May 18, 2021 Reference No. 11218041

Mr. Zachary Sasnow
Corrective Action Project Manager
U.S. EPA, Region 5
77 West Jackson Boulevard DW-8J
Chicago, Illinois
60604 3590

Dear Mr. Sasnow:

**Re: Scope of Work to Complete Additional IU H Soil Sampling**
**EPA ID #MID 041 793 340**
**RACER Nodular Facility - Saginaw, Michigan**

This letter presents the Scope of Work (Scope) to complete soil sampling of two areas in the southern portion of Investigative Unit (IU) H at the Revitalizing Auto Communities Environmental Response Trust (RACER) Former Nodular Industrial Lands (Site) in Saginaw, Michigan. This Scope was developed in accordance with the recommendations presented in the November 26, 2018 letter from GHD to the United States Environmental Protection Agency (U.S. EPA) entitled "response to U.S. EPA Comments from April 20, 2018 Soil Evaluation Memorandum".

The following figures, tables and Attachments were prepared in support of the Scope:

| | |
|---|---|
| Figure 1 | Proposed Sampling Locations |
| Table 3.1 | Summary of Analytical Methods |
| Table 3.2 | Soil Sample Parameter List-Lab Limits and Regulatory Criteria |
| Table 3.3 | Laboratory Precision and Accuracy Limits |
| Table 3.4 | Summary of Sampling and Analysis Program |
| Table 3.5 | Container, Preservation, Shipping, and Packaging Requirements |
| Attachment A | GHD Field Training Manual Section 5.0: Soil Sampling |
| Attachment B | Laboratory Standard Operating Procedures |
| Attachment C | Scope of Work Approval Form |

## 1. Background

In response to the April 20, 2018 Soil Evaluation Memorandum, U.S. EPA noted two previous sample locations at the south end of IU-H (IU-H South) that warranted further investigation; SB-05542 (herein referred to as Area 1) and MW-05443 (herein referred to as Area 2). Area 1 and Area 2 are presented in Figure 1.

**GHD**
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The 4-6 feet bgs interval in soil boring SB-05542 (Area 1) was sampled on June 13, 2000 and was the only sample listed in GHD's Soil Evaluation Memorandum dated April 20, 2018 that was analyzed for Petroleum Hydrocarbons (PHCs). Analytical results identified detections of diesel and lube oil PHCs in the soil in this sample. As part of the same sampling event, SB-05542 was also tested for VOCs in the 4-6 feet bgs interval but had no detections. The other sampling intervals at this location (0-2 feet bgs and 2-4 feet bgs) were not analyzed for PHCs or VOCs.

Soil samples collected from MW-05443 (Area 2) during installation in 1998 had a cyanide detection of 3.3 mg/kg which exceeded Non-Residential Infinite Source Volatile Soil Inhalation Criteria (1.9 mg/kg) in the 0-2 feet bgs interval. Due to the high detection limit, vertical delineation was not possible with the currently available data.

# 2. Proposed Soil Sampling Activities

To evaluate the potential impacts at both locations, soil sampling will be completed to delineate the presence PHCs in the vicinity of SB-05542 and cyanide at MW-05443. A soil boring will be completed in each area and grab samples will be collected to evaluate the extent of the impacts. Soil samples will be submitted under chain of custody procedures for laboratory analysis. Area 1 samples will be analyzed for semi-volatile organic compounds (SVOCs) as there are criteria for SVOCs to screen against. As no VOCs were detected at SB-05442, VOCs are not proposed for analysis but could be added if field observations indicate it is appropriate. Area 2 samples will be analyzed for total cyanide. In addition, samples collected from the 0-2 feet bgs interval will also be analyzed for black carbon and TOC in each area to provide information for ecological screening.

## 2.1 Sample Collection Procedure

GHD will advance a boring at location SB-05542 (SB-1-21-I)) and complete three 10-foot step-out borings, as presented on Figure 1. Grab samples will be collected from the following intervals at all four locations: 0-2 feet bgs, 4-6 feet bgs, and 8-10 feet bgs. If any indications of impact are encountered outside of the proposed sampling intervals, such as elevated PID signal, visible staining or other indicators, additional discriminatory sampling of the soil in the impacted interval will be conducted. If PID readings are above background levels, samples will be submitted for analysis for VOCs. GHD's soil sample procedures are detailed in Attachment A.

GHD will also advance a boring adjacent to MW-05443 (SB-2-21-I), with three 10-foot step-outs borings, as presented on Figure 1. Grab samples will be collected from the following intervals at all four locations: 0-2 feet bgs and 4-6 feet bgs. If any indications of impact are encountered outside of the proposed sampling intervals, such as elevated PID signal, visible staining or other indicators, additional discriminatory sampling of the soil in the impacted interval will be conducted. The samples from the step-out borings will be placed on hold pending the results of the samples collected from SB-2-21-I.

# 3. Analytical Methods and Quality Control Samples

Eurofins TestAmerica will be the laboratory company supporting the environmental sample analyses for this project utilizing their facilities in North Canton, Ohio (SVOCs, cyanide, black carbon, and TOC).

## 3.1 Laboratory Analytical Methods

Soil samples will be analyzed for specified chemical parameters by the project laboratory. The methods that will be used for sample analyses are presented in Table 3.1. Specific analytes and targeted quantitation limits for chemical parameters are presented in Table 3.2. The applicable Michigan Part 201 soil criteria are also included in Table 3.2. The precision and accuracy criteria for laboratory analyses are provided in Table 3.3. The criteria listed in Tables 3.2 and 3.3 provide the data quality objectives for the project scope. Analytical data will be validated according to the procedures outlined in Section 3.3.

## 3.2 Quality Assurance/Quality Control Procedures

### 3.2.1 Field Quality Assurance/Quality Controls

Field Quality Assurance/Quality Control Procedures (QA/QC) samples will be collected during field sampling include equipment blank samples to determine the existence and magnitude of sample contamination resulting from ambient conditions or sampling procedures, and field replicate sample to assess the overall precision of the sampling and analysis events. The specific QA/QC samples and collection frequency are summarized in Table 3.4. Equipment blank samples will be collected at a frequency of one per day, following sampling equipment decontamination procedures. Equipment blank samples will be collected by routing laboratory-provided deionized water through decontaminated sampling equipment. Equipment blank samples will be analyzed to check procedural contamination and/or ambient conditions and/or sample container contamination at the Site that may cause sample contamination. However, equipment/Field blank samples will not be required for samples collected using pre-cleaned or pre-cleaned, disposable sampling equipment.

Field duplicate samples will be collected at a minimum frequency of 1 per 10 or fewer investigative samples. Field duplicate samples will be analyzed to assess the precision of the field sample collection procedures.

Sufficient sample volume will be provided to the laboratory (as necessary) for MS/MSD analyses. The data from MS/MSD analyses provide an indication of the precision and accuracy of the analytical method relative to the sample matrix. Samples for MS/MSD analysis will be designated at a minimum frequency of 1 per 20 or fewer samples.

Samples will be collected and packed in laboratory supplied containers and transported in accordance with the container, preservation, shipping, and packaging requirements presented in Table 3.5.

### 3.2.2 Laboratory Quality Assurance/Quality Control

Laboratory QA/QC requirements for the analysis of soil samples includes analyzing method blanks, initial calibration verification standards, continuing calibration verification standards, MS/MSD samples, and

laboratory Control Samples (LCS). The analysis frequency for these QA/QC samples is identified in the applicable laboratory SOP provided in Attachment B. The acceptance criteria for these QC checks will be consistent with the analytical methods provided in Table 3.1 and applicable laboratory SOP.

### 3.2.3 Laboratory Report Deliverables

Laboratory reports for samples collected will consist of the following data deliverables:

1. Case Narrative:
    i. Date of issuance
    ii. Project name and number
    iii. Any deviations from intended analytical strategy
    iv. Condition of samples "as received"
    v. Discussion of whether or not sample holding times were met
    vi. Discussion of technical problems or other observations that may have created analytical difficulties
    vii. Discussion of any laboratory quality control checks that failed to meet project criteria
2. Chemistry Data Package
    i. Dates of sample collection, receipt, preparation, and analysis
    ii. Cross-reference of laboratory to project sample identification numbers
    iii. Description of data qualifiers used
    iv. Methods of sample preparation and analysis
    v. Sample results in tabular format
    vi. Method blank data, surrogate data, LCS data, duplicate sample data, MS/MSD data,
    vii. Fully executed chain-of-custody document

## 3.3 Data Review and Validation

Upon receipt of the final data packages from the project laboratory the data will be reviewed and validated. The data review will evaluate the final analytical results, holding time period compliance, equipment blank sample data, field duplicate sample data, method blank data, LCS data, laboratory duplicate data, surrogate compound spike data, and MS/MSD sample data. Validation of the data will consist of evaluating the QA/QC data based on the applicable review criteria specified in "National Functional Guidelines for Inorganic Superfund Methods Data Review", EPA 540-R-2017-001, January 2017 and "National Functional Guidelines for Organic Superfund Methods Data Review", EPA 540-R-2017-002, January 2017. The results of the data review and validation process will be documented in memoranda that identify all limitations on the usability of the analytical data.

## 4. Reporting

Following receipt of the soil analytical results, a letter report will be prepared summarizing the completed field program, results, conclusions, and recommendations. Sample results will compared to the same screening levels that were utilized in the April 20, 2018 Soil Evaluation Memorandum (Michigan Department of Environment, Great Lakes, and Energy (EGLE) non-residential cleanup criteria requirements for response activity (December 30, 2013)) including:

- Residential/Non-Residential Statewide Default Background Levels
- Non-Residential Soil Volatilization to Indoor Air Inhalation Criteria
- Non-Residential Infinite Source Volatile Soil Inhalation Criteria (VSIC)
- Non-Residential Finite VSIC for 5-meter source thickness
- Non-Residential Finite VSIC for 2-meter source thickness
- Particulate Soil Inhalation Criteria
- Direct Contact Criteria

In addition, the samples collected from the 0 to 2 feet bgs interval will also be screened against Ecological Screening Values (ESVs) for risks to aquatic benthos, consistent with the January 4, 2019 Ecological Screening Assessment for Isolated Wetlands Recently Formed in IU G which include:

- U.S. EPA Final Chronic Values (FCVs) from 2003 and 2008
- Region 4 ESVs

If results exceed criteria additional step-out borings may be necessary. The letter report will be submitted to U.S. EPA and will include recommendations on next steps, if required. In accordance with GHD's ISO 9001:2008 accreditation, all records will be stored in GHD's controlled filing system for a minimum 10-years including a backup and retention program.

Should you have any questions, please do not hesitate to call.

Yours truly,

GHD

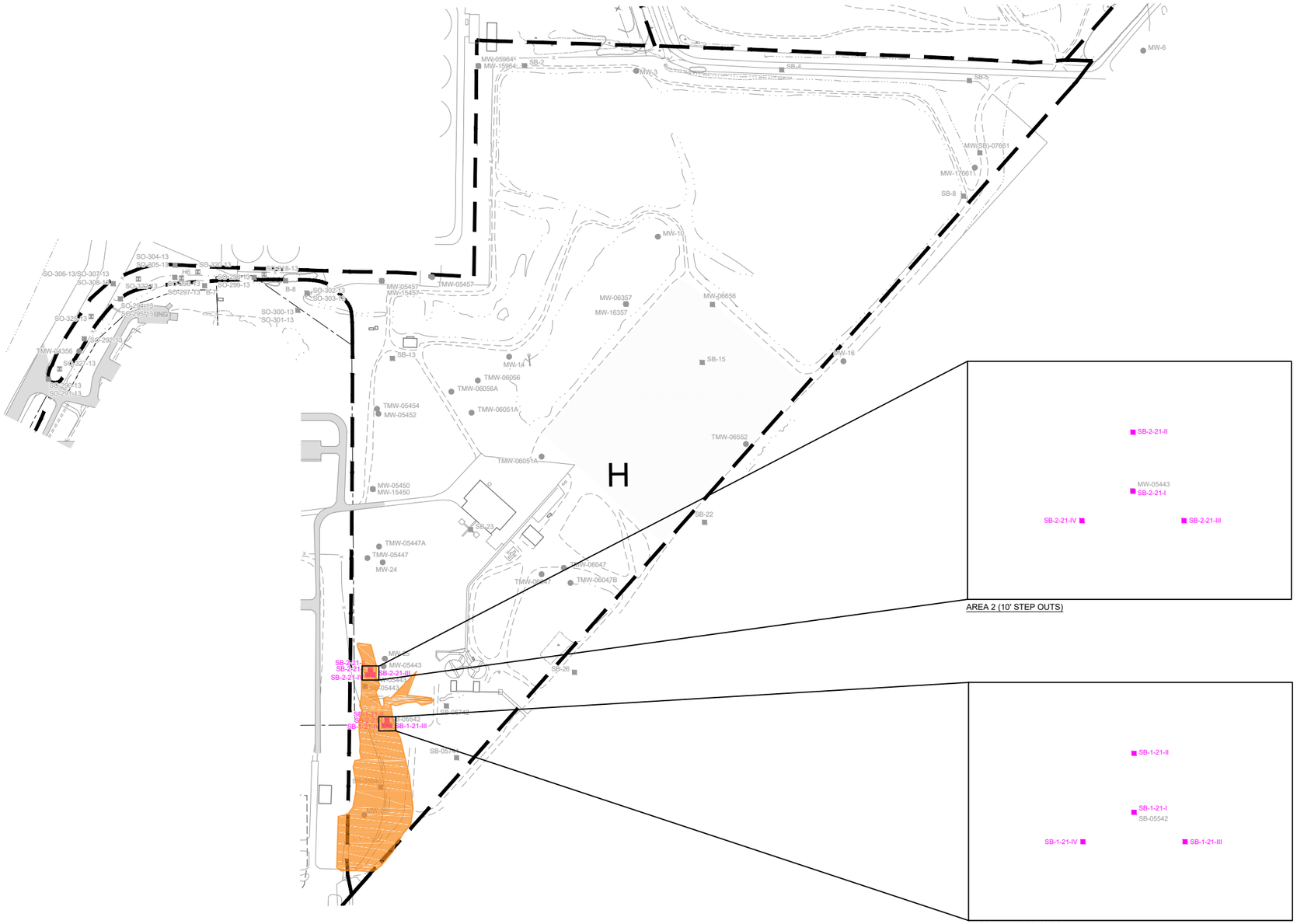
John-Eric Pardys, P. Eng.

JEP/kf/6

Encl.

cc: Dave Favero, RACER
Michael Tomka, GHD

| AREA | ANALYTES |
|---|---|
| SB-1-21 | SVOCs |
| SB-2-21 | Cyanide |




N

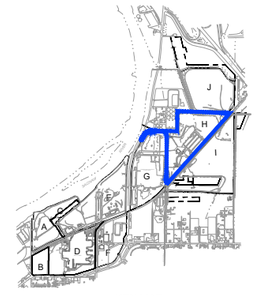
0 100.0 200 ft

LEGEND

A — INVESTIGATIVE UNIT BOUNDARY AND IDENTIFIER

SOIL BORING LOCATION

REGULATED WETLAND (PER WETLAND DELINEATION COMPLETED BY NISWANDER ENVIRONMENTAL (JULY 22, 2015))




KEY MAP

**SCALE VERIFICATION**

THIS BAR MEASURES 1" ON ORIGINAL. ADJUST SCALE ACCORDINGLY.

# RACER
# NODULAR IRON INDUSTRIAL LAND

SAGINAW, MICHIGAN

## PROPOSED SAMPLING LOCATIONS

GHD

**Source Reference:**
MICHIGAN STATE PLANE SOUTH, NAD 83 USING INTERNATIONAL FEET, NGVD 88
TOPO - SANBORN, 1996

| Project Manager: | Reviewed By: | Date: | |
|---|---|---|---|
| M.T. | J.E.P. | MAY 2021 | |
| **Scale:** | **Project Nº:** | **Report Nº:** | **Drawing Nº:** |
| 1" = 50' | 11208041 | SASNOW-06 | figure 1 |

\\ghdnet\ghd\CA\Waterloo\Projects\66211208041\Digital_Design\ACAD 2020\Figures\SASNOW-6\11208041-GHD-0000-LTR-EN-0102_WA-SASNOW6.DWG Plot Date: MAY 05, 2021

**Table 3.1**

**Summary of Analytical Methods**
**Work Plan to Complete Additional IU H Soil Sampling**
**RACER Nodular Facility**
**Saginaw, Michigan**

| Parameter | Preparation Method[1] | Analytical Method[1] |
|---|---|---|
| **Soil Samples** | | |
| TCL SVOCs | SW 3540 | SW 8270C |
| Total Cyanide | - | SW 9012B |
| Black Carbon (Lloyd Kahn) | - | Lloyd Kahn |
| Organic Carbon, Total (TOC) | - | Lloyd Kahn |

Notes:

[1] Preperation and Analytical Method References:
- SW-846 - "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods ", SW-846, 3rd Edition, and Promulgated Updates, November 1986. Actual method versions employed will include the latest promulgated version of the method adopted by the lab.
- Lloyd Kahn - EPA Region II Document Determination of Total Organic Carbon in Sediment, July 27, 1988, authored by Lloyd Kahn, Quality Assurance Specialist.

TCL -Target Compound List
SVOCs- Semi-volatile Organic Compounds

**Table 3.2**

**Soil Parameter List**
**Laboratory Limits and MI Part 201 Criteria**
**Work Plan to Complete Additional IU H Soil Sampling**
**RACER Nodular Facility**
**Saginaw, Michigan**

| Parameter | Criteria Units | Estimated Quantitation Limits (EQL)[1] Soil | Method Detection Limits (MDL)[2] Soil | Michigan Part 201 Criteria: Non_RES/Ambient Air_Finite VSIC_2M Srce Thickness | Non_RES/Ambient Air_Finite VSIC_5M Thickness | Non_RES/Ambient Air_InfiniteSrceVolatileSoilInhalation | Non_RES/Direct Contact | Non_RES/IndoorAir_SoilVolatilization_IndAirInhalation | Non_RES/Particulate Soil Inhalation | Ecological Screening Levels | Source |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **SVOCs** | | | | | | | | | | | |
| 1,1'-Biphenyl | (µg/kg) | 264 | 17.0 | - | - | - | - | - | - | | |
| 2,2'-oxybis[1-chloropropane] | (µg/kg) | 264 | 10.0 | - | - | - | - | - | - | | |
| 2,4,5-Trichlorophenol | (µg/kg) | 264 | 69.0 | - | - | - | 73000000 | - | 10000000000 | | |
| 2,4,6-Trichlorophenol | (µg/kg) | 264 | 64.0 | - | - | - | 3300000 | - | 1300000000 | | |
| 2,4-Dichlorophenol | (µg/kg) | 264 | 44.0 | - | - | - | 3900000 | - | 2300000000 | | |
| 2,4-Dimethylphenol | (µg/kg) | 264 | 40.0 | - | - | - | 36000000 | - | 2100000000 | 70 | Region 4 |
| 2,4-Dinitrophenol | (µg/kg) | 150 | 142 | - | - | - | - | - | - | | |
| 2,4-Dinitrotoluene | (µg/kg) | 264 | 62.0 | - | - | - | 220000 | - | 20000000 | | |
| 2,6-Dinitrotoluene | (µg/kg) | 264 | 56.0 | - | - | - | - | - | - | | |
| 2-Chloronaphthalene | (µg/kg) | 264 | 14.0 | - | - | - | 180000000 | - | - | | |
| 2-Chlorophenol | (µg/kg) | 264 | 10.0 | 1100000 | 1100000 | 1100000 | 4500000 | 800000 | 530000000 | | |
| 2-Methylnaphthalene | (µg/kg) | 264 | 1.96 | 1800000 | 1800000 | 1800000 | 26000000 | 4900000 | 290000000 | 890 | EPA 2003 / 10 |
| 2-Methylphenol | (µg/kg) | 264 | 31.0 | - | - | - | 36000000 | - | 2900000000 | 210 | Region 4 |
| 2-Nitroaniline | (µg/kg) | 200 | 40.0 | - | - | - | - | - | - | | |
| 2-Nitrophenol | (µg/kg) | 264 | 13.0 | - | - | - | 2000000 | - | - | | |
| 3,3'-Dichlorobenzidine | (µg/kg) | 1600 | 43.0 | - | - | - | 30000 | - | 8200000 | | |
| 3-Nitroaniline | (µg/kg) | 200 | 49.0 | - | - | - | - | - | - | | |
| 4,6-Dinitro-2-methylphenol | (µg/kg) | 150 | 80.0 | - | - | - | 260000 | - | 59000000 | | |
| 4-Bromophenyl phenyl ether | (µg/kg) | 264 | 14.0 | - | - | - | - | - | - | | |
| 4-Chloro-3-methylphenol | (µg/kg) | 264 | 45.0 | - | - | - | 15000000 | - | - | | |
| 4-Chloroaniline | (µg/kg) | 200 | 30.0 | - | - | - | - | - | - | | |
| 4-Chlorophenyl phenyl ether | (µg/kg) | 264 | 14.0 | - | - | - | - | - | - | | |
| 4-Nitroaniline | (µg/kg) | 200 | 60.0 | - | - | - | - | - | - | | |
| 4-Nitrophenol | (µg/kg) | 330 | 94.0 | - | - | - | - | - | - | | |
| Acenaphthene | (µg/kg) | 264 | 2.86 | 97000000 | 97000000 | 97000000 | 130000000 | 350000000 | 6200000000 | 980 | EPA 2003 / 10 |
| Acenaphthylene | (µg/kg) | 264 | 4.01 | 2700000 | 2700000 | 2700000 | 5200000 | 3000000 | 1000000000 | | |
| Acetophenone | (µg/kg) | 264 | 11.0 | 52000000 | 52000000 | 52000000 | 150000000 | 210000000 | 14000000000 | | |
| Anthracene | (µg/kg) | 264 | 2.41 | 1600000000 | 1600000000 | 1600000000 | 730000000 | 1000000000 | 29000000000 | 1190 | EPA 2003 / 10 |
| Atrazine | (µg/kg) | 40.0 | 36.0 | - | - | - | 330000 | - | - | | |
| Benzaldehyde | (µg/kg) | 264 | 23.0 | - | - | - | - | - | - | | |
| Benzo[a]anthracene | (µg/kg) | 264 | 3.41 | - | - | - | 80000 | - | - | 1680 | EPA 2003 / 10 |
| Benzo[a]pyrene | (µg/kg) | 264 | 9.34 | - | - | - | 8000 | - | 1900000 | 1930 | EPA 2003 / 10 |
| Benzo[b]fluoranthene | (µg/kg) | 264 | 6.50 | - | - | - | 80000 | - | - | 1960 | EPA 2003 / 10 |
| Benzo[g,h,i]perylene | (µg/kg) | 264 | 7.10 | - | - | - | 7000000 | - | 350000000 | 2190 | EPA 2003 / 10 |
| Benzo[k]fluoranthene | (µg/kg) | 264 | 6.93 | - | - | - | 800000 | - | - | 1960 | EPA 2003 / 10 |
| Bis(2-chloroethoxy)methane | (µg/kg) | 264 | 12.0 | - | - | - | - | - | - | | |
| Bis(2-chloroethyl)ether | (µg/kg) | 80.0 | 12.0 | 13000 | 13000 | 13000 | 58000 | 44000 | 12000000 | 4761000 | Region 4 |
| Bis(2-ethylhexyl) phthalate | (µg/kg) | 264 | 51.0 | - | - | - | 12000000 | - | 890000000 | 5290 | Region 4 |
| Butyl benzyl phthalate | (µg/kg) | 264 | 22.0 | - | - | - | 120000000 | - | 21000000000 | 590 | Region 4 |
| Caprolactam | (µg/kg) | 264 | 75.0 | - | - | - | 310000000 | - | 290000000 | | |
| Carbazole | (µg/kg) | 264 | 19.0 | - | - | - | 2400000 | - | 78000000 | 2200 | Region 4 |
| Chrysene | (µg/kg) | 264 | 1.49 | - | - | - | 8000000 | - | - | 1690 | EPA 2008 / 10 |
| Dibenz(a,h)anthracene | (µg/kg) | 264 | 6.92 | - | - | - | 8000 | - | - | | |
| Dibenzofuran | (µg/kg) | 264 | 13.0 | 160000 | 160000 | 160000 | - | 3600000 | 2900000 | 3400 | EPA 2008 / 10 |
| Diethyl phthalate | (µg/kg) | 264 | 31.0 | - | - | - | 550000000 | - | 1500000000 | | |
| Dimethyl phthalate | (µg/kg) | 264 | 14.0 | - | - | - | 1000000000 | - | 1500000000 | | |
| Di-n-butyl phthalate | (µg/kg) | 264 | 22.0 | - | - | - | 87000000 | - | 1500000000 | 2000000 | Region 4 |
| Di-n-octyl phthalate | (µg/kg) | 264 | 28.0 | - | - | - | 20000000 | - | 14000000000 | | |
| Fluoranthene | (µg/kg) | 264 | 4.45 | 880000000 | 880000000 | 890000000 | 130000000 | 1000000000 | 4100000000 | 1410 | EPA 2003 / 10 |
| Fluorene | (µg/kg) | 264 | 2.74 | 150000000 | 150000000 | 150000000 | 87000000 | 1000000000 | 4100000000 | 1080 | EPA 2003 / 10 |
| Hexachlorobenzene | (µg/kg) | 264 | 2.85 | 56000 | 56000 | 56000 | 37000 | 220000 | 8500000 | | |
| Hexachlorobutadiene | (µg/kg) | 40.0 | 12.0 | 460000 | 460000 | 460000 | 470000 | 710000 | 180000000 | | |
| Hexachlorocyclopentadiene | (µg/kg) | 264 | 62.0 | 60000 | 60000 | 60000 | 6700000 | 56000 | 5900000 | | |
| Hexachloroethane | (µg/kg) | 264 | 9.00 | 1400000 | 1400000 | 660000 | 730000 | 79000 | 100000000 | | |
| Indeno[1,2,3-cd]pyrene | (µg/kg) | 264 | 7.36 | - | - | - | 80000 | - | - | 2230 | EPA 2003 / 10 |
| Isophorone | (µg/kg) | 264 | 12.0 | - | - | - | 22000000 | - | 8200000000 | | |
| Naphthalene | (µg/kg) | 264 | 2.41 | 350000 | 350000 | 350000 | 52000000 | 470000 | 88000000 | 770 | EPA 2003 / 10 |
| Nitrobenzene | (µg/kg) | 264 | 13.0 | 64000 | 64000 | 64000 | 340000 | 170000 | 21000000 | | |
| N-Nitrosodi-n-propylamine | (µg/kg) | 264 | 11.0 | - | - | - | 5400 | - | 2000000 | | |
| N-Nitrosodiphenylamine | (µg/kg) | 264 | 12.0 | - | - | - | 7800000 | - | 2800000000 | | |
| Pentachlorophenol | (µg/kg) | 150 | 58.0 | - | - | - | 320000 | - | 130000000 | | |
| Phenol | (µg/kg) | 264 | 8.00 | - | - | - | 230000000 | - | 18000000000 | 240 | Region 4 |
| Phenanthrene | (µg/kg) | 264 | 2.23 | 190000 | 190000 | 190000 | 5200000 | 5100000 | 2900000 | 1200 | EPA 2003 / 10 |
| Pyrene | (µg/kg) | 264 | 2.14 | 780000000 | 780000000 | 780000000 | 84000000 | 1000000000 | 2900000000 | 1390 | EPA 2003 / 10 |
| 3 & 4 Methylphenol | (µg/kg) | 264 | 29.0 | - | - | - | 36000000 | - | 2900000000 | | |

**Table 3.2**

**Soil Parameter List**
**Laboratory Limits and MI Part 201 Criteria**
**Work Plan to Complete Additional IU H Soil Sampling**
**RACER Nodular Facility**
**Saginaw, Michigan**

| Parameter | Criteria Units | Estimated Quantitation Limits (EQL)[1] Soil | Method Detection Limits (MDL)[2] Soil | Michigan Part 201 Criteria: Non_RES/Ambient Air_Finite VSIC_2M Srce Thickness | Non_RES/Ambient Air_Finite VSIC_5M Thickness | Non_RES/Ambient Air_InfiniteSrceVolatileSoilInhalation | Non_RES/Direct Contact | Non_RES/IndoorAir_SoilVolatilization_IndAirInhalation | Non_RES/Particulate Soil Inhalation | Ecological Screening Levels | Source |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **General Chemistry** | | | | | | | | | | | |
| Total Cyanide | mg/kg | 0.500 | 0.190 | - | - | - | 250 | - | 250 | | |
| Black Carbon (Lloyd Kahn) | mg/kg | 1000 | 1,000 | | | | | | | | |
| Organic Carbon, Total (TOC) | mg/kg | 1000 | 671 | | | | | | | | |

Notes:

[1] - Please note that these are targeted quantitation limits and are presented for guidance only. Actual quantitation limits are highly matrix dependent and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes.

[2] - Method Detection Limits (MDL) are also presented for guidance only. Actual MDLs will vary depending on sample specific preparation factors. The MDLs are also highly matrix dependant and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes. Laboratory MDLs are updated on a periodic basis and the MDLs in effect when the samples are analyzed will be used for reporting purposes.

SVOCs -Semi-Volatile Organic Compounds

**Table 3.3**

**Laboratory Precision and Accuracy Limits**
**Work Plan to Complete Additional IU H Soil Sampling**
**RACER Nodular Facility**
**Saginaw, Michigan**

| Analysis | Analyte Description | LCS/LSCD Limits %Recovery | LCS/LSCD Limits RPD | MS/MSD Limits %Recovery | MS/MSD Limits RPD |
|---|---|---|---|---|---|
| **SVOCs** | 1,1'-Biphenyl | 43-120 | 40 | 38-120 | 32 |
| | 2,2'-oxybis[1-chloropropane] | 29-120 | 40 | 27-120 | 40 |
| | 2,4,5-Trichlorophenol | 28-120 | 40 | 22-120 | 40 |
| | 2,4,6-Trichlorophenol | 14-120 | 40 | 15-120 | 34 |
| | 2,4-Dichlorophenol | 40-120 | 40 | 30-120 | 40 |
| | 2,4-Dimethylphenol | 31-120 | 40 | 25-120 | 36 |
| | 2,4-Dinitrophenol | 10-120 | 40 | 10-120 | 40 |
| | 2,4-Dinitrotoluene | 49-120 | 40 | 51-120 | 21 |
| | 2,6-Dinitrotoluene | 49-120 | 40 | 51-120 | 20 |
| | 2-Chloronaphthalene | 42-120 | 40 | 39-120 | 32 |
| | 2-Chlorophenol | 42-120 | 40 | 30-120 | 40 |
| | 2-Methylnaphthalene | 42-120 | 40 | 10-133 | 40 |
| | 2-Methylphenol | 42-120 | 40 | 28-120 | 40 |
| | 2-Nitroaniline | 44-120 | 40 | 49-120 | 19 |
| | 2-Nitrophenol | 41-120 | 40 | 25-120 | 40 |
| | 3,3'-Dichlorobenzidine | 29-120 | 40 | 10-120 | 40 |
| | 3-Nitroaniline | 41-120 | 40 | 20-120 | 40 |
| | 4,6-Dinitro-2-methylphenol | 27-120 | 40 | 10-123 | 40 |
| | 4-Bromophenyl phenyl ether | 47-120 | 40 | 47-120 | 20 |
| | 4-Chloro-3-methylphenol | 39-120 | 40 | 33-120 | 40 |
| | 4-Chloroaniline | 30-120 | 40 | 21-120 | 40 |
| | 4-Chlorophenyl phenyl ether | 46-120 | 40 | 47-120 | 21 |
| | 4-Nitroaniline | 47-120 | 40 | 20-120 | 40 |
| | 4-Nitrophenol | 29-120 | 40 | 14-120 | 36 |
| | Acenaphthene | 45-120 | 40 | 41-120 | 34 |
| | Acenaphthylene | 45-120 | 40 | 39-120 | 34 |
| | Acetophenone | 42-120 | 40 | 32-120 | 40 |
| | Anthracene | 52-120 | 40 | 43-106 | 32 |
| | Atrazine | 54-120 | 40 | 50-120 | 22 |
| | Benzaldehyde | 38-120 | 40 | 18-120 | 40 |
| | Benzo[a]anthracene | 52-120 | 40 | 32-120 | 37 |
| | Benzo[a]pyrene | 50-120 | 40 | 35-120 | 38 |
| | Benzo[b]fluoranthene | 52-120 | 40 | 27-126 | 40 |
| | Benzo[g,h,i]perylene | 54-120 | 40 | 29-122 | 40 |
| | Benzo[k]fluoranthene | 54-120 | 40 | 39-120 | 37 |
| | Bis(2-chloroethoxy)methane | 43-120 | 40 | 36-120 | 39 |
| | Bis(2-chloroethyl)ether | 41-120 | 40 | 32-120 | 40 |
| | Bis(2-ethylhexyl) phthalate | 47-120 | 40 | 42-129 | 40 |
| | Butyl benzyl phthalate | 47-120 | 40 | 39-121 | 24 |
| | Caprolactam | 55-120 | 40 | 44-120 | 28 |
| | Carbazole | 51-120 | 40 | 46-120 | 28 |
| | Chrysene | 53-120 | 40 | 31-121 | 37 |
| | Dibenz(a,h)anthracene | 50-120 | 40 | 36-120 | 38 |
| | Dibenzofuran | 46-120 | 40 | 45-120 | 26 |
| | Diethyl phthalate | 45-120 | 40 | 45-120 | 19 |
| | Dimethyl phthalate | 47-120 | 40 | 47-120 | 20 |
| | Di-n-butyl phthalate | 50-120 | 40 | 46-120 | 21 |
| | Di-n-octyl phthalate | 38-120 | 40 | 44-120 | 25 |
| | Fluoranthene | 54-120 | 40 | 30-125 | 31 |
| | Fluorene | 48-120 | 40 | 44-120 | 32 |

**Table 3.3**

**Laboratory Precision and Accuracy Limits**
**Work Plan to Complete Additional IU H Soil Sampling**
**RACER Nodular Facility**
**Saginaw, Michigan**

| Analysis | Analyte Description | LCS/LSCD Limits %Recovery | LCS/LSCD Limits RPD | MS/MSD Limits %Recovery | MS/MSD Limits RPD |
|---|---|---|---|---|---|
| **SVOCs cont'd** | Hexachlorobenzene | 45-120 | 40 | 47-120 | 23 |
| | Hexachlorobutadiene | 34-120 | 40 | 27-120 | 40 |
| | Hexachlorocyclopentadiene | 10-120 | 40 | 10-120 | 40 |
| | Hexachloroethane | 36-120 | 40 | 10-120 | 40 |
| | Indeno[1,2,3-cd]pyrene | 52-120 | 40 | 34-120 | 40 |
| | Isophorone | 42-120 | 40 | 32-120 | 40 |
| | Naphthalene | 39-120 | 40 | 30-120 | 40 |
| | Nitrobenzene | 42-120 | 40 | 32-120 | 40 |
| | N-Nitrosodi-n-propylamine | 39-120 | 40 | 30-120 | 40 |
| | N-Nitrosodiphenylamine | 50-120 | 40 | 46-120 | 24 |
| | Pentachlorophenol | 16-120 | 40 | 10-120 | 40 |
| | Phenol | 39-120 | 40 | 25-120 | 40 |
| | Phenanthrene | 50-120 | 40 | 31-120 | 35 |
| | Pyrene | 50-120 | 40 | 28-122 | 30 |
| | 3 & 4 Methylphenol | 43-120 | 40 | 34-120 | 40 |
| **General Chemistry** | Total Cyanide | 65-128 | 20 | 24-140 | 40 |
| | Black Carbon (Lloyd Kahn) | 50-150 | | 50-150 | 20 |
| | Organic Carbon, Total (TOC) | 75-125 | 20 | 75-125 | 20 |

Notes:

LCS/LCSD - Lab Control Sample/Lab Control Sample Duplicate
MS/MSD - Matrix Spike/Matrix Spike Duplicte Sample
SVOCs -Semi-Volatile Organic Compounds

**Table 3.4**

**Summary of Sampling and Analysis Program**
**Work Plan to Complete Additional IU H Soil Sampling**
**RACER Nodular Facility**
**Saginaw, Michigan**

| Investigation Activity | Sample Matrix | Field Parameters | Laboratory Parameters | Investigative Samples | Quality Control Samples | | MS/MSD (2) |
|---|---|---|---|---|---|---|---|
| | | | | | Equipment Blanks(1) | Field Dup | |
| Area 1 | Soil | None | SVOCs | 12 | 1 | 1 per 10 | 1 |
| Area 2 | Soil | None | Cyanide | 8 | 1 | 1 per 10 | 1 |
| Area 1,2 (0-2 ft bgs) | Soil | None | Organic Carbon, Total (TOC) | 8 | 1 | 1 per 10 | 1 |
| Area 1,2 (0-2 ft bgs) | Soil | None | Black Carbon (Lloyd Kahn) | 8 | 1 | 1 per 10 | 1 |

Notes:

(1) - Equipment blank will be collected in the event that disposable sampling equipment is not being used.

(2) - Matrix Spike/Matrix Spike duplicate (MS/MSD) analyses are required for samples submitted for analyses are to be analyzed at a frequency of one per group of twenty (20) or fewer investigative samples for the activities detailed above. The MS/MSD is a pair a of two samples--spike and spike duplicate.

**Table 3.5**

**Container, Preservation, Shipping and Packaging Requirments**
**Work Plan to Complete Additional IU H Soil Sampling**
**RACER Nodular Facility**
**Saginaw, Michigan**

| Analyses | Sample Containers | Preservation | Maximum Holding Time from Sample Collection1 | Volume of Sample | Shipping | Normal Packaging |
|---|---|---|---|---|---|---|
| **SOLID (Soil)** | | | | | | |
| SVOCs | One 4-ounce glass jar | Iced, 4 ± 2° C | 14 days to extraction; 40 days from extraction to analysis | 4-ounce | Overnight or Hand Deliver | Bubble-wrap |
| Total Cyanide | One 4-ounce glass jar | Iced, 4 ± 2° C | 14 days to analysis | 4-ounce | Overnight or | Bubble-wrap |
| Organic Carbon, Total (TOC) | One 4 ounce glass jar | Iced, 4 ± 2° C | 14 days to analysis | Fill to shoulder of jar | Overnight or Hand Deliver | Foam Liner or Bubble-wrap |
| Black Carbon (Lloyd Kahn) | One 4 ounce glass jar | Iced, 4 ± 2° C | 14 days to analysis | Fill to shoulder of jar | Overnight or Hand Deliver | Foam Liner or Bubble-wrap |

Notes:

1 - These are technical holding times, i.e., are based on time elapsed from time of sample collection.
SVOCs - Semi-Volatile Organic Compounds

# Attachment A
# GHD Field Training Manual Section 5.0: Soil Sampling

# GHD Field Training Manual

Section 5.0
Soil Sampling Standard Operating Procedures

Part 1 - Surficial Soil Sampling, Borehole Installation and Sample Collection, and Test Pit Excavation and Sampling

(T102A)

Part 2 - GHD Approach for Soil Materials Description and Classification

(T100)

July 2015

Last Updated: September 2018

# Please adhere to the following Quality System training requirements:

- Employees who are required to conduct a specific field activity must be properly certified to do the work.
- This involves reviewing the SOP and completing the online training course and exam.
- Employees must also conduct this field work under supervised conditions on at least three occasions, and must be certified by a qualified mentor. Only then can an employee conduct a specific field activity on their own. This is documented on a Field Method Training Record (QSF-021).
- Complete the QSF-021 and forward it to trainingrecords-northamerica@ghd.com.
- Please note that four topics are discussed in this SOP. A separate QSF-021 is required for each topic:
  - Surficial Soil Sampling
  - Borehole Installation and Sample Collection
  - Test Pit Excavation and Sampling
  - GHD Approach for Soil Materials Description and Classification

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# Quality System Forms Index

# 5. Soil Sampling Standard Operating Procedures

## 5.1 Introduction

Soil sampling is conducted to characterize the physical and/or chemical conditions at a site. Standard Operating Procedures (SOPs) are presented herein for obtaining a variety of soil samples for physical and chemical analyses, including:

- Surficial soil samples (soil between ground surface and 6 to 12 inches (15 to 30 cm) below ground surface)
- Subsurface samples that require borehole installation
- Test pit excavations

This guideline is not intended to provide the basis for designing a soil sampling program, but instead assumes that a soil sampling program has been designed, a Work Plan has been established, and the sampling team is preparing to mobilize to the field.

Soil sampling procedures vary from project to project due to different parameters of concern, different guidance provided by the state/province where the site is located, or the specific objectives for the project. Therefore, it is essential that the sampling team members carefully review the Work Plan. The primary goal of surface soil sampling is to collect representative samples for examination and chemical analysis (if required).

The remainder of this section is organized as follows:

- Section 5.2 Sampling Methods
- Section 5.3 Planning and Preparation
- Section 5.4 Safety and Health
- Section 5.5 Quality Assurance/Quality Control
- Section 5.6 Equipment Decontamination
- Section 5.7 Procedures for Soil Classification
- Section 5.8 Procedures for Surficial Soil Sampling
- Section 5.9 Procedures for Borehole Installation and Sampling
- Section 5.10 Procedures for Test Pit Excavation and Sampling
- Section 5.11 Follow-up Activities
- Section 5.12 References

## 5.2 Sampling Methods

### 5.2.1 Surficial Soil Sampling

Surficial soil sampling is less frequently used than subsurface soil sampling (which involves borehole installation). Typically, surficial soil sampling is used when a large site is being assessed and the extent of contamination is unknown. In this case, surficial sampling is helpful in identifying the location of surface releases (e.g., historical spills of hydrocarbons) that may have contributed to subsurface contamination. A surficial soil sampling program is also recommended for sites with suspected atmospheric deposition of contaminants (e.g., stacks), areas of surface spills, or recent spills.

Surficial soil sampling is used when contamination is known to be restricted to the surficial region of the soil stratum. Thus, surficial sampling can be useful at brownfield sites, where it is necessary to determine if soils are contaminated with specific contaminants of concern (e.g., metals) as part of a purchaser's due diligence. Surficial soil sampling can also be required when obtaining data in order to perform a site-specific risk assessment.

For the purposes of this section, the surficial soil is considered to be the 0- to 6-inch (0 to 15 cm) soil horizon.

Samples are collected from areas where surficial soil contamination is known or suspected. Samples from a particular depth increment must not be mixed with soil from other depths. Soil horizons displaying different properties should be sampled separately, since they may behave very differently with respect to contaminant accumulation and movement.

### 5.2.2 Borehole Installation and Sampling

A significant portion of GHD's field activities involve borehole installation.

Several manual methods are available for the collection of shallow subsurface soil samples (e.g., hand augers, post-hole augers). However, the most common methods used by GHD to advance boreholes are a drill rig equipped with continuous flight hollow-stem augers (HSAs) and split-spoon samplers, or a direct-push drilling unit equipped with solid tube soil samplers.

### 5.2.3 Test Pit Excavation and Sampling

Test pits are typically excavated to explore and define geologic conditions (or buried waste/debris) and to allow the collection of subsurface soil samples for geotechnical or chemical analysis. Test pits give a more complete view of the subsurface soil conditions than soil borings. Test pits are excavated using either a rubber-tired backhoe or track-mounted excavator, and can extend 10 to 15 feet (3.0 to 4.6 m) below ground surface.

The use of test pits for investigation is determined on a site-specific basis. Experience from past projects has identified the following issues:

1. The nature and extent of contamination which may be encountered may be unknown. The Site-specific Health and Safety Plan (HASP) and Job Safety Analysis (JSA) must be specific to the level of Personal Protective Equipment (PPE); this may be Level A or B.

2. Waste materials, including drums, may be encountered. A plan must be in place specifying how this material will be handled.

3. Air emissions of some compounds may occur. A plan must be in place to ensure that employees and the public are adequately protected.

4. Community relations concerns may exist (e.g., workers in chemically protective "moon suits"). A notification plan may be required.

5. All underground utilities must be located utilizing documentation using the GHD Subsurface Clearance Protocol.

### 5.2.4 Grab Versus Composite Samples

A grab sample is collected to identify and quantify compounds at a specific location or interval. The sample is comprised of no more than the minimum amount of soil necessary to make up the volume of sample dictated by the required sample analyses. Composite samples are a mixture of a given number of sub-samples and are collected to characterize the average composition in a given surface area.

Samples to be analyzed for volatile organic compounds (VOCs) are always collected as grab samples. Mixing of soil samples to create a composite is not performed. Mixing of soil samples results in partial volatilization of VOCs from the soil, and thus compromises the integrity of the composite soil sample.

## 5.3 Planning and Preparation

The following activities are required prior to undertaking a soil sampling program:

1. Review the Work Plan, project documents, and health and safety requirements with the Project Coordinator.

2. Complete a Field Equipment Requisition Form (QSF-014) and assemble all equipment, materials, log books, and forms. Form SP-02 (Project Planning, Completion, and Follow-Up Checklist) should be used for guidance throughout the project. Borehole Installation/Soil Sampling Equipment and Supply Checklist (Form SP-12) provides a summary of the typical equipment/materials required for soil sampling. Drilling/Well Construction Checklist (Form SP-13) provides a listing of pre-planning and site activities that is designed as an aid to preparing and completing the project.

3. Obtain a site plan and any previous stratigraphic logs. Determine the exact number, location, and depths of samples to be collected.

4. Complete a Vendor Evaluation Form (QSF-012) and file in the project file for any vendors that do not have full approval status or are not listed on the Approved Vendor List (QSL-004). Completion of a Safety and Health Schedule (QSF-030 for Canadian work; QSF-031 for U.S. work) is necessary for all vendors who complete field services. Prior to mobilization on site, the vendor must submit the form to the Regional Safety and Health Manager for review and approval (if not already posted on QSL-004).

5. Contact GHD's Chemistry Group to arrange/determine:
    - SSOW (simplified Scope of Work)
    - Glassware/sample jars
    - Cooler
    - Shipping details
    - Start date
    - Laboratory
    - Expected sampling duration
6. Initiate a Property Access/Utility Clearance Data Sheet (QSF-019), if necessary. In most instances, surface sampling activities do not require utility clearances.
7. Determine notification needs with the Project Coordinator. Have the regulatory groups, client, landowner, GHD personnel, and laboratory been informed of the sampling event?
8. Determine the methods for handling and disposal of wash waters and spent decontamination fluids.

In addition to the above, the following may be required when conducting a borehole or test pit program:

1. Establish a water source for drilling and decontamination activities. Pre-plan the methods for handling and disposal of drill cuttings, wash waters, and spent decontamination fluids.
2. Arrange with driller to provide paraffin wax, melting pot, and heat source (if required).

## 5.4 Safety and Health

GHD is committed to conducting field activities in accordance with sound safety and health practices. GHD adheres to high safety standards to protect the safety and health of all employees, subcontractors, customers, and communities in which they work. The safety and health of our employees takes precedence over cost and schedule implications.

Field personnel are required to implement the Safety Means Awareness Responsibility Teamwork (SMART) program as follows:

- Assure the HASP is specific to the job and approved by a Regional Safety and Health Manager.
- Confirm that all HASP elements have been implemented for the job.
- A JSA for each task has been reviewed, modified for the specific site conditions and communicated to all appropriate site personnel. The JSAs are a component of the HASP.
- Incorporate Stop Work Authority; Stop, Think, Act, Review (STAR) process; Safe Task Evaluation Process (STEP); Observations process; Near Loss and Incident Management process in the day-to-day operations of the job.
- Review and implement applicable sections of the GHD Safety and Health Policy Manual.

- Confirm that all site personnel have the required training and medical surveillance, as defined in the HASP.
- Be prepared for emergency situations, locating safety showers, fire protection equipment, evacuation route, rally point, and first aid equipment before you begin working, and make sure the equipment is in good working order.
- Maintain all required PPE, safety equipment, and instrumentation necessary to perform the work effectively, efficiently, and safely.
- Be prepared to call the GHD Incident Hotline at 1-866-529-4886 for all incidents involving injury/illness, property damage, and vehicle incident and/or significant Near Loss.

It is the responsibility of the Project Manager to:

- Ensure that all GHD field personnel have received the appropriate health and safety and field training and are qualified to complete the work.
- Provide subcontractors with a Job Hazard Analysis to enable them to develop their own HASP.
- Ensure that all subcontractors meet GHD's (and the client's) safety requirements.

## 5.5 Quality Assurance/Quality Control

A well-designed Quality Assurance/Quality Control (QA/QC) program will:

- Ensure that data of sufficient quality are obtained in order to facilitate good site management.
- Allow for monitoring of staff and contractor performance.
- Verify the quality of the data for the regulatory agency.

The QA/QC program is developed on a site-specific basis. QA/QC requirements are discussed in detail in Section 3.9.

## 5.6 Equipment Decontamination

### *Borehole Installation and Sampling*

Prior to use and between each borehole location at an environmental site, the drilling and sampling equipment must be decontaminated in accordance with the Work Plan or the methods presented in this section.

The minimum wash procedures for decontamination of drilling or excavating equipment are:

1. High pressure hot water detergent wash (brushing as necessary to remove particulate matter).
2. Potable, hot water, high pressure rinse.

Cover the clean augers with clean plastic sheeting to prevent contact with foreign materials. For geotechnical, geologic, or hydrogeologic studies where contaminants are not present, it is sufficient to clean the drilling or excavating equipment simply by removing the excess soils.

On environmental sites, the soil sampler equipment (split spoons, trowel, spoons, shovels, bowls) are typically cleaned as follows:

1. Wash with clean potable water and laboratory detergent, using a brush as necessary to remove particulates.
2. Rinse with tap water.
3. Rinse with deionized water.
4. Air dry for as long as possible.

In addition, the following steps may be added when sampling for VOCs and metals:

1. Rinse with 10 percent nitric acid (only if samples are to be analyzed for metals).
2. Rinse with deionized water.
3. Rinse with appropriate solvent (pesticide grade isopropanol, methanol, acetone, hexane, if required).
4. Rinse again with deionized water.
5. Air dry for as long as possible.
6. Wrap split-spoon samplers in aluminum foil to prevent contamination.

> Caution: Check the Quality Assurance Project Plan (QAPP) to confirm the cleaning protocol. Use of incorrect cleaning protocol could invalidate chemical data.

## 5.7 Procedures for Soil Classification

This SOP for Soil Classification is not intended to provide complete training in soil classification. Soil Classification will require additional training and experience.

Criteria and procedures for soil classification and description include:

1. A standard method of describing the soil by name and group symbol.
2. Standard field identification methods based on visual examination and manual tests on representative soil samples by a qualified GHD representative for interpretation of subsurface conditions at the site.
3. Verifying field description descriptions through the inspection.
4. Confirming descriptive information by laboratory determination of selected soil characteristics if required in the Work Plan.
5. Factual overburden stratigraphic logs completed by GHD personnel responsible for interpreting the subsurface conditions at the site and review/confirmation of soil descriptions by the Project Coordinator.

The overburden stratigraphic log is the factual description of the soil at each borehole location and will be relied on to interpret soil characteristics at the site. The overburden stratigraphic log will also be used to interpret the soil characteristics' influence and significance on the subsurface

environment. GHD personnel responsible for interpreting the subsurface conditions at the site will also verify overburden stratigraphic log accuracy. If practical, the Project Coordinator, Geologist, or Geotechnical Engineer should confirm the soil descriptions and examine representative soil samples.

Describing and classifying soils is a skill that is learned through experience and by systematic training using laboratory results of soil composition in comparison to field descriptions.

> Note: Attendance at a soil identification course provided by GHD is mandatory.

Descriptions for natural undisturbed soils are recorded on a Stratigraphy Log (Overburden) (Form SP-14). An example of a completed Stratigraphy Log (Overburden) is presented on Figure 5.1.

Soil descriptions are completed in the following order:

1. Unified Soil Classification System (USCS) group symbol(s) (e.g., SM) of primary soil components or dual or borderline symbols.
2. Name and adjective description of primary, secondary, and minor grain size components.
3. Relative density for non-cohesive soils or consistency for cohesive soils.
4. Gradation and soil structure for non-cohesive soils or structure and plasticity for cohesive soils.
5. Color.
6. Moisture content.
7. Other physical observations including presence of staining and or odors.

> Note: When describing observed odors, be as specific as possible to classify general odor category and strength of odor. Odors are generally chemical, petroleum, or septic related, varying from slight to moderate to strong. Identification of specific chemical compounds (i.e., benzene, gasoline) is not necessary and is often inaccurate as detailed chemistry commonly shows an array of chemicals present.

When describing vegetative matter presence in soils, do not use the term organic. The use of the term organic often leads to confusion regarding the presence of organic chemicals (i.e., VOCs, semi-volatile organic compounds [SVOCs]). Similarly, as noted above, use more specific terms for odors than organic.

The description of fill soils is similar to those used to describe native undisturbed soils. Fill soils will be identified as fill (i.e., SP/GP-Sand and Gravel [Fill]). To determine if soils are fill, look for evidence that the soil has been artificially placed (e.g., brick fragments, slag, glass, wood fragments). Relative or inconsistent soil density can also assist in determining if soils are fill, along with irregular soil structure.

Soils are identified and grouped consistently to determine subsurface pattern or changes and non-conformities in the soil stratigraphy. The stratigraphy of each soil boring or test pit is compared

to ensure that patterns or changes in soil stratigraphy are noted and that consistent terminology is used.

Visual examination, physical observation, and manual tests (based on ASTM D2488, Standard Practice for Description and Identification of Soils [Visual-Manual Procedure]) are used to aid in classifying and grouping soil samples in the field. These procedures are described in the following subsection. ASTM D2488 should be reviewed for detailed explanations of the procedures. (Note that the related ASTM D2487 Standard Practice for Classification of Soils for Engineering Purposes [Unified Soil Classification System] uses slightly different percentages of soil components.) Visual-manual procedures used to aid in soil identification and classification include:

1. Visual determination of grain size, soil gradation, and percentage of various soil components to the nearest 5 percent (i.e., gravel, sand, silt, and clay).
2. Dry strength, dilatancy, toughness, and plasticity tests (i.e., thread or ribbon test) for identification of inorganic fine-grained soils (e.g., CL or CH [clays], and ML or MH [silts]).
3. Soil compressive strength and consistency estimates based on thumb indent and or pocket penetrometer (preferred) methods.

The three main soil divisions are:

1. Coarse-grained soils (e.g., sand and gravel)
2. Fine-grained soils (e.g., silts and clays)
3. Soils with high natural organic and vegetative matter content (e.g., peat, marl)

These soil divisions are presented in the table of USCS classifications below.

| Major Division | | | Group Symbol | Typical Description |
|---|---|---|---|---|
| Coarse grained soils more than 50% retained on No. 200 sieve | Gravel more than 50% of coarse fraction retained on No. 4 sieve | clean gravel <5% fines | GW | well graded gravel, gravel-sand mixtures |
| | | | GP | poorly graded gravel, gravel-sand mixtures |
| | | gravel with >15% fines | GM | silty gravel, gravel-sand-silt mixtures |
| | | | GC | clayey gravel, gravel-sand-clay mixtures |
| | Sand more than 50% of coarse fraction passes No. 4 sieve | clean sand <5% fines | SW | well graded sand, fine to coarse sand, gravelly sand |
| | | | SP | poorly graded sand |
| | | sand with >15% fines | SM | silty sand, sand-silt mixtures |
| | | | SC | clayey sand, sand-clay mixtures |
| Fine grained soils more than 50% | | inorganic | ML | Inorganic silt |
| | | | CL | Inorganic clay |

| Major Division | | | Group Symbol | Typical Description |
|---|---|---|---|---|
| passes No. 200 sieve | Silt and Clay liquid limit <50, low plasticity | organic | OL | organic silt, organic clay |
| | | | | silt of high plasticity, elastic silt |
| | Silt and Clay liquid limit ≥50, high plasticity | inorganic | MH | clay of high plasticity, fat clay |
| | | | CH | organic clay, organic silt, low plasticity |
| | | organic | OL | organic clay, organic silt, high plasticity |
| | | | OH | |
| Highly organic soils | | | Pt | peat |

### 5.7.1 Coarse Grained Soils

The USCS symbols for coarse-grained soil are primarily based on grain size, grain size distribution (gradation), and percent of fines (silt and clay content).

Grain size classification used for describing soils is in terms of particle size and sieve size (e.g., gravelly sand, trace silt). Coarse-grained soil is composed of more than 50 percent by weight, sand size, or larger (75 μm diameter, No. 200 sieve size). Note that there are other definitions for coarse-grained or coarse textured soil and for sand and for sand size as soil having greater than 70 percent particles equal to or greater than 50 μm diameter (after "Guidelines for Contaminated Sites in Ontario") or 60 μm diameter ("Canadian Foundation Manual").

The percentage descriptors for soil components are different for coarse-grained versus fine-grained soils. The following are the percentage component descriptors for coarse-grained soils:

| Noun (e.g., sand, gravel) | Major Component |
|---|---|
| Adjective (e.g., silty, clayey, sandy, gravelly) | Greater than 15% |
| With (e.g., with silt, with clay, with sand, with gravel) | 5% to 15% |
| Trace (e.g., trace silt, trace clay, trace sand, trace gravel) | <5% |

Grain size distribution of coarse-grained soils includes:

- Poorly graded (i.e., soil having a uniform or predominantly one grain size, SP and GP)
- Well graded (i.e., poorly sorted soils with a wide range of particle sizes with substantial percentage of intermediate sizes, SW and GW)
- Dirty (i.e., soil having greater than 15 percent fines, SM, SC, GM, and GC)

Coarse-grained soils are further classified based on the percentage of fine-grained soils (e.g., silts and clays) they contain. Coarse-grained soils containing greater than 15 percent fine-grained soils are described with an adjective (e.g., silty [SM, GM], clayey [SC, GC]). This description is attributed to soil particles that adhere when the soil sample is rubbed between the hands or adhere to the sides of sample jars after shaking, or rolling in the jar. The jar shake test will also result in the segregation of sand and gravel particles and can be used as a visual aid in determining sand and gravel content percentages.

Examples of the group symbol, name, and adjectives used to describe the primary, secondary, and minor components of soil are:

- GW - Sandy Gravel (e.g., 70 percent gravel and 30 percent sand, well graded)
- GW - Sandy Gravel-trace silt (less than 5 percent silt, well graded)
- SP - Sand (a uniform sand, predominantly one sand grain size)
- SM - Silty Sand, with clay (sand with greater than 15 percent silt, and 5 to 15 percent clay)

Relative density is important in establishing the engineering properties and behavior of coarse-grained soils. Relative density of non-cohesive (coarse-grained) soils is determined using the standard penetration test (SPT) blow counts (N-values) in accordance with ASTM D1586. A detailed discussion of the SPT and N values can be found in Section 5.9.2.1.

The SPT provides reliable indications of the relative density of sand and fine gravel. N-values in coarse-grained soil are influenced by a number of factors that result in overestimated relative densities. For example, in coarse-grained gravel, dilatent silty fine sands, sand below the water table and uniform coarse sand, N-values tend to be conservative and under estimate the relative density. The Project Geotechnical Engineer will assess these effects, if required.

Other methods, such as modified SPT and cone penetration tests, are used on occasion to supplement or replace the SPT method for certain site-specific conditions. All modifications to the SPT or substitute methods must be recorded as required to interpret test results and correlate relative density.

### 5.7.2 Fine-Grained Soil

A fine-grained soil is made up of more than 50 percent silt and clay (i.e., fines greater than 50 percent by weight passing the 75 μm (No. 200) sieve size). Description of visual-manual field methods and criteria to further characterize and group fine-grained soil (e.g., CL, CH, ML, and MH) are discussed in ASTM D2488.

The percentage descriptors for components is different for fine-grained versus coarse-grained soils. The following are the percentage component descriptors for fine-grained soils:

| | |
|---|---|
| Noun (e.g., silt, clay) | Major Component |
| Adjective (e.g., sandy, gravelly, silty, clayey) | Greater than 30% |
| With (e.g., with sand, with gravel, with silt, with clay) | 15% to 30% |
| Few (e.g., few sand, few gravel, few silt, few clay) | 5% to 15% |
| Trace (e.g., trace silt, trace clay, trace sand, trace gravel) | <5% |

Further soil characterization tests include dry strength, dilatency, toughness, and plasticity (thread or ribbon test).

#### *Criteria for Describing Dry Strength*

| Description | Criteria |
|---|---|
| None | The dry specimen crumbles into powder with mere pressure of handling. |
| Low | The dry specimen crumbles into powder with some finger pressure. |

| Description | Criteria |
|---|---|
| Medium | The dry specimen breaks into pieces or crumbles with considerable finger pressure. |
| High | The dry specimen crumbles into powder with finger pressure; specimen will break into pieces between thumb and a hard surface. |
| Very High | The dry specimen cannot be broken between the thumb and a hard surface. |

### *Criteria for Describing Dilatancy*

| Description | Criteria |
|---|---|
| None | No visible change in small wetted specimen when rapidly shaken in palm of hand. |
| Slow | Water appears slowly on the surface of the specimen during shaking and does not disappear or disappears slowly upon squeezing. |
| Rapid | Water appears quickly on the surface of the specimen during shaking and disappears quickly upon squeezing or stretching. |

### *Criteria for Describing Toughness*

| Description | Criteria |
|---|---|
| Low | Only slight pressure is required to roll the thread near the plastic limit; the thread and the lump are weak and soft. |
| Medium | Medium pressure is required to roll the thread to near the plastic limit; the thread and the lump have medium stiffness. |
| High | Considerable pressure is required to roll the thread to near the plastic limit; the thread and the lump have very high stiffness. |

### *Criteria for Describing Plasticity*

| Description | Criteria |
|---|---|
| Nonplastic | 1/8-inch (3 mm) thread cannot be rolled at any water content. |
| Low | The thread can barely be rolled and the lump cannot be formed when drier than the plastic limit. |
| Medium | The thread is easy to roll and not much time is required to reach the plastic limit; the thread cannot be re-rolled after reaching the plastic limit; the lump crumbles when drier than the plastic limit. |
| High | It takes considerable time rolling and kneading to reach the plastic limit; the thread can be re-rolled several times after reaching the plastic limit; the lump can be formed without crumbling when drier than the plastic limit. |

Examples of group symbol identification based on visual-manual procedures and criteria for describing fine grained soil are:

| Group Symbol | Dry Strength | Dilatancy | Toughness | Plasticity |
|---|---|---|---|---|
| ML | None to low | Slow to rapid | Low or thread cannot be formed | Slight |
| CL | Medium to high | None to slow | Medium | Low |
| MH | Low to medium | None to slow | Low to medium | Low |
| CH | High to very high | None | High | High |

Positive classification by USCS group symbols as described in ASTM D2487, is through laboratory determination of particle size characteristics, liquid limit, and plasticity index. The need for laboratory testing will be determined by the Project Hydrogeologist, Geologist, or Geotechnical Engineer and will be detailed in the Work Plan. If no laboratory testing is performed to confirm soil classification, a statement of qualification (method used) is required for group symbols.

Examples of terminology that accompany the group symbols are:

- ML - Sandy Silt (e.g., 30 percent sand)
- CL - Clay (lean) with sand (e.g., 15 to 29 percent sand)

The USCS group symbols require the use of lean clay (CL) and fat clay (CH). The use of these symbols is dependent on the plasticity of the soil. Classification such as silty clay can only be used for a very narrow set of conditions, and will only be used if Atterberg Limit results are available. The lean and fat clay designations are not universally used, but adherence to the USCS requires that these symbols be used.

Correlation of N-values and consistency for clays is unreliable. Consistency determinations will be performed using more appropriate static test methods, especially for very soft to stiff clays. N-values are more reliable in hard clays.

Estimates of unconfined compressive strength (Su) can be obtained by a pocket penetrometer test. To estimate consistency and compressive strength with a pocket penetrometer, cut a minimum 4-inch (10 cm) soil core perpendicular to the soil core length. Hold the core with moderate confining pressure so as not to deform the soil core. Slowly insert the pocket penetrometer tip into the perpendicular face of the soil core until the pocket penetrometer indents the soil core to the mark indicated on the piston of the penetrometer. The pocket penetrometer estimate of the soil compressive strength (Su) is the direct reading of the value mark on the graduated shaft indicated by the shaft ring marker, or by the graduated piston reading at the shaft body. For average estimates, complete this procedure several times on the ends and middle of the soil core. For Shelby tube samples (or thin wall samplers), perform the pocket penetrometer test at several locations on the exposed ends of the sample.

In situ shear vane tests or other test methods provide better compressive strength estimates for very soft to stiff consistency clay soil.

Describing soil consistency is an important component in evaluating the engineering properties and strength characteristics of fine-grained cohesive soil. Consistency terms like soft and hard are based on the unconfined compressive strength (Su) and shear strength or cohesion (cu) of the soil.

Patterns of soil gas and groundwater movement in fine-grained soil are influenced by natural soil structure. Soil structure is dependent on the depositional method and to a lesser extent climate. The identification of fill soil is equally important in determining soil characteristics in fine-grained soils.

## 5.8 Procedures for Surficial Soil Sampling

This section provides a limited discussion on considerations for the design of a soil sampling program in order to provide the sampling team members with a basic understanding of those considerations.

### 5.8.1 Background

Soil sampling locations are selected in order to obtain representative soils with the minimum number of samples. Prior to conducting an investigation, a site inspection may eliminate many uncertainties with respect to site characteristics and result in a more complete soil sampling study. The site inspection should identify pertinent features (e.g., rock outcrops, drainage patterns, surface runoff, surface cover characteristics (e.g., grass, gravel, concrete), wet areas, and fill areas) and evaluate the relationship between those features and potential sources of contaminants. An understanding of these relationships and conditions is important in developing a sampling plan.

### 5.8.2 Random, Biased, and Grid-Based Sampling

Unless there is a strong indication of contaminant presence, such as staining, soil sample locations may be randomly selected from several areas within the site, such as near obvious potential sources of current or historic contamination. Potential sources include large transformers, aboveground storage tanks (ASTs), mandoors, outdoor storage racks, and drainage swales.

If an area shows evidence of contamination, such as staining or vegetative stress, biased samples are collected from the area to characterize the contamination. Background and control samples are also biased, since they are collected in locations typical of non-site-impacted conditions.

When a soil sampling investigation involves a large area, grid-based soil sampling is performed. There is no single grid size that is appropriate for all sites. Common grid sizes are developed on 50- and 100-foot (15 to 30 m) centers. It is acceptable to integrate several different grid sizes in a single investigation.

For a surficial soil sampling program, it is also important to consider the presence of structures and drainage pathways that might affect contaminant migration. It is sometimes desirable to select sampling locations in low-lying areas which are capable of retaining some surface water flow since these areas could provide samples which are representative of historic site conditions (worst-case scenario if surface water flow is a concern).

### 5.8.3 Sample Interval

Surficial soil is generally considered to be soil between ground surface and 6 to 12 inches (15 to 30 cm) below ground surface. However, for risk assessment purposes, regulatory authorities often consider soil from ground surface to 2 feet (0.6 m) below ground surface to be surficial soil.

Note: Ontario regulations state that surficial soils are 0 to 6 inches (0 to 15 cm) below ground surface.

The exact interval to be considered as surficial soil is often a matter of discussion with the regulatory authorities that review the Work Plan. The sample interval is important to the sample collection method and to the manner in which the data are ultimately interpreted. Another important factor is the type of soil. If there are different types of soil present at the site, this may have a bearing on the sample interval. For example, it may be important to separately sample a layer of material with high organic carbon content which overlies a layer of fine-grained soil.

### 5.8.4 Procedures for Surficial Sampling

Soil sampling methods are dependent upon the sample interval of interest, the type of soil material to be sampled, and the requirements for handling the sample after retrieval. The most common method for collection of surficial soil samples is the use of a stainless steel trowel. Soil samples may also be collected with spoons and push tubes. Often a shovel is required to open a trench such that sampling can be conducted. Soil that has come in contact with the shovel cannot be used as sample material.

In all cases, the sampling device must be constructed of an inert material with smooth surfaces which can be easily decontaminated. The decontamination protocol employs a sequence of cleaning agents and water designed to remove surface contaminants (refer to Section 5.6). All sampling equipment is cleaned between sample locations. A typical surficial soil sampling protocol is outlined below:

1. Collect surficial soil samples using a precleaned stainless steel trowel or other appropriate tool. Each sample consists of soil from the surface (or other starting depth) to the depth specified in the Work Plan. Sample in ditches only when there is no water present.
2. Use a new pair of disposable gloves at each sample location.
3. Prior to use, at each sample location, decontaminate all sampling tools as specified in the Work Plan or as described in Section 5.5.
4. Use a precleaned sampling tool to remove the sample from the layer of exposed soil. Place the collected soil directly into a clean, prelabeled sample jar and seal with a Teflon-lined cap. If a sample is to be split for duplicate analyses, first homogenize the soil in a precleaned stainless steel bowl.
5. After collection, place the samples on ice or cooler packs in a laboratory-supplied cooler.

Surficial debris (e.g., grass cover) should be removed from the area where the sample is to be collected using a separate precleaned device.

In the event that soil conditions are not as described in the Work Plan, or if there are unexpected distinct layers of soil present (e.g., a layer of high organic carbon content overlying a layer of fine-grained soil), sampling personnel should immediately report the conditions to the Project Coordinator for direction. Similarly, if a sampling location is in a gravel or paved area, sampling personnel should confirm with the Project Coordinator whether the surface samples are to be collected from the gravel/pavement subbase material or from the first layer of soil beneath these layers.

Also, sampling team members should immediately report any conditions to the Project Coordinator that they believe may have a negative effect on the quality of the results.

It is generally inadvisable to collect samples containing excessive amounts of large particles such as gravel. Gravel presents difficulties for the laboratory in terms of sample preparation and the results may not be truly representative of contaminant concentrations in nearby soil.

All conditions at the time of sample collection are properly documented in a field log book. This includes a thorough description of the sample characteristics including grain size, color, and general appearance; date/time of sampling; and labeling information. The location of the sampling point is described in words, and three measurements are taken from adjacent permanent structures so that, if necessary, the sample location can be readily identified in the field at a future date. It is often advisable to have a licensed land surveyor accurately survey the locations.

Soil samples are homogenized in a stainless steel bowl prior to filling sample containers. This step can be bypassed if only one sample container is required to be filled, as long as the laboratory will homogenize the sample upon receipt. It is important that soil samples be mixed thoroughly to ensure that the sample is as representative as possible of the sample interval. When using a round bowl, mixing is achieved by stirring the material in a circular motion and occasionally turning the material over. Fill the sample container completely, leaving no headspace.

Do not mix soil for samples for VOC analyses as this promotes the partial volatilization of compounds from the soil.

In 1997, EPA adopted new methods for sampling soils for VOC analysis. Method 5035 calls for collecting soil using a coring device (EnCore). For analysis of low level VOCs (typically 1 to 200 μg/kg), soil is sealed in a specially prepared vial with a solution of sodium bisulfate. For higher levels of VOCs, the soil is placed in a vial with a volume of methanol. This method increases the complexity of collecting soils and makes it imperative that the sampler and laboratory work closely together. For some soil sampling programs, multiple EnCores are required for each sample interval. The number of EnCores required per sample interval should be ascertained during the prior planning and preparation stage.

### *Discrete Grab Sampling Methodology for Surficial Soils*

Discrete grab sampling is employed when the sampling location is considered to be a small area (approximately 1 square foot [0.1 square meter]) that has both a consistent soil type and a consistent level of contaminant impact.

When collecting a discrete grab surficial soil sample, use the following procedure:

1. Using the sampling device (e.g., trowel, spoon, Oakfield sampler) scoop soil from the top 2 inches (5 cm) into the sample container. If the sample is being collected for VOC analyses, perform this step as quickly as possible in order to minimize the loss of volatile compounds from the soil.
2. Collect a field screening sample from the same sampling location as the discrete grab sample and at the same time. Scoop soil into a zip-loc bag until it is no more than one quarter full.

3. Do not mix the soil for samples collected for VOC analyses (for sample homogenization purposes) as this will promote the loss of volatile compounds from the soil. The laboratory will obtain a representative sample from the container by using coring techniques before the laboratory analysis is performed.

### *Composite Sampling Methodology for Surficial Soils*

A composite sample can be obtained directly from the soil surface by combining a number of discrete grab samples from a number of sampling locations on the soil surface. For preparation of a meaningful composite sample, the soils from the sub-samples taken from the different sampling locations should have (by visual observation) similar contaminant concentrations.

When collecting a composite surface soil sample, use the following procedure:

1. Choose a number of discrete sampling locations that will give a representative sample of the defined composite area at each sampling location.
2. Using the sampling device (e.g., trowel, spoon), scoop the soil from the top 2 inches (5 cm) into the sample container. As much as practical, try to put approximately the same volume of soil from each sampling location into the container.
3. Move to the next sampling location and repeat steps 1 and 2.
4. Collect a maximum of five surface samples (to avoid the complete dilution of any hot spots).
5. When the last location has been sampled, ensure the sample container is filled with soil, leaving no headspace.
6. Since composite samples are used for semi-volatile organic compounds (SVOCs) and inorganic parameters, minimizing the sample collection time is not as important as when discrete samples for VOC analyses are being collected. However, the preferred practice is that the sampler take no longer than necessary to obtain the sample.
7. Collect a field screening sample from the same sampling location as the composite sample and at the same time. As much as practical, try to put approximately the same volume of soil from each discrete grab sampling location into a zip-loc bag. The zip-loc bag should be no more than one quarter full after all the sub-samples have been added.

Since composite samples are not analyzed for VOCs, there is no reason to avoid mixing the sub-samples from the various sampling locations in the sample container (homogenization). However, since the laboratory will use coring techniques to ensure that a sample is representative of the entire container, there is no need to perform field homogenization of the soil within the sample container.

During the sampling program, the sampling team leader will stay in contact with the GHD chemist assigned to the project such that the GHD chemist can properly inform the contract laboratory of the progress of the work. This includes submitting sample summaries and/or copies of completed chain-of-custody forms to the GHD chemist.

Finally, some GHD QAPPs require a designation of a QA/QC officer for field activities. The sampling team leader may be required to conduct certain field audit activities and, at minimum, should be familiar with and responsible for completion of all QA/QC sample activities.

## 5.9 Procedures for Borehole Installation and Sampling

Once the prior planning and preparation activities are completed, the drilling program can proceed. The typical series of events that takes place is:

1. Locating and marking boring locations.
2. Initiation of a Property Access/Utility Clearance Data Sheet (QSF-019), including obtaining appropriate signoffs by the client representative and drilling subcontractor representative.
3. Contractor mobilization; equipment and material check.
4. Site selection of decontamination pad and drum staging area (if applicable); final visual examination of proposed drilling area for utility conflicts.
5. Decontamination of sampling and drilling equipment prior to use in accordance with the Work Plan or as described in Section 5.6.
6. Borehole advancement utilizing the approved method as outlined in the Work Plan.
7. Soil sample collection; descriptions of the soil samples in accordance with GHD protocol.
8. Monitoring well installation (if applicable).
9. Sample preparation and packaging.
10. Abandonment of boreholes or installation of monitoring wells.
11. Collection of groundwater samples (if monitoring wells are installed).
12. Surveying of borehole location and elevations.
13. Field note completion and review.

### 5.9.1 Location and Marking of Drill Sites/Final Visual Check

The proposed borehole locations marked on the site plan are located in the field and staked. On most sites, this will likely be done several days in advance of the drill rig arriving on site. Unless boreholes are to be installed on a fixed grid, the proposed locations are usually strategically placed to assess site conditions.

> Note: Any borehole (and all the records thereof) which is completed with casing as a temporary or permanent monitoring well, will be designated by the monitoring well number only (i.e., MW1-yy). Boreholes drilled strictly as soil test borings in which no casing is set (even if an open-hole groundwater sample is collected) will be designated by the boring number only (i.e., BH1-yy).

Once the final location for the proposed boring has been selected and utility clearances are complete, one last visual check of the immediate area should be performed before drilling proceeds. This should confirm the locations of any adjacent utilities (subsurface or overhead) and verification

of adequate clearance. If gravity sewers or conduits exist in the area, any access manholes or chambers should be opened and the conduit/sewer alignments confirmed. Do not enter manholes unless confined space procedures are followed.

If possible, it is prudent to use a hand auger or post-hole digging equipment to a sufficient depth to confirm that there are no buried utilities or pipelines. Alternatively, a Hydrovac truck can vacuum a large diameter hole to check for utilities, although soils collected this way may require containment on site. This procedure generally clears the area to the full diameter of the drilling equipment which will follow.

> Caution: Do not assume site plan details regarding pipe alignments/position are correct. Visually check pipe position when drilling near sewers. Personnel should also be alert to additional piping presence if the plans are outdated.

If it is necessary to relocate a proposed borehole due to terrain, utilities, access, etc., the Project Coordinator must be notified and an alternate location will be selected.

### 5.9.2 Sample Collection

A boring is advanced incrementally to permit intermittent or continuous sampling. Test intervals and locations are normally stipulated by the Project Coordinator or Work Plan. Typically, the depth interval for sampling is 2.5 to 5 feet (0.75 to 1.5 m), or less in homogeneous strata, with at least one test and sampling location at every change of stratum. In some cases samples are taken continuously (i.e., 2-foot (0.6 m) long samples at 2-foot (0.6 m) intervals).

Collected soil samples are described in the field using the USCS (visual-manual procedure). The soil description is recorded on a Stratigraphic Log (Overburden) (Form SP-14) or field book in the following order:

1. USCS Soil Symbol of major component
2. Native or fill
3. Secondary and minor soil components
4. Relative densities/consistency
5. Grain-size/plasticity
6. Gradation/structure
7. Color
8. Moisture content
9. Observations of odor or visual chemical presence (i.e., non-aqueous phase liquid [NAPL])
10. Additional descriptions

For environmental sampling, always change gloves between collecting subsequent soil samples to prevent cross-contamination. Decontaminate all tools (e.g., samplers, spatulas) prior to use on each sample to prevent cross-contamination in accordance with the Work Plan or as described in Section 5.6.

Any drilling procedure that provides a suitably clean and stable hole before insertion of the sampler, and assures that the standard penetration test (SPT) or other sampling technique is performed on essentially undisturbed soil, is acceptable. The drilling method is selected based on the subsurface conditions. Each of the following methods has proven to be acceptable for specific subsurface conditions:

- HSA with inside diameter between 2.5 and 6.25 inches (5.7 to 15.9 cm)
- Solid stem auger (SSA) with auger diameter between 2.5 and 6.25 inches (5.7 to 15.9 cm)
- Direct-push (dual tube systems, discrete soil sample systems)
- Open-hole rotary drilling
- Wash boring

Several drilling methods are not acceptable. These include:

- Jetting through an open tube sampler and then sampling when the desired depth is reached.
- SSA use below the groundwater table in non-cohesive soils.
- Casing driven below the sampling depth prior to sampling.
- Advancing a borehole with bottom discharge bits.
- Advancing a boring for subsequent insertion of the sampler solely by means of previous sampling when performing SPT (the open hole must be larger in diameter than the split-spoon sampler).

### *Discrete Grab Sampling Methodology for Boreholes*

When borehole drilling, the split-spoon sample retrieved from the borehole is considered a discrete grab sample that has been taken from one sampling location, as long as both the stratigraphy of the entire sample and the level of contamination are consistent over the length of the split-spoon sample. If a single split-spoon sample contains soils from two different stratigraphic units, the soils from each of these stratigraphic units are considered separate discrete grab samples.

If a single split-spoon sample contains soils from a single stratigraphic unit, but visual observation indicated that some of the soil was heavily impacted with contaminants, while the rest of the soil was only lightly impacted, then the soils representing each of the two levels of contamination are considered two separate discrete grab samples.

### *Composite Sampling Methodology for Boreholes*

A composite sample is obtained by combining a number of discrete grab samples from the same borehole. For preparation of a meaningful composite sample, the soils from the sub-samples taken from the different split-spoon samples should be from a single stratigraphic unit and have (by visual observation) similar contaminant concentrations (or be physically similar for geotechnical testing purposes).

Use the following methodology for preparing a composite sample from these discrete grab split-spoon samples:

1. Prior to collecting a sample of the soil for field vapor screening or chemical analysis, if smearing of soil is apparent on the outside of the soil core, scrape away the outer layer of the soil using a decontaminated putty knife, stainless steel spoon, or similar implement. This should only be performed if the soil core sample is consolidated. Do not use this procedure for unconsolidated soil samples.
2. Split the sample longitudinally along the length of the split-spoon sampler. Use one half of the core sample to prepare a composite sample to be used in soil headspace vapor screening measurements, and the other half to prepare a composite sample to be submitted to the laboratory for chemical analysis or geotechnical testing.
3. Place sub-samples from various sampling locations (i.e., split-spoon samples) into a zip-loc bag for field screening. As much as practical, attempt to place approximately the same volume of soil from each sampling location into the zip-loc bag.
4. For samples where labo , ratory analysis is also desired, place sub-samples from various sampling locations into the appropriate soil sample containers. As much as practical, attempt to place approximately the same volume of soil from each sampling location into the sample container.

The following subsections describe specific protocols for split-spoon sampling, Shelby tube sampling, and methods for collecting soil samples using a direct-push rig.

#### 5.9.2.1 Split-Spoon Samplers

This method is used to obtain representative samples of subsurface soil materials and to determine a measure of the in situ relative density of the subsurface soils. The test methods described below must be followed to obtain representative samples.

SPT involves the use of split-barrel samplers (also known as split spoons). Split-spoon sampling is performed in accordance with ASTM D1586. The split-spoon sampler consists of an 18- or 24-inch (45 or 60 cm) long, 2-inch (5 cm) outside diameter tube, which comes apart lengthwise into two halves. An example of a split-spoon sampler is presented on Figure 5.2.

Note: A typical 2-inch (5 cm) outside diameter split-spoon is 1 3/8-inch (3.5 cm) diameter at the drive shoe and 1 1/2-inch (3.8 cm)diameter within the barrel of the split spoon. The volume of the soil in a completely filled 24-inch (61 cm) long split-spoon is approximately 19.8 oz (586 mL), thus the sample volume requirements are important if multiple types of parameters requiring differing analytical techniques are required (i.e., VOCs, SVOCs, metals, petroleum hydrocarbon compounds [PHC]). Soil recovery in a split spoon is often less than 24 inches (61 cm), resulting in less available volume.

Once the borehole is advanced to the target depth and cleared of cuttings, representative soil samples are collected in the following manner:

1. The split-spoon sampler is inspected to ensure it is properly cleaned and decontaminated. The driving shoe (tip) should be relatively sharp and free of severe dents and distortions.
2. The cleaned split-spoon sampler is attached to the drill rods and lowered into the borehole. Do not allow the sampler to drop onto the soil in the bottom of the borehole.
3. After the sampler has been lowered to the bottom of the hole, it is given a single blow to seat it and make sure that it is in undisturbed soil. If there still appears to be excessive cuttings in the bottom of the borehole, remove the sampler from the borehole and remove the cuttings.
4. Mark the drill rods in three or four successive 6-inch (15 cm) increments, depending on sampler length, so that the advance of the sampler under the impact of the hammer can be easily observed for each 6-inch (15 cm) increment.

The sampler is then driven continuously for either 18 or 24 inches (45 or 60 cm) by use of a 140-pound (63.5 kg) hammer. The hammer may be lifted and dropped by either the cathead and rope method, or by using a trip, automatic, or semi-automatic drop system. The hammer should free-fall a distance of 30 inches (±1 inch) (75 cm, ±25 mm) per blow. Measure the drop at least daily to ensure that the drop is correct. To ensure a free-falling hammer, no more than 2 1/4 turns of the rope may be wound around the cathead (see ASTM D1586). The number of blows applied in each 6-inch (15 cm) increment is counted until one of the following occurs:

1. A total of 50 blows have been applied during any one of the 6-inch (15 cm) increments described above.
2. A total of 100 blows have been applied.
3. There is no advancement of the sampler during the application of ten successive blows of the hammer (i.e., the spoon is 'bouncing' on a stone or bedrock).
4. The sampler has advanced the complete 18 or 24 inches (45 or 60 cm) without the limiting blow counts occurring as described above.

In some cases where the limiting number of blow counts has been exceeded, GHD may direct the driller to attempt to drive the sampler more if collection of a greater sample length is essential, as long as the sampler is still being advanced.

On the field form, record the number of blows required to drive each 6-inch (15 cm) increment of penetration. The first 6 inches (15 cm) is considered to be a seating drive. The sum of the number of blows required for the second and third 6 inches (15 cm) of penetration is termed the "standard penetration resistance" or the "N-value".

Note: If the borehole has sloughed and there is caved material in the bottom, the split spoon may push through this under its own weight, but now the spoon is partially 'pre-filled'. When the spoon is driven the 18 or 24 inches (45 or 60 cm) representing its supposedly empty length, the spoon fills completely before the end of the drive interval. Three problems arise:

1. The top part of the sample is not representative of the in-place soil at that depth.
2. The SPT value will be artificially higher toward the bottom of the drive interval since the spoon was packed full. These conditions should be noted on the field log.
3. The available sample volume is significantly reduced.

The sampler is then removed from the borehole and unthreaded from the drill rods. The open shoe (cutting end) and head of the sampler are partially unthreaded by the drill crew and the sampler is transferred to the geologist/engineer work surface.

Note: A table made out of two sawhorses and a piece of plywood is appropriate, or a drum, both covered with plastic sheeting.

The open shoe and head are removed by hand by the drill crew or GHD representative, and the sampler is tapped so that the tube separates.

Note: Handle each split spoon with clean disposable gloves if environmental samples are being collected from that split-spoon sample.

Measure and record the length of sample recovered making sure to discount any sloughed material that is present on top of the sample core.

Caution must be used when conducting split-spoon sampling below the groundwater table, particularly in sand or silt. These soils tend to heave or "blow back" into the HSA due to the difference in hydraulic pressures between the inside of the HSA and the undisturbed soil. To equalize the hydraulic pressure, it may be necessary to fill the inside of the HSA with potable water from a reliable and pre-tested source. Drilling mud is uncommonly used and presents problems for sample collection and well development. The water level within the boring or HSA needs to be maintained at or above the in situ groundwater level at all times during drilling, removal of drill rods, and sampling. Since heave or blow back is not always obvious to the driller, it is essential that the water level in the borehole always be maintained at or above the groundwater level. Split-spoon sampling below the water table in sands and silt occasionally results in non-representative samples being collected due to the heaving effect disturbing the soil. This is particularly important if the water level in the hole has not been maintained at the in situ water level.

Heaving conditions and the volume of potable water used should be noted on a Stratigraphic Log (Overburden) (Form SP-14). The volume of water added must be removed during well development prior to groundwater sampling. This practice may not be acceptable if environmental samples are to be collected.

Suspected low N-values should be noted on the field logs. If it is critical to have accurate N-values below the water table, other methods can be employed, such as conducting a dynamic cone

penetration test. This quick and easy test involves attaching a cone shaped tip to the end of the drill rods, and driving the tip into the ground similar to the split-spoon method, except that the borehole is not pre-augered. Cones may be driven 20 to 40 feet (6.1 to 12.2 m) through a formation without augering. Blow counts are recorded for each 1 foot (0.3 m) of advancement. Consult the Project Manager if such conditions are unexpectedly encountered.

> Note: A 3-inch (7.5 cm) outside diameter split spoon is available in order to obtain larger sample volumes. However, the SPT values from driving this sampler are typically much higher than those for the 2-inch (5 cm) split spoon.

#### *Larger-Diameter Barrels*

A variation of split-barrel sampling involves the use of a longer, larger diameter barrel in conjunction with a HSA. The sampling barrel is installed inside the auger with a swivel attachment to limit rotation of the barrel. After completion of a 5-foot (1.5 m) auger penetration, the auger is left in place and the barrel retrieved from the borehole. This method provides a larger diameter core, which may be desirable for bench-scale testing or where a large volume of soil is required for sample analyses. The sampler should be handled and the sample retrieved in the same way as described above for split-spoon sampling.

### 5.9.2.2 Shelby Tube Samplers

Thin-walled samplers such as Shelby tubes are used to collect relatively undisturbed samples (as compared to split-spoon samples) of soft to stiff clayey soils. The Shelby tube has an outside diameter of 2 or 3 inches (5 to 7.5 cm) and is 3 feet (0.9 m) long. These undisturbed samples are used for certain laboratory tests of structural properties (consolidation, hydraulic conductivity, shear strength) or other tests that might be influenced by sample disturbance. Procedures for conducting thin-walled tube sampling are provided in ASTM D1587, and are briefly described below:

1. The soil deposit being sampled must be cohesive in nature, and relatively free of gravel and cobble materials, as contact with these materials will damage or collapse the sampler.
2. Clean out the borehole to the sampling elevation using whatever method that will ensure the material to be sampled is not disturbed. If groundwater is encountered, maintain the liquid level in the borehole at or above groundwater level during the sampling operation.
3. Bottom discharge bits are not permitted. Side discharge bits may be used, with caution. Jetting through an open-tube sampler to clean out the borehole to sampling elevation is not permitted.
4. Remove loose material from the center of the casing or HSA as carefully as possible to avoid disturbance of the material to be sampled.
5. Place the sample tube so that its bottom rests on the bottom of the hole. Advance the sampler into the formation without rotation by a continuous and relatively rapid motion. Usually hydraulic pressure is applied to the top of the drill rods.
6. Determine the length of advance by the resistance and condition of the formation, but the length shall never exceed 5 to 10 diameters of the tube in sands and 10 to 15 diameters of the tube in clays.

7. In no case should the length of advance be greater than the sample-tube length minus an allowance for the sampler head and a minimum of 3 inches (7.5 cm) for cuttings.

8. The tube may be rotated to shear the bottom of the sample 2 to 3 minutes after pressing in, and prior to retrieval to ensure the sample does not slide out of the tube. Lift the weight of the rods off of the tube prior to rotating.

9. Withdraw the sampler from the formation as carefully as possible in order to minimize disturbance of the sample.

10. Package and transport the sample in accordance with project-specific requirements.

Occasionally, the Project Manager/Coordinator may require extraction of the sample from the tube in the field. Use the following procedure:

1. A sample extruder, which consists of a clamp arrangement to hold the tube and a hydraulic ram to push the sample through the tube, is usually provided by the driller. To prevent cross-contamination, ensure the extruder is field cleaned between each sample.

2. The sample is then extruded into a carrying tray; these are often made from a piece of 4-inch (10 cm) or 6-inch (12.5 cm) diameter polyvinyl chloride (PVC) pipe cut lengthwise. Ensure the carrying tray is field cleaned between each sample. The sample is carried to the work station for geologic description. Trim the potentially cross-contaminated exterior and place it in the appropriate container.

3. The Shelby tube sampler is then thoroughly field cleaned and decontaminated for reuse. Since they are thin-walled, the tubes are easily damaged, crimped, or otherwise distorted during handling or pushing. The Shelby tube should be inspected before use and, if significantly damaged, rejected.

#### 5.9.2.3 Direct-Push Sampling Systems

Direct-push refers to the sampler being 'pushed' into the soil material without the use of rotation to remove the soil. This method relies on the drill unit static weight combined with rapid hammer percussion for advancement of the tool string. Soil samples are continuously obtained. Groundwater and vapor samples can also be collected utilizing this method and appropriate tooling. Subsurface investigations typically sample to depths of 30 feet (9.1 m) or more; however, depth will vary based on the site-specific geology.

Direct-push methods are widely used for underground storage tank (UST) investigations and property investigations. This method is used extensively for initial site screening activities to establish site geology and to delineate vertical and horizontal plume presence. Small diameter wells (3/4 or 1 inch [2 or 2.5 cm]) diameter can be installed using direct-push methods, often using a pre-packed screen. SPT values cannot be obtained when sampling with a direct–push discrete soil sampler.

This method is also popular due to the limited cuttings produced during the drilling and sampling process and the increased sampling process speed, which can be much quicker than the sample description and sample preparation process. (It is often helpful to have two people, depending on the nature of the work program.)

Continuous soil samples are collected in tube samplers (various lengths), affixed with a cutting shoe and internal liner (PVC, Teflon, or acetate are available). The soil sampler may be operated in open-mode (when borehole collapse is not a concern), or closed-mode (when minimization of sample slough is desired). Closed-mode operation involves the placement of a temporary drill-point in the cutting shoe and driving the assembled sampler to depth. Once at the required depth, the temporary drill–point is released (via internal threading) and the sampler is driven to the desired soil interval. The drill-point slides inside the sample liner, riding above the collected soil column. Once driven to depth, the sampler is retrieved to the ground surface and the sample liner with soil, is removed for examination.

Caution: Be careful when opening interval liners with knives, as severe cuts may result from the knife slipping. A special two-blade hooked knife is available for opening the liners. Generally the driller/helper will open the liner for you.

### 5.9.3 Field Sample Screening

When soil sampling at sites with known or suspected VOC impact, it is often required to measure the soil for the presence of undifferentiated organic vapors. This field screening can be performed using a photoionization detector (PID). Immediately upon the opening of the split-spoon or discrete soil sampler, the soil is screened with a PID (HNu, Microtip, or equivalent) for the presence of undifferentiated organic vapors. This is accomplished by running the PID along the length of the soil sample. Record the highest reading.

Note: The PID measurement must be taken upwind of the drill rig or any running motors so that exhaust fumes will not affect the measurements.

Another method of field screening is head space measurement. This consists of placing a portion of the soil sample in a sealable glass jar, placing aluminum foil over the jar top, and tightening the lid. The jar is only partially filled. The jar is shaken and set aside for at least 30 minutes. After the sample has equilibrated, the lid of the jar is opened, the foil is punctured with the PID probe, and the air (headspace) above the soil sample is monitored. Record this headspace reading on the field form or in the field book. As an alternative, the soil can be placed in a sealable zip-loc bag.

Note: Perform headspace readings in an area that is not subject to wind. Also, in the winter, it is necessary to allow the samples to equilibrate in a warm area to ±70°F (20°C) (e.g., site trailer or van, but not direct heat or sunshine). The portion of the sample used for headspace analysis cannot be used for VOCs analysis.

Representative portions of the soil sample must be retained for geologic record following description. Place the soil portions into labeled, sealable sample containers (usually mason jars or zip-loc bags) without destroying any apparent stratification. If a stratigraphic change is observed within the split-spoon sampler, a separate geologic record sample is kept.

All geologic record samples are to be retained by the client. Geologic record samples must not return to or be placed in storage at a GHD office. An example of a properly completed Stratigraphy Log (Overburden) is presented on Figure 5.2.

### 5.9.4 Chemical Description

During soil examination and logging, carefully check for the presence of light or dense NAPL. NAPL may be present in gross amounts or present in small/minute quantities. The adjectives and corresponding quantities used when describing NAPL within a soil matrix are as follows:

| Visual Description | Fraction of Soil Pore Volume Containing NAPL |
|---|---|
| Saturated | >0.5 |
| Some | 0.5 - 0.25 |
| Trace | <0.25 |

A complete description of NAPL must describe the following:

- Color
- Quantity
- Density (compared to water) (i.e., light/floats or heavy/sinks)
- Odor (if observed)
- Viscosity (i.e., mobile/flowable, non-mobile/highly viscous-tar like)

The presence of an "iridescent sheen" by itself does not constitute "NAPL presence", but may be an indicator that NAPL is close to the area.

NAPL presence within a soil matrix may be confirmed by placing a small soil sample within water, shaking, and observing for NAPL separation (i.e., light or dense) from the soil matrix.

Trace amounts of NAPL are identified/confirmed by a close visual examination of the soil matrix, (i.e., separate soil by hand, wearing disposable gloves) and performing a careful inspection of the soil separation planes/soil grains for NAPL presence.

Often during sample examination with a knife, an iridescent sheen will be noted on the soil surface (i.e., clay/silts) if the knife has passed through an area of NAPL.

There are a number of more complicated tests available to confirm/identify NAPL presence, these are:

- Ultraviolet (UV) fluorescent analysis
- Hydrophobic dyes (use with care, consult the health and safety SOPs as some hydrophobic dyes are potential human carcinogens)
- Centrifugation
- Chemical analysis

GHD typically utilizes organic vapor detection results, visual examination, soil/water shake testing, and chemical analysis, to confirm NAPL presence. The more complex techniques described may be incorporated on sites where clear colorless NAPL is present and its field identification is critical to the program.

### 5.9.5 Chemical Sample Preparation and Packaging

Subsurface soil samples are usually grab samples, used to characterize the soil at a specific depth or depth interval (e.g., 2 to 4 feet [0.6 to 1.2 m]). On occasion, composite samples are collected from a borehole over a greater depth interval (e.g., 5 to 15 feet [1.5 to 4.1 m]).

The following describes the collection of grab samples for chemical analysis (all soil from one split spoon). Figure 5.2 shows the split-spoon sample selection details.

#### *Clayey Soils*

1. Discard upper and lower ends of sample core (3 inches [7.5 cm]).
2. Use a precleaned stainless steel knife.
3. Cut the remaining core longitudinally.
4. With a sample spoon, remove soil from the center portion of the core and place in a precleaned stainless steel bowl.
5. Remove large stones and natural vegetative debris.
6. Homogenize the soil and place directly into sample jars.

Note: Samples for VOC analysis must not be homogenized. Collect soil from the length of the center portion of the core and place in the sample container. Completely fill the container. No air space (headspace) should remain in the sample container.

#### *Sandy Soils*

As sandy soils have less cohesion than clayey soils, it is not easy to cut the core longitudinally to remove the center of the sample. Therefore, with a stainless steel spoon, scrape away surface soils which have likely contacted the sampler and then sample the center portion of the soil core.

Note: Place all soil samples collected for chemical analysis immediately into a cooler with ice.

Record all soil samples in the sample log book. Label samples as specified in Section 3.9.1.2.

In 1997, EPA adopted new methods for sampling soils for VOC analysis. Method 5035 calls for collecting soil using a coring device (EnCore). For analysis of low-level VOCs (typically 1 to 200 μg/kg) soil is commonly sealed in a specially prepared vial with a solution of sodium bisulfate. For higher levels of VOCs, the soil is placed in a vial with a volume of methanol. This method increases the complexity of collecting soils and makes it imperative that the sampler and laboratory work closely together. For some soil sampling programs, multiple EnCores are required for each sample interval. Holding times for samples in EnCores may be 24 to 48 hours if not field preserved; therefore, the GHD sampler, laboratory, and GHD chemist should discuss sampling and shipping procedures prior to beginning the work program.

### 5.9.6 Physical Sample Preparation and Packaging

When a sample is collected for geotechnical or hydrogeologic properties, the sample needs to be prepared and packaged in a manner to maintain its physical properties. Soil samples are usually

grab samples, collected from a specific depth or depth interval (e.g., 2 to 4 feet [0.6 to 1.2 m]). On occasion, composite samples are collected from the borehole over a greater depth interval (e.g., 5 to 15 feet [1.5 to 4.6 m]).

The following describes the collection of grab samples for geotechnical or hydrogeologic purposes for common samplers, the split-spoon, thin-wall, and direct-push discrete soil sampler. For soil samples collected for geotechnical purposes, the samples must not be allowed to freeze.

#### 5.9.6.1 Split-Spoon Samples

1. Following completion of PID screening of the split spoon, remove and dispose of soil at the top of the sample that is obviously sloughed material not representative of the soil at the sampled depth.
2. Measure the length of the sample and record as the recovered length.
3. If cohesive, perform a pocket penetrometer reading and describe the soil.
4. Carefully transfer the sample onto a sheet of aluminum or tin foil, taking care to maintain structure and bedding of the soil sample as much as possible. This may not be possible with non-cohesive soils with low silt or clay contents. The sample may need to be packaged in three 6- to 8-inch (15 to 20 cm) segments.
5. Roll the sample in the tin foil and fold over the ends to seal. Wrap in a second layer of tin foil.
6. Identify the top, middle, and bottom segments with a T, M, and B using an indelible marker.
7. For each segment record the "up" direction with an arrow.
8. Place the foil wrapped sample in a plastic bag and write the sample identification on the bag using an indelible marker. Storing the sample in foil, as opposed to a jar, has the advantage of retaining the soil's in-place structure and preventing loss of moisture.
9. If the soils are sandy and it is not possible to retain the soils structure by rolling it in tin foil, packaging the sample in a jar or zip-loc bag is also acceptable, provided the jar or zip-loc bag is filled to eliminate air space which could result in the soil sample drying out.

A split-barrel sample is approximately 4 inches (10 cm) in diameter and requires different handling than a split-spoon or Shelby tube sample. For a cohesive core sample, the section of drill core is wrapped in several layers of cheesecloth, coated with paraffin wax, and the process repeated until the entire sample is sealed adequately. These samples are usually utilized for specific bench-scale tests.

#### 5.9.6.2 Shelby Tube Samples

1. Remove any sloughed material from the top of the sample using a knife or similar long bladed instrument. If it is not possible to distinguish sloughed soil from intact soil, do not remove.
2. Following removal of sloughed material, measure the tube length and the air space in the tube above the sample and record the difference as the sample recovery. In the unusual circumstance that there is also air space at the bottom of the sample, subtract this as well and record this latter measurement as a separate entry.

3. Seal the top and bottom of the sample with wax (wax is normally provided and prepared by the driller) and first pour the liquefied wax into the top of the sample to a thickness of about 1 inch (2.5 cm). Once this is cooled, remove approximately 1/2 inch (1.3 cm) of soil from bottom of sample (unless there is already a cavity at bottom of sample) and seal similarly.
4. Fill the remaining air space above the sample with loose soil to prevent the sample from shifting in the tube, and then cap both ends of the sample with plastic caps. Tape the caps on using duct tape.
5. Write the sample identification number on the cap using an indelible marker.

Shelby tubes containing soft clays and wet silts need to be handled with care to avoid damage to the sample. Keep samples in an upright position at all times and transport either in a specifically designed cushioned box or position in your vehicle with cushioning under and around the individual tubes. Do not allow geotechnical soil samples to freeze.

#### 5.9.6.3 Direct–Push Soil Samples

1. Once removed to the ground surface, open the discrete soil sampler by removing the cutting shoe, and extract the soil liner (with recovered soil) from the sampler body.
2. Place the soil liner into a holder and cut lengthwise (using a liner knife) to expose the collected soil core.
3. Perform PID screening for organic vapors and record readings.
4. Measure length of sample and record as the recovered length.
5. If cohesive, perform pocket penetrometer reading and describe soil.
6. Carefully transfer the sample onto a sheet of aluminum or tin foil taking care to maintain structure and bedding of the soil sample as much as possible. This may not be possible with non-cohesive soils with low silt or clay contents. The sample may need to be packaged in multiple 6- to 8-inch (15 to 20 cm) segments.
7. Roll the sample in the tin foil and fold over the ends to seal. Wrap in a second layer of tin foil.
8. Identify the depth interval of each segment using an indelible marker.
9. For each segment record the "up" direction with an arrow.
10. Place the foil-wrapped sample in a plastic bag and write the sample identification on the bag using an indelible marker. Storing the sample in foil, as opposed to a jar, has the advantage of retaining the soil's in-place structure and preventing loss of moisture. If the soils are sandy and it is not possible to retain the soils structure by rolling it in tin foil, packaging the sample in one or more jars or zip-loc bags is also acceptable, provided each jar or bag is filled to eliminate air space which could result in the soil sample drying out.

The soil core is split lengthwise to allow inspection. Chemical samples can be removed from the soil core (if required), or soil record samples can be retained (if a component of the project scope). Soil record samples are often retained to allow sample collection for analysis later (depending upon analyte sensitivity/holding times), or for later inspection/geotechnical testing if required.

### 5.9.7 Communication of Field Findings

Field findings should be communicated frequently with the office technical staff responsible for the program. This communication allows the office staff to: confirm that the investigation meets the intent of the Work Plan; alter procedures and sampling protocol if soil conditions are markedly different from those assumed; and assist in determining screening intervals for piezometers or monitoring wells.

Call office staff no later than the completion of the first borehole, and sooner if possible. Be prepared to discuss the results by faxing the field logs beforehand (wherever possible) and by having a copy of the field log in hand when on the telephone. Call after each borehole and call before leaving the site.

### 5.9.8 Borehole Abandonment

Following completion of the borehole it must be properly abandoned in accordance with the project documents. Some jurisdictions have requirements or standards of practice that require filling the borehole with bentonite or cement grout.

> Note: The integrity of any underlying confining layer must be restored to prevent chemical cross-contamination or hydraulic cross-connection. This is true for all sites, regardless of the known presence or absence of contaminants. This normally requires grouting of the borehole within the zone of the confining layer.

Whenever possible, the cuttings are returned to the borehole to within 1 foot (0.3 m) of the ground surface. The remainder of the borehole is topped off with material consistent with the surrounding ground surface. Excess cuttings are usually collected in drums or a lugger box or spread on the surrounding ground surface consistent with the protocols specified in the Work Plan and as required by federal, state, provincial, and local regulations.

Check with the Project Coordinator to determine the method for handling drill cuttings.

> Note: Always include the method of abandonment in the field log book or on a Stratigraphic Log (Overburden) (Form SP-14)

### 5.9.9 Borehole Tie-In/Surveying

Recording the locations of boreholes on the site plan is extremely important, and may be accomplished by manual measurement (i.e., swing ties) and surveying. Manual measurements for each borehole must be tied into three permanent features (e.g., buildings, utility poles, hydrants). Include diagrams with measurements in the field book.

In addition to manual measurements, surveying with respect to a geodetic benchmark and a site coordinate system is often completed at larger sites for horizontal and vertical control.

Note: Manual field measurements are always necessary regardless of whether a survey is completed.
Manual measurements in field notes allow future identification of the sample/drill site without the need for a survey crew to locate positions using a grid system. This becomes important when trying to locate flushmount wells buried by snow or soils.

### 5.9.10 Field Notes

Field notes must document all the events, equipment used, calibration activities, and measurements collected during the sampling activities. The field notes must be legible and concise such that the entire borehole installation and soil sampling event can be reconstructed for future reference.

Field notes documenting events, equipment used, and related items are typically recorded in a standard GHD field book, while soil descriptions and PID readings are recorded on a Stratigraphic Log (Overburden) (Form SP-14). Standard GHD field books are available from all GHD equipment administrators. Form SP-14 is available as a printable linked document in this file or as a bound pad from each office.

Note: Use a Stratigraphic Log (Overburden) for recording all soil descriptions and related notes unless otherwise approved by the Project Coordinator/Manager.

Field book/form entries are made in black ink and any changes/corrections are stroked out with a single line, initialed, and dated to indicate when and by whom the correction was made.

The field notes should document the following for each borehole completed:

1. Identification of borehole
2. Depth
3. Static water level depth and measurement technique
4. Time started and completed
5. Measured field parameters
6. Sample appearance
7. Sample odors (if respiratory protection is not required)
8. Types of sample containers and sample identification numbers
9. Parameters requested for analysis
10. Field analysis data and method(s)
11. Sample distribution and transporter
12. Laboratory shipped to
13. Chain-of-custody number for shipment to laboratory
14. Field observations on sampling event
15. Name of collector(s)

16. Climatic conditions including air temperature

17. Problems encountered and any deviations made from the established sampling protocol

## 5.10 Procedures for Test Pit Excavation and Sampling

Once the prior planning and preparation activities are completed, the test pit excavation and subsurface soil sampling program can proceed. The typical series of events which takes place is:

1. Location and marking of test pit locations
2. Final visual examination of proposed excavation area for utility conflicts
3. Excavation of test pits and collection of the soil samples
4. Field screening of soil sample with specific air monitoring equipment (e.g., PID, LEL meter)
5. Description of soil sample and test pit
6. Completion of Test Pit Stratigraphy Log (Form SP-03)
7. Documentation, including photographs and/or videotape, as required
8. Chemical sample preparation and packaging
9. Backfilling of test pit excavation
10. Surveying of test pit locations
11. Field note completion and review.

### 5.10.1 Location and Marking of Test Pits/Final Visual Check

Proposed test pit locations marked on the site plan are located in the field and staked. The proposed test pit locations are usually strategically placed to assess site conditions, former facilities, waste areas, etc.

Once the final location for the proposed test pit has been selected and utility clearances are complete, one last check of the immediate area is performed before excavation proceeds to confirm the locations of any adjacent utilities (subsurface or overhead) and verify adequate clearance. If gravity sewers or conduits exist in the area, any access manholes or chambers are opened and the conduit/sewer alignments confirmed.

> Caution: Do not assume site plan details regarding pipe alignments/position are correct. Visually check pipe position when excavating near sewers. Personnel should also be alert to the presence of additional piping, especially if the plans are outdated.

If it is necessary to relocate a proposed test pit due to terrain, utilities, access etc., the Project Coordinator must be notified and an alternate location will be selected.

### 5.10.2 Test Pit Location Setup

The test pit location is set up as follows:

1. The excavator is positioned such that the excavation spoils are deposited by the excavator downwind of all staff.
2. A sheet of polyethylene is placed downwind of the test pit location to accept spoils, if required by the Work Plan.
3. To the extent practicable, the investigation area is set up such that water or liquids that may be excavated, freely drain back into the excavation.
4. The excavation begins at one location with the excavator backing up (as required) to extend the pit.

### 5.10.3 Sample Collection

Soil samples can be collected from the backhoe/excavator bucket or from the test pit excavation face. Samples which require a discrete depth interval are collected from the excavator bucket following excavation of all or a portion of the test pit. Samples are collected using a cleaned steel trowel, shovel, or stainless steel spoon. Samples are placed in a stainless steel bowl and mixed (except VOCs). **Do not enter the test pit**. (Confined Space Entry requirements apply and proper shoring of the excavation walls may be necessary.)

> Caution: Personnel observing or sampling test pit operations must never stand within the "turning radius" or "reach-zone" of the excavation equipment. Operator error or equipment failure could result in severe injury or death if struck by the backhoe bucket or the backhoe itself. Stand opposite the backhoe well beyond the far end of the trench for communication.
> Personnel should also be alert to test pit side wall conditions which typically undermine the ground surface and create unstable soils surrounding the test pit area.

#### *Discrete Grab Sampling From Test Pits*

When taking discrete grab samples from a test pit using an excavator bucket, the sampling location is considered a volume of soil in the bucket that has both a consistent soil type and a consistent level of contaminant impact. When sampling using an excavator bucket, the operator will dig to the desired depth and then provide a small volume of soil from a discrete position and depth in the test pit.

When collecting a discrete grab sample from the excavator bucket, use the following procedure:

1. Scrape off the top 2 inches (5 cm) of soil at the sampling location in the excavator bucket.
2. Using the sampling device (e.g., trowel, spoon) scoop the freshly exposed soil into the sample container. Ensure that the samples taken were not in contact with the excavator bucket to avoid the potential for cross-contamination.

3. Pushing the sample container into the soil in order to fill the container is not recommended. This could result in breaking the sample container and potential injury to field personnel (e.g., cutting hands on broken glass).
4. If the sample is being collected for VOC analyses, perform this step as quickly as possible in order to minimize the loss of volatile compounds from the soil.
5. Collect a field screening sample from the same sampling location as the discrete grab sample and at the same time. Scoop soil into a zip-loc bag until it is no more than one quarter full.
6. Do not mix the soil for samples collected for VOC analyses (for sample homogenization purposes) as this will promote the loss of volatile compounds from the soil. The laboratory will obtain a representative sample from the container by using coring techniques before the laboratory analysis is performed.

### *Composite Sampling*

A composite sample can be obtained by combining a number of discrete grab samples from a test pit sampling location (i.e., excavator bucket). For preparation of a meaningful composite sample, the soils from the sub-samples taken from the different sampling locations should be from a single stratigraphic unit and have (by visual observation) similar contaminant concentrations.

When taking composite samples from multiple excavator buckets, consider each excavator bucket of soil to be a sampling location. When taking a composite sample using the excavator, use the following procedure:

1. Pick a number of discrete sampling locations that will give a representative sample of the horizon of interest in the test pit.
2. From each of these sampling locations, obtain a soil sample from the excavator bucket using the same methodology described in the previous subsection for a discrete grab sample.
3. The sample container should be partially filled with soil from each discrete grab sampling location. As much as practical, try to put approximately the same volume of soil from each sampling location into the container.
4. Move to the next sampling location and obtain another discrete grab soil sample.
5. Collect a maximum of five surface samples (to avoid the complete dilution of any hot spots).
6. When the last location has been sampled, ensure the sample container is filled with soil, leaving no headspace.
7. Since composite samples are used for SVOCs and inorganic parameters, minimizing the sample collection time is not as important as when discrete samples for VOC analyses are being collected. However, the preferred practice is that the sampler take no longer than necessary to obtain the sample.
8. Collect a field screening sample from the same sampling location as the composite sample and at the same time. As much as practical, try to put approximately the same volume of soil from each discrete grab sampling location into a zip-loc bag. The zip-loc bag should be no more than one quarter full after all the sub-samples have been added.

### 5.10.4 Field Sample Screening

Upon collection of a soil sample, the soil is screened with a PID (HNu, Microtip, or equivalent) for the presence of undifferentiated organic vapors. This is accomplished by running the PID across the soil sample. Record the highest reading and sustained readings.

> Note: The PID measurement must be taken upwind of the excavating equipment or running motors so that exhaust fumes will not affect the measurements.

Another method of field screening is head space measurement. This consists of placing a portion of the soil sample in a sealable glass jar, placing aluminum foil over the jar top, and tightening the lid. The jar should only be partially filled. Shake the jar and set aside for at least 30 minutes. After the sample has equilibrated, open the lid of the jar, puncture the foil with the PID probe, and monitor the air (headspace) above the soil sample. Record this headspace reading on a Test Pit Stratigraphy Log (Form SP-03) or in the field book.

> Note: Perform all headspace readings in an area that is not subject to wind. Also, in winter it is necessary to allow the samples to equilibrate in a warm area (e.g., site trailer or van). This requirement is usually dictated by the Work Plan.

### 5.10.5 Sample Description and Logging of Test Pits

During the excavation of a test pit, samples may be collected to provide a geologic record, to assist the geologist/engineer in completing or characterizing the stratigraphic units, and to allow for physical or chemical testing.

Soil samples collected are described in the field using the USCS. The soil descriptions are recorded on the field form or field book in the following order:

1. USCS Soil Symbol of major component
2. Native or fill
3. Secondary and minor soil components
4. Relative densities/consistency
5. Grain size/plasticity
6. Gradation/structure
7. Color
8. Moisture content
9. Observations of odor or visual chemical presence (i.e., NAPL)

In addition to describing the soil properties, enter the following information into a Test Pit Stratigraphy Log (Form SP-03):

1. Presence of groundwater and the rate of seepage (if groundwater is encountered).
2. Thickness of each stratigraphic unit.

3. Description of bedding plane features (e.g., continuous, discontinuous, graded, wavy bedding).
4. Description of joints, fractures and faults, if bedrock is encountered (number and orientation).
5. Any appearance of weathering.
6. Description of fill and waste materials.

Note: When describing observed odors, be specific in terms of general odor category and strength of odor noted. Odors may typically be chemical, petroleum, or septic related, varying from slight, to moderate, to strong. Identification of specific chemical compounds (i.e., TCE or C-56 odor) is usually unnecessary and often inaccurate as a detailed analysis commonly shows an array of chemistry present.
When describing the presence of vegetative matter in the soil sample, do not use the term "organic" as this often leads to confusion with regards to the presence of organic chemicals (i.e., NAPL).

When describing the soil samples and the stratigraphy observed in the test pit, it is imperative that the sampler use consistent terms from one test pit to the next. As test pits are installed, compare the stratigraphy of completed test pits to the stratigraphy of the test pit you are currently excavating. Be aware of patterns and confirm all inconsistencies at the time the test pit is being excavated. Since soil stratigraphy is so important to understanding site conditions, soil samples are collected from each stratigraphic unit, and described in full.

### 5.10.6 Chemical Description

Representative portions of the soil sample should be retained as a geologic record along with a description. Place the soil portions into labeled, sealable, sample containers (usually mason jars) without destroying any apparent stratification.

All geologic record samples are to be retained by the client. Geologic record samples must not return to or be placed in storage at a GHD office.

An example of a properly completed Test Pit Stratigraphy Log is presented on Figure 3.12 and described in Section 3.4.1.5.

During soil examination and logging, carefully check for the presence of light or dense NAPL. NAPL may be present in gross amounts or present in small/minute quantities. The adjectives and corresponding quantities used when describing NAPL within a soil matrix are as follows:

| Visual Description | Fraction of Soil Pore Volume Containing NAPL |
|---|---|
| Saturated | >0.5 |
| Some | 0.5 - 0.25 |
| Trace | <0.25 |

A complete description of NAPL includes the following:

- Color
- Quantity

- Density (compared to water) (i.e., light/floats or heavy/sinks)
- Odor (if observed)
- Viscosity (i.e., mobile/flowable, non-mobile/highly viscous-tar like)

The presence of an iridescent sheen by itself does not constitute NAPL presence, but may be an indicator that NAPL is close to the area.

NAPL presence within a soil matrix may be confirmed by placing a small soil sample within water, shaking, and observing for NAPL separation (i.e., light or dense) from the soil matrix.

Trace amounts of NAPL are identified/confirmed by a close visual examination of the soil matrix, (i.e., separate soil by hand [wearing disposable gloves]) and perform a careful inspection of the soil separation planes/soil grains for NAPL presence.

Often during the sample examination with a knife, an iridescent sheen will be noted on the soil surface (i.e., clay/silts) if the knife has passed through an area of NAPL.

There are a number of more complicated tests available to confirm/identify NAPL presence, these are:

- UV fluorescent analysis
- Hydrophobic dyes
- Centrifugation
- Chemical analysis

GHD typically utilizes organic vapor detection results, visual examination, soil/water shake testing, and chemical analysis, to confirm NAPL presence. The more complex techniques described may be incorporated on sites where clear colorless NAPL is present and its field identification is critical to the program.

### 5.10.7 Chemical Sample Preparation and Packaging

Subsurface soil samples are usually grab samples, used to characterize the soil at a specific depth or depth interval (e.g., 2 to 4 feet [0.6 to 1.2 m]). On occasion, composite samples are collected from a test pit over a greater depth interval (e.g., 5 to 15 feet [1.5 to 4.6 m]).

The following describes the collection of grab samples for chemical analysis.

#### *Clayey Soils*

Scrape away the surface soils and collect the sample. Remove large stones and natural vegetative debris and homogenize the soil and place it directly into the sample jars.

> Note: Samples for VOC analysis must not be homogenized. Remove the outer layer of soil from the excavation face then collect the sample and place it in the sample container. Completely fill the container. No air space (headspace) should remain.

### *Sandy Soils*

As sandy soils have less cohesion than clayey soils, with a stainless steel spoon or other device scrape away surface soils which have likely contacted the backhoe/excavator bucket, then collect the sample.

> Note: All soil samples collected for chemical analysis must be placed immediately into a cooler with ice.

Record all soil samples recorded in the sample log book as described in Section 3.4.1. Labeling of samples shall be consistent with Section 3.9.1.2.

### 5.10.8 Documentation

In addition to completing all field logs and books, it will generally be necessary for test pits to be documented with photographs and/or video tape. This requirement should be fully ascertained and coordinated in advance of field activities.

### 5.10.9 Test Pit Abandonment

Following completion of the test pit, backfill the excavation using the soil excavated from the pit. To the extent practicable, replace materials in the test pit in the same intervals from which they were extracted.

It should be noted that the material will tend to "bulk" after excavation. As a result, the excavator operator must be informed to compact the materials as they are replaced within the excavation.

### 5.10.10 Restoration

The test pit location must be fully restored. Ensure that restoration activities are properly designed and incorporated within the scope of services for the test pit contractor.

Restoration could include:

- Landscaping
- Paving
- Concrete

## 5.11 Follow-up Activities

Complete the following activities at the conclusion of the field work:

1. Double check the Work Plan to ensure all samples have been collected and confirm this with the Project Coordinator.
2. Ensure that all sample locations are surveyed such that the sample location could be readily re-established.

3. Clean equipment and return to the equipment administrator with the appropriate form dated and signed. Complete water disposal (if required), and cleaning fluid disposal requirements as specified in the Work Plan.

4. Notify the contract laboratory as to when to expect the samples. Enclose the chain-of-custody and covering letter, indicating the parameters and number of samples, in the sample cooler. Ensure that the GHD chemist has all relevant information required to track the progress of the sample analysis.

5. Submit a memo to the Project Coordinator indicating sampling procedures and observations (such as surface staining), grid layout, and all QA/QC documentation.

6. Prepare and distribute a Project Planning, Completion, and Follow-Up Checklist (Form SP-02).

## 5.12 References

For additional information pertaining to this topic, the user of this manual may reference the following:

### *Surficial Soil Sampling*

ASTM D4547 Practice for Sampling Waste and Soils for Volatile Organics

ASTM D6044 Guide for Representative Sampling for Management of Waste and Contaminated Media

ASTM D6051 Guide for Composite Sampling and Field Subsampling for Environmental Waste Management Activities

### *Subsurface Soil Sampling*

ASTM D420 Guide for Site Characterization for Engineering, Design, and Construction Purposes

ASTM PS 89 Guide for Expedited Site Characterization of Hazardous Waste Contaminated Sites

ASTM D5434 Guide for Field Logging of Subsurface Explorations of Soil and Rock

ASTM D2487 Classification of Soils for Engineering Purposes (Unified Soil Classification System)

ASTM D2488 Practice for Description and Identification of Soils (Visual-Manual Procedure)

ASTM D5781 Guide for Use of Dual-Wall Reverse-Circulation Drilling for Geoenvironmental Exploration and the Installation of Subsurface Water-Quality Monitoring Devices

ASTM D5782 Guide for Use of Direct Air-Rotary Drilling for Geoenvironmental Exploration and the Installation of Subsurface Water-Quality Monitoring Devices

ASTM D5783 Guide for Use of Direct Rotary Drilling with Water-Based Drilling Fluid for Geoenvironmental Exploration and the Installation of Subsurface Water-Quality Monitoring Devices

| | |
|---|---|
| ASTM D5784 | Guide for Use of Hollow-Stem Augers for Geoenvironmental Exploration and the Installation of Subsurface Water-Quality Monitoring Devices |
| ASTM D5872 | Guide for Use of Casing Advancement Drilling Methods for Geoenvironmental Exploration and Installation of Subsurface Water-Quality Monitoring Devices |
| ASTM D5875 | Guide for Use of Cable-Tool Drilling and Sampling Methods for Geoenvironmental Exploration and Installation of Subsurface Water-Quality Monitoring Devices |
| ASTM D5876 | Guide for Use of Direct Rotary Wireline Casing Advancement Drilling Methods for Geoenvironmental Exploration and Installation of Subsurface Water-Quality Monitoring Devices |
| ASTM D4700 | Guide for Soil Sampling from the Vadose Zone |
| ASTM D1586 | Standard Test Method for Penetration Test and Split-Barrel Sampling of Soils |
| ASTM D1587 | Practice for Thin-Walled Tube Geotechnical Sampling of Soils |
| ASTM D4220 | Practices for Preserving and Transporting Soil Samples |
| ASTM D6001 | Guide for Direct-Push Water Sampling for Geoenvironmental Investigations |

# Attachment B
# Laboratory Standard Operating Procedures

# Title: Total Organic Carbon
# Lloyd Kahn Method

**Approvals (Signature):**

| | |
|---|---|
| Don Dawicki<br>Laboratory Director | Kristine Dusablon<br>Quality Assurance Manager |

## 1.0 Scope and Application

This SOP describes the laboratory procedure for the determination of total organic carbon (TOC) in soil and solid materials.

### 1.1 Analytes, Matrix(s), and Reporting Limits

This procedure may be used to determine total organic carbon in soil and solid materials. This procedure may not be amenable to oily matrices.

The routine reporting limit is 1000 mg/kg based on an initial sample weight of 10 mg.

On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in the Quality Assurance Manual.

## 2.0 Summary of Method

10 mg of dried sample is transferred to a tin capsule, treated with phosphoric acid and dried in an oven at a temperature 105°C for 30-60 minutes to separate the organic carbon from inorganic carbonates and bicarbonates. The sample is analyzed on an instrument where it is pyrolyzed in an inductive type furnace. The carbon is converted to carbon dioxide and measured by a differential thermal conductivity detector.

This procedure is based on the following reference documents:

- EPA Region II Document Determination of Total Organic Carbon in Sediment, July 27, 1988, authored by Lloyd Kahn, Quality Assurance Specialist.

If the laboratory's SOP has been modified from the above referenced document, a list of modifications is provided in Section 15.0 of this SOP.

## 3.0 Definitions

Refer to the Laboratory's Quality Assurance Manual (QAM) for the Glossary of Terms, Definitions and Acronyms except as follows:

A list of general laboratory terms and definitions are provided in Appendix A.

## 4.0 Interferences

Volatile organics in the sediments may be lost in the de-carbonation step resulting in a low bias.

## 5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe,

nonabsorbent shoes are a minimum.

### 5.1 Specific Safety Concerns or Requirements

None

### 5.2 Primary Materials Used

Table 1 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the SDS. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

## 6.0 Equipment and Supplies

- Drying Oven: Capable of maintaining a temperature of 105 ±2°C.
- Carlo Erba Elemental Analyzer Model EA1108 and Model NA 1500 or equivalent.
- Costech Elemental Analyzer: Model 4010 or equivalent.
- Analytical Balance: Capable of weighing to the nearest 0.0001g.
- Aluminum Weigh Boats.
- Tweezers
- 5mm X 9mm tin capsules
- Quartz Columns: Costech Analytical or equivalent.
- Quartz wool: for segregating and containing column materials
- Copper Wire, Reduced: Costech Analytical or equivalent.
- Tungsten on Alumina: Costech Analytical or equivalent.
- High Temperature Gloves
- Clear Plastic Sample Trays: Costech Analytical or equivalent.
- 100ul Hamilton syringe or similar

## 7.0 Reagents and Standards

### 7.1 Reagents

- Reagent water
- Phosphoric Acid, Concentrated: Reagent Grade, J.T. Baker recommended.

Phosphoric Acid Solution (1:19): Add approximately 100 mL of reagent water to a 200 mL volumetric flask. Add 18.34 g of concentrated phosphoric acid to the volumetric flask then adjust

to volume with reagent water. Mix the solution well then transfer the solution to a 250 mL polyethylene bottle. Assign an expiration date of six months from date made and store the solution at room temperature.

### 7.2 Standards

- Potassium Hydrogen Phthalate (KHP) (Primary Standard Grade) Used to calibrate the instrument. 47.05% Carbon by weight

- Laboratory Control Samples (LCS) Material, Organic Material of known Carbon percentage: Purchased from LECO Corporation.

1% Carbon KHP Solution (10,000 mg Carbon/L): Add 50 mL of reagent water to a 100 mL volumetric flask. Add 2.128 g of KHP and dissolve completely. Adjust to final volume with reagent water. To mix the solution, cap the flask and invert. Allow the air bubble to reach the top of the flask. Repeat 9 times. Assign an expiration of 6 months from the date prepared and store at room temperature.

0.1% Carbon KHP Solution (1000mg Carbon/L): Add approximately 25 mL of reagent water to a 50 mL volumetric flask. Add 5 mL of 1 % Carbon KHP solution to the flask and adjust to final volume with reagent water. To mix the solution, cap the flask and invert. Allow the air bubble to reach the top of the flask. Repeat 9 times. Assign an expiration date of 6 months from the date prepared so long as the parent solution does not expire sooner, in which case use the earliest expiration date. Store the solution at room temperature.

0.01% Carbon KHP Solution (100mg Carbon/L): Add approximately 25 mL of reagent water to a 50 mL volumetric flask. Add 0.5 mL of 1% Carbon KHP Solution and adjust to final volume with reagent water. To mix the solution, cap the flask and invert. Allow the air bubble to reach the top of the flask. Repeat 9 times. Assign an expiration date of 6 months from the date prepared so long as the parent solution does not expire sooner, in which case use the earliest expiration date. Store the solution at room temperature.

**Note: Alternatively a 10,000mg/L TOC standard may be purchased from a reputable vendor (Spex Certiprep, SCP Science or ERA) and diluted appropriately to prepare the intermediate solutions above.**

## 8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so sampling procedures are not included in this SOP. Sampling requirements may be found in the published reference method. Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

| Matrix | Sample Container | Minimum Sample Size | Preservation | Holding Time | Reference |
|---|---|---|---|---|---|
| Solids | Amber glass | 10 g | Chilled to ≤ 4°C | 14 Days | Lloyd Kahn Method |

Holding time is calculated from date of sample collection. Unless otherwise specified by client or regulatory program, after analysis, samples and extracts are retained for a minimum of 30 days after provision of the project report and then disposed of in accordance with applicable regulations.

## 9.0 Quality Control

### 9.1 Sample QC

The following QC samples are analyzed with each batch:

| QC Item | Frequency | Acceptance Criteria |
|---|---|---|
| Method Blank (MB) | 1 in 20 or fewer samples | < RL |
| Laboratory Control Sample (LCS) | 1 in 20 or fewer samples** | %R (75-125)<br>**Quad RSD 18% |
| Sample Quadruplicate | 1 in 20 or fewer samples (Only when site specific P&A has been requested) | SD ( ≤ 3x SD of site specific P&A study) |
| Matrix Spike | Client request | %R (75-125) |
| Duplicate/Matrix Spike Duplicate | Client request | RPD 20% |

**If a site specific P&A study not requested analyze the LCS in quadruplicate as a measure of method precision.

### 9.2 Instrument QC

The laboratory analyzes the following instrument check standards:

| QC Item | Frequency | Acceptance Criteria |
|---|---|---|
| Initial Calibration (ICAL) | Initial Method Set-Up, after combustion chamber is changed (approx. every 200 drops) | Correlation coefficient must be >0.995 |
| Initial Calibration Verification (ICV) | Following Calibration | %R (75-125) |
| Calibration Verification (CCV) | Every 20 drops and at the end of the analytical sequence | %R (75-125) |
| Calibration Blank (CCB) | After every CCV | <RL |

## 10.0 Procedure

### 10.1 Calibration

Analyze a calibration curve each time the combustion column is changed. Change the column after 200 drops or when you experience QC recovery issues, odd peak shapes or baseline issues. The column change procedure is provided in Appendix B.

The recommended formulations for each calibration level are provided in the following table:

| Calibration Standards | 1.0% C KHP uL | 0.1% C KHP uL | 0.01%C KHP uL | % Carbon KHP | Carbon (mg) | mg/Kg of Carbon (10mg sample) |
|---|---|---|---|---|---|---|
| Level 1 | 0 | 0 | 0 | 47.05 | 0 | 0 |
| Level 2 | 0 | 0 | 100 | 47.05 | 0.010 | 1000 |
| Level 3 | 0 | 40 | 0 | 47.05 | 0.040 | 4000 |
| Level 4 | 25 | 0 | 0 | 47.05 | 0.25 | 25000 |
| Level 5 | 50 | 0 | 0 | 47.05 | 0.500 | 50000 |
| Level 6 | 75 | 0 | 0 | 47.05 | 1.000 | 75000 |

Using a volumetric Hamilton or similar syringe, measure the specified volume of standard into a tin capsule. Dry the calibration levels completely by placing in the oven at 105$^{o}$C for 60 minutes. Fold the capsules. A blank (empty) tin must be dropped for the calibration blank. Proceed to Section 10.5 for analysis instructions.

The instrument software system plots peak area against mg of Carbon and calculates a correlation coefficient using standard linear regression. The correlation coefficient (r) must be $\geq$ 0.995 for the calibration to be considered acceptable. If it is not, repeat the calibration prior to analysis.

### 10.2 Troubleshooting

- Calibration passes at > 0.995 correlation, but LCS fails abnormally low: Re-calibrate.
- Large peak before Carbon peak; Indicates leak in system, perform leak test, isolate and repair leak.
- Carbon peak “maxes out” at instrument 1200mv (peak has flat top): Reanalyze sample at lower weight.
- No peaks on any chromatograms, no results: Gases to instrument may be off. Turn on all gasses at valve manifold.
- Autosampler will not work at all: Gasses to instrument may be off. Turn on all gasses at valve manifold.
- Carry over; Clean autosampler slide, if persists reduce sample mass. Note sample carryover in NCM. Oily samples may not be amenable to this test.
- Single chromatogram shows results at bottom of page, but no peak or baseline in chromatogram window: Re-print single chromatogram.
- Some or all chromatograms show carbon peak at same retention time as CCV, but peak is not identified as carbon, or is identified as another element: Retention time shifted. Adjust retention time in calibration window, and reprint chromatograms.
- Peaks shift later through the run, or reduced recovery of samples with known concentration. Check oxygen tank for sufficient pressure, and replace if necessary.
- Upon recalibration, peaks are not being identified as carbon: In calibration window, general tab, adjust retention time to match peaks. Starting at level 1, “Open Standard”, open level1

curve pt. in calibration directory, click “Add Peak” button, click on peak itself. Increase level #, opening standard for each curve pt and add each peak. Carbon Tab should have all five calibration points on curve, if done correctly.

- Peaks in chromatograms identified as carbon, but all results in summary table below chromatogram are zero: Current calibration not associated with run when started. Open current calibration, copy first two columns for all points (5 rows) in small table in general tab. Then, open calibration that was associated with run (should be empty) and paste into table in calibration tab. Reprint all chromatograms on run.
- Software crashes during analysis: Boot up software normally. Chromatograms already printed/analyzed are ok, but, sample that was analyzing during shutdown is lost. Restart table at next sample by un-checking “run” box for samples already run and sample that was lost.
- Autosampler error causes few samples to remain in autosampler tray after run has finished: Identify samples that got stuck. Create a new run and analyze stuck samples (with initial weights) with bracketing QC. No MB/LCS needed.
- Autosampler error causes many sequential samples to remain in autosampler tray after run has finished (usually end of run): Add rows onto existing table. Identify samples that did not get analyzed and repeat Ids and weights into added rows. Restart table. All analyzed samples’ status should be blue (analyzed), added rows should be green (not analyzed yet).

### 10.3 Sample Preparation

Homogenize the sample using the procedure described in SOP BR-QA-020. Refer to Appendix D for Marine Sediment Processing, and Appendix E for Black Carbon Processing

Dry approximately 5-10 g of sample in at 105 $^{o}$C for 12-24 hrs. (The sample from the moisture fraction may be used for this step.) Disaggregate the sample to break up clumps to ensure exposure to acidification in next step. Do not grind the sample.
Due to the sample size required by the instrumentation, if the sample matrix contains particles that are too large for analysis, the sample will be sieved using a 200 micron (#35) sieve.

For each field sample prepare a tin for analysis. Using tweezers, and working directly from the box, place a tin capsule on the analytical balance and tare the balance. Using the small sample scoop, add approximately 10 mg (or the project specified sample weight) of sample to a tin capsule. Record the actual sample weight used on sample preparation log. Remove the capsule from the balance and place into one of the aluminum holding trays.

To prepare the method blank, set an empty tin capsule into an aluminum holding tray (this tin must be acidified with the remainder of the samples).

To prepare the LCS, weigh 9 to 11 mg of the LECO LCS material into two tin capsules and set them in sequence in an aluminum holding tray. Prepare the LCS in quadruplicate if site specific P&A study has not been requested in the project.

For the matrix spike, weigh out an additional sample aliquot and record its weight. Add 35 uL of 1% KHP calibration stock.

For the sample duplicate, weigh out an additional sample aliquot.

Add one to two drops of 1:19 phosphoric acid to each tin capsule (enough to sufficiently cover the sample until reaction ceases). Place the aluminum trays into a drying oven set to a temperature of 105 ±2 ºC for 30-60 minutes or until all samples appear dry.

Using tweezers pinch the top of each tin capsule closed and compress the capsule around the material inside. Work carefully so as not to tear the capsule, but crush it down to the smallest size. Set the prepared samples in line in a clear plastic sample tray for storage, or place directly into an autosampler tray for analysis. For the latter, leave positions open for the CCV check standards and associated calibration blanks.

Prepare the ICV, CCV standards and blanks as follows:

Prepare an ICV for each sequence. To prepare the ICV, weigh 9 to11 mg of the LECO LCS material into a tin capsule.

For each CCV, transfer 35uL of 1% KHP solution into a tin capsule. Dry the capsules in a drying oven set to a temperature of 105 ±2 ºC for 30-60 minutes or until all samples appear dry. Fold the capsule up and compress down to the smallest size possible. Prepare enough CCVs to ensure a frequency of every 20 drops and the end of the analytical sequence. For each associated calibration blank, leave an empty position in the auto-sampler tray (a tin must be analyzed for calibration blanks).

### 10.4 Preparation of the ICV, CCV and Blanks

For each ICV weigh ~9-11 mg of the LECO LCS material into a tin capsule.

For each CCV, transfer 35uL of 1% KHP to a tin capsule. Dry the capsules in a drying oven at 105 $^{o}$C for 30-60 minutes or until dry. Fold the capsule and compress down to the smallest size possible. Prepare enough CCVs to ensure a CCV frequency of every 20 drops and at the beginning and end of the analytical sequence. Use a folded empty tin for each calibration blank(not acidified).

### 10.5 Software Set-up and Analysis of a Curve

If a there is not a valid curve or the valid curve is not listed in the software, create a calibration curve in the analytical software. Enter the standard type, level, and mg of KHP used for each calibration level. Enter each sample ID and their respective weights into the instrument software, enter a weight of 10 mg for the method blank and calibration blanks and save the sample table. Enter the weight for the LCS. Add the tin capsules to the autosampler tray in sequence and set the tray into the autosampler carriage.

An example analytical sequence that includes ICAL is as follows:

Initial Calibration (calibration blank and 5 calibration standards)
ICV
ICB(blank tin)
CCV
CCB(blank tin)
MB(acidified tin)
LCS (Routine=4 reps; Dixon=2reps)

Samples (Routine=1 rep; Dixon=2reps)
CCV
CCB(blank tin)
Samples (Routine=1 rep; Dixon=2reps)
CCV
CCB(blank tin)

Click the “start” icon to begin the analysis.

## 11.0 Corrective Action

When an out-of-control situation occurs that is not delineated in this corrective action table or the corrective actions listed do not adequately address the circumstances, a Corrective Action Report (CAR) (NCM), etc., must be developed (see SOP BR-QA-016) and the analyst must use his/her best analytical judgment and available resources to determine the corrective action to be taken. The out-of-control situation may be caused by more than one variable. The analyst should seek the assistance of his/her immediate supervisor, QA manager or other experienced staff if they are uncertain of the cause of the out-of-control situation. The analysis must not be resumed until the source of the problem and an in-control status is re-established. All samples associated with the out-of-control situation must be reanalyzed after in-control status has been re-established or if authorization is received from the supervisor or QA Manager for release with data qualification.

## 12.0 Calculations / Data Reduction

### 12.1 Calculations

The instrument software calculates TOC using the area response from the calibration curve and sample mass used. The determination of TOC is performed by the laboratory’s LIMS system.
See Appendix C for equations for percent recovery and relative percent difference.

### 12.2 Data Review

#### 12.2.1 Primary Data Review

Enter the results of the quadruplicate analysis into the EXCEL spreadsheet designated for this purpose. Compare the standard deviation derived from the quadruplicate sample or LCS against the standard deviation from the appropriate P&A study. If the SD of the sample quadruplicate is greater than 3 times the SD of the study, initiate a nonconformance memo and notify the PM to determine if further action is necessary.

Upload the instrument data to the laboratory information system (LIMS) “TALS”. Evaluate the sequence against the acceptance criteria given in Table 2. Perform the recommended corrective action as necessary. If corrective action is not taken or is not successful, initiate a nonconformance memo (NCM) to document the situation. Set the Batch to 1$^{st}$ level reviewed. For Dixon analysis, an additional 2 reps must be performed if the original reps yielded a RSD greater than 40. Then the four different replicates must be entered into the Dixon Outlier Template (FWC200A for 4 reps or FWC200B for 3 reps) from the lowest to the highest result.

Assemble supporting documents including the quad sample calculation spreadsheet and forward to secondary review staff.

### 12.2.2 Secondary Data Review

Spot-check the analytical results. Verify that acceptance criteria were met and if the results do not fall within the established limits verify the recommended corrective actions were performed. If corrective action was not taken or is unsuccessful, ensure the situation is documented with a nonconformance memo (NCM) and ensure data is qualified accordingly.

Set the batch to second level review. Scan and attach copies of supporting documentation such as; run logs, raw data and quad sample spreadsheet to the batch. Set the job to lab complete, review the form set, correct any problems then forward supporting documentation to report management.

### 12.2.3 Data Reporting

The report format, application of data qualifiers and creation of the data deliverable is performed by the LIMS using the formatter set by the project manager during log-in.

Retain, manage and archive electronic and hardcopy data as specified in laboratory SOP BR-QA-014 Laboratory Records.

## 13.0 Method Performance

### 13.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. An initial method detection limit study is performed in accordance with SOP No. BR-QA-005. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency.

### 13.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

**13.2.1** Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample may be equivalent to a mid- level calibration.

**13.2.2** Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

**13.2.3** If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. TNI 2016 requires consecutive passing results. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

**13.2.4** Until the IDOC is approved by the QA Manager (or designee); the trainer and trainee must be identified in the batch record.

### 13.3 Training Requirements

The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. A new analyst must be working under documented supervision prior to approval of the IDOC. Documentation that a new analyst is performing under supervision must be entered into the batch record (View Batch Information) until that analyst's IDOC has been approved by the QA Manager (or designee). See requirements for demonstration of analyst proficiency in SOP No. BR-QA-011.

## 14.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

## 15.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001 *Hazardous Waste*.

The following waste streams are produced when this method is carried out.

- Caustic waste – 2.5 L glass satellite container.
- Acidic Waste - 2.5L glass satellite container

The satellite containers are labeled "Hazardous Waste" along with the type of waste category generated. Authorized personnel routinely transfer the contents of the satellite containers to the hazardous waste storage room for future disposal in accordance with Federal, State and Local regulations.

## 16.0 References / Cross-References

- EPA Region II Document Determination of Total Organic Carbon in Sediment, July 27, 1998, authored by Lloyd Kahn, Quality Assurance Specialist.
- Corporate SOP CW-E-M-001 Corporate Environmental Health and Safety Manual
- Laboratory SOP BR-QA-005, Procedures for the Determination of Limits of Detection (LOD), Limits of Quantitation (LOQ) and Reporting Limits (RL).
- Laboratory SOP BR-QA-011 Employee Training
- Laboratory SOP BR-EH-011 Hazardous Waste
- Laboratory SOP BR-QA-014 Laboratory Records
- Laboratory Quality Assurance Manual (QAM)

## 17.0 Method Modifications

The laboratory procedure is modified from the reference method as follows:

| Modification Number | Method Reference | Modification |
|---|---|---|
| 1 | TOC by Lloyd Kahn | The Laboratory uses 1:19 (w/w) phosphoric acid to decarbonize the sample (to reduce sample loss from effervescence) and dries the sample in an oven at 105$^{o}$C. |
| 2 | TOC by Lloyd Kahn | Due to the small sample size the laboratory dries and disaggregates the sample prior to analysis. This step improves precision associated with high moisture or clay type matrices. |
| 3 | TOC by Lloyd Kahn | P&A studies are not performed per the reference method due to variability in project sites. See section 12.2 for the P&A procedure that the laboratory uses. |

## 18.0 Attachments

- Table 1: Primary Materials Used
- Table 2: QC Summary & Recommended Corrective Action
- Appendix A: Terms and Definitions
- Appendix B: Column change procedure
- Appendix C: Equations

## 19.0 Revision History

BR-WC-008, Revision 17.0

- Updated Title Page
- Updated Headers and Footers Throughout
- Section 10.2: Updated troubleshooting section to add peaks shift later through the run, or reduced recovery of samples with known concentration. Check oxygen tank for sufficient pressure, and replace if necessary.

Previous revisions are retained by the QA Department.

**Table 1: Primary Materials Used**

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Phosphoric Acid | Corrosive | 1 Mg/M3 TWA | Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

**Table 2: QC Summary, Frequency, Acceptance Criteria and Recommended Corrective Action (TOC Lloyd Kahn)**

| QC Item | Frequency | Acceptance Criteria | Recommended Corrective Action[1] |
|---|---|---|---|
| ICAL | Following each column change and when CCV failure indicates calibration may no longer be valid. | correlation coefficient $\geq$ 0.995 | Standards check, re-calibration |
| CCV | Every 20 drops and at the end of the analytical run | %R (75-125) | Re-prepare and reanalyze samples not bracketed by passing standard. If CCV fails high, and TOC is not detected in any of the bracketed samples, the samples without TOC may be reported without reanalysis. |
| CCB | Following each CCV | < RL | Re-prepare and reanalyze batch. |
| Method Blank (MB) | Once per batch of 20 samples | < RL | Re-prepare and reanalyze batch. |
| LCS | Once per batch of 20 samples. Prepared in quadruplicate unless site P&A study is performed, then analyze as single injection. | %R (75-125) | Re-prepare and reanalyze batch. |
| Sample Quadruplicate | When site specific P&A study is specified. If no quad specified for any jobs included in the batch analyze the LCS in quadruplicate. | SD ≤ 3X annual P&A SD | If sample quad, notify PM. If LCS quad, reanalyze the entire batch. |

[1]*The recommended corrective action may include some or all of the items listed in this column. The corrective action taken may be dependent on project data quality objectives and/or analyst judgment but must be sufficient to ensure that results will be valid. If corrective action is not taken or is not successful, data must be flagged with appropriate qualifiers.*

**Appendix A: Terms and Definitions**

**Batch:** environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria.

**Calibration:** the establishment of an analytical curve based on the absorbance, emission intensity or other measured characteristic of known standard.

**Calibration Standards:** a series of known standard solutions used to calibrate the instrument response with respect to analyte concentration.

**Demonstration of Capability (DOC):** procedure to establish the ability to generate acceptable accuracy and precision.

**Holding Time:** the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

**Laboratory Control Sample (LCS):** a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

**Method Blank (MB):** a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

**Non-conformance:** an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

**Preservation:** refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

**Reporting Limit (RL):** the level to which data is reported for a specific test method and/or sample.

## Appendix B: Column Change Procedure:

Turn off the helium and oxygen supplies to the instrument.

Dial the left furnace temperature to a reading of 052 (this equates to 520˚C). Wait until the temperature drops below 600˚C to remove the column.

Remove the panel covering the furnace and unscrew the autosampler connection from the top of the column.

Unscrew the fitting at the bottom of the column and remove.

Lift the column up and out of the furnace using high temperature gloves.

**CAUTION: The column will still be 500-600˚C. Do not touch the center portion of the column. Place the spent column in the metal can designated for this purpose.**

Lay a new quartz column on the bench top, measure and mark off for the following:

- One inch up from the bottom and add a ½ inch plug of quartz wool. Note: pack the quartz wool tightly enough for it to stay in place.
- Pour in 2 ½ inches of copper wire
- Pack another ½ inch quartz wool plug on top of the copper
- Pour in 3 inches of tungsten
- Pack a final ½ inch quartz wool plug on top of the tungsten

Place the new column into the furnace and reconnect the top and bottom fittings. Snug these up, but don't over tighten.
Replace the panel covering the furnace, dial the furnace temperature back to 102 (this equates to

1020˚C), and turn the helium and oxygen supplies back on.

When the instrument comes up to operating temperature, it is ready to calibrate.

## Appendix C: Equations

### Percent Recovery (%R) LCS and CCVs

$$\%R = \frac{SR}{SA} \times 100\%$$

Where:
SR= Sample Result
SA=Concentration of Spike Added

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### Relative Percent Difference (%RPD)

$$\%RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} \times 100$$

Where:
D1 = Sample result
D2 = Duplicate Result

**Appendix D: Marine Sediments High in Inorganic Carbon**

Sample Preparation

Transfer approximately 10 g of a thoroughly mixed sample to an aluminum weigh dish, and dry in the 105°C oven. Grind the sample with the pink mortar and pestle to a fine powder. Record the weight of a 250 mL Teflon beaker then transfer ~ 5 g of the ground sample to this beaker.

If the sample is to be spiked, weigh the beaker to the nearest 0.1mg and record the weight. Likewise determine and record the weight of the added sample. Add 0.1g of NIST 1632b Trace Elements in Coal (80.11% Carbon) to the sample. Record the weight added. Evenly distribute the spike over the sample and use a glass stir rod to mix the spike with the sample. Do not use that stir rod with any other sample.

Use Talc-free latex gloves from this point on to minimize the risk of acid burns. Add several drops of 1:1 HCL to each sample and stir each sample with its own glass stir rod. Carefully rinse the stir rod and beaker walls with DI water using a fine-tipped squirt bottle. Use only what is needed to bring the entire sample to the bottom of the beaker. ***When adding water to acid use necessary precautions to avoid splashing!*** Samples with high concentrations of inorganic carbon may effervesce to the point of overflowing the beaker, so take care to add the acid in small aliquots and stir vigorously. If the sample "boils over" it must be re-prepared. Continue to add 1:1 HCL in small aliquots until there is no further reaction, taking sample to dryness after each addition of acid in a 105-degree oven.

Dry the treated samples in the oven after each acid/water addition. Do not add more than a total of 200 mL of 1:1 HCL to any sample.

***NOTE****: Samples are hygroscopic and will absorb water if they are exposed to air for too long.*

Weigh beaker with residue and record the residue weight measurement. After the sample is thoroughly dry, scrape the sample residue from the beaker and grind to a powder using the pink mortar and pestle. Transfer the ground sample to a clean, dry 40-mL vial reserved for this analysis.

***NOTE:*** *Depending on the nature of the sample, it may be difficult to completely remove the dried residue from the beaker or to grind it to a homogenous powder. Where difficulties are encountered, make a note on the preparation worksheet.*

Analysis

Perform TOC analysis on processed sample material as outlined in section 10.0 of this SOP.

**Appendix E: Determination of Black Carbon in Sediment Procedure**

1. Obtain a representative subsample of the sediment. Weight 10 grams of sample into a clean pre-tared aluminum drying pan or equivalent.

2. Dry the sample at 105$^{o}$C for at least 12 hours.

3. Grind the sample using a mortar and pestle.

4. Sieve the sample using a number 35 sieve (500 um).

5. Treat the sample with phosphoric acid. Add acid drop wise until effervescence is no longer observed.

6. Dry the sample at 105$^{o}$C for 1 hour.

7. Set aside an aliquot of the sample at this stage for direct TOC analysis, reported without correction for the IN623 percent solids. Continue with the sample for Black Carbon.

8. Place the dried sample into a clean crucible and cover the sample.

9. Bake the samples at 375$^{o}$C in a muffle for 24 hours or until the LCS is +/- 50% of the true value.

10. Allow the samples to cool and transfer approximately 10.0 mg into each of two tin capsules.

11. Transfer the sample (in the tin capsules) to the TOC analyzer for analysis by the Lloyd Kahn Method.

12. The sample is pyrolyzed in an inductive type furnace, where the carbon is converted to carbon dioxide, which is measured using a differential thermal conductivity detector.

13. The results will be reported as mg/Kg Black Carbon.

Note: Black carbon LCS material: NIST Standard Reference Material 1944 New York-New Jersey Waterways Sediment.

**References:**

Orjan Gustafsson, Thomas D. Bucherli, Zofia Kukulska, Mette Andersson, Claude Largeau, Jean-Noel Rouzaud, Christopher M. Reddy and Timothy I. Eglinton (December 2001) Evaluation of a Protocol for the Quantification of Black Carbon in Sediments, Global Biogeochemical Cycles, Volume 15, pages 881-890.

Orjan Gustafsson, Farnaz Haghseta, Charmaine Chan, John MacFarlane & Philip M. Gschwend (1997) Quantification of the Dilute Sedimentary Soot Phase: Implications for PAH Speciation and Bioavailability, Environmental Science & Technology, Volume 31, pages 203-209.

# Title: GC/MS ANALYSIS BASED ON METHODS 8270C, 8270D, AND 8270E

## [Method: SW846 8270C, 8270D, and 8270E]

**Approvals (Signature/Date):**

| | | | |
|---|---|---|---|
| Technology Specialist | 06/24/19 Date | Health & Safety Coordinator | 06/21/19 Date |
| Quality Assurance Manager | 06/26/19 Date | Technical Director | 07/01/19 Date |

**This SOP was previously identified as SOP NC-MS-018, Rev 7, dated 3/30/18**



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## 1. SCOPE AND APPLICATION

1.1. This method is based upon SW846 8270C, 8270D, and 8270E, and is applicable to the determination of the concentration of semivolatile organic compounds in extracts prepared from solid and aqueous matrices. Direct injection of a sample may be used in limited applications. Refer to Tables 3a and 3b for the list of compounds applicable for this method. Note that the compounds are listed in approximate retention time order. Additional compounds may be analyzed by this method. If non-standard analytes are required, they must be validated by the procedures described in Section 13 before quantitative sample results may be reported.

1.2. The following compounds may require special treatment when being determined by this method:

1.2.1. Benzidine exhibits poor chromatography and can be subject to oxidative losses during solvent concentration. Neutral extraction should be performed if this compound is expected.

1.2.2. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

1.2.3. N-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be distinguished from diphenylamine.

1.2.4. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.2.5. Hexachlorophene is not amenable to analysis by this method.

1.2.6. 3-Methylphenol cannot be separated from 4-methylphenol under the conditions specified in this method.

1.3. Refer to the LIMS for specific reporting limits. Reporting limits will be proportionately higher for sample extracts that require dilution.

## 2. SUMMARY OF METHOD

2.1. Aqueous samples are extracted with methylene chloride using a separatory funnel and/or a continuous extractor. Solid samples are extracted with methylene chloride / acetone using sonication, or soxhlet extractor. The extract is dried, concentrated to a final volume of 2 mL for waters and soils, and analyzed by GC/MS. Extraction procedures are detailed in SOPs NC-OP-037, NC-OP-038, NC-OP-039, NC-OP-040, NC-OP-042, and NC-OP-043.

2.2. The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) equipped with a narrow-bore fused silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected directly to the GC.

2.3. Identification of target analytes is accomplished by comparing their electron impact mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard (IS), using a calibration curve appropriate to the intended application.

## 3. DEFINITIONS

3.1. Refer to the glossary in the Eurofins TestAmerica Canton Quality Assurance Manual (QAM), current version.

## 4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks (MBs) as described in the Quality Control section below. Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. If interference is detected, it is necessary to determine if the source of interference is in the instrumental analysis, preparation, and/or cleanup of the samples; then take corrective action to eliminate the problem.

4.2. The use of high purity reagents, solvents, and gases helps to minimize interference problems.

4.3. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from sample source to sample source, depending upon the nature of the site.

4.4. Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of solvent to check for cross contamination.

4.5. Phthalate contamination is commonly observed in this analysis and its occurrence must be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis.

## 5. SAFETY PRECAUTIONS

5.1. Employees must abide by the policies and procedures in the Corporate

Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.3. Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, and n-nitrosodimethylamine.

5.4. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

| Material | Hazards | Exposure Limit (1) | Signs and symptoms of exposure |
|---|---|---|---|
| Methylene Chloride | Carcinogen Irritant | 25 ppm-TWA<br><br>125 ppm-STEL | Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin. |
| **Note:** Always add acid to water to prevent violent reactions. | | | |
| 1 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

5.5. It is recommended that analysts break up work tasks to avoid repetitive motion tasks, such as opening a large number of vials or containers in one time period.

5.6. Exposure to chemicals must be maintained as low as reasonably achievable. All samples with stickers that read “Caution/Use Hood!” must be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.

5.7. The preparation of standards and reagents must be conducted in a fume hood with the sash closed as far as the operation will permit.

5.8. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents must be conducted in a fume hood with the sash closed as far as the operations will permit.

5.9. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.

5.10. All work must be stopped in the event of a known or potential compromise to the health and safety of a Eurofins TestAmerica Canton associate. The situation must be reported immediately to a Laboratory Supervisor and the EH&S Coordinator.

## 6. EQUIPMENT AND SUPPLIES

6.1. Gas Chromatograph/Mass Spectrometer (GC/MS) system: An analytical system complete with a temperature-programmable GC, suitable for split/splitless injection, and all required accessories, including syringes, analytical columns, and gases. The capillary column must be directly coupled to the MS source.

6.2. Column: 30m x 0.25mm ID, 0.5µm film thickness silicon-coated fused-silica capillary column (J & W Scientific DB-5.625 or equivalent). Alternate columns are acceptable if they provide acceptable performance.

NOTE: A suitable alternative column may be substituted as long as its performance is documented to meet the requirements of the method.

6.3. Mass Spectrometer (MS): Capable of scanning from 35 to 500 AMU every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The MS must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) that meets all of the criteria in Table 2 when the GC/MS tuning standard is injected through the GC.

6.4. GC/MS Interface: Any direct GC-to-MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used.

6.5. Data System: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search 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 the Extracted Ion Current Profile (EICP). Software must also allow integration of the abundances in any EICP between specified times or scan-number limits. (This is used to quantify TICs: The most recent version of the EPA/NIH Mass Spectral Library is recommended for TIC library searches.)

6.6. Syringes: 5 µL and 10 uL Hamilton Laboratory grade syringes or equivalent.

6.7. Carrier gas: Ultra high purity helium.

6.8. Autosampler vials, inserts, and caps

## 7. REAGENTS AND STANDARDS

7.1. A minimum five-point calibration curve is prepared. The standard preparation information and calibration levels are detailed in the LIMS. If a quadratic regression is used, six points must be analyzed for the calibration curve. The low point must be at or below the reporting limit. Other calibration levels may be used, depending on instrument capability, but the low standard must support the reporting limit (RL) and the high standard defines the upper limit or end of the range of the calibration. For Ohio VAP work, the low standard must be at, or below, the RL.

7.2. An IS solution is prepared by diluting a purchased standard. The standard preparation information is detailed in the standards and reagents module in LIMS. Compounds in the IS Mix are acenaphthene-$d_{10}$, chrysene-$d_{12}$, 1,4-dichlorobenzene-$d_4$, naphthalene-$d_8$, perylene-$d_{12}$, and phenanthrene-$d_{10}$.

7.3. Surrogate Standard Spiking Solution: Prepare as indicated in the preparative methods. Preparation information is detailed in the standards and reagents module in LIMS for the Organic Prep group. See appropriate preparation SOP. Surrogate compounds and levels are listed in Table 6.

7.4. GC/MS Tuning Standard: A methylene chloride solution containing decafluorotriphenylphosphine (DFTPP) is prepared. The standard preparation information is detailed in the standards and reagents module in LIMS. Pentachlorophenol, benzidine, and DDT, must also be included in the Tuning Standard to assess chromatographic performance. All components are at 25 ug/mL.

7.5. The standards listed in Sections 7.1 to 7.4 must be refrigerated at $\leq 6^{o}C$ when not in use. Standards may be stored at -10$^{o}$C to -20$^{o}$C if it can be demonstrated that analytes do not fall out of solution at this temperature. The standards must be replaced at least once a year. Additional information on standards preparation, tracking, and storage can be found in SOP NC-QA-017

## 8. SAMPLE PRESERVATION AND STORAGE

8.1. Sample extracts are stored at $4 \pm 2^{o}C$. Samples and extracts must be stored in suitable glass containers with Teflon®-lined caps. (Extracts will be stored for 30 days after invoicing.)

8.2. Water samples are extracted within seven days of sampling, and the extracts are analyzed within 40 days of extraction. Solids, sludges, and organic liquids are extracted within 14 days of sampling and the extracts are analyzed within 40 days of extraction.

## 9. QUALITY CONTROL

### 9.1. Batch Definition

9.1.1. The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / matrix spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank (MB). Batches are defined at the sample preparation stage. Batches must be kept together through the whole extraction process, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the Eurofins TestAmerica Canton QC Program document (QA-003) for further details of the batch definition.

### 9.2. Method Blank (MB)

9.2.1. A MB is prepared and analyzed with each batch of samples. The MB consists of reagent water for aqueous samples and sodium sulfate for soil samples. Surrogates are added and the MB is carried through the entire extraction and analysis procedure. The MB must not contain any analyte of interest at or above the reporting limit (except common lab contaminants, see below). Any MB contamination above the RL must be less than 1/10 of the measured concentration of any sample in the associated preparation batch. For Wisconsin the MB must be clean down to ½ the RL.

9.2.2. If the analyte is a common laboratory contaminant the data may be reported with qualifiers if the concentration of the analyte in the MB is less than five times the RL. Such action must be taken in consultation with the client.

9.2.3. Re-analysis of any samples with reportable concentrations of analytes found in the MB is required unless other actions are agreed upon with the client.

9.2.4. If there is no target analyte greater than the RL in the samples associated with an unacceptable MB the data may be reported with qualifiers. Such action should be taken in consultation with the client. NOTE: For Ohio VAP work, there can be no target analyte greater than the RL in the MB. All samples associated with an unacceptable MB must be re-extracted and re-analyzed. The exceptions are as follows: (a) insufficient sample for re-extraction (b) expired holding times, or (c) the analytes detected in the MB are non-detect in the associated samples.

9.2.5. The MB must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the MB has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples, re-extraction of the MB and affected samples will normally be required. Consultation with the client must take place. For Ohio VAP samples, all analytes must meet criteria or the samples must be re-extracted if sufficient volume of sample remains.

9.2.6. If re-analysis of the batch is not possible due to limited sample volume or other constraints, the MB is reported, all associated samples are flagged with a "B", and appropriate comments must be made in a narrative to provide further documentation.

9.2.7. Refer to the Eurofins TestAmerica Canton QC Program document (QA-003) for further details of the corrective actions.

9.3. Laboratory Control Sample (LCS)

9.3.1. A LCS is prepared and analyzed with every batch of samples. All control analytes must be within established control limits. The LCS is spiked with the compounds listed in Tables 4 and/or 5 unless otherwise specified by a client or agency.

9.3.2. If any control analyte in the LCS is outside the laboratory established historical control limits, corrective action must occur. All non-controlling compounds must attain a recovery of 10% or greater if the compound is on the client's list. Corrective action may include re-extraction and re-analysis of the batch. For Ohio VAP samples, all analytes must meet criteria or the samples must be re-extracted if sufficient volume of sample remains.

9.3.3. If the batch is not re-extracted and re-analyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. (An example of acceptable reasons for not re-analyzing might be that the MS and MSD are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS).

9.3.4. If re-extraction and re-analysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.3.5. The LCS must have acceptable surrogate recoveries. If surrogate recoveries are low, re-extraction of the LCS and affected samples will normally be required. Consultation with the client should take place. For Ohio VAP samples, all analytes must meet criteria or the samples must be re-extracted. The exceptions are as follows: (a) insufficient sample for re-extraction (b) expired holding times, or (c) the LCS is biased high and the samples are non-detect for those analytes.

9.3.6. Ongoing monitoring of the LCS over time provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. A MS/MSD is prepared and analyzed with every batch of samples. The MS/MSD is spiked with the same subset of analytes as the LCS (see Tables

4 and/or 5). Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically-generated limits.

9.4.2. If the recovery for any component is outside QC limits for both the MS/MSD and the LCS, the laboratory is out of control and corrective action must be taken. For client specific samples, corrective action may include re-preparation and re-analysis of the batch.

9.4.3. The MS/MSD must be analyzed at the same dilution as the un-spiked sample, even if the MS compounds will be diluted out.

9.5. Surrogates

9.5.1. Every sample, MB, and QC sample is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery [%R]) falls within the required recovery limits. The compounds routinely included in the surrogate spiking solution, along with recommended standard concentrations, are listed in Table 6.

9.5.2. If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

9.5.2.1. Check all calculations for error.

9.5.2.2. Ensure that instrument performance is acceptable.

9.5.2.3. Recalculate the data and/or re-analyze the extract if either of the above checks reveals a problem.

9.5.2.4. It is only necessary to re-prepare / re-analyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

**Note:** If all associated QC meets criteria (MB, LCS, MS/D), up to one surrogate per fraction may be outside of acceptance criteria, as long as the recovery is greater than 10%. **Note:** For Ohio VAP all surrogates must be within acceptance criteria. The exceptions for Ohio VAP are as follows: (a) insufficient sample for re-extraction, or (b) the surrogates are biased high and the samples are non-detect.

9.5.3. If the sample with surrogate recoveries outside the recovery limits was a sample used for a MS/MSD and the surrogate recoveries in the MS/MSD are also outside of the control limits, then the sample, the MS, and the MSD do not require re-analysis as this phenomenon would indicate a possible matrix problem.

9.5.4. If the sample is re-analyzed and the surrogate recoveries in the re-analysis are acceptable, then the problem was within the analyst's control and only the re-analyzed data must be reported (unless the re-analysis was outside holding times, in which case, reporting both sets of results may be appropriate).

9.5.5. If the re-analysis does confirm the original results, the original analysis is reported and the data flagged as estimated due to matrix effect.

9.6. Internal Standards

9.6.1. Every sample, MB, and QC sample (including calibration standards, ICV and CCV) is spiked with internal standards.

9.6.2. When compared to the daily CCV, internal standards must be within ± 0.5 minutes and peak area recoveries must be 50% to 200%.

9.6.3. Samples with failing internal standards must be re-analyzed "undiluted" unless matrix interference is apparent. If matrix interference is apparent, dilute the sample with methylene chloride using a syringe for re-analysis. When there is obvious interference causing the IS failure that corrective action will not remedy, data must be flagged with a qualifier indicating matrix interference. If the QC has failing internal standards, the batch must be re-prepped and re-analyzed.

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action. Deviations are not applicable for Ohio VAP projects.

## 10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. The instrument is tuned for decafluorotriphenylphosphine (DFTPP), calibrated initially with a minimum five-point calibration curve, and verified each 12-hour shift with one or more continuing calibration standard(s). Recommended instrument conditions are listed in Table 1.

10.2. All standards and extracts are allowed to warm to room temperature before injecting.

10.3. Instrument Tuning

10.3.1. At the beginning of every 12-hour shift, the GC/MS system must be checked to see if acceptable performance criteria (Table 2) are achieved for DFTPP.

10.3.2. Inject the GC/MS tuning standard (Section 7.4). Obtain background-corrected mass spectrum of DFTPP and confirm that all the key m/z criteria in Table 2 are achieved. If all the criteria are not achieved, the analyst must retune the MS and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed.

10.3.3. The GC/MS tuning standard must also be used to evaluate the inertness of the chromatographic system. The tailing factor for benzidine must be less than 3.0. The tailing factor for pentachlorophenol must be less than 5. For Method 8270D and 8270E, benzidine and pentachlorochlorophenol should not exceed a tailing factor of 2. DDT must be included in the tuning standard, and its breakdown must be < 20%. Refer to Section 12 for the appropriate calculations.

**NOTE:** Breakdown and trailing factor are not applicable for LVI PAHs.

10.4. Initial Calibration

10.4.1. Internal Standard Calibration Procedure: Internal standards are listed in Table 7. Use the base peak m/z as the primary m/z for quantitation of the standards. If interferences are noted, use one of the next two most intense masses for quantitation.

10.4.2. Compounds should be assigned to the IS with the closest retention time. Refer to Table 7 for internal standard corresponding analytes.

10.4.3. Prepare calibration standards at a minimum of five concentration levels for each parameter of interest. Six standards must be used for a quadratic least squares calibration. Add the appropriate amount of the IS mixture to result in 2 ng on column. (For example, 5 uL of 80 ppm IS mix is added to 100 uL of extract. This results in 2 ng per each 0.5 ul injection). The concentration ranges of all analytes can be easily accessed in the LIMS. For Ohio VAP work, the low standard must be at or below the reporting limit

10.4.4. For LVI analysis, 2 uL of 8 ppm IS mix is added to 100 uL of extract. The calibration standards are diluted by a factor of 10, however 10x more is injected (5 uL injected rather than the normal 0.5 uL), keeping the on-column amount the same as the non-LVI analytes (2 ng).

10.4.5. Analyze each calibration standard and tabulate the area of the primary characteristic m/z against concentration for each compound and internal standard. Table 3 lists the analytes and characteristic ions analyzed in the laboratory. Calculate response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in Section 12. For Method 8270C, verify that the SPCC and CCC criteria in Sections 10.4.6 and 10.4.8 are met. **No sample analysis maybe performed unless these criteria are met.** See section 10.4.7 for 8270D and 8270E ICAL criteria.

10.4.6. System Performance Check Compounds (SPCCs) (Method 8270C). The minimum average RF for semivolatile SPCCs is 0.050. If the minimum response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

SPCC Compounds:

N-nitroso-di-n-propylamine
Hexachlorocyclopentadiene
2,4-Dinitrophenol
4-Nitrophenol

10.4.7. Initial Calibration Criteria for Method 8270D and 8270E

10.4.7.1. The RSD should be less than 20% for each analyte. For analytes that fail, use linear or quadratic curve with 0.99 correlation coefficient.

**NOTE:** If compliance with Method 8270C is required, the RSD limit is 15%.

10.4.7.2. No more than 10% of compounds can fail the 20%/0.99 correlation coefficient requirement.

10.4.7.3. If more than 10% of analytes fail both 20% RSD and 0.99 correlation coefficient, then recalibration is necessary.

10.4.7.4. Any individual analyte that fails both 20% RSD and 0.99 correlation coefficient criteria must have any positive result flagged as estimated and must be noted in the narrative.

10.4.7.5. For any analyte non-detect associated with a calibration that fails the 20% RSD/0.99 correlation coefficient/minimum response factor criteria, there must be a demonstration of adequate sensitivity at the quantitation limit. Successful analysis of a LLCCV is considered adequate demonstration for this purpose (see section 10.4.7.7).

10.4.7.6. Minimum response factor should be met, especially for the low level standard to verify the sensitivity.

10.4.7.7. Any individual analyte that fails the minimum response factor set in the SOP must have a demonstration of sensitivity in the analytical batch to report non-detects. The demonstration of sensitivity is

analysis of a low level CCV (at or below the reporting limit). The criterion for a passing LLCCV is detection only, and a passing LLCCV allows non-detects to be reported with appropriate flagging. In general, Table 4 in the method should be used as guidance in setting minimum response factors in the SOP; but the RFs may be modified if appropriate (for example, if especially low-level analysis is performed).

10.4.7.8. For Method 8270D and 8270E, the minimum response factors are listed in Table 8 at the end of this SOP.

10.4.8. Calibration Check Compounds (CCCs) (Method 8270C). The %RSD of the response factors for each CCC in the initial calibration must be less than 30% for the initial calibration to be considered valid. This criterion must be met before sample analysis begins. Problems similar to those listed under SPCCs could also affect the CCCs.

10.4.8.1. If none of the CCCs are required analytes, project-specific calibration specifications must be agreed upon with the client.

10.4.8.2. CCC Compounds

Phenol
Acenaphthene
1,4-Dichlorobenzene
N-nitrosodiphenylamine
2-Nitrophenol
Pentachlorophenol
2,4-Dichlorophenol
Fluoranthene
Hexachlorobutadiene
Di-n-octylphthalate
4-Chloro-3-methylphenol
Benzo(a)pyrene
2,4,6-Trichlorophenol

10.4.9. Continuing Calibration Criteria for Method 8270D and 8270E

10.4.9.1. At least 80% of analytes must have a %D less than or equal to 20%.

10.4.9.2. Minimum response factors must be evaluated.

10.4.9.3. If the software in use is capable of routinely reporting curve coefficients for data validation purposes, and the necessary calibration reports can be generated, then the analyst must evaluate analytes with %RSD > 15% for calibration on a curve. If it appears that substantially better accuracy would be obtained using

quantitation from a curve, then the appropriate curve with no forced intercept must be used for quantitation.

10.4.9.4. If an analyte in the initial calibration is >15%, then calibration on a curve must be used. Quadratic curve fits must be used if the compound has historically exhibited a nonlinear response. The analyst must consider instrument maintenance to improve the linearity of response where appropriate. Use of 1/Concentration$^2$ weighting is recommended to improve the accuracy of quantitation at the low end of the curve. If Relative Standard Error (RSE) is used to evaluate the curve, it must be better than 15%. If the % RSD is >15%, the analyst may drop the low or high points in the ICAL, as long as a minimum of five points are maintained and the quantitation range is adjusted accordingly. If the % RSD is still >15%, a quadratic or linear or quadratic curve must be used. The coefficient of determination ($r^2$) must be $\geq$ 0.990. If the coefficient of determination is < 0.990, then any hits for these compounds must be flagged as estimated. If a curve is not linear for any compound that is found in a sample, the result must be flagged as estimated. Linear is defined as <15% RSD or a coefficient of determination of 0.990.

**Note:** For Method 8270C, D, and E, analytes using the linear calibration fit should have the read back concentration of the low level standard evaluated. The read back concentration should be within 50% of the true value. Any sample detects for analytes that fail the read back criterion and are using a linear calibration must be flagged as estimated, and be described in the narrative.

**Note:** Some of the later-eluting PAH compounds exhibit greater variability at the low end of the calibration curve. Analysts' judgment is critical in assessing the validity of the curve at the low end, if the 50% criterion is exceeded. Any potential effects on sample results will be narrated in the analytical report.

**Note**: Several components do not respond well by this method (poor linearity). These compounds are indene, benzoic acid, benzaldehyde, caprolactam, 1,3,5-Trinitrobenzene, dinoseb, p-phenylenediamine, benzidine, alpha alpha-dimethyl phenethylamine, acrylamide, 4-Nitroquinoline-1-oxide, famphur, benzenethiol, kepone, and 2,4-Toluenediamine. If these compounds are requested by a client and hits are found, results will be flagged as estimated. Sensitivity as demonstrated by the low standard is sufficient to substantiate a non-detect.

10.4.9.5. Quantitation is performed using the calibration curve or average response factor from the initial curve.

10.5. Initial Calibration Verification (ICV)

10.5.1. Calibration accuracy is verified by analyzing a second source standard (ICV) immediately after the initial calibration. For 8270C, the CCC compounds must have ≤ 20% difference (%D) from the ICAL. Non-CCC compounds must have ≤ 50%D with an allowance of up to six compounds >50%.

10.5.2. If time remains in the 12-hour period initiated by the DFTPP injection before the initial calibration, samples maybe analyzed. (Samples may be analyzed immediately after the ICAL and ICV) Otherwise, proceed to continuing calibration.

10.6. For Methods 8270D and 8270E, the suggested acceptance criteria limit is <30%D for all analytes. Continuing Calibration

10.6.1. At the start of each 12-hour period, analyze a GC/MS tuning standard. The injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 2.

10.6.2. Following a successful DFTPP analysis, the continuing calibration standard(s) (CCs) are analyzed. The standards must contain all semivolatile analytes, including all required surrogates. A mid-level calibration standard is used for the CC.

10.6.3. For Method 8270C, the following criteria must be met for the CC to be acceptable:

10.6.3.1. The SPCC compounds must have an average response factor of ≥ 0.05.

10.6.3.2. The percent difference or drift (both %D) of the CCC compounds from the initial calibration must be ≤ 20% (see Section 12 for calculations). In addition, the %D of all analytes must be ≤ 50%, with allowance for up to four compounds to be greater than 50%.

10.6.3.3. The IS area response must be within 50-200% of the response in the mid-level of the ICAL.

10.6.3.4. The IS retention times must be within 30 seconds of the retention times in the mid-level standard of the ICAL.

**Note**: Ohio VAP requires that samples with failing internal standards must be re-analyzed "undiluted" unless matrix interference is apparent. If matrix interference is apparent, dilute the sample with methylene chloride using a syringe for re-analysis. When there is obvious interference causing the IS failure that corrective action will not remedy, data must be flagged with a qualifier indicating matrix interference. If the QC has failing internal standards, the batch must be re-prepped and re-analyzed.

10.6.3.5. If none of the CCCs are required analytes, project specific calibration specifications must be agreed upon with the client.

10.6.3.6. For Method 8270D and 8270E, if any sample is non-detect for an analyte that fails the SOP criteria low, it must have a low level CCV at the RL) in the batch as a demonstration of sensitivity for the compound that failed criteria. The criterion for a passing LLCCV is detection only and a passing LLCCV allows non-detect samples to be reported with appropriate flagging.

10.6.4. Once the above criteria have been met, sample analysis will begin. IC average RFs (or the calibration curve) will be used for sample quantitation, not the CCRFs. Analysis will proceed until 12 hours from the injection of the DFTPP have passed. (A sample *injected* less than 12 hours after the DFTPP is acceptable.)

## 11. PROCEDURE

11.1. Sample Preparation

11.1.1. Samples are prepared following SOP NC-OP-037, NC-OP-038, NC-OP-039, NC-OP-040, NC-OP-041, or NC-OP-043.

11.2. Sample Analysis Procedure

11.2.1. Calibrate the instrument as described in Section 10. Depending on the target compounds required by the client, it may be necessary to use more than one calibration standard.

11.2.2. Analyze all samples using the same instrument conditions as the preceding CC standard.

11.2.3. Add IS to the extract to result in 2 ng injected on column. Mix thoroughly before injection into the instrument. For LVI samples, the addition should result in 2 ng injected on column.

11.2.4. Inject the sample extract into the GC/MS system using the same injection technique as used for the standards.

11.2.5. The data system will determine the concentration of each analyte in the extract using calculations equivalent to those in Section 12. Quantitation is based on the initial calibration, not the continuing calibration.

11.2.6. Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst or automatically by the data system. Chromatograms before and after manual integration, as well as the reason for performing the manual

integration are required. Additional information on manual integration can be found in SOP CA-Q-S-002.

11.2.7. Target compounds identified by the data system are evaluated using the criteria listed in Section 12.1.

11.2.8. Library searches of peaks present in the chromatogram that are not target compounds (Tentatively Identified Compounds, or TICs) must be performed if required by the client. They are evaluated using the criteria in Section 12.3.

11.3. Dilutions

11.3.1. If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. The diluent used is methylene chloride. An appropriate dilution must be in the upper half of the calibration range. Samples should be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or has hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, the sample should be re-analyzed at a dilution targeted to bring the largest hit above 50% of the calibration range if matrix allows.

11.3.2. Guidance for Dilutions Due to Matrix

11.3.2.1. If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non-target peaks are less than two times the height of the internal standards, the sample should be re-analyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgment. For example, samples containing organic acids must be analyzed at a higher dilution to avoid destroying the column.

11.3.3. Reporting Dilutions

11.3.3.1. The most concentrated dilution with target compounds within the calibration range will be reported. Other dilutions will only be reported at client request.

11.3.4. Perform all qualitative and quantitative measurements. When the extracts are not being used for analyses, refrigerate them at 4 $\pm 2^{o}$C protected from light in screw cap vials equipped with unpierced Teflon®-lined septa.

11.4. Retention Time Criteria for Samples

11.4.1. If the retention time for any internal standard changes by more than 0.5 minutes from the last continuing calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Re-analysis of samples analyzed while the system was malfunctioning is required.

11.4.2. If the retention time of any IS in any sample varies by more than 0.1 minute from the preceding CC standard, the data must be carefully evaluated to ensure no analytes have shifted outside their retention time windows.

11.5. Procedural Variations

11.5.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance Memo (NCM). The NCM must be filed in the project file.

11.6. Troubleshooting Guide

11.6.1. Daily Instrument Maintenance

11.6.1.1. In addition to the checks listed in the instrument maintenance schedule in the Eurofins TestAmerica Canton Quality Assurance Manual (QAM), current version, the following daily maintenance may be performed as needed.

11.6.1.2. Clip column as necessary.

11.6.1.3. Install new or cleaned injection port liner as necessary.

11.6.1.4. Install new septum as necessary.

11.6.1.5. Perform auto-tune.

11.6.2. Major Maintenance

11.6.2.1. A new ICAL may be necessary following major maintenance. Major maintenance includes changing the column, cleaning the source, and replacing the multiplier. Refer to the manufacturer's manual for specific guidance.

## 12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative Identification

12.1.1. An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards (target compounds) or from the NBS library (TICs). When a good user-generated spectrum for a compound cannot be produced, the NBS library must be used. Two criteria must be satisfied to

verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

12.1.1.1. The sample component retention time must compare to within ± 0.2 min. of the retention time of the standard component. For reference, the standard must be run within the same 12 hours as the sample.

12.1.1.2. All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

12.1.1.3. The characteristic ions of a compound must maximize in the same scan or within one scan of each other.

12.1.1.4. The relative intensities of ions must agree to within ±30% between the 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%.)

12.1.2. If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst must report that identification and proceed with quantitation.

12.2. Mass chromatogram searches

12.2.1. Certain compounds are unstable in the calibration standard and cannot be calibrated in the normal way. In particular, the compound hexachlorophene (CAS 70-30-4) falls into this category, and is required for Appendix IX analysis. For this analyte, a mass chromatogram (EICP) search is made.

12.2.1.1. Hexachlorophene

12.2.1.1.1. Display the mass chromatograms for mass 196 and mass 198 for the region of the chromatogram from at least 2 minutes before chrysene-$d_{12}$ to at least 4 minutes after chrysene-$d_{12}$. If peaks for both ions coincide, then the analyst evaluates the spectrum for the presence of hexachlorophene. Quantitation is not possible without calibration. This is a present/not present determination only, no quantitative information can be provided.

12.3. For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of

analyses being conducted or by client request. Computer-generated library search routines must not use normalization that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will the experienced analyst assign a tentative identification. Guidelines for making tentative identification are:

12.3.1. Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) must be present in the sample spectrum.

12.3.2. The relative intensities of the major ions must agree within ± 20 %. (Example: For an ion with an abundance of 50 % in the standard spectrum, the corresponding sample ion abundance must be between 30 % and 70 %.)

12.3.3. Molecular ions present in the reference spectrum must be present in the sample spectrum.

12.3.4. Ions present in the sample spectrum, but not in the reference spectrum, must be reviewed for possible background contamination or presence of co-eluting compounds.

12.3.5. Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

12.3.6. Automatic background subtraction can severely distort spectra from samples with unresolved hydrocarbons.

**Note:** For water samples, the TIC searches begin with compounds eluting after the first surrogate (2-Fluorophenol). For solid samples, the TIC searches begin with compounds eluting after the Aldol Condensation Product. Any compounds eluting before these analytes are considered volatile analytes are reported in the volatile analysis. A possible exception to this general rule would be if an early eluting compound were the reason for a sample dilution.

12.3.7. If a client requests 10 TICs, the laboratory supplies a minimum of 10. Choosing the largest non-target peaks present in the sample chromatogram. For a request of 20 TICS, the laboratory would supply a minimum of 20, assuming that number of compounds was available.

12.4. Anyone evaluating data must be trained to handle isomers with identical mass spectra and close elution times. These include target compounds:

Dichlorobenzenes
Methylphenols
Trichlorophenols
Phenanthrene, anthracene
Fluoranthene, pyrene

Benzo(b) and (k)fluoranthene
Chrysene, benzo(a)anthracene

12.4.1. Extra precautions concerning these compounds include closely scrutinizing retention time vs. the calibration standard and also checking that all isomers have distinct retention times.

12.4.2. A second category of problem compounds would be the poor responders or compounds that chromatograph poorly (or exhibit erratic response). Included in this category are:

Benzoic acid
Chloroanilines
Nitroanilines
2,4-Dinitrophenol
4-Nitrophenol
Pentachlorophenol
3,3'-Dichlorobenzidine
Benzyl alcohol
4,6-Dinitro-2-methylphenol

12.4.3. Manually checking the integrations is appropriate for these compounds.

12.5. Calculations

12.5.1. Percent Relative Standard Deviation for Initial Calibration

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

$RF =$ Mean of RFs from intial caibration for a compound

$SD =$ Standard deviation of RFs from initial calibration for a compound,

$$= \sqrt{\sum_{i=1}^{N} \frac{\left(RFi - \overline{RF}\right)^2}{N-1}}$$

$RFi =$ RF for each of the calibration levels

$N =$ Number of RF values

12.5.2. Continuing calibration percent drift

$$\%Drift = \frac{C_{actual} - C_{found}}{C_{actual}} \times 100\%$$

$C_{actual} =$ Known concentration in standard

$C_{found} =$ Measured concentration using selected quantitation method

12.5.3. Concentration in the extract

12.5.3.1. The concentration of each identified analyte and surrogate in the extract is calculated from the linear or quadratic curve fitted to the initial calibration points, or from the average RF of the initial calibration.

12.5.4. Average Response Factor

12.5.4.1. If the average of all the %RSDs of the response factors in the initial calibration is $\leq$ 15%, the average response factor from the initial calibration may be used for quantitation.

$$C_{ex} = \frac{R_x C_{is}}{R_{is} \overline{RF}}$$

12.5.5. Linear fit

$$X_s = \frac{\left(\frac{A_s \times C_{is}}{A_{is}}\right) - b}{a} \times C_{is}$$

Where: $X_s$ = Concentration in extract, µg/mL
$A_s$ = Response for analyte
$A_{is}$ = Concentration of internal standard
$C_{is}$ = Intercept

12.5.6. Quadratic fit

$$C_{ex} = A + B\left(\frac{R_x C_{is}}{R_{is}}\right) + C\left(\frac{R_x C_{is}}{R_{is}}^2\right)$$

Where: C = Curvature

12.5.7. The concentration in the sample is then calculated.

12.5.7.1. Aqueous Calculation

$$\text{Concentration, } \mu\text{g / L} = \frac{C_{ex}V_t}{V_o}$$

Where: $V_t$ = Volume of total extract, µL, taking into account dilutions (i.e., a 1-to-10 dilution of a 1 mL extract will mean $V_t$ = 10,000 µL. If half the base/neutral extract and half the acid extract are combined, $V_t$=2,000)
$V_o$ = Volume of water extracted (mL)

12.5.7.2. Sediment/Soil, Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis

$$\text{Concentration, } \mu\text{g / kg} = \frac{C_{ex}V_t}{W_sD}$$

Where: $W_s$ = Weight of sample extracted or diluted in grams
D = (100 - % moisture in sample)/100, for a dry weight basis or one for a wet weight basis

12.5.8. MS/MSD percent recovery calculation.

$$\text{Matrix Spike Recovery} = \frac{S_{SR} - S_R}{S_A} \times 100\%$$

Where: $S_{SR}$ = Spike sample result
$S_R$ = Sample result
$S_A$ = Concentration equivalent of spike added

12.5.9. Relative % Difference calculation for the MS/MSD

$$RPD = \frac{MS_R - MSD_R}{1/2(MS_R + MSD_R)} \times 100$$

Where: RPD = Relative percent difference
$MS_R$ = Matrix spike result
$MSD_R$ = Matrix spike duplicate result

12.5.10. Relative response factor calculation

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where: $A_x$ = Area of the characteristic ion for the compound being measured

$A_{is}$ = Area of the characteristic ion for the specific internal standard

$C_x$ = Concentration of the compound being measured (µg/L)

$C_{is}$ = Concentration of the specific internal standard (µg/L)

12.6. Calculation of TICs: The calculation of TICs) is identical to the above calculations with the following exceptions:

$A_x$ = Area of the total ion chromatogram for the compound being measured

$A_{is}$ = Area of the total ion chromatogram for the nearest internal standard without interference

RF = 1

Results for TICs are not quantitative and are always reported as estimated "J."

12.7. Percent DDT breakdown

$$\%\ \text{DDT breakdown} = \frac{\text{DDEarea} + \text{DDDarea}}{\text{DDTarea} + \text{DDEarea} + \text{DDDarea}}$$

The total ion current areas are used for this calculation

12.8. Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002

## 13. METHOD PERFORMANCE

13.1. Method Detection Limit (MDL)

13.1.1. Each laboratory must generate a valid MDL for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in Policy CA-Q-S-006 and SOP NC-QA-021.

13.2. Lower Limit of Quantitation Verification – The lowest calibration standard analyzed establishes the LLOQ or Reporting Limit. The capability to reliably detect this concentration through the preparation, clean-up and analytical procedure is verified through the annual analysis of a standard at the LLOQ/RL. The LLOQ verification shall also be performed whenever significant changes are made to the preparation and/or analytical procedure.

13.2.1. The LLOQ verification standard shall be prepared at a concentration 0.5-2 times the LLOQ/RL, and be taken through all preparation and clean-up methods which samples would be.

13.2.2. The LLOQ verification standard for aqueous matrix shall be prepared using laboratory deionized water and for the solid matrix using clean Ottawa sand.

Other clean matrices may be used in addition, for project specific requirements.

13.2.3. The LLOQ shall be verified annually on each instrument used for client sample analysis.

13.2.4. Recovery of each analyte must meet the laboratory established LCS recovery limits + 20%. (For example, if the LCS recovery limits are 70-130%, the LLOQ verification must meet recovery limits of 50-150%.) Once sufficient points have been generated, LLOQ based statistical limits may be used in place of limits based on LCS recovery. NOTE: The lower recovery limit for the LLOQ can be no lower than 10%.

13.2.5. If the LLOQ cannot be verified, it will be necessary to raise the RL to a concentration level that can be carried through the preparation and cleanup steps to meet recovery limits.

13.3. Initial Demonstration of Capability (IDOC)

13.3.1. Each analyst must make an IDOC for each individual analyte. Demonstrations of capability (DOCs) for both soil and water matrices is required. This requires analysis of four LCSs containing all of the standard analytes for the method. For some tests, it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.3.1.1. Four aliquots of the LCS are analyzed using the same procedures used to analyze samples, including sample preparation.

13.3.1.2. Calculate the average recovery and standard deviation of the recoveries for each analyte of interest.

13.3.1.3. If any analyte does not meet the LCS acceptance criteria the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.4. Training Qualification

13.4.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13.4.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

## 14. POLLUTION PREVENTION

14.1. It is Eurofins TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

## 15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of Eurofins TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.

15.3. Waste Streams Produced by the Method

15.3.1. Vials containing sample extracts: These vials are placed in the vial waste located in the GC/MS laboratory.

## 16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update III October 1994, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique, Method 8270C

16.1.2. SW846, Test Methods for Evaluating Solid Waste, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), 8270D, Rev. 4, 2007

16.1.3. SW846, Test Methods for Evaluating Solid Waste, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), 8270D, Rev. 5, 2014

16.1.4. SW846, Test Methods for Evaluating Solid Waste, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), 8270E, Rev. 6, 2018

16.1.5. J. W. Eichelberger, L. E. Harris, and W. L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography/Mass Spectrometry," Analytical Chemistry, 47, 995 (1975)

16.1.6. Eurofins TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.7. Eurofins TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and Eurofins TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.8. Corporate Quality Management Plan (CQMP), current version

16.1.9. Revision History

| | | | | |
|---|---|---|---|---|
| Historical File: | | Revision 2.1: 01/25/99 | | Revision 0: 05/28/08 (NC-MS-018) |
| (formerly CORP-MS-0001NC) | | Revision 2.2: 03/27/00 | | Revision 1: 12/16/08 |
| | | Revision 2.3: 02/15/01 | | Revision 2: 10/26/10 |
| | | Revision 2.4: 05/29/01 | | Revision 3: 04/25/13 |
| | | Revision 2.5: 04/25/02 | | Revision 4: 07/24/14 |
| | | Revision 2.6: 08/15/02 | | Revision 5: 03/01/16 |
| | | Revision 2.7: 11/12/02 | | Revision 6: 10/31/17 |
| | | Revision 2.8: 01/23/03 | | Revision 7: 03/30/18 |
| | | Revision 2.9: 06/18/03 | | |
| | | Revision 2.10: 02/24/04 | | |
| | | Revision 2.11: 02/03/06 | | |
| | | Revision 2.12: 03/01/07 | | |

16.2. Associated SOPs and policies, current version

16.2.1. Continuous Liquid/Liquid Extraction of Organic Compounds from Waters Based on Method SW-846 3520C and 600 Series, NC-OP-037

16.2.2. Separatory Funnel Extraction of Organic Compounds from Waters Based on Method SW-846 3510C and 600 Series, NC-OP-038

16.2.3. Sonication Extraction of Organic Compounds from Soils Based on Method SW-846 3550C, NC-OP-039

16.2.4. Soxhlet (Traditional) Extraction of Organic Compounds from Soils Based on Method SW-846 3540C, NC-OP-040

16.2.5. Microextraction of Organic Compounds from Waters Based on Method 3511, NC-OP-042

16.2.6. Waste Dilution, NC-OP-043

16.2.7. QA Policy, QA-003

16.2.8. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.9. Detection and Quantitation Limits, CA-Q-S-006

16.2.10. Standard and Reagents, NC-QA-017

16.2.11. Acceptable Manual Integration Practices, CA-Q-S-002

16.2.12. Calibration Curves (General), CA-Q-S-005

16.2.13. Section of Calibration Points, CA-T-P-002

## 17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. A retention time window of 0.2 minutes is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method.

17.1.2. The quantitation and qualifier ions from compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.

17.1.3. Method 8270E only requires the DFTPP tune standard to be analyzed once prior to an ICAL. There is no requirement for a daily DFTPP tune prior to sample and QC analysis. The laboratory will continue with a daily DFTPP tune following the tune criteria listed in Table 2and the tune evaluation will be the tighter criteria of methods 8270C or 8270D.

17.2. Tables and Appendices

| TABLE 1: Suggested Instrument Conditions | |
|---|---|
| Mass Range | 35-500 amu |
| Scan Time | ≤1 second/scan |
| Initial Column Temperature/Hold Time | 60°C for 1 minutes, 50°C for 1 minute for LVI |
| Column Temperature Program | 60 - 320°C at 35°C/min for 3 min<br>50 - 320°C at 35°C/min for 3 min for LVI |
| Final Column Temperature/Hold Time | 320°C (until at least one minute after benzo(g,h,i)perylene has eluted) |
| Injector Temperature | 250 - 300°C |
| Transfer Line Temperature | 250 - 300°C |
| Source Temperature | According to manufacturer's Specifications |
| Injector | Grob-type, split / splitless |
| Sample Volume | 0.5 µl, or 5.0 ul for LVI |
| Carrier Gas | Helium at 30 cm/sec |

**TABLE 2: DFTPP Key Ions and Ion Abundance Criteria**

| Mass | Ion Abundance Criteria |
|---|---|
| 51 | 30 – 80% of mass 198 |
| 68 | <2% of mass 69 |
| 69 | Present |
| 70 | <2% of mass 69 |
| 127 | 25 - 75% 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 | > 0.75% of mass 198 |
| 441 | Present, but less than mass 443 |
| 442 | 40 - 110% of mass 198 |
| 443 | 15 - 24% of mass 442 |

**TABLE 3a: Analytes (List 1) in Approximate Retention Time Order and Characteristic Ions**

| Analyte | Primary | Secondary | Tertiary |
|---|---|---|---|
| N-nitrosodimethylamine | 74 | 42 | |
| Pyridine | 79 | 52 | |
| **2-Fluorophenol (Surrogate Standard)** | 112 | 64 | 63 |
| **Phenol-$d_5$ (Surrogate Standard)** | 99 | 42 | 71 |
| Benzaldehyde | 77 | 105 | 106 |
| Aniline | 93 | 66 | |
| Phenol | 94 | 65 | 66 |
| Bis(2-chloroethyl)ether | 93 | 63 | 95 |
| 2-Chlorophenol | 128 | 64 | 130 |
| 1,3-Dichlorobenzene | 146 | 148 | 113 |
| **1,4-Dichlorobenzene-$d_4$ (Internal Standard)** | 152 | 150 | 115 |
| 1,4-Dichlorobenzene | 146 | 148 | 113 |
| Benzyl Alcohol | 108 | 79 | 77 |
| 1,2-Dichlorobenzene | 146 | 148 | 113 |
| 2-Methylphenol | 108 | 107 | 79 |
| 2,2'-oxybis(1-chloropropane)[1] | 45 | 77 | 79 |
| Indene | 115 | 116 | 89 |
| 3&4-Methylphenol | 108 | 107 | 79 |
| N-Nitroso-di-n-propylamine | 70 | 42 | 101,130 |
| Hexachloroethane | 117 | 201 | 199 |
| **Nitrobenzene-$d_5$ (Surrogate Standard)** | 82 | 128 | 54 |
| Nitrobenzene | 77 | 123 | 65 |
| Isophorone | 82 | 95 | 138 |
| 2-Nitrophenol | 139 | 65 | 109 |
| 2,4-Dimethylphenol | 107 | 121 | 122 |
| Benzoic Acid | 122 | 105 | 77 |
| Bis(2-chloroethoxy)methane | 93 | 95 | 123 |
| 2,4-Dichlorophenol | 162 | 164 | 98 |
| 1,2,4-Trichlorobenzene | 180 | 182 | 145 |
| **Naphthalene-$d_8$ (Internal Standard)** | 136 | 68 | 54 |
| Naphthalene | 128 | 129 | 127 |
| 4-Chloroaniline | 127 | 129 | 65 |
| 2,6-Dichlorophenol | 162 | 164 | 63 |
| Hexachlorobutadiene | 225 | 223 | 227 |
| Caprolactam | 113 | 55 | 56 |
| 4-Chloro-3-methylphenol | 107 | 144 | 142 |
| 1-Methylnaphthalene | 142 | 141 | 115 |
| 2-Methylnaphthalene | 142 | 141 | 115 |
| Hexachlorocyclopentadiene | 237 | 235 | 272 |
| Acetophenone | 105 | | |
| 2,4,6-Trichlorophenol | 196 | 198 | 200 |
| 2,4,5-Trichlorophenol | 196 | 198 | 200 |
| 1,1'-Biphenyl | 154 | 153 | 76 |
| **2-Fluorobiphenyl (Surrogate Standard)** | 172 | 171 | 170 |
| 2-Chloronaphthalene | 162 | 164 | 127 |
| 2-Nitroaniline | 65 | 92 | 138 |
| Dimethylphthalate | 163 | 194 | 164 |
| Acenaphthylene | 152 | 151 | 153 |
| 2,6-Dinitrotoluene | 165 | 63 | 89 |
| **Acenaphthene-$d_{10}$ (Internal Standard)** | 164 | 162 | 160 |
| 3-Nitroaniline | 138 | 108 | 92 |
| Acenaphthene | 153 | 152 | 154 |

| | | | |
|---|---|---|---|
| 2,4-Dinitrophenol | 184 | 63 | 154 |
| Dibenzofuran | 168 | 139 | 84 |
| 4-Nitrophenol | 109 | 139 | 65 |
| 2,4-Dinitrotoluene | 165 | 63 | 89 |
| Diethylphthalate | 149 | 177 | 150 |
| Fluorene | 166 | 165 | 167 |
| 4-Chlorophenylphenylether | 204 | 206 | 141 |
| 4-Nitroaniline | 138 | 92 | 108 |
| 4,6-Dinitro-2-methylphenol | 198 | 182 | 77 |
| N-Nitrosodiphenylamine | 169 | 168 | 167 |
| 1,2,4,5-Tetrachlorobenzene | 216 | | |
| **2,4,6-Tribromophenol (Surrogate Standard)** | 330 | 332 | 141 |
| Azobenzene | 77 | 182 | 105 |
| 4-Bromophenylphenylether | 248 | 250 | 141 |
| Hexachlorobenzene | 284 | 142 | 249 |
| Atrazine | 200 | 173 | 215 |
| Pentachlorophenol | 266 | 264 | 268 |
| **Phenanthrene-$d_{10}$ (Internal Standard)** | 188 | 94 | 80 |
| Phenanthrene | 178 | 179 | 176 |
| Anthracene | 178 | 179 | 176 |
| 1,3-Dinitrobenzene | 168 | | |
| Carbazole | 167 | 166 | 139 |
| Di-n-butylphthalate | 149 | 150 | 104 |
| 2,3,4,6-Tetrachlorophenol | 232 | | |
| Fluoranthene | 202 | 101 | 100 |
| Benzidine | 184 | 92 | 185 |
| Pyrene | 202 | 101 | 100 |
| **Terphenyl-$d_{14}$ (Surrogate Standard)** | 244 | 122 | 212 |
| Butylbenzylphthalate | 149 | 91 | 206 |
| Benzo(a)Anthracene | 228 | 229 | 226 |
| **Chrysene-$d_{12}$ (Internal Standard)** | 240 | 120 | 236 |
| 3,3'-Dichlorobenzidine | 252 | 254 | 126 |
| Chrysene | 228 | 226 | 229 |
| Bis(2-ethylhexyl)phthalate | 149 | 167 | 279 |
| Di-n-octylphthalate | 149 | 167 | 43 |
| Benzo(b)fluoranthene | 252 | 253 | 125 |
| Benzo(k)fluoranthene | 252 | 253 | 125 |
| Benzo(a)pyrene | 252 | 253 | 125 |
| **Perylene-$d_{12}$ (Internal Standard)** | 264 | 260 | 265 |
| Indeno(1,2,3-cd)pyrene | 276 | 138 | 277 |
| Dibenz(a,h)anthracene | 278 | 139 | 279 |
| Benzo(g,h,i)perylene | 276 | 138 | 277 |

| Table 3b: Analytes (List 2) in Approximate Retention Time Order and Characteristic Ions | | | |
|---|---|---|---|
| 2-Picoline | 93 | 66 | 92 |
| N-Nitrosomethylethylamine | 88 | 42 | 43 |
| Acrylamide | 71 | 44 | 55 |
| Methyl methanesulfonate | 80 | 79 | 65 |
| N-Nitrosodiethylamine | 102 | 44 | 57 |
| Ethyl methanesulfonate | 79 | 109 | 97 |
| Pentachloroethane | 117 | 119 | 167 |
| Acetophenone | 105 | 77 | 120 |
| 1-Chloronaphthalene | 162 | 127 | 164 |
| N-Nitrosopyrrolidine | 100 | 41 | 42 |
| N-Nitrosomorpholine | 116 | 56 | 86 |
| o-Toluidine | 106 | 107 | |
| N-Nitrosopiperidine | 114 | 42 | 55 |
| o,o,o-Triethyl-Phosphorothioate | 198 | 121 | 93 |
| a,a-Dimethyl-phenethylamine | 58 | 91 | |
| Hexachloropropene | 213 | 215 | 211 |
| p-Phenylenediamine | 108 | 80 | |
| n-Nitrosodi-n-butylamine | 84 | 57 | 41 |
| Safrole | 162 | 104 | 77 |
| Isosafrole 1 | 162 | 104 | 131 |
| Isosafrole 2 | 162 | 104 | 131 |
| 1,4-Dinitrobenzene | 168 | 75 | 122 |
| 1,4-Naphthoquinone | 158 | 104 | 102 |
| Pentachlorobenzene | 250 | 248 | 252 |
| 1-Naphthylamine | 143 | 115 | |
| 2,3,5,6-Tetrachlorophenol | 232 | 230 | 131 |
| 2-Naphthylamine | 143 | 115 | |
| 5-Nitro-o-toluidine | 152 | 77 | 106 |
| Thionazin | 97 | 96 | 143 |
| 1,3,5-Trinitrobenzene | 213 | 75 | 120 |
| Sulfotepp | 97 | 322 | 202 |
| Phorate | 75 | 97 | 121 |
| Phenacetin | 108 | 179 | 109 |
| Diallate | 86 | 234 | |
| Dimethoate | 87 | 93 | 125 |
| 4-Aminobiphenyl | 169 | | |
| Pentachloronitrobenzene | 237 | 142 | 214 |
| Pronamide | 173 | 175 | 255 |
| Disulfoton | 88 | 97 | 89 |
| 2-secbutyl-4,6-dinitrophenol (Dinoseb) | 211 | 163 | 147 |
| Methyl parathion | 109 | 125 | 263 |
| Ethyl parathion | 97 | 109 | 291 |
| 4-Nitroquinoline-1-oxide | 190 | 128 | 160 |
| Famphur | 218 | 125 | 93 |
| Methapyrilene | 97 | 58 | |
| Aramite 1 | 185 | 319 | |
| Aramite 2 | 185 | 319 | |
| p-(Dimethylamino)azobenzene | 120 | 225 | 77 |
| p-Chlorobenzilate | 251 | 139 | 253 |
| 3,3'-Dimethylbenzidine | 212 | 106 | |
| 2-Acetylaminofluorene | 181 | 180 | 223 |
| Dibenz(a,h)acridine | 279 | 280 | |
| 7,12-Dimethylbenz(a)anthracene | 256 | 241 | 120 |
| 3-Methylcholanthrene | 268 | 252 | 253 |

| Table 4: Method 8270C LCS Control Compounds | |
|---|---|
| **LCS Compounds** | **Spiking Level, Concentration Added = 20 ug/L** |
| 1,1'-Biphenyl | 20 |
| 1,2,4,5-Tetrachlorobenzene | 20 |
| 1,2,4-Trichlorobenzene | 20 |
| 1,2-Dichlorobenzene | 20 |
| 1,3-Dichlorobenzene | 20 |
| 1,3-Dinitrobenzene | 20 |
| 1,4-Dichlorobenzene | 20 |
| 1,4-Dioxane | 20 |
| 1-Methylnaphthalene | 20 |
| 2,2'-oxybis[1-chloropropane] | 20 |
| 2,3,4,6-Tetrachlorophenol | 20 |
| 2,4,5-Trichlorophenol | 20 |
| 2,4,6-Trichlorophenol | 20 |
| 2,4-Dichlorophenol | 20 |
| 2,4-Dimethylphenol | 20 |
| 2,4-Dinitrophenol | 40 |
| 2,4-Dinitrotoluene | 20 |
| 2,6-Dichlorophenol | 20 |
| 2,6-Dinitrotoluene | 20 |
| 2-Chloronaphthalene | 20 |
| 2-Chlorophenol | 20 |
| 2-Methylnaphthalene | 20 |
| 2-Methylphenol | 20 |
| 2-Nitroaniline | 20 |
| 2-Nitrophenol | 20 |
| 3&4-Methylphenol | 20 |
| 3,3'-Dichlorobenzidine | 40 |
| 3-Nitroaniline | 20 |
| 4,6-Dinitro-2-methylphenol | 40 |
| 4-Bromophenyl phenyl ether | 20 |
| 4-Chloro-3-methylphenol | 20 |
| 4-Chloroaniline | 20 |
| 4-Chlorophenyl phenyl ether | 20 |
| 4-Nitroaniline | 20 |
| 4-Nitrophenol | 40 |
| Acenaphthene | 20 |
| Acenaphthylene | 20 |
| Acetophenone | 20 |
| Aniline | 20 |
| Anthracene | 20 |
| Atrazine | 40 |
| Azobenzene | 20 |
| Benzaldehyde | 40 |
| Benzidine | 40 |
| Benzoic acid | 40 |
| Benzo[a]anthracene | 20 |
| Benzo[a]pyrene | 20 |
| Benzo[b]fluoranthene | 20 |
| Benzo[g,h,i]perylene | 20 |
| Benzo[k]fluoranthene | 20 |

| Table 4: Method 8270C LCS Control Compounds | |
|---|---|
| **LCS Compounds** | **Spiking Level, Concentration Added = 20 ug/L** |
| Benzyl alcohol | 20 |
| Bis(2-chloroethoxy)methane | 20 |
| Bis(2-chloroethyl)ether | 20 |
| Bis(2-ethylhexyl) phthalate | 20 |
| Butyl benzyl phthalate | 20 |
| Caprolactam | 40 |
| Carbazole | 20 |
| Chrysene | 20 |
| Dibenz(a,h)anthracene | 20 |
| Dibenzofuran | 20 |
| Diethyl phthalate | 20 |
| Dimethyl phthalate | 20 |
| Di-n-butyl phthalate | 20 |
| Di-n-octyl phthalate | 20 |
| Fluoranthene | 20 |
| Fluorene | 20 |
| Hexachlorobenzene | 20 |
| Hexachlorobutadiene | 20 |
| Hexachlorocyclopentadiene | 20 |
| Hexachloroethane | 20 |
| Hexadecane | 20 |
| Indene | 40 |
| Indeno[1,2,3-cd]pyrene | 20 |
| Isophorone | 20 |
| Naphthalene | 20 |
| n-Decane | 20 |
| Nitrobenzene | 20 |
| N-Nitrosodimethylamine | 20 |
| N-Nitrosodi-n-propylamine | 20 |
| N-nitrosodiphenylamine | 40 |
| n-Octadecane | 20 |
| Pentachlorophenol | 40 |
| Phenanthrene | 20 |
| Phenol | 20 |
| Pyrene | 20 |
| Pyridine | 40 |

***Spike concentrations are subject to change without notice.***

| TABLE 5: TCLP LCS Compounds | |
|---|---|
| **LCS Compounds** | **Spiking Level, mg/L in extract** |
| 1,4-Dichlorobenzene | 0.08 |
| 2,4-Dinitrotoluene | 0.08 |
| Hexachlorobenzene | 0.08 |
| Hexachlorobutadiene | 0.08 |
| Hexachloroethane | 0.08 |
| 2-Methylphenol | 0.08 |
| 3-Methylphenol | 0.08 |
| 4-Methylphenol | 0.08 |
| Nitrobenzene | 0.08 |
| Pentachlorophenol | 0.08 |
| Pyridine | 0.08 |
| 2,4,5-Trichlorophenol | 0.08 |
| 2,4,6-Trichlorophenol | 0.08 |

***Spike concentrations are subject to change without notice.***

| TABLE 6: Method 8270C Surrogate Compounds | |
|---|---|
| **Surrogate Compounds** | **Spiking Level, Conc. Added = 20 ug/L / 30 ug/L** |
| Nitrobenzene-$d_5$ | 20 |
| 2-Fluorobiphenyl | 20 |
| Terphenyl-$d_{14}$ | 20 |
| Phenol-$d_5$ | 30 |
| 2-Fluorophenol | 30 |
| 2,4,6-Tribromophenol | 30 |

***Spike concentrations are subject to change without notice.***

**Table 7: Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation**

| 1,4-Dichlorobenzene-$d_4$ | Naphthalene-$d_8$ | Acenaphthene-$d_{10}$ |
|---|---|---|
| 1,4-Dioxane | Nitrobenzene | Hexachlorocyclopentadiene |
| N-Nitrosodimethylamine | N-Nitrosopiperidine | Isosafrole |
| Pyridine | Isophorone | 1,2,4,5-Tetrachlorobenzene |
| 2-Picoline | 2-Nitrophenol | 2,4,5-Trichlorophenol |
| N-Nitrosomethylethylamine | 2,4-Dimethyphenol | 2,4,6-Trichlorophenol |
| Acrylamide | Benzoic Acid | 1,1'-Biphenyl |
| Methyl methanesulfonate | o,o',o''-Triethylphosphorothioate | 2-Chloronaphthalene |
| N-Nitrosodiethylamine | Bis(2-chloroethoxy)methane | 1-Chloronaphthalene |
| Ethyl methanesulfonate | alpha,alpha-Dimethyl phenethylamine | 2-Nitroaniline |
| Benzaldehyde | 2,4-Dichlorophenol | 1,4-Naphthoquinone |
| Phenol | 1,2,4-Trichlorobenzene | 1,4-Dinitrobenzene |
| Aniline | Naphthalene | Dimethyl phthalate |
| Bis(2-chloroethyl)ether | 4-Chloroaniline | 1,3-Dinitrobenzene |
| Pentachloroethane | 2,6-Dichlorophenol | 2,6-Dinitrotoluene |
| 2-Chlorophenol | Hexachloropropene | Acenaphthylene |
| n-Decane | Hexachlorobutadiene | 3-Nitroaniline |
| 1,3-Dichlorobenzene | Quinoline | 2,4-Dinitrophenol |
| 1,4-Dichlorobenzene | N-Nitrosodi-n-butylamine | Acenaphthene |
| Benzyl alcohol | Caprolactam | 4-Nitrophenol |
| 1,2-Dichlorobenzene | p-Phenylene diamine | 2,4-Dinitrotoluene |
| 2-Methylphenol | 4-Chloro-3-methylphenol | Pentachlorobenzene |
| 2,2'-oxybis[1-chloropropane] | Satrole, Total | Dibenzofuran |
| Indene | 1-Methylnaphthalene | 1-Naphthylamine |
| N-Nitrosopyrrolidine | 2-Methylnaphthalene | 2,3,5,6-tetrachlorophenol |
| 3 & 4 Methylphenol | Nitrobenzene-d5 | 2,3,4,6-Tetrachlorophenol |
| N-Nitrosodi-n-propylamine | | 2-Naphthylamine |
| N-Nitrosomorpholine | | Diethyl phthalate |
| Acetophenone | | Hexadecane |
| 2-Toluidine | | Thionazin |
| Hexachloroethane | | 4-Chlorophenyl phenyl ether |
| 2-Fluorophenol | | N-Nitro-o-toluidine |
| Phenol-d5 | | 4-Nitroaniline |
| | | Fluorene |
| | | 2-Fluorobiphenyl (Surr) |
| | | Hexachlorocyclopentadiene |
| | | 2,4,6-Tribromophenol |

| Phenanthrene-$d_{10}$ | Chrysene-$d_{12}$ | Perylene-$d_{12}$ |
|---|---|---|
| 4,6-Dinitro-2-methylphenol | Benzidine | Di-n-octyl phthalate |
| Diphenylamine | Pyrene | 7,12-Dimethylbenz(a)anthracene |
| N-Nitrosodiphenylamine | Aramite, Total | Benzo[b]fluoranthene |
| Azobenzene | p-Dimethylamino azobenzene | Benzo[k]fluoranthene |
| Sulfotepp | Chlorobenzilate | Benzo[a]pyrene |
| 1,3,5-Trinitrobenzene | Famphur | 3-Methylcholanthrene |
| Phenacetin | Butyl benzyl phthalate | Dibenz[a,h]acridine |
| Diallate | 3,3'-Dimethylbenzidine | Indeno[1,2,3-cd]pyrene |
| Phorate | 2-Acetylaminofluorene | Dibenz(a,h)anthracene |

| Phenanthrene-$d_{10}$ | Chrysene-$d_{12}$ | Perylene-$d_{12}$ |
|---|---|---|
| 4-Bromophenyl phenyl ether | 4,4'-Methylene bis(2-chloroaniline) | Benzo[g,h,i]perylene |
| Dimethoate | 3,3'-Dichlorobenzidine | |
| Hexachlorobenzene | Bis(2-ethylhexyl) phthalate | |
| Atrazine | Benzo[a]anthracene | |
| 4-Aminobiphenyl | Chrysene | |
| Pronamide | 6-Methylchrysene | |
| Pentachlorophenol | Terphenyl-d14 | |
| n-Octadecane | | |
| Pentachloronitrobenzene | | |
| Disulfoton | | |
| Dinoseb | | |
| Phenanthrene | | |
| Anthracene | | |
| Carbazole | | |
| Methyl parathion | | |
| Di-n-butyl phthalate | | |
| Ethyl Parathion | | |
| 4-Nitroquinoline-1-oxide | | |
| Methapyrilene | | |
| Isodrin | | |
| Fluoranthene | | |
| 4,6-Dinitro-2-methylphenol | | |

**Table 8: Recommended Minimum Response Factor Criteria for Initial and Continuing Calibration Verification**

| Semivolatile Compounds | Minimum Response Factor (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 |
| Actophenone | 0.010 |
| 3&4-Methylphenol | 0.600 |
| N-Nitros-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-Chloroanaline | 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 |

| Table 8: Recommended Minimum Response Factor Criteria for Initial and Continuing Calibration Verification | |
|---|---|
| **Semivolatile Compounds** | **Minimum Response Factor (RF)** |
| 2,4,5-Trichlorophenol | 0.200 |
| 1,1'-Biphenyl | 0.010 |
| 2-Chloronaphthalene | 0.800 |
| 2-Nitroanaline | 0.010 |
| Dimethyl phthalate | 0.010 |
| 2,6-Dinitrotoluene | 0.200 |
| Acenaphthylene | 0.900 |
| 3-Nitroaniline | 0.010 |
| Acenaphthene | 0.900 |
| 2,4-Dinitrophenol | 0.010 |
| 4-Nitrophenol | 0.010 |
| Dibenzofuran | 0.800 |
| 2,4-Dinitrotoluene | 0.200 |
| Dithyl 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 |
| Phananthrene | 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-Tetrachlorophenol | 0.010 |

# Title: TOTAL SOLIDS, PERCENT MOISTURE, AND TOTAL SETTLEABLE SOLIDS

**[Method: Standard Method 2540F and ASTM D2216-80]**

**Approvals (Signature/Date):**

| | | | |
|---|---|---|---|
| Technology Specialist | 05/21/20 Date | Health & Safety Coordinator | 05/26/20 Date |
| Quality Assurance Manager | 05/22/20 Date | Technical Director | 05/28/20 Date |

**This SOP was previously identified as SOP No. NC-WC-0004, Rev 6, dated 04/27/18**



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## 1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Total Solids; Percent Moisture; and Settleable Solids in wastewaters, sludges, and solids. It is based on Standard Method 2540F and ASTM D2216-80.

1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

## 2. SUMMARY OF METHOD

2.1. Total Solids/Percent Moisture: A homogenous sample is dried at 104 °C ± 2°C, and the difference in the weight loss of the sample represents the Total Solids.

2.2. Settleable Solids: Settleable matter is measured volumetrically with an Imhoff cone.

## 3. DEFINITIONS

3.1. Refer to the glossary in the Eurofins TestAmerica Canton Quality Assurance Manual (QAM), current version.

## 4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Samples high in concentrations of minerals must be dried longer, desiccated, and weighed quickly to prevent any excess weight added due to absorption of water from the atmosphere.

4.3. Non-homogeneous samples may give erratic results.

## 5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Oily samples or those that contain volatile chemicals may ignite during this procedure. In the case of a fire, the oven should be turned off and allowed to cool before the sample can be removed and put under a hood.

5.3. There are no materials used in this method that have a significant or serious hazard rating. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the Safety Data Sheet (SDS) for each material before using it for the first time or when there are major changes to the SDS.

5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable**. Therefore, unless they are known to be non-hazardous, all samples must be opened, transferred, and prepared in a fume hood or under other means of mechanical ventilation. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a Eurofins TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and to a Laboratory Supervisor.

## 6. EQUIPMENT AND SUPPLIES

6.1. Drying Oven

6.2. Desiccators

6.3. Evaporating dishes: various

6.4. Tongue blades

6.5. Sample containers

6.6. Top loading balance: capable of accurately weighing ± 0.01 g

6.7. Analytical balance: capable of accurately weighing ±0.0001 g

6.8. Beakers: glass, various

6.9. Volumetric flasks: various

6.10. Imhoff cones: Graduated to 20 mL, marked at 900 mL, 1000 mL, and at 1100 mL

6.11. Labels

6.12. Graduated Cylinder, 1000 mL, 2000 mL, 10mL, Class A

## 7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Reagent water

7.1.2. Ottawa sand: cleaned and dried

## 8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored in plastic or glass containers at 4°C ± 2°C.

8.3. The holding time is 48 hours for settleable solids.

8.4. There is no recommended holding time for non-water samples.

## 9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, sample duplicate) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank (MB)

9.2.1. One MB must be processed with each preparation batch of Settleable Solids samples. The MB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The MB should not contain any analyte of interest at or above the reporting limit.

**Note:** There is no MB applicable for Total Solid or Percent Moisture.

9.2.2. Corrective Action for MBs

9.2.2.1. If the analyte level in the MB exceeds the reporting limit for the analytes of interest in the sample, all associated samples are re-prepared and reanalyzed. If this is not possible due to limited sample quantity or

other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.2.2. If there is no analyte greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. For the Settleable Solids method, an LCS sample is required.

9.3.1.1 One mL of sand will be added to a 10 mL graduated cylinder. 1000 mL of water is added to a liter container. The sand mixture is added to the liter container and mixed. The resulting mixture is transferred to an Imhoff cone and allowed to settle for one hour. Control limits will be 90-110%.

9.4. Duplicates (DU)

9.4.1. A DU is a second aliquot of an environmental sample, taken from the same sample container when possible, that is processed with the first aliquot of that sample. That is, DUs are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

9.4.2. DUs are performed at a frequency of 10% and must meet laboratory-specific limits for precision.

9.4.3. DUs are not applicable for Settleable Solids.

9.5. Control Limits

9.5.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMs.

9.6. Nonconformance and Corrective Action

9.6.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action.

## 10. CALIBRATION AND STANDARDIZATION

10.1. Imhoff Cone Calibration Procedure

10.1.1. The Imhoff Cones are checked on an annual basis. Each Imhoff Cone is checked against a Class A graduated cylinder at the following volumes: 1 mL, 20 mL, and 1000 mL. Verification is visual.

## 11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.3. Total Solids (TS) and Percent Moisture

11.3.1. For solid and sludge samples, label and weigh an evaporating dish on an analytical balance that measures to ±_0.0001 g. Record the weight in the LIMS. For solid samples (TS and % Moisture), a universal tare weight is recorded in the LIMS. For solid samples, the Sample Receiving department will divide the soil sample into a pre-tared container with a label at the time of receipt. Weigh and record the wet weight in the LIMS.

11.3.2. DU for solid samples (TS and % Moisture), The Sample Receiving department will supply the sample duplicate at the time of receipt. If the sample duplicate is not supplied, split some sample off from another container into a new container with a label. Weigh and record the weight in the LIMS.

11.3.3. Place dishes with sample in the drying oven (103° - 105°C) until dry (minimum of 12 hours). Document the time samples were placed in the oven in the LIMS.

11.3.4. Remove the samples from the drying oven when they are dry. Document the time samples were removed from the oven in the LIMS.

11.3.5. Place the dishes in the desiccator for at least one hour. Weigh the sample and dish on the top loading balance. Record the weight in the LIMS.

11.4. Settleable Solids

11.4.1. An MB is prepared from one liter of reagent water. An MB must be analyzed with each batch of 20 or fewer samples to ensure Imhoff cones are clean and free of particulate contamination. An LCS sample must be analyzed as noted in Section 9.3.

11.4.2. Shake one liter of sample vigorously for ten seconds.

11.4.3. Pour the sample into an Imhoff cone, filling the cone to the one-liter mark.

**Note:** For samples containing volume less than 900 mL or greater than 1100 mL: After analysis is complete, pour the sample into a 1000 or a 2000 mL graduated cylinder to determine the exact sample volume. The exact sample volume must be entered into the LIMS, and RLs will be adjusted accordingly.

11.4.4. Allow the sample to settle for forty five minutes, gently agitate sample near the sides of the cone with a glass stir-rod. Then allow the sample to settle for another fifteen minutes.

11.4.5. Measure the volume of settleable solids by observing the location of the border between the settled matter and the supernatant liquid.

11.4.5.1. If pockets of liquid are trapped beneath large settled particles, estimate the volume of the pockets and subtract from the total measured volume.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.5.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Record all sample results and associated QC in the LIMS. Level I and Level II reviews are performed in the LIMS.

## 12. DATA ANALYSIS AND CALCULATIONS

12.1. Total Solids

$$\textit{Total Solids, \% (non-waters)} = \frac{(A - B) \times 100}{(C - B)}$$

Where: A = Final weight of dried sample and dish, g
B = Initial weight of dish, g
C = Initial weight of wet sample and dish,

12.2. Dry Weight

$$\textit{Dry Weight} = \frac{\textit{Sample Test Result x 100}}{\textit{(\%) Total Solid Results}} = \textit{Dry Weight}$$

12.3. Percent Moisture

$$\textit{\%Moisture} = 100 - \textit{\%TS (Section 12.1)}$$

## 13. METHOD PERFORMANCE

13.1. Each analyst must have initial demonstration of capability data on file for Settleable Solids. Initial Demonstrations of Capability (IDOCs) and Continuing Demonstrations of Capability (CDOCs) are filed and tracked in the analyst's technical training file.

13.2. Training Qualifications

13.2.1. The Group/Team Leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

## 14. POLLUTION PREVENTION

14.1. It is Eurofins TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

## 15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State, and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. Weighing containers and residue generated by solid sample analysis. This waste is collected in the laboratory in a designated container identified as "Solid Waste".

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of Eurofins TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

## 16. REFERENCES

16.1. References

16.1.1. Standard Methods for the Evaluation of Waters and Wastewaters, Method 2540F, Settleable Solids, current version

16.1.2. Annual Book of ASTM Standards, Volume 04.08, 1990

16.1.3. Corporate Quality Management Plan (CQMP), current version

16.1.4. Eurofins TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.5. Eurofins TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and Eurofins TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.6. Ohio Bureau of Underground Storage Tank Regulations (BUSTR) Technical Guidance Manual, April 2005

16.1.7. Revision History

| | | | | |
|---|---|---|---|---|
| Historical File: | | Revision 3.4: 12/22/09 | | |
| Revision 3.0: 08/04/00 | | Revision 3.5: 4/23/12 | | |
| Revision 3.1: 11/06/04 | | Revision 4: 05/08/14 | | |
| Revision 3.2: 02/02/06 | | Revision 5: 05/23/16 | | |
| Revision 3.3: 09/10/07 | | Revision 6: 04/27/18 | | |

**4/15/19: Changed logo and copyright information. No changes made to revision number or effective date.*

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4. Detection and Quantitation Limits, CA-Q-S-006

16.2.5. Standards and Reagents, NC-QA-017

## 17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. The reporting limit for Method SM2540F is 0.1 ml/L/hr. The reporting limit for Percent Moisture by ASTM D2216-80 is 0.1%.

17.1.2. For Settleable Solids: If sample volumes other than the volumes specified in this SOP are used, the RL will be adjusted accordingly.

# Title: CYANIDE AUTOMATED, PYRIDINE-BARBITURIC ACID METHOD

## [Method: SW846 Method 9012A, 9012B, EPA Method 335.4, and Standard Methods 4500-CN-E, 4500-CN-I, and 4500-CN-G]

**Approvals (Signature/Date):**

| | | | |
|---|---|---|---|
| Technology Specialist | Date: 10/28/20 | Health & Safety Coordinator | Date: 10/29/20 |
| Quality Assurance Officer | Date: 10/28/20 | Technical Director | Date: 10/29/20 |

**This SOP was previously identified as SOP No. NC-WC-031, Rev 15, dated 06/22/20.**



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## 1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Total, Amenable, and Weak Acid Dissociable Inorganic Cyanide in solids, liquids, and waters. It is based on SW846 Methods 9012A, 9012B, EPA Method 335.4, and Standard Methods 4500-CN-E, 4500-CN-I, and 4500-CN-G. The working linear range is 0.005 – 0.2 mg/L for waters and 0.25-10 mg/kg for solids.

1.2. Where requirements of this SOP are not met, including, but not limited to, Quality Control (QC) samples (Method Blank (MB) and Laboratory Control Sample (LCS)) associated to sample analytes, holding time, and preservation, the laboratory will narrate bias in the case narrative of the final report.

1.3. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

## 2. SUMMARY OF METHOD

2.1. The Cyanide, as HCN, is released by distilling/refluxing the sample with strong acid and then trapped in a sodium hydroxide solution.

2.2. The sodium hydroxide solution is analyzed colorimetrically on an autoanalyzer using the pyridine-barbituric acid method.

## 3. DEFINITIONS

3.1. Refer to the glossary in the Eurofins TestAmerica Canton Quality Assurance Manual (QAM), current version.

## 4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. All glassware is cleaned per SOP NC-QA-014. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Sulfides interfere, but can be eliminated by treating the sample with cadmium carbonate or bismuth nitrate prior to analysis.

## 5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

| Material | Hazards | Exposure Limit (1) | Signs and symptoms of exposure |
|---|---|---|---|
| Potassium Cyanide | Poison<br><br>Corrosive | 5 mg/m$^3$ TWA as CN | **This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.** Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heart beat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage. |
| Pyridine | Flammable<br><br>Irritant | 5 ppm-TWA | Inhalation causes severe irritation to the respiratory tract. Symptoms of overexposure include headache, dizziness, nausea, and shortness of breath. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. Absorption through the skin may occur, resulting in toxic effects similar to inhalation. May act as a photosensitizer. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage. |
| Sodium Hydroxide | Corrosive<br><br>Poison | 2 ppm,<br><br>5 mg/m$^3$<br><br>2 mg/m$^3$-Ceiling | This material will cause burns if comes into contact with the skin or eyes. Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness. |

| | | | |
|---|---|---|---|
| Potassium Phosphate | Flammable | None | Inhalation causes severe irritation to the respiratory tract. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. . |
| Sodium Phosphate | | None | Inhalation may cause respiratory tract irritation. Can produce delayed pulmonary edema. Causes mild skin and eye irritation. Ingestion may cause gastrointestinal irritation. |
| Hydrochloric Acid | Corrosive Poison | 5 ppm-Ceiling | Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. |
| Cadmium Carbonate | Probable carcinogen | 0.01 mg/ $m^3$ as Cd | Ingestion causes increased salivation, choking, vomiting, stomach pains and diarrhea. Inhalation may cause respiratory irritation, nausea and dyspnea. |
| Barbituric Acid | Irritant | Not established | Limited information. Inhalation may irritate respiratory tract. Causes skin and eye irritation. Must be treated as potential health hazard; do not ingest. |
| Potassium Hydroxide | Poison Corrosive Reactive | 2 mg/$m^3$ – Ceiling | Inhalation symptoms may include coughing, sneezing, damage to the nasal or respiratory tract. High concentrations can cause lung damage. Swallowing may cause severe burns of mouth, throat and stomach. Other symptoms may include vomiting, diarrhea. Severe scarring of tissue and death may result. Contact with skin can cause irritation or severe burns and scarring. Causes irritation of eyes with tearing, redness, swelling. Greater exposures cause severe burns with possible blindness. |
| Chloramine T Hydrate | Poison | | May be harmful by inhalation, ingestion, or skin absorption. This material is irritating to mucous membranes and upper respiratory tract. Avoid contact and inhalation. |
| Bismuth Nitrate | Irritant | None Listed | Causes eye irritation. Causes skin irritation. May cause irritation of the digestive tract. Ingestion of nitrate containing compounds can lead to methemoglobinemia. Dust is irritating to the respiratory tract. May cause methemoglobinemia, cyanosis (bluish discoloration of skin due to deficient oxygenation of the blood), convulsions, tachycardia, dyspnea (labored breathing), and death. May cause acute pulmonary edema, asphyxia, chemical pneumonitis, and upper airway obstruction caused by edema. |
| **Note:** Always add acid to water to prevent violent reactions. | | | |

1 – Exposure limit refers to the OSHA regulatory exposure limit.

5.3. Preparation of sodium hydroxide solutions produces considerable amounts of heat. Use plastic containers to mix this solution, if possible. If glass containers are used, they must be free of any cracks or irregularities.

5.4. The acidification of samples prior to extraction/preparation can result in the release of a highly toxic gas--hydrogen cyanide. Cyanide and cyanide salts such as Potassium cyanide and Sodium cyanide are extremely toxic. Addition of acid can generate hydrogen cyanide gas, which can be extremely dangerous. Inhalation of cyanide gas can cause irritation, dizziness, nausea, unconsciousness, and potentially death.

5.5. If samples are identified with cyanide concentrations equal to or greater than 200 mg/L, immediately notify the Department Manager and personnel responsible for hazardous waste shipping. Those samples must be identified as extremely hazardous for other chemists and must receive special attention during disposal.

5.6. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated must be removed and discarded. Other gloves must be cleaned.

5.7. Exposure to chemicals must be maintained **as low as reasonably achievable.** All samples with stickers that read “Caution/Use Hood!” **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a Eurofins TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and to a laboratory supervisor.

## 6. EQUIPMENT AND SUPPLIES

6.1. rAPID-T Discreet Analyzer or equivalent

6.2. rAPID-T software or equivalent

6.3. Stock standards are purchased as certified solutions. Standards are stored according to manufacturer’s instructions. All stock standards must be protected from light. Stock standard solutions must be replaced after one year, or according to manufacturer’s expiration date.

6.4. Cuvettes

6.5. 100 mL, 250 mL, 1000 mL volumetric flasks

6.6. Volumetric pipettes: various, ranging from 0.01 mL to 20 mL

6.7. Top loading balance: capable of accurately weighing ± 0.01g

6.8. Balance: Analytical, capable of accurately weighing 0.0001g

## 7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Glacial Acetic Acid ($C_2H_4O_2$): Reagent grade

7.1.2. Phosphate buffer: Add 136 g of potassium phosphate - monobasic ($KH_2PO_4$) and 2.8 g of sodium phosphate – dibasic anhydrous ($Na_2HPO_4$) to 800 mL of reagent water in a 1 liter volumetric flask. Mix, bring to volume with reagent water. This reagent may be purchased commercially.

7.1.3. Chloramine-T reagent: Add 1.0 g of chloramine-T to a 250 mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily. This reagent may be purchased commercially.

7.1.4. Pyridine reagent: Add 15.0 g of barbituric acid to a 1 liter volumetric flask. Add 75 mL of pyridine and 15 mL of concentrated hydrochloric acid (HCl) and mix. Bring to volume with reagent water and store at 4°C ± 2°C in an amber glass bottle. The maximum shelf life is six months or the vendor's expiration date, whichever is earlier

**Note:** The pyridine barbituric acid may be purchased commercially. Filter 50 ml of the pyridine barbituric acid, and bring up to 250 ml with DI water.

7.1.5. Sodium Hydroxide (NaOH): reagent grade

7.1.6. Bismuth Nitrate [BiNO3•5H2O]: Reagent Grade

7.1.7. Bismuth nitrate Solution: Dissolve 3 g of [BiNO3•5H2O] in 10 mLs DEIONIZED WATER , add 25 mLs glacial acetic acid while stirring. Once dissolved dilute to a 100 mL final volume with DI Water. Reagent is stable for 1 year.

7.1.8. 1.0 N Sodium hydroxide: Carefully add 40 g of NaOH to 800 mL reagent water. Dilute to 1 liter with reagent water.

7.1.9. 0.25 N sodium hydroxide: Add 250 mL of 1N NaOH to a 1 liter volumetric flask, and dilute to volume with reagent water.

**Note:** 0.25 N NaOH may be purchased instead.

7.2. Standards

7.2.1. Stock standards are purchased as certified solutions. Standards are stored according to manufacturer's instructions. All stock standards must be protected from light. Stock standard solutions must be replaced after one year, or according to manufacturer's expiration date.

7.2.2. PrimarySource Cyanide Stock Standard, 1000 mg/L: Add 2.51 g of potassium cyanide (KCN) and 2.0 g of potassium hydroxide (KOH) to a 1000 mL volumetric flask and dilute to volume with reagent water. Mix well and store in amber glass container. Stable for 1-3 months. Additional information can be found in SOP NC-QA-017.

**Note:** This stock standard may also be purchased.

**Note:** Prepared stock standard must be standardized prior to use. See Appendix I (SOP NC-WC-032)

7.2.3. Secondary Source Cyanide Standard, 1000 mg/L: Follow Section 7.2.1 using an alternate source of Potassium Cyanide (KCN).

**Note:** This stock standard may also be purchased.

**Note:** Prepared stock standard must be standardized prior to use. See Appendix I (SOP NC-WC-032).

7.2.4. Calibration Standards (Water and Solid Matrices)

7.2.4.1. Pipette the appropriate amount of cyanide standard into 100 mL volumetric and bring to volume with 0.25N NaOH. The low standard must be at, or below, the reporting limit. Prepare weekly.*

| Concentration CN- Calibration Standards | ML CN- | Final Volume |
|---|---|---|
| 10 mg/L | 1 mL of 1000 mg/L | 100 mL<br>Dilution from stock primary and secondary |
| 1.0 mg/L<br>(Secondary only) | 10 mL of 10 mg/L | 100 LCS/MS |
| 0.25mg/L<br>(Secondary only) | 5 mL of 10 mg/L | 200 mL ICV |
| 0.01 mg/L | 0.1 mL of 10 mg/L | 100 mL MRL check |
| * 0.5 mg/L | 5 mL of 10 mg/L | 100 mL Calibrant |

| Concentration CN- Calibration Standards | ML CN- | Final Volume |
|---|---|---|
| 0.25 mg/L | 2.5 mL of 10 mg/L | 100 mL CCV Solution |

*Denotes calibration standards

***Note:** Cyanide samples from West Virginia will be prepared and analyzed on the day that the standards are prepared.

## 8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Solid samples are not chemically preserved. Water samples are preserved with NaOH to a pH >12. All samples are stored at 4°C ± 2°C in plastic or glass containers.

8.2. The holding time for samples is 14 days from sampling to analysis.

## 9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples, excluding QC samples (Laboratory Control Sample (LCS), Method Blank (MB), Matrix Spike/Matrix Spike Duplicate (MS/ MSD)), which are processed similarly with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank (MB)

9.2.1. One MB must be processed with each preparation batch. The MB consists of reagent water or 0.25N NaOH and must contain all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated Cyanide concentrations or false positive data. The MB must not contain Cyanide at, or above, the reporting limit. For Ohio VAP Projects, the MB must not contain Cyanide above the reporting limit.

9.2.2. Corrective Action for MBs

9.2.2.1. If the level in the MB exceeds the reporting limit for Cyanide, all associated samples are re-prepared and re-analyzed. If this is not possible due to limited sample quantity, expired holding

times, or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.2.2. If there is no Cyanide result greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One LCS spiked with an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

**Note:** A purchased complex cyanide solution may be used instead as the midrange LCS for Total Cyanide analysis only.

9.3.2. Corrective Action for LCSs

9.3.2.1. If Cyanide recovery is outside established control limits, the system is out of control and corrective action must occur.

9.3.2.2. Corrective action will be re-preparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable.

9.3.2.3. The only exception is if the LCS recoveries are biased high and the associated sample is ND for Cyanide, there is insufficient sample for re-preparation, or expired holding times.. In this case, the batch is acceptable. **This must be addressed in the project narrative.**

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each analytical batch. A Matrix Spike (MS) is a field sample to which known concentrations of Cyanide have been added. A Matrix Spike Duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and MS. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates in place of, or in addition to, MS/MSD pairs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. Corrective action for MS/MSDs

9.4.2.1. If Cyanide recovery or RPD falls outside the acceptance range, the results should be evaluated to determine the cause.

9.4.2.2. If laboratory error is suspected, consultation with the PM and the client is necessary to determine the impact on data usability. Re-preparation and re-analysis may be necessary.

9.4.2.3. If matrix interference is suspected, the recovery of Cyanide must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted.

9.4.2.4. If the Cyanide concentration in the sample used to prepare the MS/MSD exceeds four times the spike level, the recovery data is automatically flagged with a “4” in TALS.

9.5. MRL Standard

9.5.1. The MRL Standard is a standard at the same concentration as the RL. It is run daily immediately after the calibration. The calibration curve cannot be accepted unless the MRL falls within ± 30% of the true value.

9.6. Additional information on QC samples can be found in QA Policy QA-003.

9.7. Method of Standard Additions (MSA)

9.7.1. The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences, such as samples, which contain sulfide.

9.8. QC Acceptance Criteria

9.8.1. Control limits are established by the laboratory as described in NC-QA-018.

**NOTE**: Control limits for LCS and MS/MSD for Method 335.4 are 90% to 110%.

9.8.2. Laboratory control limits are internally generated and updated periodically unless method specified. The latest version is easily accessible via the LIMs

9.9. Method Detection Limits (MDLs) and MDL Verifications

9.9.1. MDLs and MDL Verifications are established by the laboratory as described in SOP CA-Q-S-006.

9.9.2. MDLs are easily accessible via the LIMs

9.10. Nonconformance and Corrective Action

9.10.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

## 10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration

10.1.1 The instrument is calibrated daily using the 0.5 ppm standard, which is diluted by the instrument to the following concentrations: 0 (Blank), 0.002, 0.005, 0.010, 0.050, 0.100, 0.500. The calibration is verified by running a midrange ICV. The ICV is composed of the 0.25 ppm secondary standard. The ICV must not vary from the original curve by more than ± 10%, or recalibration is required. The correlation coefficient of the original curve must be ≥ 0.995, or recalibration is required. The curve must not be forced through the origin. An ICB sample is analyzed after the ICV. It cannot contain a Cyanide level above the reporting limit or recalibration is required.

**Note:** West Virginia requires the ICB to have no analytes of interest above the Method Detection Limit. Samples containing target analytes greater than the MDL will be flagged when the associated Initial Calibration Blank (ICB) is found to contain target analytes above the method detection limit.

**Note:** For samples that test positive for sulfides, the 0.5 ppm standard must be treated with bismuth nitrate prior to calibration. See section 11.3.2.1

10.2. Continuing Calibration

10.2.1. The run is checked every ten samples and at the end of the run using a midrange CCV to verify continued linearity. It cannot vary from the original curve by more than ± 10%, or re-analysis of all samples bracketed by the failing CCV is required. The exception is if the analytes detected in the bracketing CCV are biased high and the samples are non-detect for those analytes. Under the above circumstances result may be reported with proper narration. If CCVs continually fail to meet criteria, this would indicate a possible issue with the calibration standard or with the CCV standard solution, and re-preparation and re-analysis of the calibration curve and/or CCV solution is required. The CCV is composed of the 0.25 mg/L

primary standard.

10.2.2. System cleanliness is checked every ten samples and at the end of the run using a CCB. It cannot contain a Cyanide level above the reporting limit, or reanalysis of all bracketed samples is required. The exception is if the analytes detected in the bracketing CCB are non-detect in the associated samples. Under the above circumstances result may be reported. If CCBs continually fail to meet criteria, immediately stop the analysis and take corrective action. Corrective action can include, but is not limited to, the following: refreshing the CCB solution, recalibration, or instrument maintenance as deemed necessary. The CCB is 0.25N NaOH.

**Note:** West Virginia requires the CCB to have no analytes of interest above the Method Detection Limit. Samples containing target analytes greater than the MDL will be flagged when the associated Continuing Calibration Blank (CCB) is found to contain target analytes above the method detection limit.

10.3. High and Low Standard

10.3.1. The distillation technique is checked by distilling a high and low standard daily and comparing the values obtained to the standard curve. The method recommends that the HI/LO standards be compared to the curve with a ±10% agreement. Re-analysis must occur if the standards do not meet criteria. if the standards exhibits the same anomaly upon reanalysis, distill and re-analyze all samples and QC associated with the failing standards. The exceptions are as follows: (a) insufficient sample for re-distillation, or (b) expired holding times. Under the above circumstances results may be reported with proper narration.

10.4 Linear Calibration Range

10.4.1 The Linear Calibration Range (LCR) must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by $\pm$10%, linearity must be re-established. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

10.5 All supportive laboratory equipment is calibrated as specified in SOPs NC-QA-004 and NC-QA-015.

## 11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the

professional judgment of QA, Operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance Memo.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described. This is not applicable for OVAP.

11.3. Sample Preparation

11.3.1. See Cyanide Distillation SOP NC-WC-032.

11.3.1.1. The sample is distilled/refluxed under acidic conditions for 30 minutes. The released HCN is trapped in 2 mL of 0.25 N NaOH solution.

11.3.2. Sample Preparation Procedure

11.3.2.1 All Solid Samples: Test each sample for the presence of sulfides using lead acetate test paper. If sulfides are present (indicated by the lead acetate test paper turning a medium to dark brown in color) the method of standard additions is required.Treat each sample that test positive for sulfide by adding bismuth nitrate dropwise to the distillate. Repeat this operation until a drop of the treated distillate does not darken the lead acetate test paper. Filter the solution after addition of the bismuth nitrated is complete.

Note: All QC including the method blank (MB), laboratory control standard (LCS), CCVH, and CCVL must also be treated and placed in a separate batch with a curve that has been treated with the bismuth nitrate solution. Document this in the LIMS. See Section 11.5.1

Note: If Sulfide is present, and more than 48 hours have elapsed since sampling, the analyst must create an NCM notifying the client of the presence of Sulfide.

**Note**: Water samples must be tested prior to distillation. See Cyanide Distillation SOP NC-WC-032.

11.4. Sample Analysis

11.4.1. Recommended Instrument Conditions

11.4.1.1. See manufacturer's information for operation instructions.

11.4.1.2. Perform instrument startup.

11.4.1.3. Add reagents to the RapidT reagent tray.

11.4.1.4. Insert standards and samples into the autosampler segments.

11.4.2. Sample Analysis Procedure

11.4.2.1. See manufacturer's information for operating instructions.

11.4.2.2. Calibrate the instrument (see section 10.1.1). The correlation coefficient must be $>$ 0.995 to continue.

11.4.2.3. The ICV (from the secondary source) and the ICB are analyzed after the calibration and followed by an MRL check. CCVs (from the primary source) and CCBs are analyzed between every ten samples and at the end of the run.

11.4.2.4. Sample distillates higher than the highest calibration standard (0.5 mg/L) must be diluted with 0.25 N NaOH and re-analyzed.

11.4.2.5. Any samples analyzed after a high sample must be re-analyzed if carryover is suspected.

11.5. Dilutions

11.5.1. If the response for any sample exceeds the calibration range of the discrete analyzer, a dilution of the distillate is prepared and analyzed. The diluent used is 0.25 N NaOH Solution. An appropriate dilution must be in the upper half of the calibration range. Dilutions that result in a sample result that falls on the lower half of the calibration curve must be re-analyzed at a smaller dilution if matrix allows.

11.5.1.1. Any samples analyzed immediately after an off-scale sample must be re-analyzed if carryover is suspected.

11.6. Method of Standard Addition:

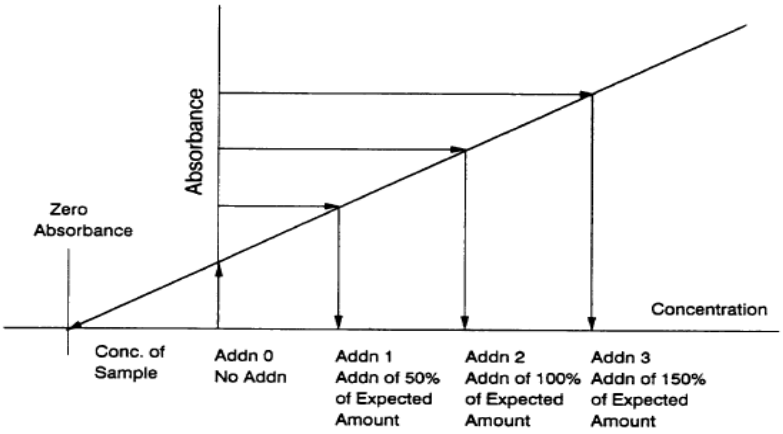
11.6.1. The standard addition technique involves the addition of known amounts of the target analyte to each of a series of replicate sample aliquots. The final concentrations of the sample replicates should span the calibration range of the method. The analytical responses versus the standard addition concentration for each of the replicates is plotted.

11.6.2. Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it

In order to determine the concentration of analyte in the sample, the analytical value of each solution is determined and a plot or linear regression performed. On the vertical axis the analytical value is plotted versus the concentrations of the standards on the horizontal axis. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbency, the analyte concentration in the original unspiked sample is equal to the inverse of the x-intercept.

FIGURE 1

STANDARD ADDITION PLOT




For the method of standard additions to be correctly applied, the following limitations must be taken into consideration:

1.) The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should reflect the aqueous standard curve.

2.) The correlation coefficient of the MSA curve must be 0.995 or greater. If the criteria is not met, the corrected ABS of the un-spiked sample will be calculated against the calibration curve to obtain a more accurate result.

11.7. Analytical Documentation

11.7.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.7.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

11.7.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.7.4. Record all sample results and associated QC directly into the LIMS. Level I and Level II review is performed in the LIMS.

## 12. DATA ANALYSIS AND CALCULATIONS

12.1.1.1. Linear Regression

The linear fit uses the following functions:

$$y = ax + b$$

*or*

$$x = \frac{(y - b)}{a}$$

Where: $y$ = Instrument response
$x$ = Concentration
$a$ = Slope
$b$ = Intercept

12.2. $$Total\,\text{Cyanide, mg/L} = \frac{\text{mg/L } CN^- \textit{ from printout x6}}{\text{mL of sample distilled}} \text{ x D}$$

12.3. $$\text{Total Cyanide, mg/kg} = \frac{\text{mg/L } CN^- \text{ from printout x6}}{\text{g of sample distilled.}} \text{ x D}$$

12.4. ***Amenable Cyanide, mg / L = Total $CN^-$ (mg / L) - Chlorinated $CN^-$ (mg / L)***

Where:

mg/L = can also be mg/kg

D = Dilution Factor $\frac{\textbf{\textit{Final Volume of Dilution}}}{\textbf{\textit{Volume of Sample Distillate Used}}}$

**Note:** Weak Acid Dissociable Cyanide has the same calculations as Total Cyanide

12.5. Laboratory Control Sample (LCS) Recovery:

$$\frac{\text{Instrument Value}}{0.25(\textit{true})} \text{ x } 100 = \% \text{ Recovery}$$

**Note:** The true value may vary by manufacturer or analysis.

12.6. CCV Recovery:

$$\frac{\textbf{\textit{Instrument Value}}}{\textbf{\textit{0.25 (true)}}} \textbf{\textit{ x 100 = \% Recovery}}$$

***NOTE:*** *CCV recovery must be between 90-110% for data to be acceptable. If CCV recovery is not within these limits, re-analysis is required.*

12.7. MS/MSD Recovery for Waters and solids

$$\frac{\textbf{\textit{A - B}}}{\textbf{\textit{0.040 (true)}}} \textbf{\textit{ x 100 = \% Recovery}}$$

Where:
A = Instrument value for MS/MSD
B = Sample instrument value

12.7 Additional equations and calculations are listed in the following SOPs: Calibration Curves and the Selection of Calibration Points, CA-Q-P-003.

## 13. METHOD PERFORMANCE

13.1. Each analyst must have initial demonstration of performance data on file and the laboratory must maintain corresponding method detection limit files.

13.2. Training Qualifications

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is

performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

## 14. POLLUTION PREVENTION

14.1. It is EurofinsTestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

## 15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2. Waste Streams Produced by the Method

15.2.1. The waste from RapidT analysis is collected in the waste bucket housed in the instrument. The waste container is emptied at the end of the day in the "Acid Waste" container.

15.2.2. Aqueous rinsates from distillation tube clean up. This waste is collected in the lab and disposed of in a container labeled "Acid Waste".

15.2.3. Standard Waste and High Concentration Samples: This waste is disposed of in the designated container labeled "High Cyanide/Basic Waste." NO ACID is added to this container.

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of Eurofins TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

## 16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste Method 9012A, Revision 1, 1996

16.1.2. SW846, Test Methods for Evaluating Solid Waste, Method 9012B, Revision 2, 2004

16.1.3. EPA 600; Determination of Total Cyanide by Semi-Automated Colorimetry, 335.4, Revision 1.0, August 1993

16.1.4. Standard Methods for the Examination of Water and Wastewater, Total, Amenable, and Weak Acid Dissociable Cyanide; Methods 4500-CN-E, 4500-CN-I, and 4500-CN-G, 1999 and 2011

16.1.5. Eurofins TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.6. Eurofins TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and Eurofins TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.7. Corporate Quality Management Plan (CQMP), current version

16.1.8. Revision History

| | | | | |
|---|---|---|---|---|
| Historical File: | | Revision 10: 08/19/15 | | |
| Revision 5: 06/24/99 | | Revision 11: 10/23/15 | | |
| Revision 6: 06/28/99 | | Revision 12a: 03/06/17 | | |
| Revision 7: 05/31/01 | | Revision 13: 11/20/17 | | |
| Revision 8: 11/08/04 | | Revision 14: 01/07/19 | | |
| Revision8.1: 05/30/08 | | Revision 15: 06/22/20 | | |
| Revision 8.2: 12/30/08 | | | | |
| Revision 8.3: 06/15/10 | | | | |
| Revision8.4A: 04/16/12 | | | | |
| Revision 9: 03/22/13 | | | | |

**4/15/19: Changed logo and copyright information. No changes made to revision number or effective date.*

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Pipette, Repeater, and Bottle-Top Dispenser Calibrations, NC-QA-004

16.2.4. Balance and Thermometer Calibration, Container Verification, NC-QA-015

16.2.5. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.6. Detection and Quantitation Limits, CA-Q-S-006

16.2.7. Cyanide Preparation Method, NC-WC-032

16.2.8. Standards and Reagents, NC-QA-017

16.2.9. Calibration Curves and the Selection of Calibration Points, CA-Q-P-003

## 17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. The reporting limit (RL) is 0.01 mg/L for waters (6 mL used) and 0.50 mg/kg for solids (0.25 g used). The lowest level of the calibration curve can be used as the reporting limit upon request.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Method Deviation

17.2.1. Methods 9012A and 9012B state that the CCV must be within $\pm$15%, or recalibration is required. The laboratory reanalyzes all samples bracketed by CCVs that are outside of $\pm$10%, and recalibrates only if deemed necessary by continual failures.

# Attachment C
# Scope of Work Approval Form

**USEPA ID Number:** MID 005 356 621
**Revision Number** 0
**February 2020**
**Prepared by:** GHD
**Prepared for:** RACER Trust Site

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Project Manager - GHD
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Date: June 3, 2021

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QA Officer - GHD
Ruth Mickle
Date: 6-2-21

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Deputy Cleanup Manager – RACER
Dave Favero
Date: June 3, 2021

Approved By: Denise Heckler
Project Manager – Eurofins TestAmerica North Canton, Ohio
Denise Heckler
Date: 5-28-21

Approved By:
USEPA Region 5 Project Manager
Zachary Sasnow
Digitally signed by ZACHARY SASNOW
Date: 2021.06.04 16:15:54 -05'00'
Date: