accuracy of their instruments and analytical methods (independent of sample or matrix effects) through the measurement of “standards,” materials of accepted reference value.

Accuracy will vary from analysis to analysis because of individual sample and matrix effects. In an individual analysis, accuracy can be measured and expressed in terms of the recovery of the surrogate compounds (organic analyses) or recovery of spiked compounds (inorganic analyses). This gives an indication of expected recovery for analytes, which tend to behave chemically like the spiked or surrogate compounds.

4.1.1.2 Precision

Precision is the agreement among a set of replicate measurements without consideration of the “true” or accurate value: i.e., variability between measurements of the same material for the same analyte. Precision is a measure of the reproducibility of a method. It may be estimated by several statistical tests, including the coefficient of variation (CV) and the relative percent difference (RPD) between duplicate samples. ARCADIS will determine the precision of the analyses conducted during remedial implementation sampling by reviewing the results of field duplicate samples and laboratory duplicate samples (where applicable). If insufficient data are obtained, the arithmetic mean and standard deviation of a group of results may be calculated.

4.1.1.3 Completeness

Completeness will be expressed both as a percentage of total tests conducted that are deemed valid and as the percentage of the total tests required in the scope of work that are deemed valid.

(Completeness = [Number of test results meeting DQOs/Total number of tests completed x 100 Percent]).

The result of this calculation must be above 90 percent before the investigation can be considered complete.

4.1.2 *Qualitative QA Objective*

This section includes a discussion of the qualitative criteria.

4.1.2.1 Representativeness

Representativeness expresses the degree to which the data accurately and precisely represent a characteristic of a population, parameter variation at a sampling point, process condition, or an environmental condition. Representativeness is a qualitative parameter that is dependent upon the proper design of the sampling program and the laboratory quality control protocol. The representative criterion is best satisfied by ensuring that the sampling locations are properly selected and that a sufficient number of samples are collected.

Representativeness has been addressed by documenting the appropriately selected sampling techniques and providing in the Work Plan the rationale used to select the sampling locations. The use of recognized procedures to collect the groundwater and soil samples ensure that the samples collected reflect the properties and conditions of the media at the location sampled.

4.2 Level of Quality Control Effort

It is required that trip blanks, field duplicates, and matrix spike samples are analyzed to assess the quality of the data resulting from the field sampling program. It is recommended that laboratory duplicates (investigative samples split by the laboratory in addition to MS/MSD samples) also be analyzed. Trip blanks, consisting of distilled water, will be submitted to the analytical laboratory with the field samples. Trip blanks are used to assess the potential volatile organic contamination of samples due to contaminant migration during sample shipment and storage. Field duplicate samples are analyzed as a check for sampling and analytical reproducibility; laboratory duplicates provide an estimate of the reproducibility of measurement. Matrix spikes provide information about the effect of the sample matrix on the digestion and measurement methodology. All matrix spikes should be performed in duplicate.

The general level of the QA effort will be one blind field duplicate and one MS/MSD per 20 or fewer field samples or a minimum of one per sampling event. Trip blank samples will associate with the samples for VOC analysis at the frequency of one per cooler containing samples for VOC analysis.

Target compounds, analytical methods, and PQLs for each matrix are presented in Table E-1.

4.3 Control Limits

Control limits are the maximum and/or minimum values defining a range for a specific parameter, as outlined within each analytical procedure, is considered to satisfactorily meet the quality control criteria. When the parameter falls outside the range, the procedure is considered to be out-of-control. Whenever the analytical procedure is or becomes out-of-control, corrective action must be taken to bring the analysis back into control. The corrective action must include: (1) finding the cause of the problem, (2) correcting the problem, (3) demonstrating the problem has been corrected by reanalyzing appropriate laboratory reference samples, and (4) repeating the analyses of any field samples that may have been affected by the control problem.

Exceptions will be made, on a case-specific basis. If the control limit is technically impracticable for a particular sample or analysis, documentation and narrative explanation should be submitted with the data report and raw data. The document must include evidence that a good faith effort was made to meet the control limit; this will generally include two attempts to analyze the sample.

5 SAMPLING PROCEDURES

Procedures and protocols for collecting samples and for performing all related field activities are presented in the RRWP and section 2.4 of this QAPP.

5.1 QA Samples

QA samples will be collected as the frequencies specifies in Table E-1. Field duplicate samples and MS/MSD samples will be collected using the procedures and protocols outlined in Section 9.2 of this QAPP.

5.2 Sample Volume, Sample Preservation and Holding Time

The required sample volume, preservation, and holding times for the soil, groundwater, and associated QC samples to be collected are presented in Table E-3.

5.3 Field Documentation of Sampling and Site Observations

Entries into the logbook or log sheets will contain a variety of information. At the beginning of each entry, the date, start and end time, weather conditions, names of all sampling team members present, level of personal protection being used, documentation of adherence to protocol, any changes made to planned protocol and the signature of the person making the entry will be entered. The names of visitors to the site work areas and the purpose of their visit will also be recorded in the field logbook or log sheets.

Measurements made and samples collected will be recorded in the field logbook or log sheets. All entries will be made in ink with no erasures. If an incorrect entry is made, the information will be crossed out with a single strike mark, initialed and dated. Whenever a sample is collected or a measurement is made, a detailed description of the location of the sampling point, which includes compass direction and distance taken from a reference point, will also be noted. All equipment used to make measurements will be identified, along with the date of calibration.

Samples will be collected in accordance with the RRWP. The equipment used to collect samples will be noted, along with the time of sampling, sample description, depth from which the sample was collected, volume of sample and number of containers, preservatives used (if any) and signature of sampler. A unique sample identification number will be assigned during sample collection. Field duplicate samples will receive unique sample identification numbers and will be submitted to the laboratory blind to avoid laboratory bias of field QC samples.

Sample Collection. For sampling event: the site name and location, date, starting and ending times, weather, names of all people involved in the sampling activities, level of personnel protection used, documentation of adherence to protocol, and changes made to planned protocol, names of visitors to the site during sampling and reason for their visit, unusual observations, and signature of the person recording the information.

For each individual sample: a detailed description of location, any measurements made, the unique sample number assigned, the time the sample was taken, physical description of sample, depth from which the sample was collected, whether grab or composite (if composite, describe technique),

equipment used to collect the sample, volume and number of sample containers, how sample is preserved, and signature of sampler. Each field duplicate must be given its own unique sampling number; the description should include the unique sample number of its duplicate.

Maps and Drawings. Sample locations will be recorded in the field on a project Site map.

Chain-of-Custody Records. Chain-of-custody records are initiated by the samplers in the field. The field portion of the custody documentation should include: (1) the project name; (2) signatures of samplers; (3) the sample number, date, and time of collection, and whether the sample is grab or composite; (4) signatures of individuals involved in sample, and (5) if applicable, air bill or other shipping number.

Calibration Records & Traceability of Standards/Reagents. If a field or mobile laboratory analysis is performed, calibrations must be performed and documented. Calibration is a reproducible reference point to which all sample measurements can be correlated. A sound calibration program shall include provisions for documentation of frequency, conditions, standards, and records reflecting the calibration history of a measurement system. The accuracy of the calibration standards is important because all data will be in reference to the standards used. A program for verifying and documenting the accuracy of all working standards against primary grade standards shall be routinely followed.

5.3.1 Sample Custody and Document Control

The custody sequence can be divided into three major segments: collection (field), laboratory analysis, and final evidence files. Within any of these segments, a sample or evidence file is in someone's custody if:

- It is in his/her actual physical possession.
- It is in his/her view, after being in his/her physical possession.
- It is in his/her physical possession and he/she has placed it in a secure (locked) location.
- It is in a designated secure area.

5.4 Field Chain-of-Custody Procedures

The sample packaging and shipment procedures summarized below will ensure that the samples will arrive at the laboratory with the chain-of-custody intact.

5.4.1 Field Procedures

1. The field sampler is personally responsible for the care and custody of the samples until transferred.
2. The sampler will keep a written record of the sampling operation and samples' identities. This documentation must include the following: chain-of-custody, air bill receipt, and sampling information sheets.
3. Each sample will be placed in a container with a completed sample label attached. The sample label must include, at a minimum: the sample number, the date and time sampled, the sample location, the parameters for which the sample is to be analyzed, and the sampler's signature.

4. Samples remain in the custody of the sampler until transfer of custody is completed. This consists of:
    a.) Delivery of samples to the laboratory sample custodian, and
    b.) Signature of laboratory sample custodian on chain-of-custody documents as receiving the samples and signature of the sampler as relinquishing samples.
    c.) If a carrier is used to take samples between the sampler and the laboratory, the carrier must also sign the chain-of-custody form (as receiver from sampler and relinquisher to laboratory). However, this does not apply to a courier service (i.e. Federal Express, Airborne, UPS). If a courier service is used, the samples along with the chain-of-custody documentation will be sealed within an appropriate container and sealed with custody seals and clear shipping tape.

5.5 Laboratory Chain-of-Custody Procedures

The sample custodian will assign a unique number to each incoming sample for use in the laboratory. The unique number and customer number will then be entered into the sample receiving log. The laboratory date of receipt will also be noted.

Laboratory custody procedures and document control for those samples analyzed by SGS North America, Inc. will be carried out as specified in the Corporate Quality Assurance Plan included in Appendix A of this QAPP.

5.6 Final Evidence/Custody Files Procedures

Evidential files for the entire project will be maintained by ARCADIS for CSX and will consist of the following:

- Project work plan
- Project logbooks
- Field data records
- Sample identification documents
- Chain-of-custody records
- Correspondence
- References, literature
- Final data packages
- Miscellaneous - photos, maps, drawings, etc.
- Final report

The laboratory will be responsible for maintaining analytical logbooks and laboratory data. Raw laboratory data files will be inventoried and maintained by the laboratory.

6 CALIBRATION PROCEDURES AND FREQUENCY

This section describes the procedures for maintaining the accuracy of the instruments and measuring equipment, which will be used for conducting laboratory analyses. All instruments and equipment will be calibrated, or the calibration verified prior to each use or according to a periodic schedule.

Equipment used to gather, generate, or measure environmental data will be calibrated with sufficient frequency and in such a manner that accuracy and reproducibility of results are consistent with the manufacturer's specification.

Equipment to be used for the field sampling will be examined to certify its operating condition. This includes checking the manufacturing's operating manual and the instruction and the instructions for each instrument to ensure that maintenance requirements are being observed. Field notes from previous sampling trips will be reviewed so that the notations on any prior equipment problems are not overlooked.

6.1 Laboratory Instruments

Calibration of laboratory equipment will be conducted by SGS North America, Inc. in accordance with the Corporate Quality Assurance Plan that is incorporated by reference (available as needed) as Appendix A and the selected respective analytical method requirements described in Section 8.

7 ANALYTICAL PROCEDURES

The groundwater and associated QC samples collected for chemical analyses will be analyzed using the methods presented in Tables E-1, E-2, and E-3.

8 INTERNAL QUALITY CONTROL CHECKS AND FREQUENCY

This section presents the internal quality control checks and the frequency of the checks, which will be employed for field collection activities and laboratory analyses. Internal laboratory control checks used by the selected laboratory will demonstrate the ability of the laboratory to produce acceptable results for the selected analytical methods listed in Tables E-1 and E-2.

8.1 Field QC

Quality control of field sampling will involve collecting field duplicates in accordance with the applicable procedures and frequencies described in Section 4.2 and the level of effort indicated in Table 1.

8.2 Laboratory QC

Specific procedures related to internal laboratory QC samples (namely, matrix spikes, matrix spike duplicates, blanks, blind check samples and laboratory duplicates) are detailed in the following subsections.

The internal QC checks for the analyses will follow the appropriate methods specified in Table E-1 and the laboratory SOPs in Appendix A.

The data will be evaluated by SGS North America, Inc. based on the following criteria (as appropriate for organic and inorganic chemical analyses):

- Method performance is evaluated using the following QA checks:
    - Instrument tuning using appropriate compounds.
    - Calibration curve relative standard deviation, calibration curve linearity, or linear range.
    - Instrument sensitivity as measured by Relative Response Factors and contract required detection limit (CRDL) standard.
    - Laboratory blanks.
    - Continuing calibration standards, as %Recovery (%R) and %Difference (%D).
    - Spike recoveries (matrix and surrogate).
    - RPD between matrix spikes and matrix spike duplicates, samples and laboratory duplicates.
    - Recoveries of laboratory control samples and independent QC check samples.
- Percent recovery of internal standard.
- Adequacy of detection limits obtained.
- Precision of duplicate analyses.

Internal QC checks of sampling procedures and laboratory analyses will be conducted periodically. These checks will consist of the preparation and submittal of trip (travel) blanks, field duplicates and MS/MSD samples for analysis of all parameters at frequencies specified in Table E-1.

The above field QC blanks and duplicates included as internal QC checks are described below:

- Trip Blanks: A trip (travel) blank is a preserved sample container filled with organic-free water in the laboratory that travels unopened with the VOC sample containers to the site. One trip blank will be returned to the laboratory with each shipment containing samples designated for VOC analyses, opened in the laboratory, and analyzed along with the field samples for VOCs.
- Field Duplicate: A field duplicate is a blind duplicate sample prepared at the sampling location from equal portions of the material in which the sample was combined for collection. Both the blind field duplicate and the primary sample are collected at the same time, in the same container type, preserved in the same way, and analyzed by the same laboratory as a measure of sampling and analytical precision. Duplicates for VOC analysis will be collected first by completely filling with no headspace the sample containers. Field duplicates will be collected at a minimum frequency of one per twenty samples collected per parameter per sampling event. The identity of the blind field duplicate sample will be recorded in the sampling log and will not be disclosed to the laboratory.

8.2.1 Initial and Continuing Calibration Checks

The compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative data. The initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of an analysis run, while the continuing calibration checks document that the initial calibration is still valid and that satisfactory maintenance and adjustment of the instrument on a day-to-day basis is achieved. The specific control criteria and corrective action requirements for these calibrations will be as specified in the respective methods presented in Table E-1 and the SOPs presented in Appendix A.

8.2.2 MS/MSD Samples

MS/MSD (or MS/DUP) sample sets will be analyzed at a minimum frequency of one per twenty verification samples. Acceptance criteria and compounds that will be used for matrix spikes are identified in the SOPs presented in Appendix A. Percent spike recoveries will be used to evaluate analytical accuracy while relative percent difference between the duplicate analyses will be used to assess analytical precision. These field QC samples will be prepared in accordance with the previously described procedures used to collect the field duplicate samples.

8.2.3 Blind Check Samples

As supplied by IDEM (if deemed necessary by IDEM), an analytical batch may contain a blind check sample. In general, the blind check sample will be obtained from IDEM and supplied to ARCADIS for submittal to the analytical laboratory.

The percent recovery of analytes will be calculated from the results of the check samples as defined in Section 12.2.4.

9 DATA REDUCTION AND REPORTING

ARCADIS may validate the analytical data to verify that the laboratory has performed in accordance with the requirements specified by the QAPP. Groundwater samples may be validated in accordance with the *National Functional Guidelines for Organic Data Review* (U.S. EPA, 1999) and *National Functional Guidelines for Inorganic Data Review* (U.S. EPA, 2002) and the precision and accuracy statements included in the selected laboratories QAPP for the analytical methods employed.

With the exception of confirmatory closure sampling, the reporting level for the groundwater and associated QC samples will be Level III as defined in Section 2.6.

9.1 Data Reduction

Data reduction is the process of converting analytical data from electronic form or instrument form (i.e. reading the mercury on a graduated thermometer) into digital form and correcting for all sample weight, dilution factors, and percent solids calculations that may be applicable. This process is performed in the field and in the laboratory.

Raw data from field measurements and sample collection activities will be recorded in the field logbook and on applicable field log sheets.

The project laboratory may perform analytical data reduction in-house under the direction of the laboratory QA officer. The laboratory QA officer will be responsible for assessing data quality and advising ARCADIS of any data, which were qualified, based on laboratory QC criteria. Data reduction, review and reporting by the laboratory will be conducted as detailed in the following. It should be noted, however, that “sign-off” will be required following completion of each step.

1. Raw data produced and reduced by the responsible analyst is turned over for independent review by another analyst.
2. The area supervisor reviews the data for attainment of quality control criteria presented in the referenced analytical methods.
3. Upon completion of all reviews and acceptance of the raw data by the laboratory operations manager, a report will be generated and sent to the laboratory quality assurance officer.
4. The laboratory QA officer will complete a thorough inspection of all reports.
5. The laboratory QA officer and area supervisor will decide whether any sample re-analysis is required.
6. Upon acceptance of the preliminary reports by the laboratory QA officer, final reports will be generated and signed by the QA officer or his designee.

9.2 Data Reporting

The following information will be included in the data package for each sample where applicable:

General Information:

- The results of sample analysis
- The parameters of interest
- The method of analysis
- The detection limits of analysis
- For large numbers of samples per report, a master list of Laboratory tracking ID numbers correlated with field sample ID numbers and sample analysis batch identification to correlate QA samples to sample analysis batch.
- Sample collection date
- Sample receipt date
- Sample preparation/extraction date
- Sample analysis date
- Copy of the chain-of-custody form signed by the Laboratory sample custodian.
- A narrative summary identifying any QA or sample problems encountered, sample manipulation (dilutions), and the corrective action taken.

Organic Analyses. Gas Chromatography (GC): For analyses by GC, the following should be provided where applicable:

- Results of blanks: Water blanks (purgeables analysis); sample preparation extraction (method) blanks; trip blanks.
- Results of Reagent Water (blank) Spikes of the compounds of interest (matrix spike compounds), amounts spiked, percent recovery, and control limits.
- Results of initial and continuing calibration standards.
- Results of matrix spikes and calculated percent recovery, control limit, and source of control limits -- matrix spikes must be sample-specific for submitted sample batches.
- Results of matrix spike duplicates, calculated percent recoveries for matrix spike duplicate, RPD between matrix spike and matrix duplicate, and control limits; if matrix spike duplicate analyzed - matrix spike duplicates must be sample-specific for submitted sample batches.
- Results of laboratory duplicates, RPD, and control limits (lab duplicates must be sample-specific for samples submitted), if matrix spike duplicate not analyzed.
- Results of surrogate spikes, percent recoveries, and control limits;
- Results of blank spike analysis for organic matrix spike parameters not meeting matrix spike recovery requirements, amount spiked, percent recovery and control limits.
- Results of GC confirmation.

- Sample Chromatograms.

The following should be provided for analyses by Gas Chromatography/Mass Spectrometer (GC/Mass Spec.), where applicable:

- Results of GC/Mass Spec. tuning with 4-bromofluoro-benzene (BFB) or decafluorotriphenylphosphine (DFTPP).
- Mass spectral data for each sample.
- Results of initial and continuing calibration standards for all volatile organic compounds as appropriate, including results of system performance check compounds and calibration check compounds.
- Results of water blanks, extraction (method) blanks analysis and trip blanks.
- Results of matrix spike and matrix spike duplicates, percent recoveries, and control limits--matrix spikes must be sample-specific for submitted sample batches.
- Results of laboratory control sample, percent recoveries, and control limits.
- Results of surrogate spike recoveries, and control limits.
- Results of calculation of relative percent difference (RPD) between matrix spike/matrix spike duplicate and RPD control limits.
- Reconstructed ion chromatograms and quantitation reports (mass spectra not required).
- Internal Standard Summaries.
- Results of tentatively identified compounds, if requested.
- Results of blank spike analysis for matrix spike or matrix spike duplicate parameters not meeting recovery requirements, amount spiked, percent recovery and control limits.

The following applies to both inorganic and organic analysis, where applicable: To the extent possible, all samples that require a preparation step should be analyzed with their associated QC samples, e.g. run on the same instrument. It is not acceptable to process QC samples independent of all samples from that QC batch.

LABORATORY NON-REPORTABLES

All raw data not included under the reportables developed by the Laboratory during sample analysis must be maintained by the Laboratory as a record for a period of seven years.

NOTE: The non-reportable inorganic and organic information is not required to be submitted with the Laboratory report but should be available for audit review upon 30-days notice. The laboratory must have available documentation supporting the source of any control limits provided in laboratory reports.

Level III deliverables will be Contract Laboratory Program (CLP) protocol and deliverables. This includes CLP detection limits, control limits, and target compounds. If CLP deliverables are not specified, Level III deliverables will be interpreted to be "CLP-Like" deliverables. These will include all of the data specified and all applicable supporting raw data and quality control data. The exact deliverables for non-CLP Level III data will be agreed upon between ARCADIS and SGS North America, Inc.

The data packages will be stored with the evidentiary files as described in Section 5.6.

10 PERFORMANCE AND SYSTEM AUDITS

Performance and system audits of both field and laboratory activities may be conducted to verify that sampling and analyses are performed in accordance with the procedures established in the RRWP and Section 8.0.

10.1 Field Audits

Internal system audits of field activities (sampling and measurements) may be conducted by the ARCADIS QA/QC Manager and will consist of a review of the field operation's quality control system and procedures. The audits will include examination of field sampling records, sample collection, handling and packaging in compliance with the established procedures, maintenance of QA procedures and chain-of-custody. These audits will be conducted to correct deficiencies and to verify that QA procedures are maintained throughout the field activity. The audits will involve review of field measurement records, instrumentation calibration records and sample documentation.

10.2 Laboratory Audits

The internal performance and system audits of the laboratory may be conducted by the ARCADIS QA/QC Manager- Analytical Activities. The system audits, which may be conducted as deemed necessary by the Project Manager or the ARCADIS QA/QC Manager, will include examination of laboratory documentation of sample handling and receiving, sample log-in, sample storage, chain-of-custody procedures, records control, sample preparation and analysis and instrument operating records. The performance audits may be conducted on a quarterly basis and will include review of analyst work sheets, on-site analyst work, blind sample analysis review and analyst proficiency test sample analysis review. Blind QC samples may be prepared and submitted along with project samples to the laboratory for analysis throughout the project. The ARCADIS QA/QC Manager will evaluate the analytical results of these blind performance samples to ensure the laboratory maintains acceptable performance.

11 PREVENTIVE MAINTENANCE

This section describes preventative maintenance procedures for laboratory equipment. All analytical instruments to be used for this project will be serviced by the laboratory personnel at regularly scheduled intervals in accordance with the manufacturer's recommendations. Instruments may also be serviced at other times due to failure. Requisite servicing beyond the abilities of the laboratory personnel will be performed by the equipment manufacturer or its designated representative.

Daily checks of each instrument will be performed by the analyst who has been assigned responsibility for that instrument. The manufacturer's recommended procedures will be followed in every case. A summary of preventative and routine maintenance is provided in the laboratory QAPP incorporated by reference as Appendix A.

12 SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY AND COMPLETENESS

The following sections include the procedures and formulae utilized to assess the levels of precision, accuracy and completeness achieved during the associated sample analyses.

12.1 Laboratory Data

Laboratory results will be assessed for compliance with the required precision, accuracy, completeness and sensitivity as follows.

12.1.1 Precision

Precision is a measure of the reproducibility of a method, and it may be estimated by several statistical tests including the CV and the RPD between duplicate samples. For the purposes of this project, precision will be evaluated using the relative percent difference (RPD) for field duplicate sample and laboratory duplicate sample data (where applicable). A description of the calculation of RPD is presented in Section 12.2.5. The control limits for this calculation are generated by the selected laboratory for each constituent being analyzed and are presented in the laboratory QAPP (incorporated by reference as Appendix A). In instances where sufficient data are obtained, the arithmetic mean and standard deviation of a group of results may be calculated.

Precision then may be assessed by using the CV, which expresses the standard deviation as a percentage of the mean. Specific statistical comparison of duplicate samples (field and laboratory), as a measure of precision evaluating both sample collection procedures and laboratory instrument performance, may be accomplished by first comparing the obtained duplicate results with the published U.S. EPA criteria for method precision. If U.S. EPA criteria are not available, the RPD may be calculated and compared to the precision criteria established by the laboratory for the analysis of laboratory duplicates.

12.1.2 Analysis of Spiked Samples

Sample-specific and batch laboratory specific analytical precision for organic analytes will be evaluated by analyzing matrix spike/matrix spike duplicates (MS/MSD). Numerical objectives for the analytical precision (as RPD) of the organic and inorganic constituents being analyzed are included in the laboratory QAPP (Appendix A) and the analytical methods. The frequency of MSD sample analysis will be the same as for matrix spiking analysis. Specific procedures for MS/MSD preparation, analysis, and evaluation are included in the specific analytical method/SOP.

12.1.3 Analysis of Duplicate Samples

The overall precision of measurement data is a function of sampling and analytical factors. Sampling precision is unique to each site. Sampling precision will be evaluated by collecting and analyzing field duplicate samples. The analytical results from the collocated or field duplicate samples provide data on overall measurement precision; analysis results from the laboratory duplicates provide data on analytical

precision. Subtracting the analytical precision from the measurement precision provides an estimate of the sampling precision.

Analytical precision for inorganic constituents will be evaluated by analyzing laboratory duplicate samples. The frequency of laboratory duplicate sample analysis will be a minimum of one per 20 field samples per analytical method per sample media. Specific procedures for laboratory duplicate sample preparation, analysis, and evaluation are included in the specific analytical method/SOP. Numerical objectives for the analytical precision (as RPD) of the organic and inorganic constituents are included in the laboratory QAPP (Appendix A) and the analytical methods.

12.1.4 Accuracy

The accuracy of a method is an estimate of the difference between the true value and the determined mean value. Certain QA parameters, such as laboratory control samples, reagent water spike samples, QC check samples, matrix spike samples, and surrogate spike samples, all have known concentrations prior to analysis. By comparing the percent recovery of the analysis of these samples to the known true value, it is possible to measure the accuracy of the analysis.

In routine practice the laboratory collects recovery data for each of these parameters from approximately 20 to 30 analytical batches. The percent recovery data are averaged, and the standard deviation of the percent recoveries is calculated. Accuracy of laboratory results will be assessed for compliance with the established QC criteria that are described in Sections 4.0 and 9.0 of the QAPP using the analytical results of method blanks, reagent/preparation blanks, and matrix spike samples. The percent recovery (%R) of matrix spike samples will be calculated using the formula in Section 12.2.4, below.

Then, based on the desired level of confidence, ranges are established as practical control limits. To be valid, these control limits must be at least as stringent as the accuracy limits specified by U.S. EPA for each analyte measured by the method. If the determined control limits are within the range established for that analyte and method by U.S. EPA, then the determined range becomes the practical control limits used by the laboratory until another set of data is developed and new control limits are calculated. The initial control limits for the constituents being analyzed will be presented in the selected laboratories QAPP.

Specific statistical comparison of percent recovery values and control limits (DQOs) reported by the laboratory, as a measure of method accuracy will be compared with the published U.S. EPA criteria for the accuracy of an individual method. Data not meeting the U.S. EPA criteria for accuracy may be considered qualitative or possibly unusable.

Sampling accuracy will be assessed by evaluating the results of field/trip blanks, while analytical accuracy will be assessed through use of known and unknown quality control samples and matrix spike samples. The accuracy of data generated during this project will be expressed as percent recovery (%R). Procedures for calculating %R are described in Section 12.2.4. Numerical goals for laboratory accuracy are presented in the laboratory QAPP (Appendix A) and analytical methods.

12.1.5 Reference Materials

The primary reference materials used for assessing accuracy include spiking compounds for matrix spikes, laboratory control samples (LCS), and surrogate spiking compounds. The identities and acceptable sources of these materials are specified in the specific methods and analytical SOPs.

12.1.6 Instrument Performance

The measurement, evaluation, and control of instrument accuracy are covered in the specific laboratory SOPs/analytical methods.

12.1.7 Recovery of Surrogates

Specific organic surrogate spiking compounds and their respective control limits for recovery are given in the laboratory QAPP (Appendix A) and analytical methods. Surrogate spikes are not applicable for field-screening tests and inorganics analyses.

12.1.8 Recovery of Spiked Compounds

Matrix spikes will be prepared from samples of site environmental media (sample specific and batch laboratory specific). Field samples to be used as matrix spikes will be collected with additional sample volume and indicated on the chain-of-custody/laboratory analysis request forms. Specific recovery control limits for matrix spikes are given in the laboratory QAPP (Appendix A).

12.1.9 Completeness

Completeness will be assessed by comparing the number of valid (usable) results (as determined by the ARCADIS QA/QC Manager to the total possible number of results using the formula presented in Section 13.2. The required level of completeness for laboratory analyses will be 80 percent or greater. Should it be determined that the completeness requirement for the project has not been satisfied, the valid data will remain usable.

12.1.10 Sensitivity

The achievement of targeted quantitation limits depends on instrumental sensitivity and matrix effects. Therefore, it is important to monitor the instrumental sensitivity to ensure the data quality through consistent instrument performance. The instrumental sensitivity will be monitored through the analysis of method blanks and calibration check samples.

12.2 Statistical Evaluations

In the evaluation of data and determination of precision and accuracy, standard statistical formulae will be used.

12.2.1 Arithmetic Mean

The arithmetic mean is the average obtained by dividing a sum by the number of its addends. A number of recovery results are averaged together to improve the accuracy of the measurement. The equation below will be used to determine the arithmetic mean.

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

Where: n = number of measurements

X_i = value of the measurements

12.2.2 Standard Deviation

The standard deviation is the square root of the average squared difference between the individual values and the average value. A number of recovery results are evaluated to find the numerical variation in the data which is then used in the determination of the percent relative standard deviation. The formula below will be used to determine the standard deviation.

$$\sigma_{n-i} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}}$$

Where: n = number of measurements

X_i = value of the measurements arithmetic mean

12.2.3 Percent Relative Standard Deviation (%RSD)

The percent relative standard deviation (%RSD) is obtained by dividing the standard deviation of the values by the arithmetic mean of the values and multiplying by 100. The %RSD is calculated on a series of measurements to evaluate an instrument's analytical precision (e.g., initial calibration). The equation below summarizes the formula to be used to determine %RSD.

$$\%\ \text{RSD} = \frac{\sigma_{n-1}}{\bar{x}} \times 100$$

Where: σ_{n-1} = standard deviation

$\bar{X}$ = arithmetic mean

12.2.4 Percent Recovery (%R)

The percent recovery of a parameter is obtained by dividing the amount recovered by the true amount added and multiplying by 100. The percent recoveries of spiked samples are evaluated to establish the analytical accuracy of a measurement. The equation below will be used to determine the percent recovery.

$$5R = \frac{SSR - SR}{SA} \times 100$$ Where: SSR = spiked sample result

SR = sample result or background

SA = spike added

12.2.5 Relative Percent Difference (RPD)

The relative percent difference is obtained by dividing the difference between two numbers by their arithmetic mean and multiplying by 100. The RPD is used to evaluate the analytical precision of two duplicate measurements. The equation below will be used to determine RPD.

$$RPD = \left(\frac{|R_1 - R_2|}{\left[\frac{R_1 + R_2}{2} \right]} \right) \times 100$$

Where: R_1 = value of the first result

R_2 = value of the second result

13 CORRECTIVE ACTION

This section describes procedures for identifying and documenting corrective actions in the field and laboratory.

13.1 Field Corrective Actions

During this investigation, the field personnel are responsible for seeing that work progresses satisfactorily and is performed in compliance with the QAPP. The field personnel are also responsible for conducting routine maintenance and QC procedures, thereby ensuring collection of valid field data.

If a problem is detected by the field personnel, the Project Manager shall be notified immediately by the field personnel, at which time the problem will be investigated further, and corrective action will begin. Similarly, if a problem is identified during a routine audit by the Project Manager or QA Manager or representatives of the IDEM, an immediate investigation will be undertaken, and the corrective measures deemed necessary will be implemented as quickly as possible.

13.2 Laboratory Corrective Actions

Within time constraints imposed by individual analysis procedures, data evaluations necessary to verify proper analytical function must be performed as early as possible in the analysis program.

A preliminary check of standard curve linearity, precision, and sensitivity should be performed as soon as it is practical. For manual procedures, it is practical to check precision, standard curve linearity, and sensitivity immediately. For automated systems, the performance check will be done after the run has been completed. Results are compared to QA control limits established by the laboratory and U.S. EPA.

Any analysis not conforming to control limits for precision, accuracy, detection limit, or linearity will be halted until the problem is identified and corrected. Laboratory batch sheets and control charts will document data evaluations and will contain all information necessary for assessment of the data quality, including: (1) information regarding indices of sensitivity, (2) precision, (3) detection limit, and (4) accuracy achieved during that run or batch.

For out-of-control incidents, it is essential to document the nature of the incident and the corrective actions taken to set the system back in control. A corrective action report, to be signed by the laboratory director and the laboratory QA Officer, should be prepared and summarized in the narrative of the laboratory report. The following topics should be discussed:

- Where did the out-of-control incident occur (laboratory name, address, telephone number, section name)?
- When did the incident occur and when was it corrected?
- Who discovered the out-of-control incident, verified the incident, and corrected the problem?
- What was the method number and name of the test?
- What was the disposition of the test or control and/or instrument?
- What was the nature of the corrective action?

- What will be done to prevent the reoccurrence of the problem?
- Why did the incident happen (if scientific explanation is available)?

A copy of the subject control charts and other data describing the out-of-control conditions should be included in the corrective action report. All out-of-control incident documentation and copies of the corrective action reports should be placed in (1) the laboratory archive record for the sample(s) in question and (2) the laboratory QA Manager's file of incidents documentation.

If the periodic quality-control audits detect unacceptable conditions or data, the project director, QA Manager, and project manager are responsible for developing and initiating appropriate changes or modifications. The condition or problem will be specifically identified, recorded in the appropriate field log or project file, investigated, and the cause determined. Then, changes or modifications will be initiated to eliminate the problem. These may include:

- Re-analyzing samples if holding time and sample volume permit.
- Resampling and re-analyzing.
- Evaluating and amending sampling and/or analytical procedures.
- Accepting data, while documenting a level of uncertainty.

Upon implementation of changes or modifications, their effectiveness will be established, and elimination of the problem verified. Details regarding the changes or modifications implemented and the results will be documented and retained in the project file.

13.3 Reporting Corrective Actions

In all cases in which corrective actions of field procedures are required, a written report describing the nature of the problem, an evaluation of the cause, if known, and the action taken will be prepared by the senior field personnel or the QA Manager.

Any corrective actions taken by the contracted laboratories will be reported to the QA Manager. The laboratory will include in each data package a summary of the problems encountered and corrective actions taken. In addition, the laboratories will maintain a file for review that documents all corrective actions taken regardless of whether the actions performed were pertinent to the analysis of samples from this project. Reports of corrective actions taken during the implementation of this Work Plan will be provided to the IDEM.

The need for corrective action may be identified by system or performance audits or by standard QC procedures. The essential steps in the corrective action system will be:

1. Checking the pre-determined limits for data acceptability beyond which corrective action is required.
2. Identifying and defining problems.
3. Assigning responsibility for investigating the problem.
4. Investigating and determining the cause of the problem.

5. Determining a corrective action to eliminate the problem (this may include re-analyses or re-sampling and analyses).
6. Assigning and accepting responsibility for implementing the corrective action.
7. Implementing the corrective action and evaluating its effectiveness.
8. Verifying that the corrective action has eliminated the problem.
9. Documenting the corrective action taken.

For each measurement system, the analyst will be responsible for identifying the need for corrective action and initiating the corrective action procedure. The laboratory supervisor will be responsible for implementing the corrective action and evaluating its effectiveness. The laboratory QA Officer will be responsible for documenting the fact that the corrective action has resolved the problem. The corrective action taken will depend upon the QA/QC criteria that did not meet the necessary criteria and may range from qualifying the data to re-sampling. All problems requiring corrective action and the corrective action employed to resolve the problem will be reported. Field corrective action will consist of re-sampling and will be documented in the field logbook.

14 QUALITY ASSURANCE REPORT TO MANAGEMENT

Management will receive reports (if deemed necessary by IDEM) on the performance of the measurement system and data quality following each sampling round and at the conclusion of the project.

Minimally, these reports may address the following:

1. QA activities and quality of collected data (results of data validation).
2. Assessment of measurement quality indicators, i.e., data accuracy, precision and completeness.
3. Results of system audits.
4. QA problems, action taken and resolutions.

The QA/QC Manager will be responsible within the organizational structure for preparing these reports. The final report for the project will also include a separate QA section which will summarize data quality information contained in the periodic QA/QC reports to management, and details on overall data assessment and validation in accordance with the data quality objectives outlined in this QAPP. This report will state limitations on use of the measurement data.

15 ACRONYMS AND GLOSSARY

The following is an alphabetical list of definitions for terms and acronyms encountered in the QA/QC process or in interactions with organizations performing sampling, laboratory, or regulatory functions. Most, but not all, are referred to in the Guidelines below. Those not used are included for informational purposes.

Accuracy	The closeness of agreement between an observed value and an accepted reference value.
ACS	American Chemical Society
Appendix VII	RCRA Hazardous Constituents List. 40 CFR 261, Appendix VII
Appendix IX	RCRA Groundwater Monitoring List. 40 CFR 264, Appendix IX
ARARs	Applicable or Relevant and Appropriate Requirements
ASTM	American Society for Testing and Materials. Organization which develops and publishes standard methods of analysis and standards for materials and procedures. Also refers to standards published by society.
Batch	A group of samples of the same matrix from the same site, not to exceed twenty, and which are processed as a unit at the laboratory. If the total number of samples of a particular matrix from a site is more than 20, each group of twenty or fewer samples is treated as a separate batch.
Bias	The deviation, due to matrix effects, of the measured value of an analyte from the “true” value. In the laboratory, this is determined from the difference between the measured value of the analyte and the known spiked amount.
Blank	Special “samples” analyzed to determine if all or a portion of an analyte detected in an environmental sample is the result of external contamination due to handling or other factors in the field or the laboratory, and not actually representative of site conditions. See Equipment Blank, Method Blank, and Trip Blank.
BTEX	Benzene, toluene, ethylbenzene, and xylenes
Calibration	Routine QC procedures performed daily or more frequently to maintain the accuracy of analytical instruments or measuring equipment by adjusting instrument response to solutions of known concentrations or to know conditions to the appropriate value; preparation of analytical curve.

Calibration Standard	Standards prepared by successive dilution of a standard solution working standards covering the full concentration range required, and expected to be seen in the samples, for the organic or inorganic analytical method. Must be prepared using the same type of acid or solvent used to prepare samples for analysis.
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act of 1980, as amended (Superfund).
Continuing Calibration	Analytical standard run periodically, as specified by method, to verify calibration of system.
CLP	U.S. EPA's Contract Laboratory Program. Refers to laboratory specifications, analytical methods, ad QA/QC protocols required for Superfund and related activities.
CRDL	Contract Required Detection Limit. Method detection limit required for a given analyte in a given matrix in the CLP SOW; generally refers to inorganic analysis.
CRQL	Contract Required Quantitation Limit. Similar to CRDL but for organic analysis.
Control Sample	A QC sample introduced into a data collection process to monitor the performance of the system.
Data Quality Objectives	The quality of data and documentation required to support decisions made in the various phases of the data collection or cleanup project (e.g., screening, characterization, risk assessment, and monitoring). They are dependent on the end uses of the data to be collected and are expressed in terms of objectives for precision, accuracy, bias, and comparability.
DL	Detection Limit
DQOs	Data Quality Objectives (see above).
Duplicate	A split sample or an independent second sample taken from the same sample location for the purpose of documenting precision. See Field Duplicate, Matrix Duplicate, and Matrix Spike Duplicate.
Equipment Blank	Also called the Equipment Rinsate. A sample of analyte-free reagent water which has been used to rinse the sampling equipment. It is collected after completion of decontamination and prior to sampling at the next sample location. It is used to document adequate decontamination; to ensure that analytes from one sample location have not contaminated a sample from the next location.
Field Blank	Analyte-free reagent water taken to the sampling site, transferred into a sample container on-site and then analyzed by the laboratory for the same parameters as the investigative samples. This sample is used to check for procedural contamination of samples.

Field Duplicate	Independent samples which are collected from the same location or source, as closely as possible to the same point in space and time. They are stored in separate containers and analyzed separately for the purpose of documenting the precision of the sampling process. (Laboratory variability will also be introduced into the samples' results.)
FSP	Field Sampling Plan.
Hazardous Constituent	Compound or element designated as a constituent of hazardous waste in the RCRA program and listed in 40 CFR 261, Appendix VIII.
Hazardous Substance	Compound or element listed in CERCLA Hazardous Substance List, 40 CFR 302.
Hazardous Waste	Material (solid waste) listed as a hazardous waste by the RCRA program by meeting any of the criteria stated in 40 CFR 261.11.
HCl	Hydrochloric acid
HNO3	Nitric Acid
Holding Time	Elapsed time, expressed in days, from the date of sampling until the date of analysis.
Interference	An element, compound, or other matrix effect present in a sample which interferes with detection of a target analyte leading to inaccurate concentration results for the target analyte.
Internal Standards	Known compounds of known concentration added to a sample by the laboratory prior to analysis to assist in quantifying the target analytes.
Laboratory Control Sample	A known matrix spiked with compounds representative of the target analytes and used to document laboratory performance.
Matrix	The substrate containing the analyte of interest. Examples are soil, sediment, sludge, groundwater, surface water, drinking water, and air. Sometimes matrix types are condensed to soils, waters, and air.
Matrix Duplicate	A duplicate field sample used to document the precision of sampling and homogeneity of a given sample matrix (same as field duplicate).
Matrix Spike	An aliquot of sample spiked with a known concentration of target analytes for the purpose of documenting the bias of a method in a particular matrix. The spiking occurs prior to sample preparation and analysis.
Matrix Spike Duplicate	A split sample, both portions of which are spiked with identical concentrations of target analytes, for the purpose of determining the bias and precision of a method in a particular sample matrix.
MCL	Maximum Contaminant Level. Maximum concentration of a contaminant allowed in drinking water systems by the National Primary Drinking Water regulations: 40 CFR 141.11 (inorganic chemicals) and 141.12 (organic chemicals).
Method Blank	An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method

	blank is carried through the complete sample preparation and analytical procedure and is used to document contamination resulting from the analytical process. (Also called Reagent Blank or Preparation Blank.)
Method Detection	The minimum concentration of an analyte that can be measured and reported with 99% confidence. It is determined by analysis of a sample with known concentrations at various dilutions. This limit is matrix-specific (i.e., soils vs. waters).
MS/MSD	Matrix Spike/Matrix Spike Duplicate (see above).
Organic-Free Reagent Water	For volatile analysis. Water prepared so that interferants or contaminants are observed below the method detection limit of the compounds of interest. Methods of preparation include passing tap water through a carbon filter containing about one pounds of activated carbon or using a water purification system to generate organic-free deionized water.
PAH	Polynuclear Aromatic Hydrocarbon
Precision	The agreement among a set of duplicate measurements without consideration of the “true” or accurate value; variability between measurements of the same material for the same analyte.
Preparation	The process used by the lab to prepare a sample for analysis.
Priority Pollutants	List of inorganic and organic analytes commonly tested for in the NPDES (water) program.
Project	Single or multiple data collection activities (or remediation activities) that are related through the same planning sequence.
QA	Quality Assurance (see below).
QAPP	Quality Assurance Project Plan.
QC	Quality Control (see below).
Quality Assurance	The management procedures and controls used to ensure data quality through the sampling and analysis stages. Sometimes refers to the entire QA/QC program.
Quality Control	The day-to-day operational measures used in the field during sampling and in the laboratory during analysis to ensure data quality.
RAS	Routine Analytical Services. Analytical procedures used exactly as written in the CLP SOW and used in the Superfund program.
RCRA	The Resource Conservation and Recovery Act of 1976, as amended.
Reagent Blank	Same as Method Blank (see above).
Reagent Grade	Chemical reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society. Also referred to as Analytical Reagent (AR) grade and ACS reagent grade.

Reagent Water	For analysis of inorganics. Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water.
Reference Material	A material containing known quantities of target analytes in solution or in a homogeneous matrix. Sometimes referred to as a "standard." It is used to document the bias of the analytical process.
Relative Percent Difference	A measurement of precision which compares the measurement of a target analyte, spiked analyte, or surrogate to a identical measurement in a duplicate sample. Especially used when sample population is small.
RRWP	Revised Remediation Work Plan
SAP	Sampling and Analysis Plan. Site-specific plan detailing sampling rationale and protocols and analyses planned per sample type.
SAS	Special Analytical Services. Used by the CLP to denote non-standard or specialized analytical protocols, perhaps requiring method development.
SOW	Statement of Work. A detailed procedure.
Spike	A known volume of a solution of target analyte(s) of known concentration added to a sample before analysis and used to document bias and accuracy in inorganic analyses. Also called analytical spike.
Split Samples	Aliquots of sample taken from the same container and analyzed independently, usually after mixing or compositing. They are used to document precision.
Standard Addition	The practice of adding a known amount of an analyte to a sample immediately prior to analysis used to evaluate interferences.
Standard Curve	A plot of concentrations of known analyte standards versus the instrument response to the analyte.
Surrogate	An organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Used to document bias and accuracy in organic analyses.
SW-846	U.S. EPA "Test Methods for Evaluating Solid Waste," 1986 (Third Edition), plus updates. Standard methods of analysis, sampling techniques, and QA/QC procedures.
TCL	Target Compound List. Organic compounds (BTEX, PAHs, Metals) included in the CLP SOW OLM01.8 as Routine Analytical Services.
Trip Blank	A sample of analyte-free media (organic-free reagent water) taken from the laboratory to the sampling site and returned to the laboratory unopened and analyzed. It is used to document contamination resulting from migration of volatile organic compounds during shipping an field handling.

VOA	Volatile Organic Analysis.
VOC	Volatile Organic Compound
VRP	Voluntary Remediation Program

TABLES

Table E-1. Sample Matrices, Analytical Parameters, and Frequencies of Sample Collection
Quality Assurance Project Plan
Former Indiana Creosoting Company
Bloomington, IN

Soil Sampling

Sample Matrix	Laboratory Parameters/ US EPA Method	US EPA Method / Method (where applicable)	Sampling Technique	Number of Samples	Trip Blanks(*)	Field Duplicates(*)	MS/MSD Sets(*)
Soils	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Quarterly Groundwater Sampling

Groundwater	VOCs (BTEX only)	SW-846 8260B	low-flow sample pump or bailer	1 per quarter	1 per cooler	1 per 20	1 per 20
Groundwater	PAHs, Phenolic Compounds, Phthalates	SW-846 8270D SIM	low-flow sample pump or bailer	1 per quarter	N/A	1 per 20	1 per 20
Groundwater	Total Metals (lead and arsenic only)	SW-846 6010C	low-flow sample pump or bailer	1 per quarter	N/A	1 per 20	1 per 20
Groundwater	Dissolved Metals (lead and arsenic only)	SW-846 6010C	low-flow sample pump or bailer	1 per quarter	N/A	1 per 20	1 per 20

Notes:
* - Indicates number of samples to be collected
MS/MSD - Matrix Spike and Matrix Spike Duplicate
Triple sample volume to be submitted for MS/MSD samples

Table E-2. Primary Constituents of Concern (COCs), Analytical Methods, and Practical Quantitation Limits
Quality Assurance Project Plan
Former Indiana Creosoting Facility
Bloomington, IN

Target Compound	Analytical Method	Practical Quantitation Limit (PQL) Groundwater (mg/L)
Benzene	SW-846 8260B	0.005
Arsenic	SW-846 6010C	0.01
Lead	SW-846 6010C	0.005
Carbazole	SW-846 8270D SIM	0.0054
Dibenzofuran	SW-846 8270D SIM	0.0054
Pentachlorophenol	SW-846 8270D SIM	0.0011
Naphthalene	SW-846 8270D SIM	0.11
Phenanthrene	SW-846 8270D SIM	0.0011
2-Methlynaphthalene	SW-846 8270D SIM	0.11

Notes:
mg/L - milligrams per liter (ppm)

Table E-3. Sample Volume, Preservation, and Holding Times for Groundwater and Soil, and Associated QC Samples
Quality Assurance Project Plan (QAPP)
Former Indiana Creosoting Facility
Bloomington, IN

Groundwater

Analyses	Matrix	Sample Container	Sample Preservative	Maximum Holding Time from Sample Collection*	Sample Volume
VOCs (BTEX only)	Water and QC (Trip Blanks, Field Duplicates, MS/MSD)	3-40 ml glass vial w/ Teflon lined lids	HCL	14 Days for Extraction and Analysis	40 ml/ vial - Fill completely with no headspace
PAHs, Phenolic Compounds, Phthalates	Water and QC (Field Duplicates, MS/MSD)	2-1 L glass jar w/ Teflon lined lids	Unpreserved	7 Days for Extraction and Analysis	Fill to neck of jar
Total Metals (lead and arsenic only)	Water and QC (Field Duplicates, MS/MSD)	1-250 ml polyethlyene jar	HNO3	180 Days for Extraction and Analysis	Fill to neck of jar
Dissolved Metals (lead and arsenic only)	Water and QC (Field Duplicates, MS/MSD)	1-250 ml polyethlyene jar	Unpreserved	180 Days for Extraction and Analysis	Fill to neck of jar

Soil

Analyses	Matrix	Sample Container	Sample Preservative	Maximum Holding Time from Sample Collection*	Sample Volume
N/A	N/A	N/A	N/A	N/A	N/A

Notes:
Triple volumes are required for MS/MSD samples

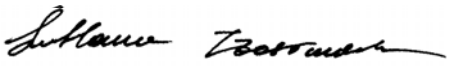
APPENDIX A

SGS North America, Inc. Laboratory Quality Assurance Plan & SOPs

Quality Systems Manual

Volume XIV, Revision I: November 2019

Caitlin Brice, General Manager, Technical Director



Svetlana Izosimova, Ph.D., Quality Assurance Officer

SGS North America, Inc. - Orlando.
4405 Vineland Road, Suite C-15
Orlando, Florida 32811
407.425.6700

The SGS North America, Inc - Orlando (acceptable designation is **SGS - Orlando**) Quality Assurance Program, detailed in this plan, has been designed to meet the quality program requirements of the National Environmental Laboratories Accreditation Conference (TNI), DoD QSM Ver 5.3, 2019, and ISO 17025. The plan establishes the framework for documenting the requirements of the quality processes regularly practiced by the Laboratory. The Quality Assurance Officer is responsible for changes to the Quality Assurance Program, which are appended to the Laboratory Quality Systems Manual (LQSM) as they occur. The plan is reviewed annually for compliance purposes by the General Manager and Technical Director and edited if necessary. Changes that are incorporated into the plan are summarized in the plan introduction. Changes to the plan are communicated to the general staff in a meeting conducted by the Quality Assurance Officer following the plan's approval.

The SGS - Orlando plan is supported by standard operating procedures (SOPs), which provide specific operational instructions on the execution of each quality element and assure that compliance with the requirements of the plan are achieved. SGS - Orlando employees are responsible for knowing the requirements of the SOPs and applying them in the daily execution of their duties. These documents are updated as changes occur and the staff is trained to apply the changes.

At SGS - Orlando, we believe that satisfying client requirements and providing a product that meets or exceeds the standards of the industry is the key to a good business relationship. However, client satisfaction cannot be guaranteed unless there is a system that assures the product consistently meets its design requirements and is adequately documented to assure that all procedural steps are executed and are traceable.

This plan has been designed to assure that this goal is consistently achieved and the SGS - Orlando product withstands the rigors of scrutiny that are routinely applied to analytical data and the processes that support its generation.

SGS - Orlando is a permanent location facility and is part of SGS, North America, Inc. (SGS-NAM), Environmental Health and Safety (EHS) Division

Summary of Changes
SGS - Orlando Quality System Manual –November 2019

Section	Description	Page #
Entire document	Updated DoD QSM references to 5.3 and TNI to 2016	
Title Page	new revision number	Title
OrgChart	Updated OrgChart,	8
Entire document	replaced CEO/President with VP of EHS	
4	Updated Inorganics Supervisor duties and removed Metals Supervisor	19
Entire Document	Added Technical Director responsibilities to General Manager	
5	Updated signatory approvals	22
6	LQSM and SOP distribution procedure updated	25
8.4	MDL procedure update	33
App II	Updated methods and methods' revisions.	Entire section
App III	Updated instrumentation list	89

Table of Contents

Appendices

QUALITY POLICY

SGS North America, Inc. - Orlando Mission:

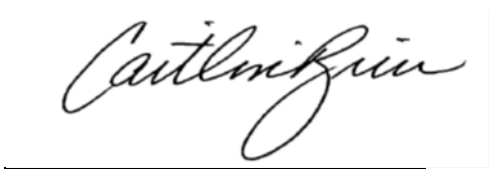
SGS - Orlando provides analytical services to commercial and government clients in support of environmental monitoring and remedial activities as requested. The Laboratory's mission is dedicated to providing reliable data that satisfies the client's requirements as explained in the following: "Provide easy access, high quality, analytical support to commercial and government clients which meet or exceeds data quality objectives and provides them with the data needed to satisfy regulatory requirements and/or make confident decisions on the effectiveness of remedial activities."

These services are provided impartially and are not influenced by undue commercial or financial pressures, which might impact the staff's technical judgment. Coincidentally, SGS - Orlando does not engage in activities that endanger the trust in our independent judgment and integrity in relation to the testing activities performed.

***Policy Statement*:**

The management and staff of SGS - Orlando share the responsibility for product quality and continually strive for its systematic improvement. Accordingly, SGS Orlando's quality assurance program is designed to assure that all processes and procedures, which are components of environmental data production, meet established industry requirements, are adequately documented from a procedural and data traceability perspective, and are consistently executed by the staff. It also assures that analytical data of known quality, meeting the quality objectives of the analytical method in use and the data user's requirements, is consistently produced in the laboratory. This assurance enables the data user to make rational, confident, cost-effective decisions on the assessment and resolution of environmental issues.

The laboratory Quality System also provides the management staff with data quality and operational feedback information. This enables them to determine if the laboratory is achieving the established quality and operational standards, which are dictated by the client or established by regulation, such as TNI, ISO 17025 or DoD QSM 5.3 revisions. The information provided to management, through the QA program, is used to assess operational performance from a quality perspective and to perform corrective action as necessary.



Caitlin Brice, General Manager

ORGANIZATION

Organizational Entity. SGS - Orlando, Inc. is a testing laboratory founded in 1956 and registered as a New Jersey Corporation. In 2016 the laboratory has changed ownership to SGS - Orlando Inc, while operations, staff and physical locations were not affected by the change, and fully transitioned into SGS North America, Inc. as of January 2018. SGS NAM headquarters are located in Rutherford, New Jersey.. Satellite laboratories are maintained in Dayton, New Jersey; Syracuse, New York; Wilmington, North Carolina; Anchorage, Alaska; Orlando, Florida; Denver, Colorado; Lafayette, Louisiana; and Houston, Texas.

Legal designations of the individual facilities follow SGS - North America, Inc – Location convention, i.e. SGS - North America, Inc. – Orlando. Legal designation of the laboratory must be used on all certification and licensure documentation. It is acceptable to display abbreviated regional designation on documents other than certificates and licenses. Example – data report from Orlando facility may be branded SGS - Orlando.

Management Responsibilities

Requirement: Each laboratory facility will have an established chain of command. The duties and responsibilities of the management staff are linked to the VP of SGS - North America, Inc, EHS division who establishes the agenda for all company activities.

VP of EHS North America. Primarily responsible for all operations and business activities. Delegates authority to laboratory directors, laboratory managers, and quality assurance director to conduct day-to-day operations and execute quality assurance duties. Each of the individual operational entities (New Jersey, New York, North Carolina, Alaska, Florida, Colorado, Louisiana, and Texas) reports to the VP of EHS.

Corporate Quality Assurance Director. Responsible for design, oversight, and facilitation of all quality assurance activities established by the Quality Program. Directly reports to the VP of EHS.

Chief Information Officer: Maintains and develops LIMS and various EDD formats to suit clients' requests. Maintains cyber security and confidentiality. Delegates daily LIMS operation to local labs.

Laboratory Director/General Manager. A Laboratory Director/General Manager is assigned to each of the following operational entities: New York, Alaska, North Carolina, New Jersey, Florida, Louisiana, Texas, and Colorado. The Laboratory Director executes day-to-day responsibility for laboratory operations including technical aspects of production activities and associated logistical procedures. The Laboratory Director reports directly to the VP of EHS.

Quality Assurance Officer *(on location).* Responsible for oversight, implementation and facilitation of all quality assurance activities established by the Quality Program. Reports to the Corporate QA Director. Also exchanges information with and submits laboratory performance data (PE scores, audit reports, accreditation changes, etc.) with Laboratory Director/General Manager. Takes program directions from Corporate QA Director.

Technical Director. Responsible for oversight and implementation of all technical aspects of production activities in the environmental testing laboratory, including method development and compliance. Laboratory Director/General Manager is designated as Technical Director on location.

In the event that the technical director, quality assurance officer, or laboratory director is absent for a period of time that exceeds 15 consecutive calendar days, the designated appointees shall temporarily perform the technical director, quality assurance officer's, or laboratory director's job function. If this absence exceeds 65 consecutive calendar days, the Accreditation Body(ies), including DoD ELAP, will be notified in writing. Current list of appointed deputies located in restricted access controlled document directory.

Project Manager/Customer Service Manager: primary contact for clients requesting laboratory services. Evaluates and processes client specifications for routine and non-routine analytical services. Identifies, evaluates, and documents the requested specifications to determine if adequate resources are available to perform the analysis. Communicates the specifications to the laboratory staff for execution and verifies that specifications have been executed.

Purchasing Manager (Corporate): Evaluates vendors of services and supplies following established policies. Procures services and supplies. Maintains purchasing documentation and database.

Department Supervisor*.* Executes day-to-day responsibility for specific laboratory areas including technical aspects of production activities and associated logistical procedures. Orders consumable supplies, inspects supplies upon receipt. Directly reports to the Technical Director and Laboratory Manager.

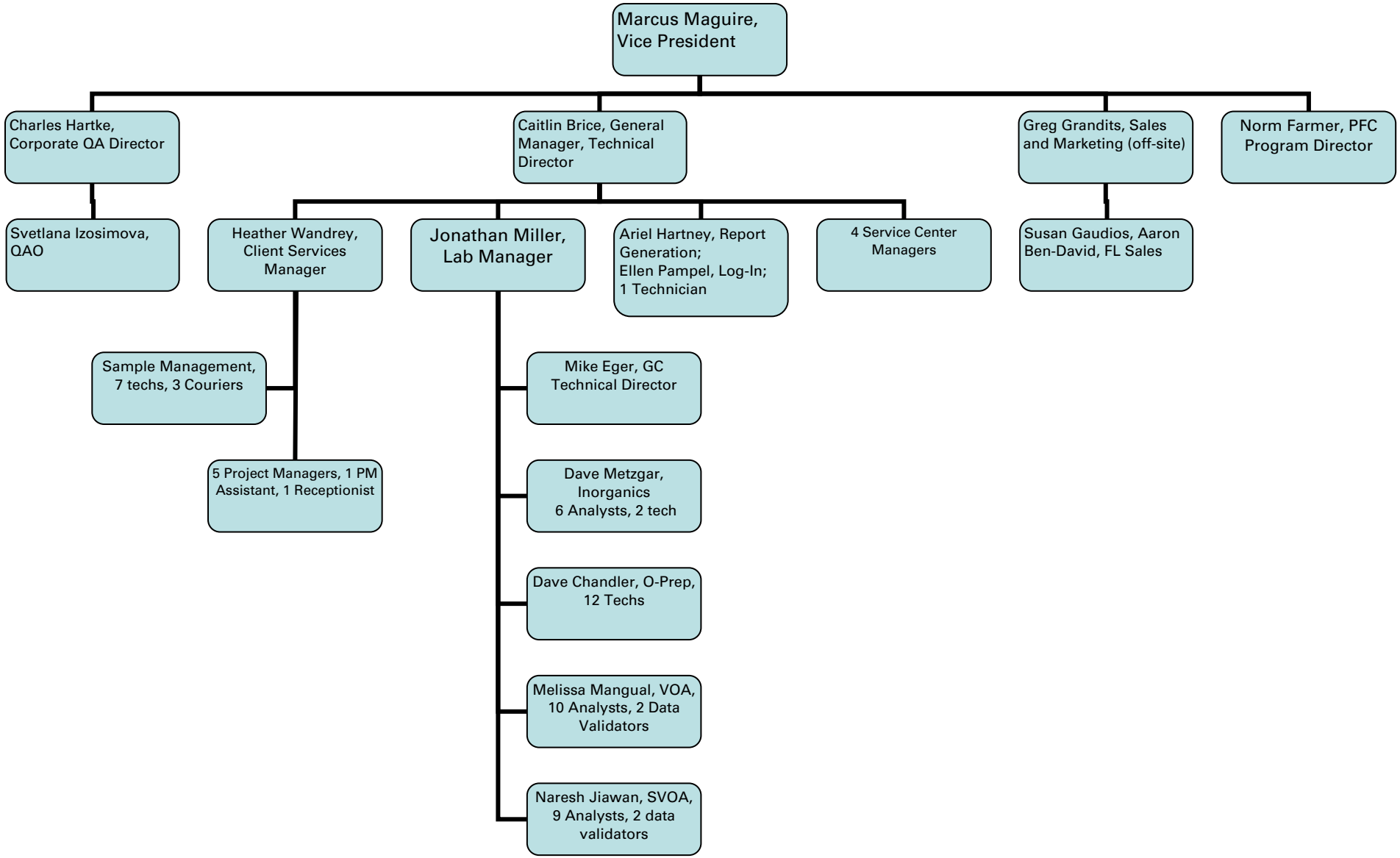
Team Leader*.* Executes day-to-day responsibility for specific laboratory units including technical aspects of production activities and associated logistical procedures. Directly report to the Department Supervisor.

Chain of Command

The responsibility for managing all aspects of the Company's operation is delegated to specific individuals, who have been assigned the authority to act in the absence of the senior staff. These individuals are identified in the following Chain of Command:

Caitlin Brice, General Manager (Operations)
Heather Wandrey, Client Service Manager

SGS - Orlando Organizational Chart



QUALITY RESPONSIBILITIES OF THE MANAGEMENT TEAM

***Requirement*:** Each member of the management team has a defined responsibility for the Quality Program. Program implementation and operation is designated as an operational management responsibility. Program design and implementation is designated as a Quality Assurance Responsibility.

VP of SGS EHS North America*:* Primary responsibility for all quality activities. Delegates program responsibility to the Quality Assurance Director. Serves as the primary alternate in the absence of the Quality Assurance Director. Has the ultimate responsibility for implementation of the Quality Program.

Laboratory Director/General Manager*.* Responsible for implementing and operating the Quality Program in all laboratory areas. Responsible for the design and implementation of corrective action for defective processes. Has the authority to delegate Quality Program implementation responsibilities.

Corporate Quality Assurance Director*.* Responsible for design, implementation support, training, and monitoring of the quality system. Identifies product, process, or operational defects using statistical monitoring tools and processes audits for elimination via corrective action. Empowered with the authority to halt production if warranted by quality problems. Monitors implemented corrective actions for compliance.

Quality Assurance Officer *(on location).* Responsible for design support, implementation support, and monitoring support of the quality system. Training personnel in various aspects of quality system. Conducts audits and product reviews to identify product, process, or operational defects using statistical monitoring tools and processes audits for elimination via corrective action. Empowered with the authority to halt production if warranted by quality problems. Monitors implemented corrective actions for compliance.

Technical Director. Responsible for oversight and implementation of technical aspects of Quality System as they are integrated into method applications and employed to assess analytical controls on daily basis. The Technical Director reviews and acknowledges the technical feasibility of proposed quality system involving technical applications. Empowered with the authority to halt production if warranted by quality problems.

Laboratory Manager. Responsible for oversight and implementation of various aspects of Quality System as they are integrated into method applications and employed to assess analytical controls on daily basis. The Laboratory Manager reviews and acknowledges the technical and logistical feasibility of proposed quality system involving technical applications. Empowered with the authority to halt production if warranted by quality problems.

Department Supervisors. Responsible for applying the requirements of the Quality Program in their section and assuring subordinate supervisors and staff apply all program requirements. Initiates, designs, documents, and implements corrective action for quality deficiencies.

Team Leaders. Responsible for applying the requirements of the Quality Program to their operation and assuring the staff applies all program requirements. Initiates, designs, documents, and implements corrective action for quality deficiencies.

Bench Analysts. Responsible for applying the requirements of the Quality Program to the analyses they perform, evaluating QC data and initiating corrective action for quality control deficiencies within their control. Implements global corrective action as directed by superiors.

Program Authority:

Authority for program implementation on corporate level originates with the VP of EHS North America who bears ultimate responsibility for program design, implementation, and enforcement of requirements. This authority and responsibility is delegated to the Director of Quality Assurance who performs quality functions independently without the encumbrances or biases created by operational or production responsibilities to ensure an honest, independent assessment of quality issues.

Laboratory Director/General Manager and Quality Assurance Officer mirror this authority on location.

Data Integrity Policy:

The SGS - Orlando Data Integrity Policy reflects a comprehensive, systematic approach for assuring that data produced by the laboratory accurately reflects the outcome of the tests performed on field samples and has been produced in a bias free environment by ethical professionals. The policy includes a commitment to technical ethics, staff training in ethics and data integrity, an individual attestation to data integrity and procedures for evaluating data integrity. Senior management assumes the responsibility for assuring compliance with all technical ethics elements and operation of all data integrity procedures. The staff is responsible for compliance with the ethical code of conduct and for practicing data integrity procedures.

The SGS - Orlando Data Integrity Policy is as follows:

"SGS - Orlando is committed to producing data that meets the data integrity requirements of the environmental regulatory community. This commitment is demonstrated through the application of a comprehensive data integrity program that includes ethics and data integrity training, data integrity evaluation procedures, staff participation and management oversight. Adherence to the specifications of the program assures that data provided to

our clients is of the highest possible integrity and can be used for decision making processes with high confidence."

Data Integrity Responsibilities

***Management*.** Senior management retains oversight responsibility for the data integrity program and retains ultimate responsibility for execution of the data integrity program elements. Senior management is responsible for providing the resources required to conduct ethics training and operate data integrity evaluation procedures. They also include responsibility for creating an environment of trust among the staff and being the lead advocate for promoting the data integrity policy and the importance of technical ethics.

***Staff*.** The staff is responsible for adhering to the company ethics policy as they perform their duties and responsibilities associated with sample analysis and reporting. By executing this responsibility, data produced by SGS - Orlando retains its high integrity characteristics and withstands the rigors of all data integrity checks.

The staff is also responsible for adhering to all laboratory requirements pertaining to manual data edits, data transcription and data traceability. These include the application of approved manual peak integration and documentation procedures. It also includes establishing traceability for all manual results calculations and data edits.

***Ethics Statement*.** The SGS - Orlando ethics statement reflects the standards that are expected for businesses that provide environmental services to regulated entities and regulatory agencies on a commercial basis. The Ethics Policy is comprised of key elements that are essential to organizations that perform chemical analysis for a fee. As such, it focuses on elements related to personal, technical and business activities.

SGS - Orlando provides analytical chemistry services on environmental matters to the regulated community. The data the company produces provides the foundation for determining the risk presented by a chemical pollutant to human health and the environment. The environmental industry is dependent upon the accurate portrayal of environmental chemistry data. This process is reliant upon a high level of scientific and personal ethics.

It is essential to the Company that each employee understands the ethical and quality standards required to work in this industry. Accordingly, SGS - Orlando has adopted a code of ethics, which each employee is expected to adhere to as follows:

- Perform chemical and microbiological analysis using accepted scientific practices and principles.
- Perform tasks in an honest, principled and incorruptible manner inspiring peers & subordinates.
- Maintain professional integrity as an individual.
- Provide services in a confidential, honest, and forthright manner.

- Produce results that are accurate and defensible.
- Report data without any considerations of self-interest.
- Comply with all pertinent laws and regulations associated with assigned tasks and responsibilities.

Data Integrity Procedures.

Four key elements comprise the SGS - Orlando data integrity system:

1) data integrity training,

2) signed data integrity documentation for all laboratory employees,

3) in-depth, periodic monitoring of data integrity, and

4) data integrity procedure documentation.

Procedures have been implemented for conducting data integrity training and for documenting that employees conform to the SGS – Orlando Data Integrity and Ethics policy.

The data integrity program consists of routine data integrity evaluation and documentation procedures to periodically monitor and document data integrity. These procedures are documented in SOPs. SOPs are approved and reviewed annually following the procedures employed for all SGS - Orlando SOPs. Documentation associated with data integrity evaluations is maintained on file and is available for review.

Data Integrity Training. SGS – Orlando employees receive technical ethics training during new employee orientation. Employees are also required to attend annual ethics refreshment training and sign an ethical conduct agreement annually, which verifies their understanding of SGS – Orlando's technical ethics policy and their ethical responsibilities. The agreement is refreshed annually and appended to each individual's training file.

The training focuses on the reasons for technical ethic training, explains the impact of data fraud on human health and the environment, and illustrates the consequences of criminal fraud on businesses and individual careers. Multiple examples of prohibited practices are reviewed and discussed. SGS - Orlando's ethics policy and code of ethics are reviewed and explained for each new employee.

Training on department-specific data integrity procedures are conducted by individual departments for groups involved in data operations. These include procedures for manual chromatographic peak integration, standards traceability, etc.

Data Integrity Training Documentation. Records of all data integrity training are maintained in individual training folders. Attendance at all training sessions is documented and appended to the training file.

SGS - Orlando Data Integrity and Ethical Conduct Agreement. All employees are required to sign a Data Integrity and Ethical Conduct Agreement annually – See Appendix VI This document is archived in individual training files, which are retained for duration of employment.

Data Integrity Monitoring. Several documented procedures are employed for performing data integrity monitoring. These include regular data review procedures by supervisory and management staff (Section 12.7), supervisory review and approval of manual integrations and periodic reviews of data audit trails from the LIMS and all computer controlled analysis.

Data Review. All data produced by the laboratory undergoes several levels of review, which includes two levels of management review. Detected data anomalies that appear to be related to data integrity issues are isolated for further investigation. The investigation is conducted following the procedures described in this section.

Manual Peak Integration Review and Approval. Routine data review procedures for all chromatographic processes includes a review of all manual chromatographic peak integrations. This review is performed by the management staff and consists of a review of the machine integration compared to the manual integration. Manual integrations, which have been performed in accordance with SGS - Orlando's manual peak integration procedures are approved for further processing and release. Manual integrations which are not performed to SGS - Orlando's specifications are set aside for corrective action, which may include analyst retraining or further investigation as necessary.

Data Audit Trail Review. Data integrity audits are comprehensive data package audits that include a review of raw data, process logbooks, processed data reports and data audit trails from individual instruments and LIMS. Data audit trails, which record all electronic data activities, are available for the majority of computerized methodology and the laboratory information management system (LIMS). These audit trails are periodically reviewed to determine if interventions performed by technical staff constitute an appropriate action. The review is performed on a recently completed job and includes interviews with the staff that performed the analysis. Findings indicative of inappropriate interventions or data integrity issues are investigated to determine the cause and the extent of the anomaly.

Confidential Reporting Of Data Integrity Issues. Data integrity concerns may be raised by any individual to their supervisor. Employees with data integrity concerns should always discuss those concerns with their immediate supervisors as a first step unless the employee is concerned with the confidentiality of disclosing data integrity issues or is uncomfortable discussing the issue with their immediate supervisors. The supervisor makes an initial assessment of the situation to determine if the concern is

related to a data integrity violation. Those issues that appear to be violations are documented by the supervisor and referred to the QA Officer (local) for investigation.

Documented procedures for the confidential reporting of data integrity issues in the laboratory are part of the data integrity policy. These procedures assure that laboratory staff can privately discuss ethical issues or report items of ethical concern without fears of repercussions with senior staff.

Employees with data integrity concerns that they consider to be confidential are directed to the Human Resources Specialist in Dayton, New Jersey. The HR Specialist acts as a conduit to arrange a private discussion between the employee and the Corporate QA Director or a local QA Officer.

During the employee - QA discussion, the QA representative evaluates the situation presented by the employee to determine if the issue is a data integrity concern or a legitimate practice. If the practice is legitimate, the QA representative clarifies the process for the employee to assure understanding. If the situation appears to be a data integrity concern, the QA representative initiates a Data Integrity Investigation following the procedures specified in SOPs QA038-QA041.

Data Integrity Investigations. Follow-up investigations are conducted for all reported instances of ethical concern related to data integrity. Investigations are performed in a confidential manner by senior management according to a documented procedure. The outcome of the investigation is documented and reported to the VP of EHS who has the ultimate responsibility for determining the final course of action in the matter. Investigation documentation includes corrective action records, client notification information and disciplinary action outcomes, which is archived for a period of five years.

The investigations are conducted by the senior staff and supervisory personnel from the affected area. The investigation team includes the Laboratory Director and the Quality Assurance Officer. Investigations are conducted in a confidential manner until it is completed and resolved.

The investigation includes a review of the primary information in question by the investigations team. The team performs a review of associated data and similar historical data to determine if patterns exist. Interviews are conducted with key staff to determine the reasons for the observed practices.

Following data compilation, the investigations team reviews all information to formulate a consensus conclusion. The investigation results are documented along with the recommended course of action.

Corrective Action, Client Notification & Discipline. Investigations that reveal systematic data integrity issues will go through corrective action for resolution and disposition (Section 13). If the investigation indicates that an impact to data has

occurred and the defective data has been released to clients, client notification procedures will be initiated following the steps in Section 17.6.

In all cases of data integrity violations, some level of disciplinary action will be conducted on the responsible individual. The level of discipline will be consistent with the violation and may range from retraining and/or verbal reprimand to termination.

JOB DESCRIPTIONS OF KEY STAFF

***Requirement*:** Descriptions of key positions within the organization must be defined to ensure that clients and staff understand duties and the responsibilities of the management staff and the reporting relationships between positions.

VP of EHS. Responsible for all company EHS division operations and business activities. Establishes the company mission and objectives in response to business needs. Direct supervision of the Vice President of Operations, each laboratory director, client services, management information systems, and Corporate quality assurance.

Laboratory Director/General Manager. Reports to the VP of EHS. Establishes regional laboratory operations strategy and business development. Authorized to enter into contractual agreements on Company's behalf. Directs the day-to-day operations of entire laboratory, direct supervision of organic chemistry, inorganic chemistry, field services, and sample management. Oversees daily work schedule as developed by respective departments. Supervises method implementation. Responsible for following Quality Program requirements. Maintains laboratory instrumentation in an operable condition.

Director, Quality Assurance. Reports to the VP of EHS. Establishes the company quality agenda, develops quality procedures, provides assistance to operations on quality procedure implementation, coordinates all quality control activities monitors the quality system and provides quality system feedback to management to be used for process improvement.

Vice President, Information Technologies Reports to the VP of EHS. Develops the MIS software and hardware agenda. Provides system strategies to compliment company objectives. Maintains all software and hardware used for data handling.

Client Services, Sales, Account Manager(s). Reports to the VP of EHS. Establishes and maintains communications between clients and the laboratory pertaining to client requirements which are related to sample analysis and data deliverables. Initiates client orders and supervises sample login operations.

Quality Assurance Officer *(on location)*. Reports to the Corporate QA Director. Develops quality procedures, provides assistance to operations on quality procedure implementation, coordinates all quality control activities, monitors the quality system, and provides quality system feedback to management to be used for process improvement. In the event of prolonged absence QAO also designated a Deputy Technical Director, unless otherwise specified by internal memo from Laboratory Director.

Manager Client Services *(on location)*. Reports to the Laboratory Director. Establishes and maintains communications between clients and the laboratory

pertaining to client requirements which are related to sample analysis and data deliverables. Initiates client orders and supervises sample login operations.

Technical Director (*on Location***)**. Laboratory Director/General Manager is designated Technical Director. Establishes laboratory operations strategy. Direct supervision of organic chemistry and inorganic chemistry. Directs the operations, preparation and instrumental analysis. Responsible for following Quality Program requirements. .

Supervisors, Shipping and Receiving Departments. Reports to the Laboratory Director. Develops, maintains and executes all procedures required for transport and receipt of samples, verification of preservation, and chain of custody documentation. Responsible for maintaining and documenting secure storage, delivery of samples to laboratory units on request, and disposal following completion of all analytical procedures.

Supervisor, Inorganics. Reports to the Laboratory Director. Directs the operations of the General Chemistry and Metals group. Establishes and executes daily work schedule. Supervises method implementation, application, and data production. Supervises the analysis of samples for Inorganics parameters using valid, documented methodology. Maintains instrumentation in an operable condition. Reviews data for compliance to quality and methodological requirements. Responsible for following Quality Program requirements.

requirements. Responsible for following Quality Program requirements

Supervisor, Organic Preparation. Reports to the Laboratory Director. Directs the operations of the sample preparation group. Establishes and executes daily work schedule. Supervises method implementation, and application. Supervises the preparation of samples for organic compounds using valid, documented methodology. Documents all procedures and data production activities. Maintains laboratory equipment in an operable condition. Reviews records for compliance to quality and methodological requirements. Responsible for following Quality Program requirements.

Volatile and Semivolatie Supervisors, Organics. Reports to the Laboratory Director. Directs the operations of the respective organics group. Establishes and executes daily work schedule. Supervises method implementation, application, and data production. Supervises the analysis of samples for organic compounds using valid, documented methodology. Documents all procedures and data production activities. Maintains instrumentation in an operable condition. Reviews data for compliance to quality and methodological requirements. Responsible for following Quality Program requirements

Report Generation Supervisor. Reports to Laboratory Director. Oversees report generation and fulfillment of client specifications as applied to data deliverables. Responsible for data delivery in timely manner.

Detailed Job descriptions of lab personnel are found in training folders

4.2 ***Employee Screening, Orientation, and Training***.

All potential laboratory employees are screened and interviewed by human resources and technical staff prior to their hire. The pre-screen process includes a review of their qualifications including education, training and work experience to verify that they have adequate skills to perform the tasks of the job. Minimum qualifications for non-technical personnel require High School diploma (couriers also must posses clean driving record), technical personnel must also demonstrate basic laboratory experience, such as balance and syringe use, aseptic practices, etc. College-level science coursework is favored.

Newly hired employees receive orientation training beginning the first day of employment by the Company. Orientation training consists of initial health and safety training and a detailed review of the personal protection policies, technical ethics and data integrity procedures training (for detailed description refer to Sec. 3.3) and quality assurance program training (including Company's goals, objectives, mission, and vision).

All technical staff receives training to develop and demonstrate proficiency for the methods they perform. New analysts work under supervision until the supervisory staff is satisfied that a thorough understanding of the method is apparent. Organics/Inorganics analysts are required to demonstrate method proficiency through a precision and accuracy study (Demonstration of Capability). Data from the study is reviewed by appropriate technical supervisor and compared to method acceptance limits. If the data is unacceptable, additional training is required. The analyst must also demonstrate the ability to produce acceptable data through the analysis of an independently prepared proficiency sample.

Proficiency is demonstrated annually. Data from initial and continuing proficiency demonstration is archived in the individual's training folder. In the instance where analyte can not be spiked in the clean matrix, such as TSS or pH, the results of an external Performance Evaluation (PE) sample may be used to document analyst's proficiency.

Minimum training required for administrative staff consists of laboratory safety and ethical conduct.

4.3 ***Training Documentation***. The QA Officer prepares a training file for every new employee. All information related to qualifications, experience, external training courses, and education are placed into the file. Verification documentation for orientation, health & safety, quality assurance, and ethics training is also included in the file.

Additional training documentation is added to the file as it occurs. This includes data for initial and continuing demonstrations of proficiency, performance evaluation study data and notes and attendance lists from group training sessions.

The Quality Assurance Department also maintains the employee training database – SGS - Orlando University. This database is a comprehensive inventory of training documentation for each individual employee. The database enables supervisors to obtain current status information on training data for individual employees on a job specific basis. It also enables the management staff to identify training documentation in need of completion.

Employee specific database records are created by QA Staff on the date of hire. Reports are produced which summarize the qualifications of individual employees or departments.

SIGNATORY APPROVALS

Requirement: Procedures are required for establishing the traceability of data and documents. The procedure consists of a signature hierarchy, indicating levels of authorization for signature approvals of data and information within the organization. Signature authority is granted for approval of specific actions based on positional hierarchy within the organization and knowledge of the operation that requires signature approval. A log of signatures and initials of all employees is maintained for cross-referencing purposes.

Signature Hierarchy.

Vice-President of EHS North America. Authorization for contracts and binding agreements with outside parties up to $150,000. Contract signature authority in excess of $150,000 resides with Executive VP of EHS Global in Geneva, Switzerland.

Laboratory Director/General Manager (however named). Authorization for binding agreements with outside parties up to $25,000. General Manager may also sign non-binding agreements such as work authorizations, purchase orders, confidentiality agreements, etc. Approval of final reports and quality assurance policy. Approval of project-specific QAPs. Review and approval of technical and quality systems policies (LQSM). In the event of prolonged absence refer to list of approved deputies – sec 2.2.

Technical Director: Approval of final reports and quality assurance policy in the absence of the Laboratory Director. Approval of SOPs, project specific QAPs. Review and approval of technical and quality systems policies (LQSM). In the event of prolonged absence refer to list of approved deputies – sec 2.2.

Director, Quality Assurance. Approval of final reports and quality assurance policy in the absence of the President. Approval of SOPs, project specific QAPs, data review and approval in lieu of technical managers.

Quality Assurance Officer (on location). Approval of final reports and quality assurance policy in the absence of the Laboratory Director. Approval of SOPs, project specific QAPs, data review and approval in lieu of technical managers. In the event of prolonged absence refer to list or appointed deputies – see sec. 2.2.

Manager, Sample Management. Initiation of laboratory sample custody and acceptance of all samples. Approval of department policies and procedures. Department specific supplies purchase. Waste manifesting and disposal.

Project Manager, Client Services. QAP and sampling and analysis plan approval. Project specific contracts, pricing, and price modification agreements. Approval and acceptance of incoming work, Client services policy.

Supervisors, Technical Departments. Data review and approval, department specific supplies purchase. Technical approval of SOPs.

Signature Requirements. All laboratory activities related to sample custody and generation or release of data must be approved using either initials or signatures. The individual, who applies his signature or initial to an activity or document, is authorized to do so within the limits assigned to them by their supervisor. All signatures and initials must be applied in a readable format that can be cross-referenced to the signatures and initials log if necessary.

Signature and Initials Log. The QA Officer maintains a signature and initials log. New Employee signatures and initials are appended to the log on the first day of employment. Electronic signatures are appended to Electronic signature log. Signature of individuals no longer employed by the company are retained**.**

DOCUMENTATION and DOCUMENT CONTROL

Requirement: Document control policies have been established which specify that any document used as an information source or for recording analytical or quality control information must be managed using defined document control procedures. Accordingly, policies and procedures required for the control, protection, and storage of any information related to the production of analytical data and the operation of the quality system to assure its integrity and traceability have been established and implemented in the laboratory. The system contains sufficient controls for managing, archiving and reconstructing all process steps, which contributed to the generation of an analytical test result. Using this system, an audit trail for reported data can be produced, establishing complete traceability for the result.

> **Administrative Records**. The Quality Assurance Officer manages Administrative (non-analytical) records. These records consist of electronic documents that are retained in a limited access electronic directory, which are released to the technical staff upon specific request.

Form Generation & Control. The Quality Assurance Officer approves all forms used as either stand-alone documents or in logbooks to ensure their traceability. Forms are generated as computer files only and maintained in a limited access master directory. Access to the electronic forms and applications is granted to QA Officer, Laboratory Manager and Technical Director(s) (local and regional). Approved forms must display the date of current revision and initials of person who revised the form. Modifications to existing forms are approved by QA, obsolete forms moved to archive directory and retained for minimum of five years.

New forms must include SGS - Orlando identification and appropriate spaces for signatures of approvals and dates. Further design specifications are the responsibility of the originating department.

Technical staff is required to complete all forms to the maximum extent possible. If information for a specific item is unavailable, the analyst is required to cross out the information block. The staff is also required to cross out the uncompleted portions of a logbook or logbook form if the day's analysis does not fill the entire page of the form.

Logbook Control. All laboratory logbooks are controlled documents that are comprised of approved forms used to document specific processes. Logbook control is maintained by QA staff.

New logs are numbered and issued to a specific individual who is assigned responsibility for the log. Supervisor performs periodical review of the logbooks. Old logs are returned to QA for entry into the document archive system where they are retained for minimum of five (5) years. Laboratory staff may hold a maximum of two consecutively dated logbooks of the same type in the laboratory, not including the most recently issued book to simplify review of recently completed analysis.

Controlled Documents. Key laboratory documents are designated for controlled document status to assure that identities of individuals receiving copies and the number of copies that have been distributed are known. Controlled status simplifies document updates and **retrieval** of outdated documents. Control is maintained through a document numbering procedure and document control logbook designating the individual receiving the controlled document. Document control is also maintained by pre-designating the numbers of official copies of documents that are placed into circulation within the laboratory.

Quality Systems Manual (QSM). QSMs distributed to outside entities are considered tracked documents – since there is no possibility of collecting them back and ensuring that current revision is in use. These situations include bid submissions, client requests, etc. These copies can be watermarked as "Uncontrolled Documents". The date of distribution, and identity of the individual receiving the document are captured in the digital communications.

Standard Operating Procedures (SOPs). SOPs are maintained by pre-designating the numbers of official copies of documents that are placed into circulation within the laboratory. Official documents are printed and placed into the appropriate laboratory section as follows:

Sample Management: One copy for the sample receiving file, copy may be electronic
Bottle preparation area – One copy for shipping area, copy may be electronic
Organics Laboratories: One for each affected laboratory area. Copy may be electronic.
Inorganics Laboratories: One for each affected laboratory area. Copy may be electronic.

The original, signed copy of the SOP is maintained in the master SOP binder by the QA staff.

Documents are controlled using an "Official Copy" stamp in red ink. Additional copies could be issued to individuals for training purposes. Distribution is documented on SOP cover page. Superseded copies collection is conducted accordingly to cover page distribution list.

SOPs distributed to clients as part of bid submission, pre-audit evaluation, etc. can be watermarked as "Proprietary Information".

Quick reference cards: These documents are compiled for lab staff convenience and are based on current SOP revision and/or recent regulatory updates. These one- or two-sided documents are footnoted with reference to SOP/regulatory standard, stamped with "Official Copy" stamp in red ink and laminated for durability. ***Use of these quick references does not substitute reading and acknowledging the parent SOP.***

Operators' Manuals are considered controlled documents and stored in appropriate departments. QA staff maintains current listing of Operator's manuals.

Technical Records. All records related to the analysis of samples and the production of analytical results are archived in secure document storage or on electronic media and contain sufficient detail to produce an audit trail, which re-creates the analytical result. These records include information related to the original client request, bottle order, sample login and custody, storage, sample preparation, analysis, data review and data reporting.

Records that cannot be maintained on electronic media are considered irretrievable records, segregated into separate secured storage and access controlled with access log maintained by QA Staff. Examples of such records are employee training files, obsolete SOPs and acknowledgement form originals, training files, logbooks, etc.

Each department involved in this process maintains controlled documents, which enable them to maintain records of critical information relevant to their department's process.

Quality Assurance Directory. All Quality Assurance documentation and quality control limit data is stored in a restricted QA directory on the network server. The directory has been designated as read only. The QA staff, technical director and the laboratory manager have write capability in this directory. Information on this directory is backed-up weekly.

This directory contains all current and archived Quality System Manuals, SOPs, control limits, MDL studies, precision and accuracy data, internal and external audit reports, official forms, Health and Safety materials, PT scores, State Certifications and metrics calibration information.

Analytical Records. All data related to the analysis of field samples are retained as either paper or electronic records that can be retrieved to compile a traceable audit trail for any reported result. All information is linked to the client job and sample number, which serves as a reference for all sample related information tracking.

Critical times in the life of the sample from collection through analysis to disposal are documented. This includes date and time of collection, receipt by the laboratory, preparation times and dates, analysis times and dates and data reporting information. Analysis times are calculated in hours for methods where holding time is specified in hours (≤72 hours).

Sample preparation information is recorded in a separate controlled logbook or on controlled forms in three-ring binder. It includes sample identification numbers, types of analysis, preparation and cleanup methods, sample weights and volumes, reagent lot numbers and volumes and any other information pertinent to the preparation procedure.

Information related to the identification of the instrument used for analysis is permanently attached to the electronic record. The record includes an electronic data file that indicates all instrument conditions employed for the analysis, including the type of analysis conducted. The analyst's identification is electronically attached to the record. The instrument tuning and calibration data is electronically linked to the sample or linked though paper logs, which were used in the documentation of the analysis. Quality control and performance criteria are permanently linked to the paper archive or electronic file.

Paper records for the identity, receipt, preparation and evaluation of all standards and reagents used in the analysis are documented in prepared records and maintained in controlled documents or files. Lot number information linking these materials to the analysis performed is recorded in the logbooks associated with the samples in which they were used.

Manual calculations or peak integrations that were performed during the data review are retained as paper or electronically generated PDF documents and included as part of the electronic archive. Signatures for data review are retained on paper or as electronic stamps on PDF versions of the paper record for the permanent electronic file.

Confidential Business Information (CBI). Operational documents including SOPs, Quality Manuals, personnel information, internal operations statistics, and laboratory audit reports are considered confidential business information. Strict controls are placed on the release of this information to outside parties.

Release of CBI to outside parties or organizations may be authorized upon execution of a confidentiality agreement between SGS - Orlando and the receiving organization or individual. CBI information release is authorized for third party auditors and commercial clients in electronic mode as Adobe Acrobat .PDF format only.

Software Change Documentation & Control. Changes to software are documented as text within the code of the program undergoing change. Documentation includes a description of the change, reason for change and the date the change was placed into effect. Documentation indicating the adequacy of the change is prepared following the evaluation by the user who requested the change.

Report and Data Archiving. SGS - Orlando maintains electronic image file copies of original reports in archive for a minimum period of five (5) years. After five years, the files are automatically discarded unless contractual arrangements exist which dictate different requirements. Client specific data retention practices are employed for government organizations such as the Department of Defense Agencies and MA DEP that require a retention period of ten (10) years, as well as commercial clients upon contractual requirements agreement.

Complete date and time stamped client reports are generated from LIMS using the source documents archived on Document server. These source documents are

maintained on document server and backed up to removable primary and clone hard drives. SGS - Orlando archives the original report (organized by job number) and the organic and inorganic support data. Organic support data is archived according to instrument batch numbers and datafile. All organics data is backed up to an archive drive via Baculla backup software and/or AccuBack backup software. Data from the archive drive is then written to removable hard drives at periodic intervals. Drives are cloned for an offsite archival.

Wet chemistry support data is archived by analytical batch (GN…). Metals support data is archived by instrument batch (MA…). Metals digestion data is archived as digestion logbooks. Additionally all Wet chemistry and Metals data is scanned to PDF and archived electronically.

The reports generation group electronically scans completed reports and stores them by job number on the document server. The document server is backed up daily to a removable hard drive. Copies of these files remain active on the document server for easy review access. The removable hard drives remain in secure storage for the remainder of the archive period.

Training. Ongoing training ensures competence of all relevant personnel. At the minimum personnel should possess knowledge of the technology used in the testing, general requirements expressed in legislature and industry standards, and understand the significance of deviations with regard to approved procedures. The company maintains a training record for all employees that documents that they have received instruction on administrative and technical tasks that are required for the job they perform. Training records for individuals employed by the company are retained for a period of five years following their termination of employment.

Training File Origination. The Quality Assurance Officer (QAO) initiates training files. Quality Assurance officer retains the responsibility for the maintenance and tracking of all training related documentation in the file. The file is started on the first day of employment. Information required for the file includes a copy of the individual's most current resume, detailing work experience and a copy of any college diplomas or transcript(s), if applicable. Information added on the first day includes documentation of health and safety training and a signed Ethics and Data Integrity agreement. Classroom content is standardized across entire SGS - Orlando network and administered using SGS - Orlando University database. Safety and Ethics training constitute minimal necessary training for Project Management and Administrative staff. Analyst training documentation, training requirements, analyst proficiency information and other training related support documentation is tracked using a customized database applications. Database extracts provide an itemized listing of specific training requirements by job function. Training status summaries for individual analysts portray dates of completion for job specific training requirements.

Technical Training. The supervisor of each new employee is responsible for developing a training plan for each new employee. The supervisor updates the outline, adding signatures and dates as training elements are completed at regular

frequency. Supporting documentation, such as precision and accuracy studies, which demonstrate analyst capability for a specific test, are added as completed. When analyte can not be spiked, such as pH or TSS, external PE sample is purchased and analyzed. Where no external PE sample is available, sample duplicates must be successfully analyzed. Method review records are retained where analysis of duplicates is not possible. Employees and supervisors verify documentation of understanding (DOU) for all assigned standard operating procedures in the training files. Certificates or diplomas for any off-site training are added to the file.

7.0 REFERENCE STANDARD TRACEABILITY

Requirement: Documented procedures, which establish traceability between any measured value and a national reference standard, must be in place in the laboratory. All metric measurements must be traceable to NIST reference weights or thermometers that are calibrated on a regular schedule. All chemicals used for calibration of a quantitative process must be traceable to an NIST reference that is documented by the vendor using a certificate of traceability. The laboratory maintains a documentation system that establishes the traceability links. The procedures for verifying and documenting traceability must be documented in standard operating procedures.

Traceability of Metric Measurements - Thermometers. SGS – Orlando uses NIST-traceable thermometers to calibrate commercially purchased working laboratory thermometers prior to their use in the laboratory and annually thereafter for liquid in glass thermometers or quarterly for electronic temperature measuring devices. If necessary, these working thermometers are assigned correction factors that are determined during their calibration using an NIST-traceable thermometer as the standard. The correction factor is documented in a thermometer log and on a tag attached to the working thermometer. Both original observation and corrected measurement are recorded in the temperature log. The NIST-traceable reference thermometer is checked for accuracy by an outside vendor minimum every five (5) years following the specifications for NIST-traceable thermometer calibration verification detailed in the United States Environmental Protection Agency's "Manual for the Certification of Laboratories Analyzing Drinking Water", Fifth Edition, January 2005. Currently the NIST thermometer is verified by outside vendor on triennial basis due to contract-specific requirements. Calibration log and Certificate(s) of calibration are maintained on file with QAO.

Traceability of Metric Measurements – Calibration Weights. SGS – Orlando uses calibrated weights, which are traceable to NIST standard weights to calibrate all balances used in the laboratory. Balances must be calibrated to specific tolerances within the intended use range of the balance. Calibration checks are required on each day of use. If the tolerance criteria are not achieved, corrective action specified in the balance calibration SOP must be applied before the balance can be used for laboratory measurements. All weights are recalibrated by outside vendor every five years following the specifications for weight calibration verification detailed in the United States Environmental Protection Agency's "Manual for the Certification of Laboratories Analyzing Drinking Water", Fifth Edition, January 2005. Certificate(s) of calibration are maintained on file with QAO. Balances are inspected and maintained by professional service technicians annually. Certificate(s) of inspection are maintained with QAO.

Traceability of Chemical Standards and Reagents. All chemicals and reagents, purchased as reference standards for use in method calibration must establish traceability to NIST referenced material through a traceability certificate (Certificate of Analysis, CoA). Process links are established that enable a calibration standard

solution to be traced to its NIST reference certificate. Solvents, acids and other supplies are being tested to verify their suitability for the analytical process.

Assignment Of Reagent and Standard Expiration Dates. Expiration date information for all purchased standards and reagents is provided to SGS – Orlando with all prepared standard solutions and unstable reagents as a condition of purchase. Neat materials and inorganic reagents are not required to be purchased with expiration dates. Certified prepared solutions are labeled with the expiration date provided by the manufacturer. In-house prepared solutions are assigned expiration dates that are consistent with the method that employs their use unless documented experience indicates that an alternate date can be applied. If alternate expiration dates are employed, their use is documented in the method SOP. Expiration dates for prepared inorganic reagents, which have not exhibited instability, are established at two years form the date of preparation for tracking purposes. All containers shall be labeled with the date of preparation and expiration date clearly indicated.

The earliest expiration date is always the limiting date for assigning expiration dates to prepared solutions. Expiration dates that are later than the expiration date of any derivative solution or material are prohibited.

Documentation of Traceability. Traceability information is documented in individual logbooks designated for the measurement process in use. The QA Officer maintains calibration documentation for metric references in pertinent folders and logbooks.

Balance calibration verification is documented in logbooks that are assigned to each balance. The individual conducting the verification is required to initial and date all calibration activities. Any defects that occur during verification are also documented along with the corrective action applied and a demonstration of return to control. Annual service and calibration reports and certificates retained on file with QA staff.

Temperature control is documented in logbooks assigned to the equipment being monitored. A verified (see 7.1) thermometer is assigned to each individual item. Measurements are recorded along with date and initials of the individual conducting the measurement on a daily or as used basis. Corrective action, if required, is also documented including the demonstration of return to control.

Initial traceability of chemical standards and reagents is documented via a vendor-supplied certificate (see also 7.3) that includes lot number and expiration date information. Solutions prepared using the vendor supplied chemical standards are documented in logbooks assigned to specific analytical processes. Alternatively, documentation may be entered into the electronic standards and reagent tracking log The documentation includes links to the vendors lot number, an internal lot number, dates of preparation, and the preparer's initials. Standards received without certificate of analysis can not be used for calibration or calibration verification and are rejected.

Supervisors conduct regular reviews of logbooks, which are verified using a word rev'd", signature and date. QA Staff monitors the process and documents it in the same manner.

TEST PROCEDURES, METHOD REFERENCES, AND REGULATORY PROGRAMS

Requirements: The laboratory must use client specified or regulatory agency approved methods for the analysis of environmental samples. The laboratory maintains a list of active methods, which specifies the type of analysis performed, and cross-references the methods to applicable environmental regulation. Routine procedures used by the laboratory for the execution of a method must be documented in a standard operating procedure. Method performance and sensitivity must be demonstrated annually where required. Defined procedures for the use of method sensitivity for data reporting purposes must be established by the Director of Quality Assurance and used consistently for all data reporting purposes.

Method Selection. SGS - Orlando employs methods for environmental sample analysis that are consistent with the client's application, which are appropriate and applicable to the project objectives. SGS – Orlando informs the client if the method proposed is inappropriate or outdated and suggests alternative approaches.

SGS - Orlando employs documented, validated regulatory methods in the absence of a client specification and informs the client of the method selected. These methods are available to the client and other parties as determined by the client. Documented and validated in-house methods may be applied if they are appropriate to the project. The client is informed of the method selection.

Method Validation. Standard methods from regulatory sources are primarily used for all analysis. Standard methods do not require validation by the laboratory. Non-standard, in-house methods are validated prior to use. Validation is also performed for standard methods applied outside their intended scope of use. Validation is dependent upon the method application and may include analysis of quality control samples to develop precision and accuracy information for the intended use. A final method validation report is generated, which includes all data in the validation study. A statement of adequacy and/or equivalency is included in the report. A copy of the report is archived in the quality assurance directory of the company server.

Non-standard methods are validated prior to use. This includes the validation of modified standard methods to demonstrate comparability with existing methods. Demonstrations and validations are performed and documented prior to incorporating technological enhancements and non-standard methods into existing laboratory methods used for general applications. The demonstration includes method specific requirements for assuring that significant performance differences do not occur when the enhancement is incorporated into the method. Validation is dependent upon method application and may include the analysis of quality control samples to develop precision and accuracy information for intended use.

The study procedures and specifications for demonstrating validation include comparable method sensitivity, calibration response, method precision, method accuracy and field sample consistency for several classes of analytical methods are

detailed in this document. These procedures and specifications may vary depending upon the method and the modification.

Standard Operating Procedures. Standard operating procedures (SOP) are prepared for routine methods executed by the laboratory and processes related to sample or data handling. The procedures describe the process steps in sufficient detail to enable an individual, who is unfamiliar with the procedure to execute it successfully. SOPs are reviewed annually and edited if necessary. SOPs can be edited on a more frequent basis if systematic errors dictate a need for process change or the originating regulatory agency promulgates a new version of the method. Procedural modifications are indicated using a revision number. SOPs are available for client review at the SGS - Orlando facility upon request.

Method Detection Limit Determination and verification. Continuous method detection limit (MDL) studies are performed as appropriate for routine methods used in the laboratory. MDL studies are also performed when there is a change to the method that affects how the method is performed or when an instrumentation change that impacts sensitivity occurs. The procedure used for determining MDLs is described in 40 CFR, Part 136, Appendix B, revision 2, December 2016. Studies are performed for each method on water, soil and air matrices for every instrument that is used to perform the method. MDLs are established at the instrument level. The highest MDL of the pooled instrument data is used to establish a laboratory MDL. MDLs are experimentally verified through the analysis of spiked quality control samples at 2-3 times the concentration of the experimental MDL, or 1-4 times for multicomponent methods. The verification is performed on every instrument used to perform the analysis. The quality assurance staff manages the continuous MDL determination process and is responsible for retaining MDL data on file. Approved MDLs are appended to the LIMS and used for data reporting purposes. MDL values are used as DL values for DOD projects and verification spiking concentrations are listed as LOD values.

Methods certified under DOD ELAP requirements must undergo verification procedure on quarterly basis – see DOD QSM 5-series,Volume 1, Module 4, 1.5.2.1.g)

Method Reporting Limit. The method reporting limit is established at the lowest concentration calibration standard in the calibration curve. The low calibration standard is selected by department managers as the lowest concentration standard that can be used while continuing to meet the calibration linearity criteria of the method being used. The validity of the Method Reporting Limits is confirmed via analysis of a spiked quality control sample at 1 – 2x Method reporting limit concentration. RL values are referred to as LOQ for DOD projects.

By definition, detected analytes at concentrations below the low calibration standard cannot be accurately quantitated and must be qualified accordingly.

Methods certified under DOD ELAP requirements must undergo verification procedure on quarterly basis – see DOD QSM 5.0 and 5.1,Volume 1, Module 4, 1.5.2.2.e).

Reporting of Quantitative Data. Analytical data for all methods is reported without qualification to the reporting limit established for each method. Data may be reported to MDL depending upon the client's requirements provided that all qualitative identification criteria for the parameter have been satisfied. All parameters reported at concentrations between the reporting limit and MDL are qualified as an estimated concentration.

Measured concentrations of detected analytes that exceed the upper limit of the calibration range are either diluted into the range and reanalyzed or qualified as an estimated value. The only exception to this applies to ICP and ICP/MS analysis, which can be reported to the upper limit of the experimentally determined linear range without qualification.

Estimated Uncertainty. A statement of the estimated uncertainty of an analytical measurement accompanies the test result when required. Estimated uncertainty is derived from the performance limits established for spiked samples of similar matrices. The degree of uncertainty is derived from the negative or positive bias for spiked samples accompanying a specific parameter. When the uncertainty estimate is applied to a measured value, the possible quantitative range for that specific parameter at that measured concentration is defined. Well recognized regulatory methods that specify values for the major sources of uncertainty and specify the data reporting format do not require a further estimate of uncertainty.

Precision and Accuracy Studies. Annual precision and accuracy (P&A) studies, which demonstrate the laboratories ability to generate acceptable date, are performed for all routine methods used in the laboratory. The procedure used for generating P&A data is referenced in the majority of the regulatory methodology in use. The procedure requires quadruplicate analysis of a sample spiked with target analytes at a concentration in the working range of the method. This data may be compiled from a series of existing blank spikes or laboratory control samples. Accuracy (percent recovery) of the replicate analysis is averaged and compared to established method performance limits. Values within method limits indicate an acceptable performance demonstration. (See also Sec 4, Training, Demonstration of capability)

Method Sources, References and Update Mechanism. The Quality Assurance Staff maintains a list of active methods used for the analysis of samples. This list includes valid method references such as EPA, American Society of Testing and Materials (ASTM) or Standard Methods designations and the current version and version date.

Updated versions of approved reference methodology are placed into use as changes occur. The Quality Assurance Director informs operations management of changes in method versions as they occur. The operations management staff selects an implementation date. The operations staff is responsible for completing all method requirements prior to the implementation date. This includes modification to SOPs, completion of MDL and precision and accuracy studies and staff training. Documentation of these activities is provided to the QA staff who retains this

information on file. The updated method is placed into service on the implementation date and the old version is de-activated.

Multiple versions of selected methods may remain in use to satisfy client specific needs. In these situations, the default method version becomes the most recent version. Client specific needs are communicated to the laboratory staff using method specific analytical codes, which clearly depict the version to be used. The old method version is maintained as an active method until the specified client no longer requires the use of the older version.

SGS - Orlando will not use methodology that represents significant departures from the reference method ***unless specifically directed by the client***. In cases where clients direct the laboratory to use a method modification that represents a significant departure from the reference method, the request will be documented in the project file. The LQSM lists active methods used for the analysis of samples in Table 8.1. This list includes valid method references from sources such as USEPA, ASTM or Standard Methods designations and the current version and version date.

Analytical Capabilities. Appendix II provides a detailed listing of the methodology employed for the analysis of test samples.

SAMPLE MANAGEMENT, LOGIN, CUSTODY, STORAGE AND DISPOSAL

Requirement: A system to ensure that client supplied product is adequately evaluated, acknowledged, and secured upon delivery to the laboratory must be practiced by the laboratory. The system must assure that chain of custody is maintained and that sample receipt conditions and preservation status are documented and communicated to the client and internal staff. The login procedure must assign, document, and map the specifications for the analysis of each unique sample to assure that the requested analysis is performed on the correct sample and enables the sample to be tracked throughout the laboratory analytical cycle. The system must include procedures for reconciling defects in sample condition or client provided data, which occur at sample arrival. The system must specify the procedures for proper sample storage, transfer to the laboratory, and disposal after analysis. The system must be documented in a standard operating procedure.

Order Receipt and Entry. New orders are initiated and processed by the client services group (See Chapter 14, Procedures for Executing Client Specifications). The new order procedure includes mechanisms for providing sampling containers to clients. These containers must meet the size, cleanliness, and preservation specifications for the analysis to be performed.

For new orders, the project manager prepares a bottle request form, which is submitted to sample management department. This form provides critical project details to the sample management staff, which are used to prepare and assemble the sample bottles for shipment to the client prior to sampling.

The bottle order is assembled using bottles that meet USEPA specifications for contaminant-free sample containers. SGS - Orlando checks all sample containers for cleanliness. Data are reviewed by both the analyst and sample management technician. Results of bottle analyses are retained for minimum of 5 years.

All preservative solutions are prepared in the laboratory and are checked to assure that they are free of contamination from analytes of interest before being released for use. Sample management department retains a copy of the documentation of in-house contamination checks.

Reagent water for trip and field blanks is poured into appropriately labeled containers. Sample bottleware is labeled with durable labels printed on waterproof printing medium with indelible laser or heat transfer printer ink. All bottles are packed into ice chests with blank chain of custody forms and the original bottle order form. Completed bottle orders are delivered to clients using SGS - Orlando couriers or commercial carriers for use in field sample collection.

Sample Receipt and Custody. Samples are delivered to the laboratory using a variety of mechanisms including SGS - Orlando couriers, commercial shippers, and client self-delivery. Documented procedures are followed for arriving samples to

assure that custody and integrity are maintained and that handling and preservation requirements are documented and continued.

Sample custody documentation is initiated when the individual collecting the sample collects field samples. Custody documentation includes all information necessary to provide an unambiguous record of sample collection, sample identification, and sample collection chronology. Initial custody documentation employs either SGS - Orlando or client generated custody forms.

SGS - Orlando generates a Sample Receipt Confirmation form in situations where the individuals who collected the sample did not generate custody documentation in the field. SGS - Orlando Project Manager then contacts the client for the CoC information to be faxed or e-mailed from the client to the lab.

SGS - Orlando defines sample custody as follows:

- The sample is in the actual custody or possession of the assigned responsible person,

- The sample is in a secure area.

The SGS -Orlando facility is defined as a secure facility. Perimeter security has been established, which limits access to authorized individuals only. Visitors enter the facility through the building lobby and must register with the receptionist prior to entering controlled areas. While in the facility, visitors must be accompanied by their hosts at all times. After hours, building access is controlled using a computerized pass-key reader system. This system limits building access to individuals with a pre-assigned authorization status. After hours visitors are not authorized to be in the building. Clients delivering samples after hours must make advanced arrangements through client services and sample management to assure that staff is available to take delivery and maintain custody.

Upon arrival at SGS - Orlando, the sample custodian reviews the chain of custody and generates Sample Receipt Confirmation form for the samples received to verify that the information on the form corresponds with the samples delivered. This includes verification that all listed samples are present and properly labeled, checks to verify that samples were transported and received at the required temperature, verification that the sample was received in proper containers, verification that sufficient volume is available to conduct the requested analysis, and a check of individual sample containers to verify test specific preservation requirements including the absence of headspace for volatile compound analysis.

Sample conditions and other observations are documented on the Sample Receipt Confirmation form by the sample custodian prior to completing acceptance of custody. The sample custodian accepts sample custody upon verification that the custody document is correct. Discrepancies or non-compliant situations are documented, flagged and communicated to the SGS - Orlando project manager, who contacts the

client for resolution. The resolution is documented and communicated to sample management for execution.

Laboratory preservation of Improperly preserved field samples. SGS - Orlando extends every effort to preserve samples which were received without proper field preservation.

Field/Equipment negative controls also receive the same amount of preservation as incorrectly preserved samples, and record made in the preservation logbook.

Sample Tracking Via Status Change. An automated, electronic LIMS procedure records sample exchange transactions between departments and changes in analytical status. This system tracks all preparation, analytical, and data reporting procedures to which a sample is subjected while in the possession of the laboratory. Each individual receiving samples must acknowledge the change in custody and operational status in the LIMS. This step is required to maintain an accurate electronic record of sample status, dates of analytical activity, and custody throughout the laboratory.

Sample tracking is initiated at login where all chronological information related to sample collection dates and holding times are entered into the LIMS. This information is entered on an individual sample basis

Sample Acceptance Policy. Incoming samples must satisfy SGS - Orlando sample acceptance criteria before being logged into the system. Sample acceptance is based on the premise that clients have exercised proper protocols for sample collection. This includes sufficient volume, proper chemical preservation, temperature preservation, sample container sealing and labeling, and appropriate shipping container packing.

The sample management staff will make every attempt to preserve improperly preserved samples upon arrival. However, if preservation is not possible, the samples may be refused unless the client authorizes analysis. No samples will be accepted if holding times have been exceeded or will be exceeded before analysis can take place unless the client authorizes analysis.

Sample acceptance criteria include proper custody and sample labeling documentation. Proper custody documentation includes an entry for all physical samples delivered to the laboratory with an identification code that matches the sample bottle and a date and signature of the individual who collected the sample and delivered them to the laboratory. Labeling is done using durable waterproof labels printed with indelible heat-transfer ink.

SGS - Orlando reserves the right to refuse any sample which in its sole and absolute discretion and judgement is hazardous, toxic and poses or may pose a health, safety or environmental risk during handling or processing. The company will not accept samples for analysis using methodology that is not performed by the laboratory or for methods

that lab does not hold valid accreditation unless arrangements have been made to have the analysis conducted by a qualified subcontractor.

Assignment of Unique Sample Identification Codes. Unique identification codes must be assigned to each sample bottle to assure traceability and unambiguously identify the tests to be performed in the laboratory.

The sample identification coding process begins with the assignment of a unique alphanumeric job number. A job is defined as a group of samples received on the same day, from a specific client pertaining to a specific project. A job may consist of groups of samples received over multi-day period. The first character of the job number is an alpha-character that identifies the laboratory facility. The next characters are numeric and sequence by one number with each new job.

Unique sample numbers are assigned to each bottle collected as a discrete entity from a designated sample point. This number begins with the job number and incorporates a second series of numbers beginning at one and continuing chronologically for each point of collection. The test to be performed is clearly identified on the bottle label.

Alpha suffixes may be added to the sample number to identify special designations such as subcontracted tests, in-house QC checks, or re-logs. Multiple sample bottles for a specific analysis are labeled Bottle 1, Bottle 2, etc.

Subcontracted Analysis. Subcontract laboratories are employed to perform analysis not performed by SGS - Orlando. The quality assurance staff evaluates subcontract laboratories to assure their quality processes meet the standards of the environmental laboratory industry prior to engagement. Throughout the subcontract process, SGS - Orlando follows established procedures to assure that sample custody is maintained and the data produced by the subcontractor meets established quality criteria.

SGS - Orlando network laboratories are considered primary subcontractors.

*Subcontracting Procedure***.** Subcontracting procedures are initiated through several mechanisms, which originate with sample management. Samples for analysis by a subcontractor are logged into the SGS - Orlando system using regular login procedures. If subcontract parameters are part of the project or sample management has received subcontracting instructions for a specific project, a copy of the chain of custody is given to the appropriate project manager with the subcontracted parameters highlighted. This procedure triggers the subcontract process at the project management level. The Sample Management supervisor contacts an approved subcontractor to place the subcontract order. Subcontract chain of custody is processed in Sample Management Department and copy is filed with the original CoC. Sample management signs the subcontract chain of custody and ships the sample(s) to the subcontractor. The subcontract COC is filed with the original COC and the request for subcontract. Copies are distributed to the login department, the project manager, and sample management.

Client is verbally notified by Project Manager of the requirement to subcontract to the outside laboratory as soon as need is identified by the SGS - Orlando staff. Client notification must be verified in writing, i.e. by e-mail. Client notification may take place during the initial project set-up, or at the time of sample receipt and login.

Subcontractor data packages are reviewed by the QA Staff to assess completeness and quality compliance. If completeness defects are detected, the subcontractor is asked to immediately upgrade the data package. If data quality defects are detected, the package is forwarded to the QA staff for further review. The QA staff will pursue a corrective action solution before releasing data to the client.

Approved subcontract data is entered into the laboratory information management system (LIMS) if possible and incorporated into the final report. All subcontract data is footnoted to provide the client with a clear indication of its source. Copies of original subcontract data are always included in the data report whether in hardcopy or PDF file, depending on the data submission requirements.

*Subcontract Laboratory Evaluation***.** The QA staff evaluates subcontract laboratories prior to engagement. As a minimum, the subcontract laboratory must provide SGS - Orlando with proof of a valid certification to perform the requested analysis for the venue where they were collected, QC criteria summary (LOD/LOQ, LCS, MS/MSD, %RPD, etc.), copy of the most recent regulatory agency audit report, and a copy of the laboratory's Summary of Qualifications (SOQ). Other beneficial materials are QSM, copies of SOPs used for the subcontracted analysis, a copy of the most recent performance evaluation study for the subcontracted parameter, and copies of the most recent third party accreditor's audit report.

Certification verification must be submitted to SGS - Orlando annually. If possible, the QA staff may conduct a site visit to the laboratory to inspect the quality system. SGS - Orlando assumes the responsibility for the performance of all subcontractors who have successfully demonstrated their qualifications. When selecting a subcontractor for analysis not performed by SGS - Orlando, assure qualifications of the subcontractor through local QA officer.

Qualification process of a subcontract laboratory may be bypassed if the primary client directs SGS - Orlando to employ a specific subcontractor

Subcontract Laboratory Database. SGS - Orlando maintains centralized database of preferred contractors in order to optimize sample handling and data submission process, as well as obtain competitive priced services of uniform quality throughout the network. Individual SGS - Orlando facilities are assigned "Center of Expertise" status according to unique capabilities.

Sample Storage. Following sample custody transfer, samples are assigned to various refrigerated storage areas by the sample management staff depending upon the test to be performed and the matrix of the samples. The location (refrigerator and shelf) of each sample is entered into sample location database on the line

corresponding to each sample number. Samples remain in storage until the laboratory technician retrieves them into the laboratory for analysis.

Samples for volatile organics analysis are placed in storage in designated refrigerators by the sample management staff and immediately transferred to the organics group control. Sample custody is transferred to the VOC department staff. These samples are segregated according to matrix to limit opportunities for cross contamination to occur.

Organics staff is authorized to retrieve samples from these storage areas for analysis. When analysis is complete, the samples are placed back into storage.

Sample Login. Following sample custody transfer to the laboratory, the documentation that describes the clients analytical requirements are delivered to the sample login group for coding and entry to the Laboratory Information management System (LIMS). This process translates all information related to collection time, turnaround time, sample analysis, and deliverables into a code which enables client requirements to be electronically distributed to the various departments within the laboratory for scheduling and execution.

The technical staff is alerted to client or project specific requirements through the use of a unique project code that is electronically attached to the job during login. The unique project code directs the technical staff to controlled specifications documents detailing the unique requirements.

Sample Retrieval for Analysis. It is a responsibility of individual analyst to retrieve samples for analysis. Sample Management employs a program to facilitate sample placement and retrieval. Sample is traced around the laboratory using Status feature of LIMS.

After sample analysis has been completed, the analyst places the sample back into the storage and updates sample status.

Sample Disposal. SGS - Orlando retains all samples under proper storage for a minimum of 30 days following completion of the analysis report. Longer storage periods are accommodated on a client specific basis if required. Samples may also be returned to the client for disposal.

SGS - Orlandodisposes of all laboratory wastes following the requirements of the Resource Conservation and Recovery Act (RCRA). The Company has obtained and maintains a waste generator identification number, FLR00001263309002 (FLR designates State of Florida).

Sample management generates a sample disposal dump sheet from the LIMS tracking system each week, which lists all samples whose holding period has expired. Data from each sample is compared to the hazardous waste criteria established by the Florida Department of Environmental Protection (FDEP).

Samples containing constituents at concentrations above the criteria are labeled as hazardous and segregated into the following waste categories for disposal as follows:

Chlorinated Waste (Closed Top Steel Drum)- Methylene Chloride

Non-Chlorinated Waste (Closed Top Steel Drum)- Hexane, Methanol, and mixed solvents

Sodium Sulfate/Used Charcoal (Open Top Steel Drum)- Charcoal and paper filters used in the filtering of samples.

Hazardous Flammable Vials (Open Top Polypropylene Drum)- Methylene Chloride, Hexane.

Hazardous Aqueous waste (Closed Top Polypropylene Drum)- High Odor Samples, Lachat Waste.

Non Hazardous Soil (Open Top Steel Drum)- Soils.

Hazardous Solid Waste- (Open Top Steel Drum).

Non-Aqueous/Oil Samples- (Closed Top Steel Drum)

Difference between Open and Closed type of drums is whether it is possible to remove entire lid or just threaded stopper. Drums are closed at all times while in storage.

Non-hazardous aqueous samples are neutralized and collected in HDPP 500 Gal holding tank to be removed by waste company.

Non-hazardous solids are drummed and disposed of by contract waste company. Sample bottles are disposed of as recyclable waste in order to crush the bottles and destroy the labels. VOC vials are crushed on site using PRODEVA glass crusher. Supernatant liquid is siphoned off into the HDPP holding tank and solid residue drummed separately.

Laboratory wastes are collected by waste stream in designated areas throughout the laboratory. Waste streams are consolidated twice a week by the waste custodian and transferred to stream specific drums for disposal through a permitted waste management contractor. Filled, consolidated drums are tested for hazardous characteristics and scheduled for removal from the facility for appropriate disposal based on the laboratory data.

LABORATORY INSTRUMENTATION AND MEASUREMENT STANDARDS

Requirement: Procedures, which assure that instrumentation is performing to a pre-determined operational standard prior to the analysis of any samples, must be established by the laboratory. In general, these procedures will follow the regulatory agency requirements established in promulgated methodology. The instrumentation selected to perform specified analysis is capable of providing the method-specified uncertainty and sufficient sensitivity of measurement needed. These procedures must be documented and incorporated into the standard operating procedures for the method being executed. SASE Equipment List attached as Appendix III.

Mass Tuning – Mass Spectrometers. The mass spectrometer tune and sensitivity must be monitored to assure that the instrument is assigning masses and mass abundances correctly and that the instrument has sufficient sensitivity to detect compounds at low concentrations. This is accomplished by analyzing a specific mass tuning compound at a fixed concentration. If the sensitivity is insufficient to detect the tuning compound, corrective action must be performed prior to the analysis of standards or samples. If the mass assignments or mass abundances do not meet criteria, corrective action must be performed prior to the analysis of standards or samples.

Wavelength Verification – Spectrophotometers. Spectrophotometer detectors are checked on a regular schedule to verify proper response to the wavelength of light needed for the test in use. If the detector response does not meet specifications, corrective action (detector adjustment or replacement) is performed prior to the analysis of standards or samples.

Inter-element Interference Checks (Metals). Inductively Coupled Plasma Emission Spectrophotometers (ICP) are subject to a variety of spectral interferences, which can be minimized or eliminated by applying interfering element correction factors and background correction points. Interfering element correction factors are checked on a specified frequency through the analysis of check samples containing high levels of interfering elements. Analysis of single element interferent solutions is also conducted at a specified frequency.

If the check indicates that the method criteria has not been achieved for any element in the check standard, the analysis is halted and data from the affected samples are not reported. Sample analysis is resumed after corrective action has been performed and the correction factors have been re-calculated.

New interfering element correction factors are calculated and applied whenever the checks indicate that the correction factors are no longer meeting criteria. At a minimum, correction factors are replaced once a year.

Calibration and Calibration Verification. Many tests require calibration using a series of reference standards to establish the concentration range for performing quantitative analysis. Method specific procedures for calibration are followed prior to any sample analysis.

Calibration is performed using a linear or quadratic regression calculation or calibration factors calculated from the curve. The calibration must meet method specific criteria for linearity or precision. If the criteria are not achieved, corrective action (instrument maintenance or re-calibration) is performed. The instrument must be successfully calibrated before analysis of samples can be conducted.

Initial calibration for metals analysis performed using inductively coupled plasma (ICP) employs the use of two standards and a calibration blank to establish linearity. The calibration blank contains all reagents that are placed into the calibration standard with the exception of the target elements. Valid calibration blanks must not contain any target elements.

Initial calibrations must be initially verified using a single concentration calibration standard from a second source (i.e. separate lot or different provider). The continuing validity of an existing calibration must be regularly verified using a single concentration calibration standard. The response to the standard must meet pre-established criteria that indicate the initial calibration curve remains valid. Samples must be bracketed by passing CCVs. If the criteria are not achieved corrective action (re-calibration) is performed before any additional samples may be analyzed.

Linear Range Verification and Calibration Linear range verification is performed for all ICP, ICP/MS and select General Chemistry methods. The regulatory program or analytical method specifies the verification frequency. A series of calibration standards are analyzed over a broad concentration range. The data from these analyses are used to determine the valid analytical range for the instrument.

Some methods or analytical programs require a low concentration calibration check to verify that instrument is sufficient to detect target elements at the reporting limit. The analytical method or regulatory program defines the criteria used to evaluate the low concentration calibration check. If the low calibration check fails criteria, corrective action is performed and verified through reanalysis of the low concentration calibration check before continuing with the field sample analysis.

In accordance with TNI standards minimum number of calibration points in the absence of method-specific requirements is two calibration points and a blank.

Retention Time Verification (GC/HPLC/IC). Chromatographic retention time windows are developed for all analysis performed using gas chromatographs with conventional detectors. An initial experimental study is performed, which establishes the width of the retention window for each compound. The retention time range of the window defines the time ranges for elution of specified target analytes on the primary and

confirmation columns. Retention time windows are established upon initial calibration, applying the retention time range from the initial study to each target compound. Retention times are regularly confirmed through the analysis of an authentic standard during calibration verification. If the target analytes do not elute within the defined range during calibration verification, the instrument must be recalibrated and new windows defined. New studies are performed when major changes, such as column replacement are made to the chromatographic system.

INSTRUMENT MAINTENANCE

***Requirement*.** Procedures must be established for equipment maintenance. The procedure may include a maintenance schedule if required or documentation of daily maintenance related activities. All instrument maintenance activities must be documented in instrument specific logbooks. All equipment out of service (both analytical and auxiliary) must be clearly marked "Out of Order".

Routine, Daily Maintenance. Routine, daily maintenance is required on an instrument specific basis. It is performed each time the instrument is used. Daily maintenance traditionally includes activities to insure a continuation of good analytical performance. In some cases, they include performance checks that indicate whether non-routine maintenance is required. If the performance check indicates a need for higher level maintenance, the equipment is taken out of service until maintenance is performed. Analysis cannot be continued until the performance checks meet established criteria. Document return to control. Daily maintenance is the responsibility of the individual assigned to the instrument used for the analysis he is performing.

Non-routine Maintenance. Non-routine maintenance is reserved for catastrophic occurrences such as instrument failure. The need for non-routine maintenance is indicated by failures in general operating systems that result in an inability to conduct required performance checks or calibration. Equipment in this category are taken out of service and repaired before attempting further analysis. Analysis cannot continue until the instrument meets all performance check criteria and is capable of being calibrated. Section supervisors are responsible for identifying non-routine maintenance episodes and initiating repair activities to bring the equipment on-line. This may include initiating telephone calls to maintenance contractors if necessary. They are also responsible for documenting all details related to the occurrence and the repair.

Scheduled Maintenance. Modern laboratory instrumentation rarely requires traditional scheduled maintenance. Where required, the equipment is placed on a schedule, which dictates when maintenance is required. Examples include annual balance calibration by an independent provider and pump oil changes. Section supervisors are responsible for initiating scheduled maintenance on equipment that requires scheduled preventative attention. Scheduled maintenance is documented using routine documentation practices.

Maintenance Documentation. Routine and non-routine maintenance activities are documented in logbooks assigned to instruments and equipment used for analytical measurements. The logbooks contain preprinted forms, which specify the maintenance activities required with each use. SGS - Orlando has adopted a problem – action – follow-up format to conduct instrument maintenance. The analyst or supervisor who performs or initiates the maintenance activity is required to check the activity upon its completion, verify complete statement of return to normal conditions and initial the form. Non-routine maintenance (i.e. repairs, upgrades, etc.) is

documented as well either electronically via e-mail from the service provider or receipt attached to the maintenance log.

QUALITY CONTROL PARAMETERS, PROCEDURES, AND CORRECTIVE ACTION

Requirement: All procedures used for test methods must incorporate quality control parameters to monitor elements that are critical to method performance. Each quality parameter includes acceptance criteria that have been established by regulatory agencies for the methods in use. Criteria may also be established through client dictates or through the accumulation and statistical evaluation of internal performance data. Data obtained from these parameters must be evaluated by the analyst, and compared to established method criteria. If the criteria are not achieved, the procedures must specify corrective action and conformation of control before proceeding with sample analysis. QC parameters, procedures, and corrective action must be documented within the standard operating procedures for each method. In the absence of client specific objectives the laboratory must define qualitative objectives for completeness and representativeness of data.

Procedure. Bench analysts are responsible for methodological quality control and sample specific quality control. Each method specifies the control parameters to be employed for the method in use and the specific procedures for incorporating them into the analysis. These control parameters are analyzed and evaluated with every designated sample group (batch).

The data from each parameter provides the analyst with critical decision making information on method performance. The information is used to determine if corrective action is needed to bring the method or the analysis of a specific sample into compliance. These evaluations are conducted throughout the course of the analysis. Each parameter being indicative of a critical control feature. Failure of a methodological control parameter is indicative of either instrument or batch failure. Failure of a sample control parameter is indicative of control difficulties with a specific sample or samples.

Sample Batch. All samples analyzed in the laboratory are assigned to a designated sample batch, which contains all required quality control samples and a defined maximum number of field samples that are prepared and/or analyzed over a defined time period. The maximum number of investigative and field QC samples in the batch is 20. SGS - Orlando has incorporated the TNI batching policy as the sample-batching standard. This policy incorporates the requirement for blanks and spiked blanks as a time based function as defined by TNI. The typical batch contains a blank, laboratory control sample (LCS or spiked blank), matrix spike and matrix spike duplicate. Batch documentation includes lot specifications for all reagents and standards used during preparation of the batch.

Methodological Control Parameters and Corrective Action. Prior to the analysis of field sample the analyst must determine that the method is functioning properly. Specific control parameters indicate whether critical processes meet specified requirements before continuing with the analysis. Method specific control parameters must meet criteria before sample analysis can be conducted. Each of these

parameters is related to processes that are under the control of the laboratory and can be adjusted if out of control.

Method Blank. A method blank is analyzed during the analysis of any field sample. The method blank is defined as a sample. It contains the same standards (internal standards, surrogates, matrix modifiers, etc.) and reagents that are added to the field sample during analysis, with the exception of the sample itself. If the method blank contains target analyte(s) at concentrations that exceed method or client requirements (typically defined as 1/2 RL concentrations), the source of contamination is eliminated before proceeding with sample analysis. Systematic contamination is documented for corrective action and resolved following the established corrective action procedures. In specific cases, contamination detected in the method blank may be acceptable if the concentrations do not exceed regulatory limits or client defined reporting limits.

Laboratory Control Samples (LCS or Spiked Blanks). A laboratory control sample (spiked blank or commercially prepared performance evaluation sample) is analyzed along with field samples to demonstrate that the method accuracy is within acceptable limits. These spike solutions are derived from different sources than the solutions used for method calibration. The performance limits are derived from published method specifications or from statistical controls generated from laboratory method performance data. Spiked blanks are blank matrices (reagent water, clean sand, Teflon chips, or granular sodium sulfate) spiked with the targeted parameters and analyzed using the same method used for samples. Accuracy data is compared to laboratory experimentally derived limits to determine if the method is in control. Laboratory control samples (LCS) may be laboratory or commercially prepared spiked samples in an inert material.

Accuracy data is compared to the applicable performance limits. If the spike accuracy exceeds the performance limits, corrective action, as specified in the SOP for the method is performed and verified before continuing with a field sample analysis. In some cases, decisions are made to continue with sample analysis if performance limits are exceeded; provided the unacceptable result has no negative impact on the sample data.

Marginal exceedance (ME) values are calculated for methods containing more than eleven (11) targeted analytes. The ME is calculated as $\pm$ 4 standard deviations about the mean. MEs are considered for multi-analyte methods because of the increased likelihood of LCS failure as the number of analytes in the method increase. The number of allowable MEs is based on the number of target analytes in the method. Analytes that regularly fall into the ME category are treated as systematic problems, which are resolved using established trend monitoring and corrective action procedures. Marginal Exceedances are not applied to parameters that are detected in field samples. Routine corrective action is initiated for all cases where LCS spike accuracy criteria is beyond the established control limits and the parameter is detected in field samples corresponding to the unacceptable LCS. Use of ME may be disallowed on project-specific basis. Use of ME may be disallowed or limited on State-

specific basis; of note are the Commonwealth of Massachusetts (demonstrated low bias) and State of South Carolina (complete prohibition).

Blanks and spikes are routinely evaluated before samples are analyzed. However, in situations where sample analysis is performed using an autosampler, they may be evaluated after sample analysis has occurred. If the blanks and spikes do not meet criteria, sample analysis is repeated.

Proficiency Testing. Performance Evaluation (Proficiency Testing) samples (PEs, PTs) are single or double blind samples spiked with known amount of analytes on interest and introduced to the laboratory to assess method performance. PEs may be introduced as double blinds submitted by commercial clients, single or double blinds from regulatory agencies, or internal blinds submitted by the QA group.

A minimum of two single blind studies must be performed each year for every parameter in aqueous and solid matrices for each field of proficiency testing (FOPT) for which the laboratory maintains accreditation. Proficiency Testing samples must be purchased as blinds from an accredited vendor for every combination of analyte-matrix-method. Data from these studies are provided to the laboratory by the vendor and reported to accrediting agencies. If unsatisfactory performance is noted, corrective action is performed to identify and eliminate any sources of error. A new PT must be analyzed to demonstrate continuing proficiency.

PE samples performed for accrediting agencies or clients, which do not meet performance specifications, require a written summary that documents the corrective action investigation, findings, and corrective action implementation.

Single or double blind PT samples are employed for self-evaluation purposes. Data from these analyses are compared to established performance limits. If the data does not meet performance specifications, the system is evaluated for sources of acute or systematic error. If required, corrective action is performed and verified before initiating or continuing sample analysis.

Trend Analysis for Control Parameters. Accuracy data for selected spiked parameters from the laboratory control sample (LCS) is statistically evaluated daily for trends. Data from selected LCS parameters and surrogates are pooled on a method, matrix, and instrument basis. This data is evaluated by comparison to existing control and warning limits. Trend analysis is performed automatically as follows:

- Any point outside the control limit
- Any three consecutive points between the warning and control limits
- Any eight consecutive points on the same side of the mean
- Any six consecutive points increasing or decreasing

The results of the trend analysis are printed for supervisory evaluation prior to sample analysis. Trends that indicate the potential loss of statistical control are further

evaluated to determine the impact on data quality and to determine if corrective action is necessary. If corrective action is indicated, the supervisor informs the analysts of the corrective actions to be performed. Return to control is demonstrated before analysis resumes.

Sample Control Parameters and Corrective Action. The analysis of samples can be initiated following a successful demonstration that the method is operating within established controls. Additional controls are incorporated into the analysis of each sample to determine if the method is functioning within established specifications for each individual sample. Sample QC data is evaluated and compared to established performance criteria. If the criteria are not achieved the method or the SOP specifies the corrective action required to continue sample analysis. In many cases, failure to meet QC criteria is a function of sample matrix and cannot be remedied. Each parameter is designed to provide quality feedback on a defined aspect of the sampling and analysis episode.

Duplicates. Duplicate sample analysis is used to measure analytical precision. This can also be equated to laboratory precision for homogenous samples. Precision criteria are method dependent. If precision criteria are not achieved, corrective action or additional action may be required. Recommended action must be completed before sample data can be reported.

Laboratory Control Duplicate, Spikes & Spiked Duplicates. Spikes and spiked duplicates are used to measure analytical precision and accuracy for the sample matrix selected. Precision and accuracy criteria are method dependent. If precision and accuracy criteria are not achieved, corrective action or additional action may be required. Recommended action must be completed before sample data can be reported.

Serial Dilution (Metals). Serial dilutions of metals samples are analyzed to determine if analytical matrix effects may have impacted the reported data. If the value of the serially diluted samples does not agree with the undiluted value within a method-specified range, the sample matrix may be causing interference, which may lead to either a high or low bias. If the serial dilution criterion is not achieved, it must be flagged to indicate possible bias from matrix effects. SGS - Orlando *uses this procedure as opposed to post-digestion spike unless contractual obligations absolutely require latter*

Post Digestion Spikes (Metals). Digested samples are spiked and analyzed to determine if matrix interferences are creating biases in the results. It may also be used to determine potential interferences per client's specification. Spike concentration is determined as per analytical method. No action is necessary if the post digestion spike is outside of the method criteria, unless a preparation problem is suspected with the spike, in which case the post digestion spike should remade and reanalyzed.

Surrogate Spikes (Organics). Surrogate spikes are organic compounds that are similar in behavior to the target analytes but unlikely to be found in nature. They are added to all quality control and field samples to measure method performance for each individual sample. Surrogate accuracy limits are derived from published method specifications or by statistical evaluation of laboratory generated surrogate accuracy data. Accuracy data is compared to the applicable performance limits. If the surrogate accuracy exceeds performance limits, corrective action, as specified in the method or SOP is performed before sample data can be reported.

Internal Standards (Organic Methods). Internal standards are retention time and instrument response markers added to every sample to be used as references for quantitation. Their response is compared to reference standards and used to evaluate instrument sensitivity on a sample specific basis. Internal standard retention time is also compared to reference standards to assure that target analytes are capable of being located by their individual relative retention time.

If internal standard response criteria are not achieved, corrective action or additional action may be required. The recommended action must be completed before sample data can be reported.

If the internal standard retention time criteria are not achieved corrective action or additional action may be required. This may include re-calibration and re-analysis. Additional action must be completed before sample data is reported.

Internal Standards (ICP and ICP-MS Metals). Internal standards are used on ICP instruments to compensate for variations in response caused by differences in sample matrices. This adjustment is performed automatically during sample analysis. The internal standard response of replicated sample analysis is monitored to detect potential analytical problems. If analytical problems are suspected, then the field samples are reanalyzed.

Laboratory Derived Quality Control Criteria. Control criteria for in-house methods and client specific modifications that exceed the scope of published methodology are defined and documented prior to the use of the method. The Quality Assurance staff identifies the responsibility for control criteria needs. Control parameters and criteria, based on best technical judgment are established using input provided by the operations staff. These control parameters and criteria are documented and incorporated into the method.

The laboratory derived criteria are evaluated for technical soundness on spiked samples prior to the use of the method on field samples. The technical evaluation is documented and archived by the Quality Assurance staff.

When sufficient data form the laboratory developed control parameter is accumulated, the data is statistically processed and the experimentally derived control limits are incorporated into the method.

Bench Review & Corrective Action. The bench chemists are responsible for all QC parameters. Before proceeding with sample analysis, they are required to successfully meet all instrumental QC criteria. They have the authority to perform any necessary corrective action before proceeding with sample analysis. Their authority includes the responsibility for assuring that departures from documented policies and procedures do not occur.

The bench chemists are also responsible for all sample QC parameters. If the sample QC criteria are not achieved, they are authorized and required to perform the method specified corrective action before reporting sample data.

***Data Qualifiers*.** An alpha character coding system is employed for defining use limitations for reported data. These limitations are applied to analytical data by the analyst to clarify the usefulness of the reported data for data user. SGS - Orlando qualifies data in accordance with program-specific requirements, such as State of Florida DEP, DoD QSM, etc., and these qualifiers are hard-coded in the LIMS on project level. Definitions of common qualifiers could be found at the bottom of the sample report form.

QA Monitoring. The QA staff prior to client release conducts a spot review of completed data packages. This review includes an examination of QC data for compliance and trends indicative of systematic difficulties. If non-conformances are detected, the QA staff places an immediate stop on the release of the data and initiates corrective action to rectify the situation. The data package is released when the package becomes compliant with all quality requirements.

If the review reveals trends indicative of systematic problems, QA initiates an investigation to determine the cause. If process defects are detected, a corrective action is implemented and monitored for effectiveness.

Performance Limits. The Technical Director is responsible for compilation and maintenance of all precision and accuracy data used for performance limits. Quality control data for all test methods are accumulated and stored in the laboratory information management system (LIMS). Parameter specific QC data is extracted annually and statically processed to eliminate outliers and develop laboratory specific warning limits and confidence limits. The new limits are reviewed and approved by the supervisory staff prior to their use for data assessment. The new limits are used to evaluate QC data for compliance with method requirements for a period of one year. Laboratory generated limits appear on all data reports unless method specifies hard-coded limits (mostly General Chemistry and Metals)

Data Package Review. SGS - Orlando employs multiple levels of data review to assure that reported data has satisfied all quality control criteria and that client specifications and requirements have been met. Production departments have

developed data review procedures which must be conducted before data is released to the client.

Analytical Review. The analyst conducts the primary review of all data. This review begins with a check of all instrument and method quality control and progresses through sample quality control concluding with a check to assure that the client's requirements have been executed. Analyst checks focuses on a review of qualitative determinations and checks of precision and accuracy data to verify that existing laboratory criteria have been achieved. Checks at this level may include comparisons with project specific criteria if applicable. The analyst has the authority and responsibility to perform corrective action for any out-of-control parameter or nonconformance at this stage of review.

Secondary data reviews are performed at the peer level by analysts who have met the qualification criteria for the method in use. Qualification requirements include a valid demonstration of capability and demonstrated understanding of the method SOP. Section supervisors may perform secondary review in-lieu of a peer review Secondary review is performed on 100% of the data produced by their department. It includes a check of all manual calculations; an accuracy check of manually transcribed data from bench sheets to the LIMS, a check of all method and instrument QC criteria, baseline manipulations (if applicable) and a comparison of the data package to client specified requirements. Also included are checks to assure the appropriate methodology was applied and that all anomalous information was properly flagged for communication in the case narrative. Supervisors have the authority to reject data and initiate re-analysis, corrective action, or reprocessing.

All laboratory data requiring manual entry into LIMS system is double-checked by the analysts performing initial data entry and the section supervisor. Verification of supervisory review is indicated on the raw data summary by the supervisor's initials and date.

Electronic data that is manually edited at the bench by the primary analysts is automatically flagged by the instrument data system indicating an override by the analyst. All manual overrides must be verified and approved by a supervisor who initials and dates all manual changes.

Hard copies of manually integrated chromatographic peaks are printed that clearly depict the manually drawn baseline. The hard copy is reviewed and approved by the reviewer (initialed and dated) and included in the data package of all full tier reports or the archived batch records of commercial report packages.

Electronic data that has been committed to the LIMS can only be edited by a manager or supervisor. These edits may be required if needs for corrections are indicated during the final review. An audit record for all electronic changes in the LIMS is automatically appended to the record.

The section leader performs a tertiary review on a spot check basis. This review includes an evaluation of QC data against acceptance criteria and a check of the data package contents to assure that all analytical requirements and specifications were executed.

Report Generation (Administrative) Review. The report generation group reviews all data and supporting information delivered by the laboratory for completeness and compliance with client specifications. Missing deliverables are identified and obtained from the laboratory. The group also reviews the completed package to verify that the delivered product complies with all client specifications. Non-analytical defects are corrected before the package is sent to the client.

Project Management/Quality Assurance Review. Spot-check data package reviews are performed by the project manager. Project management reviews focus on project specifications. If the project manager identifies defects in the product prior to release, he initiates immediate corrective action to rectify the situation.

The QA Staff reviews approximately 10% of the data produced. The QA review focuses on all elements of the deliverable including the client's specifications and requirements, analytical quality control, sample custody documentation and sample identification. QA reviews at this step in the production process are geared towards systematic process defects, which require procedural changes to effect a corrective action. However, if defects are identified that can be corrected prior to data release, the QA staff returns the package to the laboratory for corrective action. QA data review cannot be used in lieu of a peer level review or a supervisory review.

Data Reporting. Analytical data is released to clients following secondary departmental review. Data release at this stage of the process is limited to electronic information, which is released to clients through a secure, encrypted, password protected, Internet connection.

Hard copy support data is compiled by the report generation group and assembled into the final report. The report is sent to the client following administrative review by report generation staff, and spot-check by QA staff.

All data reports include specified information, which is required to identify the report and its contents. This information includes a title, name and address of the laboratory, a unique report number, total number of pages in the report, clients name and address, analytical method identification, arriving sample condition, sampling, preparation/digestion/extraction and analysis dates, test results with units of measurement, authorized signature of data release, statement of applicability, report reproduction restrictions and TNI requirements certification. Subcontracted data is clearly identified.
Laboratory might be required either by State-specific program or federal program(s) to identify certification status and certification exceptions of the analyses performed.

Examples include TNI 2009/2016 standards, DoD Ver. 5.x and 310 CMR 42 (Massachusetts). For accreditation status review see sec. 14.1.

In the event of report revision date of the revision, nature of revision and identity of the person revising the report must be clearly stated in the body of the report. All levels of deliverables incorporate letter(s) of report reissue into all subsequent reports. This letter(s) is addressed to the client and briefly outlines reasons for report revision.

Electronic Data Reduction. Raw data from sample analysis is entered into the laboratory information management system (LIMS) using automated processes or manual entry. Final data processing is performed by the LIMS using procedures developed by the Company.

All LIMS programs and internally developed software (including Excel spreadsheets) are tested and validated prior to use to assure that they consistently produce correct results. Validation testing is performed by the Information Technology Staff. The testing procedures are documented in an SOP. Programs are not approved for use until they have demonstrated that they are capable of performing the required calculations.

Representativeness. Data representativeness is based on the premise that qualitative and quantitative information developed for field samples is characteristic of the sample that was collected by the client and analyzed in the laboratory. The laboratory objective for representativeness defines data as representative if the criteria for all quality parameters associated with the analysis of the sample are achieved.

Comparability. Analytical data is defined as comparable when data from a sample set analyzed by the laboratory is representatively equivalent to other sample sets analyzed separately regardless of the analytical logistics. The laboratory will achieve 100% comparability for all sample data which meets the criteria for the quality parameters associated with its analysis using the method requested by the client.

CORRECTIVE ACTION SYSTEM

Requirement. The laboratory must have policies and procedures for correcting defective processes, systematic errors, and quality defects, which enables the staff to systematically improve product quality. The system must include procedures for communicating items requiring corrective action, corrective action tracking procedures, corrective action documentation, monitoring of effectiveness, and reports to management. The system must be documented in a standard operating procedure.

Procedure. Corrective action is the step that follows the identification of a process defect. The type of defect determines the level of documentation, communication, and training necessary to prevent re-occurrence of the defect or non-conformance.

Routine Corrective Action. Routine corrective action is defined as the procedures used to return out of control analytical systems back to control. This level of corrective action applies to all analytical quality control parameters or analytical system specifications.

Bench analysts have full responsibility and authority for performing routine corrective action. The resolution of defects at this level does not require a procedural change or staff re-training. The analyst is free to continue work once corrective action is complete and the analytical system has been returned to control. Documentation of routine corrective action is limited to bench logbook or maintenance logbook comment.

Process Changes. Corrective actions in this category require procedural modifications. They may be the result of systematic defects identified during audits, the investigation of client inquiries, failed proficiency tests, product defects identified during data review, or method updates. Resolution of defects of this magnitude requires formal identification of the defect, development and documentation of a corrective action plan, and staff training to communicate the procedural change.

Technical Corrective Action. Technical corrective action encompasses routine corrective action performed by bench analysts for out of control systems and corrective actions performed for data produced using out of control systems. Technical corrective action for routine situations is conducted using the procedures detailed above.

Non-routine corrective actions apply to situations where the bench analysts failed to perform routine corrective action before continuing analysis. Supervisors and Department Managers perform corrective action in these situations. Documentation of all non-routine corrective actions is performed using the corrective action system.

Sample re-analysis is conducted if sufficient sample and holding time remain to repeat the analysis using an in-control system. If insufficient sample or holding time remains, the data is processed and qualifiers applied that describe the out of control situation. The occurrence is further documented in the case narrative and in the corrective

action response. The corrective action must include provisions for retraining the analysts who failed to perform routine corrective action.

Documentation & Communication. Routine corrective actions are documented as part of the analytical record. Notations are made in the comments section of the analytical chronicle or data sheet detailing the nonconformance. Continuation of the analysis indicates that return to control was successful.

Corrective actions for process changes are documented, tracked and monitored for effectiveness. Corrective actions may be initiated by any supervisor or senior staff member by completing the corrective action form in Corrective Action database

The corrective action database is an Access application. The initiator generates the corrective action investigation form, which is documented, tracked, distributed to responsible parties and archived through the application. The application assigns a tracking number initiation data and due date to each corrective action initiated and copies the corrective action form to the corrective action database. The application also distributes an E-mail message containing the form to the responsible parties for resolution.

Corrective Action system employs Deficiency – Root Cause – Immediate Fix – Corrective action approach, further divided into categories of Analytical Error, Omission Error, Random Error, Systemic Error and Training Issue.

The responsible party develops and implements the procedural change. Existing documentation such as SOPs are edited to reflect the change. The affected staff is informed of the procedural change through a formal training session. The training is documented and copies are placed into individual training files. The corrective action form is completed and closed in CA database.

Initial and completed corrective action forms are maintained in the Corrective Action directory. This information is archived daily. Copies of training records describing corrective actions are appended to the involved individuals training files.

Monitoring. The QA Staff monitors the implemented corrective action until it is evident that the corrective action has been effective and the systematic deficiency has been eliminated. The corrective action database is updated by QA to reflect closure of the corrective action. The QA staff also assigns an error code to the corrective action for classification of the type of errors being committed.

If QA determines that the corrective action procedure has not effectively remedied the deficiency, the process continues with a re-initiation of the corrective action. Corrective action continues until the defective process is eliminated. If another procedural change is required, it is treated as a new corrective action, which is documented and monitored using established procedures.

Client Notification. Defective processes, systematic errors, and quality defects, detected during routine audits may have negative impacts on data quality. In some cases, data that has been released to clients may be affected. If defective data has been released for use, SGS - Orlando will notify the affected clients of the defect and provide specific details regarding the magnitude of the impact to their data.

PROCEDURES FOR EXECUTING CLIENT SPECIFICATIONS

***Requirement*.** Systems must be established for evaluating and processing client specifications for routine and non-routine analytical services. The systems must enable the client services staff to identify, evaluate, and document the requested specifications to determine if adequate resources are available to perform the analysis. The system must include procedures for communicating the specifications to the laboratory staff for execution and procedures for verifying the specifications have been executed.

Client Specific Requirements. The project manager is the primary contact for clients requesting laboratory services. Client specifications are communicated using several mechanisms. The primary source of information is the client's quality assurance project plan (QAPP) which details analytical and quality control specifications for the project. In the absence of a QAPP, projects specifications can also be communicated using contracts, letters of authorization, or letters of agreement, which may be limited to a brief discussion of the analytical requirements and the terms and conditions for the work. These documents may also include pricing information, liabilities, scope of work, in addition to the analytical requirements. QAPPs include detailed analytical requirements and data quality objectives, which supersede those found in the referenced methods. This information is essential to successful project completion.

Laboratory also reviews its Accreditation status to evaluate whether it is possible to accept proposed project. Discrepancies must be resolved before the work commences.

The client services staff provides additional assistance to clients who are unsure of the specifications they need to execute the sampling and analysis requirements of their project. They provide additional support to clients who require assistance in results interpretation as needed, provided they possess the expertise required to render an opinion.

The project manager is responsible for obtaining project documents, which specify the analytical requirements. Following project management review, copies are distributed to the QA staff and the appropriate departmental managers for review and comment. The original QAPP is numbered with a document control number and filed in a secure location.

Requirements for Non-Standard Analytical Specifications. Client requirements that specify departures from documented policies, procedures, or standard specifications must be submitted to SGS - Orlando in writing. These requirements are reviewed and approved by the technical staff before the project is accepted. Once accepted, the non-standard requirements become analytical specifications, which follow the routine procedure for communicating client specifications. Departures from documented policies, procedures, or standard specifications that do not follow this procedure are not permitted.

Exception Policy: With respect to the quality system, incoming non-conforming product refers to received samples that do not meet requirements of custody documentation, are improperly packaged or stored or are contaminated. An internal non-conformance refers to a problem, caused internally due to improper handling of samples, improper sampling methods, and equipment malfunction or data management errors. The individual who identifies the incoming non-conformance is responsible for notifying the project manager. The project manager resolves the issue with the client. The individual who recognizes an internal non-conformance is responsible for initiating corrective action

Departures from standard practices, policies and specifications are reviewed and approved by Technical Director, QA Officer and by Project Manager of the project affected.

Corrective & Preventative Action: Once a quality problem has been identified, the analytical or review process stops, until the reason is identified. Primary responsibility for identifying the cause of the problem rests with the instrument operator. Other staff may be called on to assist in reaching the root cause. The problem prevention tracking system, using Corrective Action Tracking Records, provides a method to track systemic problems until resolved/removed. The QA Officer is responsible for the record management with respect to the disposition of problems.

Deviations that do not limit themselves to a single department and/or client are cited on Corrective Action Record. This may include but not limited to: sample arrival outside of EPA specified holding time, analysis completion outside of EPA specified holding time (with explanation of the reason), inconsistencies between chain of custody and cooler contents, including labeling errors, improper preservation, etc.

Deviations from analytical methods' SOP's are reported by the Analyst to the Section Leader. Single occurrences warrant completion of Corrective Action Tracking record, repetitive occurrences may indicate that either an additional training session is in order, or that the SOP does not reflect proper laboratory practice. Training session is conducted by the Technical Director or by QA Officer. In case where SOP does not reflect current laboratory practice, SOP review and correction process may be initiated.

Evaluation of Resources. A resource evaluation is completed prior to accepting projects submitted by clients. The evaluation is initiated by the client services staff receives project requirements (usually in the form of QAPjP) and distributes these requirements to the laboratory departments affected. The specifications are evaluated by the department managers from a scheduling and hardware resources perspective. The project is not accepted unless the department managers have the necessary resources to execute the project according to client specifications.

Documentation. New projects are initiated using a project set up form, which is completed prior to the start of the project. This form details all of the information needed to correctly enter the specifications for each client sample into the laboratory information management system (LIMS, see example). The form includes data reporting requirements, billing information, data turnaround times, QA level, state of origin, and comments for detailing project specific requirements. The project manager is responsible for obtaining this information from the client and completing the form prior to sample arrival and login.

Sample receipt triggers project creation and the login process. The information on the set-up form is entered into the LIMS immediately prior to logging in the first sample. The set up form may be accompanied by a quotation, which details the analytical product codes and sample matrices. These details are also entered into the LIMS during login.

Special information is distributed to the laboratory supervisors and login department in electronic or hardcopy format upon project setup. All project specific information is retained by the project manager in a secure file. The project manager maintains a personal telephone log, which details conversations with the client regarding the project.

Communication. A pre-project meeting is held between client services and the operations managers to discuss the specifications described in the QAPjP and/or related documents. Project logistics are discussed and finalized and procedures are developed to assure proper execution of the client's analytical specifications and requirements. Questions, raised in the review meeting, are discussed with the client for resolution. Exceptions to any requirements, if accepted by the client, are documented and incorporated into the QAPjP or project documentation records.

Non-standard specifications for individual clients are documented in the LIMS at the client account level. Once entered into the LIMS, these specifications become memorialized for all projects related to the client account. Upon sample arrival, these specifications are accessed through a terminal or printed as a hard copy and stored in a binder for individuals who require access to the specification. Specifications that are not entered into the LIMS are prohibited unless documented in an interdepartmental memo, which clearly identifies the project, client and effective duration of the specification.

Operational Execution. A work schedule is prepared for each analytical department on a daily basis. Analytical specifications from recently arrived samples have now been entered into the LIMS database. The database is sorted by analytical due date and holding time, into product specific groups. Samples are scheduled for analysis by due date and holding time. The completed schedule, which is now defined as a work list, is printed. The list contains the client requested product codes and specifications required for the selected sample(s). Special requirements are communicated to the analyst using the comments section or relayed through verbal instructions provided by

the supervisor. The bench analyst assumes full responsibility for performing the analysis according to the specifications printed on the work sheet.

Verification. Prior to the release of data to the client, laboratory section managers and the report generation staff review the report and compare the completed product to the client specifications documentation to assure that all requirements have been met. Project managers perform a spot check of projects with unique requirements to assure that the work was executed according to specifications.

CLIENT COMPLAINT RESOLUTION PROCEDURE

Requirement. A system for managing and reconciling client complaints must be implemented in the laboratory. The system must include procedures for documenting client complaints and communicating the complaint to the appropriate department for resolution. The system must also include a quality assurance evaluation to determine if the complaint is related to systematic defects requiring process changes.

Procedure. Client complaints are communicated to client services representatives, quality assurance staff, or senior management staff for resolution. The individual receiving the complaint retains the responsibility for documentation and communicating the nature of the complaint to the responsible department(s) for resolution. The responsible party addresses the complaint. The resolution is communicated to quality assurance (QA) and the originator for communication to the client. QA reviews the complaint and resolution to determine if systematic defects exist. If systematic defects are present, QA works with the responsible party to develop a corrective action that eliminates the defect.

Documentation. Client's complaints are documented by the client service representative receiving the complaint. A record of the telephone conversation is maintained by client services. Client service staff enters the complaint into Data Challenge database or Client Complaint database, depending on the nature of complaint. These databases are cross-linked with corrective action database – see sec. 13. Complaint is communicated to the production departments concerned via auto e-mail. The complaint resolution is documented in the database by the responsible party and resultant e-mail returned to the originator. QA staff is copied on the correspondence.

Corrective Action. Responses to Data Challenges/Client Complaints are required from the responsible party. At a minimum, the response addresses the query and provides an explanation to the complaint. Corrective action may focus on the single issue expressed in the complaint. Corrective action may include job case narrative generation, reprocessing of data, editing of the initial report, and re-issue to the client. If the QA review indicates a systematic error, process modification is required. The defective process at the root of the complaint is changed. SOPs are either created or modified to reflect the change. The party responsible for the process implements process changes.

QA Monitoring. Process changes, implemented to resolve systematic defects, are monitored for effectiveness by QA. If monitoring indicates that the process change has not resolved the defect, QA works with the department management to develop and implement an effective process. If monitoring indicates that the defect has been resolved, monitoring is slowly discontinued. Continued monitoring is incorporated as an element of the annual system audit and annual Management Report (see 18.8).

CONTROL OF NONCONFORMING PRODUCT

Requirement: Policies and procedures have been developed and implemented that describe the procedures employed by the laboratory when any aspect of sample analysis or data reporting do not conform to established procedures or client specifications. These procedures include steps to ensure that process defects are corrected and affected work is evaluated to assess its impact to the client.

Procedure. Nonconforming product is identified through multiple channels, such as second level analytical data review, routine internal review and audit practices, external auditing or through client inquiry. Responsibility and authority for the management of the non-conforming product is directly defined by a nature of a non-conformance. For example, non-conformances resulting from internal and external reviews are evaluated and managed by QA Staff. Corrective Action items are issued and followed to completion and verification that defect is prevented from reoccurring. Non-conformances stemming from client inquiry are managed by Project Management staff with QA staff oversight.

Data associated with out-of compliance QC are evaluated by bench personnel and section supervisors. The analyst has the authority and responsibility to perform corrective action for any out-of-control parameter or nonconformance at this stage of review.

If non-conformances are detected, the QA staff places an immediate stop on the release of the data and initiates corrective action to rectify the situation

Non-conformances and their significance are communicated in case narrative and sample report footnotes. Case narrative comments and sample repot footnotes must state the impact on data quality.

Corrective Action. The outcome of the evaluation dictates the course of action. The type of defect determines the level of documentation, communication, and training necessary to prevent re-occurrence of the defect or non-conformance This may include at a minimum client notification, but may also include corrective action. Immediate corrective action is performed using the SOP-specified procedures. However, additional action may be required including cessation of analysis and withholding and/or recalling data reports. If the evaluation indicates that nonconforming data may have been issued to clients, the client is immediately notified and data may be recalled following the procedures specified in respective SOPs. If work has been stopped because of a nonconformance, the Laboratory Director is the only individual authorized to direct a resumption of analysis.

Non-conformances caused by systematic process defects require retraining of the personnel involved as an element of the corrective action solution. Routine corrective actions are documented as part of the analytical record.

CONFIDENTIALITY PROTECTION PROCEDURES

Requirements: Policies and procedures are required to protect client data from release to unauthorized parties or accidental release of database information through accidental electronic transmission or illegal intrusion. These policies must be communicated to clients and staff. Electronic systems must be regularly evaluated for effectiveness.

Client Anonymity. Information related to the Company's clients is granted to employees on a "need to know" basis. An individual's position within the organization defines his "need to know". Individuals with "need to know" status are given password access to systems that contain client identity information and access to documents and document storage areas containing client reports and information. Access to client information by individuals outside of the Company is limited to the client and individuals authorized by the client.

Individuals outside of the Company may obtain client information through subpoena issued by a court of valid jurisdiction. Clients are informed when subpoenas are received ordering the release of their information.

Documents. Access to client documents is restricted to employees in need to know positions. Copies of all client reports are stored in secure archive with restricted access. Reports and report copies are distributed to individuals who have been authorized by the client to receive them. Documents are not released to third parties without verbally expressed or written permission from the client.

Confidential Business Information (CBI). Operational documents including SOPs, Quality Manuals, personnel information, internal operations statistics, and laboratory audit reports are considered confidential business information. Strict controls are placed on the release of this information to outside parties.

Release of CBI to outside parties or organizations may be authorized upon execution of a confidentiality agreement between SGS - Orlando and the receiving organization or individual. CBI information release is authorized for third party auditors and commercial clients in electronic mode as Adobe Acrobat .PDF format only. See also Sec. 6.5.

Electronic Data.

Database Intrusion. Direct database entry is authorized for employees of SGS - Orlando only on a need to know basis. Entry to the database is restricted through a user specific multiple password entry system. Direct access to the database outside of the facility is possible through a VPN connection. A unique user and password is required for access to the local area network. A second unique password is required to gain access to the database. All Passwords are required to be changed

semiannually. The staff receives read or write level authorization on a hierarchical privilege basis.

Internet Access. Access to client information is through an HTTPS Web application only. It does not contain a mechanism that allows direct access to the database. Clients can gain access to their data only using a series of SGS - Orlando assigned accounts, and client specific passwords. The viewable data, which is encrypted during transmission, consists of an extraction of database information only.

Client Accessibility. Accessibility to client data delivered via electronic means follows strict protocols to insure confidentiality. Clients accessing electronic data are assigned a company account. The account profile, which is established by the MIS staff, grants explicit access to explicit information pertaining to the client's project activity. Passwords are assigned on an individual basis within a client account. These accounts can be activated or deactivated by the MIS staff only.

Information Requests. Client specific data or information is not released to third parties without verbally expressed or written permission from the client. Written permission is required from third parties, who contact the Company directly for the release of information. Verbal requests will be honored only if they are received directly from the client. These requests must be documented in a record of communication maintained by authorized recipient.

Transfer of Records. Archived data, which has previously been reported and transmitted to clients, is the exclusive property of SGS - Orlando. In the event of a cessation of business activities due to business failure or sale, The Company's legal staff will be directed to arrange for the final disposition of archived data.

The final disposition of archived data will be accomplished using the approach detailed in the following sequence:

1. All data will be transferred to the new owners for the duration of the required archive period as a condition of sale.

2. If the new owners will not accept the data or the business has failed, letters will be sent to clients listed on the most recent active account roster offering them the option to obtain specific reports (identified by SGS – Orlando Job Number) at their own expense.

3. A letter will be sent to the TNI accrediting authority with organizational jurisdiction over the company offering them the option to obtain all unclaimed reports at their own expense.

4. All remaining archived data will be recycled using the most expedient means possible.

QUALITY AUDITS AND SYSTEM REVIEWS

Requirement: The quality assurance group will conduct regularly scheduled audits of the laboratory to assess compliance with quality system requirements, technical requirements of applied methodology, and adherence to documentation procedures. The information gathered during these audits will be used to provide feedback to senior management and perform corrective action where needed for quality improvement purposes.

Quality Systems Review. Quality system audits are performed annually by the Quality Assurance Director for the VP of EHS. In this audit, the laboratory is evaluated for compliance with the Laboratory Quality Systems Manual (LQSM) and the quality system standards of TNI/DoD. Findings, which indicate non-compliance or deviation from the LQSM, are flagged for corrective action. Corrective actions require either a return to compliance or a plan change to reflect an improved quality process. The QA Officer is responsible for making and documenting changes to the LQSM. These changes are reviewed by the Laboratory Director and Technical Director prior to the approval of the revised system.

Quality System Audits. Quality system audits are conducted to evaluate the effectiveness and laboratory compliance with individual quality system elements. These audits are conducted on an established schedule. Audit findings are documented and communicated to the management staff and entered into the corrective action system for resolution. If necessary, retraining is conducted to assure complete understanding of the system requirements.

Technical Compliance Audits. Technical compliance audits are performed throughout the year following the established schedule. Selected analytical procedures are evaluated for compliance with standard operating procedures (SOPs) and method requirements. If non-conformances exist, the published method serves as the standard for compliance. SOPs are edited for compliance if the document does not reflect method requirements. Analysts are trained to the new requirements and the process is monitored by quality assurance. Analysts are retrained in method procedures if an evaluation of bench practices indicates non-compliance with SOP requirements.

Documentation Audits. Documentation audits are conducted periodically. This audit includes a check of measurement processes that require manual documentation and non-analytical logbook review. It also includes checks of data archiving systems and a search to find and remove any inactive versions of SOPs that may still be present in the laboratory and being accessed by the analysts. Non-conformances are corrected on the spot. Procedural modifications are implemented if the evaluation indicates a systematic defect.

Corrective Action Monitoring. Defects or non-conformances that are identified during client or internal audits are shared with management and entered into CA

database for attention by the responsible party. Audit findings are corrected through process modifications and/or retraining. Once a corrective action has been designed and implemented, it is monitored for compliance on a regular basis by the QA staff. Monitoring of the corrective action continues until satisfactory implementation has been verified.

Preventive Action. Laboratory systems or processes, which may be faulty and pose the potential for nonconformances, errors, confusing reports or difficulties establishing traceability may be identified during internal audits. These items are highlighted for systematic change using the corrective action system and managed to resolution using appropriate procedures for corrective action.

Client Notification. Defective processes, systematic errors, and quality defects detected during routine audits may have negative impact on data quality. In some cases, data that has been released to the client may be affected. If defective data has been released for use, SGS - Orlando will immediately notify the affected clients of the defect and provide specific details regarding the magnitude of the impact to their data.

Management Reports. Formal reports of all audit activities are prepared for the management staff. These reports are prepared annually. The report details the status of the Quality System.

The formal report also addresses the following topics:

- *the suitability of policies and procedures;*
- *reports from managerial and supervisory personnel;*
- *the outcome of recent internal audits;*
- *corrective and preventive actions;*
- *assessments by external bodies;*
- *the results of inter-laboratory comparisons or proficiency tests;*
- *changes in the volume and type of the work;*
- *customer feedback;*
- *complaints;*
- *recommendations for improvement;*
- *other relevant factors, such as quality control activities, resources, and staff training.*

19.0 HEALTH AND SAFETY

Requirement. The company operates a formal health and safety program that complies with the requirements of the Occupational Health and Safety Administration. The program consists of key policies and practices that are essential to safe laboratory operation. All employees are required to receive training on the program elements. Job specific training is conducted to assure safe practices for specific tasks. All employees are required to participate in the program, receive initial and annual training, and comply with the program requirements. All plan and program requirements are detailed in the Health and Safety Program Manual.

19.1 Policy. SGS - Orlando will provide a safe and healthy working environment for its employees and clients while protecting the public and preserving the Company's assets and property. The company will comply with all applicable government regulations pertaining to safety and health in the laboratory and the workplace.

The objective of the SGS - Orlando Health and Safety Program is to promote safe work practices that minimize the occurrence of injuries and illness to the staff through proper health and safety training, correct laboratory technique application and the use of engineering controls.

19.2 Responsibilities. The Health and Safety Program assists managers, supervisors and non-supervisory employees in control of hazards and risks to minimize the potential for employee and client injuries, damage to client's property and damage or destruction to SGS - Orlando's facilities.

The Health and Safety Officer is responsible for implementing the Program's elements and updating its contents as necessary. He also conducts periodic audits to monitor compliance and assess the program's effectiveness and is also responsible for creating and administering safety training for all new and existing employees.

The employee is responsible for following all safety rules established for their protection, the protection of others and the proper use of protective devices provided by the Company. The employee is also expected to comply with the requirements of the program at all times. Department Managers and Supervisors are responsible for ensuring the requirements of the Safety Program are practiced daily. The Company President retains the ultimate responsibility for the program design and implementation.

19.3 Program Elements. The SGS - Orlando Health and Safety Program consists of key program elements that compliment the company's health and safety objective. These elements form the essence of the health and safety policy and assure that the objectives of the program are achieved.

Safety Education and Training and Communication. Training is conducted to increase the staff's awareness of laboratory hazards and their knowledge of the safety

practices and procedures required to protect them from those hazards. It is also used to communicate general safety procedures required for safe operation in a chemical laboratory.

Initial health and safety training for new employees is conducted during new employee orientation and administered through SGS - Orlando University database.. The training focuses on the SGS - Orlando Safety and Health Program and includes specific training for the hazards that may be associated with the employees' duties. Training is also conducted for all program elements focusing on general, acceptable, laboratory safety procedures. Targeted training is conducted to address hazards or safety procedures that are specific to individual employee's work assignments. All training activities are documented and archived in individual training folders. A health and safety training inventory is maintained in the training database.

SGS - Orlando maintains personnel trained in HAZWOPER, DOT and HazMat operations, as well as respirator fit certification.

Safety Officer. The safety officer provides the employees with an opportunity to express their views and concerns on safety issues in an environment where those concerns will be addressed to ensure that the interests of the company and the well being of the employee are protected. Safety Officer is entrusted with elevating the level of safety awareness among their peers.

***Hazard Identification and Communication*.** The hazard communication program enables employees to readily identify laboratory hazards and the procedures to protect themselves from those hazards. This program complies with OSHA's Hazard Communication Standard, Title 29 Code of Federal Regulations 1910.1200 that requires the company to adopt and adhere to the following key elements:

- Material Safety Data Sheets (MSDS) and/or Safety Data Sheets (SDS) must be available to any employee wishing to view them,
- The Company must maintain a Hazardous Chemicals Inventory (by location), which is updated on an annual basis,
- Containers are properly labeled,
- All employees must be provided with annual Personal Protection, Hazard Communication and Right to Know training,

Chemical Hygiene Plan. The Chemical Hygiene Plan complies with the requirements of the Occupational Safety and Health Administration's Occupational Exposure to Hazardous Chemicals in the Laboratory Standard, 29 CFR 1910.1450. This plan establishes procedures, identifies safety equipment, personal protective equipment, and work practices that protect employees from the potential health hazards presented by hazardous chemicals in the laboratory if properly used and/or applied.

Emergency Action & Evacuation Plan. The Emergency Action and Evacuation Plan details the procedures used to protect and safeguard SGS - Orlando employees and property during emergencies. Emergencies are defined as fires or explosions, gas leaks, building collapse, hazardous material spills, emergencies that immediately threaten life and health, bomb threats and natural disasters such as floods, hurricanes or tornadoes. The plan identifies and assigns responsibility for executing specific roles in situations requiring emergency action.

Lockout/Tagout Plan. Lockout/tagout procedures have been established to assure that laboratory employees and outside contractors take steps to render equipment inoperable and/or safe before conducting maintenance activities. The plan details the procedures for conducting maintenance on equipment that has the potential to unexpectedly energize, start up, or release energy or can be operated unexpectedly or accidentally resulting in serious injury to employees. The plan ensures that employees performing maintenance render the equipment safe through lock out or tag out procedures.

Personal Protection Policy. Policies have been implemented which detail the personal protection requirements for employees. The policy includes specifications regarding engineering controls, personal protective equipment (PPE), hazardous waste, chemical exposures, working with chemicals and safe work practices. Safety requirements specific to processes or equipment are reviewed with the department supervisor or the Health and Safety Officer before beginning operations.

Emergency Preparedness Plan. This plan identifies the actions to be taken by SGS - Orlando staff in the event of terrorism or terrorist actions, to ensure the safety of the employees and the facility. The plan describes the building security actions coinciding with the “Alert Condition”, designated by the Department of Homeland Security.

Appendix I

Glossary of Terms

GLOSSARY OF TERMS

Acceptance Criteria: specified limits placed on characteristics of an item, process, or service defined in requirement documents.

Accreditation: the process by which an agency or organization evaluates and recognizes a laboratory as meeting certain predetermined qualifications or standards, thereby accrediting the laboratory. In the context of TNI program, this process is a voluntary one.

Accuracy: the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

Analyst: the designated individual who performs the "hands-on" analytical methods and associated techniques and who is the one responsible for applying required laboratory practices and other pertinent quality controls to meet the required level of quality.

Analytical Uncertainty: A subset of Measurement Uncertainty that includes all laboratory activities performed as part of the analysis.

Audit: a systematic evaluation to determine the conformance to quantitative *and qualitative* specifications of some operational function or activity.

Batch: environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one to 20 environmental samples of the same quality-system matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

Blank: a sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

Blind Sample: a sub-sample for analysis with a composition known to the submitter. The analyst/laboratory may know the identity of the sample but not its composition. It is used to test the analyst's or laboratory's proficiency in the execution of the measurement process.

Case Narrative: a statement of non-conformances associated with particular data report

Calibration: to determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter, instrument, or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

Calibration Curve: the mathematical relationship between the known values, such as concentrations, of a series of calibration standards and their instrument response.

Calibration Method: a defined technical procedure for performing a calibration.

Calibration Standard: a substance or reference material used to calibrate an instrument.

Certified Reference Material (CRM): a reference material one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body.

Chain of Custody: an unbroken trail of accountability that ensures the physical security of samples and includes the signatures of all who handle the samples.

Clean Air Act: the enabling legislation in 42 U.S.C. 7401 *et seq.*, Public Law 91-604, 84 Stat. 1676 Pub. L. 95-95, 91 Stat., 685 and Pub. L. 95-190, 91 Stat., 1399, as amended, empowering EPA to promulgate air quality standards, monitor and to enforce them.

Comprehensive Environmental Response, Compensation and Liability Act (CERCLA/Superfund): the enabling legislation in 42 U.S.C. 9601-9675 *et seq*., as amended by the Superfund Amendments and Reauthorization Act of 1986 (SARA), 42 U.S.C. 9601*et seq.*, to eliminate the health and environmental threats posed by hazardous waste sites.

Confirmation: verification of the identity of a component through the use of an approach with a different scientific principle from the original method. These may include, but are not limited to second column confirmation, alternate wavelength, derivatization, mass spectral interpretation, alternative detectors or, additional cleanup procedures.

Conformance: an affirmative indication or judgement that a product or service has met the requirements of the relevant specifications, contract, or regulation; also the state of meeting the requirements.

Corrective Action: the action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

Data Audit: a qualitative and quantitative evaluation of the documentation and procedures associated with environmental measurements to verify that the resulting data are of acceptable quality (i.e., that they meet specified acceptance criteria).

Data Reduction: the process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

Demonstration of Capability: a procedure to establish the ability of the analyst to generate acceptable accuracy.

Document Control: the act of ensuring that documents (and revisions thereto) are proposed, reviewed for accuracy, approved for release by authorized personnel, distributed properly and controlled to ensure use of the correct version at the location where the prescribed activity is performed.

Duplicate Analyses: the analyses or measurements of the variable of interest performed identically on two sub-samples of the same sample. The results from duplicate analyses are used to evaluate analytical or measurement precision but not the precision of sampling, preservation or storage internal to the laboratory.

Environmental Health and Safety (EHS) – SGS North America line of business to which SGS – Orlando laboratory belongs.

Federal Water Pollution Control Act (Clean Water Act, CWA): the enabling legislation under 33 U.S.C. 1251 *et seq.*, Public Law 92-50086 Stat. 816, that empowers EPA to set discharge limitations, write discharge permits, monitor, and bring enforcement action for non-compliance.

Field of Testing: TNI's approach to accrediting laboratories by program, method and analyte. Laboratories requesting accreditation for a program-method-analyte combination or for an up-dated/improved method are required submit to only that portion of the accreditation process not previously addressed (see TNI, section 1.9ff).

Holding Times (Maximum Allowable Holding Times) the maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standards or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix (or Quality System Matrix): the component or substrate that contains the analyte of interest. For purposes of batch and QC requirement determinations, the following matrix distinctions shall be used:

Aqueous: any aqueous sample excluded from the definition of Drinking Water matrix or Saline/Estuarine source. Includes surface water, groundwater, effluents, and TCLP or other leachates.

Drinking Water: any aqueous sample that has been designated a potable or potential potable water source. Saline/Estuarine: any aqueous sample from an ocean or estuary, or other salt-water source such as the Great Salt Lake. Non-aqueous Liquid: any organic liquid with <15% settleable solids.

Biological Tissue, Biota: any sample of a biological origin such as fish tissue, shellfish, or plant material. Such samples shall be grouped according to origin.

Solids: includes soils, sediments, sludges and other matrices with >15% settleable solids.

Chemical Waste: a product or by-product of an industrial process that results in a matrix not previously defined.

Air: whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas or vapor that are collected with a sorbent tube, impinger solution, filter, or other device.

Matrix Spike (spiked sample or fortified sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of Target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (spiked sample or fortified sample duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Method Blank: a sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest, which is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

Method Detection Limit: the minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

National Institute of Standards and Technology (NIST): an agency of the US Department of Commerce's Technology Administration that is working with EPA, States, TNI, and other public and commercial entities to establish a system under which private sector companies and interested States can be accredited by NIST to provide NIST-traceable proficiency testing (PT) to those laboratories testing drinking water and wastewater.

The NELAC institute (TNI): a voluntary organization of State and Federal environmental officials and interest groups purposed primarily to establish mutually acceptable standards for accrediting environmental laboratories.

TNI Standards: the plan of procedures for consistently evaluating and documenting the ability of laboratories performing environmental measurements to meet nationally defined standards established by the The NELAC Institute.

Performance Audit: the routine comparison of independently obtained *qualitative and quantitative* measurement system data with routinely obtained data in order to evaluate the proficiency of an analyst or laboratory.

Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

Preservation: refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

PT Fields of Testing: TNI's approach to offering proficiency testing by regulatory or environmental program, matrix type, and analyte.

Proficiency Testing: a means of evaluating a laboratory's performance under controlled conditions relative to a given set of criteria through analysis of unknown samples provided by an external source.

Proficiency Test Sample (PT): a sample, the composition of which is unknown to the analyst and is provided to test whether the analyst/laboratory can produce analytical results within specified acceptance criteria.

Quality Assurance: an integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

Quality Control: the overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

Quality Manual: a document stating the management policies, objectives, principles, oganizational structure and authority, responsibilities, accountability, and implementation of an agency, organization, or laboratory, to ensure the quality of its product and the utility of its product to its users.

Quality System: a structured and documented management system describing the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products (items), and services. The quality system provides the framework for planning, implementing, and assessing work performed by the organization and for carrying out required QA and QC.

Quantitation Limits: the maximum or minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be quantified with the confidence level required by the data user.

Range: the difference between the minimum and the maximum of a set of values.

Raw Data: any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

Reagent Blank (method reagent blank or method blank): a sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

Reference Material: a material or substance one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.

Reference Method: a method of known and documented accuracy and precision issued by an organization recognized as competent to do so.

Reference Standard: a standard, generally of the highest metrological quality available at a given location, from which measurements made at that location are derived.

Replicate Analyses: the measurements of the variable of interest performed identically on two or more sub-samples of the same sample within a short time interval.

Requirement: denotes a mandatory specification; often designated by the term “shall”.

Resource Conservation and Recovery Act (RCRA): the enabling legislation under 42 USC 321 *et seq.* (1976), that gives EPA the authority to control hazardous waste from the “Cradle-to-grave”, including its generation, transportation, treatment, storage, and disposal.

Safe Drinking Water Act (SDWA): the enabling legislation, 42 USC 300f *et seq.* (1974), (Public Law 93-523), that requires the EPA to protect the quality of drinking water in the U.S. by setting maximum allowable contaminant levels, monitoring, and enforcing violations.

Sample Duplicate: two samples taken from and representative of the same population and carried through all steps of the sampling and analytical procedures in an identical manner.

Duplicate samples are used to assess variance of the total method including sampling and analysis.

Spike: a known mass of target analyte added to a blank sample or sub-sample; used to determine recovery efficiency or for other quality control purposes.

Standard: the document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of TNI and meets the approval requirements of TNI procedures and policies.

Toxic Substances Control Act (TSCA): the enabling legislation in 15 USC 2601 *et seq.*, (1976), that provides for testing, regulating, and screening all chemicals produced or imported into the United States for possible toxic effects prior to commercial manufacture.

Traceability: the property of a result of a measurement whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons.

United States Environmental Protection Agency (EPA): federal governmental agency with the responsibility for protecting public health and safeguarding and improving the natural environment (i.e., the air, water, and land) upon which human life depends.

Validation: the process of substantiating specified performance criteria.

Verification: confirmation by examination and provision of evidence that specified requirements have been met.

NOTE: In connection with the management of measuring equipment, verification provides a means for checking that the deviations between values indicated by a measuring instrument and corresponding known values of a measured quantity are consistently smaller than the maximum allowable error defined in a standard, regulation or specification peculiar to the management of the measuring equipment. The result of verification leads to a decision either to restore in service, to perform adjustment, to repair, to downgrade, or to declare obsolete. In all cases, it is required that a written trace of the verification performed shall be kept on the measuring instrument's individual record.

Appendix II

Analytical Capabilities

TNI-Accredited Fields of Testing

Method Type	Method Number	Regulatory Program
Organics		
EDB and DBCP	EPA 504.1	Drinking Water
Perfluorinated Carboxylic Acids and Sulfonates	EPA 537	Drinking Water
Organics		
EDB and DBCP	EPA 504, SW846 8011**	Non-Potable Water
Volatile Organics	EPA 624**, SW846 8260B**, 8260B SIM**, 8260C**, 8260C SIM**, 8260D**, 8260D SIM**	Non-Potable Water
Semi-Volatile Organics	EPA 625**, SW846 8270D**	Non-Potable Water
Semi-Volatile Organics	SW846 8270D SIM**, 8270E**, 8270E** SIM	Non-Potable Water
Chlorinated Pesticides & PCBs	EPA 608**, SW846 8081B**, 8082A**	Non-Potable Water
Poly-Aromatic Hydrocarbons	EPA 610**	Non-Potable Water
Explosives	SW846 8330A**, 8332**	Non-Potable Water
Explosives	SW846 8330B**,	Non-Potable Water
Chlorinated Herbicides	SW846 8151A**	Non-Potable Water
Organophosphorus Pesticides	SW846 8141B**	Non-Potable Water
Perchlorate	SW846 6850**	Non-Potable Water
Perfluorinated Carboxylic Acids and Sulfonates	EPA 537 MOD** (ALS MS014)	Non-Potable Water
Dissolved Gases	RSK SOP 147-175**	Non-Potable Water
Alcohols	SW846 8015C**,8015D**	Non-Potable Water
Gasoline Range Organics	SW846 8015C**,8015D**	Non-Potable Water
Diesel Range Organics	SW846 8015C**,8015D**	Non-Potable Water
Total Petroleum Hydrocarbons	FLPRO**	Non-Potable Water
Tennessee EPH	TN-EPH**	Non-Potable Water
Tennessee GRO	TN-GRO**	Non-Potable Water
Wisconsin DRO	WI-DRO**	Non-Potable Water
Petroleum Hydrocarbons	Iowa OA-1**	Non-Potable Water
Petroleum Hydrocarbons	Iowa OA-2**	Non-Potable Water
Volatile Petro. Hydrocarbons	Massachusetts VPH, 2004**	Non-Potable Water
Extractable Petro. Hydrocarbons	Massachusetts EPH, 2004**	Non-Potable Water
Acrylamide	SW846 8316	Non-Potable Water

Method Type	Method Number	Regulatory Program
Metals		
ICP: General – EPA WW	EPA 200.7**, 1994; SW-846 6010C**6010D**	Non-Potable Water
ICP/MS: General – EPA WW	EPA 200.8**, 1994; SW-846 6020A**, 6020B**	Non-Potable Water
Cold Vapor Mercury – EPA WW	EPA 245.1, 1994; SW-846 7470A**	Non-Potable Water
Inorganic WetChem		
Alkalinity	SM2320B-11**	Non-Potable Water
CBOD	SM5210B-11	Non-Potable Water
COD	SM5220C-11	Non-Potable Water
BOD	SM5210B-11	Non-Potable Water
Color, Apparent	SM2120B-11	Non-Potable Water
Ion Chromatography (Bromide, Fluoride, Chloride, Sulfate, Nitrite, Nitrate,) – Aqueous	EPA 300.0**, SW846 9056A**	Non-Potable Water
Nitrate/Nitrite	EPA 353.2**	Non-Potable Water
Total Kjeldahl Nitrogen	EPA 351.2**	Non-Potable Water
Ammonia	EPA 350.1**	Non-Potable Water
Oil & Grease, Gravimetric – AQ	EPA 1664A**, 1664B, SW846 9070A**	Non-Potable Water
Orthophosphate	EPA 365.3**	Non-Potable Water
pH by electrode (Waters)	SM4500H+B-11**; SW846 9040C**	Non-Potable Water
Specific Conductance	EPA 120.1**	Non-Potable Water
Sulfide	SM4500S=F-11**	Non-Potable Water
Total Dissolved Solids	SM2540C-11**	Non-Potable Water
Total Organic Carbon	SM5310B-11, SW846 9060A**	Non-Potable Water
Total Phosphorus	EPA 365.3**	Non-Potable Water
Total Solids	SM2540B-11**	Non-Potable Water
Total Suspended Solids	SM2540D-11**	Non-Potable Water
Turbidity	EPA 180.1	Non-Potable Water
Total CN	EPA 335.4, SW846 9012B**	Non-Potable Water
Un-Ionized Ammonia - calculation	FDEP SOP10/03/83	Non-Potable Water
Calcium Hardness by Calculation	SM2340B-11	Non-Potable Water
Hardness, Total by Calculation	SM2340B-11	Non-Potable Water

Method Type	Method Number	Regulatory Program
Corrosivity & pH – aqueous	SW846 9040C**	Non-Potable Water
Hexavalent Chromium	SW846 7196A**	Non-Potable Water
Organics		
EDB and DBCP	SW846 8011 Mod**	Solid and Chemical Material
Volatile Organics	SW846 8260B**, 8260B SIM, 8260C**, 8260C SIM**	Solid and Chemical Material
Semi-Volatile Organics	SW846 8270D**, 8270E**	Solid and Chemical Material
Semi-Volatile Organics	SW846 8270D SIM**, 8270E SIM**	Solid and Chemical Material
Gasoline Range Organics	SW846 8015C**,8015D**	Solid and Chemical Material
Diesel Range Organics	SW846 8015C**,8015D**	Solid and Chemical Material
Alcohols	SW846 8015C**,8015D**	Solid and Chemical Material
Explosives	SW846 8330A**, 8332**	Solid and Chemical Material
Explosives	SW846 8330B**	Solid and Chemical Material
Organochlorine Pesticides	SW846 8081B**	Solid and Chemical Material
Polychlorinated Biphenyls	SW846 8082A**	Solid and Chemical Material
Chlorinated Herbicides	SW846 8151A**	Solid and Chemical Material
Organophosphorus Pesticides	SW846 8141B**	Solid and Chemical Material
Perchlorate	SW-846 6850**	Solid and Chemical Material
Perfluorinated Carboxylic Acids and Sulfonates	EPA 537 MOD** (ALS MS014)	Solid and Chemical Material
Total Petroleum Hydrocarbons	FLPRO**	Solid and Chemical Material
Tennessee EPH	TN-EPH**	Solid and Chemical Material
Tennessee GRO	TN-GRO**	Solid and Chemical Material
Wisconsin DRO	WI-DRO**	Solid and Chemical Material

Method Type	Method Number	Regulatory Program
Petroleum Hydrocarbons	Iowa OA-1**	Solid and Chemical Material
Petroleum Hydrocarbons	Iowa OA-2**	Solid and Chemical Material
Volatile Petro. Hydrocarbons	Massachusetts VPH, 2004**	Solid and Chemical Material
Extractable Petro. Hydrocarbons	Massachusetts EPH, 2004**	Solid and Chemical Material
Acrylamide	SW846 8316	Solid and Chemical Material
Metals		
ICP: General	SW846 6010C**, 6010D**	Solid and Chemical Material
ICP/MS: General	SW846 6020A**, 6020B**	Solid and Chemical Material
Cold Vapor Mercury	SW846 7471B**	Solid and Chemical Material
Inorganic WetChem		
Ion Chromatography (Bromide, Fluoride, Chloride, Sulfate, Nitrite, Nitrate,) – Aqueous	SW846 9056A**	Solid and Chemical Material
Total CN	SW846 9012B**	Solid and Chemical Material
Ammonia	EPA 350.1	Solid and Chemical Material
Total Kjeldahl Nitrogen	EPA 351.2	Solid and Chemical Material
Total Phosphorus	EPA 365.3	Solid and Chemical Material
Waste Ignitability	SW846 1010A**	Solid and Chemical Material
Hexavalent Chromium	SW846 7196A**	Solid and Chemical Material
Corrosivity & pH – aqueous	SW846 9040C**	Solid and Chemical Material
Corrosivity & pH – solid	SW846 9045D**	Solid and Chemical Material

Method Type	Method Number	Regulatory Program
Cyanide Reactivity	SW846 Chapter 7**	Solid and Chemical Material
Sulfide Reactivity	SW846 Chapter 7**	Solid and Chemical Material
Organics		
Volatile Organics	TO-3	Air and Emissions
Preparation Methods*		
Liquid/Liquid Extraction, Water	SW846 3510C	
Micro-extraction, Water	SW846 3511	
Solid Phase Extraction, Water	SW846 3535A	
Solids Extraction by Sonication	SW846 3550B	
Microwave-assisted extraction, solids	SW846 3546	
Acid/Base Partitioning	SW846 3650B	
Sulfur Cleanup of Extracts	SW846 3660B	
Sulfuric Acid Cleanup	SW846 3665A	
Purge & Trap - Aqueous	SW846 5030B	
Purge & Trap – Solids	SW846 5035A	
Total Recoverable Metals Digestion	EPA 200.7, 200.8	
Non-Pot. Water Digest: ICP	SW846 3010A	
Alkaline Digestion of Soils for Hexavalent Chromium	SW846 3060A	
Digestion of Soils for ICP	SW846 3050B	
TCLP	SW846 1311	
SPLP	SW846 1312	

* Preparation methods are not listed on Primary TNI Accreditation per State of Florida DOH rules. However, for the benefit of other accrediting authorities, these methods are inspected during FDOH visits. Listing of surveyed and approved preparation methods is available from on-site inspection report.
** Methods certified by DoD ELAP

Non-TNI-Accredited Fields of Testing

Method Type	Method Number	Regulatory Program
Thiodiglycol	SGS - Orlando in-house method (HPLC)	Non-Potable Water, Solid and Chemical Material
Perfluorinated Carboxylic Acids and Sulfonates	DoD QSM 5.1 table B-15 compliant**	Non-Potable Water, Solid and Chemical Material
Volatile Organics	SM6200B-11	Non-Potable Water
Volatile Petroleum Hydrocarbons	Missouri Gasoline Range Organics	Non-Potable Water, Solid and Chemical Material
Extractable Hydrocarbons	Missouri Diesel Range Organics	Non-Potable Water, Solid and Chemical Material
Extractable Hydrocarbons	Missouri Oil Range Organic	Non-Potable Water, Solid and Chemical Material
Volatile Petroleum Hydrocarbons	KS-LRH**	Non-Potable Water, Solid and Chemical Material
Extractable Hydrocarbons	KS-MRH**, KS-HRH**	Non-Potable Water, Solid and Chemical Material
Volatile Petroleum Hydrocarbons	NW-TPH	Non-Potable Water, Solid and Chemical Material
Extractable Hydrocarbons	NW-TPH	Non-Potable Water, Solid and Chemical Material
Volatile Petroleum Hydrocarbons	Alaska AK-101**	Non-Potable Water, Solid and Chemical Material
Extractable Hydrocarbons	Alaska AK-102**	Non-Potable Water, Solid and Chemical Material
Extractable Hydrocarbons	Alaska AK-103**	Non-Potable Water, Solid and Chemical Material
Volatile Petroleum Hydrocarbons	OK GRO**	Non-Potable Water, Solid and Chemical Material
Extractable Hydrocarbons	OK DRO**	Non-Potable Water,

Method Type	Method Number	Regulatory Program
		Solid and Chemical Material
Inorganic WetChem		
Percent Ash (dry basis)	ASTM D2974-87, D482-91	Solid and Chemical Material
Sieve Testing	ASTM D422-63	Solid and Chemical Material
Dissolved Oxygen	EPA 360.1	Non-Potable Water
Mineral Suspended Solids	EPA 160.2/160.4	Non-Potable Water
Oil & Grease, Gravimetric – AQ	EPA 1664B	Non-Potable Water
Percent Solids	SM2540G-11	Solid and Chemical Material
Settleable Solids	EPA 160.5	Non-Potable Water
Total Mineral Solids	EPA 160.4	Non-Potable Water
Total Residual Chlorine	EPA 330.5	Non-Potable Water
Total Volatile Solids	EPA 160.4	Non-Potable Water
Volatile Suspended Solids	EPA 160.2/160.4	Non-Potable Water
CN Amenable to Chlorination	EPA 335.4	Solid and Chemical Material
Bicarbonate, Carbonate, CO2 - calculation	SM2320B-11, SM4500 CO2D-11	Non-Potable Water
Ferrous Iron	SM3500 FE-D-11	Non-Potable Water
Salinity - calculation	SM2520B-11	Non-Potable Water
Paint Filter Test	SW846 9095	Solid and Chemical Material
Corrosivity & pH – aqueous	SW846 9040C	Solid and Chemical Material

Appendix III

Equipment List

Instrument	Model	Location	Serial #	Year
GC/MS	Agilent 5975TAD MSD/OI 4551/4660	MS-VOA	US13042A19	2013
GC/MS	Agilent 5975TAD MSD/OI 4551/4660	MS-VOA	US11172705	2011
GC/MS	Agilent 5975TAD MSD/OI 4551/4660	MS-VOA	US11322911	2011
GC/MS	Agilent 5975TAD MSD/OI 4551/4660	MS-VOA	US11282930	2011
GC/MS	Agilent 5975TAD MSD/OI 4551/4660	MS-VOA	US10102029	2010
GC/MS	Agilent 5975TAD MSD/OI 4551/4660	MS-VOA	US10452710	2010
GC/MS	Agilent 5975TAD MSD/OI 4551/4660	MS-VOA	US83120965	2008
GC/MS	Agilent 5975N MSD/Agilent 7683 AS	SVOC Lab	US71225975	2007
GC/MS	Agilent 5975N MSD/Agilent 7683 AS	SVOC Lab	US62724401	2006
GC/MS	Agilent 5975TAD MSD/OI 4551/4660	MS-VOA	US62733661	2006
GC/MS	Agilent 5975N MSD/Agilent 7683 AS	SVOC Lab	US53921303	2005
GC/MS	Agilent 5973N MSD/Agilent 7683 AS	SVOC Lab	US40620599	2004
GC/MS	Agilent 5973 MSD/OI 4551/4660	MS-VOA	US41746628	2004
GC/MS	Agilent 5973 MSD/OI 4551/4660	MS-VOA	US41746633	2004
GC/MS	Agilent 5973 MSD/OI 4560/4552 Archon	Soil VOA	US21843765	2002
GC/MS	Agilent 5973 MSD/OI 4551/4660	MS-VOA	US21844034	2002
GC/MS	Agilent 5973 MSD/OI 4660/4552 Archon	Soil VOA	US02440350	2000
GC/MS	Agilent 5973 MSD/OI 4551/4660	MS-VOA	US94240108	1999
GC/MS	Agilent 5973 MSD/Agilent 7683 AS	SVOC Lab	US82311290	1998
GC/MS	Agilent 5973 MSD/Agilent 7683 AS	SVOC Lab	US81211109	1998
GC/MS	Agilent 5973A MSD/OI 4660/4552 Archon	Soil VOA	US82321728	1998
GC/MS	Agilent 5973A MSD/OI 4660/4551	MS-VOA	US63810329	1996
GC	Agilent 7890A/Dual FID/7693 AS	SVOC Lab	CN13161042	2013
GC	Agilent 7890A/Dual FID/7683B AS	SVOC Lab	CN12121006	2012
GC	Agilent 7890A/Dual ECD/7683B AS	SVOC Lab	CN10842133	2008

Instrument	Model	Location	Serial #	Year
GC	Agilent 7890A/Dual FID/7693 AS	SVOC Lab	CN10902149	2009
GC	Agilent 7890A/Dual ECD/7683B AS	SVOC Lab	CN10741128	2007
GC	Agilent 6890/Dual FPD/7683B AS	SVOC Lab	US10643024	2006
GC	Agilent 6890/Dual FID/7683B AS	SVOC Lab	CN10641049	2006
GC	Agilent 6890/Dual ECD/7683B AS	SVOC Lab	CN10641081	2006
GC	Agilent 6890/Dual ECD/7683B AS	SVOC Lab	US10613003	2006
GC	Agilent 6890/PID/PID/OI 4560/4552 Archon	GC VOA	CN10421047	2004
GC	Agilent 6890/PID/FID/ENTECH 7032A-LB	GC VOA	US10239007	2002
GC	Agilent 6890N/Dual FID/HP 7683 AS	SVOC Lab	CN10425061	2004
GC	Agilent 6890N/Dual ECD/HP 7683 AS	SVOC Lab	US10333015	2003
GC	Agilent 6890/Dual ECD/HP 7683 AS	SVOC Lab	US00036916	2000
GC	Agilent 6890/Dual ECD/HP 7683 AS	SVOC Lab	US00028304	1999
GC	Hewlett-Packard 5890/PID/FID/ OI 4560/4552 Archon	GC VOA	3336A60617	1993
GC	Hewlett-Packard 5890/PID/FID/ OI 4560/4552 Archon	Soil VOA	3336A61096	1993
GC	Hewlett-Packard 5890/PID/FID/ OI 4560/4552 Archon	GC VOA	3336A51045	1993
GC	Hewlett-Packard 5890/PID/FID/OI 4560/4552 Archon	GC VOA	3203A41646	1992
GC	Hewlett-Packard 5890/PID/FID/OI 4560/4552 Archon (screening instrument)	GC VOA	3223A42867	1992
GC	Hewlett-Packard 5890/PID/FID OI 4560/4552 Archon	Soil VOA	3029A29748	1990
GC	Hewlett-Packard 5890/FID	GC VOA	2843A20183	1988
GC	Hewlett-Packard 5890/FID	GC VOA	2728A12705	1987
HPLC	Agilent 1100 Automated LC System	HPLC Room	DE91606857	1999
HPLC	Agilent 1100 Automated LC System	HPLC Room		2002

Instrument	Model	Location	Serial #	Year
HPLC	Agilent 1100 Automated LC System	HPLC Room	DE01608404	2000
HPLC	Agilent 1100 Automated LC System	HPLC Room	DE40522115	2004
HPLC	Agilent 1100 Automated LC System	HPLC Room	DE03000863	2003
HPLC	Agilent 1100 Automated LC System	HPLC Room	DE61800775	2006
HPLC	Agilent 1100 Automated LC System	HPLC Room	DE33219455	2003
LC/MS/MS	Agilent 1200/6460 LC/Triple Quad	HPLC Room	SG10447001	2011
LC/MS/MS	Agilent 1200/6460 LC/Triple Quad	HPLC Room	SG163G008	2016
O-Prep	ESSA LM2-P Ring and Puck mill	Explosives Prep Lab	215090-004	2008
O-prep	Microwave extractor MARS 6, 2 units	Organic Prep Lab	Multiple	Various
O-Prep	TurboVap concentrators, 8 units	Organic Prep Lab	Multiple	Various
O-Prep	Buchi solvent recovery system, 4 units	Organic Prep Lab	Multiple	2014
O-Prep	Sonicator 4 units	Organic Prep Lab		Various
O-Prep	N-Vap	Organic Prep Lab	479200-2000	2000
Data System	Hewlett-Packard/MS ChemStation	Labwide		1999, with subsequent upgrades

Instrument	Model	Location	Serial #	Year
ICP/MS	Agilent 7700 Series	Metals Lab	JP12151709	2012
ICP	Thermo ICAP 6000 Series	Metals Lab	20100903	2010
ICP	Thermo ICAP 6000 Series	Metals Lab	20103825	2010
Mercury Analyzer	Leeman Hydra AA II	Metals Lab	2019	2012
Mercury Analyzer	Leeman Hydra AA II	Metals Lab	2004	2012
TOC Analyzer	Teledyne TORCH	VOC GC Room	US18151009	2019

Instrument	Model	Location	Serial #	Year
TOC Analyzer	Shimadzu	VOC GC room	H51404735099	2010
IC	Dionex IC-2100	VOC MS room	1930200035126	2019
IC	Dionex IC-2000	WetChem IC room	04070250	2004
Auto Analyzer	QuickChem 8500 Series	WetChem main room	050500000130	2005
Auto Analyzer	QuickChem 8500 Series 2	WetChem main room	111200001380	2011
Spectrophotometer	Milton-Roy Spectronic 200	WetChem main room	2 units	2000
Digestion block	DigiPrep	WetChem main room	2units	2005
Digestion block	DigiPrep	WetChem main room	2 units	2018
Centrifuge	CentraCL2	WetChem main room	42613052	2003
Autoclave	ThermoFisher NAPCO	WetChem IC room	124977-418	2015
MicroDistillation Block	Lachat	WetChem main room	2 units	2005

LIMS		
Instrument	**Model**	**Year**
LIMS	Stratus Dual Server; Oracle 10G Database	2013

Appendix IV

Certification Summary

Alaska	Contaminated Sites	UST-088
Arizona	Solid/Hazardous Waste	
Arkansas	Solid/Hazardous Wastes, Non-Potable Water	88-0620
		04226CA
Department of Defense (DoD)	Non-Potable Water, Solid and Chemical Materials	L-2229
Florida (NELAP)	Potable, Non-Potable, Solid Waste, UST, Air Toxics	E83510
Georgia	Wastewater/Microbiology analyst	Not Applicable
Illinois	Solid/Hazardous Wastes, Non-Potable Water	
Iowa	UST, Solid/Hazardous Wastes, Non-Potable Water	IA366
Kansas (NELAP)	Solid/Hazardous Wastes, Non-Potable Water	E-10327
Kentucky	Underground Storage Tank Program	0065
Kentucky		98023
Louisiana (NELAP)	Solid/Hazardous Wastes	38582
Massachusetts	Non-Potable Water	M-FL946
Mississippi	Potable Water	Not Applicable
Nevada	Non-Potable Water, Solid/Hazardous Wastes	FL009462008A
New Hampshire	Non-Potable Water, Solid/Hazardous Wastes	
New Jersey (NELAP)	Solid/Hazardous Wastes, Non-Potable Water	FL002
New York	Solid/Hazardous Wastes, Non-Potable Water	12022
North Carolina	Solid/Hazardous Wastes, Non-Potable Water	573
North Dakota	Solid/Hazardous Wastes, Non-Potable Water	
Oklahoma	Non-Potable Water, Solid/Hazardous Waste	9959
Oregon	Non-Potable Water, Solid/Hazardous Waste	
South Carolina	Solid/Hazardous Wastes, Non-Potable Water	96038001
Texas (NELAP)	Non-Potable Water, Solid/Hazardous Waste	T104704040-08-TX
US Dept. of Agriculture	Foreign Soils Permit	P330-16-00126
Utah (NELAP)	Potable, Non-Potable, Solid/Chemical Materials	FL009462008A
Virginia (NELAP)	Potable, Non-Potable, Solid/Chemical Materials	460177
Washington	Potable, Non-Potable, Solid/Chemical Materials, Air	C2046
West Virginia	Solid/Hazardous Wastes, Non-Potable Water	304

Appendix V

SOP List

SOP #	TITLE
	Organic Preparation Department
OP002	SOP for Glassware Cleaning and Storage
OP003	SOP for Reagent Prep
OP006	SOP for the Extraction of Semi-volatile Organics (BNAs) from Aqueous Samples
OP007	SOP for the Extraction of Semi-volatile Organics (BNAs) from Solid Samples
OP007TV	SOP for the Extraction of Semi-volatile Organics (BNAs) from Solid Samples, TurboVap option
OP008	SOP for the Extraction of Pesticides/PCBs from Aqueous Samples
OP009	SOP for the Extraction of Pesticides/PCBs from Solid Samples
OP009MW	SOP for the Extraction of Pesticides/PCBs from Solid Samples, microwave
OP010	SOP for the Extraction of Diesel Range Organics (DRO) from Aqueous Samples
OP011	SOP for the Extraction of Diesel Range Organics (DRO) from Solid Samples
OP011MW	SOP for the Extraction of Diesel Range Organics (DRO) from Solid Samples
OP012	SOP for the Extraction of Petroleum Related Organics (FL-PRO) from Aqueous Samples
OP013	SOP for the Extraction of Petroleum Related Organics (FL-PRO) from Solid Samples
OP014	SOP for the Extraction of PAHs from Aqueous Samples (HPLC)
OP015	SOP for the Extraction of PAHs from Solid Samples (HPLC)
OP016	SOP for the Extraction of EDB/DBCP from Aqueous Samples
OP017	SOP for the Extraction of EDB/DBCP from Solid Samples
OP018	SOP for the Extraction of Explosives from Aqueous Samples, 8330A/B
OP019	SOP for the Extraction of Explosives from Solid Samples, 8330A
OP020	SOP for Sample Introduction via SW846-5035
OP021	SOP for Sample Introduction via SW846-5030B
OP024	Standard Operating Procedure For The Extraction Of Nitroaromatics From Water Samples
OP025	SOP For Sample Preparation For Dissolved Gases In Aqueous Samples
OP026	SOP For The Extraction Of Extractable Petroleum Products (OA-2) From Water Samples
OP027	SOP For The Extraction Of Extractable Petroleum Products (OA-2) From Solid Samples
OP028	SOP For The Extraction Of Diesel And Oil Range Organics From Water Samples
OP029	SOP For The Extraction Of Diesel And Oil Range Organics From Solid Samples
OP030	SOP For The Extraction Of Extractable Petroleum Hydrocarbons From Water Samples (Tennessee EPH)

SOP #	TITLE
OP031	SOP For The Extraction Of Extractable Petroleum Hydrocarbons From Solid Samples (Tennessee EPH)
OP032	SOP For The Extraction Of Volatile Petroleum Hydrocarbons From Soil Samples, MA-VPH
OP033	SOP For The Extraction Of PCBs From Wipes
OP034	SOP For The Extraction Of Diesel Range Organics (DRO) From Aqueous Samples WI-DRO
OP035	SOP For The Extraction Of Massachusetts Extractable Petroleum Hydrocarbons From Water Samples
OP036MW	SOP For The Extraction Of Massachusetts Extractable Petroleum Hydrocarbons From Solid Samples, Microwave option
OP037	SOP For The Extraction Of Chlorinated Herbicides From Water Samples
OP038MW	SOP For The Extraction Of Chlorinated Herbicides From Soil Samples, microwave
OP039	SOP For The Solid Phase Extraction (SPE) Cartridge Cleanup Of Pesticide Extracts
OP040	SOP For SPLP Leaching Of SVOC And Metals
OP041	SOP For TCLP Leaching Of VOC
OP042	SOP For SPLP Leaching Of SVOC And Metals
OP043	SOP For SPLP Leaching Of VOC
OP044	SOP For The Extraction Of Organophosphorus Pesticides From Water Samples
OP044SP	SOP For The Extraction Of Organophosphorus Pesticides From Water Samples, Solid Phase Extraction
OP045MW	SOP For The Extraction Of Organophosphorus Pesticides From Soil Samples, microwave
OP046	SOP for the Extraction of Explosives from Solid Samples, SW-8330B
OP048	SOP for the Extraction of PCB Congeners from Aqueous Samples
OP049	SOP for the Extraction of PCB Congeners from Solid Samples
OP050	SOP For The Extraction Of Alaska Extractable Petroleum Hydrocarbons From Water Samples
OP051	SOP For The Extraction Of Alaska Extractable Petroleum Hydrocarbons From Solid Samples
OP052	SOP For The Extraction Of Oklahoma Extractable Petroleum Hydrocarbons From Water Samples
OP053	SOP For The Extraction Of Oklahoma Extractable Petroleum Hydrocarbons From Solid Samples
OP054	SOP For The Extraction Of 1,4-Dioxane From Water Samples
OP055	SOP For The Extraction Of Petroleum Hydrocarbons From Water Samples, TX-1005
OP056	SOP For The Extraction Of Petroleum Hydrocarbons From Solid Samples, TX-1005
OP057	SOP for Sample Introduction via AK-101
OP058	SOP For Extraction Perfluorinated Alkyl Compounds From Water Samples

SOP #	TITLE
OP059	SOP for Extraction of PAH and select analytes for 8270 SIM analysis from Aqueous samples
OP060	SOP for Extraction of PAH and select analytes for 8270 SIM analysis from Solid samples
OP061	SOP for Reduced Volume Extraction of PAH from water sample for GC/MS LVI
OP062	SOP for microextraction of PAH from water samples 3511.

Gas Chromatography/ HPLC SOPs

GC002	Analysis Of 1,2-Dibromoethane (EDB) And 1,2-Dibromo-3-Chloropropane (DBCP) By Gas Chromatography, Electron Capture Detector
GC005	Analysis Of Organochlorine Pesticides By Gas Chromatography, Electron Capture Detector EPA 608
GC006	Analysis Of Polychlorinated Biphenyls By Gas Chromatography, Electron Capture Detector EPA 608
GC007	Analysis Of Polynuclear Aromatic Hydrocarbons By Gas Chromatography, Flame Ionization Detector EPA 610
GC008	Analysis Of Petroleum Range Organics By Gas Chromatography Using Flame Ionization Detector
GC009	Analysis Of 1,2-Dibromoethane (EDB) And 1,2-Dibromo-3-Chloropropane (DBCP) By Gas Chromatography, Electron Capture Detector SW-846 8011
GC010	Analysis Of Gasoline Range Organics By Gas Chromatography Using Flame Ionization Detector
GC011	Analysis Of Diesel Range Organics By Gas Chromatography Using Flame Ionization Detector
GC014	Analysis Of Polychlorinated Biphenyls By Gas Chromatography, Electron Capture Detector SW-846 8082
GC015	Analysis Of Organochlorine Pesticides By Gas Chromatography, Electron Capture Detector SW-846 8081
GC016	Analysis Of Nitroaromatics And Nitramines By HPLC
GC019	Analysis Of Dissolved Gases By Gas Chromatography, Flame Ionization Detector
GC020	Analysis Of Nitroglycerine And PETN By HPLC
GC021	Analysis Of Volatile Petroleum Hydrocarbons By Gas Chromatography
GC022	Analysis Of Extractable Petroleum Products By Gas Chromatography Using Flame Ionization Detector OA-2
GC023	Analysis Of Diesel And Oil Range Organics By Gas Chromatography Using Flame Ionization Detector
GC024	Analysis Of Petroleum Hydrocarbons By Gas Chromatography Using Flame Ionization Detector (Tennessee EPH)
GC025	Analysis Of Nitroaromatics By Gas Chromatography Using Electron Capture Detector
GC026	Method For Determination Of Volatile Petroleum Hydrocarbons By GC-

SOP #	TITLE
	PID/FID
GC027	Analysis Of Non-Halogenated Organics By Gas Chromatography Using Flame Ionization Detector
GC028	Analysis Of Gasoline Range Organics By Gas Chromatography Using Flame Ionization Detector TDEC GRO
GC029	Analysis Of Diesel Range Organics By Gas Chromatography Using Flame Ionization Detector Wi DRO
GC030	Analysis Of Extractable Petroleum Hydrocarbons By Gas Chromatography Using Flame Ionization Detector MA-EPH
GC031	Analysis Of Chlorinated Herbicides Using GC-ECD
GC032	Analysis Of Organophosphorus Pesticides Using GC-NPD Or FPD
GC033	Air Analysis By GC-PID/FID
GC034	Analysis Of Nitroaromatics, Nitramines And Nitrate Esters By HPLC Method 8330B
GC035	Screening Of Volatile Organics By GC-PID/FID
GC036	Analysis of PCB Congeners by ECD
GC037	Analysis of Diesel and Oil Range Organics by GC/FID, AK-102, AK-103
GC038	Analysis of Gasoline Range Organics by GC/FID, AK-101
GC039	Analysis of Diesel Range Organics by GC/FID, OK-GRO
GC040	Analysis of Gasoline Range Organics by GC/FID, OK-GRO
GC041	Analysis of N-Nitroso-N-Ethylurea by HPLC
GC042	Analysis of Thiodiglycol by HPLC
GC043	Analysis of Acrylamide by HPLC
GC044	Analysis of Petroleum Organics by TX-1005
GC045	Automated Fractionation of MA-EPH extracts
GC046	SOP for Screening Petroleum Range Organics by FID
GC047	Nitroguanidine by HPLC
GC048	Analysis of KS LRH by GC-FID
GC049	Analysis of KS MRH-HPH by GC-FID

Mass-Spectrometry SOPs

MS003	Analysis of Volatile Organics by EPA Method 624
MS004	Analysis of Semi-volatile Organics by EPA Method 625
MS005	Analysis of Volatile Organics by EPA Method 8260B
MS006	Analysis of Semi-volatile Organics by EPA Method 8270C
MS008	Analysis of Semi-volatile Organics by EPA Method 8270C SIM
MS009	Analysis of Volatile Organics by GC/MS
MS010	Analysis of Volatile Organics by GC/MS SIM
MS011	Analysis of Semi-volatile Organics by EPA Method 8270D
MS012	Analysis of 1,4-Dioxane by EPA 522
MS013	Analysis of Perchlorate by SW-846 6850
MS014	Analysis of PFOS/PFOA by LC/MS/MSD
MS015	Analysis of 8270 SIM LVI

SOP #	TITLE
MS016	Analysis of Volatile Organics by EPA Method 8260C
MS017	Analysis of PFOS/PFOA by LC/MS/MSD, method EPA 537, Drinking water
MS018	Analysis of Amines by LC/MS/MSD,
MS019	Analysis of PFOS/PFOA by LC/MS/MSD, Isotope Dilution

Quality Assurance SOPs

QA001	Preparation, Approval, Distribution & Archiving Of Standard Operating Procedures (SOPs)
QA002	Calibration Of Thermometers
QA003	Personnel Training And Analyst Proficiency
QA004	Temperature Monitoring
QA005	Calibration Of Analytical Balances
QA006	Eppendorf Pipette Calibration
QA007	Sample Batching Procedure
QA008	Creating New Accounts
QA009	Creating New Projects
QA010	Confidentiality Protection Procedures
QA011	Signature Authority
QA012	Employee Technical Ethics Responsibilities
QA013	Client Complaint Resolution Procedure
QA014	Procedures For The Purchase Of Laboratory Supplies
QA015	Procedures For The Preparation, Distribution, Use And Archiving Of Laboratory Logbooks
QA016	Corrective Action Procedure
QA017	Standards Traceability Documentation Procedure
QA018	Procedure For Login, Management, Handling, And Reporting Of Proficiency Test (Pt) Samples
QA019	Quality System Review
QA020	Procedure For Developing Method Performance Criteria And Experimental Method Detection Limits
QA021	Subcontracting Procedures
QA022	Internal Audit Procedure
QA023	Fume Hood Inspection
QA027	Review Of Inorganics Data
QA028	Review Of Organics Data
QA029	Manual Integration Of Chromatographic Peaks
QA030	Procedure For The Development And Use Of in-house Quality Control Criteria
QA031	Air Quality Monitoring Of Extraction Laboratory
QA032	Routine Maintenance For Major Analytical Instrumentation
QA033	Laboratory Safety
QA034	Sample Homogenizing
QA035	Solvent Testing And Approval

SOP #	TITLE
QA036	Data Package Generation
QA037	Deionized Water Quality Control Procedure
QA038	Data Integrity Training Procedure
QA039	Data Integrity Monitoring Procedure
QA040	Procedure For Conducting Data Integrity Investigations
QA041	Procedure For The Confidential Reporting Of Data Integrity Issues
QA042	Basic Calculations For General Chemistry Methods
QA043	Data Qualifier SOP
QA044	Calibration Of Micro-Distillation Tubes
QA045	Estimation of Uncertainty
QA046	Document Control
QA047	Management of Client Project
QA048	Data Entry for Log-In
QA049	MA DEP DW Notification
QA050	PA DW Notification

General Chemistry SOPs

GNSOP: 101	Acidity (pH 8.2)
GNSOP: 102	Alkalinity, Total (pH 4.5)
GNSOP: 103	Ammonia – Distillation Procedure
GNSOP: 104	Nitrogen, Ammonia
GNSOP: 104GD	Nitrogen, Ammonia, Gas Diffusion option
GNSOP: 105	Bicarbonate, Carbonate, Free Carbon Dioxide
GNSOP: 106	Chemical Oxygen Demand
GNSOP: 109	Color, Apparent
GNSOP: 110	Chromium, Hexavalent (Water)
GNSOP: 113	Cyanide Distillation/Aqueous And Solid Samples
GNSOP: 115	Cyanide, Total
GNSOP: 116	Dissolved Oxygen
GNSOP: 121	Ignitability
GNSOP: 123	Nitrogen, Nitrite
GNSOP: 126	Ortho Phosphate
GNSOP: 127	Paint Filter Liquids Test
GNSOP: 128	Phenols Distillation, Soil And Water Samples
GNSOP: 130	Phenols, Total Recoverable
GNSOP: 133	Settleable Solids
GNSOP: 134	Total Suspended Solids (Non Filterable Residue)
GNSOP: 135	Total Dissolved Solids (Total Filterable Residue)
GNSOP: 136	Reactive Sulfide And Reactive Cyanide
GNSOP: 137	pH By Electrode - Water
GNSOP: 140	Sulfide
GNSOP: 144	Total Phosphorus

SOP #	TITLE
GNSOP: 145	Turbidity
GNSOP: 147	Winkler Titration For DO Standardization
GNSOP: 161	Percent Solids
GNSOP: 163	Specific Conductance At 25 C.
GNSOP: 166	pH By Electrode – Soil
GNSOP: 167	Biochemical Oxygen Demand (BOD)
GNSOP: 171	Hexachromium In Soils
GNSOP: 179	Corrosivity (Soil pH By Electrode)
GNSOP: 182	Total Kjeldahl Nitrogen
GNSOP: 189	Corrosivity Toward Steel
GNSOP: 190	Total Nitrogen, Organic Nitrogen
GNSOP: 191	Nitrogen, Nitrate
GNSOP: 192	Carbonaceous Biochemical Oxygen Demand (CBOD)
GNSOP: 193	Oxidation-Reduction Potential
GNSOP: 194	Ferrous Iron
GNSOP: 196	Glassware Cleaning
GNSOP: 211	Oil & Grease And PHC By 1664
GNSOP: 212	Fractional Organic Carbon
GNSOP: 213	Walkley-Black Total Organic Carbon
GNSOP: 214	Particle Size By Sieve
GNSOP: 215	TOC In Water
GNSOP: 218	Perchlorate
GNSOP: 219	Bulk Density
GNSOP: 222	Un-Ionized Ammonia Calculation
GNSOP: 224	Hardness By Calculation
GNSOP: 225	Cation Exchange Capacity Of Soils (Sodium Acetate)
GNSOP: 226	TOC In Soil
GNSOP: 227	Oil And Grease – Gravimetric Analysis (Soils)
GNSOP: 228	Anions By Ion Chromatography
GNSOP: 231	% Ash
GNSOP: 232	Determination Of Nitrate and Nitrite by Lachat
GNSOP: 233	Sulfite
GNSOP: 234	Total Solids, Gravimetric
GNSOP: 235	Total Volatile Solids, Gravimetric

Metals SOPs

MET 100	Metals By Inductively Coupled Plasma, EPA 6010C
MET 103	Digestion Of Water Samples For Flame And ICP Analysis
MET 104	Digestion Of Soils For ICP Analysis
MET 105	Cold Vapor Analysis Of Mercury For Soils
MET 106	Cold Vapor Analysis Of Mercury For Water Samples
MET 107	Metals By Inductively Coupled Plasma, Mass-Spectrometry
MET 108	Metals By Inductively Coupled Plasma, EPA 6010D

SOP #	TITLE

Sample Management SOPs

SAM101	Sample Receipt And Storage
SAM102	Procedure For Sample Bottle Preparation And Shipment
SAM104	Sample Container Quality Control
SAM108	Sample And Laboratory Waste Disposition
SAM109	Foreign Soil receipt and Handling

Appendix VI

Data Integrity Training Acknowledgement and Ethical Conduct Agreement

I understand that SGS Accutest is committed to having its employees perform their duties ethically and responsibly. By signing this document, I agree to uphold SGS Accutest commitment to ethics and integrity as follows:

I. *I understand the high ethical standards required of me with regard to the duties I perform and the data I report in connection with my employment at SGS Accutest.*

II. *I have received formal instruction on the code of ethics that has been adopted by SGS Accutest during my orientation and agree to comply with these requirements.*

III. *I have received formal instruction on the elements of SGS Accutest's Data Integrity Policy and have been informed of the following specific procedures:*

   a. *Formal procedures for the confidential reporting of data integrity issues are available, which can be used by any employee,*

   b. *A data integrity investigation is conducted when data issues are identified that may negatively impact data integrity.*

   c. *Routine data integrity monitoring is conducted on sample data, which may include an evaluation of the data I produce,*

IV. *I have attended the Data Integrity training detailing SGS Accutest Data Integrity and Ethics Program as required.*

V. *I am aware that data fraud is a punishable crime that may include fines and/or imprisonment upon conviction.*

VI. *I also agree to the following:*

   a. *I shall not intentionally report data values, which are not the actual values observed or measured.*

   b. *I shall not intentionally modify data values unless the modification can be technically justified through a measurable analytical process.*

   c. *I shall not intentionally report dates and times of data analysis that are not the true and actual times the data analysis was conducted.*

   d. *I shall not condone any accidental or intentional reporting of inauthentic data by other employees and immediately report it's occurrence to my superiors.*

   e. *I shall immediately report any accidental reporting of inauthentic data by myself to my superiors.*

   f. *I will, at all times, handle client samples and SGS Accutest instrumentation as required by the SGS Accutest Standard Operating Procedures.*

g. *I will not intentionally deviate from, or fail to follow, the SGS Accutest Standard Operating Procedures at any time except as authorized by this document.*

h. *I understand that deviations from a Standard Operating procedure are allowed only when the deviations are clearly presented in writing by supervisory, managerial or director level staff and when those deviations do not contradict any part of the SGS Accutest ethics policy. No other personnel are allowed to approve Standard Operating Procedure deviations.*

i. *Anytime someone suggests, recommends, or requests that I do not follow an SGS Accutest Standard Operating Procedure, other than as noted in h above, I shall immediately notify my supervisor, manager, a Quality Assurance Officer, the Lab Director, or the Director of Human Resources.*

j. *Anytime I am uncomfortable or unsure about an action that I am requested to perform, I shall immediately notify my supervisor, manager, a Quality Assurance officer, the Lab Director, or the Director of Human Resources. By doing so, I understand that I will not be punished or penalized for asking for guidance or reporting potential wrongdoing.*

k. *If I intentionally disregard the SGS Accutest Standard Operating Procedures without written authorization to do so, I may face disciplinary action up to and including termination of my employment. Note: unintentional deviation from a Standard Operating Procedure must be documented on discovery and appropriate corrective actions followed.*

l. *If I become aware of another person who appears to be disregarding the SGS Accutest Standard Operating Procedures without written authorization to do so, I shall immediately report it to my supervisor, manager, a Quality Assurance Officer, the Lab Director, or the Director of Human Resources. By failing to do so, I may face disciplinary action up to and including termination of my employment.*

m. *I am aware that intentionally failing to follow an SGS Accutest Standard Operating Procedure, other than as noted in h above, may be illegal and could be considered data fraud. In addition, providing instruction to another person to deviate from a Standard Operation, other than as noted in c above, may be illegal and could be considered data fraud.*

n. *I am aware that data fraud is a crime and is punishable by fines and/or imprisonment upon conviction. It is the general policy of SGS Accutest to cooperate with law enforcement authorities in the investigation and prosecution of such matters.*

o. *I understand that SGS Accutest strictly prohibits unlawful retaliation and I understand that, if I report a violation of the SGS Accutest Standard Operating Procedures or an instruction that would violate the SGS Accutest Standard Operating Procedures, I will not be subjected in any way to any adverse employment action because of my report. I agree that if I believe I am being, or have been, subjected to an adverse employment action because of my report, then I will immediately notify my supervisor, manager, a Quality Assurance officer, the Lab Director, or the Director of Human Resources. I agree that SGS Accutest cannot address or correct any such retaliatory behavior unless it is reported and SGS Accutest is given an opportunity to address or correct such behavior.*

Printed Name	Signature	Date

ANALYSIS OF VOLATILE ORGANICS BY GC/MS

Prepared by: Norm Farmer Date: 08/26/19

Approved by: Juan Garcia Date: 08/27/19

Annual Review

Reviewed by: _____ Date: _____

Reviewed by: _____ Date: _____

Reviewed by: _____ Date: _____

Document Control

Issued to: QA Department Date: 08/28/19

Issued to: MS Volatile Department Date: * 08/28/19

Issued to: MS Volatile Soil Lab Date: 08/28/19

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Effective 7 days after "*" date

CONTROLLED COPY
DO NOT DUPLICATE

TITLE: ANALYSIS OF VOLATILE ORGANICS BY GC/MS

REFERENCES: SW846 8260B

REVISED SECTIONS: 1.1.6 and 7.5.2.8

1.0 SCOPE AND APPLICATION, SUMMARY

1.1 Scope and Application

1.1.1 This method is used to determine the concentrations of various volatile organic compounds in water and solid matrices utilizing a gas chromatograph equipped with a mass spectrometer detector. Routine compounds can be found in Table 1.

1.1.2 The Lower Limit of Quantitation (LLOQ) or Reporting limits (RL) are based on the sample amount and the lowest calibration standard. LLOQs may vary depending on matrix complications and sample volumes. LLOQs for this method are in the range of 1.0-5.0 ug/l for aqueous samples and 5-25 ug/kg for solid samples. Solid matrices are reported on a dry weight basis.

1.1.3 The Method Detection Limit (MDL) for each analyte is evaluated on an annual basis for each matrix and instrument. MDLs are pooled for each matrix, and the final pooled MDLs are verified. The verified MDLs are stored in the LIMS and should be at least 2 to 3 times lower than the LLOQ. Exceptions may be made on a case by case basis; however, at no point shall the MDL be higher than the reported LLOQ.

1.1.4 The LLOQ for each analyte is evaluated on an annual basis for each matrix and instrument. The LLOQ verifications are prepared by spiking a clean matrix at 0.5 to 2 times the current LLOQ level. This LLOQ verification is carried through the same preparation and analytical procedures as the samples. Recovery of the analytes should be within the established limits. The DOD QSM requirements for Limit of Detection (LOD) and Limit of Quantitation (LOQ) verifications are different. See SOP QA020 for complete requirements for MDL, LOD, LOQ, and LLOQ.

1.1.5 Compounds detected at concentrations between the LLOQ and MDL are quantitated and qualified as estimated values and reported with either a “J” or “I” qualifier. Some program or project specifications may require that no values below the LLOQ be reported.

1.1.6 For DOD projects, refer to QSM 5.0, Table 4; QSM 5.1, Table B-4; or QSM 5.3, Table B-4 for additional method requirements and data qualifying guidance.

1.2 Summary

1.2.1 This method is adapted from SW846 method 8260B.

1.2.2 Samples are received, stored, and analyzed within the appropriate holding times.

1.2.3 Sample preparation is performed in accordance with SGS Orlando SOP OP020 and OP021.

1.2.4 The samples are analyzed on a gas chromatograph equipped with mass spectrometer detector.

1.2.5 The peaks detected are identified by comparison to characteristic ions and retention times specific to the known target list of compounds.

1.2.6 Additional unknown peaks with a response > 10% of the closest internal standard may be processed through a library search with comparison to an NIST database of approximately 129,000 compound spectra. An estimated concentration is quantitated by assuming a response factor of 1.

1.2.7 Manual integrations are performed in accordance with SOP QA029.

2.0 PRESERVATION AND HOLDING TIME

2.1 Preservation

Aqueous Samples:

2.1.1 Samples should be preserved to a pH < 2. The pH should be checked and recorded immediately after the sample analysis. If the sample is not preserved to a pH < 2, it must be noted on the report.

2.1.2 If 2-chloroethyl vinyl ether is a compound of concern, the sample should not be preserved. If acrolein and acrylonitrile are compounds of concern, the sample should be adjusted to a pH 4 – 5 in the field.

2.1.3 The samples must be stored in capped vials, with minimum headspace, at ≤ 6 °C in an area free of solvent fumes. The size of any bubble caused by degassing upon cooling should not exceed 5-6mm.

Solid Samples:

2.1.4 Special 40ml vials for purge-and-trap of solid samples, as well as the collection and preservation options are described in OP020.

2.1.5 Low level soil samples are preserved by storing them in sealed VOA vials at temperatures between –10 °C to –20 °C. High level soil samples are preserved by storing them in methanol at a ratio of 1 gram of soil to 1ml of methanol.

2.2 Holding Time

2.2.1 Aqueous samples are to be analyzed within 14 days of collection, unless otherwise specified by the contract. Samples that are not preserved should be analyzed within 7 days of collection; however, the preservation deficiency must be noted in the report.

2.2.2 Solid and waste samples must be analyzed within 14 days of collection.

3.0 INTERFERENCES

3.1 Data from all blanks, samples, and spikes must be evaluated for interferences.

3.2 Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory blanks. The use of non-TFE tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.3 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank can serve as a check on such contamination.

3.4 Contamination by carry-over can occur whenever high level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for carry-over.

3.5 Acidification with HCl or bisulfate solution may cause the loss of 2-chloroethyl vinyl ether, acrolein, and acrylonitrile.

3.6 Soils and sediment that contain limestone ($CaCO_3$) may react with the sodium bisulfate and effervesce. The effervescing can result in significant losses of volatile organics.

3.7 Certain naturally occurring compounds (humic acids, etc.) will decompose when exposed to the bisulfate solution and form ketones, notably acetone. The amount of acetone formed is extremely matrix dependent but may be produced in significant concentrations.

3.8 The purge efficiency of select fuel oxygenates may be improved by using a heated purge. These fuel oxygenates generally include: methyl tert butyl ether (MTBE), ethyl tert butyl ether (ETBE), tert amyl methyl ether (TAME), di-isopropyl ether (DIPE), tert amyl ethyl ether (TAEE), tert amyl alcohol (TAA), tert butyl alcohol (TBA), and ethanol (ETOH).

3.8.1 Methyl tert butyl ether (MTBE) may be converted to TBA under acidic preservation and elevated purging temperatures.

3.8.2 If samples containing MTBE, TAME, ETBE or other fuel ethers have been preserved with hydrochloric acid and will be analyzed by purging at elevated temperatures, these samples must be adjusted to pH >10 with tri-sodium phosphate dodecahydrate (TSP) prior to initiation of the analysis.

3.8.3 Dibromofluoromethane (surrogate) may degrade and fail low in samples with a basic pH.

3.8.4 Tert butyl formate (TBF) may degrade at elevated purge temperatures.

4.0 DEFINITIONS

4.1 Batch: A group of samples which are similar with respect to matrix and the testing procedures being employed and which are processed as a unit. A sample batch is limited to a maximum of 20 samples or samples loaded on an instrument within the same 12-hour shift, whichever comes first.

4.2 Blank Spike (BS): An analyte-free matrix spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. Blank Spike Recoveries are used to document laboratory performance for a given method. This may also be called a Laboratory Control Sample (LCS).

4.3 Continuing Calibration Verification (CCV): A check standard used to verify instrument calibration throughout an analytical run. For all MS methods, a CCV must be analyzed at the beginning of each analytical run. For DoD QSM 5.x projects, an additional CCV must be analyzed at the end of the run.

4.4 Holding Time: The maximum times that samples may be held prior to preparation and/or analysis and still be considered valid.

4.5 Internal Standards: An organic compound which is similar to the target analyte(s) in chemical composition and behavior, but which is not normally found in environmental samples. Internal standards for mass spec methods are often deuterated forms of target analytes. Internal standards are used to compensate for retention time and response shifts during an analytical run.

4.6 Initial Calibration (ICAL): A series of standards used to establish the working range of a particular instrument and detector. The low point should be at a level equal to or below the LLOQ.

4.7 Initial Calibration Verification (ICV): A standard from a source different than that used for the initial calibration. A different vendor should be used whenever possible. The ICV is used to verify the validity of an Initial Calibration. This may also be called a QC check standard.

4.8 Matrix Spike (MS): A sample aliquot spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. The

matrix spike recoveries are used to document the bias of a method in a given sample matrix.

4.9 Matrix Spike Duplicate (MSD): A replicate sample aliquot spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. The matrix spike duplicate recoveries are used to document the precision and bias of a method in a given sample matrix.

4.10 Method Blank (MB): An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is processed simultaneously with the samples through all the steps of the analytical procedure. The method blank is used to document contamination resulting from the analytical process.

4.11 Sample Duplicate (DUP): A replicate sample which is used to document the precision of a method in a given sample matrix.

4.12 Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical integrity of the sample.

4.13 Surrogate: An organic compound which is similar to the target analyte(s) in chemical composition and behavior, but which is not normally found in environmental samples. Surrogates are used to measure the purge efficiency.

4.14 Trip Blank: A sample of analyte-free matrix taken from the laboratory to the sampling site and returned to the laboratory unopened. A trip blank is used to document contamination attributable to shipping and field handling procedures. This type of blank is useful in documenting contamination of volatile organic samples.

5.0 REAGENTS

5.1 Reagent water – distilled or deionized water free of interferences

5.2 Methanol – purge-and-trap grade or equivalent

5.3 Hydrochloric acid (HCl) – ACS reagent grade or equivalent

5.4 Sodium Bisulfate Solution – free of interferences

5.5 Tri-sodium phosphate dodecahydrate (TSP) – ACS reagent grade or equivalent

5.6 Inert Gas – UHP Helium or UHP Nitrogen

5.7 Volatile stock standards – Various mixes, traceable to Certificate of Analysis

5.8 4-Bromofluorobenzene (BFB) – instrument tuning mix

5.9 Surrogate standards –

Dibromofluoromethane	1,2-Dichloroethane-d_4
Toluene-d_8	4-Bromofluorobenzene

5.10 Internal standards –

Fluorobenzene	Chlorobenzene-d_5
1,4-Dichlorobenzene-d_4	Tert-butyl alcohol-d_{10}

6.0 APPARATUS

6.1 Gas Chromatograph – Agilent Technologies 6890 or 7890

6.1.1 Gas Chromatograph

The analytical system that is complete with a temperature programmable gas chromatograph and all required accessories, analytical columns, and gases.

6.1.2 The injection port is designed for split-splitless injection with capillary columns. The injection port must have an appropriate interface for sample introduction.

6.2 Mass Spectrometer – Agilent Technologies 5973 or 5975

The mass spectrometer must be capable of scanning from 35-300 amu every second or less utilizing 70-volt (nominal) electron energy in the electron impact ionization mode. It must also be capable of producing a mass spectrum that meets all the criteria in section 7.5.1.1 when injecting 50 ng of Bromofluorobenzene (BFB).

6.3 Purge and Trap – OI Analytical 4660 with OI Analytical 4552 or 4551 or EST Evolution with EST Centurion

6.3.1 The following autosampler models are used for purging, trapping and desorbing the sample onto GC column.

- O.I. Model 4660 sample concentrator with 4552 Water/Soil multisampler
- O.I. Model 4660 sample concentrator with 4551 Water multisampler
- EST Evolution sample concentrator with Centurion Water/Soil multisampler

6.3.2 The sample purge vessel must be designed to accept 5 or 10ml samples with a water column at least 3 cm deep.

6.3.3 The multisampler is equipped with a heater capable of maintaining the purge chamber at 40 °C to improve purging efficiency. The heater is to be used for soil and sediment analysis.

6.3.4 The desorber should be capable of rapidly heating the trap to the manufacturer recommended desorb temperature.

6.4 Data System – Agilent Technologies MS Chemstation rev. DA 02.0x, DA 03.0x or EA02.0x.

6.4.1 A computer system interfaced to the mass spectrometer that allows for the continuous acquisition and storage of all mass spectral data obtained throughout the duration of the chromatographic program.

6.4.2 The computer utilizes software that allows searching any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP).

6.4.3 The software should allow for integrating the abundances in any EICP between specific time or scan number limits. Characteristic ions for each analyte are listed in Table 2.

6.4.4 The most recent version of the EPA/NIST mass spectral library should be available. Current NIST database contains approximately 129,000 compound spectra.

6.4.5 Data is archived to a backup server for long term storage.

6.5 Trap – OI #10 or equivalent: Tenax, Silica Gel, and Carbon Molecular Sieve.
Trap – Vocarb 3000 (K) or equivalent: Carbopack B, Carboxen 1000, Carboxen 1001

The trap should be conditioned according to the manufacturer‘s recommendations.

6.6 Columns – RTX-624 or equivalent: 60m X 0.25mm 1.4um.
- RTX-VMS or equivalent: 40m X 0.18mm 1.0um

6.7 Gas-tight syringes and class “A” volumetric glassware for dilutions of standards and samples.

7.0 PROCEDURE

7.1 Standards Preparation

Standards are prepared from commercially available certified reference standards. All standards must be logged in the Volatile Standards Logbook. All standards shall be traceable to their original source. The standards should be stored at temperatures between –10 °C and –20 °C, or as recommended by the manufacturer. Calibration levels, spike and surrogate concentrations, preparation information, and vendor part numbers can be found in the MSVOA STD Summary in the Active SOP directory.

7.1.1 Stock Standard Solutions

Stock standards are available from several commercial vendors. All vendors must supply a “Certificate of Analysis” with the standard. The certificate will be retained by the lab. Hold time for unopened stock standards is until the vendor’s expiration

date. Once opened, the hold time is reduced to six months (one month for gases) or the vendor's expiration date (whichever is shorter).

7.1.2 Intermediate Standard Solutions

Intermediate standards are prepared by quantitative dilution of the stock standard with methanol. The hold time for intermediate standards is one month (one week for gases) or the vendor's expiration date (whichever is shorter). Intermediate standards may need to be remade if comparison to other standards indicates analyte degradation or concentration changes.

7.1.3 Calibration Standards

Calibration standards for the volatile organics are prepared at a minimum of five concentration levels through quantitative dilutions of the intermediate standard. The low standard is at a concentration at or below the LLOQ and the remaining standards define the working range of the detector.

Calibration standard concentrations are verified by the analysis of an initial calibration verification (ICV) standard.

7.2 Instrument Conditions

Gas Chromatograph/ Mass Spectrometer

Carrier gas flow	1.0-1.3 ml/min
Transfer line temperatures	220 - 280 °C
Analyzer temperature	150 °C

Oven program – 45 °C for 2.5 minutes (RTX-VMS 40m)
10 °C/min to 80 °C for 0 minutes
15 °C/min to 185 °C for 0 minutes
30 °C/min to 240 °C for 2.5 minutes

Oven program – 35 °C for 2.5 minutes (RTX-VMS 40m)
4 °C/min to 60 °C for 0 minutes
25 °C/min to 220 °C for 0 minutes
30 °C/min to 240 °C for 1.2 minutes

Oven program – 45 °C for 2.0 minutes (RTX-624)
10 °C/min to 80 °C for 0 minutes
14 °C/min to 210 °C for 0 minutes
16 °C/min to 240 °C for 4.2 minutes

GC conditions are optimized for each instrument. Actual conditions may vary slightly from those listed above.

7.3 Purge and Trap Device conditions

OI Autosampler

Purge Gas:	Helium or Nitrogen at 30-45 ml/min
Sample Temp:	Aqueous (Ambient) Soils (40°C)
Trap Temp:	<25°C
Purge Time:	6 or 11 min
Desorb:	2 min. at 190°C
Bake:	5 min. at 210°C

EST Autosampler

Purge Gas:	Helium at 35-45 ml/min
Sample Temp:	Aqueous (Ambient to 35°C) Soils (40°C)
Trap Temp:	<35°C
Purge Time:	6 or 11 min
Desorb:	1-2 min. at 250°C
Bake:	6 min. at 235°C

Purge and Trap conditions are optimized for each instrument. Actual conditions may vary slightly from those listed above.

7.4 Sample Preparation

7.4.1 Water Samples

A 5ml aliquot of sample is loaded onto the purge-and-trap device and purged for either 6 or 11 minutes depending on the system. Detailed procedures are described in SOP OP021.

7.4.2 Solid Samples

A 5-gram aliquot of sample is loaded onto the purge-and-trap device. 5mls of reagent water is added along with internal standards and surrogates. Depending on the system, the sample is then purged for either 6 or 11 minutes while heated to 40°C and mechanically agitated. Detailed procedures are described in SOP OP020.

Alternatively, a methanol aliquot from the sample is loaded onto the purge-and-trap device. 5mls of reagent water is added along with internal standards and surrogates. The sample is then purged for either 6 or 11 minutes depending on the system. Detailed procedures are described in SOP OP020 and OP021.

7.5 Gas Chromatographic Analysis

Instrument calibration consists of two major sections:

Initial Calibration Procedures
Continuing Calibration Verification

7.5.1 Initial Calibration Procedures

Before samples can be run, the GC/MS system must be tuned, the injection port inertness must be verified, and the instrument must be calibrated.

7.5.1.1 Tune Verification (BFB)

The instrument should be hardware tuned per manufacturer's instructions. Verify the instrument tune by injecting 50ng of BFB solution onto the instrument. The BFB standard may also be purged. The resulting BFB spectra should meet the criteria in the following table.

BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15-40% of mass 95
75	30-60% of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5-9 % of mass 174
176	>95% and <101% of mass 174
177	5-9% of mass 176

Evaluate the tune spectrum using three mass scans from the chromatographic peak and a subtraction of instrument background. This procedure is performed automatically by the MS Chemstation software by running "autofind" on the BFB peak.

Select the scans at the peak apex and one to each side of the apex. Calculate an average of the mass abundances from the three scans.

Background subtraction is required. Select a single scan in the chromatogram that is absent of any interfering compound peak and no more than 20 scans prior to the elution of BFB. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the tuning compound peak.

Alternatively, the average spectra over the entire peak may be used. **All subsequent tune evaluations must use the same procedure that was used for the Initial Calibration.**

If the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are met.

Analysis must not begin until the tuning criteria are met. The injection time of the acceptable tune analysis is considered the start of the 12-hour clock. The same mass spec settings must be used for the calibration standards and samples that were used for the tune evaluation standard.

7.5.1.2 Internal Standard Calibration

A minimum 5-point calibration curve is created for the volatile organic compounds and surrogates using an internal standard technique. SGS Orlando routinely performs a 6-point calibration to maximize the calibration range.

NOTE: West Virginia requires that samples preserved with sodium bisulfate be analyzed against a calibration curve that was also preserved with sodium bisulfate. In this instance, 2-chloroethyl vinyl ether and acrolein will not be reportable.

Historically, many analytical methods have relied on linear models of the calibration relationship, where the instrument response is directly proportional to the amount of a target compound. The linear model has many advantages including simplicity and ease of use. However, given the advent of new detection techniques and because many methods cannot be optimized for all the analytes to which they may be applied, the analyst is increasingly likely to encounter situations where the linear model neither applies nor is appropriate. The option of using non-linear calibration may be necessary to address specific instrumental techniques. However, it is not EPA's intent to allow non-linear calibration to compensate for detector saturation or avoid proper instrument maintenance.

NOTE: Because of this concern, select programs including SC DHEC do not support the use of non-linear regressions.

The low point may be omitted from the calibration table for any compound with an LLOQ set at the level two standard. Additionally, the high point may be omitted for any compound that exhibits poor linearity at the upper end of the calibration range.

An entire level may be omitted provided that a minimum of 5 points remain. There must be technical justification to omit an entire level. This should be documented in the run log.

Response factors (RF) for each analyte are determined as follows:

$$RF = (A_{analyte} \mathbf{X} C_{istd})/(A_{istd} \mathbf{X} C_{analyte})$$

$A_{analyte}$ = area of the analyte
A_{istd} = area of the internal standard
$C_{analyte}$ = concentration of the analyte

C_{istd} = concentration of the internal standard.

The mean RF and standard deviation of the RF are determined for each analyte. The percent relative standard deviation (%RSD) of the response factors is calculated for each analyte as follows:

%RSD = (Standard Deviation of RF X 100) / Mean RF

If the %RSD ≤ 15%, linearity through the origin can be assumed and the mean RF can be used to quantitate target analytes in the samples. Alternatively, a calibration curve of response vs. amount can be plotted. This method allows for the use of average response factors, linear regressions, and non-linear regressions. Linear regressions may be unweighted or weighted as $1/x$ or $1/x^2$. If the correlation coefficient (r) is ≥0.995 (r^2 ≥0.990) then the curve can be used to quantitate target analytes in the samples. Regardless of which calibration model is chosen, the laboratory should visually inspect the curve plots to see how the individual calibration points compare to the plot.

Alternatively, either of the two techniques described below may be used to determine whether the calibration function meets acceptable criteria. These involve refitting the calibration data back to the model. Both % Error and Relative Standard Error (RSE) evaluate the difference between the measured and the true amounts or concentrations used to create the model.

Calculation of the % Error

% ERR = (xi-x'i) / xi * 100

x'i = Measured amount of analyte at calibration level i, in mass or concentration units.

xi = True amount of analyte at calibration level i, in mass or concentration units.

Percent error between the calculated and expected amounts of an analyte should be ≤ 30% for all standards. For some data uses, ≤50% may be acceptable for the lowest calibration point.

Calculation of Relative Standard Error (%RSE)

$$RSE = 100 \times \sqrt{\sum_{i=1}^{n} \left[\frac{x_i' - x_i}{x_i}\right]^2 \Big/ (n-p)}$$

x'i = Measured amount of analyte at calibration level i, in mass or concentration units.

xi = True amount of analyte at calibration level i, in mass or concentration units.

p = Number of terms in the fitting equation. (average = 1, linear = 2, quadratic = 3)

n = Number of calibration points.

The %RSE acceptance limit criterion is ≤15% for good performing compounds and ≤30% for poor performing (PP) compounds.

The method also employs a series of Calibration Check Compounds (CCC) and System Performance Check Compounds (SPCC). The %RSD for any CCC must be ≤ 30 % and the average relative response factor for any SPCC must be at least 0.10 or 0.30 (See tables below). If the %RSD for any CCC is ≤ 30% but > 15% the compound should be evaluated by curve fit.

Calibration Check Compounds (CCC)

Vinyl chloride	1,1-Dichloroethene
Chloroform	1,2-Dichloropropane
Toluene	Ethylbenzene

System Performance Check Compounds (SPCC)

Compound	**Minimum RF**
Chloromethane	0.1
1,1-Dichloroethane	0.1
Bromoform	0.1
1,1,2,2-Tetrachloroethane	0.3
Chlorobenzene	0.3

7.5.1.3 Initial Calibration Verification (ICV)

The validity of the initial calibration curve must be verified through the analysis of an initial calibration verification (ICV) standard. The ICV should be prepared from a second source at a mid-range concentration.

The %D for all normal analytes of interest should be ≤ 20%, and the %D for all poor performing (PP) analytes of interest should be ≤ 40%. These analytes are identified in Table 1. If the %D > 20% (>40% for PP), the analysis of samples may still proceed if the analyte failed high and the

analyte is not expected to be present in the samples. However, if a reportable analyte is detected in a sample and the %D for that analyte was greater than 20% (>40% for PP) in the ICV, the sample will need to be reanalyzed on a system with a passing ICV for that analyte.

NOTE: For any DoD QSM project, the %D for all target compounds should be ≤ 20%. If samples must be analyzed with an analyte of interest having a %D > 20%, then the data must be qualified accordingly.

If the ICV does not meet this criteria, a second standard should be prepared. If the ICV still does not meet criteria, analyze an ICV prepared from a third source. If this ICV meets criteria, proceed with sample analysis. If the ICV still does not meet criteria, determine which two standards agree. Make fresh calibration standards and an ICV from the two sources that agree. Recalibrate the instrument.

7.5.2 Continuing Calibration Verification (CCV)

7.5.2.1 Inject 2ul of the tune evaluation mix at the beginning of each 12-hour shift. Evaluate the resultant peaks against the criteria in section 7.5.1.1. The injection time of this standard starts the 12-hour window.

When the analyst is running an unattended second 12-hour window, they may opt to purge the BFB standard. This can be performed by purging an additional blank (which contains BFB) just prior to the second CCV.

7.5.2.2 Analyze a continuing calibration check standard. The CCV should be at or below the mid-point of the calibration curve.

7.5.2.3 The RF of check standard for SPCC compounds must meet the minimum RF requirement as listed in the table.

7.5.2.4 The %D for the CCC compounds must be ≤ 20%. If the CCCs are not part of the target list, then all target analytes must meet the 20 %D criteria.

7.5.2.5 The %D for all analytes of interest should be ≤ 20%; however, the large number of analytes in this method presents a substantial probability that a few of the analytes will fall outside of this range.

If less than 10 percent of the analytes have a %D > 20% but ≤ 50% then the analysis of samples may still proceed provided that the following criteria is met.

The CCV exceeds the upper limit (+20%) and the analyte is not expected to be present in the samples.

The CCV exceeds the lower limit (-20%) but not more than -50% and the analyte is not expected to be present in the samples. An additional check standard at the LLOQ must be analyzed and the analytes in question be detected and meet all of the qualitative identification criteria.

However, if a reportable analyte is detected in a sample and the %D for that analyte was greater than 20% in the CCV, the sample will need to be reanalyzed on a system with a passing CCV for that analyte, or the data must be qualified.

NOTE: For any DoD QSM project, the %D for all target compounds should be ≤ 20%. If samples must be reported with an analyte of interest having a %D > 20%, then the data must be qualified accordingly, regardless of whether the analyte was detected or not.

7.5.2.6 The criteria in 7.5.2.3 and 7.5.2.4 must be met for the continuing calibration to be considered valid. Additionally, only analytes that are being reported for a given sample must meet the criteria in 7.5.2.5.

If the first continuing calibration verification does not meet criteria, a second standard may be injected. If the second standard does not meet criteria, the system must be recalibrated. If the second standard meets criteria then the system is considered in control and results may be reported.

Rationale for second standard such as instrument maintenance, clipped column, remade standard, etc should be documented in the run log or maintenance log. Reanalysis of second standard without valid rationale may require the analysis of a third standard (in which case both the second and third standard would have to pass).

NOTE: For any DoD QSM project, if the second standard meets criteria, then a third standard must be analyzed. If the third standard also meets criteria, then the system is considered in control and results may be reported.

If the |%D| is greater than 20%, then documented corrective action is necessary. This may include recalibrating the instrument and reanalyzing the samples, performing instrument maintenance to correct the problem and reanalyzing the samples, or qualifying the data. Under certain circumstances, the data may be reported, i.e., the CCV failed high, the associated QC passed, and the samples were ND.

NOTE: For any DoD QSM project, if samples must be reported with a target analyte having a %D > 20%, then the data must be qualified accordingly, regardless of whether the analyte was detected or not.

NOTE: Any target analytes that are detected in the samples must be bracketed by an acceptable initial calibration curve and acceptable CCV standards; otherwise, the samples must be reanalyzed, or the data must be qualified.

7.5.2.7 For DoD QSM 5.x compliance, an additional CCV must be analyzed at the end of each run. The closing CCV should be within the 12-hour Tune window.

The %D for all target compounds in this CCV should be ≤ 50%. If the %D > %50 for any target compound, the samples may need to be reanalyzed. If samples must be reported with an analyte of interest having a %D > 50%, then the data must be qualified accordingly, regardless of whether the analyte was detected or not.

NOTE: If samples are ND and an analyte in the CCV fails high, then the sample does not need to be reanalyzed.

7.5.2.8 If any of the internal standard response changes by more than a factor of two (-50% to +100%) or retention time changes by more than 30 seconds (10 seconds for DOD QSM 5.x compliance) from the midpoint standard of the last initial calibration or from the daily CCV, the mass spectrometer must be inspected for malfunctions and corrections made, as appropriate. Corrective action may include re-calibration (initial calibration) of the instrument.

7.5.3 Sample Analysis

7.5.3.1 Samples are analyzed in a set referred to as an analysis sequence or batch. A batch consists of the following:

Tune Evaluation Mix
Initial Calibration Standards (or CCV)
QC Samples
Samples

7.5.3.2 One microliter (OI) or five microliter (EST) of internal standard/ surrogate solution is added to every 5ml of sample in the sparge vessel. Generally, 5ml of sample are transferred to the sparge vessel.

7.5.3.3 After purging, the system will automatically reverse flow and rapidly heat the trap to desorb the sample analytes onto the GC column.

7.5.3.4 Qualitative identification

The target compounds shall be identified by analysts with competent knowledge in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. The criteria required for a positive identification is:

The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

The sample component must elute at the same relative retention time (RRT) as the daily standard. The RRT of sample component must be within ± 0.06 RRT units of the standard.

All ions present in the standard mass spectra at a relative intensity greater than 10% (major abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

The relative intensities of these ions must agree within ± 30% between the daily standard and sample spectra, (e.g., for an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20 and 80%).

Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

If peak identification is prevented by the presence of interferences, the sample must be diluted so that the interference does not mask any analytes.

7.5.3.5 Quantitative analysis

When a target compound has been identified, concentration will be based on the integrated area of the quantitation ion, which is normally the base peak.

The sample matrix may produce an interference with the primary ion. This may be characterized by an excessive background signal of the same ion, which distorts the peak shape beyond a definitive integration. The interference could also, severely inhibit the response of the internal standard ion.

If the analyte response exceeds the linear range of the system, the extract must be diluted and reanalyzed. It is recommended that samples be diluted so that the response falls into the middle of the calibration curve.

7.5.3.6 Library search for tentatively identified compounds

If a library search is requested, the analyst should perform a forward library search of the NIST mass spectral library to tentatively identify 10 to 20 non-target compounds.

Guidelines for making tentative identification are:

These compounds should have a response greater than 10% of the nearest internal standard. The response is obtained from the Total Ion Chromatogram.

The search is to include a spectral printout of the best library match for a particular substance. The results are to be interpreted by the analyst.

Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

The relative intensities of the major ions should agree within ±20%.

Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

Ions present in the reference spectrum but not in the sample spectrum should be verified by performing further manual background subtraction to eliminate the interference created by co-eluting peaks and/or matrix interference.

Quantitation of the tentatively identified compounds is obtained from the total ion chromatogram based on a response factor of 1 from the nearest internal standard and is to be tabulated on the library search summary data sheet.

7.6 Maintenance and Trouble Shooting

7.6.1 Refer to SOP GC001 for routine instrument maintenance and trouble shooting.

7.6.2 All instrument maintenance must be documented in the appropriate “Instrument Repair and Maintenance” log. The log will include such items as problem, action taken, correction verification, date, and analyst.

7.6.3 Repairs performed by outside vendors must also be documented in the log. The analyst or Department Supervisor responsible for the instrument must complete the log if the repair technician does not.

7.6.4 PC and software changes must be documented in the “Instrument Repair and Maintenance” log. Software changes may require additional validation.

8.0 METHOD PERFORMANCE

Method performance is monitored through the routine analysis of negative and positive control samples. These control samples include method blanks (MB), blank spikes (BS), matrix spikes (MS), and matrix spike duplicates (MSD). The MB and BS are used to monitor overall method performance, while the MS and MSD are used to evaluate the method performance in a specific sample matrix.

Blank spike, matrix spike, and matrix spike duplicate samples are compared to statistically generated control limits. These control limits are reviewed and updated annually. Control limits are stored in the LIMS. Additionally, blank spike accuracy is regularly evaluated for statistical trends that may be indicative of systematic analytical errors.

9.0 QUALITY ASSURANCE / QUALITY CONTROL

Accuracy and matrix bias are monitored by the use of surrogates and by the analysis of a QC set that is prepared with each batch (maximum of 20 samples) of samples. The QC set consists of a method blank (MB), blank spike (BS), matrix spike (MS), and matrix spike duplicate (MSD).

9.1 Internal Standards

9.1.1 Fluorobenzene, chlorobenzene-d_5, 1,4-dichlorobenzene-d_4, and tert butyl alcohol-d_{10} are used as internal standards for this method. The response of the internal standard in all subsequent runs should be within a factor of two (-50% to +100%) of the internal standard response in the opening CCV for each sequence. On days that an initial calibration is performed, the internal standard responses should be compared to the internal standard responses for the mid-point standard. The response for tert butyl alcohol-d_{10} need only be monitored if target analytes are being reported that reference that particular internal standard.

9.1.2 If the internal standard responses are not within limits, the following are required.

9.1.2.1 Check to be sure that there are no errors in calculations, integrations, or internal standards solutions. If errors are found, recalculate the data accordingly.

9.1.2.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample. If the recovery is high due to interfering peaks, it may be possible to get a more accurate recovery by analyzing the sample on a different column type.

9.1.2.3 If no problem is found, prepare a second aliquot of sample and reanalyze the sample. If there is insufficient sample for reanalysis, footnote this on the report.

9.1.2.4 If upon reanalysis, the responses are still not within limits, the problem is considered matrix interference. The sample may need to be diluted or the results qualified.

9.1.3 Historical data has shown that when soils are preserved with sodium bisulfate the 4th internal standard (tert butyl alcohol-d_{10}) will very often fail high. If the analytes that reference tert butyl alcohol-d_{10} are non-detect, then the sample does not need to be reanalyzed; however, they should be footnoted with "Associated internal standard response outside of control limits.

9.2 Surrogates

9.2.1 Dibromofluoromethane, 1,2-dichloroethane-d_4, toluene-d_8, and 4-Bromofluorobenzene are used as the surrogate standards to monitor the efficiency of the purge-and-trap system.

A known amount of surrogate standard is added to each sample including the QC set prior to purging. The percent recovery for each surrogate is calculated as follows:

% Recovery = (Sample Amount / Amount Spiked) X 100

The percent recovery must fall within the established control limits for all surrogates for the results to be acceptable.

9.2.2 If any surrogate recovery is not within the established control limits, the following are required.

9.2.2.1 Check to be sure that there are no errors in calculations, dilutions, integrations, surrogate solutions or internal standard solutions. If errors are found, recalculate the data accordingly.

9.2.2.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample. If the recovery is high due to interfering peaks, it may be possible to get a more accurate recovery by analyzing the sample on a different column type.

9.2.2.3 If no problem is found, reanalyze the sample. **NOTE:** If the recoveries are high and the sample is non-detect, then reanalysis may not be necessary. **For any DoD QSM projects, the resulting data must be qualified accordingly.** If there is insufficient sample for reanalysis, footnote this on the report.

9.2.2.4 If upon reanalysis, the recovery is still not within control limits, the problem is considered matrix interference. Surrogates from both sets of analysis should be reported on the final report.

9.2.2.5 Historical data has shown that samples with pH > 11 will cause dibromofluoromethane to degrade and fail low. If the remaining surrogates are within control limits, then samples with pH > 11 should be footnoted, but they do not need to be reanalyzed for dibromofluoromethane failures.

9.3 Method Blank

9.3.1 The method blank is de-ionized water or de-ionized water with 5 grams of clean sand (depending upon sample matrix) to which the surrogate standard has been added. An appropriate aliquot of methanol should also be added. The method blank is then purged along with the other samples to determine any contamination from the system or ambient sources. The method blank must be free of any analytes of interest or interferences at ½ the required LLOQ to be acceptable. Common laboratory contaminants such as methylene chloride must be below the LLOQ if present. If the method blank is not acceptable, corrective action must be taken to determine the source of the contamination. Samples associated with a contaminated method blank shall be evaluated as to the best corrective action for each particular sample. This may include reanalyzing the samples or qualifying the results with a "B" or "V" qualifier.

9.3.2 If the MB is contaminated but the samples are non-detect, then the source of contamination should be investigated and documented. The sample results can be reported. **For any DoD QSM projects the resulting data must be qualified accordingly.**

9.3.3 If the MB is contaminated but the samples results are > 10 times the contamination level, the source of the contamination should be investigated and documented. The samples results may be reported with the appropriate "B" or "V" qualifier. This must be approved by the department supervisor.

9.3.4 If the MB is contaminated but the samples results are < 10 times the contamination level, the source of the contamination should be investigated and documented. The samples should be reanalyzed for confirmation. If there is insufficient sample to reanalyze, or if the sample is reanalyzed beyond hold time, the appropriate footnote and qualifiers should be added to the results. This must be approved by the department supervisor.

9.4 Blank Spike

9.4.1 The blank spike is de-ionized water or de-ionized water with 5 grams of clean sand (depending upon sample matrix) to which the surrogate standard and spike standard have been added. An appropriate aliquot of methanol should also be added. The blank spike is then processed along with the other samples to monitor the efficiency of the purge-and-trap procedure. The percent recovery for each analyte is calculated as follows:

% Recovery = (Blank Spike Amount / Amount Spiked) X 100

The percent recovery for each analyte of interest should fall within the established control limits for the results to be acceptable. The large number of analytes in this method presents a substantial probability that a few of the analytes will fall outside of the established control limits. This may not indicate that the system is out of control; therefore, corrective action may not be necessary.

Upper and lower marginal exceedance (ME) limits can be established to determine when corrective action is necessary. A marginal exceedance in the Blank Spike is defined as a recovery being outside of 3 standard deviations but within 4 standard deviations of the mean.

The number of allowable marginal exceedances is based on the number of analytes in the Blank Spike. Marginal Exceedances must be random. If the same analyte exceeds the BS control limits repeatedly, it is an indication of a systematic problem and corrective action must be taken.

Marginal exceedances are not permitted for analytes that are deemed to be "Compounds of Interest" for a specific project. "Compounds of Concern" are different from "Target Compounds". "Target Compounds" are all analytes that are being reported for a site where "Compounds of Concern" are those analytes expected to be present at the site.

The number of allowable marginal exceedances is as follows:

1) > 90 analytes in BS, 5 analytes allowed in ME range;

2) 71-90 analytes in BS, 4 analytes allowed in ME range;

3) 51-70 analytes in BS, 3 analytes allowed in ME range;

4) 31-50 analytes in BS, 2 analytes allowed in ME range;

5) 11-30 analytes in BS, 1 analyte allowed in ME range;

6) < 11 analytes in BS, no analytes allowed in ME range.

NOTE: SC DHEC does not recognize the concept of Marginal Exceedances. Additionally, a secondary check against 70-130% limits should be performed for all analytes reported to SC DHEC.

9.4.2 If the blank spike recoveries are not within the established control limits, the following are required.

9.4.2.1 Check to be sure that there are no errors in calculations, dilutions, integrations, spike solutions or internal standard solutions. If errors are found, recalculate the data accordingly.

9.4.2.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample.

9.4.2.3 Check to see if the recoveries that are outside of control limits are analytes of concern. If the analytes are not being reported, additional corrective action is not necessary and the sample results can be reported without qualification.

9.4.2.4 If the recovery of an analyte in the BS is high **and the associated sample is non-detect, the data may be reportable. For any DoD QSM projects, the resulting data must be qualified accordingly.**

9.4.2.5 If no problem is found, the department supervisor shall review the data and determine what further corrective action is best for each particular sample. That may include reanalyzing the samples or qualifying the results as estimated.

9.4.2.6 If there is insufficient sample to reanalyze, or if the sample is reanalyzed beyond hold time, the appropriate footnote and qualifiers should be added to the results. This must be approved by the department supervisor.

9.4.2.7 Because of their problematic nature, 2-chloroethyl-vinyl-ether and acrolein are generally not evaluated in the blank spike unless they are of specific concern for a given project.

9.5 Matrix Spike and Matrix Spike Duplicate

9.5.1 Matrix spike and spike duplicates are replicate sample aliquots to which the surrogate standard and spike standard have been added. The matrix spike and spike duplicate are then processed along with the other samples to monitor the precision and accuracy of the purge-and-trap procedure. The percent recovery for each analyte is calculated as follows:

% Recovery = ([Spike Amount – Sample Amount] / Amount Spiked) X 100

The percent recovery for each analyte of interest must fall within the established control limits for the results to be acceptable.

9.5.2 If the matrix spike recoveries are not within the established control limits, the following are required.

9.5.2.1 Check to be sure that there are no errors in calculations, dilutions, integrations, spike solutions or internal standard solutions. If errors are found, recalculate the data accordingly.

9.5.2.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample. If the recovery is high due to interfering peaks, it may be possible to get a more accurate recovery by analyzing the sample on a different column type.

9.5.2.3 If no problem is found, compare the recoveries to those of the blank spike. If the blank spike recoveries indicate that the problem is sample related, document this on the run narrative. Matrix spike recovery failures are not grounds for reanalysis but are an indication of the sample matrix effects.

9.5.3 Precision

Matrix spike and spike duplicate recoveries for each analyte are used to calculate the relative percent difference (RPD) for each compound.

RPD = (| MS Result – MSD Result | / Average Result) X 100

The RPD for each analyte should fall within the established control limits. If more than 33% of the RPDs fall outside of the established control limits, the department supervisor shall review the data and determine if any corrective action is necessary. RPD failures are generally not grounds for batch reanalysis.

10.0 CALCULATIONS

The concentration of each target compound in the original sample is calculated as follows:

Water (ug/l) = ($CONC_{inst}$) X DF

Soil (ug/kg) = [($CONC_{inst}$) X (5 / W_I)] / %solids (*low level soils)*

Soil (ug/kg) = [($CONC_{inst}$) X (V_F / V_A) X (5 / W_I) X DF] / %solids (*high level soils)*

$CONC_{inst}$	=	Instrument concentration calculated from the initial calibration using mean RF or curve fit.
DF	=	Dilution Factor
V_F	=	Volume of methanol extract (ul)
V_A	=	Volume of methanol aliquot (ul)
W_I	=	Weight of sample (g)
%solids	=	Dry weight determination in decimal form

For high level soils, V_F is calculated as follows:

V_F = {ml of solvent + [(%moisture X W_I) / 100]} X 1000 ul/ml

11.0 SAFETY AND POLLUTION PREVENTION

11.1 Safety

The analyst should follow normal safety procedures as outlined in the SGS Health and Safety Program, which includes the use of safety glasses, gloves, and lab coats.

The toxicity of each reagent and target analyte has not been precisely defined; however, each reagent and sample should be treated as a potential health hazard. Material Safety Data Sheets (MSDS) or Safety Data Sheets (SDS) are available for all reagents and many of the target analytes. Exposure must be reduced to the lowest possible level. Personal protective equipment should be used by all analysts.

11.2 Pollution Prevention

Waste solvents from the sample analysis, methanol extraction, and standards preparation are collected in waste storage bottles and are eventually transferred to the non-chlorinated waste drum.

Old stock standards are disposed of in the waste vial drum.

Samples are archived and stored for 30 days after analysis. After the storage time has elapsed, the remaining aqueous and soil samples are transferred to the appropriate drums for disposal.

12.0 REFERENCES

SW846 Method 8000D Revision 4, July 2014

SW846 Method 8260B Revision 2, December 1996

TABLE 1

Routine Target Analytes

Dichlorodifluoromethane	**2-Butanone**	n-Propylbenzene
Chloromethane	1,1-Dichloropropene	Bromobenzene
Vinyl Chloride	Propionitrile	1,1,2,2-Tetrachloroethane
Bromomethane	Methacrylonitrile	1,3,5-Trimethylbenzene
Chloroethane	Benzene	2-Chlorotoluene
Trichlorofluoromethane	TAME	**trans-1,4-Dichloro-2-Butene**
Ethyl Ether	1,2-Dichloroethane	1,2,3-Trichloropropane
1,2-Dichlorotrifluoroethane	Trichloroethene	**Cyclohexanone**
1,1-Dichloroethene	Methylcyclohexane	4-Chlorotoluene
Freon 113	Dibromomethane	tert-Butylbenzene
Carbon Disulfide	1,2-Dichloropropane	1,2,4-Trimethylbenzene
Iodomethane	Bromodichloromethane	**Pentachloroethane**
Acrolein	Methyl methacrylate	sec-Butylbenzene
Allyl chloride	**2-Chloroethyl vinyl ether**	4-Isopropyltoluene
Methylene Chloride	cis-1,3-Dichloropropene	1,3-Dichlorobenzene
Acetone	Toluene	1,4-Dichlorobenzene
Methyl acetate	2-Nitropropane	n-Butylbenzene
trans-1,2-Dichloroethene	4-Methyl-2-pentanone	**Benzyl Chloride**
Hexane	trans-1,3-Dichloropropene	1,2-Dichlorobenzene
Methyl Tert Butyl Ether	Tetrachloroethene	**1,2-Dibromo-3-Chloropropane**
Acetonitrile	Ethyl methacrylate	Hexachlorobutadiene
Di-isopropyl ether	1,1,2-Trichloroethane	1,2,4-Trichlorobenzene
Chloroprene	Dibromochloromethane	Naphthalene
1,1-Dichloroethane	1,3-Dichloropropane	1,2,3-Trichlorobenzene
Acrylonitrile	1,2-Dibromoethane	**Ethanol**
ETBE	**2-hexanone**	Tert Butyl Alcohol
Vinyl acetate	1-Chlorohexane	Isobutyl alcohol
cis-1,2-Dichloroethene	Ethylbenzene	Tert Amyl Alcohol
2,2-Dichloropropane	Chlorobenzene	**1,4-Dioxane**
Bromochloromethane	1,1,1,2-Tetrachloroethane	3,3-Dimethyl-1-butanol
Cyclohexane	m,p-Xylene	Tert Amy Alcohol
Chloroform	o-Xylene	**Tert Butyl Formate**
Ethyl acetate	Styrene	1,2,3-Trimethylbenzene
Tetrahydrofuran	Bromoform	
Carbon Tetrachloride	Isopropylbenzene	
1,1,1-Trichloroethane	cis-1,4-Dichloro-2-butene	

Bolded analytes are considered "Poor Performing"

TABLE 2

Characteristic Ions

Analyte	Quant. Ion	Q1	Q2	Q3
Fluorobenzene	96	70		
Dichlorodifluoromethane	85	87		
Chloromethane	50	52		
Vinyl Chloride	62	64		
Bromomethane	94	96	93	
Chloroethane	64	66	49	
Trichlorofluoromethane	101	103		
Ethyl Ether	59	45	74	
1,2-Dichlorotrifluoroethane	67	117	85	69
1,1-Dichloroethene	61	96	98	63
Freon 113	101	151	103	85
Carbon Disulfide	76	44		
Iodomethane	142	127	141	
Allyl chloride	41	39	38	76
Methylene Chloride	49	84	86	51
Acetone	58	43		
Methyl acetate	74	43	42	
trans-1,2-Dichloroethene	61	96	98	63
Hexane	56	57	43	41
Methyl Tert Butyl Ether	73	57	43	41
Acetonitrile	40	41	39	
Di-isopropyl ether	45	43	87	
Chloroprene	53	88	51	50
1,1-Dichloroethane	63	65		
Acrylonitrile	53	52	51	
ETBE	59	87	57	
Vinyl acetate	43	42		
cis-1,2-Dichloroethene	96	61	98	63
2,2-Dichloropropane	77	97		
Bromochloromethane	128	49	130	51
Cyclohexane	56	84	41	55
Chloroform	83	85	47	
Ethyl acetate	43	45		
Tetrahydrofuran	42	41	72	
Dibromofluoromethane	113	111	192	
Carbon Tetrachloride	117	119	121	82
1,1,1-Trichloroethane	97	99	61	
2-Butanone	43	72		

TABLE 2 (cont)

Characteristic Ions

Analyte	Quant. Ion	Q1	Q2	Q3
1,1-Dichloropropene	75	39	110	77
Propionitrile	54	52	55	
Methacrylonitrile	41	39	40	52
Benzene	78	51		
TAME	73	43	55	
1,2-Dichloroethane-d_4	65	67	102	
1,2-Dichloroethane	62	49	64	
Trichloroethene	95	130	97	132
Methylcyclohexane	83	55	98	42
Dibromomethane	93	95	174	172
1,2-Dichloropropane	63	62	41	76
Bromodichloromethane	83	85	47	
Methyl methacrylate	41	69	39	100
2-Chloroethyl vinyl ether	63	43	44	65
cis-1,3-Dichloropropene	75	77	39	
Chlorobenzene-d_5	117	82		
Toluene-d_8	98	100		
Toluene	91	92		
2-Nitropropane	41	43	39	
4-Methyl-2-pentanone	43	58	57	41
trans-1,3-Dichloropropene	75	77	39	49
Tetrachloroethene	166	164	129	131
Ethyl methacrylate	69	41	39	99
1,1,2-Trichloroethane	83	97	61	99
Dibromochloromethane	129	127	131	
1,3-Dichloropropane	76	78	41	39
1,2-Dibromoethane	107	109		
2-hexanone	43	58	57	
1-Chlorohexane	91	55	41	43
Ethylbenzene	91	106		
Chlorobenzene	112	77	114	51
1,1,1,2-Tetrachloroethane	131	133	119	117
m,p-Xylene	91	106	105	
o-Xylene	91	106	105	
Styrene	104	78	103	51
Bromoform	173	175	171	91
Isopropylbenzene	105	120		
1,4-Dichlorobenzene-d_4	152	151		

TABLE 2 (cont)

Characteristic Ions

Analyte	Quant. Ion	Q1	Q2	Q3
4-Bromofluorobenzene	95	174	176	
cis-1,4-Dichloro-2-butene	53	75	88	39
n-Propylbenzene	91	120		
Bromobenzene	156	158		
1,1,2,2-Tetrachloroethane	83	85		
1,3,5-Trimethylbenzene	105	120		
2-Chlorotoluene	91	126	89	
trans-1,4-Dichloro-2-Butene	53	89	75	
1,2,3-Trichloropropane	110	61	112	49
Cyclohexanone	55	98	42	69
4-Chlorotoluene	91	126		
tert-Butylbenzene	91	41	134	
1,2,4-Trimethylbenzene	105	120	119	
1,2,3-Trimethylbenzene	105	120		
Pentachloroethane	167	117	119	165
sec-Butylbenzene	105	134		
4-Isopropyltoluene	119	134		
1,3-Dichlorobenzene	146	111	148	75
1,4-Dichlorobenzene	146	111	148	75
n-Butylbenzene	92	91	134	
Benzyl Chloride	126	91	65	
1,2-Dichlorobenzene	146	111	148	75
1,2-Dibromo-3-Chloropropane	75	155	157	39
Hexachlorobutadiene	225	190	118	260
1,2,4-Trichlorobenzene	180	182	145	109
Naphthalene	128	127		
1,2,3-Trichlorobenzene	180	182	145	109
Tert Butyl Alcohol-d10	65	46		
acrolein	56	55		
Tert Butyl Alcohol	59	41	43	
tert Amyl alcohol	59	55	73	
Isobutyl alcohol	42	43	41	39
1,4-Dioxane	88	58	43	
tert-Butyl Formate	59	57	41	56
Ethanol	45	46		
3,3-Dimethyl-1-butanol	57	69	41	56

ANALYSIS OF VOLATILE ORGANICS BY GC/MS

Prepared by: Norm Farmer Date: 08/15/19

Approved by: Juan Garcia Date: 08/19/19

Annual Review

Reviewed by: _____ Date: _____

Reviewed by: _____ Date: _____

Reviewed by: _____ Date: _____

Document Control

Issued to: QA Department Date: 08/25/19

Issued to: MS Volatile Department Date: * 08/25/19

Issued to: MS Volatile Soil Lab Date: 08/25/19

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Effective 7 days after "*" date

CONTROLLED COPY
DO NOT DUPLICATE

TITLE: ANALYSIS OF VOLATILE ORGANICS BY GC/MS

REFERENCES: SW846 8260C

REVISED SECTIONS: 1.1.6

1.0 SCOPE AND APPLICATION, SUMMARY

1.1 Scope and Application

1.1.1 This method is used to determine the concentrations of various volatile organic compounds in water and solid matrices utilizing a gas chromatograph equipped with a mass spectrometer detector. Routine compounds can be found in Table 1.

1.1.2 The Lower Limit of Quantitation (LLOQ) or Reporting limits (RL) are based on the sample amount and the lowest calibration standard. LLOQs may vary depending on matrix complications and sample volumes. LLOQs for this method are in the range of 1.0-5.0 ug/l for aqueous samples and 5-25 ug/kg for solid samples. Solid matrices are reported on a dry weight basis.

1.1.3 The Method Detection Limit (MDL) for each analyte is evaluated on an annual basis for each matrix and instrument. MDLs are pooled for each matrix, and the final pooled MDLs are verified. The verified MDLs are stored in the LIMS and should be at least 2 to 3 times lower than the LLOQ. Exceptions may be made on a case by case basis; however, at no point shall the MDL be higher than the reported LLOQ.

1.1.4 The LLOQ for each analyte is evaluated on an annual basis for each matrix and instrument. The LLOQ verifications are prepared by spiking a clean matrix at 0.5 to 2 times the current LLOQ level. This LLOQ verification is carried through the same preparation and analytical procedures as the samples. Recovery of the analytes should be within the established limits. The DOD QSM requirements for Limit of Detection (LOD) and Limit of Quantitation (LOQ) verifications are different. See SOP QA020 for complete requirements for MDL, LOD, LOQ, and LLOQ.

1.1.5 Compounds detected at concentrations between the LLOQ and MDL are quantitated and qualified as estimated values and reported with either a “J” or “I” qualifier. Some program or project specifications may require that no values below the LLOQ be reported.

1.1.6 For DOD projects refer to QSM 5.0, Table 4; QSM 5.1, Table B-4; or QSM 5.3, Table B-4 for additional method requirements and data qualifying guidance.

1.2 Summary

1.2.1 This method is adapted from SW846 method 8260C.

1.2.2 Samples are received, stored, and analyzed within the appropriate holding times.

1.2.3 Sample preparation is performed in accordance with SGS Orlando SOP OP020 and OP021.

1.2.4 The samples are analyzed on a gas chromatograph equipped with mass spectrometer detector.

1.2.5 The peaks detected are identified by comparison to characteristic ions and retention times specific to the known target list of compounds.

1.2.6 Additional unknown peaks with a response > 10% of the closest internal standard may be processed through a library search with comparison to a NIST database of approximately 129,000 compound spectra. An estimated concentration is quantitated by assuming a response factor of 1.

1.2.7 Manual integrations are performed in accordance with SOP QA029.

2.0 PRESERVATION AND HOLDING TIME

2.1 Preservation

Aqueous Samples:

2.1.1 Samples should be preserved to a pH < 2. The pH should be checked and recorded immediately after the sample analysis. If the sample is not preserved to a pH < 2, it must be noted on the report.

2.1.2 If 2-chloroethyl vinyl ether is a compound of concern, the sample should not be preserved. If acrolein and acrylonitrile are compounds of concern, the sample should be adjusted to a pH 4 – 5 in the field. These analytes may also be analyzed from an unpreserved sample.

2.1.3 The samples must be stored in capped vials, with minimum headspace, at ≤ 6 °C in an area free of solvent fumes. The size of any bubble caused by degassing upon cooling should not exceed 5-6mm.

Solid Samples:

2.1.4 Special 40ml vials for purge-and-trap of solid samples, as well as the collection and preservation options are described in OP020.

2.1.5 Low level soil samples are preserved by storing them in sealed VOA vials at temperatures between –10 °C to –20 °C. High level soil samples are preserved by storing them in methanol at a ratio of 1 gram of soil to 1ml of methanol.

2.2 Holding Time

2.2.1 Aqueous samples are to be analyzed within 14 days of collection, unless otherwise specified by the contract. Samples that are not preserved should be analyzed within 7 days of collection; however, the preservation deficiency must be noted in the report.

2.2.2 Samples that are preserved to pH 4-5 for the analysis of acrolein and acrylonitrile must be analyzed with 7 days of collection.

2.2.3 Solid and waste samples must be analyzed within 14 days of collection.

3.0 INTERFERENCES

3.1 Data from all blanks, samples, and spikes must be evaluated for interferences.

3.2 Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory blanks. The use of non-TFE tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.3 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank can serve as a check on such contamination.

3.4 Contamination by carry-over can occur whenever high level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for carry-over.

3.5 Acidification with HCl or bisulfate solution may cause the loss of 2-chloroethyl vinyl ether, acrolein, and acrylonitrile.

3.6 Soils and sediment that contain limestone ($CaCO_3$) may react with the sodium bisulfate and effervesce. The effervescing can result in significant losses of volatile organics.

3.7 Certain naturally occurring compounds (humic acids, etc.) will decompose when exposed to the bisulfate solution and form ketones, notably acetone. The amount of acetone formed is extremely matrix dependent but may be produced in significant concentrations.

3.8 The purge efficiency of select fuel oxygenates may be improved by using a heated purge. These fuel oxygenates generally include: methyl tert butyl ether (MTBE), ethyl tert butyl

ether (ETBE), tert amyl methyl ether (TAME), di-isopropyl ether (DIPE), tert amyl ethyl ether (TAEE), tert amyl alcohol (TAA), tert butyl alcohol (TBA) and ethanol (ETOH).

3.8.1 Methyl tert butyl ether (MTBE) may be converted to TBA under acidic preservation and elevated purging temperatures.

3.8.2 If samples containing MTBE, TAME, ETBE or other fuel ethers have been preserved with hydrochloric acid and will be analyzed by purging at elevated temperatures, these samples must be adjusted to pH >10 with tri-sodium phosphate dodecahydrate (TSP) prior to initiation of the analysis.

3.8.3 Dibromofluoromethane (surrogate) may degrade and fail low in samples with a basic pH.

3.8.4 Tert butyl formate (TBF) may degrade at elevated purge temperatures.

4.0 DEFINITIONS

4.1 Batch: A group of samples which are similar with respect to matrix and the testing procedures being employed and which are processed as a unit. A sample batch is limited to a maximum of 20 samples or samples loaded on an instrument within the same 12-hour shift, whichever comes first.

4.2 Blank Spike (BS): An analyte-free matrix spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. Blank Spike recoveries are used to document laboratory performance for a given method. This may also be called a Laboratory Control Sample (LCS).

4.3 Continuing Calibration Verification (CCV): A check standard used to verify instrument calibration throughout an analytical run. For all MS methods, a CCV must be analyzed at the beginning of each analytical run. For DoD QSM 5.x projects, an additional CCV must be analyzed at the end of the run.

4.4 Holding Time: The maximum times that samples may be held prior to preparation and/or analysis and still be considered valid.

4.5 Internal Standards: An organic compound which is similar to the target analyte(s) in chemical composition and behavior, but which is not normally found in environmental samples. Internal standards for mass spec methods are often deuterated forms of target analytes. Internal standards are used to compensate for retention time and response shifts during an analytical run.

4.6 Initial Calibration (ICAL): A series of standards used to establish the working range of a particular instrument and detector. The low point should be at a level equal to or below the reporting level.

4.7 Initial Calibration Verification (ICV): A standard from a source different than that used for the initial calibration. A different vendor should be used whenever possible. The ICV is

used to verify the validity of an Initial Calibration. This may also be called a QC check standard.

4.8 Matrix Spike (MS): A sample aliquot spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. The matrix spike recoveries are used to document the bias of a method in a given sample matrix.

4.9 Matrix Spike Duplicate (MSD): A replicate sample aliquot spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. The matrix spike duplicate recoveries are used to document the precision and bias of a method in a given sample matrix.

4.10 Method Blank (MB): An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is processed simultaneously with the samples through all the steps of the analytical procedure. The method blank is used to document contamination resulting from the analytical process.

4.11 Sample Duplicate (DUP): A replicate sample which is used to document the precision of a method in a given sample matrix.

4.12 Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical integrity of the sample.

4.13 Surrogate: An organic compound which is similar to the target analyte(s) in chemical composition and behavior, but which is not normally found in environmental samples. Surrogates are used to measure the purge efficiency.

4.14 Trip Blank: A sample of analyte-free matrix taken from the laboratory to the sampling site and returned to the laboratory unopened. A trip blank is used to document contamination attributable to shipping and field handling procedures. This type of blank is useful in documenting contamination of volatile organic samples.

5.0 REAGENTS

5.1 Reagent water – distilled or deionized water free of interferences

5.2 Methanol – purge-and-trap grade or equivalent

5.3 Hydrochloric acid (HCl) – ACS reagent grade or equivalent

5.4 Sodium Bisulfate Solution – free of interferences

5.5 Tri-sodium phosphate dodecahydrate (TSP) – ACS reagent grade or equivalent

5.6 Inert Gas – UHP Helium or UHP Nitrogen

5.7 Volatile stock standards – Various mixes, traceable to Certificate of Analysis

5.8 4-Bromofluorobenzene (BFB) – instrument tuning mix

5.9 Surrogate standards –

Dibromofluoromethane	1,2-Dichloroethane-d_4
Toluene-d_8	4-Bromofluorobenzene

5.10 Internal standards –

Fluorobenzene	Chlorobenzene-d_5
1,4-Dichlorobenzene-d_4	tert-Butyl alcohol-d_{10}

6.0 APPARATUS

6.1 Gas Chromatograph – Agilent Technologies 6890 or 7890

6.1.1 Gas Chromatograph

The analytical system that is complete with a temperature programmable gas chromatograph and all required accessories, analytical columns, and gases.

6.1.2 The injection port is designed for split-splitless injection with capillary columns. The injection port must have an appropriate interface for sample introduction.

6.2 Mass Spectrometer– Agilent Technologies 5973 or 5975

The mass spectrometer must be capable of scanning from 35-300 amu every second or less utilizing 70-volt (nominal) electron energy in the electron impact ionization mode. It must also be capable of producing a mass spectrum that meets all the criteria in section 7.5.1.1 when injecting 50 ng of Bromofluorobenzene (BFB).

6.3 Purge and Trap – OI Analytical 4660 with OI Analytical 4552 or 4551 or EST Evolution with EST Centurion

6.3.1 The following autosampler models are used for purging, trapping, and desorbing the sample onto GC column.

- O.I. Model 4660 sample concentrator with 4552 Water/Soil multisampler
- O.I. Model 4660 sample concentrator with 4551 Water multisampler
- EST Evolution sample concentrator with Centurion Water/Soil multisampler

6.3.2 The sample purge vessel must be designed to accept 5 or 10ml samples with a water column at least 3 cm deep.

6.3.3 The multisampler is equipped with a heater capable of maintaining the purge chamber at 40 °C to improve purging efficiency. The heater is to be used for soil and sediment analysis.

6.3.4 The desorber should be capable of rapidly heating the trap to the manufacturer recommended desorb temperature.

6.4 Data System – Agilent Technologies MS Chemstation rev. DA 02.0x, DA 03.0x or EA02.0x.

6.4.1 A computer system interfaced to the mass spectrometer that allows for the continuous acquisition and storage of all mass spectral data obtained throughout the duration of the chromatographic program.

6.4.2 The computer utilizes software that allows searching any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP).

6.4.3 The software should allow for integrating the abundances in any EICP between specific time or scan number limits. Characteristic ions for each analyte are listed in Table 3.

6.4.4 The most recent version of the EPA/NIST mass spectral library should be available. Current NIST database contains approximately 129,000 compound spectra.

6.4.5 Data is archived to a backup server for long term storage.

6.5 Trap – OI #10 or equivalent: Tenax, Silica Gel, and Carbon Molecular Sieve.
Trap – Vocarb 3000 (K) or equivalent: Carbopack B, Carboxen 1000, Carboxen 1001

The trap should be conditioned according to the manufacturer ‘s recommendations.

6.6 Columns – RTX-624 or equivalent: 60m X 0.25mm 1.4um.
- RTX-VMS or equivalent: 40m X 0.18mm 1.0um

6.7 Gas-tight syringes and class “A” volumetric glassware for dilutions of standards and samples.

7.0 PROCEDURE

7.1 Standards Preparation

Standards are prepared from commercially available certified reference standards. All standards must be logged in the Volatile Standards Logbook. All standards shall be traceable to their original source. The standards should be stored at temperatures between –10 °C and –20 °C, or as recommended by the manufacturer. Calibration levels, spike and surrogate concentrations, preparation information, and vendor part numbers can be found in the MSVOA STD Summary in the Active SOP directory.

7.1.1 Stock Standard Solutions

Stock standards are available from several commercial vendors. All vendors must supply a "Certificate of Analysis" with the standard. The certificate will be retained by the lab. Hold time for unopened stock standards is until the vendor's expiration date. Once opened, the hold time is reduced to six months (one month for gases) or the vendor's expiration date (whichever is shorter).

7.1.2 Intermediate Standard Solutions

Intermediate standards are prepared by quantitative dilution of the stock standard with methanol. The hold time for intermediate standards is one month (one week for gases) or the vendor's expiration date (whichever is shorter). Intermediate standards may need to be remade if comparison to other standards indicates analyte degradation or concentration changes.

7.1.3 Calibration Standards

Calibration standards for the volatile organics are prepared at a minimum of five concentration levels through quantitative dilutions of the intermediate standard. The low standard is at a concentration at or below the LLOQ and the remaining standards define the working range of the detector.

Calibration standard concentrations are verified by the analysis of an initial calibration verification (ICV) standard.

7.2 Instrument Conditions

<u>Gas Chromatograph/ Mass Spectrometer</u>

Carrier gas flow	1.0-1.3 ml/min
Transfer line temperature	220 - 280 °C
Analyzer temperature	150 °C

Oven program – 45 °C for 2.5 minutes (RTX-VMS 40m)
10 °C/min to 80 °C for 0 minutes
15 °C/min to 185 °C for 0 minutes
30 °C/min to 240 °C for 2.5 minutes

Oven program – 35 °C for 2.5 minutes (RTX-VMS 40m)
4 °C/min to 60 °C for 0 minutes
25 °C/min to 220 °C for 0 minutes
30 °C/min to 240 °C for 1.2 minutes

Oven program – 45 °C for 2.0 minutes (RTX-624)
10 °C/min to 80 °C for 0 minutes
14 °C/min to 210 °C for 0 minutes
16 °C/min to 240 °C for 4.2 minutes

GC conditions are optimized for each instrument. Actual conditions may vary slightly from those listed above.

7.3 Purge and Trap Device conditions

OI Autosampler

Purge Gas:	Helium or Nitrogen at 30-45 ml/min
Sample Temp:	Aqueous (Ambient) Soils (40°C)
Trap Temp:	<25°C
Purge Time:	6 or 11 min
Desorb:	2 min. at 190°C
Bake:	5 min. at 210°C

EST Autosampler

Purge Gas:	Helium at 35-45 ml/min
Sample Temp:	Aqueous (ambient - 35°C) Soils (40°C)
Trap Temp:	<35°C
Purge Time:	6 or 11 min
Desorb:	1-2 min. at 250°C
Bake:	6 min. at 235°C

Purge and Trap conditions are optimized for each instrument. Actual conditions may vary slightly from those listed above

7.4 Sample Preparation

7.4.1 Water Samples

A 5ml aliquot of sample is loaded onto the purge-and-trap device and purged for either 6 or 11 minutes depending on the system. Detailed procedures are described in SOP OP021.

7.4.2 Solid Samples

A 5-gram aliquot of sample is loaded onto the purge-and-trap device. 5mls of reagent water is added along with internal standards and surrogates. Depending on the system, the sample is then purged for either 6 or 11 minutes while heated to 40ºC and mechanically agitated. Detailed procedures are described in SOP OP020.

Alternatively, a methanol aliquot from the sample is loaded onto the purge-and-trap device. 5mls of reagent water is added along with internal standards and surrogates. The sample is then purged for either 6 or 11 minutes depending on the system. Detailed procedures are described in SOP OP020 and OP021.

7.5 Gas Chromatographic Analysis

Instrument calibration consists of two major sections:

Initial Calibration Procedures
Continuing Calibration Verification

7.5.1 Initial Calibration Procedures

Before samples can be run, the GC/MS system must be tuned, the injection port inertness must be verified, and the instrument must be calibrated.

7.5.1.1 Tune Verification (BFB)

The instrument should be hardware tuned per manufacturer's instructions. Verify the instrument tune by injecting 50ng of BFB solution onto the instrument. The BFB standard may also be purged. The resulting BFB spectra should meet the criteria in the following table.

BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15-40% of mass 95
75	30-60% of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5-9 % of mass 174
176	>95% and <101% of mass 174
177	5-9% of mass 176

Evaluate the tune spectrum using three mass scans from the chromatographic peak and a subtraction of instrument background. This procedure is performed automatically by the MS Chemstation software by running "autofind" on the BFB peak.

Select the scans at the peak apex and one to each side of the apex. Calculate an average of the mass abundances from the three scans.

Background subtraction is required. Select a single scan in the chromatogram that is absent of any interfering compound peak and no more than 20 scans prior to the elution of BFB. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the tuning compound peak.

Alternatively, the average spectra over the entire peak may be used. **All subsequent tune evaluations must use the same procedure that was used for the Initial Calibration.**

If the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are met.

Analysis must not begin until the tuning criteria are met. The injection time of the acceptable tune analysis is considered the start of the 12-hour clock. The same mass spec settings must be used for the calibration standards and samples that were used for the tune evaluation standard.

7.5.1.2 Internal Standard Calibration

A minimum 5-point calibration curve is created for the volatile organic compounds and surrogates using an internal standard technique. SGS Orlando routinely performs a 6-point calibration to maximize the calibration range.

NOTE: West Virginia requires that samples preserved with sodium bisulfate be analyzed against a calibration curve that was also preserved with sodium bisulfate. In this instance, 2-chloroethyl vinyl ether and acrolein will not be reportable.

Historically, many analytical methods have relied on linear models of the calibration relationship, where the instrument response is directly proportional to the amount of a target compound. The linear model has many advantages including simplicity and ease of use. However, given the advent of new detection techniques and because many methods cannot be optimized for all the analytes to which they may be applied, the analyst is increasingly likely to encounter situations where the linear model neither applies nor is appropriate. The option of using non-linear calibration may be necessary to address specific instrumental techniques. However, it is not EPA's intent to allow non-linear calibration to compensate for detector saturation or avoid proper instrument maintenance.

NOTE: Because of this concern, select programs including SC DHEC do not support the use of non-linear regressions.

The low point may be omitted from the calibration table for any compound with an LLOQ set at the level two standard. Additionally, the high point may be omitted for any compound that exhibits poor linearity at the upper end of the calibration range.

An entire level may be omitted provided that a minimum of 5 points remain. There must be technical justification to omit an entire level. This should be documented in the run log.

Response factors (RF) for each analyte are determined as follows:

$RF = (A_{analyte} \mathbf{X} C_{istd})/(A_{istd} \mathbf{X} C_{analyte})$

$A_{analyte}$ = area of the analyte
A_{istd} = area of the internal standard
$C_{analyte}$ = concentration of the analyte
C_{istd} = concentration of the internal standard.

The mean RF and standard deviation of the RF are determined for each analyte. The percent relative standard deviation (%RSD) of the response factors is calculated for each analyte as follows:

%RSD = (Standard Deviation of RF X 100) / Mean RF

If the %RSD $\leq$ 20%, linearity through the origin can be assumed and the mean RF can be used to quantitate target analytes in the samples. **The %RSD should be ≤ 15% for any DoD QSM projects.**

Alternatively, a calibration curve of response vs. amount can be plotted. This method allows for the use of average response factors, linear regressions, and non-linear regressions. Linear regressions may be unweighted or weighted as $1/x$ or $1/x^2$. If the correlation coefficient (r) is $\geq$0.995 ($r^2 \geq$0.990) then the curve can be used to quantitate target analytes in the samples. Regardless of which calibration model is chosen, the laboratory should visually inspect the curve plots to see how the individual calibration points compare to the plot.

NOTE: If a linear regression is used for an analyte, then the low standard must be recalculated against the current initial calibration. The recovery of any analyte using a linear regression must be 70-130% of the expected value. This requirement does not apply to non-linear regressions.

Alternatively, either of the two techniques described below may be used to determine whether the calibration function meets acceptable criteria. These involve refitting the calibration data back to the model. Both % Error and Relative Standard Error (RSE) evaluate the difference between the measured and the true amounts or concentrations used to create the model.

Calculation of the % Error

% ERR = (xi-x'i) / xi * 100

x'i = Measured amount of analyte at calibration level i, in mass or concentration units.

xi = True amount of analyte at calibration level i, in mass or concentration units.

Percent error between the calculated and expected amounts of an analyte should be ≤ 30% for all standards. For some data uses, ≤50% may be acceptable for the lowest calibration point.

Calculation of Relative Standard Error (%RSE)

$$RSE = 100 \times \sqrt{\sum_{i=1}^{n} \left[\frac{x_i' - x_i}{x_i}\right]^2 \Big/ (n-p)}$$

x'i = Measured amount of analyte at calibration level i, in mass or concentration units.

xi = True amount of analyte at calibration level i, in mass or concentration units.

p = Number of terms in the fitting equation. (average = 1, linear = 2, quadratic = 3)

n = Number of calibration points.

The %RSE acceptance limit criterion is ≤20% for good performing compounds and ≤30% for poor performing (PP) compounds.

The method also employs minimum response factor (RF) criteria for select target analytes. See Table 2 for the analytes and associated minimum response factors. Unlike previous revisions that only set a minimum for the average RF, 8260C requires that the minimum RF be met for each level of the calibration curve.

If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.99) for alternate curve fits, then the chromatographic system is considered too imprecise for analysis to begin. Adjust moisture control parameters, replace analytical trap or column, replace moisture trap or adjust desorb time, and then repeat the calibration procedure.

7.5.1.3 Initial Calibration Verification (ICV)

The validity of the initial calibration curve must be verified through the analysis of an initial calibration verification (ICV) standard. The ICV

should be prepared from a second source at a mid-range concentration.

The %D for all normal analytes of interest should be ≤ 30%, the %D for all poor performing (PP) analytes of interest should be ≤ 40%. (These analytes are identified in Table 1) If the %D > 30% (>40% for PP), the analysis of samples may still proceed if the analyte failed high and the analyte is not expected to be present in the samples. However, if a reportable analyte is detected in a sample and the %D for that analyte was greater than 30% (>40% for PP) in the ICV, the sample will need to be reanalyzed on a system with a passing ICV for that analyte.

NOTE: For any DoD QSM project, the %D for all target compounds should be ≤ 20%. If samples must be analyzed with an analyte of interest having a %D > 20%, then the data must be qualified accordingly.

If the ICV does not meet this criteria, a second standard should be prepared. If the ICV still does not meet criteria, analyze an ICV prepared from a third source. If this ICV meets criteria, proceed with sample analysis. If the ICV still does not meet criteria, determine which two standards agree. Make fresh calibration standards and an ICV from the two sources that agree. Recalibrate the instrument.

7.5.2 Continuing Calibration Verification (CCV)

7.5.2.1 Inject 2ul of the tune evaluation mix at the beginning of each 12-hour shift. Evaluate the resultant peaks against the criteria in section 7.5.1.1. The injection time of this standard starts the 12-hour window.

When the analyst is running an unattended second 12-hour window, they may opt to purge the BFB standard. This can be performed by purging an additional blank (which contains BFB) just prior to the second CCV.

7.5.2.2 Analyze a continuing calibration check standard. The CCV should be at or below the mid-point of the calibration curve.

7.5.2.3 The response factor for any target analyte listed in Table 2 should meet the listed minimum value under 8260C but must meet the minimum value listed under SOM 2.3.

7.5.2.4 The %D for all analytes of interest should be ≤ 20%; however, the large number of analytes in this method presents a substantial probability that a few of the analytes will fall outside of this range.

If less than 10 percent of the analytes have a %D > 20% but ≤ 50% then the analysis of samples may still proceed provided that the following criteria is met.

The CCV exceeds the upper limit (+20%) and the analyte is not expected to be present in the samples.

The CCV exceeds the lower limit (-20%) but not more than -50% and the analyte is not expected to be present in the samples. An additional check standard at the LLOQ must be analyzed and the analytes in question be detected and meet all of the qualitative identification criteria.

However, if a reportable analyte is detected in a sample and the %D for that analyte was greater than 20% in the CCV, the sample will need to be reanalyzed on a system with a passing CCV for that analyte, or the data must be qualified.

NOTE: For any DoD QSM project, the %D for all target compounds should be ≤ 20%. If samples must be reported with an analyte of interest having a %D > 20%, then the data must be qualified accordingly, regardless of whether the analyte was detected or not.

7.5.2.5 The criteria in 7.5.2.3 and 7.5.2.4 must be met for the continuing calibration to be considered valid. Only analytes that are being reported for a given sample must meet the criteria in 7.5.2.3 and 7.5.2.4.

If the first continuing calibration verification does not meet criteria, a second standard may be injected. If the second standard does not meet criteria, the system must be recalibrated. If the second standard meets criteria then the system is considered in control and results may be reported.

Rationale for second standard such as instrument maintenance, clipped column, remade standard, etc should be documented in the run log or maintenance log. Reanalysis of second standard without valid rationale may require the analysis of a third standard (in which case both the second and third standard would have to pass).

NOTE: For any DoD QSM project, if the second standard meets criteria, then a third standard must be analyzed. If the third standard also meets criteria then the system is considered in control and results may be reported.

If the |%D| is greater than 20%, then documented corrective action is necessary. This may include recalibrating the instrument and reanalyzing the samples, performing instrument maintenance to correct the problem and reanalyzing the samples, or qualifying the data. Under certain circumstances, the data may be reported, i.e., the CCV failed high, the associated QC passed, and the samples were ND.

NOTE: For any DoD QSM project, if samples must be reported with a target analyte having a %D > 20%, then the data must be qualified accordingly, regardless of whether the analyte was detected or not.

NOTE: Any target analytes that are detected in the samples must be bracketed by an acceptable initial calibration curve and acceptable CCV standards; otherwise, the samples must be reanalyzed or the data must be qualified.

7.5.2.6 For DoD QSM 5.x compliance, an additional CCV must be analyzed at the end of each run. The closing CCV should be within the 12-hour Tune window.

The %D for all target compounds in this CCV should be ≤ 50%. If the %D > %50 for any target compound, then the samples should be reanalyzed at least once at the appropriate dilution. If the %D > %50 for the analytes in the reanalysis, the department supervisor shall review the data and determine what further action is necessary. This may include reanalyzing the samples at a higher dilution or qualifying the data.

NOTE: If samples are ND and an analyte in the CCV fails high, then the sample does not need to be reanalyzed.

7.5.2.7 If any of the internal standard response changes by more than a factor of two (-50% to +100%) or retention time changes by more than 10 seconds from the midpoint standard of the last initial calibration or from the daily CCV, the mass spectrometer must be inspected for malfunctions and corrections made, as appropriate. Corrective action may include re-calibration (initial Calibration) of the instrument.

7.5.3 Sample Analysis

7.5.3.1 Samples are analyzed in a set referred to as an analysis sequence or batch. A batch consists of the following:

Tune Evaluation Mix
Initial Calibration Standards (or CCV)
QC Samples
Samples

7.5.3.2 One microliter (OI) or five microliter (EST) of internal standard/ surrogate solution is added to every 5ml of sample in the sparge vessel. Generally, 5ml of sample are transferred to the sparge vessel.

7.5.3.3 After purging, the system will automatically reverse flow and rapidly heat the trap to desorb the sample analytes onto the GC column.

7.5.3.4 Qualitative identification

The target compounds shall be identified by analysts with competent knowledge in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. The criteria required for a positive identification are:

The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

The sample component must elute at the same relative retention time (RRT) as the daily standard. The RRT of sample component must be within ± 0.06 RRT units of the standard.

All ions present in the standard mass spectra at a relative intensity greater than 10% (major abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

The relative intensities of these ions must agree within ± 30% between the daily standard and sample spectra, (e.g., for an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20 and 80%).

Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

If peak identification is prevented by the presence of interferences, the sample must be diluted so that the interference does not mask any analytes.

7.5.3.5 Quantitative analysis

When a target compound has been identified, concentration will be based on the integrated area of the quantitation ion, which is normally the base peak.

The sample matrix may produce an interference with the primary ion. This may be characterized by an excessive background signal of the same ion, which distorts the peak shape beyond a definitive integration.

The interference could also, severely inhibit the response of the internal standard ion.

If the analyte response exceeds the linear range of the system, the extract must be diluted and reanalyzed. It is recommended that samples be diluted so that the response falls into the middle of the calibration curve.

7.5.3.6 Library search for tentatively identified compounds

If a library search is requested, the analyst should perform a forward library search of the NIST mass spectral library to tentatively identify 10 to 20 non-target compounds.

Guidelines for making tentative identification are:

These compounds should have a response greater than 10% of the nearest internal standard. The response is obtained from the Total Ion Chromatogram.

The search is to include a spectral printout of the best library match for a particular substance. The results are to be interpreted by the analyst.

Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

The relative intensities of the major ions should agree within ±20%.

Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

Ions present in the reference spectrum but not in the sample spectrum should be verified by performing further manual background subtraction to eliminate the interference created by co-eluting peaks and/or matrix interference.

Quantitation of the tentatively identified compounds is obtained from the total ion chromatogram based on a response factor of 1 from the nearest internal standard and is to be tabulated on the library search summary data sheet.

7.6 Maintenance and Trouble Shooting

7.6.1 Refer to SOP GC001 for routine instrument maintenance and trouble shooting.

7.6.2 All instrument maintenance must be documented in the appropriate “Instrument Repair and Maintenance” log. The log will include such items as problem, action taken, correction verification, date, and analyst.

7.6.3 Repairs performed by outside vendors must also be documented in the log. The analyst or Department Supervisor responsible for the instrument must complete the log if the repair technician does not.

7.6.4 PC and software changes must be documented in the "Instrument Repair and Maintenance" log. Software changes may require additional validation.

8.0 METHOD PERFORMANCE

Method performance is monitored through the routine analysis of negative and positive control samples. These control samples include method blanks (MB), blank spikes (BS), matrix spikes (MS), and matrix spike duplicates (MSD). The MB and BS are used to monitor overall method performance, while the MS and MSD are used to evaluate the method performance in a specific sample matrix.

Blank spike, matrix spike, and matrix spike duplicate samples are compared to statistically generated control limits. These control limits are reviewed and updated annually. Control limits are stored in the LIMS. Additionally, blank spike accuracy is regularly evaluated for statistical trends that may be indicative of systematic analytical errors.

9.0 QUALITY ASSURANCE / QUALITY CONTROL

Accuracy and matrix bias are monitored by the use of surrogates and by the analysis of a QC set that is prepared with each batch (maximum of 20 samples) of samples. The QC set consists of a method blank (MB), blank spike (BS), matrix spike (MS), and matrix spike duplicate (MSD).

9.1 Internal Standards

9.1.1 Fluorobenzene, chlorobenzene-d_5, 1,4-dichlorobenzene-d_4, and tert butyl alcohol-d_{10} are used as internal standards for this method. The response of the internal standard in all subsequent runs should be within a factor of two (-50% to +100%) of the internal standard response in the opening CCV for each sequence. On days that an initial calibration is performed, the internal standard responses should be compared to the internal standard responses for the mid-point standard. The response for tert butyl alcohol-d_{10} need only be monitored if target analytes are being reported that reference that particular internal standard.

9.1.2 If the internal standard responses are not within limits, the following are required.

9.1.2.1 Check to be sure that there are no errors in calculations, integrations, or internal standards solutions. If errors are found, recalculate the data accordingly.

9.1.2.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample. If the recovery is high due to interfering peaks, it may be possible to get a

more accurate recovery by analyzing the sample on a different column type.

9.1.2.3 If no problem is found, prepare a second aliquot of sample and reanalyze the sample. If there is insufficient sample for reanalysis, footnote this on the report.

9.1.2.4 If upon reanalysis, the responses are still not within limits, the problem is considered matrix interference. The sample may need to be diluted or the results qualified.

9.1.3 Historical data has shown that when soils are preserved with sodium bisulfate the 4th internal standard (tert butyl alcohol-d_{10}) will very often fail high. If the analytes that reference tert butyl alcohol-d_{10} are non-detect, then the sample does not need to be reanalyzed; however, they should be footnoted with "Associated internal standard response outside of control limits.

9.2 Surrogates

9.2.1 Dibromofluoromethane, 1,2-dichloroethane-d_4, toluene-d_8, and 4-Bromofluorobenzene are used as the surrogate standards to monitor the efficiency of the purge-and-trap system.

A known amount of surrogate standard is added to each sample including the QC set prior to purging. The percent recovery for each surrogate is calculated as follows:

% Recovery = (Sample Amount / Amount Spiked) X 100

The percent recovery must fall within the established control limits for all surrogates for the results to be acceptable.

9.2.2 If any surrogate recovery is not within the established control limits, the following are required.

9.2.2.1 Check to be sure that there are no errors in calculations, dilutions, integrations, surrogate solutions or internal standard solutions. If errors are found, recalculate the data accordingly.

9.2.2.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample. If the recovery is high due to interfering peaks, it may be possible to get a more accurate recovery by analyzing the sample on a different column type.

9.2.2.3 If no problem is found, reanalyze the sample. **NOTE:** If the recoveries are high and the sample is non-detect, then reanalysis may not be necessary. For any DoD QSM projects the resulting data must be

qualified accordingly. If there is insufficient sample for reanalysis, footnote this on the report.

9.2.2.4 If upon reanalysis, the recovery is still not within control limits, the problem is considered matrix interference. Surrogates from both sets of analysis should be reported on the final report.

9.2.2.5 Historical data has shown that samples with pH > 11 will cause dibromofluoromethane to degrade and fail low. If the remaining surrogates are within control limits, then samples with pH > 11 should be footnoted, but they do not need to be reanalyzed for dibromofluoromethane failures.

9.3 Method Blank

9.3.1 The method blank is de-ionized water or de-ionized water with 5 grams of clean sand (depending upon sample matrix) to which the surrogate standard has been added. An appropriate aliquot of methanol should also be added. The method blank is then purged along with the other samples to determine any contamination from the system or ambient sources. The method blank must be free of any analytes of interest or interferences at ½ the required LLOQ to be acceptable. Common laboratory contaminants such as methylene chloride must be below the LLOQ if present. If the method blank is not acceptable, corrective action must be taken to determine the source of the contamination. Samples associated with a contaminated method blank shall be evaluated as to the best corrective action for each particular sample. This may include reanalyzing the samples or qualifying the results with a “B” or “V” qualifier.

9.3.2 If the MB is contaminated but the samples are non-detect, then the source of contamination should be investigated and documented. The sample results can be reported. **For any DoD QSM projects the resulting data must be qualified accordingly.**

9.3.3 If the MB is contaminated but the samples results are > 10 times the contamination level, the source of the contamination should be investigated and documented. The samples results may be reported with the appropriate “B” or “V” qualifier. This must be approved by the department supervisor.

9.3.4 If the MB is contaminated but the samples results are < 10 times the contamination level, the source of the contamination should be investigated and documented. The samples should be reanalyzed for confirmation. If there is insufficient sample to reanalyze, or if the sample is reanalyzed beyond hold time, the appropriate footnote and qualifiers should be added to the results. This must be approved by the department supervisor.

9.4 Blank Spike

9.4.1 The blank spike is de-ionized water or de-ionized water with 5 grams of clean sand (depending upon sample matrix) to which the surrogate standard and spike

standard have been added. An appropriate aliquot of methanol should also be added. The blank spike is then processed along with the other samples to monitor the efficiency of the purge-and-trap procedure. The percent recovery for each analyte is calculated as follows:

% Recovery = (Blank Spike Amount / Amount Spiked) X 100

The percent recovery for each analyte of interest should fall within the established control limits for the results to be acceptable. The large number of analytes in this method presents a substantial probability that a few of the analytes will fall outside of the established control limits. This may not indicate that the system is out of control; therefore, corrective action may not be necessary.

Upper and lower marginal exceedance (ME) limits can be established to determine when corrective action is necessary. A marginal exceedance in the Blank Spike is defined as a recovery being outside of 3 standard deviations but within 4 standard deviations of the mean.

The number of allowable marginal exceedances is based on the number of analytes in the Blank Spike. Marginal Exceedances must be random. If the same analyte exceeds the BS control limits repeatedly, it is an indication of a systematic problem and corrective action must be taken.

Marginal exceedances are not permitted for analytes that are deemed to be "Compounds of Interest" for a specific project. "Compounds of Concern" are different from "Target Compounds". "Target Compounds" are all analytes that are being reported for a site where "Compounds of Concern" are those analytes expected to be present at the site.

The number of allowable marginal exceedances is as follows:

1) > 90 analytes in BS, 5 analytes allowed in ME range;

2) 71-90 analytes in BS, 4 analytes allowed in ME range;

3) 51-70 analytes in BS, 3 analytes allowed in ME range;

4) 31-50 analytes in BS, 2 analytes allowed in ME range;

5) 11-30 analytes in BS, 1 analyte allowed in ME range;

6) < 11 analytes in BS, no analytes allowed in ME range.

NOTE: SC DHEC does not recognize the concept of Marginal Exceedances. Additionally, a secondary check against 70-130% limits should be performed for all analytes reported to SC DHEC.

9.4.2 If the blank spike recoveries are not within the established control limits, the following are required.

9.4.2.1 Check to be sure that there are no errors in calculations, dilutions, integrations, spike solutions or internal standard solutions. If errors are found, recalculate the data accordingly.

9.4.2.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample.

9.4.2.3 Check to see if the recoveries that are outside of control limits are analytes of concern. If the analytes are not being reported, additional corrective action is not necessary, and the sample results can be reported without qualification.

9.4.2.4 If the recovery of an analyte in the BS is high and the associated sample is non-detect, the data may be reportable. **For any DoD QSM projects the resulting data must be qualified accordingly.**

9.4.2.5 If no problem is found, the department supervisor shall review the data and determine what further corrective action is best for each particular sample. That may include reanalyzing the samples or qualifying the results as estimated.

9.4.2.6 If there is insufficient sample to reanalyze, or if the sample is reanalyzed beyond hold time, the appropriate footnote and qualifiers should be added to the results. This must be approved by the department supervisor.

9.4.2.7 Because of their problematic nature, 2-chloroethyl-vinyl-ether and acrolein are generally not evaluated in the blank spike unless they are of specific concern for a given project.

9.5 Matrix Spike and Matrix Spike Duplicate

9.5.1 Matrix spike and spike duplicates are replicate sample aliquots to which the surrogate standard and spike standard have been added. The matrix spike and spike duplicate are then processed along with the other samples to monitor the precision and accuracy of the purge-and-trap procedure. The percent recovery for each analyte is calculated as follows:

% Recovery = [(Spike Amount – Sample Amount) / Amount Spiked] X 100

The percent recovery for each analyte of interest must fall within the established control limits for the results to be acceptable.

9.5.2 If the matrix spike recoveries are not within the established control limits, the following are required.

9.5.2.1 Check to be sure that there are no errors in calculations, dilutions, integrations, spike solutions or internal standard solutions. If errors are found, recalculate the data accordingly.

9.5.2.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample. If the recovery is high due to interfering peaks, it may be possible to get a more accurate recovery by analyzing the sample on a different column type.

9.5.2.3 If no problem is found, compare the recoveries to those of the blank spike. If the blank spike recoveries indicate that the problem is sample related, document this on the run narrative. Matrix spike recovery failures are not grounds for reanalysis but are an indication of the sample matrix effects.

9.5.3 Precision

Matrix spike and spike duplicate recoveries for each analyte are used to calculate the relative percent difference (RPD) for each compound.

RPD = (| MS Result – MSD Result | / Average Result) X 100

The RPD for each analyte should fall within the established control limits. If more than 33% of the RPDs fall outside of the established control limits, the department supervisor shall review the data and determine if any corrective action is necessary. RPD failures are generally not grounds for batch reanalysis.

10.0 CALCULATIONS

The concentration of each target compound in the original sample is calculated as follows:

Water (ug/l) = ($CONC_{inst}$) X DF

Soil (ug/kg) = [($CONC_{inst}$) X (5 / W_I)] / %solids (*low level soils)*

Soil (ug/kg) = [($CONC_{inst}$) X (V_F / V_A) X (5 / W_I) X DF] / %solids (*high level soils)*

$CONC_{inst}$	=	Instrument concentration calculated from the initial calibration using mean RF or curve fit.
DF	=	Dilution Factor
V_F	=	Volume of methanol extract (ul)
V_A	=	Volume of methanol aliquot (ul)
W_I	=	Weight of sample (g)
%solids	=	Dry weight determination in decimal form

For high level soils, V_F is calculated as follows:

V_F = {ml of solvent + [(%moisture X W_I) / 100]} X 1000 ul/ml

11.0 SAFETY AND POLLUTION PREVENTION

11.1 Safety

The analyst should follow normal safety procedures as outlined in the SGS Health and Safety Program, which includes the use of safety glasses, gloves, and lab coats.

The toxicity of each reagent and target analyte has not been precisely defined; however, each reagent and sample should be treated as a potential health hazard. Material Safety Data Sheets (MSDS) or Safety Data Sheets (SDS) are available for all reagents and many of the target analytes. Exposure must be reduced to the lowest possible level. Personal protective equipment should be used by all analysts.

11.2 Pollution Prevention

Waste solvents from the sample analysis, methanol extraction, and standards preparation are collected in waste storage bottles and are eventually transferred to the non-chlorinated waste drum.

Old stock standards are disposed of in the waste vial drum.

Samples are archived and stored for 30 days after analysis. After the storage time has elapsed, the remaining aqueous and soil samples are transferred to the appropriate drums for disposal.

12.0 REFERENCES

SW846 Method 8000D Revision 4, July 2014

SW846 Method 8260C Revision 3, August 2006

SW846 Method 8260D Revision 4, June 2018

EPA CLP SOW for Organics Superfund Methods, SOM02.3, September 2015

TABLE 1

Routine Target Analytes

Dichlorodifluoromethane	**2-Butanone**	n-Propylbenzene
Chloromethane	1,1-Dichloropropene	Bromobenzene
Vinyl Chloride	Propionitrile	1,1,2,2-Tetrachloroethane
Bromomethane	Methacrylonitrile	1,3,5-Trimethylbenzene
Chloroethane	Benzene	2-Chlorotoluene
Trichlorofluoromethane	TAME	**trans-1,4-Dichloro-2-Butene**
Ethyl Ether	1,2-Dichloroethane	1,2,3-Trichloropropane
1,2-Dichlorotrifluoroethane	Trichloroethene	**Cyclohexanone**
1,1-Dichloroethene	Methylcyclohexane	4-Chlorotoluene
Freon 113	Dibromomethane	tert-Butylbenzene
Carbon Disulfide	1,2-Dichloropropane	1,2,4-Trimethylbenzene
Iodomethane	Bromodichloromethane	**Pentachloroethane**
Acrolein	Methyl methacrylate	sec-Butylbenzene
Allyl chloride	**2-Chloroethyl vinyl ether**	4-Isopropyltoluene
Methylene Chloride	cis-1,3-Dichloropropene	1,3-Dichlorobenzene
Acetone	Toluene	1,4-Dichlorobenzene
Methyl acetate	2-Nitropropane	n-Butylbenzene
trans-1,2-Dichloroethene	4-Methyl-2-pentanone	**Benzyl Chloride**
Hexane	trans-1,3-Dichloropropene	1,2-Dichlorobenzene
Methyl Tert Butyl Ether	Tetrachloroethene	**1,2-Dibromo-3-Chloropropane**
Acetonitrile	Ethyl methacrylate	Hexachlorobutadiene
Di-isopropyl ether	1,1,2-Trichloroethane	1,2,4-Trichlorobenzene
Chloroprene	Dibromochloromethane	Naphthalene
1,1-Dichloroethane	1,3-Dichloropropane	1,2,3-Trichlorobenzene
Acrylonitrile	1,2-Dibromoethane	**Ethanol**
ETBE	**2-hexanone**	Tert Butyl Alcohol
Vinyl acetate	1-Chlorohexane	Isobutyl alcohol
cis-1,2-Dichloroethene	Ethylbenzene	Tert Amyl Alcohol
2,2-Dichloropropane	Chlorobenzene	**1,4-Dioxane**
Bromochloromethane	1,1,1,2-Tetrachloroethane	3,3-Dimethyl-1-butanol
Cyclohexane	m,p-Xylene	Tert Amy Alcohol
Chloroform	o-Xylene	**Tert Butyl Formate**
Ethyl acetate	Styrene	1,2,3-Trimethylbenzene
Tetrahydrofuran	Bromoform	
Carbon Tetrachloride	Isopropylbenzene	
1,1,1-Trichloroethane	cis-1,4-Dichloro-2-butene	

Bolded analytes are considered "Poor Performing"

TABLE 2

Recommended Minimum Response Factors

Analyte	8260C Min RF	SOM2.3 Min RF
Dichlorodifluoromethane	0.1	0.01
Chloromethane	0.1	0.01
Vinyl chloride	0.1	0.01
Bromomethane	0.1	0.01
Chloroethane	0.1	0.01
Trichlorofluoromethane	0.1	0.01
1,1-Dichloroethene	0.1	0.02
1,1,2-Trichloro-1,2,2-trifluoroethane	0.1	0.01
Acetone	0.1	0.01
Carbon disulfide	0.1	0.01
Methyl Acetate	0.1	0.01
Methylene chloride	0.1	0.01
trans-1,2-Dichloroethene	0.1	0.07
cis-1,2-Dichloroethene	0.1	0.1
Methyl tert-Butyl Ether	0.1	0.01
1,1-Dichloroethane	0.2	0.1
2-Butanone	0.1	0.01
Chloroform	0.2	0.04
1,1,1-Trichloroethane	0.1	0.05
Cyclohexane	0.1	0.1
Carbon tetrachloride	0.1	0.02
Benzene	0.5	0.3
1,2-Dichloroethane	0.1	0.01
Trichloroethene	0.2	0.1
Methylcyclohexane	0.1	0.2

Analyte	8260C Min RF	SOM2.3 Min RF
1,2-Dichloropropane	0.1	0.1
Bromodichloromethane	0.2	0.09
cis-1,3-Dichloropropene	0.2	0.1
trans-1,3-Dichloropropene	0.1	0.01
4-Methyl-2-pentanone	0.1	0.01
Toluene	0.4	0.4
1,1,2-Trichloroethane	0.1	0.04
Tetrachloroethene	0.2	0.1
2-Hexanone	0.1	0.01
Dibromochloromethane	0.1	0.05
1,2-Dibromoethane	0.1	0.01
Chlorobenzene	0.5	0.4
Ethylbenzene	0.1	0.5
meta-/para-Xylene	0.1	0.2
ortho-Xylene	0.3	0.3
Styrene	0.3	0.2
Bromoform	0.1	0.01
Isopropylbenzene	0.1	0.7
1,1,2,2-Tetrachloroethane	0.3	0.05
1,3-Dichlorobenzene	0.6	0.5
1,4-Dichlorobenzene	0.5	0.7
1,2-Dichlorobenzene	0.4	0.4
1,2-Dibromo-3-chloropropane	0.05	0.01
1,2,4-Trichlorobenzene	0.2	0.3

TABLE 3
Characteristic Ions

Analyte	Quant. Ion	Q1	Q2	Q3
Fluorobenzene	96	70		
Dichlorodifluoromethane	85	87		
Chloromethane	50	52		
Vinyl Chloride	62	64		
Bromomethane	94	96	93	
Chloroethane	64	66	49	
Trichlorofluoromethane	101	103		
Ethyl Ether	59	45	74	
1,2-Dichlorotrifluoroethane	67	117	85	69
1,1-Dichloroethene	61	96	98	63
Freon 113	101	151	103	85
Carbon Disulfide	76	44		
Iodomethane	142	127	141	
Allyl chloride	41	39	38	76
Methylene Chloride	49	84	86	51
Acetone	58	43		
Methyl acetate	74	43	42	
trans-1,2-Dichloroethene	61	96	98	63
Hexane	56	57	43	41
Methyl Tert Butyl Ether	73	57	43	41
Acetonitrile	40	41	39	
Di-isopropyl ether	45	43	87	
Chloroprene	53	88	51	50
1,1-Dichloroethane	63	65		
Acrylonitrile	53	52	51	
ETBE	59	87	57	
Vinyl acetate	43	42		
cis-1,2-Dichloroethene	96	61	98	63
2,2-Dichloropropane	77	97		
Bromochloromethane	128	49	130	51
Cyclohexane	56	84	41	55
Chloroform	83	85	47	
Ethyl acetate	43	45		
Tetrahydrofuran	42	41	72	
Dibromofluoromethane	113	111	192	
Carbon Tetrachloride	117	119	121	82
1,1,1-Trichloroethane	97	99	61	
2-Butanone	43	72		

TABLE 3 (cont)
Characteristic Ions

Analyte	Quant. Ion	Q1	Q2	Q3
1,1-Dichloropropene	75	39	110	77
Propionitrile	54	52	55	
Methacrylonitrile	41	39	40	52
Benzene	78	51		
TAME	73	43	55	
1,2-Dichloroethane-d_4	65	67	102	
1,2-Dichloroethane	62	49	64	
Trichloroethene	95	130	97	132
Methylcyclohexane	83	55	98	42
Dibromomethane	93	95	174	172
1,2-Dichloropropane	63	62	41	76
Bromodichloromethane	83	85	47	
Methyl methacrylate	41	69	39	100
2-Chloroethyl vinyl ether	63	43	44	65
cis-1,3-Dichloropropene	75	77	39	
Chlorobenzene-d_5	117	82		
Toluene-d_8	98	100		
Toluene	91	92		
2-Nitropropane	41	43	39	
4-Methyl-2-pentanone	43	58	57	41
trans-1,3-Dichloropropene	75	77	39	49
Tetrachloroethene	166	164	129	131
Ethyl methacrylate	69	41	39	99
1,1,2-Trichloroethane	83	97	61	99
Dibromochloromethane	129	127	131	
1,3-Dichloropropane	76	78	41	39
1,2-Dibromoethane	107	109		
2-hexanone	43	58	57	
1-Chlorohexane	91	55	41	43
Ethylbenzene	91	106		
Chlorobenzene	112	77	114	51
1,1,1,2-Tetrachloroethane	131	133	119	117
m,p-Xylene	91	106	105	
o-Xylene	91	106	105	
Styrene	104	78	103	51
Bromoform	173	175	171	91
Isopropylbenzene	105	120		
1,4-Dichlorobenzene-d_4	152	151		

TABLE 3 (cont)
Characteristic Ions

Analyte	Quant. Ion	Q1	Q2	Q3
4-Bromofluorobenzene	95	174	176	
cis-1,4-Dichloro-2-butene	53	75	88	39
n-Propylbenzene	91	120		
Bromobenzene	156	158		
1,1,2,2-Tetrachloroethane	83	85		
1,3,5-Trimethylbenzene	105	120		
2-Chlorotoluene	91	126	89	
trans-1,4-Dichloro-2-Butene	53	89	75	
1,2,3-Trichloropropane	110	61	112	49
Cyclohexanone	55	98	42	69
4-Chlorotoluene	91	126		
tert-Butylbenzene	91	41	134	
1,2,4-Trimethylbenzene	105	120	119	
1,2,3-Trimethylbenzene	105	120		
Pentachloroethane	167	117	119	165
sec-Butylbenzene	105	134		
4-Isopropyltoluene	119	134		
1,3-Dichlorobenzene	146	111	148	75
1,4-Dichlorobenzene	146	111	148	75
n-Butylbenzene	92	91	134	
Benzyl Chloride	126	91	65	
1,2-Dichlorobenzene	146	111	148	75
1,2-Dibromo-3-Chloropropane	75	155	157	39
Hexachlorobutadiene	225	190	118	260
1,2,4-Trichlorobenzene	180	182	145	109
Naphthalene	128	127		
1,2,3-Trichlorobenzene	180	182	145	109
Tert Butyl Alcohol-d10	65	46		
acrolein	56	55		
Tert Butyl Alcohol	59	41	43	
tert Amyl alcohol	59	55	73	
Isobutyl alcohol	42	43	41	39
1,4-Dioxane	88	58	43	
tert-Butyl Formate	59	57	41	56
Ethanol	45	46		
3,3-Dimethyl-1-butanol	57	69	41	56

ANALYSIS OF SEMIVOLATILE ORGANICS BY GC/MS

Prepared by: Norm Farmer Date: 08/26/19

Approved by: Mike Eger Date: 08/26/19

Annual Review

Reviewed by: _____ Date: _____

Reviewed by: _____ Date: _____

Reviewed by: _____ Date: _____

Document Control

Issued to: QA Department Date: 08/27/19

Issued to: SVOC Department Date: * 08/27/19

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Effective 7 days after "*" date

CONTROLLED COPY
DO NOT DUPLICATE

TITLE: ANALYSIS OF SEMIVOLATILE ORGANICS BY GC/MS

REFERENCES: SW846 8270D

REVISED SECTIONS: 1.1.6, 4.3 and 12.0

1.0 SCOPE AND APPLICATION, SUMMARY

1.1 Scope and Application

1.1.1 This method is used to determine the concentrations of various semivolatile organic compounds in water and solid matrices utilizing a gas chromatograph equipped with a mass spectrometer detector. Routine compounds can be found in Table 1.

1.1.2 The Lower Limits of Quantitation (LLOQ) or Reporting limits (RL) are based on the extraction procedure and the lowest calibration standard. LLOQs may vary depending on matrix complications and sample volumes. LLOQs for this method are in the range of 5.0-25.0 ug/l for aqueous samples and 170-850 ug/kg for solid samples. Solid matrices are reported on a dry weight basis.

1.1.3 The Method Detection Limit (MDL) for each analyte is evaluated on an annual basis for each matrix and instrument. MDLs are pooled for each matrix, and the final pooled MDLs are verified. The verified MDLs are stored in the LIMS and should be at least 2 to 3 times lower than the LLOQ. Exceptions may be made on a case by case basis; however, at no point shall the MDL be higher than the reported LLOQ.

1.1.4 The LLOQ for each analyte is evaluated on an annual basis for each matrix and instrument. The LLOQ verifications are prepared by spiking a clean matrix at 0.5 to 2 times the current LLOQ level. This LLOQ verification is carried through the same preparation and analytical procedures as the samples. Recovery of the analytes should be within the established limits. The DOD QSM requirements for Limit of Detection (LOD) and Limit of Quantitation (LOQ) verifications are different. See SOP QA020 for complete requirements for MDL, LOD, LOQ, and LLOQ.

1.1.5 Compounds detected at concentrations between the LLOQ and MDL are quantitated and qualified as estimated values and reported with either a “J” or “I” qualifier. Some program or project specifications may require that no values below the LLOQ be reported.

1.1.6 For DOD projects refer to QSM 5.0, Table 4; QSM 5.1, Table B-4; or QSM 5.3, Table B-4 for additional method requirements and data qualifying guidance.

1.2 Summary

1.2.1 This method is adapted from SW846 Method 8270D.

1.2.2 Samples are received, stored, and extracted within the appropriate holding times.

1.2.3 Sample preparation is performed in accordance with SGS Orlando SOPs OP006 and OP007.

1.2.4 The extracts are analyzed on a gas chromatograph equipped with mass spectrometer detector.

1.2.5 The peaks detected are identified by comparison to characteristic ions and retention times specific to the known target list of compounds.

1.2.6 Additional unknown peaks with a response > 10% of the closest internal standard may be processed through a library search with comparison to an NIST database of approximately 129,000 compound spectra. An estimated concentration is quantitated by assuming a response factor of 1.

1.2.7 Manual integrations are performed in accordance with SOP QA029.

2.0 PRESERVATION AND HOLDING TIME

2.1 Preservation

2.1.1 Samples shall be collected in amber glass bottles with Teflon lined caps. One-liter bottles are recommended for aqueous samples, and 300ml jars are recommended for solid samples.

2.1.2 The samples must be protected from light and refrigerated at ≤ 6°C from the time of collection until extraction. The extracts must be refrigerated at –10°C to –20°C until analysis.

2.2 Holding Time

2.2.1 Aqueous samples must be extracted within 7 days of collection.

2.2.2 Solid and waste samples must be extracted within 14 days of collection.

2.2.3 Extracts must be analyzed within 40 days of extraction.

3.0 INTERFERENCES

3.1 Data from all blanks, samples, and spikes must be evaluated for interferences.

3.2 Method interferences may be caused by contaminants in solvents, reagents, or glassware. Interferences from phthalate esters can be eliminated by using plastic-free solvent containers and solvent rinsed glassware.

3.3 Other organic compounds, including chlorinated hydrocarbons, petroleum hydrocarbons, and phthalate esters may be co-extracted by this method.

3.4 Aldol condensation byproducts may form when samples are extracted using solvent mixes containing acetone. Concrete samples in particular are prone to forming aldol condensation byproducts at levels that can interfere with the analysis. Therefore, concrete samples should be extracted with 100% methylene chloride.

3.5 Benzidine and benzaldehyde are extremely reactive in the calibration mix and will quickly break down. Analytes may need to be calibrated separately.

4.0 DEFINITIONS

4.1 Batch: A group of samples which are similar with respect to matrix and the testing procedures being employed and which are processed as a unit. A sample batch is limited to a maximum of 20 samples.

4.2 Blank Spike (BS): An analyte-free matrix spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. Blank Spike recoveries are used to document laboratory performance for a given method. This may also be called a Laboratory Control Sample (LCS).

4.3 Continuing Calibration Verification (CCV): A check standard used to verify instrument calibration throughout an analytical run. For all MS methods, a CCV must be analyzed at the beginning of each analytical run. For DoD QSM 5.x projects, an additional CCV must be analyzed at the end of the run.

4.4 Holding Time: The maximum times that samples may be held prior to preparation and/or analysis and still be considered valid.

4.5 Internal Standards: An organic compound which is similar to the target analyte(s) in chemical composition and behavior, but which is not normally found in environmental samples. Internal standards for mass spec methods are often deuterated forms of target analytes. Internal standards are used to compensate for retention time and response shifts during an analytical run.

4.6 Initial Calibration (ICAL): A series of standards used to establish the working range of a particular instrument and detector. The low point should be at a level equal to or below the LLOQ.

4.7 Initial Calibration Verification (ICV): A standard from a source different than that used for the initial calibration. A different vendor should be used whenever possible. The ICV is used to verify the validity of an Initial Calibration. This may also be called a QC check standard.

4.8 Matrix Spike (MS): A sample aliquot spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. The matrix spike recoveries are used to document the bias of a method in a given sample matrix.

4.9 Matrix Spike Duplicate (MSD): A replicate sample aliquot spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. The matrix spike duplicate recoveries are used to document the precision and bias of a method in a given sample matrix.

4.10 Method Blank (MB): An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is processed simultaneously with the samples through all the steps of the analytical procedure. The method blank is used to document contamination resulting from the analytical process.

4.11 Sample Duplicate (DUP): A replicate sample which is used to document the precision of a method in a given sample matrix.

4.12 Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical integrity of the sample.

4.13 Surrogate: An organic compound which is similar to the target analyte(s) in chemical composition and behavior, but which is not normally found in environmental samples. Surrogates are used to measure the extraction efficiency.

5.0 REAGENTS

5.1 Methylene Chloride – pesticide grade or equivalent

5.2 Semivolatile stock standards – Various mixes, traceable to Certificate of Analysis

5.3 Decafluorotriphenylphosphine mix (DFTPP) – Also contains pentachlorophenol, benzidine, and DDT.

5.4

Base/neutral surrogate standards –	Acid surrogate standards –
Nitrobenzene-d_5	Phenol-d_6
2-Fluorobiphenyl	2-Fluorophenol
p-Terphenyl-d_{14}	2,4,6-Tribromophenol

5.5 Internal standards –

1,4-Dichlorobenzene-d_4	Naphthalene-d_8
Acenaphthene-d_{10}	Phenanthrene-d_{10}
Chrysene-d_{12}	Perylene-d_{12}

6.0 APPARATUS

6.1 Gas Chromatograph – Agilent Technologies 6890 or 7890 with 7683 or 7693 Autosampler

6.1.1 Gas Chromatograph

The analytical system that is complete with a temperature programmable gas chromatograph and all required accessories, analytical columns, and gases.

6.1.2 The injection port is designed for split-splitless or on-column injection with capillary columns.

6.1.3 Autosampler allows for unattended sample and standard injection throughout the analytical run.

6.2 Mass Spectrometer – Agilent Technologies 5973 and 5975

The mass spectrometer must be capable of scanning from 35-500 amu every second or less utilizing a 70-volt (nominal) electron energy in the electron impact ionization mode. It must also be capable of producing a mass spectrum that meets all the criteria in section 7.4.1.1 when injecting 50 ng of Decafluorotriphenylphosphine (DFTPP).

6.3 Data System – Agilent Technologies MS Chemstation rev. DA 02.0x, DA 03.0x or EA 02.0x.

6.3.1 A computer system interfaced to the mass spectrometer that allows for the continuous acquisition and storage of all mass spectral data obtained throughout the duration of the chromatographic program.

6.3.2 The computer utilizes software that allows searching any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP).

6.3.3 The software should allow for integrating the abundances in any EICP between specific time or scan number limits. See Table 2.

6.3.4 The most recent version of the EPA/NIST mass spectral library should be available. Current NIST database contains approximately 129,000 compound spectra.

6.3.5 Data is archived to a backup server for long term storage.

6.4 Column – TG-5MS or equivalent: 30m X 0.25mm X 0.25um
– ZB-Semivolatiles: 30m X 0.25mm X 0.25um

6.5 Gas-tight syringes and class “A” volumetric glassware for dilutions of standards and extracts.

7.0 PROCEDURE

7.1 Standards Preparation

Standards are prepared from commercially available certified reference standards. All standards must be logged in the Semivolatile Standards Logbook. All standards shall be traceable to their original source. The standards should be stored at temperatures between –10 °C and –20 °C, or as recommended by the manufacturer. Calibration levels, spike and surrogate concentrations, preparation information, and vendor part numbers can be found in the MS STD Summary in the Active SOP directory.

7.1.1 Stock Standard Solutions

Stock standards are available from several commercial vendors. All vendors must supply a “Certificate of Analysis” with the standard. The certificate will be retained by the lab. Hold time for unopened stock standards is until the vendor’s expiration date. Once opened, the hold time is reduced to one year or the vendor’s expiration date (whichever is shorter).

7.1.2 Intermediate Standard Solutions

Intermediate standards are prepared by quantitative dilution of the stock standard with methylene chloride. The hold time for intermediate standards is six months or the vendor’s expiration date (whichever is shorter). Intermediate standards may need to be remade if comparison to other standards indicates analyte degradation or concentration changes.

7.1.3 Calibration Standards

Calibration standards for the semivolatile organics are prepared at a minimum of five concentration levels through quantitative dilutions of the intermediate standard. The low standard is at a concentration at or below the LLOQ, and the remaining standards define the working range of the detector.

Benzidine and benzaldehyde are extremely reactive in the calibration mix and will quickly break down. Fresh standards may need to be made if these analytes are requested.

Calibration standard concentrations are verified by the analysis of an initial calibration verification (ICV) standard.

7.2 Gas Chromatograph Conditions

Split/Splitless Injection Port

1 or 2ul autosampler injection

Pulsed splitless or 4:1 split injection

Carrier gas – UHP Helium (7.7psi to 40psi @1.5 psi/min ramp pressure)

Injection port temperature – 280 °C Transfer line temperature – 280 °C

Multimode Injection Port

1 or 2ul autosampler injection

Pulsed 4:1 split injection at 25psi for 0.3 min or 10:1 split injection

Carrier gas – UHP Helium (7.7psi to 38psi @2psi/min ramp pressure)

Injection port temperature – 280 °C Transfer line temperature – 280 °C

Oven program – 40 °C for 2.0 minutes
20 °C/min to 260 °C for 0 minutes
10 °C/min to 280 °C for 0 minutes
15 °C/min to 320 °C for 1.0 minutes

Source temperature – 230 °C Quad temperature – 150 °C

GC conditions are optimized for each instrument. Actual conditions may vary slightly from those listed above.

7.3 Sample Preparation

7.3.1 Water Samples

A 1000ml aliquot of sample is pH adjusted and extracted with methylene chloride utilizing separatory funnel extraction. The extract is concentrated to 1.0ml.

7.3.2 Solid Samples

A 30-gram aliquot of sample is extracted with methylene chloride and acetone utilizing pulse sonication or microwave extraction. The extract is concentrated to 1.0ml.

7.4 Gas Chromatographic Analysis

Instrument calibration consists of two major sections:

Initial Calibration Procedures
Continuing Calibration Verification

7.4.1 Initial Calibration Procedures

Before samples can be run, the GC/MS system must be tuned, the injection port inertness must be verified, and the instrument must be calibrated.

7.4.1.1 Tune Verification (DFTPP)

The instrument should be hardware tuned per manufacturer's instructions. Verify the instrument tune by injecting 50ng of DFTPP solution onto the instrument. The resulting DFTPP spectra should meet the criteria in the following table.

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30-60 of mass 198
68	<2 % of mass 69
70	<2 % of mass 69
127	40-60 % of mass 198
197	<1 % of mass 198
198	Base peak, 100 % relative abundance
199	5-9 % of mass 198
275	10-30 % of mass 198
365	>1 % of mass 198
441	Present but less than mass 443
442	>40 % of mass 198
443	17-23 % of mass 442

Evaluate the tune spectrum using three mass scans from the chromatographic peak and a subtraction of instrument background. This procedure is performed automatically by the MS Chemstation software by running "autofind" on the DFTPP peak.

Select the scans at the peak apex and one to each side of the apex. Calculate an average of the mass abundances from the three scans.

Background subtraction is required. Select a single scan in the chromatogram that is absent of any interfering compound peak and no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or

instrument background ions. Do not subtract part of the tuning compound peak.

If the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are met.

Analysis must not begin until the tuning criteria are met. The injection time of the acceptable tune analysis is considered the start of the 12-hour clock. The same mass spec settings must be used for the calibration standards and samples that were used for the tune evaluation standard.

7.4.1.2 Injection Port Inertness Verification

DDT, pentachlorophenol, and benzidine must also be evaluated in the tune standard. These compounds are used to assess injection port inertness and column performance.

Pentachlorophenol and benzidine should be present at their normal responses and, no peak tailing should be visible. The tailing factor for both benzidine and pentachlorophenol must be less than 2.

DDT breakdown should not exceed 20%. Breakdown is calculated as follows:

$$\%DDT_{BREAKDOWN} = \frac{(DDE\ Area + DDD\ Area) \times 100}{(DDE\ Area + DDD\ Area + DDT\ Area)}$$

If degradation is excessive or peak tailing is noticed, injection port maintenance is required.

This performance test must be passed before any samples or standards are analyzed.

7.4.1.3 Internal Standard Calibration

A minimum 5-point calibration curve is created for the semivolatile organic compounds and surrogates using an internal standard technique. SGS Orlando routinely performs a 6-point calibration to maximize the calibration range.

Historically, many analytical methods have relied on linear models of the calibration relationship, where the instrument response is directly proportional to the amount of a target compound. The linear model has many advantages including simplicity and ease of use. However, given the advent of new detection techniques and because many methods cannot be optimized for all the analytes to which they may be applied, the analyst is increasingly likely to encounter situations where the linear model neither applies nor is appropriate. The option of using non-linear calibration may be necessary to address specific instrumental

techniques. However, it is not EPA's intent to allow non-linear calibration to compensate for detector saturation or avoid proper instrument maintenance.

NOTE: Because of this concern, select programs including SC DHEC do not support the use of non-linear regressions.

The low point may be omitted from the calibration table for any compound with an LLOQ set at the level two standard. Additionally, the high point may be omitted for any compound that exhibits poor linearity at the upper end of the calibration range.

An entire level may be omitted provided that a minimum of 5 points remain. There must be technical justification to omit an entire level. This should be documented in the run log.

Response factors (RF) for each analyte are determined as follows:

$$RF = (A_{analyte} \mathbf{X} C_{istd})/(A_{istd} \mathbf{X} C_{analyte})$$

$A_{analyte}$ = area of the analyte
A_{istd} = area of the internal standard
$C_{analyte}$ = concentration of the analyte
C_{istd} = concentration of the internal standard.

The mean RF and standard deviation of the RF are determined for each analyte. The percent relative standard deviation (%RSD) of the response factors is calculated for each analyte as follows:

%RSD = (Standard Deviation of RF X 100) / Mean RF

If the %RSD $\leq$ 20%, linearity through the origin can be assumed and the mean RF can be used to quantitate target analytes in the samples. **The %RSD should be ≤ 15% for any DoD QSM projects.**

Alternatively, a calibration curve of response vs. amount can be plotted. This method allows for the use of average response factors, linear regressions, and non-linear regressions. Linear regressions may be unweighted or weighted as $1/x$ or $1/x^2$. If the correlation coefficient is $\geq$0.995 ($r^2 \geq$0.990) then the curve can be used to quantitate target analytes in the samples. Regardless of which calibration model is chosen, the laboratory should visually inspect the curve plots to see how the individual calibration points compare to the plot.

NOTE: If a linear regression is used for an analyte, then the low standard must be recalculated against the current initial calibration. The recovery of any analyte using a linear regression must be 70-130% of the expected value. This requirement does not apply to non-linear regressions.

Alternatively, either of the two techniques described below may be used to determine whether the calibration function meets acceptable criteria. These involve refitting the calibration data back to the model. Both % Error and Relative Standard Error (RSE) evaluate the difference between the measured and the true amounts or concentrations used to create the model.

Calculation of the % Error

% ERR = (xi-x'i) / xi * 100

x'i = Measured amount of analyte at calibration level i, in mass or concentration units.

xi = True amount of analyte at calibration level i, in mass or concentration units.

Percent error between the calculated and expected amounts of an analyte should be ≤ 30% for all standards. For some data uses, ≤50% may be acceptable for the lowest calibration point.

Calculation of Relative Standard Error (%RSE)

$$RSE = 100 \times \sqrt{\sum_{i=1}^{n} \left[\frac{x_i' - x_i}{x_i}\right]^2 \Big/ (n-p)}$$

x'i = Measured amount of analyte at calibration level i, in mass or concentration units.

xi = True amount of analyte at calibration level i, in mass or concentration units.

p = Number of terms in the fitting equation.
(average = 1, linear = 2, quadratic = 3)

n = Number of calibration points.

The %RSE acceptance limit criterion is ≤20% for good performing compounds and ≤30% for poor performing (PP) compounds.

The method also employs minimum response factor (RF) criteria for select target analytes. See Table 2 for the analytes and associated minimum response factors. Unlike previous revisions that only set a

minimum for the average RF, 8270D requires that the minimum RF be met for each level of the calibration curve.

7.4.1.4 Initial Calibration Verification (ICV)

The validity of the initial calibration curve must be verified through the analysis of an initial calibration verification (ICV) standard. The ICV should be prepared from a second source at a mid-range concentration. Because of compound interactions, the ICV for this method is prepared as two separate standards that cover the entire list of compounds.

The %D for all analytes of interest should be ≤ 30%. If the %D > 30%, the analysis of samples may still proceed if the analyte failed high and the analyte is not expected to be present in the samples. However, if a reportable analyte is detected in a sample and the %D for that analyte was greater than 30% in the ICV, the sample will need to be reanalyzed on a system with a passing ICV for that analyte.

NOTE: For any DoD QSM project, the %D for all target compounds should be ≤ 20%. If samples must be analyzed with an analyte of interest having a %D > 20%, then the data must be qualified accordingly.

If the ICV does not meet this criteria, a second standard should be prepared. If the ICV still does not meet criteria, analyze an ICV prepared from a third source. If this ICV meets criteria, proceed with sample analysis. If the ICV still does not meet criteria, determine which two standards agree. Make fresh calibration standards and an ICV from the two sources that agree. Recalibrate the instrument.

7.4.2 Continuing Calibration Verification (CCV)

7.4.2.1 Inject 1ul of the tune evaluation mix at the beginning of each 12-hour shift. Evaluate the resultant peaks against the criteria in sections 7.4.1.1 and 7.4.1.2. The injection time of this standard starts the 12-hour window.

7.4.2.2. Analyze a continuing calibration check standard. The CCV should be at or below the mid-point of the calibration curve.

7.4.2.3. The response factor for any target analyte listed in Table 2 must meet the listed minimum value.

7.4.2.4. The %D for all analytes of interest should be ≤ 20%; however, the large number of analytes in this method presents a substantial probability that a few of the analytes will fall outside of this range.

If less than 10 percent of the analytes have a %D > 20% but ≤ 50%, then the analysis of samples may still proceed provided that the following criteria is met.

The CCV exceeds the upper limit (+20%) and the analyte is not expected to be present in the samples.

The CCV exceeds the lower limit (-20%) but not more than -50% and the analyte is not expected to be present in the samples. An additional check standard at the LLOQ must be analyzed and the analytes in question be detected and meet all of the qualitative identification criteria.

However, if a reportable analyte is detected in a sample and the %D for that analyte was greater than 20% in the CCV, the sample will need to be reanalyzed on a system with a passing CCV for that analyte, or the data must be qualified.

NOTE: For any DoD QSM project, the %D for all target compounds should be ≤ 20%. If samples must be reported with an analyte of interest having a %D > 20%, then the data must be qualified accordingly, regardless of whether the analyte was detected or not.

7.4.2.5. The criteria in 7.4.2.3 and 7.4.2.4 must be met for the continuing calibration to be considered valid. Only analytes that are being reported for a given sample must meet the criteria in 7.4.2.3 and 7.4.2.4.

If the first continuing calibration verification does not meet criteria, a second standard may be injected. If the second standard does not meet criteria, the system must be recalibrated. If the second standard meets criteria, then the system is considered in control and results may be reported.

Rationale for second standard such as instrument maintenance, clipped column, remade standard, etc. should be documented in the run log or maintenance log. Reanalysis of second standard without valid rationale may require the analysis of a third standard (in which case both the second and third standard would have to pass).

NOTE: For any DoD QSM project, if the second standard meets criteria, then a third standard must be analyzed. If the third standard also meets criteria, then the system is considered in control and results may be reported.

If the |%D| is greater than 20%, then documented corrective action is necessary. This may include recalibrating the instrument and reanalyzing the samples, performing instrument maintenance to correct the problem and reanalyzing the samples, or qualifying the data. Under certain circumstances, the data may be reported, i.e., the CCV failed high, the associated QC passed, and the samples were ND.

NOTE: For any DoD QSM project, if samples must be reported with a target analyte having a %D > 20%, then the data must be qualified accordingly, regardless of whether the analyte was detected or not.

NOTE: Any target analytes that are detected in the samples must be bracketed by an acceptable initial calibration curve and acceptable CCV standards; otherwise, the samples must be reanalyzed or the data must be qualified.

7.4.2.6. For DoD QSM 5.x compliance, an additional CCV must be analyzed at the end of each run. The closing CCV should be within the 12-hour tune window.

The %D for all target compounds in this CCV should be ≤ 50%. If the %D > %50 for any target compound, the samples may need to be reanalyzed. If samples must be reported with an analyte of interest having a %D >50%, then the data must be qualified accordingly, regardless of whether the analyte was detected or not.

NOTE: If samples are ND and an analyte in the CCV fails high, then the sample does not need to be reanalyzed.

7.4.2.7. If any of the internal standard response changes by more than a factor of two (-50% to +100%) or retention time changes by more than 30 seconds (10 seconds for DOD QSM 5.x compliance) from the midpoint standard of the last initial calibration or the daily CCV, the mass spectrometer must be inspected for malfunctions and corrections made, as appropriate. Corrective action may include re-calibration (initial calibration) of the instrument.

7.4.3 Sample Extract Analysis

7.4.3.1 Samples are analyzed in a set referred to as an analysis sequence or batch. A batch consists of the following:

Tune Evaluation Mix
Initial Calibration Standards (or CCV)
QC Extracts
Sample Extracts

7.4.3.2 Four microliters of internal standard solution is added to every 100ul of extract in the autosampler vial. Generally, 400ul of extract are transferred to the autosampler vial with a gas tight syringe.

7.4.3.3 One or two microliters (same amount as standards) of extract is injected into the GC by the autosampler. The data system then records the resultant peak responses and retention times.

7.4.3.4 Qualitative identification

The target compounds shall be identified by analysts with competent knowledge in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. The criteria required for a positive identification is:

The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

The sample component must elute at the same relative retention time (RRT) as the daily standard. The RRT of sample component must be within ± 0.06 RRT units of the standard.

All ions present in the standard mass spectra at a relative intensity greater than 10% (major abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

The relative intensities of these ions must agree within ± 30% between the daily standard and sample spectra, (e.g., for an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20 and 80%).

Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

If peak identification is prevented by the presence of interferences, further cleanup may be required or the extract must be diluted so that the interference does not mask any analytes.

7.4.3.5 Quantitative analysis

When a target compound has been identified, concentration will be based on the integrated area of the quantitation ion, which is normally the base peak.

The sample matrix may produce an interference with the primary ion. This may be characterized by an excessive background signal of the same ion, which distorts the peak shape beyond a definitive integration. The interference could also severely inhibit the response of the internal standard ion.

If the analyte response exceeds the linear range of the system, the extract must be diluted and reanalyzed. It is recommended that extracts be diluted so that the response falls into the middle of the calibration curve.

7.4.3.6 Library search for tentatively identified compounds

If a library search is requested, the analyst should perform a forward library search of the NIST mass spectral library to tentatively identify 10 to 20 non-target compounds.

Guidelines for making tentative identification are:

These compounds should have a response greater than 12.5% of the nearest internal standard. The response is obtained from the Total Ion Chromatogram.

The search is to include a spectral printout of the best library match for a particular substance. The results are to be interpreted by the analyst.

Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

The relative intensities the major ions should agree within ±20%.
Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

Ions present in the reference spectrum but not in the sample spectrum should be verified by performing further manual background subtraction to eliminate the interference created by co-eluting peaks and/or matrix interference.

Quantitation of the tentatively identified compounds is obtained from the total ion chromatogram based on a response factor of 1 from the nearest internal standard and is to be tabulated on the library search summary data sheet.

7.5 Maintenance and Trouble Shooting

7.5.1 Refer to SOP GC001 for routine instrument maintenance and trouble shooting.

7.5.2 All instrument maintenance must be documented in the appropriate “Instrument Repair and Maintenance” log. The log will include such items as problem, action taken, correction verification, date, and analyst.

7.5.3 Repairs performed by outside vendors must also be documented in the log. The analyst or Department Supervisor responsible for the instrument must complete the log if the repair technician does not.

7.5.4 PC and software changes must be documented in the "Instrument Repair and Maintenance" log. Software changes may require additional validation.

8.0 METHOD PERFORMANCE

Method performance is monitored through the routine analysis of negative and positive control samples. These control samples include method blanks (MB), blank spikes (BS), matrix spikes (MS), and matrix spike duplicates (MSD). The MB and BS are used to monitor overall method performance, while the MS and MSD are used to evaluate the method performance in a specific sample matrix.

Blank spike, matrix spike, and matrix spike duplicate samples are compared to statistically generated control limits. These control limits are reviewed and updated annually. Control limits are stored in the LIMS. Additionally, blank spike accuracy is regularly evaluated for statistical trends that may be indicative of systematic analytical errors.

9.0 QUALITY ASSURANCE / QUALITY CONTROL

Accuracy and matrix bias are monitored by the use of surrogates and by the analysis of a QC set that is prepared with each batch (maximum of 20 samples) of samples. The QC set consists of a method blank (MB), blank spike (BS), matrix spike (MS), and matrix spike duplicate (MSD).

9.1 Internal Standards

9.1.1 1,4-Dichlorobenzene-d_4, Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrysene-d_{12} and Perylene-d_{12} are used as internal standards for this method. The response of the internal standard in all subsequent runs should be within a factor of two (-50% to +100%) of the internal standard response in the opening CCV for each sequence. On days that an initial calibration is performed, the internal standard responses should be compared to the internal standard responses for the mid-point standard.

9.1.2 If the internal standard responses are not within limits, the following are required.

9.1.2.1 Check to be sure that there are no errors in calculations, integrations, or internal standards solutions. If errors are found, recalculate the data accordingly.

9.1.2.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample. If the recovery is high due to interfering peaks, it may be possible to get a more accurate recovery by analyzing the sample on a different column type.

9.1.2.3 If no problem is found, prepare a second aliquot of extract and reanalyze the sample.

9.1.2.4 If upon reanalysis, the responses are still not within limits, the problem is considered matrix interference. The extract may need to be diluted or the results qualified.

9.2 Surrogates

9.2.1 Nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14} are used as the base neutral surrogate standards, and phenol-d_5, 2-fluorophenol, and 2,4,6-tribromophenol are used as the acid surrogate standards to monitor the efficiency of the extraction.

A known amount of surrogate standard is added to each sample including the QC set prior to extraction. The percent recovery for each surrogate is calculated as follows:

% Recovery = (Sample Amount / Amount Spiked) X 100

The percent recovery must fall within the established control limits for all surrogates for the results to be acceptable.

9.2.2 If any surrogate recovery is not within the established control limits, the following are required. Note: If the samples are being analyzed for only base neutral compounds or only acid compounds, then only the relative surrogates need to be monitored.

9.2.2.1 Check to be sure that there are no errors in calculations, dilutions, integrations, surrogate solutions, or internal standard solutions. If errors are found, recalculate the data accordingly. If errors are suspected, re-vial and re-inject the extract to verify.

9.2.2.2 Check instrument performance. It may be necessary to re-vial and re-inject the extract in order to verify performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample.

9.2.2.3 If no problem is found, re-extract and reanalyze the sample. **NOTE:** If the recoveries are high and the sample is non-detect, then re-extraction may not be necessary. **For any DoD QSM projects, the resulting data must be qualified accordingly.** If there is insufficient sample for re-extraction, reanalyze the sample and footnote this on the report.

9.2.2.4 If upon reanalysis, the recovery is still not within control limits, the problem is considered matrix interference. Surrogates from both sets of analysis should be reported on the final report.

9.3 Method Blank

9.3.1 The method blank is either de-ionized water or a mixture of sodium sulfate and clean sand (depending upon sample matrix) to which the surrogate standard has been added. The method blank is then extracted and taken through all cleanup procedures along with the other samples to determine any contamination from reagents, glassware, or high-level samples. The method blank must be free of any analytes of interest or interferences at ½ the required LLOQ to be acceptable. If the method blank is not acceptable, corrective action must be taken to determine the source of the contamination. Samples associated with a contaminated method blank shall be evaluated as to the best corrective action for each particular sample. This may include reanalyzing the samples, re-extracting and reanalyzing the samples or qualifying the results with a "B" or "V" qualifier.

9.3.2 If the MB is contaminated but the samples are non-detect, then the source of contamination should be investigated and documented. The sample results can be reported. **For any DoD QSM projects the resulting data must be qualified accordingly.**

9.3.3 If the MB is contaminated but the samples results are > 10 times the contamination level, the source of the contamination should be investigated and documented. The samples results may be reported with the appropriate "B" or "V" qualifier. This must be approved by the department supervisor.

9.3.4 If the MB is contaminated but the samples results are < 10 times the contamination level, the source of the contamination should be investigated and documented. The samples should be re-extracted and reanalyzed for confirmation. If there is insufficient sample to re-extract, or if the sample is re-extracted beyond hold time, the appropriate footnote and qualifiers should be added to the results. This must be approved by the department supervisor.

9.4 Blank Spike

9.4.1 The blank spike is either de-ionized water or a mixture of sodium sulfate and clean sand (depending upon sample matrix) to which the surrogate standard and spike standard have been added. The blank spike is then extracted and taken through all cleanup procedures along with the other samples to monitor the efficiency of the extraction procedure. The percent recovery for each analyte is calculated as follows:

$$\% \text{ Recovery} = (\text{Blank Spike Amount} / \text{Amount Spiked}) \times 100$$

The percent recovery for each analyte of interest should fall within the established control limits for the results to be acceptable. The large number of analytes in this method presents a substantial probability that a few of the analytes will fall outside of the established control limits. This may not indicate that the system is out of control; therefore, corrective action may not be necessary.

Upper and lower marginal exceedance (ME) limits can be established to determine when corrective action is necessary. A marginal exceedance in the Blank Spike is defined as a recovery being outside of 3 standard deviations but within 4 standard deviations of the mean.

The number of allowable marginal exceedances is based on the number of analytes in the Blank Spike. Marginal Exceedances must be random. If the same analyte exceeds the BS control limits repeatedly, it is an indication of a systematic problem and corrective action must be taken.

Marginal exceedances are not permitted for analytes that are deemed to be "Compounds of Concern" for a specific project. "Compounds of Concern" are different from "Target Compounds". "Target Compounds" are all analytes that are being reported for a site where "Compounds of Concern" are those analytes expected to be present at the site.

The number of allowable marginal exceedances is as follows:

1) > 90 analytes in BS, 5 analytes allowed in ME range;

2) 71-90 analytes in BS, 4 analytes allowed in ME range;

3) 51-70 analytes in BS, 3 analytes allowed in ME range;

4) 31-50 analytes in BS, 2 analytes allowed in ME range;

5) 11-30 analytes in BS, 1 analyte allowed in ME range;

6) < 11 analytes in BS, no analytes allowed in ME range

NOTE: SC DHEC does not recognize the concept of Marginal Exceedances. Additionally, a secondary check against 70-130% limits should be performed for all analytes reported to SC DHEC.

9.4.2 If the blank spike recoveries are not within the established control limits, the following are required:

9.4.2.1 Check to be sure that there are no errors in calculations, dilutions, integrations, spike solutions, or internal standard solutions. If errors are found, recalculate the data accordingly. If errors are suspected, re-vial and re-inject the extract to verify.

9.4.2.2 Check instrument performance. It may be necessary to re-vial and re-inject the extract in order to verify performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample.

9.4.2.3 Check to see if the recoveries that are outside of control limits are analytes of concern. If the analytes are not being reported, additional corrective action is not necessary and the sample results can be reported without qualification.

9.4.2.4 If the recovery of an analyte in the BS is high and the associated sample is non-detect, the data may be reportable. **For any DoD QSM projects the resulting data must be qualified accordingly.**

9.4.2.5 If no problem is found, the department supervisor shall review the data and determine what further corrective action is best for each particular sample, which may include reanalyzing the samples, re-extracting and reanalyzing the samples, or qualifying the results as estimated.

9.4.2.6 If there is insufficient sample to re-extract, or if the sample is re-extracted beyond hold time, the appropriate footnote and qualifiers should be added to the results. This must be approved by the department supervisor.

9.4.2.7 Because of their problematic nature, benzidine, benzaldehyde, and benzoic acid are generally not evaluated in the blank spike unless they are of specific concern for a given project.

9.5 Matrix Spike and Matrix Spike Duplicate

9.5.1 Matrix spike and spike duplicates are replicate sample aliquots to which the surrogate standard and spike standard have been added. The matrix spike and spike duplicate are then extracted and taken through all cleanup procedures along with the other samples to monitor the precision and accuracy of the extraction procedure. The percent recovery for each analyte is calculated as follows:

% Recovery = ([Spike Amount – Sample Amount] / Amount Spiked) X 100

The percent recovery for each analyte of interest must fall within the established control limits for the results to be acceptable.

9.5.2 If the matrix spike recoveries are not within the established control limits, the following are required.

9.5.2.1 Check to be sure that there are no errors in calculations, dilutions, integrations, spike solutions, or internal standard solutions. If errors are found, recalculate the data accordingly. If errors are suspected, re-vial and re-inject the extract to verify.

9.5.2.2 Check instrument performance. It may be necessary to re-vial and re-inject the extract in order to verify performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample. If the recovery is high due to interfering peaks, it may be

possible to get a more accurate recovery by analyzing the sample on a different column type.

9.5.2.3 If no problem is found, compare the recoveries to those of the blank spike. If the blank spike recoveries indicate that the problem is sample related, document this on the run narrative. Matrix spike recovery failures are not grounds for re-extraction but are an indication of the sample matrix effects.

9.5.3 Precision

Matrix spike and spike duplicate recoveries for each analyte are used to calculate the relative percent difference (RPD) for each compound.

RPD = (| MS Result – MSD Result | / Average Result) X 100

The RPD for each analyte should fall within the established control limits. If more than 33% of the RPDs fall outside of the established control limits, the MS and MSD should be reanalyzed to ensure that there was no injection problem. If upon reanalysis the RPDs are still outside of the control limits, the department supervisor shall review the data and determine if any further action is necessary. RPD failures are generally not grounds for re-extraction.

10.0 CALCULATIONS

The concentration of each analyte in the original sample is calculated as follows:

Water (ug/l) = ($CONC_{inst}$) X (V_F / V_I) X DF

Soil (ug/kg) = ([$CONC_{inst}$] X [V_F / W_I] X DF) / %solids

$CONC_{inst}$	=	Instrument concentration calculated from the initial calibration using mean RF or curve fit.
DF	=	Dilution Factor
V_F	=	Volume of final extract (ul)
V_I	=	Volume of sample extracted (ml)
W_I	=	Weight of sample extracted (g)
%solids	=	Dry weight determination in decimal form

All soils are reported on a dry weight basis.

11.0 SAFETY AND POLLUTION PREVENTION

11.1 Safety

The analyst should follow normal safety procedures as outlined in the SGS Health and Safety Program, which includes the use of safety glasses, gloves, and lab coats.

The toxicity of each reagent and target analyte has not been precisely defined; however, each reagent and sample should be treated as a potential health hazard. Material Safety Data Sheets (MSDS) or Safety Data Sheets (SDS) are available for all reagents and many of the target analytes. Exposure must be reduced to the lowest possible level. Personal protective equipment should be used by all analysts.

11.2 Pollution Prevention

Waste solvents from the sample analysis and standards preparation are collected in waste storage bottles and are eventually transferred to the chlorinated waste drum.

Sample Extracts are archived and stored for 60 days after analysis. Old extracts and standards are disposed of in the waste vial drum.

12.0 REFERENCES

SW846 Method 8000D Revision 4, July 2014

SW846 Method 8270D Revision 5, July 2014

TABLE 1: Routine Target Analytes

	Benzyl Alcohol	1,4-Dioxane	5-Nitro-o-toluidine
Benzoic Acid	1,1'-Biphenyl	Diphenylamine	N-Nitrosodiethylamine
Caprolactam	4-Bromophenyl Phenyl Ether	Diphenyl Ether	N-Nitrosodimethylamine
4-Chloro-3-methyl Phenol	Butyl Benzyl Phthalate	1,2-Diphenylhydrazine	N-Nitrosodi-n-butylamine
2-Chlorophenol	Carbazole	Disulfoton	N-Nitrosodi-n-propylamine
4-Chlorophenol	4-Chloroaniline	bis(2-Ethylhexyl)phthalate	N-Nitrosodiphenylamine
2,4-Dichlorophenol	Chlorobenzilate	Ethyl Methanesulfonate	N-Nitrosomethylethylamine
2,6-Dichlorophenol	bis(2-Chloroethoxy)methane	Famphur	N-Nitrosomorpholine
2,4-Dimethylphenol	bis(2-Chloroethyl)ether	Fluoranthene	N-Nitrosopiperidine
2,4-Dinitrophenol	bis(2-Chloroisopropyl)ether	Fluorene	N-Nitrosopyrrolidine
4,6-Dinitro-o-cresol	1-Chloronaphthalene	Hexachlorobenzene	4-Nitroquinoline 1-Oxide
Dinoseb	2-Chloronaphthalene	Hexachlorobutadiene	n-Octadecane
2-Methylphenol	4-Chlorophenyl Phenyl Ether	Hexachlorocyclopentadiene	Octamethylcyclotetrasiloxane
3&4-Methylphenol	Chrysene	Hexachloroethane	O,O,O-Triethyl Phosphorothioate
2-Nitrophenol	n-Decane	**Hexachlorophene**	Parathion
4-Nitrophenol	Decamethylcyclopentasiloxane	Hexachloropropene	Pentachlorobenzene
Pentachlorophenol	Diallate		Pentachloroethane
Phenol	Dibenz(a,h)acridine	Indeno(1,2,3-cd)pyrene	Pentachloronitrobenzene
2,3,4,6-Tetrachlorophenol	Dibenz(a,j)acridine	Isodrin	
2,4,5-Trichlorophenol	Dibenzo(a,h)anthracene	Isophorone	Phenacetin
2,4,6-Trichlorophenol	Dibenzofuran	Isosafrole	Phenanthrene
Acenaphthene	1,2-Dichlorobenzene	**Kepone**	**p-Phenylenediamine**
Acenaphthylene	1,3-Dichlorobenzene	Methapyrilene	Phorate
Acetophenone	1,4-Dichlorobenzene	3-Methylcholanthrene	2-Picoline
2-Acetylaminofluorene	3,3'-Dichlorobenzidine		Pronamide
4-Aminobiphenyl	Diethyl Phthalate	4,4'-Methylenebis(2-chloroaniline)	
	Dimethoate	Methyl Methanesulfonate	Pyrene
Aniline	p-(Dimethylamine)azobenzene	1-Methylnaphthalene	Pyridine
Anthracene	7,12-Dimethylbenz(a)anthracene	2-Methylnaphthalene	
Aramite	3,3'-Dimethylbenzidine	Methyl Parathion	Safrole
Atrazine	Dimethylnaphthalenes (total)	Naphthalene	Simazine
Azobenzene	**A,A-Dimethylphenethylamine**	1,4-Naphthoquinone	alpha-Terpineol
Benzaldehyde	Dimethyl Phthalate	1-Naphthylamine	1,2,4,5-Tetrachlorobenzene
Benzidine	Di-n-butyl Phthalate	2-Naphthylamine	Tetraethyl dithiopyrophosphate
Benzo(a)anthracene	Di-n-octyl Phthalate		Thionazin
Benzo(a)pyrene	m-Dinitrobenzene	2-Nitroaniline	Toluene-2,4-diamine
Benzo(b)fluoranthene	p-Dinitrobenzene	3-Nitroaniline	o-Toluidine
Benzo(g,h,i)perylene	2,4-Dinitrotoluene	4-Nitroaniline	1,2,4-Trichlorobenzene
Benzo(k)fluoranthene	2,6-Dinitrotoluene	Nitrobenzene	sym-Trinitrobenzene

Bolded analytes are considered "Poor Performing"

TABLE 2: Minimum Response Factors

Analyte	Min. RF
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl)ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitroso-di-n-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxy)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
4-Chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenol	0.010
2-Chloronaphthalene	0.800
2-Nitroaniline	0.010
Dimethyl phthalate	0.010
2,6-Dinitrotoluene	0.200
Acenaphthalene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010

Analyte	Min. RF
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
Diethyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3'-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,I)perylene	0.500
2,3,4,6-Trichlorophenol	0.010

Note: 2,4-Dinitrophenol and 4-Nitrophenol will also need to have an average RF greater than 0.050 for any DOD QSM projects.

TABLE 3: Characteristic Ions

Analyte	Quant. Ion	Q1	Q2
Benzoic Acid	105	122	77
2-Chlorophenol	128	64	130
4-Chloro-3-methyl phenol	107	144	142
2,4-Dichlorophenol	162	164	98
2,4-Dimethylphenol	107	121	122
2,4-Dinitrophenol	184	63	154
2,6-Dichlorophenol	162	164	98
4,6-Dinitro-o-cresol	198	51	105
2-Methylphenol	108	107	77
3&4-Methylphenol	108	107	79
2-Nitrophenol	139	65	109
4-Nitrophenol	109	39	65,139
Pentachlorophenol	266	264	268
Phenol	94	65	66
2,3,4,6-Tetrachlorophenol	232	230	131
2,4,5-Trichlorophenol	196	198	200
2,4,6-Trichlorophenol	196	198	200
Acenaphthene	153	152	154
Acenaphthylene	152	151	153
Acetophenone	105	120	106
Aniline	93	66	65
Anthracene	178	179	176
Atrazine	200	58	215
Benzaldehyde	106	77	105
Benzidine	184	92	185
Benzo(a)anthracene	228	226	229
Benzo(a)pyrene	252	253	125
Benzo(b)fluoranthene	252	253	125
Benzo(g,h,i)perylene	276	138	277
Benzo(k)fluoranthene	252	253	125
4-Bromophenyl phenyl ether	248	250	141
Butyl benzyl phthalate	149	91	206
Benzyl Alcohol	108	79	77
1,1'-Biphenyl	154	153	152
2-Chloronaphthalene	162	164	127
4-Chloroaniline	127	129	65
Caprolactam	113	55	85
Carbazole	167	166	139
Chrysene	228	226	229

Analyte	Quant. Ion	Q1	Q2
bis(2-Chloroethoxy)methane	93	95	123
bis(2-Chloroethyl)ether	93	63	95
bis(2-Chloroisopropyl)ether	45	77	121
4-Chlorophenyl phenyl ether	204	206	141
1,2-Dichlorobenzene	146	148	111
1,2-Diphenylhydrazine	77	105	182
1,3-Dichlorobenzene	146	148	111
1,4-Dichlorobenzene	146	148	111
2,4-Dinitrotoluene	165	89	63
2,6-Dinitrotoluene	165	89	63
3,3'-Dichlorobenzidine	252	254	126
Dibenzo(a,h)anthracene	278	139	279
Dibenzofuran	168	139	169
m-Dinitrobenzene	168	50	76
Di-n-butyl phthalate	149	150	104
Di-n-octyl phthalate	149	150	43
Diethyl phthalate	149	177	150
Dimethyl phthalate	163	194	164
1,4-Dioxane	88	58	43
bis(2-Ethylhexyl)phthalate	149	167	279
Fluoranthene	202	101	203
Fluorene	166	165	167
Hexachlorobenzene	284	142	249
Hexachlorobutadiene	225	223	227
Hexachlorocyclopentadiene	237	235	272
Hexachloroethane	117	201	119
Indeno(1,2,3-cd)pyrene	276	138	277
Isophorone	82	138	95
1-Methylnaphthalene	142	141	115
2-Methylnaphthalene	142	141	115
2-Nitroaniline	65	92	138
3-Nitroaniline	138	108	92
4-Nitroaniline	138	92	108
Naphthalene	128	129	127
Nitrobenzene	77	123	65
N-Nitrosodimethylamine	42	74	43
N-Nitroso-di-n-propylamine	70	42	130
N-Nitrosodiphenylamine	169	168	167
Phenanthrene	178	179	176

TABLE 3: Characteristic Ions (continued)

Analyte	Quant. Ion	Q1	Q2
Pyrene	202	101	203
Pyridine	79	52	
1,2,4,5-Tetrachlorobenzene	216	214	218
1,2,4-Trichlorobenzene	180	182	145
Simazine	201	186	173
alpha-Terpineol	59	93	121
2-Acetylaminofluorene	181	223	152
4-Aminobiphenyl	169	168	141
Aramite	185	63	135
1-Chloronaphthalene	162	164	127
Chlorobenzilate	137	251	111
7,12-Dimethylbenz(a)anthracene	256	241	120
Diallate	43	86	234
Dibenz(a,j)acridine	279	139	125
Diphenyl ether	170	141	77
p-(Dimethylamine)azobenzene	120	225	77
3,3'-Dimethylbenzidine	212	213	106
Ethyl methanesulfonate	79	109	97
A,A-Dimethylphenethylamine	58	91	134
Hexachlorophene	196	198	209
Hexachloropropene	213	211	215
Isodrin	193	195	66
Isosafrole	162	131	104
Kepone	272	274	237
3-Methylcholanthrene	268	252	126
Methyl methanesulfonate	80	79	65
Methapyrilene	58	97	72
1,4-Naphthoquinone	158	102	76
1-Naphthylamine	143	115	116
2-Naphthylamine	143	115	116
5-Nitro-o-toluidine	152	77	106
4-Nitroquinoline 1-Oxide	190	160	89
N-Nitrosodi-n-butylamine	84	57	41
N-Nitrosodiethylamine	102	42	44
N-Nitrosomethylethylamine	42	88	43
N-Nitrosomorpholine	56	86	116
N-Nitrosopiperidine	42	114	55
N-Nitrosopyrrolidine	100	41	42
p-Phenylenediamine	108	80	107

Analyte	Quant. Ion	Q1	Q2
2-Picoline	93	66	92
Pentachlorobenzene	250	248	252
Pentachloroethane	167	119	117
Pentachloronitrobenzene	237	214	142
Phenacetin	108	109	179
Pronamide	173	175	145
Safrole	162	131	104
o-Toluidine	106	107	77
sym-Trinitrobenzene	75	74	213
Benzenethiol	110	66	109
Dibenz(a,h)acridine	279	139	280
Indene	116	115	63
6-Methyl Chrysene	242	241	239
Quinoline	129	102	128
Dimethoate	87	83	125
Disulfoton	88	97	142
Famphur	218	125	93
Methyl parathion	109	125	263
O,O,O-Triethyl phosphorothioate	198	121	97
Parathion	97	109	291
Phorate	75	121	97
Sulfotep	97	202	322
Thionazin	97	107	143
Resorcinol	110	81	53
Nicotine	84	133	42
2,4-Diaminotoluene	121	122	94
MOCA	231	266	140
1,4-Dichlorobenzene-d4	152	115	150
Naphthalene-d8	136	68	
Acenaphthene-d10	164	162	160
Phenanthrene-d10	188	94	80
Chrysene-d12	240	120	236
Perylene-d12	264	260	265
2-Fluorophenol	112	64	
Phenol-d5	99	42	71
Nitrobenzene-d5	82	128	54
2-Fluorobiphenyl	172	171	
2,4,6-Tribromophenol	330	332	141
Terphenyl-d14	244	122	212

Some analytes listed may not be applicable to this method due to certification requirements.

ANALYSIS OF SEMIVOLATILE ORGANICS BY GC/MS SELECT ION MONITORING (SIM)

Prepared by: Norm Farmer Date: 08/17/19

Approved by: Mike Eger Date: 08/19/19

Annual Review

Reviewed by: _____ Date: _____

Reviewed by: _____ Date: _____

Reviewed by: _____ Date: _____

Document Control

Issued to: QA Department Date: 08/21/19

Issued to: SVOC Department Date: * 08/21/19

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Effective 7 days after "*" date

CONTROLLED COPY
DO NOT DUPLICATE

TITLE: ANALYSIS OF SEMIVOLATILE ORGANICS BY GC/MS SELECT ION MONITORING (SIM)

REFERENCES: SW846 8270D and 8270E

REVISED SECTIONS: 1.1.7, 1.2.3, 7.1.4, 7.4.1.3, 7.4.2.4, 7.4.2.7 and 12.0

1.0 SCOPE AND APPLICATION, SUMMARY

1.1 Scope and Application

1.1.1 This method is used to determine the concentrations of various semivolatile organic compounds in water and solid matrices utilizing a gas chromatograph equipped with a mass spectrometer detector. Routine compounds can be found in Table 1.

1.1.2 Unlike convention full scan 8270; this method utilizes the instrument's select ion monitoring (SIM) capabilities. By monitoring for a few specific ions the sensitivity can be increased 10 to 20 fold.

1.1.3 The Lower Limit of Quantitation (LLOQ) or Reporting limits (RL) are based on the extraction procedure and the lowest calibration standard. LLOQs may vary depending on matrix complications and sample volumes. LLOQs for this method are in the range of 0.2 to 1.0 ug/l for aqueous samples and 10 to 50 ug/kg for solid samples. Solid matrices are reported on a dry weight basis.

1.1.4 The Method Detection Limit (MDL) for each analyte is evaluated on an annual basis for each matrix and instrument. MDLs are pooled for each matrix, and the final pooled MDLs are verified. The verified MDLs are stored in the LIMS and should be at least 2 to 3 times lower than the LLOQ. Exceptions may be made on a case by case basis; however, at no point shall the MDL be higher than the reported LLOQ.

1.1.5 The LLOQ for each analyte is evaluated on an annual basis for each matrix and instrument. The LLOQ verifications are prepared by spiking a clean matrix at 0.5 to 2 times the current LLOQ level. This LLOQ verification is carried through the same preparation and analytical procedures as the samples. Recovery of the analytes should be within the established limits. The DOD QSM requirements for Limit of Detection (LOD) and Limit of Quantitation (LOQ) verifications are different. See SOP QA020 for complete requirements for MDL, LOD, LOQ, and LLOQ.

1.1.6 Compounds detected at concentrations between the LLOQ and MDL are quantitated and qualified as estimated values and reported with either a "J" or "I" qualifier. Some program or project specifications may require that no values below the LLOQ be reported.

1.1.7 For DOD projects refer to QSM 5.1 Table B-22 and QSM 5.3 B-22 for additional method requirements and data qualifying guidance. QSM 5.0 did not have requirements specific to SIM analysis.

1.2 Summary

1.2.1 This method is adapted from SW846 method 8270D.

1.2.2 Samples are received, stored and extracted within the appropriate holding times.

1.2.3 Sample preparation is performed in accordance with SGS Orlando SOP OP006, OP007, OP059 and OP060.

1.2.4 The extracts are analyzed on a gas chromatograph equipped with mass spectrometer detector.

1.2.5 The peaks detected are identified by comparison to characteristic ions and retention times specific to the known target list of compounds.

1.2.6 Library searches cannot be performed on data acquired in SIM mode because data was only acquired for selected ions.

1.2.7 Manual integrations are performed in accordance with SOP QA029.

2.0 PRESERVATION AND HOLDING TIME

2.1 Preservation

2.1.1 Samples shall be collected in amber glass bottles with Teflon lined caps. One-liter bottles are recommended for aqueous samples and 4oz jars are recommended for solid samples.

2.1.2 The samples must be protected from light and refrigerated at ≤ 6°C from the time of collection until extraction. The extracts must be refrigerated at –10°C to –20°C until analysis.

2.2 Holding Time

2.2.1 Aqueous samples must be extracted within 7 days of collection.

2.2.2 Solid and waste samples must be extracted within 14 days of collection.

2.2.3 Extracts must be analyzed within 40 days of extraction.

3.0 INTERFERENCES

3.1 Data from all blanks, samples, and spikes must be evaluated for interferences.

3.2 Method interferences may be caused by contaminants in solvents, reagents, or glassware. Interferences from phthalate esters can be eliminated by using plastic-free solvent containers and solvent rinsed glassware.

3.3 Other organic compounds, including chlorinated hydrocarbons, petroleum hydrocarbons, and phthalate esters may be co-extracted by this method.

3.4 SIM may provide a lesser degree of confidence in compound identification unless multiple ions are monitored for each compound. In general, SGS Orlando monitors 3 ions per target compound.

4.0 DEFINITIONS

4.1 Batch: A group of samples which are similar with respect to matrix and the testing procedures being employed and which are processed as a unit. A sample batch is limited to a maximum of 20 samples.

4.2 Blank Spike (BS): An analyte-free matrix spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. Blank Spike Recoveries are used to document laboratory performance for a given method. This may also be called a Laboratory Control Sample (LCS).

4.3 Continuing Calibration Verification (CCV): A check standard used to verify instrument calibration throughout an analytical run. For all MS methods, a CCV must be analyzed at the beginning of each analytical run. For DoD QSM 5.x Projects an additional CCV must be analyzed at the end of the run.

4.4 Holding Time: The maximum times that samples may be held prior to preparation and/or analysis and still be considered valid.

4.5 Internal Standards: An organic compound which is similar to the target analyte(s) in chemical composition and behavior, but which is not normally found in environmental samples. Internal standards for Mass Spec methods are often deuterated forms of target analytes. Internal standards are used to compensate for retention time and response shifts during an analytical run.

4.6 Initial Calibration (ICAL): A series of standards used to establish the working range of a particular instrument and detector. The low point should be at a level equal to or below the LLOQ.

4.7 Initial Calibration Verification (ICV): A standard from a source different than that used for the initial calibration. A different vendor should be used whenever possible. The ICV is used to verify the validity of an Initial Calibration. This may also be called a QC check standard.

4.8 Matrix Spike (MS): A sample aliquot spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. The matrix spike recoveries are used to document the bias of a method in a given sample matrix.

4.9 Matrix Spike Duplicate (MSD): A replicate sample aliquot spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. The matrix spike duplicate recoveries are used to document the precision and bias of a method in a given sample matrix.

4.10 Method Blank (MB): An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is processed simultaneously with the samples through all the steps of the analytical procedure. The method blank is used to document contamination resulting from the analytical process.

4.11 Sample Duplicate (DUP): A replicate sample which is used to document the precision of a method in a given sample matrix.

4.12 Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical integrity of the sample.

4.13 Surrogate: An organic compound which is similar to the target analyte(s) in chemical composition and behavior, but which is not normally found in environmental samples. Surrogates are used to measure the extraction efficiency.

5.0 REAGENTS

5.1 Methylene Chloride – pesticide grade or equivalent

5.2 Semivolatile stock standards – Various mixes, traceable to Certificate of Analysis

5.3 Decafluorotriphenylphosphine mix (DFTPP) – Also contains pentachlorophenol, benzidine and DDT.

5.4 Base/neutral surrogate standards – dependent on the analytes being analyzed

Nitrobenzene-d5
2-Fluorobiphenyl
P-Terphenyl-d14
OR
2-Methylnaphthalene-d10
Fluoranthene-d10

5.5 Acid surrogate standards – dependent on the analytes being analyzed

Phenol-d6
2-Fluorophenol
2,4,6-Tribromophenol

5.6 Internal standards – dependent on the analytes being analyzed

1,4-Dichlorobenzene-d4	Naphthalene-d8
Acenaphthene-d10	Phenanthrene-d10
Chrysene-d12	Perylene-d12

6.0 APPARATUS

6.1 Gas Chromatograph – Agilent Technologies 6890 or 7890 with 7683 Autosampler

6.1.1 Gas Chromatograph

The analytical system that is complete with a temperature programmable gas chromatograph and all required accessories, analytical columns, and gases.

6.1.2 The injection port is designed for split-splitless or on-column injection with capillary columns.

6.1.3 Autosampler allows for unattended sample and standard injection throughout the analytical run.

6.2 Mass Spectrometer – Agilent Technologies 5973 and 5975

The mass spectrometer must be capable of scanning from 35-500 amu every second or less utilizing a 70-volt (nominal) electron energy in the electron impact ionization mode. It must also be capable of producing a mass spectrum that meets all the criteria in section 7.4.1.1 when injecting 50 ng of Decafluorotriphenylphosphine (DFTPP).

For this method it also must be capable of operating in Select Ion Mode (SIM). The selected ions are nominal ions but may have small mass defect, usually less than 0.2 amu, in their spectra. The acquisition table should be set to include these mass defects. The dwell time may be automatically calculated by the laboratory's GC/MS software. The total scan time should be less than 1,000 msec and produce at least 5 to 10 scans per chromatographic peak.

The mass spectrometer must be capable of analyzing multiple groups for up to 30 specific ions. Use the primary ion for quantitation and the secondary ions for confirmation. The start and end of each group should be time programmable and can be determined from the full scan analysis. Each group of specific ions is referred to as a descriptor.

6.3 Data System – Agilent Technologies MS Chemstation rev. DA 02.0x, DA 03.0x or EA 02.0x.

6.3.1 A computer system interfaced to the mass spectrometer that allows for the continuous acquisition and storage of all mass spectral data obtained throughout the duration of the chromatographic program.

6.3.2 The computer utilizes software that allows searching any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP).

6.3.3 The software should allow for integrating the abundances in any EICP between specific time or scan number limits. See Table 3.

6.3.4 Data is archived to a backup server for long term storage.

6.4 Column – TG-5MS or equivalent: 30m X 0.25mm X 0.25um
– ZB-Semivoaltiles or equivalent: 30m X 0.25mm X 0.25um

6.5 Gas-tight syringes and class "A" volumetric glassware for dilutions of standards and extracts.

7.0 PROCEDURE

7.1 Standards Preparation

Standards are prepared from commercially available certified reference standards. All standards must be logged in the Semivolatile Standards Logbook. All standards shall be traceable to their original source. The standards should be stored at temperatures between –10 °C and –20 °C, or as recommended by the manufacturer. Calibration levels, spike and surrogate concentrations, preparation information, and vendor part numbers can be found in the MS STD Summary in the Active SOP directory.

7.1.1 Stock Standard Solutions

Stock standards are available from several commercial vendors. All vendors must supply a "Certificate of Analysis" with the standard. The certificate will be retained by the lab. Hold time for unopened stock standards is until the vendor's expiration date. Once opened, the hold time is reduced to one year or the vendor's expiration date (whichever is shorter).

7.1.2 Intermediate Standard Solutions

Intermediate standards are prepared by quantitative dilution of the stock standard with methylene chloride. The hold time for intermediate standards is six months or the vendor's expiration date (whichever is shorter). Intermediate standards may need to be remade if comparison to other standards indicates analyte degradation or concentration changes.

7.1.3 Calibration Standards

Calibration standards for the semivolatile organics are prepared at a minimum of five concentration levels through quantitative dilutions of the intermediate standard. The low standard is at a concentration at or below the LLOQ and the remaining standards define the working range of the detector. See Table 4

Calibration standard concentrations are verified by the analysis of an initial calibration verification (ICV) standard.

7.1.4 Low Level Spike and Surrogates

Spikes and Surrogates for this method should be injected into the samples at levels appropriate to the analysis. 2-Methylnaphthalene-d10 and Flouranthene-d10 must be used for the low-level SIM surrogates when preparing split batches for SIM and Full Scan or when preparing samples for PAH analysis. Nitrobenzene-d5, 2-Fluorobiphenyl, and P-Terphenyl-d14 should be used for the Full Scan batches. Nitrobenzene-d5, 2-Fluorobiphenyl, and P-Terphenyl-d14 may be used for the SIM batches if spiked at lower concentrations. An additional set of low-level Spikes must be prepared with the SIM batch.

7.2 Gas Chromatograph Conditions and Mass Spectrometer Descriptors

1 or 2ul autosampler injection Pulsed splitless or splitless

Carrier gas – UHP Helium (10psi hold for 2min. to 32psi @2 psi/min to 38 psi @ 3ml/min ramp pressure)
Injection port temperature – 280 °C Transfer line temperature – 280 °C

Oven program – 45 °C for 1.0 minutes
27.5 °C/min to 265 °C for 0 minutes
5 °C/min to 295 °C for 0 minutes
20 °C/min to 320 °C for 0 minutes

OR

Oven program – 40 °C for 1.5 minutes
30 °C/min to 190 °C for 0 minutes
10 °C/min to 260 °C for 0 minutes
25 °C/min to 320 °C for 2.0 minutes

Source temperature – 230 °C Quad temperature – 150 °C

GC conditions are optimized for each instrument. Actual conditions may vary slightly from those listed above.

MS Descriptors – Monitor 3 characteristic ions for each target analyte, and 2 characteristic ions for each surrogate and internal standard. Each descriptor may have up to 30 ions; however, the more ions in a descriptor, the less the sensitivity. Therefore, it is beneficial to use multiple descriptors for longer analytes lists.

GC conditions and mass spectrometer descriptors are dependent on the analytes being analyzed. Refer to the specific instrument methods for actual conditions and descriptors.

7.3 Sample Preparation

7.3.1 Water Samples

A 1000ml aliquot of sample is pH adjusted and extracted with methylene chloride utilizing separatory funnel extraction. The extract is concentrated to 1.0ml.

7.3.2 Solid Samples

A 15 or 30-gram aliquot of sample is extracted with methylene chloride and acetone utilizing pulse sonication or microwave extraction. The extract is concentrated to 1.0ml.

7.4 Gas Chromatographic Analysis

Instrument calibration consists of two major sections:

Initial Calibration Procedures
Continuing Calibration Verification

7.4.1 Initial Calibration Procedures

Before samples can be run, the GC/MS system must be tuned, the injection port inertness must be verified, and the instrument must be calibrated.

7.4.1.1 Tune Verification (DFTPP)

The instrument should be hardware tuned per manufacturer's instructions. Verify the instrument tune by injecting 50ng of DFTPP solution onto the instrument. The resulting DFTPP spectra should meet the criteria in the following table.

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30-60 of mass 198
68	<2 % of mass 69
70	<2 % of mass 69
127	40-60 % of mass 198
197	<1 % of mass 198
198	Base peak, 100 % relative abundance
199	5-9 % of mass 198
275	10-30 % of mass 198
365	>1 % of mass 198
441	Present but less than mass 443
442	>40 % of mass 198
443	17-23 % of mass 442

Evaluate the tune spectrum using three mass scans from the chromatographic peak and a subtraction of instrument background. This procedure is performed automatically by the MS Chemstation software by running “autofind” on the DFTPP peak.

Select the scans at the peak apex and one to each side of the apex. Calculate an average of the mass abundances from the three scans. Background subtraction is required. Select a single scan in the chromatogram that is absent of any interfering compound peak and no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the tuning compound peak.

If the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are met.

Analysis must not begin until the tuning criteria are met. The injection time of the acceptable tune analysis is considered the start of the 12-hour clock. The same mass spec settings must be used for the calibration standards and samples that were used for the tune evaluation standard. The exception being that the tune evaluation standard must be acquired in full scan mode and all others in SIM mode.

7.4.1.2 Injection Port Inertness Verification

This requirement is optional if samples are being analyzed for PAHs (including carbazole and dibenzofuran) only. It must be evaluated if any other analytes are being reported.

NOTE: DOD QSM requires that the injection port inertness be verified every 12 hours even for PAHs.

DDT, pentachlorophenol, and benzidine must also be evaluated in the tune standard. These compounds are used to assess injection port inertness and column performance.

Pentachlorophenol and benzidine should be present at their normal responses and, no peak tailing should be visible. The tailing factor for Benzidine must be less than 2 and the tailing factor for pentachlorophenol must be less than 2.

DDT breakdown should not exceed 20%. Breakdown is calculated as follows:

$$\%DDT_{BREAKDOWN} = \frac{(\text{DDE Area} + \text{DDD Area}) \times 100}{(\text{DDE Area} + \text{DDD Area} + \text{DDT Area})}$$

If degradation is excessive or peak tailing is noticed, injection port maintenance is required.

This performance test must be passed before any samples or standards are analyzed.

7.4.1.3 Internal Standard Calibration

A minimum 5-point calibration curve is created for the semivolatile organic compounds and surrogates using an internal standard technique. SGS Orlando routinely performs a 6-point calibration to maximize the calibration range.

Historically, many analytical methods have relied on linear models of the calibration relationship, where the instrument response is directly proportional to the amount of a target compound. The linear model has many advantages including simplicity and ease of use. However, given the advent of new detection techniques and because many methods cannot be optimized for all the analytes to which they may be applied, the analyst is increasingly likely to encounter situations where the linear model neither applies nor is appropriate. The option of using non-linear calibration may be necessary to address specific instrumental techniques. However, it is not EPA's intent to allow non-linear calibration to compensate for detector saturation or avoid proper instrument maintenance.

NOTE: Because of this concern, select programs including SC DHEC do not support the use of non-linear regressions.

The low point may be omitted from the calibration table for any compound with an LLOQ set at the level two standard. Additionally, the high point may be omitted for any compound that exhibits poor linearity at the upper end of the calibration range.

An entire level may be omitted provided that a minimum of 5 points remain. There must be technical justification to omit an entire level. This should be documented in the run log.

Response factors (RF) for each analyte are determined as follows:

$$RF = (A_{analyte} \mathbf{X} C_{istd})/(A_{istd} \mathbf{X} C_{analyte})$$

$A_{analyte}$ = area of the analyte
A_{istd} = area of the internal standard
$C_{analyte}$ = concentration of the analyte
C_{istd} = concentration of the internal standard.

The mean RF and standard deviation of the RF are determined for each analyte. The percent relative standard deviation (%RSD) of the response factors is calculated for each analyte as follows:

%RSD = (Standard Deviation of RF X 100) / Mean RF

If the %RSD $\leq$ 20%, linearity through the origin can be assumed and the mean RF can be used to quantitate target analytes in the samples.

NOTE: DOD QSM allows %RSD $\leq$ 40% for Pentachlorophenol (PCP). It the %RSD > 20% for PCP it may be best to use a curve fit.

Alternatively, a calibration curve of response vs. amount can be plotted. This method allows for the use of average response factors, linear regressions, and non-linear regressions. Linear regressions may be unweighted or weighted as $1/x$ or $1/x^2$. If the correlation coefficient (r) is $\geq$0.995 (r^2 $\geq$0.990) then the curve can be used to quantitate target analytes in the samples. Regardless of which calibration model is chosen, the laboratory should visually inspect the curve plots to see how the individual calibration points compare to the plot.

NOTE: If a linear regression is used for an analyte, then the low standard must be recalculated against the current initial calibration. The recovery of any analyte using a linear regression must be 70-130% of the expected value. This requirement does not apply to non-linear regressions.

Alternatively, either of the two techniques described below may be used to determine whether the calibration function meets acceptable criteria. These involve refitting the calibration data back to the model. Both % Error and Relative Standard Error (RSE) evaluate the difference between the measured and the true amounts or concentrations used to create the model.

Calculation of the % Error

% ERR = (xi-x'i) / xi * 100

x'i = Measured amount of analyte at calibration level i, in mass or concentration units.

xi = True amount of analyte at calibration level i, in mass or concentration units.

Percent error between the calculated and expected amounts of an analyte should be ≤ 30% for all standards. For some data uses, ≤50% may be acceptable for the lowest calibration point.

Calculation of Relative Standard Error (%RSE)

$$RSE = 100 \times \sqrt{\sum_{i=1}^{n} \left[\frac{x_i' - x_i}{x_i}\right]^2 \Big/ (n-p)}$$

x'i = Measured amount of analyte at calibration level i, in mass or concentration units.

xi = True amount of analyte at calibration level i, in mass or concentration units.

p = Number of terms in the fitting equation. (average = 1, linear = 2, quadratic = 3)

n = Number of calibration points.

The %RSE acceptance limit criterion is ≤15% for good performing compounds and ≤30% for poor performing (PP) compounds.

The method also employs minimum response factor (RF) criteria for select target analytes. See Table 2 for the analytes and associated minimum response factors. Unlike previous revisions that only set a minimum for the average RF, 8270D and 8270E requires that the minimum RF be met for each level of the calibration curve.

7.4.1.4 Initial Calibration Verification (ICV)

The validity of the initial calibration curve must be verified through the analysis of an initial calibration verification (ICV) standard. The ICV should be prepared from a second source at a mid-range concentration.

The %D for all analytes of interest should be ≤ 30%. If the %D > 30%, the analysis of samples may still proceed if the analyte failed high and the analyte is not expected to be present in the samples. However, if a reportable analyte is detected in a sample and the %D for that analyte was greater than 30% in the ICV, the sample will need to be reanalyzed on a system with a passing ICV for that analyte.

NOTE: For any DoD QSM project, the %D for all target compounds except PCP should be ≤ 20% (PCP ≤ 50%). If samples must be analyzed with an analyte of interest having a %D > 20%, then the data must be qualified accordingly.

If the ICV does not meet this criteria, a second standard should be prepared. If the ICV still does not meet criteria, analyze an ICV prepared from a third source. If this ICV meets criteria, proceed with sample analysis. If the ICV still does not meet criteria, determine which two standards agree. Make fresh calibration standards and an ICV from the two sources that agree. Recalibrate the instrument.

7.4.2 Continuing Calibration Verification (CCV)

7.4.2.1 Inject 1ul of the tune evaluation mix at the beginning of each 12-hour shift. Evaluate the resultant peaks against the criteria in sections 7.4.1.1 and 7.4.1.2. The injection time of this standard starts the 12-hour window.

7.4.2.2. Analyze a continuing calibration check standard. The CCV should be at or below the mid-point of the calibration curve.

7.4.2.3. The response factor for any target analyte listed in Table 2 must meet the listed minimum value.

7.4.2.4. The %D for all other analytes of interest should be ≤ 20%. If the %D > 20%, the analysis of samples may still proceed if the analyte failed high and the analyte is not expected to be present in the samples. However, if a reportable analyte is detected in a sample and the %D for that analyte was greater than 20% in the CCV, the sample will need to be reanalyzed on a system with a passing CCV for that analyte, or the data must be qualified.

NOTE: For any DoD QSM project, the %D for all target compounds should be ≤ 20% (PCP ≤ 50%). If samples must be reported with an analyte of interest having a %D > 20% (PCP > 50%), then the data must be qualified accordingly, regardless of whether the analyte was detected or not.

7.4.2.5. The criteria in 7.4.2.3 and 7.4.2.4 must be met for the continuing calibration to be considered valid. Only analytes that are being reported for a given sample must meet the criteria in 7.4.2.3 and 7.4.2.4.

If the first continuing calibration verification does not meet criteria, a second standard may be injected. If the second standard does not meet criteria, the system must be recalibrated. If the second standard meets criteria then the system is considered in control and results may be reported.

Rationale for second standard such as instrument maintenance, clipped column, remade standard, etc should be documented in the run log or maintenance log. Reanalysis of second standard without valid rationale may require the analysis of a third standard (in which case both the second and third standard would have to pass).

NOTE: For any DoD QSM project, if the second standard meets criteria, then a third standard must be analyzed. If the third standard also meets criteria then the system is considered in control and results may be reported.

If the |%D| is greater than 20%, then documented corrective action is necessary. This may include recalibrating the instrument and reanalyzing the samples, performing instrument maintenance to correct the problem and reanalyzing the samples, or qualifying the data. Under certain circumstances, the data may be reported. i.e. The CCV failed high, the associated QC passed, and the samples were ND.

NOTE: For any DoD QSM project, if samples must be reported with a target analyte having a %D > 20% (PCP > 50%), then the data must be qualified accordingly, regardless of whether the analyte was detected or not.

NOTE: Any target analytes that are detected in the samples must be bracketed by an acceptable initial calibration curve and acceptable CCV standards; otherwise, the samples must be reanalyzed, or the data must be qualified.

7.4.2.6. For DoD QSM 5.x compliance an additional CCV must be analyzed at the end of each run. The closing CCV should be within the 12-hour Tune window

.

The %D for all target compounds in this CCV should be ≤ 50%. If the %D > %50 for any target compound, the samples may need to be reanalyzed. If samples must be reported with an analyte of interest having a %D > 50%, then the data must be qualified accordingly, regardless of whether the analyte was detected or not.

NOTE: If samples are ND and an analyte in the CCV fails high, then the sample does not need to be reanalyzed.

7.4.2.7. If any of the internal standard response changes by more than a factor of two (-50% to +100%) or retention time changes by more than 30 seconds (10 seconds for DOD QSM 5.x compliance) from the midpoint standard of the last initial calibration or the daily CCV, the mass spectrometer must be inspected for malfunctions and corrections made, as appropriate. Corrective action may include re-calibration (initial Calibration) of the instrument.

7.4.3 Sample Extract Analysis

7.4.3.1 Samples are analyzed in a set referred to as an analysis sequence or batch. A batch consists of the following:

Tune Evaluation Mix
Initial Calibration Standards (or CCV)
QC Extracts
Sample Extracts

7.4.3.2 Two microliters of internal standard solution is added to every 100ul of extract in the autosampler vial. Generally, 400ul of extract are transferred to the autosampler vial with a gas tight syringe.

7.4.3.3 One or two microliters (same amount as standards) of extract is injected into the GC by the autosampler. The data system then records the resultant peak responses and retention times.

7.4.3.4 Qualitative identification

The target compounds shall be identified by analysts with competent knowledge in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. The criteria required for a positive identification is:

The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

The sample component must elute at the same relative retention time (RRT) as the daily standard. The RRT of sample component must be within ± 0.06 RRT units of the standard.

All ions monitored in the standard mass spectra should be present in the sample spectrum.

The relative intensities of these ions must agree within ± 30% between the daily standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20 and 80%.

Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

If peak identification is prevented by the presence of interferences, further cleanup may be required, or the extract must be diluted so that the interference does not mask any analytes.

7.4.3.5 Quantitative analysis

When a target compound has been identified, concentration will be based on the integrated area of the quantitation ion, which is normally the base peak.

The sample matrix may produce an interference with the primary ion. This may be characterized by an excessive background signal of the same ion, which distorts the peak shape beyond a definitive integration. The interference could also, severely inhibit the response of the internal standard ion.

If the analyte response exceeds the linear range of the system, the extract must be diluted and reanalyzed. It is recommended that extracts be diluted so that the response falls into the middle of the calibration curve.

7.5 Maintenance and Trouble Shooting

7.5.1 Refer to SOP GC001 for routine instrument maintenance and trouble shooting.

7.5.2 All instrument maintenance must be documented in the appropriate “Instrument Repair and Maintenance” log. The log will include such items as problem, action taken, correction verification, date, and analyst.

7.5.3 Repairs performed by outside vendors must also be documented in the log. The analyst or Department Supervisor responsible for the instrument must complete the log if the repair technician does not.

7.5.4 PC and software changes must be documented in the “Instrument Repair and Maintenance” log. Software changes may require additional validation.

8.0 METHOD PERFORMANCE

Method performance is monitored through the routine analysis of negative and positive control samples. These control samples include method blanks (MB), blank spikes (BS), matrix spikes (MS), and matrix spike duplicates (MSD). The MB and BS are used to monitor overall method performance, while the MS and MSD are used to evaluate the method performance in a specific sample matrix.

Blank spike, matrix spike, and matrix spike duplicate samples are compared to statistically generated control limits. These control limits are reviewed and updated annually. Control limits are stored in the LIMS. Additionally, blank spike accuracy is regularly evaluated for statistical trends that may be indicative of systematic analytical errors.

9.0 QUALITY ASSURANCE / QUALITY CONTROL

Accuracy and matrix bias are monitored by the use of surrogates and by the analysis of a QC set that is prepared with each batch (maximum of 20 samples) of samples. The QC set consists of a method blank (MB), blank spike (BS), matrix spike (MS), and matrix spike duplicate (MSD).

9.1 Internal Standards

9.1.1 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12 and Perylene-d12 can be used as internal standards for this method. The internal standards used are dependent on the compounds being analyzed. The response of the internal standard in all subsequent runs should be within a factor of two (-50% to +100%) of the internal standard response in the opening CCV for each sequence. On days that an initial calibration is performed, the internal standard responses should be compared to the internal standard responses for the mid-point standard.

9.1.2 If the internal standard responses are not within limits, the following are required.

9.1.2.1 Check to be sure that there are no errors in calculations, integrations, or internal standards solutions. If errors are found, recalculate the data accordingly.

9.1.2.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample. If the recovery is high due to interfering peaks, it may be possible to get a more accurate recovery by analyzing the sample on a different column type.

9.1.2.3 If no problem is found, prepare a second aliquot of extract and reanalyze the sample.

9.1.2.4 If upon reanalysis, the responses are still not within limits, the problem is considered matrix interference. The extract may need to be diluted or the results qualified.

9.2 Surrogates

9.2.1 Nitrobenzene-d5, 2-Fluorobiphenyl, and p-Terphenyl-d14 (or 2-Methylnaphthalene-d10 and Fluoranthene-d10) are used as the base neutral surrogate standards and Phenol-d5, 2-Fluorophenol, and 2,4,6-Tribromophenol are used as the acid surrogate standards to monitor the efficiency of the extraction. The surrogates used are dependent on the compounds being analyzed.

A known amount of surrogate standard is added to each sample including the QC set prior to extraction. The percent recovery for each surrogate is calculated as follows:

% Recovery = (Sample Amount / Amount Spiked) X 100

The percent recovery must fall within the established control limits for all surrogates for the results to be acceptable.

9.2.2 If any surrogate recovery is not within the established control limits, the following are required. Note: If the samples are being analyzed for only base neutral compounds or only acid compounds, then only the relative surrogates need to be monitored.

9.2.2.1 Check to be sure that there are no errors in calculations, dilutions, integrations, surrogate solutions or internal standard solutions. If errors are found, recalculate the data accordingly. If errors are suspected, re-vial and re-inject the extract to verify.

9.2.2.2 Check instrument performance. It may be necessary to re-vial and re-inject the extract in order to verify performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample.

9.2.2.3 If no problem is found, re-extract and reanalyze the sample. **NOTE:** If the recoveries are high and the sample is non-detect, then re-extraction may not be necessary. For any DoD QSM projects the resulting data must be qualified accordingly. If there is insufficient sample for re-extraction, reanalyze the sample and footnote this on the report.

9.2.2.4 If upon reanalysis, the recovery is still not within control limits, the problem is considered matrix interference. Surrogates from both sets of analysis should be reported on the final report.

9.3 Method Blank

9.3.1 The method blank is either de-ionized water or sodium sulfate (depending upon sample matrix) to which the surrogate standard has been added. The method blank is then extracted and taken through all cleanup procedures along with the other samples to determine any contamination from reagents, glassware, or high level samples. The method blank must be free of any analytes of interest or interferences at ½ the required LLOQ to be acceptable. If the method blank is not acceptable, corrective action must be taken to determine the source of the contamination. Samples associated with a contaminated method blank shall be evaluated as to the best corrective action for each particular sample. This may include reanalyzing the samples, re-extracting and reanalyzing the samples or qualifying the results with a “B” or “V” qualifier.

9.3.2 If the MB is contaminated but the samples are non-detect, then the source of contamination should be investigated and documented. The sample results can be reported without qualification.

9.3.3 If the MB is contaminated but the samples results are > 10 times the contamination level, the source of the contamination should be investigated and documented. The samples results may be reported with the appropriate "B" or "V" qualifier. This must be approved by the department supervisor.

9.3.4 If the MB is contaminated but the samples results are < 10 times the contamination level, the source of the contamination should be investigated and documented. The samples should be re-extracted and reanalyzed for confirmation. If there is insufficient sample to re-extract, or if the sample is re-extracted beyond hold time, the appropriate footnote and qualifiers should be added to the results. This must be approved by the department supervisor.

9.4 Blank Spike

9.4.1 The blank spike is either de-ionized water or sodium sulfate (depending upon sample matrix) to which the surrogate standard and spike standard have been added. The blank spike is then extracted and taken through all cleanup procedures along with the other samples to monitor the efficiency of the extraction procedure. The percent recovery for each analyte is calculated as follows:

% Recovery = (Blank Spike Amount / Amount Spiked) X 100

The percent recovery for each analyte of interest should fall within the established control limits for the results to be acceptable. The large number of analytes in this method presents a substantial probability that a few of the analytes will fall outside of the established control limits. This may not indicate that the system is out of control; therefore, corrective action may not be necessary.

Upper and lower marginal exceedance (ME) limits can be established to determine when corrective action is necessary. A marginal exceedance in the Blank Spike is defined as a recovery being outside of 3 standard deviations but within 4 standard deviations of the mean.

The number of allowable marginal exceedances is based on the number of analytes in the Blank Spike. Marginal Exceedances must be random. If the same analyte exceeds the BS control limits repeatedly, it is an indication of a systematic problem and corrective action must be taken.

Marginal exceedances are not permitted for analytes that are deemed to be "Compounds of Concern" for a specific project. "Compounds of Concern" are different from "Target Compounds". "Target Compounds" are all analytes that are being reported for a site where "Compounds of Concern" are those analytes expected to be present at the site.

The number of allowable marginal exceedances is as follows:

1) 31-50 analytes in BS, 2 analytes allowed in ME range;

2) 11-30 analytes in BS, 1 analyte allowed in ME range;

3) < 11 analytes in BS, no analytes allowed in ME range

NOTE: SC DHEC does not recognize the concept of Marginal Exceedances. Additionally a secondary check against 70-130% limits should be performed for all analytes reported to SC DHEC.

9.4.2 If the blank spike recoveries are not within the established control limits, the following are required.

9.4.2.1 Check to be sure that there are no errors in calculations, dilutions, integrations, spike solutions or internal standard solutions. If errors are found, recalculate the data accordingly. If errors are suspected, re-vial and re-inject the extract to verify.

9.4.2.2 Check instrument performance. It may be necessary to re-vial and re-inject the extract in order to verify performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample.

9.4.2.3 Check to see if the recoveries that are outside of control limits are analytes of concern. If the analytes are not being reported, additional corrective action is not necessary and the sample results can be reported without qualification.

9.4.2.4 If the recovery of an analyte in the BS is high and the associated sample is non-detect, the data may be reportable. For any DoD QSM projects the resulting data must be qualified accordingly.

9.4.2.5 If no problem is found, the department supervisor shall review the data and determine what further corrective action is best for each particular sample. That may include reanalyzing the samples, re-extracting and reanalyzing the samples, or qualifying the results as estimated.

9.4.2.6 If there is insufficient sample to re-extract, or if the sample is re-extracted beyond hold time, the appropriate footnote and qualifiers should be added to the results. This must be approved by the department supervisor.

9.4.2.7 Because of their problematic nature, benzidine, benzaldehyde, and benzoic acid are generally not evaluated in the blank spike unless they are of specific concern for a given project.

9.5 Matrix Spike and Matrix Spike Duplicate

9.5.1 Matrix spike and spike duplicates are replicate sample aliquots to which the surrogate standard and spike standard have been added. The matrix spike and spike duplicate are then extracted and taken through all cleanup procedures along

with the other samples to monitor the precision and accuracy of the extraction procedure. The percent recovery for each analyte is calculated as follows:

% Recovery = [(Spike Amount – Sample Amount) / Amount Spiked] X 100

The percent recovery for each analyte of interest must fall within the established control limits for the results to be acceptable.

9.5.2 If the matrix spike recoveries are not within the established control limits, the following are required.

9.5.2.1 Check to be sure that there are no errors in calculations, dilutions, integrations, spike solutions or internal standard solutions. If errors are found, recalculate the data accordingly. If errors are suspected, re-vial and re-inject the extract to verify.

9.5.2.2 Check instrument performance. It may be necessary to re-vial and re-inject the extract in order to verify performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample. If the recovery is high due to interfering peaks, it may be possible to get a more accurate recovery by analyzing the sample on a different column type.

9.5.2.3 If no problem is found, compare the recoveries to those of the blank spike. If the blank spike recoveries indicate that the problem is sample related, document this on the run narrative. Matrix spike recovery failures are not grounds for re-extraction but are an indication of the sample matrix effects.

9.5.3 Precision

Matrix spike and spike duplicate recoveries for each analyte are used to calculate the relative percent difference (RPD) for each compound.

RPD = [| MS Result – MSD Result | / Average Result] X 100

The RPD for each analyte should fall within the established control limits. If more than 33% of the RPDs fall outside of the established control limits, the MS and MSD should be reanalyzed to ensure that there was no injection problem. If upon reanalysis the RPDs are still outside of the control limits, the department supervisor shall review the data and determine if any further action is necessary. RPD failures are generally not grounds for re-extraction.

10.0 CALCULATIONS

The concentration of each analyte in the original sample is calculated as follows:

Water (ug/l) = $(CONC_{inst})$ X (V_F / V_I) X DF

Soil (ug/kg) = [($CONC_{inst}$) X (V_F / W_I) X DF] / %solids

$CONC_{inst}$	=	Instrument concentration calculated from the initial calibration using mean RF or curve fit.
DF	=	Dilution Factor
V_F	=	Volume of final extract (ul)
V_I	=	Volume of sample extracted (ml)
W_I	=	Weight of sample extracted (g)
%solids	=	Dry weight determination in decimal form

All soils are reported on a dry weight basis.

11.0 SAFETY AND POLLUTION PREVENTION

11.1 Safety

The analyst should follow normal safety procedures as outlined in the SGS Health and Safety Program, which includes the use of safety glasses, gloves, and lab coats.

The toxicity of each reagent and target analyte has not been precisely defined; however, each reagent and sample should be treated as a potential health hazard. Material Safety Data Sheets (MSDS) or Safety Data Sheets (SDS) are available for all reagents and many of the target analytes. Exposure must be reduced to the lowest possible level. Personal protective equipment should be used by all analysts.

11.2 Pollution Prevention

Waste solvents from the sample analysis and standards preparation are collected in waste storage bottles and are eventually transferred to the chlorinated waste drum.

Sample Extracts are archived and stored for 60 days after analysis. Old extracts and standards are disposed of in the waste vial drum.

12.0 REFERENCES

SW846 Method 8000D Revision 4, July 2014

SW846 Method 8270D Revision 5, July 2014

SW846 Method 8270E Revision 6, June 2018

EPA CLP SOW for Organics Superfund Methods, SOM02.3, September 2015

TABLE 1

Routine Target Analytes

Naphthalene	Pentachlorophenol
2-Methylnaphthalene	2,4-Dinitrotoluene
1-Methylnaphthalene	2,6-Dinitrotoluene
Acenaphthylene	Hexachlorobenzene
Acenaphthene	Hexachlorobutadiene
Fluorene	bis(2-Chloroethyl)ether
Phenanthrene	2,4-Dichlorophenol
Anthracene	1,4-Dioxane
Fluoranthene	1,1'-Biphenyl
Pyrene	Diphenyl Ether
Benzo[a]anthracene	4-Nitrophenol
Chrysene	2,4-Dinitrophenol
Benzo[b]fluoranthene	N-Nitroso-di-n-propylamine
Benzo[k]fluoranthene	N-nitrosodimethylamine
Benzo[a]pyrene	Nitrobenzene
Indeno[1,2,3-cd]pyrene	Dibenzofuran
Dibenz[a,h]anthracene	bis(2-Ethylhexyl)phthalate
Benzo[g,h,i]perylene	Hexachlorocyclopentadiene
Carbazole	

TABLE 2

Minimum Response Factors

Analyte	Min. RF
Naphthalene	0.700
2-Methylnaphthalene	0.400
1-Methylnaphthalene	0.400
Acenaphthylene	0.900
Acenaphthene	0.900
Fluorene	0.900
Phenanthrene	0.700
Anthracene	0.700
Fluoranthene	0.600
Pyrene	0.600
Benzo[a]anthracene	0.800
Chrysene	0.700
Benzo[b]fluoranthene	0.700
Benzo[k]fluoranthene	0.700
Benzo[a]pyrene	0.700
Indeno[1,2,3-cd]pyrene	0.500
Dibenz[a,h]anthracene	0.400
Benzo[g,h,i]perylene	0.500

Analyte	Min. RF
N-nitroso-di-n-propylamine	0.500
Hexachlorocyclopentadiene	0.050
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Pentachlorophenol	0.050
bis(2-chloroethyl)ether	0.700
2,4-Dinitrotoluene	0.200
2,6-Dinitrotoluene	0.200
Hexachlorobenzene	0.100
1,4-Dioxane	n/a
1,1' Biphenyl	0.010
Diphenyl Ether	n/a
Carbazole	0.010
Dibenzofuran	0.800
bis(2-Ethylhexyl)phthalate	0.010
2-Methylnaphthalene-d10	0.400
Flouranthene-d10	0.400

TABLE 3

Characteristic Ions

Analyte	Quant. Ion	Q1	Q2
Naphthalene-d8 IS	136	68	
Nitrobenzene-d5 SS	82	128	54
Naphthalene	128	129	127
2-Methylnaphthalene	142	141	115
1-Methylnaphthalene	142	141	115
Acenaphthene-d10 IS	164	162	160
2-Fluorobiphenyl SS	172	171	
Acenaphthylene	152	151	153
Acenaphthene	153	152	154
Fluorene	166	165	167
Phenanthrene-d10 IS	188	94	80
Phenanthrene	178	179	176
Anthracene	178	179	176
Fluoranthene	202	101	203
Chrysene-d12 IS	240	120	236
Pyrene	202	101	203
Terphenyl-d14 SS	244	122	212
Benzo[a]anthracene	228	226	229
Chrysene	228	226	229
Perylene-d12 IS	264	260	265
Benzo[b]fluoranthene	252	253	125
Benzo[k]fluoranthene	252	253	125
Benzo[a]pyrene	252	253	125
Indeno[1,2,3-cd]pyrene	276	138	277
Dibenz[a,h]anthracene	278	139	279
Benzo[g,h,i]perylene	276	138	277

Analyte	Quant. Ion	Q1	Q2
N-nitroso-di-n-propylamine	42	70	
Hexachlorocyclopentadiene	237	235	
2,4-Dinitrophenol	184	154	
4-Nitrophenol	139	65	
2,4,6-Tribromophenol	330	332	141
Pentachlorophenol	266	264	268
bis(2-chloroethyl)ether	93	63	95
2,4-Dinitrotoluene	165	63	182
2,6-Dinitrotoluene	165	89	121
Hexachlorobenzene	284	142	249
1,4 Dioxane	88	58	43
1,1' Biphenyl	154	153	152
Diphenyl Ether	170	141	77
Carbazole	167	166	139
Dibenzofuran	168	139	169
bis(2-Ethylhexyl)phthalate	149	167	279
2-Methylnaphthalene-d10	152	151	125
Fluoranthene-d10	212	111	213

TABLE 4

Calibration, Spike, and Surrogate Levels for PAHs and PCP

COMPOUND (ng/ul)	ICAL							ICV	SPIKE	SURR
Naphthalene-d8 IS	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0		
Nitrobenzene-d5 SS	0.4	2.0	5.0	10.0	15.0	20.0	40.0			10.0
Naphthalene	0.4	2.0	5.0	10.0	15.0	20.0	40.0	10.0	10.0	
2-Methylnaphthalene-d10 SS	0.2	1.0	2.5	5.0	7.5	10.0	20.0			5.0
2-Methylnaphthalene	0.4	2.0	5.0	10.0	15.0	20.0	40.0	10.0	10.0	
1-Methylnaphthalene	0.4	2.0	5.0	10.0	15.0	20.0	40.0	10.0	10.0	
Acenaphthene-d10 IS	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0		
2-Fluorobiphenyl SS	0.4	2.0	5.0	10.0	15.0	20.0	40.0			10.0
Acenaphthylene	0.4	2.0	5.0	10.0	15.0	20.0	40.0	10.0	10.0	
Acenaphthene	0.4	2.0	5.0	10.0	15.0	20.0	40.0	10.0	10.0	
Fluorene	0.4	2.0	5.0	10.0	15.0	20.0	40.0	10.0	10.0	
Phenanthrene-d10 IS	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0		
2,4,6-Tribromophenol	0.8	4.0	10.0	20.0	30.0	40.0	80.0			20.0
Pentachlorophenol	1.0	5.0	12.5	25.0	37.5	50.0	100.0	20.0	20.0	
Dibenzofuran	0.4	2.0	5.0	10.0	15.0	20.0	40.0	10.0	10.0	
Phenanthrene	0.4	2.0	5.0	10.0	15.0	20.0	40.0	10.0	10.0	
Anthracene	0.2	1.0	2.5	5.0	7.5	10.0	20.0	5.0	5.0	
Fluoranthene-d10 SS	0.2	1.0	2.5	5.0	7.5	10.0	20.0			5.0
Fluoranthene	0.4	2.0	5.0	10.0	15.0	20.0	40.0	10.0	10.0	
Carbazole	0.2	1.0	2.5	5.0	7.5	10.0	20.0	5.0	5.0	
Chrysene-d12 IS	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0		
Pyrene	0.4	2.0	5.0	10.0	15.0	20.0	40.0	10.0	10.0	
Terphenyl-d14 SS	0.4	2.0	5.0	10.0	15.0	20.0	40.0			10.0
Benzo[a]anthracene	0.2	1.0	2.5	5.0	7.5	10.0	20.0	5.0	5.0	
Chrysene	0.2	1.0	2.5	5.0	7.5	10.0	20.0	5.0	5.0	
Perylene-d12 IS	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0		
Benzo[b]fluoranthene	0.2	1.0	2.5	5.0	7.5	10.0	20.0	5.0	5.0	
Benzo[k]fluoranthene	0.2	1.0	2.5	5.0	7.5	10.0	20.0	5.0	5.0	
Benzo[a]pyrene	0.2	1.0	2.5	5.0	7.5	10.0	20.0	5.0	5.0	
Indeno[1,2,3-cd]pyrene	0.2	1.0	2.5	5.0	7.5	10.0	20.0	5.0	5.0	
Dibenz[a,h]anthracene	0.2	1.0	2.5	5.0	7.5	10.0	20.0	5.0	5.0	
Benzo[g,h,i]perylene	0.2	1.0	2.5	5.0	7.5	10.0	20.0	5.0	5.0	

Note: DoD QSM 5.x lists the ISTD concentration at 0.4 ng/ul; however, that is based on a PAH calibration range of 0.1 to 1.0 ng/ul. Since SGS Orlando calibrates the PAHs from 0.2 to 20 ng/ul and 0.4 to 40 ng/ul the ISTD concentration of 4.0 ng/ul is appropriate.

METALS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

Prepared by: David Metzgar III Date: 07/24/2019

Approved by: Svetlana Izosimova Date: 07/31/2019

Annual Review

Reviewed by: _____ Date: _____

Reviewed by: _____ Date: _____

Reviewed by: _____ Date: _____

Document Control

Issued to: QA Department Date: 07/31/2019

Issued to: Metals Date: * 07/31/2019

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Effective 7 days after "*" date

CONTROLLED COPY
DO NOT DUPLICATE

TITLE: METALS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

REFERENCES: SW846 6010C, EPA 200.7 Rev 4.4 1994, WV 47CSR32

REVISED SECTIONS:

1.0 update MDL procedure
6.6 added detail

INSTRUMENT: THERMO 6500, SERIAL # 20100903 SSTRACE 1
INSTRUMENT: THERMO 6500, SERIAL # 20103825 SSTRACE 2
AUTOSAMPLER: CETAC 240 POSITION, SERIAL # 031038A520 SSTRACE 1
AUTOSAMPLER: CETAC 240 POSITION, SERIAL # 041048A520 SSTRACE 2

SUGGESTED WAVELENGTH (S): TABLE 2

1.0 SCOPE AND APPLICATION

SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

Method EPA 200.7 has been modified within the flexibility allowed in 40CFR136.6.

1.1 This method is applicable for the determination of metals in water, sludges, sediments, and soils. Elements that can be reported by this method include: Aluminum, Antimony, Arsenic, Barium, Beryllium, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Molybdenum, Nickel, Potassium, Selenium, Silver, Sodium, Strontium, Titanium, Thallium, Tin, Vanadium, and Zinc.

1.2 Sample matrices are pretreated following SW846 and EPA methods for digestion of soil, sediment, sludge or water samples. Refer to specific metals department digestion SOP's for more information on digestion techniques.

1.3 This inductively coupled argon plasma optical emission spectrometer (s) (ICP-OES) uses an Echelle optical design and a Charge Injection Device (CID) solid-state detector to provide elemental analysis. Control of the spectrometer is provided by PC based iTEVA software. In the instrument, digested samples are introduced into the Thermo 6500 ICP, passed through a nebulizer and transported to a plasma torch. The element-specific emission spectra are produced by a radio frequency inductively coupled plasma. The spectra are dispersed by a

spectrometer, and the intensities of the emission lines are monitored with the solid state detector.

1.4 Reporting limits (RL) are based on the extraction procedure. Reporting limits may vary depending on matrix complications, volumes and by client needs, but the reporting limits must always be verified with a low check which meets the criteria outlined in this SOP. Solid matrices are reported on a dry weight basis. Refer to table 1 of this SOP for SGS - Orlando typical reporting limits. Refer to scheduling sheets and/or project specific QAPP for further information regarding client specific reporting limits.

1.5 MDLs should be established for all appropriate methods using a solution spiked at approximately 2-10 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The samples used for the MDL must be prepared in at least three batches on three separate calendar dates and analyzed on three separate calendar days. If there are multiple instruments that will be assigned the same MDL, then the sample analyses must be distributed across all instruments. A minimum of 2 MDL's prepared and analyzed on different calendar days is required for each instrument. The same prepared extract may be analyzed on multiple instruments so long as the minimum requirement of seven preparations in at least three separate batches is maintained. Please refer to SOP QA020, current revision for further information regarding MDL's.

1.6 An MDL (LOD) check standard will be analyzed at the time of the MDL study and on a quarterly basis for verification. The concentration of the MDL check standard must be 2x-4x the statistical MDL. The MDL Check Standard is carried through the entire preparation and analytical procedure. This is a qualitative check; therefore, the analyte needs to be detected only. If the analyte is not detected, the concentration of the MDL check standard must be increased to a level where the analyte is detected.

1.7 Lower limit of quantitation check sample (LOQ). The lower limit of quantitation check (LLQC) sample should be analyzed after establishing the lower laboratory reporting limits and on a quarterly basis to demonstrate the desired detection capability. The LLQC sample is carried through the entire preparation and analytical procedure. Lower limits of quantitation are verified when all analytes in the LLQC sample are detected within 20 percent of their true value.

1.8 Compounds detected at concentrations between the RL and MDL are quantitated and qualified as estimated values and reported with either a "J" or "I" qualifier. Some program or project specifications may require that no values below the RL be reported.

1.9 Instrument Detection Limits (IDL). IDL's should be completed upon initial instrument installation. SGS - Orlando does not report to IDL.

2.0 PRESERVATION AND BOTTLEWARE

All samples should be preserved with nitric acid to a pH of <2 at the time of collection. All sample pH are checked in sample receiving and within the metals department. Samples that are received with a pH >2 must be preserved to pH <2 and held for 24 hours prior to metals digestion to dissolve any metals that absorb to the container walls. Refer to SOP SAM101, current revision for further instruction. Final pH of TCLP extracts are checked and recorded in SGS - Orlando Extractions Department. Please refer to TCLP (1311) fluid determination logbook and SPLP (1312) fluid determination logbook for further information. TCLP extracts received from SGS - Orlando Extractions Department are prepared as soon as possible, no longer than 24 hours from time of receipt. If precipitation is observed during the sample preparation process the sample(s) are immediately re-prepped on dilution until no precipitation is observed. Samples received for dissolved metals analysis should be filtered and preserved to pH<2 as soon as possible and held for 24 hours prior to digestion. Refer to SGS - Orlando Sample Filtration Logbook for further information.

All soil samples must be stored in a refrigerator at $\leq$ 6^{o}C upon receipt. Refer to SOP SAM101, current revision for further instruction.

All bottleware used by SGS - Orlando is tested for cleanliness prior to shipping to clients. Analysis results must be less than one half the reporting limit to be acceptable. Refer to SOP SAM104, current revision for further instruction.

3.0 HOLDING TIME AND BATCH SIZE

All samples must be prepared and analyzed within 6 months of the date of collection. Refer to appropriate SGS - Orlando digestion SOP, current revision for batch size criteria.

4.0 INTERFERENCES

Several types of interferences can cause inaccuracies in trace metals determinations by ICP. These interferences are discussed below.

4.1 Spectral interferences are caused by overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution from continuous or recombination phenomena, and background contribution from stray light from the line emission of high concentration elements. Corrections for these interferences can be made by using interfering element corrections, by choosing an alternate analytical line, and/or by applying background correction points. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak.

Note: Refer to section 17.0 of this SOP for further instruction regarding interfering element correction factor generation.

4.2 Physical interferences can be caused by changes in sample viscosity or surface tension, by high acid content in a sample, or by high dissolved solids in a sample. These interferences can be reduced by making sample dilutions.

4.3 Matrix interferences in high solid samples can be overcome by using an internal standard. Yttrium/Indium mix is used for the Thermo 6500 ICP. The concentration must be sufficient for optimum precision but not so high as to alter the salt concentration of the matrix. The element intensity is used by the instrument as an internal standard to ratio the analyte intensity signals for both calibration and quantitation.

4.3 Chemical interferences are not pronounced with ICP due to the high temperature of the plasma, however if they are present, they can be reduced by optimizing the analytical conditions (i.e. power level, torch height, etc.).

5.0 APPARATUS

5.1 Currently there are two solid state ICPs available for use in the lab. Both are Thermo 6500 ICP units. These units have been optimized to obtain lower detection limits for a wide range of elements. Since they are solid state systems, different lines may be included for elements to obtain the best analytical results. However, the lines which are normally included in the normal analysis program are shown in Table 2.

5.2 Instrument auto samplers. For random access during sample analysis.

5.3 Class A volumetric glassware and pipettes.

5.4 Polypropylene auto sampler tubes.

5.5 Eppendorf Pipette (s) - Pipette (s) are checked daily for accuracy and to ensure they are in good working condition prior to use. Volumes are checked at 100% of maximum volume (nominal volume). Pipettes are checked within the metals department and results are stored electronically in the “Pipette Calibration Log”. Refer to SOP QA006, current revision for further information regarding pipette calibration. BIAS: mean must be within 2% of nominal volume. Precision: RSD must be $\leq$1% of nominal volume based on three replicates.

5.6 Fisher Brand 0.45 micron (um) filter or equivalent. Filter lots are checked for cleanliness through the Method Blank process. All Method Blank analytical results must be less than one half the reporting limit to be acceptable, if not, the contaminated lot must be identified and removed from laboratory use. Samples filtered through the contaminated filters must be re-filtered through acceptable filters.

5.7 Fisher Brand disposable 10 ml syringes or equivalent. Syringe lots are checked for cleanliness through the Method Blank process. All Method Blank results must be less than one half the reporting limit to be acceptable, if not , the contaminated lot must be identified and removed from laboratory use. Samples filtered through the contaminated syringes must be re-filtered through acceptable syringes.

5.8 Data System

Microsoft Windows XP Professional Version 2002
Instrument software SST1 – Thermo iTEVA version 2.8.0.89
Instrument software SST2 – Thermo iTEVA version 2.7.0.87

5.8.1 A computer system interfaced to the Thermo 6500 ICP that allows for the continuous acquisition and storage of all data obtained throughout the duration of the analytical run sequence.

5.8.2 Data is archived to a backup server for long term storage.

6.0 REAGENTS

All chemicals listed below are trace metal grade unless otherwise specified. Refer to Acid Certificate of Analysis logbook for Certificates of Analysis and compliance with the specifications of the grade listed. SGS - Orlando produces DI water to the specifications for the ASTM Type II standard designation based on the system manufacturer's performance specifications. The DI water is used exclusively for laboratory purposes. De-ionized (DI) water should be used whenever water is required. Refer to SOP QA037, current revision for more information regarding testing and monitoring. Refer to the Metals Department Standard Prep Logbook for the make-up and concentrations of standards and stock solutions being used within this SOP. Some of the information included in the logbook is as follows: standard name, elements in mix, manufacturer, lot number, parent expiration date, acid matrix, stock concentration, volume of standard added, total volume, final prepared concentration, prep date, initials, MET number, and prepared standard expiration date. Standards and prepared reagents must be prepared every 6 months or before stock standard expiration date, whichever comes first**.** Refer to tables 3 through 7 of this SOP for concentration levels of standards used. Unless otherwise approved, the calibration curve must contain 3 points determined by a blank and a series of standards representing the elements of interest.

6.1 2.5 ppm Yttrium and 10 ppm Indium internal standard, made from ICP quality standard.

6.2 Hydrochloric acid, trace metals grade.

6.3 Nitric Acid, trace metals grade.

6.4 ICP quality standard stock solutions are available from Inorganic Ventures, Spex, Plasma Pure, Ultra, Environmental Express, or equivalent.

6.5 Calibration Standards. These can be made up by diluting the stock solutions to the appropriate concentrations. The calibration standards should be prepared using the same type of acid (s) and at approximately the same concentration as will result in the samples following sample preparation.

6.5.1 For calibration and quantitation an internal standard (Yttrium/Indium) is used to limit nebulization problems. If it is known that the samples contain a significantly different acid matrix, the samples must be diluted so that they are in a similar matrix to the

curve. All sample results are referenced to the initial calibration blank (ICB) Internal Standard counts. The criteria is 60-125 percent of the initial calibration blank (ICB) counts. If the internal standard counts fall outside these criteria matrix effects must be suspected and the sample diluted until it meets the criteria or footnoted in LIMS as suspected matrix interference.

6.5.2 Standards must be prepared so that there is minimal spectral interference between analytes.

Note: All Ag stock and intermediate solutions must be stored away from direct sunlight.

6.6 Analytical Quality Control Solutions.

All solutions listed below are prepared by adding either mixed or single element metals solutions to a solution prepared using the same type of acid (s) and at approximately the same concentration as will result in the samples following sample preparation. Please refer to electronic standard preparation logbook for further details.

6.6.1 Blank (Calibration, ICB, CCB)

This reagent blank contains Nitric Acid at 3 percent and Hydrochloric Acid at 5 percent.

6.6.2 Initial Calibration Verification solution.

This standard solution must be made from a different source than the calibration curve. The concentrations for each element must be within the range of the calibration curve and should be approximately at the midpoint of the curve. This solution is used to verify the accuracy of the initial calibration. Levels for the ICV standard are shown in Table 4.

6.6.3 Continuing Calibration Verification solution.

The metals concentrations for this standard should be at approximately the mid point of the calibration curve for each element. This standard should be prepared from the same source that is used for the calibration curve. Levels for the CCV standard are shown in Table 5.

6.6.4 Interference Element Check Solutions.

These solutions must be analyzed to check the interfering element correction factors (IEC's) on the ICP instruments. Refer to section 17.0 of this SOP for further information regarding generation of IEC's.

6.6.4.1 ICSA Solution.

The ICSA solution contains only the interfering elements. Levels for the ICSA are shown in Table 9.

6.6.4.2 ICSAB Solution.

The ICSAB solution contains both the interferents and the analytes of interest. Levels for the ICSAB are shown in Table 10.

6.6.4.3 Single element interference check solutions

Prepared as single solutions. Levels for the single element interference solutions are shown in Table 11.

6.7 CRIA Standard Solution (Also referred to as LLCCV)

The CRIA standard contains the elements of interest at levels equal to SGS - Orlando quantitation limits (RL). Please refer to Table 6 for list of elements of interest and concentration levels for the CRIA. If special client reporting limits are requested, then low checks corresponding to those reporting limits must also be analyzed.

6.8 Matrix Spike, Matrix Spike duplicate, and Spike Blank Solution.

This solution is prepared by adding either mixed or single element metals solutions to a solution containing 3 percent nitric acid and 5 percent hydrochloric acid and diluting to a fixed final volume with this acid mixture. Spiking solution (s) must be added to the spike blank, matrix spike, and the matrix spike duplicate prior to digestion. Levels for the MS and MSD and Spike Blank standard are shown in Table 7.

6.9 Liquid Argon or Argon Gas. (99.999% purity)

7.0 ANALYTICAL PROCEDURE

Note: Please refer to section 8 of this SOP for further detail on quality control standards. Please refer to scheduling sheets and/or project specific QAPP for further information regarding client specific QC requirements.

7.1 General procedure on how to operate the Thermo 6500 is described below. Refer to the Thermo 6500 operation manual for further details.

7.2 Before starting up the instrument, make sure that the pump tubing is in good condition, the torch assembly, the nebulizer, and the spray chamber are clean, the dehumidifier (if used) is filled with DI water up to the level between Minimum and Maximum, and that there are no leaks in the torch area.

7.3 Turn on the recirculating cooler. Verify that the argon is turned on and there is enough for the entire days analytical run.

7.4 Tighten the pump platens and engage the peristaltic pump. Make sure sample and internal standard solutions are flowing smoothly.

7.5 Put a new solution of acid rinse into the rinse reservoir. The composition of the rinse solution may be periodically changed to minimize sample introduction problems and sample carryover. If internal standard is being used, make sure that sufficient amount of internal standard is prepared for the entire analytical run.

7.6 Start up the instrument following the sequence show below.

7.6.1 Double click the **iTEVA Control Center** Icon on the desktop. Type ***admin*** in User Name field, and then click **OK**.

7.6.2 Once the iTEVA Control Center window is opened, click on **Plasma** Icon at status bar area. Then click on **Instrument Status** to check the interlock indicators (torch compartment, purge gas supply, plasma gas supply, water flow and exhaust should be in green; drain flow and busy should be in gray) and the Optics Temperature. (It should be around 38^{o}C.) Click on the Close box.

7.6.3 Click **Plasma On**. When the plasma is on, click close. Let the instrument warm up for 15 to 20 minutes before starting the analysis. New tubing may take an hour to stabilize.

7.7 Torch Alignment and Auto Peak

7.7.1 If the torch has been cleaned, then the torch alignment procedure must be performed.

7.7.2 Open the method and then click on **Sequence** tab, then click on **List View** Icon until you reach rack display.

7.7.3 Go to S-6 position (you can assign any position in the rack for torch alignment), then right click to select **Go** to empty sample S:6. (Now, the auto sampler tip moves from Rinse to this position).

7.7.4 Click on **Analysis** tab, then select **Torch Alignment** from Instrument drop down menu. There will be a pop up dialog box present. Click **Run**. Then there will be another dialog pop up box (This is a reminder for Torch Alignment Solution (2 ppm Zn)), click **Ok**. Now, the instrument is initializing an automated torch alignment. It takes about 7 minutes to complete this step. Progress is indicated in the progress bar.

7.7.5 After torch alignment is complete, click **Close**. Click on **Sequence** tab, then followed by **List View** Icon.

7.7.6 Go to Rinse position at rack display, right click to select Go to rinse and let it rinse for approximately 5 minutes.

7.7.7 Perform Auto Peak

7.7.8 It is recommended that the Auto Peak Adjust procedure be performed daily prior to calibration. A standard that contains all of the lines of interest is used and the system automatically makes the appropriate fine adjustments. (High standard solution should be used for this process.)

7.7.9 Click **Sequence** tab, then click on **List View** Icon until the rack is displayed.

7.7.10 Go to S-5 position (you can assign any position in the rack for auto peak adjust), then right click to select **Go** to empty sample S:5. (Now, the auto sampler tip moves from the Rinse position to this position). Click on **Analysis** tab. All elements result is shown in the display area. From Instrument drop down menu, select **Perform Auto Peak**. There will be a pop up dialog box present. Highlight "All Elements", and then click **Run**. Then there will another pop up dialog box (This is a reminder for Auto Peak Solution), click **Ok**. Now, the instrument is performing auto peak adjust. It takes about 5 minutes to complete this process. The Auto Peak dialog box will show a green check mark in front of "All Elements", which indicates Auto Peak is complete.

7.8 Open the method and start up the run.

7.8.1 Click on **Analyst** Icon at the workspace. Go to the method and choose Open from the drop down menu. Select the method with the latest revision number.

7.8.2 Go to **Method** tab at the bottom of left hand corner to click on **Automated Output** at the workspace area. Type a filename in Filename field in the data display area (i.e. : SA101010M1, starts with SA, then followed by MM-DD-YY, then M1; M1 indicates the first analytical run for that day, then followed by M2, M3 and so on for the second and third runs.) Click on **Apply To All Sample Types**.

7.8.3 Click on **Sequence** tab at the bottom of left hand corner. From Auto Session drop down menu bar, click on **New Auto sampler** to create a sequence. This will pop up a dialog box, then click on **New** and fill in number of samples (i.e.: 100) in the Number of Samples field and the sample I.D. (leave this field empty) in Sample Name field. Type a sequence name (i.e. : SEQ101010M1, starts with SEQ, then MM-DD-YY, then M1; M1 indicates the first analytical run for that day, then followed by M2, M3 and so on for the second and third runs) in the Sequence Name field. Click Ok, then put in "0" as settle time between between sequences, and click **Ok**.

7.8.4 Right click on **Untitled** (Cetac ASX-520 Enviro 5 Named Rack is the rack that is currently used) at the workspace area, click on **Auto-Locate All** to locate all sample positions.

7.8.5 Double click on **Untitled** again, then click on the sequence name (i.e. : SEQ101010M1), on the data display area, type the sequence in Samplename column, dilution factor (if needed) in CorrFact column, check the box in front of Check column, and select an appropriate check table.

7.8.6 Once done with creating sequence, go to **Method** drop down menu and save all changes as **Save As**. There will be a Save a Method dialog box present, go to the

save option to check on “Overwrite Method and bump revision number” box, and then click **Ok**.

7.8.7 Go to Sequence tab, click on List View Icon from tool bar, then click on Connect Autosampler to PC and Initialize Icon.

7.8.8 See table 8 for a typical run sequence.

7.9 Calibrate the instrument as outlined below. See table 3 for calibration standards concentrations. This calibration procedure is done a minimum of once every 24 hours. The calibration standards may be included in the auto sampler program or they may be run manually from the **Calibrate Instrument (graduated cylinder)** icon located on the Analyst tab. All curves must be determined from a linear calibration prepared in the normal manner using the established analytical procedure for the instrument. Refer to instrument manual for further detail. Unless otherwise approved, the calibration curve must be determined by a blank and a series of three standards representing the elements of interest. Three exposures will be used with a percent relative standard deviation of less than 5 percent. The resulting correlation coefficient must be $\geq$0.998. If the calibration curves do not meet these criteria, analysis must be terminated, the problem corrected, and instrument re-calibrated. Correlation coefficients, slopes, and y-intercepts for each wavelength are printed and included in each analytical data package.

Note:Refer to scheduling sheets and/or project specific QAPP for further information regarding client specific QA/QC requirements.

7.10 After the instrument is properly calibrated, begin by reanalyzing the high standard(s) for each element. The standards can be combined into one solution for this analysis. The analyzed value must be within 5 percent of the true value or that element must be re-calibrated. The High Standard Check shall be used for 200.7 only. After the high standards are analyzed, the ICV check standard shall be run. For the ICV, all elements to be reported must be within 5 percent of the true value for 200.7 and 10 percent of the true value for 6010C. If the ICV fails, analysis shall be terminated, problem corrected, and the instrument re-calibrated.

7.11 After analyzing the ICV, the ICB must be analyzed. The results of the ICB must be less than one half the reporting limit. The instrument blank may be failing the criteria due to contamination or instrument drift. Samples associated with the failing blank shall be evaluated as to the best corrective action for each particular sample. This may include reanalyzing the samples bracketed by the failing blank, qualifying the results with a “B” or “V” qualifier, or raising the reporting limit for all samples to greater than two times the background concentration.

7.12 Before analyzing any real samples the CRIA (also referred to as LLCCV) must be analyzed. The CRIA contains elements of interest at the reporting limit. The CRIA will be analyzed at the beginning and end of each analytical run. For all elements the results must be within 20 percent of the true value for client specific reporting limits (CRIA Requirement). For all others a 30 percent criterion will be applied. If the initial CRIA fails no samples associated with the failing CRIA can be reported, and the CRIA should be reanalyzed for the failing elements. If the closing CRIA fails the criteria, the samples associated with the CRIA shall be evaluated

as to the best corrective action for each particular sample. This may include reanalyzing the samples associated with the CRIA, or qualifying the results in LIMS.

7.13 Before analyzing any real samples, the interference check standards (ICSA, ICSAB) must be analyzed. For all spiked elements, the analyzed results must be within 20 percent of the true value. For non-spiked elements, the interfering element solutions must be ± the absolute value of the reporting limit for each element. Also, on an as needed basis (i.e.: instrument repair), analyze the single element interference check solutions (SIC). The same criteria as outlined above apply. If the ICSA and/or the ICSAB fall outside this criterion the problem must be corrected and the instrument re-calibrated or data footnoted in LIMS system. If the closing ICSA/ICSAB fails the criteria, the samples associated with the ICSA/ICSAB shall be evaluated as to the best corrective action for each particular sample. This may include reanalyzing the samples associated with the ICSA/ICSAB, or qualifying the results in LIMS. Refer to section 17.0 of this SOP for Interfering Element Correction (IEC) procedure.

7.14 After the initial analytical quality control has been analyzed, the samples and the preparation batch matrix quality control shall be analyzed. Each sample analysis must be a minimum of 3 readings using at least a 5 second integration time. Between each sample, flush the nebulizer and the solution uptake system with a blank rinse solution for at least 60 seconds or for the required period of time to ensure that analyte memory effects are not occurring.

7.15 Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCV solution is not within 10 percent of the true value for method 6010C and 5 percent for method 200.7 (for the initial CCV (ICCV)), the CCV shall be reanalyzed to confirm the initial value. If the CCV is not within criteria after the reanalysis, no samples can be reported in the area bracketed by the failing CCV. Immediately following the analysis of the CCV the CCB shall be analyzed. The results of the CCB must be less than one half the reporting limit for all elements. The instrument blank may be failing the criteria due to contamination or instrument drift. Samples associated with the failing blank shall be evaluated as to the best corrective action for each particular sample. This may include reanalyzing the samples bracketed by the failing blank, qualifying the results with a “B” or “V” qualifier, or raising the reporting limit for all samples to greater than two times the background concentration.

7.16 One sample per preparation batch, or whenever matrix interferences are suspected for a batch of samples, a serial dilution (SDL) must be prepared. For the serial dilution, a 1:5 dilution must be made on the sample. The results of the 1:5 dilution shall agree within 10 percent of the true value as long as the sample and the dilution result are greater than 10 times the method detection limit or greater than 50 times the IDL. If the results are outside these criteria then matrix interference should be suspected and the proper footnote entered into LIMS. A post digestion spike (PDS) must be performed if the SDL fails. The PDS must recover within ± 20 percent for method SW846-6010C and ± 15 percent for method EPA 200.7. If the PDS is outside these limits then matrix interference must be suspected and the proper footnote entered into LIMS.

7.17 The upper limit of quantitation may exceed the highest concentration calibration point and can be defined as the “linear dynamic” range. Sample results above the linear dynamic range shall be diluted under the linear dynamic range and reanalyzed. Samples following a sample with high concentrations of analyte (s) must be examined for possible carryover.

Verification may be done by rinsing the lines with an acid solution and then reanalyzing the sample. A limit check table is built into the autosampler file so that samples exceeding the standardization range are flagged on the raw data.

7.18 After the instrument is optimized and all initial QC has been run, click on **Run Auto-Session** Icon to start the analytical run sequence.

7.18.1 If you need to add or delete samples once the run is started, follow the steps shown below.

7.18.2 Click on **Sequence** tab, then click on **List View** Icon at the tool bar. There is the sequence table shown on the display area.

7.18.3 Click on **Add Samples** Icon. This will pop up a dialog box, and then fill in number of samples that need to be added. Click **Ok**. By doing this, samples will be added to the end of the current sequence without a rack location.

7.18.4 On the Samplename column type in the sample I.D., correction factors, and check tables. **Click on Auto Locate All.**

7.18.5 The added samples will be analyzed at the end of the original sequence run order unless they are assigned a different run order.

7.18.6 Deleting Samples

7.18.7 Click on **Sequence** tab, and then click on **List View** Icon under the sequence display area.

7.18.8 Highlight all samples that need to be deleted and then click on the **Delete Samples** icon.

7.19 When the analysis is completed export the data to LIMS following the procedure outlined below.

7.19.1 Double click on **ePrint** Icon on desktop. There will be a **LEADTOOLS ePRINT** pop up box, click on **Finish Jobs** and **OK** boxes.

7.19.2 Double click the **PDF** Icon on the desktop; the PDF file will be present as Document_#. Right click on that file, select **rename** to change the filename to an assigned analytical run I.D. (i.e.: MA9000). This is the raw data file for MA9000.

7.19.3 Drop the raw data to the **LIMS Data Drop** icon located on the desktop.

7.19.4 By completing the above steps, the raw data (i.e.: MA9000) can be viewed and/or printed from the Raw Data Search function.

7.19.5 Go to **Analysis** tab, right click on sample header, and select export all samples. A pop up dialog box will come up, type in the analytical run I.D. (i.e.: SA101010M1) and click **Ok**. Go to **LIMS Export** folder located on the desktop, right click on analytical

run and change extension from .TXT to .ICP. Open the analytical file and make any necessary changes, such as deleting any samples that need to be re-run on dilution. **Save** the file. Drop the data file to the **LIMS Data Drop** icon located on the desktop. This will then send the export file to LIMS for review.

7.20 The data can be evaluated by running an automated data evaluation program, which will help to generate quality control summary pages. Each run must be evaluated as quickly as possible to make sure that all required quality control has been analyzed. With each data package include: cover sheet, copies of all prep sheets, autosampler run sequence, dilution sheets, and raw data. Label each folder with MA#, instrument run I.D., instrument used, and date.

7.21 At the end of the analysis day the ICP must be shutdown using the following sequence.

7.21.1 Place the auto sampler tip in the rinse cup and rinse in a mixed solution of approximately 5 percent nitric acid and 5 percent hydrochloric acid for 10 minutes and then in DI water for 20 minutes.

7.21.2 Turn off the plasma by clicking on the **Plasma** Icon and then by clicking **Plasma Off.**

7.21.3 Close all iTeva programs/windows.

7.21.4 Release the tension on the sample pump platens.

7.21.5 Turn off recirculating chiller.

8.0 QUALITY CONTROL

This section outlines the QA/QC operations necessary to satisfy the analytical requirements for method SW846 6010C. Please refer to scheduling sheets and/or project specific QAPP for further information regarding client specific QC requirements. Check with the area supervisor or lab manager for any non compliant quality control for further information.

8.1 High Standard Check.

After the instrument is properly calibrated, the high standard(s) shall be reanalyzed for each element. The analyzed value must be within 5 percent of the true value. If the High Standard falls outside this criteria analysis shall be terminated, problem corrected, and the instrument re-calibrated.

Note: High Standard Check is for method 200.7 only. The standards can be combined into one solution for this analysis.

8.2 Initial Calibration Verification Standard (ICV).

After each calibration, a standard from a different source than the calibration standard shall be analyzed. For the ICV, all elements to be reported must be within 10 percent of the true value for 6010C and within 5 percent for 200.7. If the ICV is outside these criteria then the analysis must be terminated, problem corrected, and the instrument re-calibrated.

8.3 Continuing Calibration Blank/Initial Calibration Blank.

Analyze the Initial calibration blank solution at the beginning of each run and the continuing calibration blank after every tenth sample and at the end of the sample run. The ICB/CCB must be less than one half the reporting limit for each element. The instrument blank may be failing the criteria due to contamination or instrument drift. Samples associated with the failing blank shall be evaluated as to the best corrective action for each particular sample. This may include reanalyzing the samples bracketed by the failing blank, qualifying the results with a "B" or "V" qualifier, or raising the reporting limit for all samples to greater than two times the background concentration.

8.4 Low Standard Check (CRIA).

The CRIA (also referred to as LLCCV) contains elements of interest at the reporting limit. The CRIA will be analyzed at the beginning and end of each analytical run. For all elements the results must be within 20 percent of the true value for client specific reporting limits (CRIA Requirement). For all others a 30 percent criterion will be applied. If the initial CRIA fails no samples associated with the failing CRIA can be reported, and the CRIA should be reanalyzed for the failing elements. If the closing CRIA fails the criteria, the samples associated with the CRIA shall be evaluated as to the best corrective action for each particular sample. This may include reanalyzing the samples associated with the CRIA, or qualifying the results in LIMS.

8.5 ICSA and ICSAB and Single Element Interference Solutions

Analyze the ICSA and ICSAB at the beginning and end of each run following the analysis of the CRIA. Also, on an as needed basis (i.e.: instrument repair), analyze the single element interference check solutions (SIC). For all spiked elements, the analyzed results must be within 20 percent of the true value. For non-spiked elements, the interfering element solutions must be $\pm$ the absolute value of the reporting limit for each element. If the ICSA and/or the ICSAB fall outside this criterion the problem must be corrected and the instrument re-calibrated or data footnoted in LIMS system. If the closing ICSA/ICSAB fails the criteria, the samples associated with the ICSA/ICSAB shall be evaluated as to the best corrective action for each particular sample. This may include reanalyzing the samples associated with the ICSA/ICSAB, or qualifying the results in LIMS. Refer to section 17.0 of this SOP for Interfering Element Correction (IEC) procedure.

8.6 Continuing Calibration Verification.

Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCV solution is not within 10 percent of the true value for method 6010C and 5 percent for method 200.7 (for the initial CCV (ICCV)) the CCV must be reanalyzed to confirm the initial value. If the CCV is not within criteria after reanalysis no samples can be reported in the area bracketed by the failing CCV.

8.7 Method Blank.

The laboratory must digest and analyze a method blank with each batch of samples. The method blank must contain elements at less than one half the reporting limit for each element. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit. Samples associated with the contaminated blank shall be evaluated as to the best corrective action for each particular sample. This may include reanalyzing the samples, re-digesting and reanalyzing the samples, qualifying the results with a "B" or "V" qualifier, or raising the reporting limit to greater than two times the background concentration. **Note:** 200.7 Method Blanks associated with samples originated in West Virginia are evaluated to MDL (WV 47CSR32)

8.8 Blank Spike Sample.

The laboratory must digest and analyze a spike blank sample with each batch of samples. Blank Spikes must be within 20 percent of the true value for method SW846-6010C and within 15 percent for method EPA 200.7. If the lab control is outside of the control limits for a reportable element, all samples must be re-digested and reanalyzed for that element. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results may be reported with no flag. For solid standard reference materials (SRMs) $\pm$ 20 percent accuracy may not be achievable and the manufacturer's established acceptance criterion should be used for all soil SRMs.

8.9 Matrix Spike and Matrix Spike Duplicate Recovery.

The laboratory must digest and analyze a matrix spike and matrix spike duplicate with each batch of samples. The matrix spike recovery is calculated as shown below and must be within 20 percent of the true value for method SW846-6010C and within 30 percent for method EPA 200.7. If a matrix spike is out of control, then the results must be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and must be footnoted to that effect.

Note: Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

$$\frac{\textbf{(Spiked Sample Result - Sample Result)}}{\textbf{Amount Spiked}} \textbf{ x 100 = matrix spike recovery}$$

8.10 Matrix Duplicate/Matrix Spike Duplicate Relative Percent Difference.

The laboratory must digest a duplicate with each batch of samples. The relative percent difference (RPD) between the duplicate and the sample must be assessed and must be $\leq$ 20 percent for sample results at or above the reporting limit. If the RPD is outside the 20 percent criteria the results must be qualified in LIMS. RPD's are also calculated in LIMS for sample results below the reporting limit. RPD's outside the 20 percent criteria are not considered failing and LIMS automatically footnotes these as "RPD acceptable due to low duplicate and sample concentrations."

Note: Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

8.11 Serial Dilution Analysis and Post Digestion Spike.

For one sample per preparation batch, or whenever matrix interferences are suspected for a batch of samples, a serial dilution must be prepared. For the serial dilution, a 1:5 dilution must be made on the sample. The results of the 1:5 dilution must agree within 10 percent of the true value as long as the sample and the dilution result are greater than 10 times the method detection limit and/or greater than 50 times the IDL. If the dilution does not agree, then the sample must be post digestion spiked (PDS) at a level no less than 10 times but no greater than 100 times the MDL concentration. The PDS must recover within ± 20 percent for method SW846-6010C and ± 15 percent for method EPA 200.7. If the PDS is outside these limits then matrix interference must be suspected and the proper footnote entered into LIMS.

$$\frac{\text{(Sample Result - Serial Dil. Result)} \times 100}{\text{Sample Result}} = \text{Serial Dilution RPD}$$

8.12 Linear Calibration ranges.

The upper limit of the linear calibration ranges must be established for all elements by determining the signal responses from a minimum of three concentration standards, one of which is close to the upper limit of the linear range. The linear calibration range, which may be used for the analysis of samples must be judged by the analyst from the resulting data. The upper range limit should be an observed signal no more than 10% below the level extrapolated from lower standards. Linear calibration ranges must be determined whenever there is a significant change in instrument response or at a minimum, every 6 months.

8.13 Sample RSD

For samples containing levels of elements greater than five times the reporting limits, the relative standard deviation for the replicates should be less than 5%. If not, reanalyze the sample. If upon reanalysis, the RSD's are acceptable then report the data from the reanalysis. If RSD's are not acceptable upon reanalysis, then the results for that element should be footnoted that there are possible analytical problems and/or matrix interference indicated by a high RSD between replicates.

8.14 Interelement Spectral Interference Correction Validity

For the interelement spectral interference corrections to remain valid during sample analysis, the interferent concentration must not exceed its linear range. If the interferent concentration exceeds its linear range or its correction factor is big enough to affect the element of interest even at lower concentrations, sample dilution with reagent blank and

reanalysis is required. In these circumstances, analyte dilution limits are raised by an amount equivalent to the dilution factor.

8.15 Internal Standard (Yttrium/Indium)

For any readings where the internal standard is outside of the range 60-125 percent of the internal standard level in the reference standard (Initial Calibration Blank), then the sample must be diluted until the internal standard is within range and all sample results must be footnoted in LIMS.

8.16 MSA (Method of Standard Additions)

SGS - Orlando uses the internal standard technique as an alternative to the MSA per SW846-6010C section 4.4.2. However, in certain circumstances MSA may be needed by some project specific requirements. SGS - Orlando may perform an MSA when sample matrix interference is confirmed through the post digestion spike process or may qualify the results in LIMS. SGS - Orlando will use a single addition method as described in SW846-7000B.

9.0 GLASSWARE CLEANING

All glassware must be washed with soap and tap water and then rinsed with 5 percent nitric acid. It must then be rinsed at least 3 times with DI water. Refer to SOP GN196, current revision for further information regarding glassware cleaning.

10.0 DOCUMENTATION REQUIREMENTS

Refer to the Laboratory Quality Assurance Manual for documentation requirements. All raw data is printed to .PDF format and archived to a backup server for long term storage.

11.0 SAFETY

The analyst must follow normal safety procedures as outlined in the SGS - Orlando Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor. Follow proper safety precautions when working with gas cylinders.

12.0 CALCULATIONS

For water samples, the following calculations must be used. Refer to the QC section for the calculations to be used for the QC samples.

Original sample concentration of metal (ug/l) =

$$\frac{\text{(conc. in the digestate (ug/l)) x (final digestate volume (ml))}}{\text{(initial sample volume (ml))}}$$

For soil samples, the following calculations must be used.

Concentration of the metal in the dry sample (mg/kg) =

$$\frac{\text{(conc. in the digestate (mg/l) x final digestate volume(L))}}{\text{(sample wt. (kg)) x (\% solids/100)}}$$

13.0 INSTRUMENT MAINTENANCE

Recommended periodic maintenance includes the items outlined below. All maintenance must be recorded in the instrument maintenance log.

13.1 Change the pump tubing as needed.

13.2 Clean the filter on the recirculating pump approximately once a month and dust off the power supply vents as needed.

13.3 Clean or replace the nebulizer, torch assembly, and injector tube as needed.

13.4 Change the sampler tip as needed.

13.5 Clean the recirculating pump lines and internal sock filter every 3 months or as needed.

13.6 Clean the radial view quartz surface weekly or more often if needed.

14.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

14.1 Pollution Prevention

Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids must be followed. All method users must be familiar with the waste management practices described in Section 14.2.

14.2 Waste Management

Individuals performing this method must follow established waste management procedures as described in the Sample and Laboratory Waste Disposal SOP SAM108, current revision. This document describes the proper disposal of all waste materials generated during the testing of samples.

15.0 GENERIC DEFINITIONS

15.1 Batch: A group of samples which are similar with respect to matrix and the testing procedures being employed and which are processed as a unit. A sample batch is limited to a maximum of 20 samples or 24 hours whichever comes first.

15.2 Blank Spike (BS): An analyte-free matrix spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. Blank Spike Recoveries are used to document laboratory performance for a given method. This may also be called a Laboratory Control Sample (LCS).

15.3 Continuing Calibration Verification (CCV): A check standard used to verify instrument calibration throughout an analytical run. A CCV must be analyzed at the beginning of the analytical run, after every 10 samples, and at the end of the run.

15.4 Holding Time: The maximum times that samples may be held prior to preparation and/or analysis and still be considered valid.

15.5 Initial Calibration (ICAL): A series of standards used to establish the working range of a particular instrument and detector. The low point must be at a level equal to or below the reporting level.

15.6 Initial Calibration Verification (ICV): A standard from a source different than that used for the initial calibration. A different vendor must be used whenever possible. The ICV is used to verify the validity of an Initial Calibration. This may also be called a QC check standard.

15.7 Matrix Spike (MS): A sample aliquot spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. The matrix spike recoveries are used to document the performance of a method in a given sample matrix.

15.8 Matrix Spike Duplicate (MSD): A replicate sample aliquot spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. The matrix spike recoveries are used to document the precision and performance of a method in a given sample matrix.

15.9 Method Blank (MB): An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is processed simultaneously with the samples through all the steps of the analytical procedure. The method blank is used to document contamination resulting from the analytical process.

15.10 Sample Duplicate (DUP): A replicate sample which is used to document the precision of a method in a given sample matrix.

15.11 Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical integrity of the sample.

16.0 METHOD PERFORMANCE

Method performance is monitored through the routine analysis of negative and positive control samples. These control samples include method blanks (MB), blank spikes (BS), matrix spikes (MS), and matrix spike duplicates (MSD). The MB and BS are used to monitor overall method performance, while the MS and MSD are used to evaluate the method performance in a specific sample matrix.

Blank spike, matrix spike, and matrix spike duplicate samples are compared to method defined control limits. Statistical control limits are stored in the LIMS for QA purposes only. Additionally, blank spike accuracy is regularly evaluated for statistical trends that may be indicative of systematic analytical errors.

17.0 GENERATION OF INTERFERING ELEMENT CORRECTION FACTORS

17.1 It is recommended that all IEC's be verified and updated approximately every 6 months or whenever instrument conditions change significantly. It is also recommended that elements with frequent high concentrations or with large IEC's should be checked more frequently.

17.2 Calculate the IEC correction factors and enter them into the method (refer to Thermo 6500 instrument manual). Calculate the correction factor using the equation shown below. This correction factor must be added to the correction factor already in place in the method for a given element.

$$\text{IEC} = \frac{\text{Concentration Result of the element with the interference}}{\text{Concentration result of the interfering element}}$$

17.3 Verify the new correction factors by reanalyzing the ICSA/ICSAB solutions and/or the SIC solutions or by reloading and recalculating the previously stored results. If the reanalysis is not within QC limits, make additional changes to the IEC factors and then re-verify both the individual and combined solution values.

17.4 Save and update the method.

17.5 Interfering element correction factors are saved as raw data along with the run printouts on a daily basis so that the IEC's for a given run are traceable.

TABLE 1: REPORTING LIMIT BY ELEMENT

Analyte	Water Reporting Limit (ug/L)	Soil Reporting Limit (mg/kg)	TCLP Reporting Limit (mg/L)/MCL
Tin	50	5	
Aluminum	200	20	
Antimony	5	1	
Arsenic	10	0.5	0.10 / 5.0
Barium	200	20	10 / 100
Beryllium	4	0.5	
Cadmium	5	0.4	0.05 / 1.0
Calcium	1000	500	
Chromium	10	1	0.10 / 5.0
Cobalt	50	5	
Copper	25	2.5	
Iron	300	10	
Lead	5	1	0.5 / 5.0
Magnesium	5000	500	
Manganese	15	1.5	
Nickel	40	4.0	
Potassium	5000	500	
Selenium	10	1	0.5 / 1.0
Silver	10	1	0.10 / 5.0
Sodium	5000	500	
Thallium	10	1	
Vanadium	50	5	
Zinc	20	2	
Molybdenum	50	2.5	
Strontium	10	0.5	
Titanium	10	0.5	

TABLE 2. THERMO 6500 ANALYSIS LINES

Element	Wavelength
Al	396.1
As	189.042
Ca	317.933
Fe	259.9
Mg	279.078
Mn	257.610
Pb	220.353
Se	196.026
Tl	190.864
V	292.402
Ag	328.068
Ba	455.4
Be	313.042
Cd	226.502
Co	228.616
Cr	267.716
Cu	324.753
K	766.491
Na	589.5
Ni	231.604
Sb	206.838
Zn	206.2
Mo	202.030
Sn	189.900
Sr	407.7
Ti	334.9

TABLE 3: LOW, MID AND HIGH STANDARD LEVELS

Element	Low	Mid	High
	ug/l	ug/l	ug/l
Al	10000	40000	80000
As	500	2000	4000
Ca	10000	40000	80000
Fe	10000	40000	80000
Mg	10000	40000	80000
Mn	500	2000	4000
Pb	500	2000	4000
Se	500	2000	4000
Tl	500	2000	4000
V	500	2000	4000
Ag	62.5	250	500
Ba	500	2000	4000
Be	500	2000	4000
Cd	500	2000	4000
Co	500	2000	4000
Cr	500	2000	4000
Cu	500	2000	4000
K	10000	40000	80000
Na	10000	40000	80000
Ni	500	2000	4000
Sb	500	2000	4000
Zn	500	2000	4000
Mo	500	2000	4000
Sn	500	2000	4000
Sr	500	2000	4000
Ti	500	2000	4000

TABLE 4: ICV STANDARD LEVELS

Element	Concentration
	ug/l
Al	40000
As	2000
Ca	40000
Fe	40000
Mg	40000
Mn	2000
Pb	2000
Se	2000
Tl	2000
V	2000
Ag	250
Ba	2000
Be	2000
Cd	2000
Co	2000
Cr	2000
Cu	2000
K	40000
Na	40000
Ni	2000
Sb	2000
Zn	2000
Mo	2000
Sn	2000
Sr	2000
Ti	2000

TABLE 5: CCV STANDARD LEVELS

Element	Concentration
	ug/l
Al	40000
As	2000
Ca	40000
Fe	40000
Mg	40000
Mn	2000
Pb	2000
Se	2000
Tl	2000
V	2000
Ag	250
Ba	2000
Be	2000
Cd	2000
Co	2000
Cr	2000
Cu	2000
K	40000
Na	40000
Ni	2000
Sb	2000
Zn	2000
Mo	2000
Sn	2000
Sr	2000
Ti	2000

TABLE 6: CRIA STANDARD LEVELS

Element	CRIA
	ug/l
Al	200
As	10
Ca	1000
Fe	300
Mg	5000
Mn	15
Pb	5
Se	5
Tl	10
V	50
Ag	10
Ba	200
Be	5
Cd	5
Co	50
Cr	10
Cu	25
K	5000
Na	5000
Ni	40
Sb	5
Zn	20
Mo	50
Sn	50
Sr	10
Ti	10

TABLE 7: BLANK SPIKE, MATRIX SPIKE AND MATRIX SPIKE DUPLICATE LEVELS

Element	Concentration
	ug/l
Al	27000
As	2000
Ca	25000
Fe	26000
Mg	25000
Mn	500
Pb	500
Se	2000
Tl	2000
V	500
Ag	50
Ba	2000
Be	50
Cd	50
Co	500
Cr	200
Cu	250
K	25000
Na	25000
Ni	500
Sb	500
Zn	500
Mo	500
Sn	500
Sr	500
Ti	500

TABLE 8: TYPICAL RUN SEQUENCE

BLANK
LOW
MID
HIGH
HIGH STD
ICV
ICB
CRIA
ICSA
ICSAB
CCV
CCB
MB
SB
SAMPLE1
DUPLICATE
SERIAL DILUTION
MATRIX SPIKE
MATRIX SPIKE DUPLICATE
POST DIGESTION SPIKE
SAMPLE2
SAMPLE3
CCV
CCB
SAMPLE4
SAMPLE5
SAMPLE6
SAMPLE7
SAMPLE8
SAMPLE9
SAMPLE10
SAMPLE11
SAMPLE12
SAMPLE13
CRIA CLOSING
ICSA CLOSING
ICSAB CLOSING
CCV
CCB

TABLE 9: ICSA SOLUTION LEVELS

Element	Concentration
	mg/l
Al	500
As	0
Ca	500
Fe	200
Mg	500
Mn	0
Pb	0
Se	0
Tl	0
V	0
Ag	0
Ba	0
Be	0
Cd	0
Co	0
Cr	0
Cu	0
K	0
Na	0
Ni	0
Sb	0
Zn	0
Mo	0
Sn	0
Sr	0
Ti	0

TABLE 10: ICSAB SOLUTION LEVELS

Element	Concentration
	mg/l
Al	500
As	1.0
Ca	500
Fe	200
Mg	500
Mn	0.5
Pb	1.0
Se	1.0
Tl	1.0
V	0.5
Ag	1.0
Ba	0.5
Be	0.5
Cd	1.0
Co	0.5
Cr	0.5
Cu	0.5
K	0
Na	0
Ni	1.0
Sb	1.0
Zn	1.0
Mo	1.0
Sn	1.0
Sr	1.0
Ti	1.0

TABLE 11: SINGLE ELEMENT INTERFERENCE CHECK SOLUTION (SIC) LEVELS

Element	Concentration
	mg/l
Al	500
As	0
Ca	500
Fe	200
Mg	500
Mn	0
Pb	0
Se	0
Tl	0
V	0
Ag	0
Ba	0
Be	0
Cd	0
Co	0
Cr	0
Cu	0
K	0
Na	0
Ni	0
Sb	0
Zn	0
Mo	0
Sn	0
Si	50
Sr	0
Ti	0

COLD VAPOR ANALYSIS OF MERCURY FOR WATER SAMPLES

Prepared by: David Metzgar III Date: 07/24/2019

Approved by: Svetlana Izosimova Date: 07/30/2019

Annual Review

Reviewed by: _____ Date: _____

Reviewed by: _____ Date: _____

Reviewed by: _____ Date: _____

Document Control

Issued to: QA Department Date: 07/30/2019

Issued to: Metals Date: * 07/30/2019

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Effective 7 days after "*" date

CONTROLLED COPY
DO NOT DUPLICATE

TITLE: COLD VAPOR ANALYSIS OF MERCURY FOR WATER SAMPLES

REFERENCES: EPA 245.1 Rev.3, 1994, SW-846 7470A, WV 47CSR32

INSTRUMENT SERIAL #: 2004 (HG4), 2019 (HG5)

WAVELENGTH: 253.7 nm

REVISED SECTIONS:
4.0 updated MDL procedure
7.0 added detail
7.8 added 10 percent HCL

1.0 SCOPE AND APPLICATION, SUMMARY

1.1 The method outlined in this SOP is based on EPA method 245.1 and SW846 7470A for waters. The types of samples that can be analyzed include drinking, surface and saline waters, as well as domestic and industrial wastes.

1.2 The mercury is reduced to the elemental state and aerated from the solution in a closed system. The mercury vapor passes through a cell in the light path of an atomic spectrophotometer, where the absorbance is measured as a function of mercury concentration.

2.0 PRESERVATION AND BOTTLEWARE

All samples should be preserved with nitric acid to a pH of <2 at the time of collection. All sample pH are checked in sample receiving and within the metals department. Samples that are received with a pH >2 must be preserved to pH <2 and held for 24 hours prior to metals digestion to dissolve any metals that absorb to the container walls. Refer to SOP SAM101, current revision for further instruction. Final pH of TCLP extracts are checked and recorded in SGS - Orlando Extractions Department. Please refer to TCLP (1311) fluid determination logbook and SPLP (1312) fluid determination logbook for further information. TCLP extracts received from SGS - Orlando Extractions Department are prepared as soon as possible, no longer than 24 hours from time of receipt. If precipitation is observed during the sample preparation process the sample(s) are immediately re-prepped on dilution until no precipitation is observed. Samples received for dissolved metals analysis should be filtered and preserved to pH<2 as soon as possible and held for 24 hours prior to digestion. Refer to SGS - Orlando Sample Filtration Logbook for further information regarding sample filtration and preservation. All bottleware used by SGS - Orlando is tested for cleanliness prior to shipping to clients. Bottleware analysis results must be < ½ RL to be acceptable. Refer to SOP SAM104, current revision for further instruction.

3.0 HOLDING TIME AND STORAGE

All samples should be prepared and analyzed within 28 days of the date of collection.

Aqueous samples do not require refrigeration.

4.0 REPORTING and METHOD DETECTION LIMITS

Please refer to SOP QA020, current revision for further information regarding MDL's.

4.1 Reporting Limit. The reporting limit for this method has been established at 0.0005 mg/l.

4.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

4.3 MDLs should be established for all appropriate methods using a solution spiked at approximately 2-10 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The samples used for the MDL must be prepared in at least three batches on three separate calendar dates and analyzed on three separate calendar days. If there are multiple instruments that will be assigned the same MDL, then the sample analyses must be distributed across all instruments. A minimum of 2 MDL's prepared and analyzed on different calendar days is required for each instrument. The same prepared extract may be analyzed on multiple instruments so long as the minimum requirement of seven preparations in at least three separate batches is maintained.

4.4 An MDL (LOD) check standard will be analyzed at the time of the MDL study and on a quarterly basis. The concentration of the MDL check standard should be 2-4 times the statistical MDL. This is a qualitative check; therefore, the analyte needs to be detected only. If the analyte is not detected, the concentration of the MDL check standard must be increased until the analyte is detected.

4.5 An LOQ check standard will be analyzed at the time of the MDL study and on a quarterly basis. The concentration of the LOQ check standard should be at the current method RL. LOQ check standard must recover within the methods blank spike requirements to be considered valid.

4.5 Compounds detected at concentrations between the RL and MDL are quantitated and qualified as estimated values and reported with either a "J" or "I" qualifier. Some program or project specifications may require that no values below the RL be reported.

5.0 INTERFERENCES

Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations of sulfide as sodium sulfide as high as 20 mg/l do not interfere with mercury recoveries when following this method. Copper concentrations > 10 mg/l may also interfere with mercury recoveries. Samples that are high in chloride such as seawater, brine and industrial effluent may require as much as 12.5 ml of additional permanganate.

Note: When chloride concentrations are high, hydroxylamine sulfate and stannous sulfate should be used in place of corresponding chlorides.

Finally, certain volatile organic materials will also absorb at this wavelength and can interfere. It can be determined if this type of interference is present by doing a preliminary run without reagents.

6.0 APPARATUS

6.1 A Leeman HYDRA AA II automated analyzer is used for all analysis. Currently there are two Hydra AA's in service at SGS - Orlando. Refer to the instrument manual for further details on this instrumentation.

6.2 Automatic repipettor (s).

6.3 Fisher Brand 0.45 micron (um) filter or equivalent. Filter lots are checked for cleanliness through the Method Blank process. All Method Blank analytical results must be <1/2 RL to be acceptable, if not, the contaminated lot must be identified and removed from laboratory use. Samples filtered through the contaminated filters must be re-filtered through acceptable filters.

6.4 Fisher Brand disposable 10 ml syringes or equivalent. Syringe lots are checked for cleanliness through the Method Blank process. All Method Blank results must be < ½ RL to be acceptable, if not, the contaminated lot must be identified and removed from laboratory use. Samples filtered through the contaminated syringes must be re-filtered through acceptable syringes.

6.5 Environmental Express Hot Block or equivalent capable of maintaining 90-95 ^{o}C.

6.6 Environmental Express digestion vessels or equivalent, 65ml capacity. Each Lot of digestion tubes comes with a Certificate of Analysis which demonstrates cleanliness as well as volume accuracy. Please refer to Digestion Tube Certificate Logbook for further information. Tube Lots are also checked through the Method Blank process. All Method Blank analytical results must be < ½ RL to be acceptable, if not, the contaminated lot must be identified and removed from laboratory use. Re-digestion is required for all samples prepared with the contaminated tube lot.

6.7 Class A volumetric pipette (s), flask (s), and cylinder (s)

6.8 Thermometer(s), capable of measuring a temperature of at least 125 ^{o}C, checked against NIST traceable thermometers. Refer to SOP QA002, current revision for further information.

6.9 Eppendorf Pipette (s) - Pipette (s) are checked daily for accuracy and to ensure they are in good working condition prior to use. Volumes are checked at 100% of maximum volume (nominal volume). Pipettes are checked within the metals department and results are stored electronically in the "Pipette Calibration Log". Refer to SOP QA006, current revision for further information regarding pipette calibration. BIAS: mean must be within 2% of nominal volume. Precision: RSD must be $\leq$ 1% of nominal volume based on three replicates.

6.10 Top Loader Balance (used to prepare reagents) – Capable of accurately weighing 0.01 g. Refer to SOP QA005, current revision for further information.

6.11 Data System

Microsoft Windows 7 Professional
Instrument software – HG4 - Leeman Labs Envy 1.9 sp1
Instrument software – HG5 - Leeman Labs Envy 2.0 sp0

6.11.1 A computer system interfaced to the Leeman Hydraa II that allows for the continuous acquisition and storage of all data obtained throughout the duration of the analytical run sequence.

6.11.2 Data is archived to a backup server for long term storage.

7.0 REAGENTS

All chemicals listed below are trace metal grade unless otherwise specified. Refer to Acid Certificate of Analysis logbook for Certificate of Analysis and compliance with the specifications of the grade listed. SGS - Orlando produces DI water to the specifications for the ASTM Type II standard designation based on the system manufacturer's performance specifications. The DI water is used exclusively for laboratory purposes. De-ionized (DI) water should be used whenever water is required. Refer to SOP QA037, current revision for more information regarding testing and monitoring. All standards and prepared reagents must be prepared every 6 months or before stock standard expiration date, whichever comes first, except as noted elsewhere in this SOP. Refer to Metals Electronic Standard Prep Logbook for further information. Some of the information included in the logbook is as follows: standard name, elements in mix, manufacturer, lot number, parent expiration date, acid matrix, stock concentration, volume of standard added, total volume, final prepared concentration, prep date, initials, MET number, and prepared standard expiration date.

7.1 Sulfuric acid, concentrated, trace metal grade

7.2 Nitric acid, concentrated, trace metal grade

7.3 Stannous chloride, reagent grade. To 400 ml of DI water, add 50 ml of concentrated Hydrochloric acid, and 50 g of stannous chloride. Dilute to 500 ml with DI water. Stannous sulfate may be used in place of stannous chloride. Stannous chloride is prepared daily. Lot number is recorded in Hg Digestion logbook.

7.4 Sodium chloride-hydroxylamine hydrochloride, reagent grade. Add 120 g of sodium chloride and 120 g of hydroxylamine hydrochloride to 1 liter of DI water. Mix well; hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.5 Potassium permanganate, reagent grade. Add 50 g of potassium permanganate to 1 liter of DI water and mix well.

Caution: Potassium permanganate is a strong oxidizing agent. Handle with care.

7.6 Potassium persulfate, reagent grade. Add 50.0 g of potassium persulfate to 1 liter of DI water and mix well.

Caution: Potassium persulfate is a strong oxidizing agent. Handle with care.

7.7 2 percent HCl Carrier Solution. 40 mls concentrated HCl, diluted to 2 liters with DI water. 2 percent HCL carrier solution is prepared daily. Lot number is recorded in Hg Digestion logbook.

7.8 10 percent HCL rinse solution. Add 100mls of concentrated HCL to final volume of 1 liter of DI water.

7.9 Mercury working standards. Mercury standard solutions are made from a purchased stock solution of 1000 ppm mercury.

7.9.1 10 ppm Hg solution. (Used to prepare 100ppb Mercury solution) Using a 10 ml class A volumetric pipette, add 10 ml of 1000 ppm stock to a 1.00 liter class A volumetric flask containing approximately 750 ml of DI water and 10 ml of concentrated nitric acid. Dilute to volume with DI water and mix well. This 10ppm standard must be prepared every six months.

7.9.2 100 ppb Hg solution. (Used to prepare calibration curve, CCV, CRI). Using a 10 ml class A volumetric pipette, add 10 ml of 10 ppm Hg solution to a 1.00 liter class A volumetric flask containing approximately 750 ml of DI water and 10 ml of concentrated nitric acid. Dilute to volume with DI water and mix well. This 100ppb standard must be prepared every month.

7.9.3 Second source working solutions are prepared at the same concentrations as the calibration standards listed above in sections 7.8.1 and 7.8.2 except they must be from a second source.

7.9.4 Daily working standards used in section 8.0 are prepared and digested daily using 100ppb standard solutions.

8.0 WATER DIGESTION AND ANALYSIS PROCEDURE

Below is a step-by-step procedure for the digestion and analysis of water samples for mercury.

8.1 Make up the standard curve as shown below. Clearly label each digestion vessel with the standard's ID. The standard ID's should be recorded in the Mercury Digestion Logbook.

ml of 100 ppb Hg solution	ml of DI water	Total µg/L of Hg
0.0	50	0.0
0.10	50	0.20
0.50	50	1.0
1.50	50	3.0
2.50	50	5.0
3.00	50	6.0

Dilute to the 50ml mark on the digestion vessel with DI water.

8.2 Make up the quality control samples as shown below. Make sure to clearly label each digestion vessel.

Sample ID	ml of 100ppb Hg solution	ml of DI water	Total µg/L of Hg
*Spike Blank	1.5	50	3.0
CCV	1.5	50	3.0
Low Check (CRI)	0.10	50	0.20
Method Blank	0.0	50	0.0
*ICV	1.5	50	3.0

Dilute to the 50ml mark on the digestion vessel with DI water.

Sample ID	ml of 100 ppb Hg solution	ml of sample	Total µg/L of Hg
*Matrix Spike	1.5	50	3.0 + sample
*Matrix Spike Dup	1.5	50	3.0 + sample
Duplicate		50	sample

Dilute to the 50ml mark on the digestion vessel with DI water.
*Use second source 100ppb solution.

8.3 Shake sample vigorously to ensure thorough mixing. Measure out 50 ml of each sample into a labeled digestion vessel. The sample may be measured by using a Class A graduated cylinder or by using the calibrated digestion tube. If no information is available about the level of mercury in the samples to be analyzed set up a 50 ml sample size. If information is available, select a sample size that will result in an analysis value near the

mid-range of the curve. For TCLP / SPLP samples, use a 5 ml initial volume. Record the volume used in the Mercury Digestion Logbook.

8.4 To all samples, QC and standards add the following reagents:

- 1.25 ml of concentrated nitric acid
- 2.5 ml of concentrated sulfuric acid
- 7.5 ml of permanganate solution
- 4.0 ml of persulfate solution

Swirl the samples well after each addition of reagent. More potassium permanganate solution may be required for some samples. Enough should be added so that the purple color persists for at least 15 minutes. Ensure that equal amounts of potassium permanganate are added to the standards and blanks.

8.5 Pre-heat the Hot Block to 90-95 degree C. Place the sample vessels in the Hot Block. Heat the samples for 2 hours, remove and cool to room temperature. Allow samples to stand quietly without manual agitation.

8.6 While the samples are digesting, begin setting up the Leeman HYDRA AA II mercury analyzer following the steps outlined below. Further details are available in the instrument manual.

8.6.1 Turn the Argon gas on. Check that the vent line is connected to the exhaust hood.

8.6.2 Inspect all pump tubing and replace if necessary. Put the tubing on the cassettes and attach to the pump head, making sure the cassette adjusters are properly adjusted to provide a smooth flow of sample and reagents. Place the fresh stannous chloride solution in the bottle. Fill the rinse bottle with 2 percent HCL carrier solution. Connect stannous chloride and HCL rinse lines.

8.6.3 Double click on the Envoy icon on the desktop. This will open the Envoy mercury analysis software. Click on the green and black arrow icon. This will start the pump, turn on the gas, and turn on the lamp.

8.6.4 Locate the “Sequence” tab at the bottom of the Envoy software page. Now click on “sequence” at the top of the page and click “new”. Type in the run sequence starting with the MB. After typing in the entire days run sequence click on the “Update” button. Click on “sequence” at the top of the page and choose “save”. Type in run sequence name as follows: Instrument-month-day-matrix-run number. (i.e. h40606w1).

8.6.5 Locate “Analysis” tab at bottom of Envoy page. Now click on “Analysis” at the top of the page and click “new”. Enter analysis dataset as follows: Instrument-month-day-matrix-run number (i.e. h40606w1).

8.6.6 Add 3 ml of hydroxylamine hydrochloride solution to each standard and sample and swirl until the solution has been completely decolorized before analyzing. Bring samples to a final volume of 50mls using DI water. If the sample (s) contain

particulate matter, it should be filtered (performed at the analytical bench), along with the method blank and blank spike through a 0.45 um syringe filter before analysis. Samples are now ready for analysis.

8.6.7 Calibration is performed by analyzing a series of 5 standards and a blank. All calibration curves must be determined from a linear calibration prepared in the normal manner using the established analytical procedure for the instrument. Refer to instrument manual for further detail. A correlation coefficient of $\geq$0.995 must be achieved, if not, analysis must be terminated, the problem corrected, and instrument re-calibrated. Calibration data is printed and included with each analytical data package. Click on the "Run sequence" icon. Instrument will start calibration. Once the calibration is complete the instrument will automatically accept the curve if correlation coefficient >0.995. The instrument will then proceed to analyze the High standard, ICV, ICB, CRI, CCV, and CCB. The calibration curve and all initial QC are compared to check tables set up in the software. If any standard fails the set criteria it will be flagged on the screen as to alert the analyst. The instrument will continue the analysis of the run sequence if all QC criteria has been met.

8.6.8 After analysis has been completed flush the entire system with 10% HCL, then DI water, and then allow to pump dry. Unclamp all tubing, turn off gas and lamp.

8.6.9 Raw data generation (PDF File)

Open the "PDF Creator" icon located on the desktop. Click on the green light, it will turn red. Go to the Envoy software. Click on the "Method" tab and then locate that days calibration curve. Click on print to PDF creator. Now go to the "Analysis" tab, click on "report" and "clear all." Click on "Load" and choose "Accutest" profile. Select all samples to be reported. Choose "report" as output. Next click on "Printer" and send to PDF creator. Leave the report title blank and click "OK". Now go back to the "PDF Creator" which should still be open on the desktop and click on "Document", "combine all." Click on the red light which should now turn green. Close the PDF creator. Go to the "Pdf shortcut" icon located on the desktop and rename .PDF to MAxxxx.pdf. Right click on MAxxxx.pdf, copy, then paste to the "Lims Data" icon on the desktop. Open the pdf file (MAxxxx.pdf) and print to metals printer. This will generate the raw data that will be included in the run package. Now close the pdf file and archive.

8.6.10 LIMS data generation

Choose "CSV" as output under the "Analysis" tab. Type in analysis dataset (h40606w1), no extension. Go to the "Export" shortcut located on the desktop. Locate analysis dataset (h40606w1.csv), right click on file and open with wordpad. Change Blank, 0.2ppb, 1.0ppb, 3.0ppb, 5.0ppb, and 6.0ppb to STD1 (STD1_1 for 245.1, STD1_2 for 7470A), STD2, STD3, STD4, STD5, and STD6. Remove all percent recoveries from the file and the save and close the file. Right click on the analysis dataset, copy/paste to "Lims Data" icon on desktop. If the run contains any errors an "error report" will be generated to the metals printer. Correct any

errors and re-send the file. Archive run sequence (.SEQ) and analysis dataset (.CSV) when done.

9.0 QUALITY CONTROL

All QC calculations should be done as outlined in the method. Please refer to scheduling sheets and/or project specific QAPP for further information regarding client specific QC requirements. Check with area supervisor or lab manager for any non-compliant quality control for further information.

9.1 Method Blank – An acceptable method blank or reagent blank must be analyzed with every batch of samples processed. The method blank must be less than one half the reporting limit. If the method blank is greater than one half the reporting limit, the samples associated with the contaminated blank shall be evaluated as to the best corrective action for each particular sample. This may include reanalyzing the samples, re-digesting and reanalyzing the samples, or qualifying the results with a "B" or "V" qualifier. **Note:** 245.1 Method Blanks associated with samples originated in West Virginia are evaluated to MDL (WV 47CSR32)

9.2 High Standard Check (for method 245.1 only) – The high calibration standard must be analyzed after the initial calibration has been performed. The results of the high standard check must agree within 5 percent of the true value for the analysis to be valid. If the high standard check fails criteria, a new HSTD or initial calibration must be performed and all samples must be re-analyzed.

9.3 Initial Calibration Verification – An initial calibration verification (ICV) sample must be analyzed after the initial calibration has been performed. This sample must be prepared at or near the midpoint of the initial calibration from a reference material independent from the initial calibration solution. The results of the ICV must agree within 10 percent of the true value for the analysis to be valid. For method 245.1 the ICV must agree within 5 percent of the true value for the analysis to be valid. If the ICV fails, a new ICV or initial calibration must be performed and all samples must be re-analyzed with an acceptable ICV.

9.4 Continuing Calibration Verification – If more than 10 samples are to be analyzed in a single day, a Continuing Calibration Verification sample prepared at or near the mid point of the initial calibration must be analyzed after every 10^{th} sample and at the end of the analytical run. The results of the initial CCV analysis must be within 10 percent of the true value to be considered valid. All subsequent CCV's must be within 20 percent of the true value to be considered valid. For method 245.1 the results of the initial CCV must be within 5 percent of the true value for the analysis to be valid. All subsequent CCV's must be within 10 percent of the true value to be considered valid. If the CCV fails, all samples analyzed after the first passing CCV must be reanalyzed.

9.5 Continuing Calibration Blank/Initial Calibration Blank – Analyze the Initial calibration blank solution at the beginning of each run and the continuing calibration blank after every tenth sample and at the end of the sample run. The ICB/CCB must be less than one half the reporting limit to be considered valid. The instrument blank may be failing the criteria due to

contamination or instrument drift. Samples associated with the failing blank shall be evaluated as to the best corrective action for each particular sample. This may include reanalyzing the samples bracketed by the failing blank, or qualifying the results with a "B" or "V" qualifier, or raising the reporting limit for all samples to greater than two times the background concentration.

9.6 Low Level Check Standard (CRI) – A standard prepared at the low calibration concentration should be prepared and analyzed at the beginning and end of each analytical run. The CRI should agree within 20 percent of the true value to be acceptable. If the initial CRI does not meet the acceptance criteria, the samples must be reanalyzed. If the closing CRI fails the criteria, the samples associated with the failing CRI shall be evaluated as to the best corrective action for each particular sample. This may include reanalyzing the samples associated with the CRI or qualifying the results in LIMS.

9.7 Blank Spike – A blank spike (BSP) or Laboratory Control Spike (LCS) should be prepared using DI water spiked at the midpoint of the calibration curve. The blank spike must be within 20 percent of the true value for the analysis to be considered valid. For method 245.1 the results of the BSP must be within 15 percent of the true value for the analysis to be valid. If the blank spike exceeds the acceptance criteria, the samples must be re-digested and reanalyzed. A blank spike is required for every 20 field samples or for each analysis batch. Statistical control limits are generated for LCS's for QA purposes only. Refer to section 15.0 of this SOP for further detail.

9.8 Duplicate - The laboratory must digest a duplicate for a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample must be assessed and must be $\leq$ 20 percent for sample results at or above the reporting limit. If the RPD is outside the 20 percent criteria the results must be qualified in LIMS. RPD's are also calculated in LIMS for sample results below the reporting limit. RPD's outside the 20 percent criteria are not considered failing and LIMS automatically footnotes these as "RPD acceptable due to low duplicate and sample concentrations."

9.9 Matrix Spike/Matrix Spike Duplicate/MSA – At least on Matrix Spike/Matrix Spike Duplicate pair must be prepared and analyzed with every 20 field samples. The MS/MSD recovery must agree within 30 percent of the true value for method 245.1 and within 20 percent of the true value for method 7470A. Relative standard deviation (RSD) for the MSD should be $\leq$ 20 percent. If the results of the MS/MSD are outside the acceptance criteria, the data should be footnoted as possible matrix effect. In certain circumstances the Method of Standard Additions (MSA) may be needed by some project specific requirements. SGS - Orlando may perform an MSA when sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards. If an MSA is not performed the results may be footnoted in LIMS. SGS - Orlando will use a single addition method as described in SW846-7000B.

9.10 When sample concentrations exceed the upper limit of the calibration curve, samples shall be diluted back into the calibration range and reanalyzed.

9.11 When preparing TCLP/SPLP samples, prepare an additional leachate blank and leachate blank spike from the extraction fluid used to extract the samples. See section 9.1 and 9.7 for acceptance criteria.

9.12 When preparing dissolved metals, an additional method blank must be prepared. The method blank must be filtered through the same filter media as the samples and then digested as usual. This is performed to ensure there is no cross contamination from the filter media into the samples. See section 9.1 for acceptance criteria.

9.13 Serial Dilution - For one sample per preparation batch, or whenever matrix interferences are suspected for a batch of samples, a serial dilution should be prepared. For the serial dilution, a 1:5 dilution should be made on the sample. The results of the 1:5 dilution should agree within 10 percent of the true value as long as the sample and the dilution result are greater than 10 times the method detection limit and/or greater than 50 times the IDL. If the dilution is not within 10 percent then a footnote must be entered into LIMS.

9.14 For each digestion batch of 20 samples (10 samples for method EPA 245.1), a serial dilution (performed at the analytical bench), a matrix spike (MS), a matrix spike duplicate (MSD), a duplicate (DUP), a blank spike (LCS), and a method blank should be prepared. Re-digestion is suggested for QC that does not meet the SGS - Orlando QC limits. The appropriate lab supervisor or lab manager will notify the analyst of samples that need re-digestion.

10.0 DOCUMENTATION REQUIREMENTS

All digestion information should be documented in the Sample Digestion Logbook. The information required includes the sample identification (including the sample bottle number), the initial sample volume, and the final sample volume, the acids used (including lot number and manufacturer), the spiking solutions used, the digestion vessel lot number, the observed temperature, corrected temperature, the thermometer ID, analyst's signature, the date of digestion, digestion start time, and digestion end time. The analyst should write additional information such as unusual sample characteristics and samples that need to be filtered (dissolved analysis) in the comment section. All raw data is printed to .PDF format and archived to a backup server for long term storage.

11.0 SAFETY

The analyst should follow normal safety procedures as outline in the SGS - Orlando Laboratory Safety Manual. Particular care should be observed in handling the strong acids and oxidizing agents. Safety glasses and lab coats should be worn at all times in the lab. Gloves should be worn when handling samples.

12.0 CALCULATIONS

Below are the calculations, which should be used for soil samples. The concentration of the sample in µg should be obtained from the linear calibration curve.

$$\textbf{Final concentration in mg/kg} = \frac{\textbf{Concentration of sample in µg}}{}$$

(Sample wt in g)(%solids/100)

Matrix Spike and Matrix Spike Duplicate Recovery:

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{Amount Spiked}} \times 100 = \text{matrix spike recovery}$$

Matrix Duplicate/Matrix Spike Duplicate Relative Percent Difference:

$$\frac{\text{(|Sample Result - Duplicate Result|) x 100}}{\text{(Sample Result + Duplicate Result)/2}} = \text{Duplicate RPD}$$

13.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

13.1 Pollution Prevention

Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids must be followed. All method users must be familiar with the waste management practices described in Section 13.2.

13.2 Waste Management

Individuals performing this method must follow established waste management procedures as described in the Sample and Laboratory Waste Disposal SOP SAM108, current revision. This document describes the proper disposal of all waste materials generated during the testing of samples.

14.0 GENERIC DEFINITIONS

14.1 Batch: A group of samples which are similar with respect to matrix and the testing procedures being employed and which are processed as a unit. A sample batch is limited to a maximum of 20 samples or 24 hours whichever comes first.

14.2 Blank Spike (BS): An analyte-free matrix spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. Blank Spike Recoveries are used to document laboratory performance for a given method. This may also be called a Laboratory Control Sample (LCS).

14.3 Continuing Calibration Verification (CCV): A check standard used to verify instrument calibration throughout an analytical run. A CCV must be analyzed at the beginning of the analytical run, after every 10 samples, and at the end of the run.

14.4 Holding Time: The maximum times that samples may be held prior to preparation and/or analysis and still be considered valid.

14.5 Initial Calibration (ICAL): A series of standards used to establish the working range of a particular instrument and detector. The low point should be at a level equal to or below the reporting level.

14.6 Initial Calibration Verification (ICV): A standard from a source different than that used for the initial calibration. A different vendor should be used whenever possible. The ICV is used to verify the validity of an Initial Calibration. This may also be called a QC check standard.

14.7 Matrix Spike (MS): A sample aliquot spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. The matrix spike recoveries are used to document the performance of a method in a given sample matrix.

14.8 Matrix Spike Duplicate (MSD): A replicate sample aliquot spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. The matrix spike recoveries are used to document the precision and performance of a method in a given sample matrix.

14.9 Method Blank (MB): An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is processed simultaneously with the samples through all the steps of the analytical procedure. The method blank is used to document contamination resulting from the analytical process.

14.10 Sample Duplicate (DUP): A replicate sample which is used to document the precision of a method in a given sample matrix.

14.11 Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical integrity of the sample.

15.0 METHOD PERFORMANCE

Method performance is monitored through the routine analysis of negative and positive control samples. These control samples include method blanks (MB), blank spikes (BS), matrix spikes (MS), and matrix spike duplicates (MSD). The MB and BS are used to monitor overall method performance, while the MS and MSD are used to evaluate the method performance in a specific sample matrix.

Blank spike, matrix spike, and matrix spike duplicate samples are compared to method defined control limits. Statistical control limits are stored in the LIMS for QA purposes only. Additionally,

blank spike accuracy is regularly evaluated for statistical trends that may be indicative of systematic analytical errors

16.0 GLASSWARE CLEANING

All glassware should be washed with soap and tap water, rinsed with 5 percent nitric acid solution, and then rinsed at least three times with DI water. Refer to SOP GN196, current revision for further information regarding glassware cleaning.

17.0 INSTRUMENT MAINTENANCE

Recommended periodic maintenance includes the items outlined below. All maintenance must be recorded in the instrument maintenance log.

17.1 Change the pump tubing weekly or as needed.

17.2 Clean the optical cell and lenses once per week or as needed.

17.3 Change the sampler tip as needed.

17.4 Inspect the liquid/gas separator, mixing coil, and all tubing connections once per week and replace as needed.

STANDARD OPERATING PROCEDURE FOR THE TOXICITY CHARACTERISTIC LEACHING OF VOLATILE ORGANICS (TCLP)

Prepared by: Norm Farmer Date: 08/25/18

Approved by: Mark Erstling Date: 08/25/18

Annual Review

Reviewed by: _____ Date: _____

Reviewed by: _____ Date: _____

Reviewed by: _____ Date: _____

Document Control

Issued to: QA Department Date: 09/13/18

Issued to: TCLP Prep Department Date: * _____

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Effective 7 days after "*" date

CONTROLLED COPY
DO NOT DUPLICATE

TITLE: STANDARD OPERATING PROCEDURE FOR THE TOXICITY CHARACTERISTIC LEACHING OF VOLATILE ORGANICS (TCLP)

REFERENCES: SW846 1311

REVISED SECTIONS: 1.2.2 and 7.5.11.2, reformatted SOP

1.0 SUMMARY, SCOPE AND APPLICATION

1.1 Summary

For liquid and aqueous samples containing less than 5.0% solids, the sample is filtered via ZHE through TCLP filter paper and the filtrate is defined as the TCLP leachate. The leachate can then be analyzed for volatile organics.

For solid samples, the solid portion of the sample is extracted via ZHE by adding extraction fluid equal to 20 times the weight of the sample and rotating the sample for 18 hours at 30 rpm. After leaching, the sample is filtered through TCLP filter paper. The leachate can then be analyzed for volatile organics.

1.2 Scope and Application

This procedure is applicable to samples submitted for TCLP volatile analysis.

1.2.1 Volatiles by 8260

1.2.2 Volatile TPH by 8015

2.0 DISCUSSION AND COMMENTS

This procedure is adapted from SW-846 method 1311. The method utilizes a zero headspace extraction (ZHE) vessel and rotary agitation device to evaluate the presence and mobility of volatile analytes. It is not applicable for evaluating the mobility of semivolatile organics or metals analytes.

3.0 PRESERVATION AND HOLDING TIMES

3.1 Preservation

3.1.1 Samples shall be collected in amber glass bottles with Teflon lined caps. One-liter bottles are recommended for aqueous samples and 300ml jars are recommended for solid samples. Samples should be collected with minimal headspace.

3.1.2 The samples must be protected from light and refrigerated at ≤ 6°C from the time of collection until leaching.

3.1.3 Samples for TCLP analysis should not be chemically preserved prior to leaching.

3.1.4 TCLP Leachates for volatile organics must be protected from light and stored at ≤ 6°C from the time of filtration until analysis.

3.2 Holding Time

3.2.1 Samples submitted for the analysis of volatile organics must be leached within 14 days of collection.

3.2.2 Leachates for volatile organics must be analyzed by the appropriate procedure within 14 days of filtration.

4.0 DEFINITIONS

4.1 Batch: A group of samples which are similar with respect to matrix and the testing procedures being employed and which are processed as a unit. A sample batch is limited to a maximum of 20 samples.

4.2 Blank Spike (BS): An analyte-free matrix spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. Blank Spike Recoveries are used to document laboratory performance for a given method. This may also be called a Laboratory Control Sample (LCS).

4.3 Holding Time: The maximum times that samples may be held prior to preparation and/or analysis and still be considered valid.

4.4 Matrix Spike (MS): A sample aliquot spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. The matrix spike recoveries are used to document the bias of a method in a given sample matrix.

4.5 Matrix Spike Duplicate (MSD): A replicate sample aliquot spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. The matrix spike duplicate recoveries are used to document the precision and bias of a method in a given sample matrix.

4.6 Method Blank (MB): An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is processed simultaneously with the samples through all the steps of the analytical procedure. The method blank is used to document contamination resulting from the analytical process.

4.7 Leachate Blank Spike (LBS): An aliquot of TCLP fluid spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. Leachate blank spike recoveries are used to document laboratory

performance for a given method. This may also be called a Laboratory Control Sample (LCS).

4.8 Leachate Blank (LB): An aliquot of TCLP fluid to which all reagents are added in the same volumes or proportions as used in sample processing. The leachate blank is processed simultaneously with the samples through all the steps of the analytical procedure. The Leachate blank is used to document contamination resulting from the analytical process.

4.9 Leachate Spike (LS): A sample leachate aliquot spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. The leachate spike recoveries are used to document the bias of a method in a given sample matrix.

4.10 Sample Duplicate (DUP): A replicate sample which is used to document the precision of a method in a given sample matrix.

4.11 Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical integrity of the sample.

4.12 Surrogate: An organic compound which is similar to the target analyte(s) in chemical composition and behavior, but which is not normally found in environmental samples. Surrogates are used to measure the purge efficiency.

5.0 REAGENTS

5.1 Reagent water – distilled or deionized - free of interferences

5.2 Sodium Hydroxide, 10.0N Fisher brand or equivalent

5.3 Glacial Acetic Acid, Reagent Grade

5.4 Extraction Fluid #1: Add 57 ml of glacial acetic acid and 64.3 ml of 10.0N sodium hydroxide to a 1000ml graduated cylinder and dilute to 1 liter with reagent water. Transfer to a PTFE lined carboy. Using a 1000ml graduated cylinder, transfer an additional 9 liters of reagent water to the carboy. Mix thoroughly. This will prepare 10 liters of Fluid #1. The preparation of all TCLP fluids must be logged in the Organics Reagent Logbook and the pH must be verified prior to use. The pH of this solution should be 4.93 $\pm$ 0.05.

NOTE: If the pH of the fluid is out of range, remake the fluid.

5.5 Buffer solution at pH 2, pH 4, pH 7 and pH 10. Commercially available solutions that have been validated by comparison to NIST standards are recommended for routine use. All buffers must be labeled on receipt and after opening. Buffer solutions must be refreshed at least weekly. **When analyzing samples from West Virginia the buffers must be refreshed on the day of use.**

6.0 GLASSWARE AND APPARATUS

6.1 Agitation apparatus – Environmental Express, Millipore Corp., or equivalent. Must be capable of rotating the extraction vessels in an end-over-end fashion at 30 ± 2 rpm.

6.2 Zero Headspace Extraction (ZHE) Vessels – Millipore Corp., or equivalent. The vessel should have an internal volume of 500 ml and be able to accommodate a 90 mm filter. The vessel must be gas tight and free of organic contaminants.

ZHE vessels must be leak tested prior to being placed into service. Additional leak testing should be performed whenever a loss of pressure during an extraction is observed. To leak test an extractor, pressurize the ZHE to 50 psi and allow it to stand unattended for one hour, and recheck the pressure.

6.2.1 If pressure is lost, check all fittings and o-rings. Replace any worn o-rings and repeat the leak test procedure.

6.2.2 If the pressure still does not hold at 50 psi, then pressurize the extractor to 10 psi and allow it to stand unattended for one hour and recheck the pressure. If it does not hold at 10 psi, the ZHE must be removed from all service until the problem is resolved.

6.2.3 If the ZHE will hold pressure at 10 psi and can maintain a filtering pressure of 50 psi when gas pressure is applied, then it can be used for extractions. Notify the Department Supervisor that further maintenance is required on this extractor.

6.3 Filtration device – Millipore Corp.142 mm, or equivalent, capable of exerting pressures of up to 50 psi (for %solids evaluation).

6.4 Fluid metering pump – Environmental Express Model TP1200, or equivalent

6.5 Filters – Environmental Express or equivalent, 0.7um glass fiber, 90 mm diameter.

6.6 VOA Vials – 40ml

6.7 Tedlar Bags

6.8 Luer Tip Syringe – 50 to 60 ml capacity.

6.9 Teflon Tubing

6.10 pH meter - capable of reading ± 0.05 pH units

6.11 Balance - capable of weighing ± 0.01 g

6.12 Graduated cylinders – 100ml, 250ml, and 1000ml

6.13 PTFE lined 20 liter carboy

6.14 Thermometer, calibrated against an NIST traceable thermometer

7.0 PROCECDURE

7.1 The preparation of all samples must be documented. See Section 8.1 for the various logbooks and prep sheets that are required for this method. The prep sheet will include such items as: sample ID, bottle number, initial volume, final volume, pHs, lot numbers, batch numbers, and leachate dates and times.

The extraction technician is responsible for filling out all the required information. A copy of the prep sheet will be submitted to the analyst with the leachates. The leaching start date and time are entered into LIMS.

7.2 Determination of Percent Solids

7.2.1 If the sample will obviously yield no liquid when subjected to pressure filtration, proceed to Section 7.5.

7.2.2 If the sample is liquid or mixed-phase (solid and liquid), proceed as follows. **NOTE:** If the sample appears to contain an organic liquid phase, notify the Department Supervisor. It is recommended that samples containing organic phases be analyzed as “totals” instead of TCLP.

7.2.3 Pre-weigh the filter and container that will receive the filtrate. Document all weights in the TCLP_SPLP Description Log.

7.2.4 Assemble the filtering apparatus as per the manufacturer's instructions.

7.2.5 Transfer a 100-gram aliquot of the sample to a beaker and record the weight. If a 100-gram aliquot is not available, inform the Department Supervisor.

7.2.6 Quantitatively transfer the sample aliquot to the filter apparatus. Slurries may be allowed to settle, and the liquid portion filtered prior to transferring the solid portion of the sample. **NOTE**: If sample material has adhered to the sample container, obtain the weight of this residue and subtract from the total weight of the sample.

7.2.7 Complete the assembly of the filtration device, and gradually apply pressure until fluid is expelled or 10 psi is obtained. If no fluid is expelled, gradually increase the pressure in 10 psi increments to a maximum of 50 psi. If no fluid is expelled in any 2-minute period, stop the filtration. Shut off the pressurizing gas and vent the filtration system using the top vent.

CAUTION: Do not remove flange clamps while system is pressurized! Serious injury may result.

NOTE: Instantaneous application of high pressure can cause the filter to clog prematurely.

7.2.8 The material in the filtration apparatus is defined as the solid phase.

NOTE: Some high viscosity liquids (oils, paints) will not filter under these circumstances. The material remaining within the filtration device is defined as the solid phase.

NOTE: If the sample appears to contain an organic liquid phase, notify the Department Supervisor. It is recommended that samples containing organic phases be analyzed as "totals" instead of TCLP.

7.2.9 Remove the solid phase of the sample and the filter from the filtration apparatus. If there is a noticeable amount of filtrate entrained in the filter, then dry at 100 °C ± 20 until two successive readings yield the same value within ±1%. Record the final weight.

7.2.10 Determine the percent solids as follows:

$$\% \text{ solids} = \frac{(W - F) \times 100}{T}$$

W = Weight of sample remaining on filter
F = Weight of filter
T = Initial weight of sample used

7.2.11 If the sample contains <5.0% solids, the filtrate is defined as the sample leachate.

NOTE: This aliquot can NOT be used for the analysis of Volatile Organics. Proceed to Section 7.5.

7.3 Determination of Particle Size

7.3.1 Evaluate the solid portion of the sample for particle size. If the solid portion of sample has a surface area equal to or greater than 3.1 cm^2/gram, then the sample does not require particle size reduction. This would apply to samples such as paper or rags.

7.3.2 Alternatively, if the solid portion of the sample is smaller than 1 cm in its narrowest dimension (i.e. is capable of passing through a 9.5 mm sieve), then the sample does not require particle size reduction.

7.3.3 If the sample does not meet the particle size criteria listed above, then prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the sample. This should be performed as quickly as possible in order to minimize the amount of volatile analytes that may be lost.

7.3.4 Document the sample description and any particle size reduction in the TCLP_SPLP Description Log.

7.4 Determination of Extraction Fluid

Samples submitted for the analysis of volatile organics by TCLP are always extracted with Fluid #1.

See Section 7.4.1 of OP040 for pH meter calibration.

7.5 Zero Headspace Extraction

7.5.1 Percent solids is 100%.

7.5.1.1 If the sample is 100% solid, weigh out a 10 to 25 gram aliquot and quickly transfer to the ZHE. Record the weight to ± 0.1 gram on the TCLP_SPLP ZHE Sample Prep Sheet.

7.5.1.2 Insert the filter and screens. Seal the vessel. Connect the gas supply to the lower fitting on the ZHE. Close the lower vent.

7.5.1.3 Apply 10 to 15 psi of pressure to the ZHE. Slowly open the top valve to expel any air from the ZHE. Slowly increase the pressure to keep the piston moving. DO NOT EXCEED 50 PSI.

7.5.1.4 Once the piston will no longer move, close the top valve.

7.5.1.5 Add 20 times the sample weight of extraction fluid to a graduated cylinder. Attach the pump and the transfer line to the ZHE.

7.5.1.6 Disconnect the gas supply from the lower ZHE fitting and open the lower vent.

7.5.1.7 Open the top valve to the transfer line and then turn on the pump. Transfer the fluid to the ZHE. After the fluid has been transferred, close the top valve and remove the transfer line.

7.5.1.8 Close the lower vent and reattach the gas supply line. Pressurize the ZHE to 5-10 psi. Disconnect the gas supply line.

7.5.1.9 Rotate the ZHE 2-3 times. Open the top valve and expel any residual headspace. Stop at the first sign of liquid. Disconnect the gas supply line.

7.5.1.10 Check the ZHE carefully for leaks and make sure that the pressure is holding to within 2 psi of the initial pressure. If not, discard the sample and set up a new aliquot in a different ZHE. Record the initial pressure on the TCLP_SPLP ZHE Prep Sheet. Proceed to section 7.5.4.

7.5.2 Percent solids is <5.0%.

7.5.2.1 If the waste contains <5.0% solids, transfer at least 200ml of sample to the zero headspace extractor (ZHE).

7.5.2.2 Insert the filter and screens. Seal the vessel. Connect the gas supply to the lower fitting on the ZHE. Close the lower vent.

7.5.2.3 Apply 10 to 15 psi of pressure to the ZHE. Slowly open the top valve to expel any air from the ZHE. At the first appearance of any liquid, close the valve.

7.5.2.4 Attach a 50 ml Luer tip syringe to the ZHE. Open the valve to expel approximately 50 ml of filtrate. If the flow stops, gradually increase the gas pressure. Once you have collected 50 ml of filtrate, close the top valve.

7.5.2.5 Transfer the filtrate to a 40 ml VOA vial and cap the vial. Make sure that there is no headspace in the vial. Repeat the process to obtain three vials of filtrate. Store at ≤ 6°C until analysis. Proceed to section 7.5.11.

7.5.3 Mixed phase samples

7.5.3.1 If the sample is mixed-phase (solid and liquid), proceed as follows. **NOTE:** If the sample appears to contain an organic liquid phase, notify the Department Supervisor. It is recommended that samples containing organic phases be analyzed as "totals" instead of TCLP.

7.5.3.2 Charge the ZHE with enough sample to obtain 10-25 grams of solid using the formula shown below:

$$\text{Grams of Solid} = \frac{(\text{Grams of Total Sample}) \times (\%\ \text{solids})}{100}$$

7.5.3.3 Insert the filter and screens. Seal the vessel. Connect the gas supply to the lower fitting on the ZHE. Close the lower vent.

7.5.3.4 Apply 10 to 15 psi of pressure to the ZHE. Slowly open the top valve to expel any air from the ZHE. Slowly increase the pressure to keep the piston moving. At the first appearance of any liquid, close the valve.

7.5.3.5 Attach a 50 ml Luer tip syringe to the ZHE. Open the valve to expel the liquid phase. If the flow stops, gradually increase the gas pressure to a maximum of 50 psi. Once you have collected the liquid phase, close the top valve.

7.5.3.6 Transfer the liquid phase to a Tedlar bag or a 40 ml VOA vial. Make sure that there is no headspace in the vial.

7.5.3.7 Add 20 times the sample weight of extraction fluid into a graduated cylinder. Attach the pump and the transfer line to the ZHE.

7.5.3.8 Disconnect the gas supply from the lower ZHE fitting and open the lower vent.

7.5.3.9 Open the top valve to the transfer line and then turn on the pump. Transfer the fluid to the ZHE. After the fluid has been transferred, close the top valve and remove the transfer line.

7.5.3.10 Close the lower vent and reattach the gas supply line. Pressurize the ZHE to 5-10 psi. Disconnect the gas supply line.

7.5.3.11 Rotate the ZHE 2-3 times. Open the top valve and expel any residual headspace. Stop at the first sign of liquid. Disconnect the gas supply line.

7.5.3.12 Check the ZHE carefully for leaks and make sure that the pressure is holding to within 2 psi of the initial pressure. If not, discard the sample and set up a new aliquot in a different ZHE. Record the initial pressure on the TCLP_SPLP ZHE Prep Sheet. Proceed to section 7.5.4.

7.5.4 Rotate at 30 ±2 rpm. Make sure to measure and record the rotation rate and tumbler ID on the TCLP_SPLP ZHE Sample Prep Sheet. Allow the extraction to proceed for 18 ± 2 hrs.

NOTE: The temperature of the extraction room must be 23 ± 2 °C during the extraction period. Record the temperature on TCLP_SPLP ZHE Sample Prep Sheet. Use a Hi/Lo thermometer to monitor the room temperature through out the extraction period.

7.5.5 After the leaching period has elapsed, remove the extraction vessels from the rotary agitator and allow them to settle.

7.5.6 Check and record the pressure of each ZHE on the TCLP_SPLP ZHE Prep Sheet. If the pressure has dropped by more than 10 psi, the samples should be discarded and reprepped.

7.5.7 Attach a 50 ml Luer tip syringe to the ZHE. Connect the gas supply to the lower fitting on the ZHE. Open the top valve to expel approximately 50 ml of filtrate. If the flow stops, gradually increase the gas pressure (DO NOT EXCEED 50 PSI). Once you have collected 50 ml of filtrate, close the top valve.

Transfer the filtrate to a 40 ml VOA vial and cap the vial. Make sure that there is no headspace in the vial. Repeat the process to obtain three vials of filtrate. Store at ≤ 6°C until analysis.

7.5.8 Alternatively, connect one end of the Teflon tubing to the ZHE. Place the other end in a 40 ml VOA vial. Connect the gas supply to the lower fitting on the ZHE. Open the top valve to transfer the filtrate to the VOA vial. If the flow stops, gradually increase the gas pressure (DO NOT EXCEED 50 PSI). Once you have completely filled the VOA vial, close the top valve.

Cap the vial. Make sure that there is no headspace in the vial. Repeat the process to obtain three vials of filtrate. Store at ≤ 6°C until analysis.

7.5.9 If a compatible liquid was obtained in Section 7.5.3.6, combine the liquids at this time. It may be easier to transfer the initial filtrate and the final leachate to a Tedlar bag for mixing.

7.5.10 If the liquids are not compatible, record the total volume of the expelled liquid in the sample description logbook and submit both fractions for analysis. Notify the Department Supervisor.

NOTE: Department Supervisor will notify the Project Manager to determine if the phases are to be mathematically combined as in Section 7.5.13, or to be report separately.

7.5.11 Aliquot the leachate for the necessary analyses. Listed below are the minimum quantities required for analysis. Additional aliquots will be needed for QC samples.

7.5.11.1	Volatiles by 8260	3 x 40ml
7.5.11.2	Volatile TPH by 8015	3 x 40ml

7.5.12 All aliquots for volatile organics are transferred to 40 ml VOA vials and stored at ≤ 6°C until analysis.

7.5.13 If individual phase are analyzed separately (see 7.5.10) conduct the appropriate analysis and combine the results mathematically by using the following formula:

Final Analyte Conc. = [(V1*C1)+(V2*C2)] / (V1+V2)

V1 = The volume of the first phase (l)
C1 = The conc. of the analyte of concern in the first phase (mg/l)
V2 = The volume of the second phase (l)
C2 = The conc. of the analyte of concern in the second phase (mg/l)

8.0 DOCUMENTATION

8.1 Documentation for this analysis is quite extensive. At minimum the following logbooks or prep sheets must be filled out completely.

8.1.1 TCLP_SPLP Description Log

8.1.2 TCLP_SPLP ZHE Sample Prep Sheet

8.1.3 ZHE Tracking Log

8.1.4 Organics Reagent Log

8.2 For every 20 extractions performed in an extraction vessel, a leachate blank must be performed using that vessel. Document this in the ZHE Tracking Log.

8.3 For each original matrix type extracted, (soil, water, sludge, etc.) a leachate spike must be performed. Various unique matrices may require their own leachate spikes.

9.0 QUALITY ASSURANCE, QUALITY CONTROL AND METHOD PERFORMANCE

9.1 An extraction batch is defined as samples of a similar matrix that are prepared for a particular parameter. The batch size is limited to 20 samples. A batch may be held open for up to 6 hours; however, samples should not be added after the QC set has been completed. **NOTE:** All samples and QC samples must leached for the required amount of time.

9.2 A leachate blank (LB) and sample duplicate (DUP) must be leached with each batch of samples.

9.3 All spiking for the matrix spike (MS) and matrix spike duplicate (MSD), leachate spike (LS), and leachate blank spike (LBS) occurs after filtration.

9.4 Method performance is monitored through the routine analysis of negative and positive control samples. Leachate blank spikes and matrix spikes are not applicable to the leaching portion of this test; however, they will be used later to assess the purge efficiency of the specific methods performed on the leachate.

9.5 A sample duplicate is used to assess method precision. Sample duplicate %RPD is compared to method defined control limits. Control limits are stored in the LIMS.

10.0 SAFETY AND WASTE DISPOSAL

10.1 Safety

10.1.1 Safety glasses, gloves and lab coats should be worn when handling acids, samples, standards or solvents.

10.1.2 Perform all filtration in a fume hood.

10.1.3 Material Safety Data Sheets (MSDS) or Safety Data Sheets (SDS) are available for all reagents and solvents used in the lab. Technicians should review the MSDS or SDS prior to using any new reagents or solvents.

10.2 Waste Disposal

10.2.1 The TCLP filter and remaining sample is placed in a waste container.

10.2.2 Extra leachate is rinsed down the drain with large amounts of water.

10.2.3 Waste soil from the homogenizing process should be place in the “soil waste” container. **NOTE:** Waste soil from foreign soils must follow “foreign soil” disposal requirements.

11.0 REFERENCES

SW-846 Method 1311, Rev. 0, 07/92

SW-846 Method 1312, Rev. 0, 09/94

STANDARD OPERATING PROCEDURE FOR THE TOXICITY CHARACTERISTIC LEACHING OF SEMIVOLATILE ORGANICS AND METALS (TCLP)

Prepared by: Norm Farmer Date: 12/17/18

Approved by: Mark Erstling Date: 12/19/18

Annual Review

Reviewed by: _____ Date: _____

Reviewed by: _____ Date: _____

Reviewed by: _____ Date: _____

Document Control

Issued to: QA Department Date: 12/24/18

Issued to: Organics Prep Department Date: * 01/28/19

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Issued to: _____ Date: _____

Effective 7 days after "*" date

CONTROLLED COPY
DO NOT DUPLICATE

TITLE: STANDARD OPERATING PROCEDURE FOR THE TOXICITY CHARACTERISTIC LEACHING OF SEMIVOLATILE ORGANICS AND METALS (TCLP)

REFERENCES: SW846 1311

REVISED SECTIONS: 6.2 and reformatted SOP

1.0 SUMMARY, SCOPE AND APPLICATION

1.1 Summary

For liquid and aqueous samples containing less than 0.5% solids, the sample is filtered through TCLP filter paper and the filtrate is defined as the TCLP leachate. The leachate can then be analyzed for semivolatile organics and metals.

For solid samples, the solid portion of the sample is extracted by adding extraction fluid equal to 20 times the weight of the sample and rotating the sample for 18 hours at 30 rpm. The extraction fluid used is based on the alkalinity of the solid portion of the sample. After leaching, the sample is filtered through TCLP filter paper. The leachate can then be analyzed for semivolatile organics and metals.

1.2 Scope and Application

This procedure is applicable to samples submitted for TCLP semivolatile analysis and/or TCLP metals analysis.

1.2.1 Metals by 6010

1.2.2 Mercury by 7470

1.2.3 Semivolatiles by 8270

1.2.4 Pesticides by 8081

1.2.5 Herbicides by 8151

1.2.6 Extractable TPH by 8015

2.0 DISCUSSION AND COMMENTS

This procedure is adapted from SW-846 method 1311. The method utilizes an extraction bottle and rotary agitation device to evaluate the presence and mobility of semivolatile analytes and metals. It is not applicable for evaluating the mobility of volatile analytes.

3.0 PRESERVATION AND HOLDING TIMES

3.1 Preservation

3.1.1 Samples shall be collected in amber glass bottles with Teflon lined caps. One-liter bottles are recommended for aqueous samples and 300ml jars are recommended for solid samples. Liquid samples for the analysis of metals only may be collected in HDPE bottles.

3.1.2 The samples must be protected from light and refrigerated at ≤ 6°C from the time of collection until leaching.

3.1.3 Samples for TCLP analysis should not be chemically preserved prior to leaching. After filtration, the TCLP leachate for metals should be preserved to a pH <2 with nitric acid unless the leachates will be digested immediately.

3.1.4 TCLP Leachates for semivolatile organics must be protected from light and stored at ≤ 6°C from the time of filtration until extraction.

3.2 Holding Time

3.2.1 Samples submitted for the analysis of semivolatile organics including pesticides and herbicides must be leached within 14 days of collection.

3.2.2 Samples submitted for the analysis of mercury must be leached within 28 days of collection.

3.2.3 Samples submitted for the analysis of metals (except mercury) must be leached within 180 days of collection.

3.2.4 Leachates for semivolatile organics must be extracted by the appropriate procedure within 7 days of filtration.

4.0 DEFINITIONS

4.1 Batch: A group of samples which are similar with respect to matrix and the testing procedures being employed and which are processed as a unit. A sample batch is limited to a maximum of 20 samples.

4.2 Blank Spike (BS): An analyte-free matrix spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. Blank Spike Recoveries are used to document laboratory performance for a given method. This may also be called a Laboratory Control Sample (LCS).

4.3 Holding Time: The maximum times that samples may be held prior to preparation and/or analysis and still be considered valid.

4.4 Matrix Spike (MS): A sample aliquot spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. The matrix spike recoveries are used to document the bias of a method in a given sample matrix.

4.5 Matrix Spike Duplicate (MSD): A replicate sample aliquot spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. The matrix spike duplicate recoveries are used to document the precision and bias of a method in a given sample matrix.

4.6 Method Blank (MB): An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is processed simultaneously with the samples through all the steps of the analytical procedure. The method blank is used to document contamination resulting from the analytical process.

4.7 Leachate Blank Spike (LBS): An aliquot of TCLP fluid spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. Leachate blank spike recoveries are used to document laboratory performance for a given method. This may also be called a Laboratory Control Sample (LCS).

4.8 Leachate Blank (LB): An aliquot of TCLP fluid to which all reagents are added in the same volumes or proportions as used in sample processing. The leachate blank is processed simultaneously with the samples through all the steps of the analytical procedure. The Leachate blank is used to document contamination resulting from the analytical process.

4.9 Leachate Spike (LS): A sample leachate aliquot spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. The leachate spike recoveries are used to document the bias of a method in a given sample matrix.

4.10 Sample Duplicate (DUP): A replicate sample which is used to document the precision of a method in a given sample matrix.

4.11 Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical integrity of the sample.

4.12 Surrogate: An organic compound which is similar to the target analyte(s) in chemical composition and behavior, but which is not normally found in environmental samples. Surrogates are used to measure the extraction efficiency.

5.0 REAGENTS

5.1 Reagent water – distilled or deionized - free of interferences

5.2 Hydrochloric Acid, 1.0N Fisher brand or equivalent

5.3 Sodium Hydroxide, 10.0N Fisher brand or equivalent

5.4 Glacial Acetic Acid, Reagent Grade

5.5 Extraction Fluid #1: Add 57 ml of glacial acetic acid and 64.3 ml of 10.0N sodium hydroxide to a 1000ml graduated cylinder and dilute to 1 liter with reagent water. Transfer to a PTFE lined carboy. Using a 1000ml graduated cylinder, transfer an additional 9 liters of reagent water to the carboy. Mix thoroughly. This will prepare 10 liters of Fluid #1. The preparation of all TCLP fluids must be logged in the Organics Reagent Logbook and the pH must be verified prior to use. The pH of this solution should be 4.93 $\pm$ 0.05.

NOTE: If the pH of the fluid is out of range, remake the fluid.

5.6 Extraction Fluid #2: Add 57 ml of glacial acetic acid to a 1000ml graduated cylinder and dilute to 1 liter with reagent water. Transfer to a PTFE lined carboy. Using a 1000ml graduated cylinder, transfer an additional 9 liters of reagent water to the carboy. Mix thoroughly. This will prepare 10 liters of Fluid #2. The preparation of all TCLP fluids must be logged in the Organics Reagent Logbook and the pH must be verified prior to use. The pH of this solution should be 2.88 $\pm$ 0.05.

NOTE: If the pH of the fluid is out of range, remake the fluid.

5.7 Buffer solution at pH 2, pH 4, pH 7 and pH 10. Commercially available solutions that have been validated by comparison to NIST standards are recommended for routine use. All buffers must be labeled on receipt and after opening. Buffer solutions should be refreshed weekly. **When analyzing samples from West Virginia the buffers must be refreshed on the day of use.**

6.0 GLASSWARE AND APPARATUS

6.1 Agitation apparatus – Environmental Express, Millipore Corp., or equivalent. Must be capable of rotating the extraction vessels in an end-over-end fashion at 30 $\pm$ 2 rpm.

6.2 Extraction Vessels – 2.2 liter PTFE coated HDPE bottles OR 2.2 liter Amber glass bottles. Bottles must have enough volume for the 100 gram sample and 2.0 liters of leaching fluid.

6.3 Filtration device - Millipore Corp.142 mm, or equivalent, capable of exerting pressures of up to 50 psi

6.4 Filters – Environmental Express or equivalent, 0.7um glass fiber, 142 mm diameter. Filters are acid washed by the manufacturer.

6.5 pH meter - capable of reading $\pm$ 0.05 pH units

6.6 Balance - capable of weighing $\pm$ 0.01 g

6.7 Graduated cylinders – 100ml and 1000ml

6.8 Beakers – 250 ml glass or plastic

6.9 Watch glass - appropriate to cover beaker

6.10 Magnetic Stirrer and stir bars

6.11 PTFE lined 20 liter carboy

6.12 Thermometer, calibrated against an NIST traceable thermometer

6.13 Water bath – adjustable temperature control

7.0 PROCEDURE

7.1 The preparation of all samples must be documented. See Section 8.1 for the various logbooks and prep sheets that are required for this method. The prep sheet will include such items as: sample ID, bottle number, initial volume, final volume, pHs, lot numbers, batch numbers, and leachate dates and times.

The extraction technician is responsible for filling out all the required information. A copy of the prep sheet will be submitted to the analyst with the leachates. The leaching start date and time are entered into LIMS.

7.2 Determination of Percent Solids

7.2.1 If the sample will obviously yield no liquid when subjected to pressure filtration, proceed to Section 7.5.

7.2.2 If the sample is liquid or mixed-phase (solid and liquid), proceed as follows. **NOTE:** If the sample appears to contain an organic liquid phase, notify the Department Supervisor. It is recommended that samples containing organic phases be analyzed as “totals” instead of TCLP.

7.2.3 Pre-weigh the filter and container that will receive the filtrate. Document all weights in the TCLP_SPLP Description Log.

7.2.4 Assemble the filtering apparatus as per the manufacturer's instructions.

7.2.5 Transfer a 100 gram aliquot of the sample to a beaker and record the weight. If a 100 gram aliquot is not available, inform the Department Supervisor.

7.2.6 Quantitatively transfer the sample aliquot to the filter apparatus. Slurries may be allowed to settle and the liquid portion filtered prior to transferring the solid portion of the sample. **NOTE**: If sample material has adhered to the sample container, obtain the weight of this residue and subtract from the total weight of the sample.

7.2.7 Complete the assembly of the filtration device, and gradually apply pressure until fluid is expelled or 10 psi is obtained. If no fluid is expelled, gradually increase the pressure in 10 psi increments to a maximum of 50 psi. If no fluid is expelled in any 2

minute period, stop the filtration. Shut off the pressurizing gas and vent the filtration system using the top vent.

CAUTION: DO NOT REMOVE FLANGE CLAMPS WHILE SYSTEM IS PRESSURIZED! SERIOUS INJURY MAY RESULT.

NOTE: Instantaneous application of high pressure can cause the filter to clog prematurely.

7.2.8 The material in the filtration apparatus is defined as the solid phase.

NOTE: Some high viscosity liquids (oils, paints) will not filter under these circumstances. The material remaining within the filtration device is defined as the solid phase.

NOTE: If the sample appears to contain an organic liquid phase, notify the Department Supervisor. It is recommended that samples containing organic phases be analyzed as "totals" instead of TCLP.

7.2.9 Remove the solid phase of the sample and the filter from the filtration apparatus. If there is a noticeable amount of filtrate entrained in the filter, then dry at 100 °C ± 20 until two successive readings yield the same value within ±1%. Record the final weight.

7.2.10 Determine the percent solids as follows:

$$\% \text{ solids} = \frac{(W - F) \times 100}{T}$$

W = Weight of sample remaining on filter
F = Weight of filter
T = Initial weight of sample used

7.2.11 If the sample contains <0.5% solids, the filtrate is defined as the sample leachate. **NOTE:** Additional aliquots may need to be filtered to generate sufficient volume for all of the analysis. Proceed to Section 7.5.10.

7.3 Determination of Particle Size

7.3.1 Evaluate the solid portion of the sample for particle size. If the solid portion of sample has a surface area equal to or greater than 3.1 cm^2/gram, then the sample does not require particle size reduction. This would apply to samples such as paper, filter material or rags.

7.3.2 Alternatively, if the solid portion of the sample is smaller than 1 cm in its narrowest dimension (i.e. is capable of passing through a 9.5 mm sieve), then the sample does not require particle size reduction.

7.3.3 If the sample does not meet the particle size criteria listed above, then prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the sample. Care should be taken to minimize any potential metals contamination.

7.3.4 Document the sample description and any particle size reduction in the TCLP_SPLP Description Log.

7.4 Determination of Extraction Fluid

7.4.1 pH Meter Calibration

Make sure that the pH electrode is clean. If the electrode is coated with oil or grease, then it must be washed with a 50% water-methanol solution and then rinse it well with DI water. Do not soak the electrode in the acetone solution. Soak the electrode in a beaker containing pH 7 buffer for approximately 2 hours before using.

Connect the pH electrode to the pH meter. Calibrate the meter using three of the following buffers: pH 2, pH 4, pH 7 or pH 10. Buffers chosen must bracket the pH range. Read back the remaining buffer. For details on specific calibration procedure, see the instruction manual for the meter being used.

After the calibration is complete, analyze the 3 buffer solutions to ensure that an accurate calibration was obtained. Record the results in the TCLP Fluid Determination Log. Readings must be within 0.05 pH units of the buffer solution's true value.

7.4.2 Transfer a 5.0 gram aliquot of the solid phase of the sample to a 250 ml beaker. Record the actual weight in the fluid determination log.

NOTE: The particle size of the solid phase should be < 1mm for this step. This may require some particle size reduction.

7.4.3 Add 96.5 ml of DI water to the beaker. Place a magnetic stir bar in the beaker and cover with a watch glass. Stir vigorously for 5 minutes. Measure and record the pH in the TCLP Fluid Determination Log. If the pH is <5.0, use extraction fluid #1, and proceed to step 7.5.

7.4.4 If the pH is >5.0, add 3.5 ml of 1.0N HCl and swirl gently. Cover the beaker with a watch glass and heat to 50°C for 10 minutes.

7.4.5 Allow the solution to cool. Stir vigorously for 5 minutes. Measure and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2.

NOTE: All pH measurements must be recorded to two places after the decimal point.

7.5 Extraction of Semivolatile Organics and Metals

7.5.1 If the sample contains 100% solids, and the sample does not need particle size reduction transfer a minimum of 100g aliquot of the sample to the extraction vessel. Record the weight to ± 0.1 gram on the TCLP_SPLP Sample Prep Sheet. Add 20 times the sample weight of the appropriate extraction fluid to the leaching vessel. Swirl gently and watch for the evolution of carbon dioxide. If no gasses are evolved, cap the container and mount on the rotary agitator. Proceed to section 7.5.4.

7.5.2 If the sample contains <0.5% solids, the filtrate obtained in step 7.2 is defined as the sample leachate. Proceed to section 7.5.10.

7.5.3 If the sample is mixed phase and/or contains >0.5% solids, transfer a 100g aliquot of the sample or more, based on % solids to the filtration device. Assemble the filtration apparatus, and gradually apply pressure to remove any free liquids. Expelled liquid is stored in a glass container and is to be recombined with sample leachate. Transfer the solid portion of the sample to the appropriate extraction vessel. Add a volume of the appropriate TCLP fluid, calculated as follows:

$$\frac{20 \times \text{sample wt (g)} \times \%\ \text{solids}}{100} = \text{ml extraction fluid}$$

Swirl gently and watch for evolution of carbon dioxide. Cap the extraction bottle and attach to rotary agitator. Allow the extraction to proceed 18 ± 2 hrs.

NOTE: If the sample contains <25% solids, more sample can be filtered to obtain sufficient solids for leaching such that all analyses may be performed. Consult the Department Supervisor.

7.5.4 Rotate at 30 ±2 rpm. Make sure to measure and record the rotation rate and tumbler ID on the TCLP_SPLP Sample Prep Sheet. Allow the extraction to proceed for 18 ± 2 hrs.

The vessels should be vented periodically during the first hour to prevent pressure build up.

NOTE: The temperature of the extraction room must be 23 ± 2 °C during the extraction period. Record the temperature on TCLP_SPLP Sample Prep Sheet. Use a Hi/Lo thermometer to monitor the room temperature throughout the extraction period.

7.5.5 After the leaching period has elapsed, remove the extraction vessels from the rotary agitator and allow them to settle.

7.5.6 Assemble the filtration device. Filter each sample into an appropriately labeled container. Multiple filters may be used. Be sure to thoroughly clean the filtration apparatus between samples.

7.5.7 If a compatible liquid was obtained in Section 7.5.3, combine the liquids at this time.

7.5.8 If the liquids are not compatible, record the total volume of the expelled liquid in the sample description logbook and submit both fractions for analysis. Notify the Department Supervisor.

NOTE: Department Supervisor will notify the Project Manager to determine if the phases are to be mathematically combined as in Section 7.5.13, or to be report separately.

7.5.9 Measure and record the pH of each leachate in the TCLP Fluid Determination Log. See Section 7.4.1 for pH meter calibration.

NOTE: All pH measurements must be recorded to two places after the decimal point.

7.5.10 Aliquot the leachate for the necessary analyses. Listed below are the minimum quantities required for analysis. Additional aliquots will be needed for QC samples.

7.5.10.1	Metals (including Mercury)	100ml
7.5.10.2	Semivolatiles by 8270	100ml
7.5.10.3	Pesticides by 8081	100ml
7.5.10.4	Herbicides by 8151	10ml
7.5.10.5	TPH by 8015	100ml

7.5.11 Leachates for metals analysis are stored in labeled plastic bottles and transferred to the metals department.

7.5.12 All other aliquots (semi-volatile organics) are transferred to amber glass bottles and stored at ≤ 6°C until the subsequent extractions can be performed.

7.5.13 If individual phases are analyzed separately (see 7.5.8) conduct the appropriate analysis and combine the results mathematically by using the following formula:

Final Analyte Conc. = [(V1*C1)+(V2*C2)] / (V1+V2)

V1 = The volume of the first phase (l)
C1 = The conc. of the analyte of concern in the first phase (mg/l)
V2 = The volume of the second phase (l)
C2 = The conc. of the analyte of concern in the second phase (mg/l)

8.0 DOCUMENTATION

8.1 Documentation for this analysis is quite extensive. At minimum the following logbooks or prep sheets must be filled out completely.

8.1.1 TCLP_SPLP Description Log

8.1.2 TCLP Fluid Determination Log

8.1.3 TCLP_SPLP Sample Prep Sheet

8.1.4 Extraction Bottle Tracking Log

8.1.5 Organics Reagent Log

8.2 For every 20 extractions performed in an extraction vessel, a leachate blank must be performed using that vessel. Document this in the Extraction Bottle Tracking Log.

8.3 For each original matrix type extracted, (soil, water, sludge, etc.) a leachate spike must be performed. Various unique matrices may require their own leachate spikes.

9.0 QUALITY ASSURANCE, QUALITY CONTROL AND METHOD PERFORMANCE

9.1 An extraction batch is defined as samples of a similar matrix that are prepared for a particular parameter. The batch size is limited to 20 samples. A batch may be held open for up to 6 hours; however, samples should not be added after the QC set has been completed. **NOTE:** All samples and QC samples must leached for the required amount of time.

9.2 A leachate blank (LB) and sample duplicate (DUP) must be leached with each batch of samples. A leachate blank must be prepared for each fluid type used in a given batch.

9.3 All spiking for the matrix spike (MS) and matrix spike duplicate (MSD), leachate spike (LS), and leachate blank spike (LBS) occurs after filtration.

9.4 Method performance is monitored through the routine analysis of negative and positive control samples. Leachate blank spikes and matrix spikes are not applicable to the leaching portion of this test; however, they will be used later to assess the extraction and digestion efficiency of the specific methods performed on the leachate.

9.5 A sample duplicate is used to assess method precision. Sample duplicate %RPD is compared to method defined control limits. Control limits are stored in the LIMS.

10.0 SAFETY AND WASTE DISPOSAL

10.1 Safety

10.1.1 Safety glasses, gloves and lab coats should be worn when handling acids, samples, standards or solvents.

10.1.2 Perform all filtration in a fume hood.

10.1.3 Material Safety Data Sheets (MSDS) or Safety Data Sheets (SDS) are available for all reagents and solvents used in the lab. Technicians should review the MSDS or SDS prior to using any new reagents or solvents.

10.2 Waste Disposal

10.2.1 The TCLP filter and remaining sample is placed in a waste container.

10.2.2 Extra leachate is rinsed down the drain with large amounts of water.

10.2.3 Waste soil from the homogenizing process should be placed in the “soil waste” container. **NOTE:** Waste soil from foreign soils must follow “foreign soil” disposal requirements.

11.0 REFERENCES

SW-846 Method 1311, Rev. 0, 07/92

SW-846 Method 1312, Rev. 0, 09/94

Compound List Report
Product: V8260BTX BTEX
Matrix: AQ Aqueous

Jun 18, 2020 05:07 pm

Method List: VAIX8260 AQ
Report List: BTEX ALL
LOQ/MDL Factor: 1

Method Ref: SW846 8260B
Purgeable Aromatics

LF27173
LF3702

Compound	CAS No.	LOQ	LOD	MDL	Units	Control Limits (%) Rev: 04/29/19 MS/MSD	RPD	BS	DUP
Benzene	71-43-2	1	0.5	0.31	ug/l	81-122	14	81-122	14
Ethylbenzene	100-41-4	1	0.5	0.36	ug/l	81-121	14	81-121	14
Toluene	108-88-3	1	0.5	0.3	ug/l	80-120	14	80-120	14
Xylene (total)	1330-20-7	3	1.5	0.72	ug/l	80-126	15	80-126	15
Dibromofluoromethane	1868-53-7					Surrogate Limits:		83-118	
1,2-Dichloroethane-D4	17060-07-0					Surrogate Limits:		79-125	
Toluene-D8	2037-26-5					Surrogate Limits:		85-112	
4-Bromofluorobenzene	460-00-4					Surrogate Limits:		83-118	

4 compounds and 4 surrogates reported in list BTEX

Compound List Report
Product: V8260TCLP TCLP, Volatiles
Matrix: AQ Aqueous

Jun 18, 2020 05:07 pm

Method List: VAIX8260 LEACHATE | Method Ref: SW846 8260B | LF24671
Report List: VTCLP ALL | VOA TCLP List | LF14778
LOQ/MDL Factor: 10

Compound	CAS No.	LOQ	LOD	MDL	Units	Control Limits (%) Rev: 04/15/17 MS/MSD	RPD	BS	DUP
Benzene	71-43-2	0.01	0.005	0.0031	mg/l	81-122	14	81-122	14
2-Butanone (MEK)	78-93-3	0.05	0.035	0.02	mg/l	56-143	18	56-143	18
Carbon Tetrachloride	56-23-5	0.01	0.005	0.0036	mg/l	76-136	23	76-136	23
Chlorobenzene	108-90-7	0.01	0.005	0.002	mg/l	82-124	14	82-124	14
Chloroform	67-66-3	0.01	0.005	0.003	mg/l	80-124	15	80-124	15
1,4-Dichlorobenzene	106-46-7	0.01	0.005	0.0026	mg/l	78-120	15	78-120	15
1,2-Dichloroethane	107-06-2	0.01	0.005	0.0031	mg/l	75-125	14	75-125	14
1,1-Dichloroethylene	75-35-4	0.01	0.005	0.0032	mg/l	78-137	18	78-137	18
Tetrachloroethylene	127-18-4	0.01	0.005	0.0022	mg/l	76-135	16	76-135	16
Trichloroethylene	79-01-6	0.01	0.005	0.0035	mg/l	81-126	15	81-126	15
Vinyl Chloride	75-01-4	0.01	0.005	0.0041	mg/l	69-159	18	69-159	18

Dibromofluoromethane	1868-53-7	Surrogate Limits:	83-118
1,2-Dichloroethane-D4	17060-07-0	Surrogate Limits:	79-125
Toluene-D8	2037-26-5	Surrogate Limits:	85-112
4-Bromofluorobenzene	460-00-4	Surrogate Limits:	83-118

11 compounds and 4 surrogates reported in list VTCLP

Compound List Report
Product: AB8270SL Semivolatiles, Special List
Matrix: AQ Aqueous Jun 18, 2020 04:15 pm
CSXT10083: AGMININD: 9415829/ENV53216, Former Indiana Creosote Co, Bloomington, IN
Method List: AB8270 AQ Method Ref: SW846 8270D LF24600
Report List: ABSL ALL ABN Special List LF15681 (a)
LOQ/MDL Factor: 1

Compound	CAS No.	LOQ	LOD	MDL	Units	Control Limits (%) Rev: 04/15/17 MS/MSD	RPD	BS	DUP
2,4-Dichlorophenol	120-83-2	5	1	0.84	ug/l	53-103	26	53-103	26
2,4-Dimethylphenol	105-67-9	5	2	0.74	ug/l	43-90	27	43-90	27
2-Methylphenol	95-48-7	5	1	0.56	ug/l	43-90	28	43-90	28
3&4-Methylphenol		5	2	0.98	ug/l	36-88	28	36-88	28
Pentachlorophenol	87-86-5	25	10	5	ug/l	61-115	26	61-115	26
Phenol	108-95-2	5	2	0.5	ug/l	19-56	35	19-56	35
2,4,6-Trichlorophenol	88-06-2	5	2	0.75	ug/l	59-107	23	59-107	23
Acenaphthene	83-32-9	5	1	0.63	ug/l	61-107	22	61-107	22
Acenaphthylene	208-96-8	5	1	0.64	ug/l	60-104	22	60-104	22
Anthracene	120-12-7	5	1	0.8	ug/l	65-108	20	65-108	20
Benzo(a)anthracene	56-55-3	5	1	0.76	ug/l	66-111	22	66-111	22
Benzo(a)pyrene	50-32-8	5	1	0.78	ug/l	62-107	23	62-107	23
Benzo(b)fluoranthene	205-99-2	5	1	0.78	ug/l	65-114	23	65-114	23
Benzo(g,h,i)perylene	191-24-2	5	1	0.82	ug/l	66-116	23	66-116	23
Benzo(k)fluoranthene	207-08-9	5	1	0.86	ug/l	65-114	24	65-114	24
Butyl Benzyl Phthalate	85-68-7	5	2	1	ug/l	65-112	24	65-112	24
Carbazole	86-74-8	5	1	0.6	ug/l	59-113	21	59-113	21
Chrysene	218-01-9	5	1	0.85	ug/l	66-111	22	66-111	22
Dibenzo(a,h)anthracene	53-70-3	5	1	0.8	ug/l	66-119	24	66-119	24
Dibenzofuran	132-64-9	5	1	0.6	ug/l	61-106	21	61-106	21
bis(2-Ethylhexyl)phthalate	117-81-7	5	2	1	ug/l	61-117	23	61-117	23
Fluoranthene	206-44-0	5	1	0.55	ug/l	63-106	21	63-106	21
Fluorene	86-73-7	5	1	0.7	ug/l	62-108	20	62-108	20
Indeno(1,2,3-cd)pyrene	193-39-5	5	1	0.71	ug/l	64-119	24	64-119	24
2-Methylnaphthalene	91-57-6	5	1	0.6	ug/l	51-102	26	51-102	26
Naphthalene	91-20-3	5	1	0.5	ug/l	47-100	29	47-100	29
Phenanthrene	85-01-8	5	1	0.86	ug/l	66-110	21	66-110	21
Pyrene	129-00-0	5	1	0.68	ug/l	64-113	23	64-113	23

2-Fluorophenol	367-12-4	Surrogate Limits:	14-67
Phenol-d5	4165-62-2	Surrogate Limits:	10-50
2,4,6-Tribromophenol	118-79-6	Surrogate Limits:	33-118
Nitrobenzene-d5	4165-60-0	Surrogate Limits:	42-108
2-Fluorobiphenyl	321-60-8	Surrogate Limits:	40-106
Terphenyl-d14	1718-51-0	Surrogate Limits:	39-121

28 compounds and 6 surrogates reported in list ABSL

(a) Custom list for CSXT10083.

Compound List Report
Product: AB8270SLSIM Semivolatiles by SIM
Matrix: AQ Aqueous Jun 18, 2020 04:15 pm
CSXT10083: AGMININD: 9415829/ENV53216, Former Indiana Creosote Co, Bloomington, IN
Method List: AB8270SIM AQ Method Ref: SW846 8270D BY SIM LF25579
Report List: ABSIMSL ALL ABN Special List LF11788 (a)
LOQ/MDL Factor: 1

Compound	CAS No.	LOQ	LOD	MDL	Units	Control Limits (%) Rev: 10/10/17 MS/MSD	RPD	BS	DUP
Pentachlorophenol	87-86-5	1	0.5	0.3	ug/l	43-110	30	43-110	30
Acenaphthene	83-32-9	1	0.5	0.4	ug/l	56-101	24	56-101	24
Acenaphthylene	208-96-8	1	0.5	0.4	ug/l	54-104	25	54-104	25
Anthracene	120-12-7	1	0.5	0.25	ug/l	67-106	21	67-106	21
Benzo(a)anthracene	56-55-3	0.2	0.05	0.04	ug/l	65-106	22	65-106	22
Benzo(a)pyrene	50-32-8	0.2	0.05	0.04	ug/l	58-111	23	58-111	23
Benzo(b)fluoranthene	205-99-2	0.2	0.05	0.04	ug/l	59-113	24	59-113	24
Benzo(g,h,i)perylene	191-24-2	0.2	0.05	0.04	ug/l	43-112	24	43-112	24
Benzo(k)fluoranthene	207-08-9	0.2	0.05	0.04	ug/l	58-110	23	58-110	23
Chrysene	218-01-9	0.2	0.1	0.04	ug/l	66-107	22	66-107	22
Dibenzo(a,h)anthracene	53-70-3	0.2	0.05	0.04	ug/l	40-113	25	40-113	25
Fluoranthene	206-44-0	1	0.5	0.25	ug/l	64-110	22	64-110	22
Fluorene	86-73-7	1	0.5	0.4	ug/l	60-106	24	60-106	24
Indeno(1,2,3-cd)pyrene	193-39-5	0.2	0.05	0.04	ug/l	44-112	25	44-112	25
2-Methylnaphthalene	91-57-6	1	0.5	0.4	ug/l	53-105	26	53-105	26
Naphthalene	91-20-3	1	0.5	0.4	ug/l	56-105	27	56-105	27
Phenanthrene	85-01-8	1	0.5	0.25	ug/l	62-105	22	62-105	22
Pyrene	129-00-0	1	0.5	0.25	ug/l	62-109	21	62-109	21

2-Fluorophenol	367-12-4	Surrogate Limits:	14-67
Phenol-d5	4165-62-2	Surrogate Limits:	10-50
2,4,6-Tribromophenol	118-79-6	Surrogate Limits:	33-118
Nitrobenzene-d5	4165-60-0	Surrogate Limits:	42-108
2-Fluorobiphenyl	321-60-8	Surrogate Limits:	40-106
Terphenyl-d14	1718-51-0	Surrogate Limits:	39-121
2-Methylnaphthalene-d10	7297-45-2	Surrogate Limits:	50-150
Fluoranthene-d10	93951-69-0	Surrogate Limits:	50-150
1,4-Dithiane-d4		Surrogate Limits:	40-140

18 compounds and 9 surrogates reported in list ABSIMSL

(a) Custom list for CSXT10083.

Compound List Report
Product: AB8270TCLP TCLP, Semivolatiles
Matrix: LIQ Liquid

Jun 18, 2020 05:07 pm

Method List: AB8270 LEACHATE | Method Ref: SW846 8270D | LF24651
Report List: ABTCLP ALL | ABN TCLP List | LF14777
LOQ/MDL Factor: 10

Compound	CAS No.	LOQ	LOD	MDL	Units	Control Limits (%) Rev: 04/15/17 MS/MSD	RPD	BS	DUP
2-Methylphenol	95-48-7	0.05	0.01	0.0056	mg/l	43-90	28	43-90	28
3&4-Methylphenol		0.05	0.02	0.0098	mg/l	36-88	28	36-88	28
Pentachlorophenol	87-86-5	0.25	0.1	0.05	mg/l	61-115	26	61-115	26
2,4,5-Trichlorophenol	95-95-4	0.05	0.02	0.0074	mg/l	62-109	22	62-109	22
2,4,6-Trichlorophenol	88-06-2	0.05	0.02	0.0075	mg/l	59-107	23	59-107	23
1,4-Dichlorobenzene	106-46-7	0.05	0.02	0.005	mg/l	45-98	25	45-98	25
2,4-Dinitrotoluene	121-14-2	0.05	0.01	0.0081	mg/l	61-110	21	61-110	21
Hexachlorobenzene	118-74-1	0.05	0.01	0.0069	mg/l	63-108	22	63-108	22
Hexachlorobutadiene	87-68-3	0.05	0.01	0.005	mg/l	42-102	28	42-102	28
Hexachloroethane	67-72-1	0.05	0.02	0.016	mg/l	42-100	29	42-100	29
Nitrobenzene	98-95-3	0.05	0.02	0.0093	mg/l	50-104	28	50-104	28
Pyridine	110-86-1	0.1	0.035	0.02	mg/l	23-74	34	23-74	34

2-Fluorophenol	367-12-4	Surrogate Limits:	14-67
Phenol-d5	4165-62-2	Surrogate Limits:	Oct-50
2,4,6-Tribromophenol	118-79-6	Surrogate Limits:	33-118
Nitrobenzene-d5	4165-60-0	Surrogate Limits:	42-108
2-Fluorobiphenyl	321-60-8	Surrogate Limits:	40-106
Terphenyl-d14	1718-51-0	Surrogate Limits:	39-121

12 compounds and 6 surrogates reported in list ABTCLP

	6010 AQ				TCLP			TCLP
Parm_Syn	Units	MDL/DL	LOD	RL/LOQ	Units	MDL/DL	LOD	RL/LOQ
Aluminum	ug/l	14	25	200	mg/L			
Antimony	ug/l	1	5	6	mg/L			
Arsenic	ug/l	1.3	5	10	mg/L	0.013	0.05	0.1
Barium	ug/l	1	5	200	mg/L	0.05	0.1	2
Beryllium	ug/l	0.2	1	4	mg/L			
Cadmium	ug/l	0.2	1	5	mg/L	0.002	0.01	0.05
Calcium	ug/l	50	100	1000	mg/L			
Chromium	ug/l	1	5	10	mg/L	0.01	0.05	0.1
Cobalt	ug/l	0.2	1	50	mg/L			
Copper	ug/l	1	2	25	mg/L			
Iron	ug/l	17	50	300	mg/L			
Lead	ug/l	1.1	2	5	mg/L	0.011	0.02	0.05
Magnesium	ug/l	35	100	5000	mg/L			
Manganese	ug/l	1	2	15	mg/L			
Molybdenum	ug/l	0.3	2	50	mg/L			
Nickel	ug/l	0.4	1	40	mg/L			
Potassium	ug/l	200	500	10000	mg/L			
Selenium	ug/l	2.9	5	10	mg/L	0.029	0.05	0.1
Silver	ug/l	0.7	2	10	mg/L	0.007	0.02	0.1
Sodium	ug/l	500	2000	10000	mg/L			
Strontium	ug/l	0.5	1	10	mg/L			
Thallium	ug/l	1.4	2	10	mg/L			
Tin	ug/l	1	2	50	mg/L			
Titanium	ug/l	1	2	10	mg/L			
Vanadium	ug/l	0.6	2	50	mg/L			
Zinc	ug/l	4.4	5	20	mg/L			
Mercury	ug/l	0.03	0.1	0.5	mg/L	0.0005	0.001	0.005

Arcadis U.S., Inc.

150 W. Market Street

Suite 728

Indianapolis, Indiana 46204

Tel 317 231 6500

Fax 317 231 6514

www.arcadis.com