October 31, 2019 Reference No. 058502

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

Dear Mr. Sasnow:

**Re: Work Plan to Complete Additional North Ditch Sediment Sampling**
**EPA ID #MID 041 793 340**
**RACER Nodular Facility - Saginaw, Michigan**

This letter presents the Work Plan to complete additional sampling of the sediments present in the North Ditch at Revitalizing Auto Communities Environmental Response Trust's (RACER) Former Nodular Industrial Lands (Site) in Saginaw, Michigan. Additional sampling and evaluation of the sediments in the North Ditch was recommended in the North Ditch Ecological Screening Assessment (ESA) submitted to the United States Environmental Protection Agency (U.S. EPA) on March 14, 2019 and as discussed in subsequent communications.

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

| | |
|---|---|
| Figure 1 | Proposed North Ditch Sediment Sample Locations |
| Table 3.1 | Summary of Analytical Methods |
| Table 3.2 | Sediment Sample Parameter List |
| 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's Standard Operating Procedures for sediment sampling |
| Attachment B | Laboratory Standard Operating Procedures |
| Attachment C | Work Plan Approval Form |

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# 1. Background

As part of Resource Conservation and Recovery Act (RCRA) corrective action the North Ditch surface water, underlying sediments, and bank soils have been sampled for Nodular-specific chemicals: target analyte list (TAL) metals, PCB Aroclors, and others (e.g., nitrate, ammonia, and cyanide). The North Ditch sample results identified elevated concentrations of the same constituents, e.g., PCBs, organic carbon, and metals, especially zinc and manganese which were found in high concentrations in the heretofore upstream Secondary Ponds (GHD 2017).

The North Ditch previously received flow from the Secondary Ponds, and had low detections of PCBs. Importantly, subsequent testing of the Secondary Pond sediments found very high contributions of black carbon (2.9 percent, GHD 2018c), which presumably also occurs in the North Ditch.

Compared to typical organic carbon, black carbon binds much more aggressively (5 to 100 times more) to hydrophobic substances, like PCBs, greatly reducing their bioavailability and potential for bioaccumulation (e.g., see Cornelissen et al. 2005; Driscoll et al. 2009; USEPA 2012). The likely presence of significant amounts of black carbon in the North Ditch would significantly reduce PCB concentrations in forage fish compared to those estimated with Tracey and Hansen's results. The relative reduction in bioavailability associated with black carbon versus typical organic carbon is inversely related to the amount of total organic carbon (TOC). That is, the more typical TOC there is, the less black carbon reduces bioavailability. Hence, the relationship between typical TOC, BC, and bioavailability is complex and can only be estimated with iterative calculations (USEPA 2012).

Hence, the black carbon and TOC will be evaluated consistent with the approach taken with the Secondary Pond data. See GHD letter dated January 29, 2018, which was prepared in response to Booz Allen Hamilton's technical review comments on GHD's Ecological Screening Assessment for Secondary Pond Under Future Use Scenario's Memorandum dated August 18, 2017. That is, it will be assumed that black carbon binds PCBs 10 times more aggressively than regular TOC. Bioavailability of PCBs will then be estimated with an effective TOC concentration that includes binding of both types of organic carbon. More specifically, the effective [TOC] would be estimated with the following equation,

([TOC] – [BC]) + 10 * [BC], where [TOC] and [BC] are concentrations of TOC and BC, respectively.

# 2. Additional Sampling Activities

In order to evaluate the composition of the Total Organic Carbon (TOC) in the North Ditch, and more specifically the Black Carbon component, ten sediment samples will be collected from seven locations in the North Ditch. The samples will be submitted under chain of custody procedures for laboratory analysis of Total Organic Carbon and Black Carbon, as recommended in the ESA. In addition, to further evaluate the historic detections of PCBs in the North Ditch sediments, sediment samples will also be collected at the seven locations and submitted for laboratory analysis of PCBs. Approximate sediment sample

locations are presented on Figure 1. Sediment samples have been generally evenly distributed along the centerline of the channel.

### 2.1 Sample Collection Procedure

The sediment samples will be collected from below the water surface using an Ekman Dredge in accordance with GHD's standard operating procedure (SOP) for sediment sampling, which is presented in Attachment A. Alternative techniques may be implemented if the Ekman Dredge does not produce a representative sample given the sediment composition. Sediment samples will be recovered and the upper 3-inches of the sediment column will be collected and sent to the laboratory for analyses as this zone is considered to be representative of the biological exposure zone. Oxygen is expected to be depleted below the surficial layer of sediment (top 3-inches), consequently, the sediment infaunal macrobenthos in the North Ditch will likely be restricted to the top layers of sediment. In order to show that the oxygen-depleted layer contains sufficient black carbon to minimize PCB diffusion, three additional sediment samples will be collected from the 3-6-inch interval at three of the seven proposed sediment sample locations. One of these additional deep samples will be located near the historical sediment sample location, H7A. Additionally, since the area near historical sediment sample location H7A is of interest for this work plan, a field duplicate will be collected from the proposed sediment sample location near H7A.

## 3. Analytical Methods and Quality Control Samples

Eurofins TestAmerica will be the laboratory company supporting the environmental sample analysis for this project utilizing their facilities in North Canton, Ohio (PCBs, polynuclear aromatic hydrocarbons (PAHs), and TOC) and Burlington, Vermont (Black Carbon).

### 3.1 Laboratory Analytical Methods

Sediment samples will be analyzed for specified chemical constituents by the project laboratory. The methods that will be used for sample analysis are presented in Table 3.1. Specific analytes and targeted quantitation limits for chemical constituents are presented in Table 3.2. The precision and accuracy criteria for laboratory analyses are provided in Table 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 a field duplicate 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 1 per 20 or fewer 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. Equipment/Field blank samples will not be required for samples collected using pre-cleaned or pre-cleaned, disposable sampling equipment.

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

Additional 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 sediment samples includes analyzing method blanks, initial calibration verification standards, continuing calibration verification standards, surrogate 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, LCS data, duplicate sample data, MS/MSD data,

vii. surrogate compound spike data

viii. 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. Validation of the data will consist of evaluating the QA/QC data based on the applicable review criteria specified in "National Functional Guidelines for Superfund Organic Methods Data Review", EPA 540-R-2017-002, January 2017 and "National Functional Guidelines for Inorganic Superfund Methods Data Review", EPA 540-R-2017-001, January 2017.

The PCB 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.

The National Functional Guidelines (NFG) do not specifically cover validation methods for TOC and black carbon. However, the NFG validation procedures will be applied to several validation components including: final analytical results, holding time period compliance, equipment blank sample data, field duplicate sample data, method blank data, LCS data, laboratory duplicate data, and MS/MSD sample data.

The sample results and quality control data will be evaluated against NFG criteria and laboratory control limits, where applicable. Field duplicate samples will be evaluated against a relative percent difference maximum of 100 for solid samples. 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.

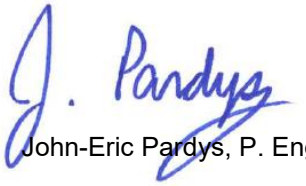
## 4. Reporting

Following the completion of the sediment investigation, a report will be prepared summarizing the completed field program and the analytical results and will include an update to the ESA. The report will be submitted to U.S. EPA and will include recommendations on next steps, if required.

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

Yours truly,

GHD

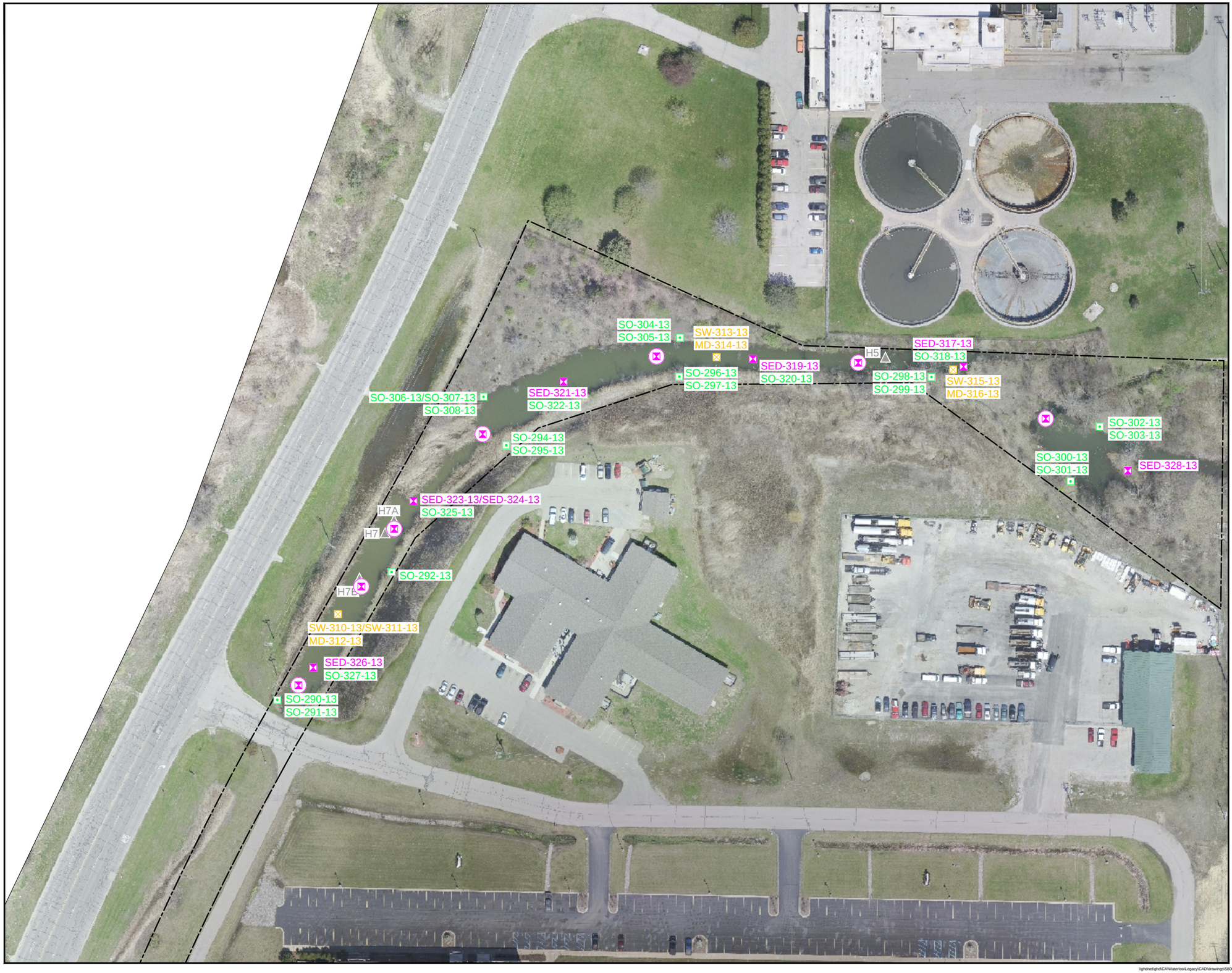


John-Eric Pardys, P. Eng.

JEP/kf/4-rev.1

Encl.

cc: Dave Favero, RACER
Michael Tomka, GHD




N

0 20 50ft

LEGEND

- SURVEYED PROPERTY BOUNDARY
- HISTORICAL SEDIMENT SAMPLE LOCATION
- SEDIMENT SAMPLE LOCATION
- SOIL SAMPLE LOCATION
- SURFACE WATER SAMPLE LOCATION
- PROPOSED SEDIMENT SAMPLE LOCATION

SCALE VERIFICATION

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

# REVITALIZING AUTO COMMUNITES ENVIRONMENTAL RESPONSE

SAGINAW, MICHIGAN

## PROPOSED NORTH DITCH SEDIMENT SAMPLE LOCATIONS

GHD

Source Reference:
MICHIGAN STATE PLANE SOUTH, NAD 83 USING INTERNATIONAL FEET, NGVD 88
AERIAL: GHD UAV ORTHOIMAGERY - MAY 3, 2016.

| Project Manager: | Reviewed By: | Date: | |
|---|---|---|---|
| JEP | GR | JULY 2019 | |
| Scale: 1" = 50' | Project Nº: 58502-T02 | Report Nº: SAGN004 | Drawing Nº: figure 1 |

\\ghdnet\ghd\CA\Waterloo\Legacy\CAD\drawings\58000s\58502\58502-CORR\58502-T02\SAGN004\58502-T02\SAGN004\GN\58502-T02\SAGN004\GN-WA001.DWG Plot Date: SEP 10, 2019

**Table 3.1**

**Summary of Analytical Methods**
**Work Plan to Complete Additional North Ditch Sediment Sampling**
**RACER Nodular Facility**
**Saginaw, Michigan**

| Parameter | Preparation Method[1] | Analytical Method[1] |
|---|---|---|
| **Sediment Samples** | | |
| Polynuclear Aromatic Hydrocarbons (PAH) | SW-846 3510 | SW-846 8270 |
| Polychlorinated Biphenyls (PCB) | SW-846 3545 | SW-846 8082 |
| Organic Carbon, Total (TOC) | Lloyd Kahn | Lloyd Kahn |
| Black Carbon (Lloyd Kahn) | Lloyd Kahn | 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.

**Table 3.2**

**Sediment Sample Parameter List**
**Work Plan to Complete Additional North Ditch Sediment Sampling**
**RACER Nodular Facility**
**Saginaw, Michigan**

| Compound | Estimated Quantitation Limits (EQL)[1] Sediment (µg/kg) | Method Detection Limits (MDL)[2] Sediment (µg/kg) |
|---|---|---|
| **Polychlorinated Biphenyls (PCB) as Aroclors** | | |
| Aroclor-1016 | 264 | 21 |
| Aroclor-1221 | 264 | 16 |
| Aroclor-1232 | 264 | 14 |
| Aroclor-1242 | 264 | 13 |
| Aroclor-1248 | 264 | 17 |
| Aroclor-1254 | 264 | 17 |
| Aroclor-1260 | 264 | 17 |
| **Polynuclear Aromatic Hydrocarbons (PAH)** | | |
| Benzo[a]anthracene | 15.0 | 3.41 |
| Benzo[a]pyrene | 15.0 | 9.34 |
| Benzo[b]fluoranthene | 15.0 | 6.50 |
| Benzo[g,h,i]perylene | 15.0 | 7.10 |
| Benzo[k]fluoranthene | 15.0 | 6.93 |
| Anthracene | 15.0 | 2.41 |
| Chrysene | 15.0 | 1.49 |
| Dibenz(a,h)anthracene | 15.0 | 6.92 |
| Fluoranthene | 15.0 | 4.45 |
| Fluorene | 15.0 | 2.74 |
| Indeno[1,2,3-cd]pyrene | 15.0 | 7.36 |
| Phenanthrene | 15.0 | 2.23 |
| Pyrene | 15.0 | 2.14 |
| Acenaphthene | 15.0 | 2.86 |
| Acenaphthylene | 15.0 | 4.01 |
| Naphthalene | 15.0 | 2.41 |

| Compound | Estimated Quantitation Limits (EQL)[1] Sediment (mg/kg) | Sediment (mg/kg) |
|---|---|---|
| **Organic Carbon, Total (TOC)** | 1000 | 684 |
| **Black Carbon (Lloyd Kahn)** | 1000 | NR |

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.

NR Not Reported

**Table 3.3**

**Laboratory Precision and Accuracy Limits**
**Work Plan to Complete Additional North Ditch Sediment Sampling**
**RACER Nodular Facility**
**Saginaw, Michigan**

| Analysis | Analyte Description | LCS Limits | MS/MSD Limits | Surrogate Limits |
|---|---|---|---|---|
| Polychlorinated Biphenyls (PCBs) | Aroclor-1016 | 47-120 (30) | 31-120 (30) | |
| | Aroclor-1260 | 46-120 (30) | 21-122 (30) | |
| | *Tetrachloro-m-xylene* | | | 14-128 |
| | *DCB Decachlorobiphenyl* | | | 10-132 |
| Polynuclear Aromatic Hydrocarbons (PA | Benzo[a]anthracene | 53-120 (40) | 35-120 (40) | |
| | Benzo[a]pyrene | 50-120 (40) | 33-120 (40) | |
| | Benzo[b]fluoranthene | 48-120 (40) | 26-120 (40) | |
| | Benzo[g,h,i]perylene | 50-120 (40) | 16-120 (40) | |
| | Benzo[k]fluoranthene | 51-120 (40) | 33-120 (40) | |
| | Anthracene | 51-120 (40) | 42-120 (32) | |
| | Chrysene | 54-1209 40) | 33-120 (40) | |
| | Dibenz(a,h)anthracene | 48-120 (40) | 30-120 (40) | |
| | Fluoranthene | 53-120(40) | 26-121 (40) | |
| | Fluorene | 50-120 (40) | 36-120 (28) | |
| | Indeno[1,2,3-cd]pyrene | 49-120(40) | 24-120 (40) | |
| | Phenanthrene | 52-120 (40) | 28-120 (40) | |
| | Pyrene | 55-120 (40) | 28-120 (40) | |
| | Acenaphthene | 48-120 (40) | 36-120 (28) | |
| | Acenaphthylene | 46-120 (40) | 35-120 (26) | |
| | Naphthalene | 48-120 (40) | 29-120 (34) | |
| | *2-Fluorobiphenyl* | | | 32-120 |
| | *2-Fluorophenol* | | | 29-120 |
| | *2,4,6-Tribromophenol* | | | 10-120 |
| | *Nitrobenzene-d5* | | | 30-120 |
| | *Phenol-d5* | | | 29-120 |
| | *Terphenyl-d14* | | | 41-120 |
| Black Carbon (Lloyd Kahn) | Black Carbon | 50-150 | 50-150 (20) | |
| Organic Carbon, Total (TOC) | Total Organic Carbon | 75-125 (20) | 75-125 (20) | |

Notes:

LCS - Laboratory Control Sample
MS/MSD - Matrix Spike/Matrix Spike Duplicte Sample

**Table 3.4**

**Summary of Sampling and Analysis Program**
**Work Plan to Complete Additional North Ditch Sediment Sampling**
**RACER Nodular Facility**
**Saginaw, Michigan**

| Investigation Activity | Sample Matrix | Field Parameters | Laboratory Parameters | Investigative Samples | Quality Control Samples | | | Total |
|---|---|---|---|---|---|---|---|---|
| | | | | | Equipment Blanks | Field Duplicates | MS/MSD (1) | |
| North Ditch Sediment Sampling | Sediment | None | Polynuclear Aromatic Hydrocarbons, Polychlorinated Biphenyls, Total Organic Carbon, Black Carbon | 10 | 1 | 1 | 1 | 13 |

Notes:

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

**Table 3.5**

**Container, Preservation, Shipping and Packaging Requirments**
**Work Plan to Complete Additional North Ditch Sediment Sampling**
**RACER Nodular Facility**
**Saginaw, Michigan**

| Analyses | Sample Containers[1] | Preservation | Maximum Holding Time from Sample Collection[2] | Volume of Sample | Shipping | Normal Packaging |
|---|---|---|---|---|---|---|
| **SOLID (Sediment)** | | | | | | |
| Polychlorinated Biphenyls (PCB) | One 4-ounce glass jar | Iced, 4 ± 2° C | One year for extraction 40 days after extraction for analysis | Fill to shoulder of jar | Overnight or Hand Deliver | Foam Liner or Bubble-wrap |
| Polynuclear Aromatic Hydrocarbons (PA | One 4-ounce glass jar | Iced, 4 ± 2° C | 14 days for extraction 40 days after extraction for analysis | Fill to shoulder of jar | Overnight or Hand Deliver | Foam Liner or Bubble-wrap |
| Organic Carbon, Total (TOC) | One 4 ounce glass jar | Iced, 4 ± 2° C | 14 days to analysis | Fill to shoulder | Overnight or | Foam Liner or |
| Black Carbon (Lloyd Kahn) | Same 4 ounce glass jar | Iced, 4 ± 2° C | 14 days to analysis | of jar | Hand Deliver | Bubble-wrap |

Notes:

[1] - Multiple parameters on a single sample may be combined into one single 16 ounce glass jar.

[2] - These are technical holding times, i.e., are based on time elapsed from time of sample collection.
- ASTM - "Annual Book of ASTM Standards", American Society for Testing and Materials.

# Attachment A
# GHD's Standard Operating Procedures for Sediment Sampling

**This procedure makes reference to Australian legislation and guidelines. Reference should be made to relevant state and country legal requirements and relevant guidelines where appropriate.**

# 1. PURPOSE

This procedure describes the approach to be taken for collection of representative marine, coastal and freshwater sediment samples. This procedure focuses primarily on conducting sediment sampling and analysis programs in accordance with *The National Assessment Guidelines for Dredging*, Commonwealth of Australia, Canberra, 2009.

# 2. SCOPE

This procedure applies to all jobs where marine, coastal and freshwater sediment samples are to be collected using vibracoring, piston sampling and grab sampling methods.

# 3. SAFETY REQUIREMENTS

A health and safety plan should be prepared prior to commencing all field work on site and should be reviewed regularly and updated throughout the project as changes in conditions or work methods occurs.

Reference should be made to safety requirements and considerations described in specific sampling procedures and SOP 19 *Site Safety Plan Preparation and PPE.*

When conducting sediment sampling along any waterway, always work in the company of at least one other person who is able to assist in case of an emergency. When working in open water, ensure the vessel is appropriate for the works to be conducted and the boat is sufficient for local weather and water conditions. The vessel needs to have appropriate safety equipment, is in survey and a licenced commercial skipper is operating it (refer to your local Maritime Safety department for further information). Ensure that all personnel are aware of current and proposed weather conditions and maintain regular checks of forecasts throughout the day. Note wind direction and tidal effects may affect the return of the vessel to your departure point.

# 4. PROCEDURE

## 4.1 Background

The following procedure describes the methodology for collecting sediment samples from marine, coastal and freshwater environments. A number of different methods may be employed in collection of sediment samples. Selection of the method for sediment sampling may be dependent on the following factors and constraints:

- project objectives

- likely depth of contaminated sediment
- proposed depth of dredging
- site location
- depth of water
- weather and sea conditions
- lithology likely to be encountered during sampling
- budget constraints
- access to sampling contractors and equipment

Each site is different and site specific sampling plans are required to be developed prior to the commencement of works. Sampling should be adapted to be appropriate for each specific location.

Sampling locations should be selected following appropriate consideration of project objectives and requirements of the relevant guidelines [for example if the project objective is to obtain a sea dumping permit than the number of sampling locations selected should be conducted in accordance with the NAGD (2009)].

Sampling sites should be identified in a Sediment Sampling and Analysis Plan (SAP).

## 4.2 Fieldwork Planning and Equipment Requirements

The following actions should be completed prior to conducting sampling, also refer to SOP 03 *Field Sampling Design and Preparation*:

- Sediment Sampling and Analysis Plan (SAP) that has been technically reviewed by a GHD person competent to do so (if the project objective is to obtain a sea dumping permit then approval by the Determining Authority is required)
- Ensure subcontractors are engaged with GHD under GHD's Subcontractor's Agreement (QA023)
- Occupational Health and Safety and Environmental documentation and permits have been completed that addresses GHD requirements, client contractual obligations, Australian laws and any stakeholder requirements (i.e. harbour master, port authorities)
- Dial before you dig (DBYD) must be undertaken (allowing at least two weeks for asset owners to respond)
- Brief the primary and secondary laboratories on the proposed sampling and analysis program and ensure they can meet the required practical quantification limits (PQL) and holding times
- Ensure the logistics for sample delivery to the laboratory have been satisfactorily arranged
- Organisation of field equipment/ requirements. Equipment and supplies that may be required during sediment sampling is listed, but not limited to those identified in Attachment A.
- Where specialist equipment is required to support a sediment investigation, personnel should be fully trained or be able to appropriately supervise operation prior to arriving on site. Equipment should be tested prior to going to site to ensure it is operational.

## 4.3 Sampling Methods and Procedures

### 4.3.1 Field Information and Sample Logging

The following field measurements must be recorded on an appropriate field data sheet at each sampling location:

- Date and time of sampling of each core/sample
- Subcontractor conducting sampling, client, project, sample location identifier, type of sampler used, GPS coordinates of sampling location and name of sampler
- Tides – daily tide charts will be included and water depth from the sampling point (including if on a vessel) at the time of sampling recorded. If applicable, a tide graph should additionally be used to calculate the elevation of the seafloor in Lowest Astronomical Tide (LAT) so that it can be checked against the bathymetry maps and if different, the dredge depth at that location recalculated.
- Weather – relevant conditions including wind speed, sea state (if applicable), currents and rainfall for each day of sampling will be recorded
- General comments – noting issues which may affect the sampling program and/or interpretation of results
- Depth of penetration of core into the sediment.
- Core logs – each core will be logged in accordance with SOP 09 *Lithological Logging*, before samples are processed. Details recorded will include depth, physical appearance, colour, contaminant odour and staining (if present), plasticity, field texture, sand grain size and presence of organic matter, marine organisms, shell layers, fill material, odour and other relevant features
- Digital photographs – documenting the sampling program, methods and the sediment cores. The photographs taken during logging should include details such as a coring plate stating project, date and time, location, and sample identification (ID)

Examples of finalised field data sheets / core logs are provided in Attachment B.

### 4.3.2 Grab Sampling Method

Grab sampling is the simple process of bringing up surface sediments from below the water.. It cannot be used to characterise different sedimentary layers since a mixture of sediments is produced (as a result of the equipment used when they are brought up; therefore, it is only used to sample approximately the top 0 m to 0.3 m. of sediments. The procedure for grab sampling is as follows:

1. Ensure the sampling locations are away from underground utilities and overhead hazards. If possible or appropriate, obtain signed clearance from the client or a site representative.
2. Prepare a sampling record (sediment) and record the date and time of sampling.
3. Decontaminate all equipment in accordance with SOP 20 *Decontamination of Sampling Equipment* and make sure that all equipment is in working order.
4. At each location, lay out equipment on a plastic sheet to prevent cross contamination (from contact of sampling equipment with the ground or water bodies).

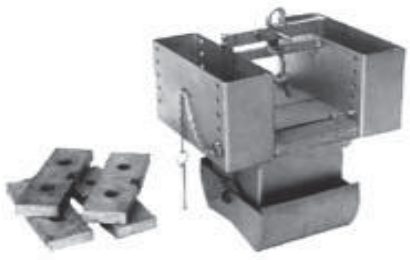
5. Ensure the sediment is not disturbed prior to sampling.
6. Collect sample using sampling equipment selected to suit the sediment texture likely to be encountered (see section 5.3.3 below).
7. Place the sample in an appropriate (labelled) and sterile sample container/ bags (depending on analytical analysis required) provided by the analytical laboratory.
8. If required, take a photo ionisation detector (PID) reading of the collected sample (see SOP 29 *Field Equipment Calibration*).
9. Record the location of the sampling point and the soil/ sediment type and depths at which samples were collected in the field notes and logbook. Classify the soil in accordance with SOP 09.
10. Store and transport the samples in accordance with SOP 18 *Sample Storage and Handling*.
11. Dispose of all sampling wastes in accordance with SOP 22 *Disposal of Waste Materials*.

### 4.3.3 Sediment Sampling Equipment

Sediment samples can be recovered using grabs described in the table below.

| Sediment Sampling Device | Suitability and Form of Use |
|---|---|
| Ekman Grab<br>  | This grab is used for soft, finely divided littoral bottoms that are free from vegetation, such as sticks and decayed leaves as well as intermixtures of sand, stones and other coarse debris. This dredge is mostly used for taking quantitative and qualitative samples of macroscopic bottom fauna to determine the productivity of soft bottoms, particularly those composed of finely divided muck, mud, ooze, submerged marl and fine peaty materials. It is not recommended for rocky or sandy bottoms or moderate macrophyte growth because small pebbles or macrophyte stems prevent proper jaw closure. Two thin, hinged overlapping lids on top open during descent to let water pass through. They close during retrieval and are held shut by water pressure to reduce washout.<br>Best used from a boat, lowered through water by rope to the depth required. |

| | |
|---|---|
| Van Veen Grab<br>  | This lightweight large grab is used for taking large samples in soft bottoms. Its long lever arms and sharp cutting edges on the bottom of the scoops allow it to cut deep into softer bottoms. A self-releasing pin attached to the two closing arms holds the grab open before it hits the bottom. Upon impact, the tension on the chains is released, and it pulls the closing arms together to close the scoops when the cable is lifted. The top of each scoop is covered with stainless steel screen for water to flow through during descent. The screen is covered with a neoprene rubber flap to prevent sample washout during retrieval.<br>Best used from a boat, lowered through water by rope to the depth required as it weighs 18.5 kg. |
| Smith-Macintyre<br>  | Used for sampling sediment in deep water. It has spring-loaded jaws that close when triggered using a rope from the surface. It can collect between 8 and 14 cm in depth of sediment, usually with a well-preserved water/sediment interface and with water still contained above the sampled sediments. Frequently used by research institutes during oceanographic surveys.<br>Best used from a boat, lowered through water by rope to the depth required. |
| Petersen Grab<br>  | The Petersen grab is used for collecting macroscopic fauna in sand, gravel, marl, clay or clay combinations. Vent holes permit water to flow through while the grab is being lowered, minimizing diagonal movement as well as reducing the frontal shock wave generated by descent. Jaws close clamshell fashion. The bayonet-style trip mechanism is designed to release when the sampler is on the bottom and the cable is slack. A deliberately heavy device for biting deep into hard bottoms.<br>Best used from a boat, lowered through water by rope to the depth required. Weighs around 34 kg. Use of a crane and winch is recommended due to the weight. |

| | |
|---|---|
| Ponar Grab<br>  | Widely used in fresh and salt water for taking samples of hard bottoms such as sand, gravel, consolidated marl or clay, this sturdy dredge is a deliberately heavy device for biting deep into the bottom and has proven success at invertebrate recovery. The simple design means it is easy to use. Self-closing scoops have centre pivot closing action. When the scoops strike the bottom, their tapered cutting edges penetrate well with very little sample disturbance. An attached underlip wipes the scoop clean of pebbles and cobble that would interfere with closing. Side plates prevent the lateral loss of sample as scoops close. Removable screens on top of each scoop allow water to flow through as it descends. This lessens the frontal shock wave and reduces surface disturbance. Both screens are covered with neoprene rubber flaps that close during retrieval. Use of a crane and winch is recommended due to the 34 kg working weight. |
| Box Corer<br>  | This patented device is designed to take larger samples in harder bottoms more easily and safely than spring-powered grabs. It is especially effective in finely divided muck, clays, mud, ooze, submerged marl, or fine peaty materials like a big bruiser, the sole driving force is the box corer's weight, which can total 49 kg. The body itself weighs about 14 kg and is augmented by up to 12 extra weights, each weighing 4 kg, securely fastened in two side bins. The heavy duty linkage and scoops dig as deep as the weight will allow. The inside of the box is smooth and free of projections, allowing an acrylic liner to easily slip in and out. |

Note: the above grab descriptions, apart from that for the Smith-Macintyre grab, are taken from the Wildlife Supply Company catalogue (www.wildco.com).

### 4.3.4 Vibracoring Method

Vibracoring is a technology and a technique for collecting core samples of underwater sediments and wetland soils to a depth of approximately 3 m to 20 m plus (below top of sediment) depending on the sediments encountered and power of equipment used.

The vibrating mechanism of a vibracorer operates on hydraulic, pneumatic, mechanical or electrical power from an external source. The attached core tube is driven into sediment by the force of gravity, enhanced by vibration energy. When the maximum depth of refusal is encountered, the vibracorer is turned off, and the tube is withdrawn with the aid of hoist equipment. Vibracoring works best on unconsolidated, waterlogged, heterogeneous sediments and soils. Silty sediments of mixed grain size are easiest to core. Vibracoring is less effective for relatively dry clays, packed sand or any consolidated (cemented) materials. In good conditions, vibracoring can produce continuous cores of over 20 metres depth. As this process involves the use of machinery, it is likely a contractor will be required to supply the

equipment and undertake the methods outlined above. The necessary procedures to be undertaken are as follows:

1. Prepare a sediment sampling record
2. Decontaminate all equipment (sediment core trays, stainless steel buckets etc) in accordance with SOP 20 and make sure that all equipment is in working order
3. Once the sediment core is unconfined from the vibracoring tube and placed on the sediment tray follow the appropriate procedures outlined in section 5.3.1
4. Follow general sampling processing and preservation procedures outlined in section 5.4
5. If applicable, undertake any necessary laboratory or field QA/QC outlined in section 5.5
6. Dispose of all sampling wastes in accordance with SOP 22

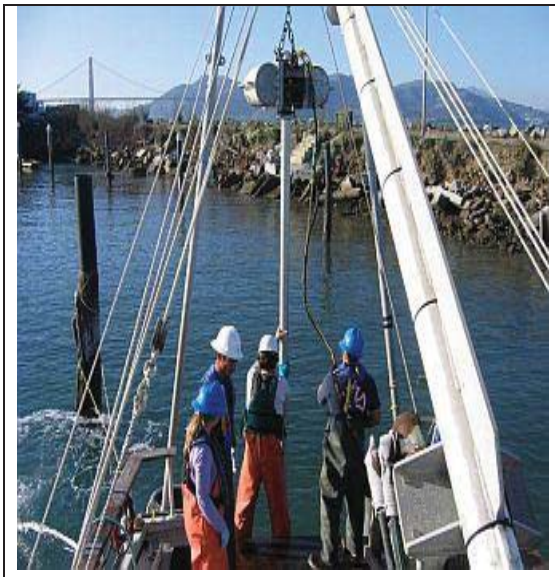


**Figure 1: Deployment of Vibrocore**

**Figure 2: Samples collected in steel casing from vibrocoring**

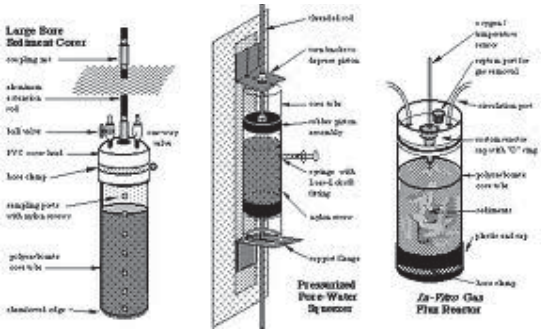
### 4.3.5 Piston Sampling Method

Piston sampling can be used on both small and large scale projects. It involves manual sampling using a piston sampler (mainly used by a diver deployed to the sea floor from a vessel) where the piston sampler is released to draw a sediment core into the tube. The piston sampler is then plugged and brought to the surface for logging and sampling) by contractors on the vessel.

For large scale piston sampling, the sampling procedure will be similar to the vibracoring method in the respect that the equipment and sample collection are likely to be undertaken by a subcontractor due to

the use of machinery. In regards to piston sampling, divers are to collect cores from the seafloor using hand piston samplers. These cores are transported to the surface in the piston sampler where they are extruded onto the sample trays. Often two to three cores are required from the one sample site in order to provide a sufficient quantity of sample from each depth range. The procedure to be undertaken is similar to that of the vibracoring procedure and is as follows:

1. Prepare a sediment sampling record
2. Decontaminate all equipment (sediment core trays, stainless steel buckets etc) in accordance with SOP 20 and make sure that all equipment is in working order
3. Once the sediment core is extruded from the piston sampling tube and placed on the sediment tray, follow the appropriate procedures outlined in section 4.3.1
4. Follow general sampling processing and preservation procedures outlined in section 4.4
5. If applicable, undertake any necessary laboratory or field QC/QA outlined in section 4.5
6. Dispose of all sampling wastes in accordance with Procedure E22

| Sediment Sampling Device | Suitability and Form of Use |
|---|---|
| Piston Sampling<br>  | Piston sampling is used for soft, finely divided littoral bottoms that are free from vegetation, such as sticks and decayed leaves as well as intermixtures of sand, stones and other coarse debris. This sample type is used for collecting samples from soft bottom. . It is not recommended for rocky or sandy bottoms or in areas that have moderate to high organic matter located on the surface of the silt, as this can impact on the collection of the sample. A plug like feature can be used following the collection of the core, to ensure that the core remains intact within the piston during the transportation to the surface for logging and sampling.<br>Best used from a boat, lowered through water by rope to the depth required. |

## 4.4 Sample Processing and Preservation

### 4.4.1 General - Collection of Samples

The following should be considered prior to and during field work:

- Prior to fieldwork, contact should be made with the analytical laboratories regarding the minimum quantity (grams/ kilograms) of sediment that is required for each sample (based on the analysis that is proposed). It should also be noted that water samples at each sample site will need to be collected should elutriate/ bioavailability testing be required.

- When sampling for analytical (including acid sulphate soils) and physical parameters samples should be collected from half meter depth ranges (ie 0-0.5 m, 0.5-1.0 m 1.0-1.5 m etc to the required depth). It is important that the required quantity of sediment is collected from each sample depth, therefore, depending on the sampling methodology (ie piston sampling) a number of cores may need to be collected from the sample site (within 1 m squared) in order to collected the required volume. If a number of cores are required, the depth profile from each core (ie 0-0.5 m) will need to be collected from each core and mixed in a stainless steel bucket, prior to the collection of sample. Further information is identified in section 5.4.2.

### 4.4.2 Sample Processing

Once cores have been collected from a sample site and field information and logging is completed, the following sample processing should be undertaken:

- Sediment from each sample interval (i.e. 0.0 - 0.5 m) should be mixed well to ensure a thoroughly homogenised sample, with the exception of a portion of the core that will be analysed for volatile contaminants. The portion of the core that will be analysed for volatiles should not be mixed, and should be collected from midway of the cores in accordance with NAGD (2009).
- Sediment will then be placed directly into pre-treated laboratory supplied jars and/or air tight zip lock bags (depending on the analyses required). The table below outlines the sample containers and volumes required based on information provided in the NAGD (2009) though this should be confirmed with the laboratory.
- For organic analyses, sediment is placed into the jars with minimum possible headspace to prevent volatilisation.
- At each location (where required), ensure additional sediment and water is collected for potential elutriate, bioavailability and toxicity testing. The table below outlines approximate required volumes though this should be confirmed with the laboratory

| Analytical Parameter | Required Container | Required Volume (grams, wet weight) |
|---|---|---|
| Moisture content | Glass Jar | 10-50 |
| Particle size (by hydrometer) | Plastic Zip Lock Bag | 50-200 |
| Total organic carbon | Glass Jar | 10-50 |
| Total recoverable hydrocarbons (TRH) / benzene, toluene, ethylbenzene, xylenes (BTEX) | Glass Jar | 100-250 |
| Phenol/ phenolics | Glass Jar | |
| Organochlorine pesticides (OCP) | Glass Jar | |
| Polychlorinated biphenyls (PCB) | Glass Jar | |
| Polycyclic aromatic | Glass Jar | |

| Analytical Parameter | Required Container | Required Volume (grams, wet weight) |
|---|---|---|
| hydrocarbons (PAH) | | |
| Organophosphorous pesticides (OPP) | Glass Jar | 100-250 |
| Heavy metals/metalloids | Glass jar / Plastic zip lock bag | 10-100 |
| Nutrients | Glass jar | 50-200 |
| Ammonia (in solids) | Glass jar | |
| Organotins | Glass jar | 50-200 |
| Acid sulphate soils (ASS) | Plastic zip lock bag | 500 |
| Toxicity testing | As per primary contaminant | 2000 |
| Elutriate testing (Metals) | As per primary contaminant | 1000 |
| Elutriate testing (Organics) | As per primary contaminant | 2000 |
| Porewater analysis | As per primary contaminant | 1000 |
| Seawater for elutriate testing | Sterile Plastic Container | 20 - 40 litres of water per sample from the site |

#### 4.4.3 Preservation of Physical and Chemical Soil Testing Samples

Chemical preservation of sediment is generally not recommended. Cooling the sample to minimise degradation (with the exception of ASS samples, see Section 4.4.4 coupled with a short holding time is usually sufficient. For general requirements refer to SOP 18.

#### 4.4.4 Preservation of Potential Acid Sulphate Soil Samples

ASS samples should be collected in a labelled plastic zip lock bag. If samples cannot be delivered to the laboratory within 24 hours of sampling, they should be frozen and then delivered to prolong holding times.

## 4.5 Field Quality Control and Quality Assurance Procedures

Field QA/QC sampling should be collected and conducted in accordance with the NAGD (2009) requirements, and must include the analyses of the following types of samples (refer SOP 30 *Quality Assurance Sampling*):

**Table 4 Field QA/QC Sample Details**

| Field QA/QC sample type | Collection/Analysis Rate | Details |
|---|---|---|
| Field Triplicate | 10% of all sample locations | Field triplicate samples are two replicate sites collected at the same location as a primary site and analysed to determine the variability of the sediment physical and chemical characteristics. The replicate sites are not homogenised with each other or with the primary site. At least two additional cores per replicate site will need to be collected to allow for sufficient sample. |
| Intra Laboratory Field Duplicate | 5% of all locations | An intra-laboratory field duplicate samples is a replicate sample (at 0.5 m sampling interval) collected from the same homogenised sediment as a primary sample and analysed by the primary laboratory to identify variation associated with sub sample handling. One extra core may need to be collected at the primary site to allow for sufficient sample. |
| Inter Laboratory Field Duplicate (Split) | 5% of all locations | An inter laboratory field duplicate sample is a replicate sample (at 0.5 m sampling interval) collected from the same homogenised sediment as a primary sample and analysed to identify any variation in analytical protocol of the primary laboratory. One extra core may need to be collected at the primary site to allow for sufficient sample. |
| Trip Blank | One per day of sampling | Field trip blank samples provide an indication of cross contamination from volatile substances during field sampling. |

# 5. SUGGESTED FURTHER READING

## 5.1 Procedures

- SOP 03: *Field Sampling Design and Preparation*
- SOP 08: *Field Documentation*
- SOP 09: *Lithological Logging*
- SOP 18: *Sample Storage and Handling*
- SOP 19: *Safety Plan Preparation and PPE*
- SOP 20: *Decontamination of Sampling Equipment*
- SOP 21: *Validation Sampling*
- SOP 22: *Disposal of Waste Materials*
- SOP 25: *Underground Services Search*
- SOP 27: *Report Writing*
- SOP 30: *Quality Assurance Sampling*

- SOP 31: *Acid Sulphate Soil Sampling*

### 5.2 Standards

- AS4482.1—1997 Guide to the sampling and investigation of potentially contaminated soil. Part 1 & 2
- AS 1726 — 1993 Geotechnical Site Investigations
- AS5667.12—1999 Water Quality – Sampling – Guidance on sampling of bottom sediments

### 5.3 Associated Documents

- *National Assessment Guidelines of Dredging* (NAGD), Commonwealth of Australia, Canberra, 2009.
- Queensland Acid Sulfate Soils Investigation Team (QASSIT), NEPM Schedule B(2) Guideline on Data Collection, Sample Design and Reporting.
- Australia and New Zealand Environment and Conservation Council (ANZECC), 2000
- USEPA Environmental Response Team Standard Operating Procedure #: 2016 Sediment Sampling.
- Handbook for Sediment Quality Assessment (CSIRO2005)

## 6. ATTACHMENTS

Attachment A: Equipment and supplies that may be required during sediment sampling is listed in Attachment A (2 pages)

The following equipment may be required during sediment sampling:

- Personal protection equipment including (but not limited to) slip on steel cap boots, long sleeve shirt, long pants, sunscreen, wide brim hat, aeroguard
- Site plan marked with sampling locations including GPS coordinates, depth of sample required and analysis;
- Photo log tablet
- GPS unit with sampling site coordinates preloaded
- Tape measure
- Compass
- Camera and spare battery (if required)
- Stainless steel or plastic core trays and sediment bowls (stainless steel)
- Stainless steel wire for cutting cores, for photos:
- Nitrile disposable gloves
- Wide-mouthed sample containers provided by analysing laboratory (including jars, plastic bags and water containers (for elutriate testing)
- Sediment sampling tubes (supplied by contractor)
- Sampling grab (supplied by contractor)
- Nylon rope or steel cable for grab sampler (supplied by contractor)
- Boat with safety equipment
- Plastic zip lock bags
- Logbook, field data sheets (borelogs), SAP specific to works, any other reference material (NAGD 2009 guidelines), job safety and analysis plan and safety plan specific to works
- Writing equipment (including pen, pencil, permanent / water proof marker)
- Labels
- Chain of custody forms from the laboratory
- Contact numbers (including JM, Lab contact, courier contact and emergency contact numbers (which should also be on the JSEA/ Safety Plan)
- Cool storage containers (Eskys or similar provided by the lab)
- Ice (sufficient for chilling and preserving samples for the day and/ or holding time before courier arrives
- Freezer for acid sulfate soil (ASS) samples
- Protective packing (bubble wrap) for glass jars
- PID (if required)
- Plastic sheets (for storing/ protecting field notes)
- Decontamination equipment (see Procedure E20)
- Trowel

- Spatula
- First aid kit (also supplied by contractor)
- Laptop (for downloading and storing)
- Paper towel

# Attachment B
# Laboratory Standard Operating Procedures

# Title: GAS CHROMATOGRAPHIC ANALYSIS of PCBs BASED ON METHODS 8082 and 8082A

**Approvals (Signature/Date):**

| | | | |
|---|---|---|---|
| Technology Specialist | 04/17/18 Date | Health & Safety Coordinator | 04/06/18 Date |
| Quality Assurance Manager | 04/17/18 Date | Technical Director | 04/06/18 Date |

**This SOP was formerly known as NC-GC-045 Rev. 1, dated 1/14/16**



**Facility Distribution No. _____ Distributed To:_____**

**The controlled copies of this SOP are the PDF copy that is posted to the laboratory's SOP Directory and, where applicable, the copy that is printed and placed in the General Chemistry SOP binder. Printed or electronic copies distributed outside of the facility are considered uncontrolled.**

## 1. SCOPE AND APPLICATION

1.1. This SOP describes procedures to be used when SW-846 Method 8082 or 8082A are applied to the analysis of polychlorinated biphenyls (PCB) as Aroclors by GC/ECD. This SOP is applicable to extracts derived from any matrices which are prepared according to the appropriate sample extraction SOPs. PCBs are determined and quantitated as Aroclor mixes.

1.2. Table 1 lists compounds routinely determined by this method and the CAS Number. RLs are easily accessible via the Laboratory Information Management System (LIMS). Matrix interferences and/or high concentrations of PCB compounds may result in higher RLs.

## 2. SUMMARY OF METHOD

2.1. PCBs in aqueous samples are prepared for analysis using continuous liquid/liquid or separatory funnel extraction (SOP NC-OP-037 and NC-OP-038). Solid samples are prepared using sonication or soxhlet extraction (SOP NC-OP-039 and NC-OP-040). After the initial preparation step, the sample is introduced into the GC and the concentration of each target analyte is measured by the detector response within a defined retention time (RT) window, relative to the response of the reference standards.

## 3. DEFINITIONS

3.1. Refer to the Test America Canton Quality Assurance Manual (QAM), current version, for definitions of terms and acronyms used in this document.

## 4. INTERFERENCES

4.1. Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. Co-elution of target analytes with non-targets can occur, resulting in false positives or biased high results. All glassware is cleaned per SOP NC-QA-014.

4.2. Interferences in the GC analysis can arise from many compounds which are amenable to gas chromatography and give a measurable response on the electron capture detector (ECD). Phthalate esters, which are common contaminants found in plastics, can pose a major problem in the determinations. Avoiding contact with any plastic materials minimizes interferences from phthalates.

4.3. Compounds extracted from the sample matrix to which the detector will respond, such as single-component chlorinated pesticides, including the DDT analogs (DDT, DDE, and DDD) will cause interference. A standard of the DDT analogs should be injected to determine which of the PCB or Aroclor peaks may be subject to interferences on the analytical columns used. There may be substantial DDT interference with the last major Aroclor 1254 peak in some soil and sediment samples.

4.4. Sulfur will interfere and can be removed using procedures described in SOP NC-OP-025.

4.5. Interferences co-extracted from samples will vary considerably. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts. These cleanup procedures are included in SOP NC-OP-025.

## 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. Eye protection that prevents splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Refer to the TestAmerica Canton Corporate Environmental Health and Safety Manual for a complete description of personal protection equipment.

5.2. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have become contaminated must be removed and discarded; other gloves must be cleaned immediately. Nitrile gloves provide adequate protection against the solvents used in this method.

5.3. 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 (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Acetone | Flammable | 1000 ppm-TWA | Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache. |
| Hexane | Flammable Irritant | 500 ppm-TWA | Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes. |
| Methylene Chloride | Carcinogen Irritant | 25 ppm-TWA 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. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

5.4. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

5.5. All $^{63}$Ni sources (ECD) must be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.

5.6. All $^{63}$Ni sources must be inventoried every six months. If a detector is missing, the EH&S Director must be immediately notified and a letter sent to the NRC or local state agency.

5.7. Exposure to chemicals must be limited as much 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. Opened containers of neat standards must be handled in a fume hood.

5.9. Sample extracts and standards, which are in a flammable solvent, must be stored in an explosion-proof refrigerator.

5.10. When using hydrogen gas as a carrier, all precautions listed in the CSM must be observed.

5.11. Standard preparation and dilution must be performed inside an operating fume hood.

5.12. The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.13. There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

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

## 6. EQUIPMENT AND SUPPLIES

6.1. Gas Chromatograph (GC) equipped with Electron Capture Detectors (ECDs)

6.2. Software: ChemStation or equivalent

6.3. Refer to Table 2 for analytical columns and run conditions

6.4. Microsyringes and syringes: various sizes, for standards preparation, sample injection, and extract dilution

6.5. Autosampler vials, inserts, and caps

6.6. Class A volumetric flasks: various sizes

6.7. Transfer pipettes: disposable

6.8. VOA vials

6.9. Carrier gas: Hydrogen

6.10. Makeup gas: Nitrogen

## 7. REAGENTS AND STANDARDS

7.1. Stock Standards: Stock standards are purchased as certified solutions or prepared from pure solutions.

7.1.1. Other stock standard solutions are stored as recommended by the manufacturer. All stock standards must be protected from light. Stock standard solutions must be brought to room temperature before using.

7.1.2. Stock standard solutions must be replaced after one year.

7.1.3. Expiration times for all standards are measured from the time the standard is prepared or from the time that the standard ampoule is opened, if the standard is supplied in a sealed ampoule. If vendor-supplied standard has an earlier expiration date then the vendor's expiration date is used. Refer to SOP NC-QA-017, Standards and Reagents, for additional information. The standard preparation information is detailed in the LIMS standards and reagents module.

7.2. Calibration Standards

7.2.1. PCB Calibration Standards

7.2.1.1. PCB calibration standards are prepared as dilutions of the stock standards. Surrogates and internal standards are used as specified in the method. PCB calibration solutions must be refrigerated at 4° C ± 2° C and protected from light. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem.

7.2.1.2. See the LIMS Reagent module for details on standard concentration and preparation.

7.3. Surrogate Standards

7.3.1. Tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) are the surrogate standards. Refer to the LIMS for details of surrogate standards.

7.4. Internal Standard

7.4.1. The internal standard used for PCB analysis is 1-Bromo-2-nitrobenzene (BNB)

## 8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Unless otherwise specified by regulatory or client programs, holding time for PCB samples (regardless of matrix) is 1 year.

8.2. Sample extracts are stored at 4 ± 2°C. The holding time for PCB sample extracts is 40

days.

## 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 at the same time using the same procedures and reagents. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank (MB). Laboratory generated QC samples (Method Blank, LCS and MS/MSD do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count. In some cases, at client request, the MS/MSD may be replaced with an MS and an un-spiked sample duplicate (DU).

9.2. Method Blank (MB)

9.2.1. For each batch of samples, analyze an MB. The MB consists of reagent water for aqueous PCB samples and sodium sulfate for PCB soils tests and all surrogates required for the analysis. Refer to SOPs NC-OP-037, NC-OP-038, NC-OP-039, and NC-OP-040 for details.

9.2.2. The MB must not contain any analyte of interest at, or above, the reporting limit or at, or above, 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

**Note:** Some programs require that the MB be clean to ½ the RL. Method notes should inform the analyst if the samples are part of a special program. Analysts are responsible for checking the program requirements.

9.2.3. Corrective action

9.2.3.1. Corrective action may include re-analysis of the MB. If the re-analysis fails to meet criteria, re-extraction and re-analysis of samples associated with an unacceptable MB is required when concentrations greater than the RL are detected in the samples.

9.2.3.2. 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.

**Note:** For Ohio VAP projects, the MB result must be below the reporting limit or samples must be re-extracted, unless the samples have no detections above the RL.

9.3. Laboratory Control Samples (LCS)

9.3.1. For each batch of samples, analyze an LCS. The LCS contains a representative subset of the analytes of interest and all surrogates required for the analysis. The LCS standard contains the same analytes as the matrix

spike. If any LCS analyte is outside the laboratory established historical control limits, corrective action must occur.

9.3.2. Corrective Action

9.3.2.1. Corrective action may include re-analysis of the LCS. If the re-analysis fails to meet criteria, re-extraction and re-analysis of the batch may be needed. If the LCS is biased high, samples that have no analytes detectable above the RL may be reported with proper narration.

**Note:** For Ohio VAP samples, re-analyze an aliquot of the LCS to verify the outlier; if the LCS exhibits the same anomaly upon re-analysis, the sample batch 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 LCS is biased high and the samples have no detections above the RL for those analytes. Under the above circumstances, results may be reported with proper narration.

9.3.3. LCS compound lists and surrogates are included in the reagent module of the LIMS.

9.4. Matrix Spikes/Spike Duplicates (MS/MSD)

9.4.1. For each QC batch, analyze an MS/MSD. Compare the percent recovery and relative percent difference (RPD) to those in the laboratory-specific historically generated limits.

9.4.2. If any individual recovery or RPD falls outside the acceptable range, corrective action must occur unless samples for this compound are ND. The initial corrective action must be to check the recovery of that analyte in the LCS. Generally, if the recovery of the analyte in the LCS is within limits, adverse matrix effect is indicated, the laboratory operation is in control and analysis may proceed.

9.4.3. If the recovery for any component is outside QC limits for both the MS/MSD and the LCS, the laboratory process is out of control and corrective action must be taken.

9.4.4. The MS/MSD must be analyzed at the same dilution as the un-spiked sample, unless the matrix spike components would then be above the calibration range.

9.5. Surrogates

9.5.1. Surrogates are added to all samples, and batch QC during the preparation procedure. Surrogates are added to instrument QC for the 1016/1260 Aroclor mix, which includes the calibration standards, and the CCVs. Surrogate recoveries in samples and QC samples must be assessed to ensure that recoveries are within established limits.

9.5.2. Method Blank

9.5.2.1. Surrogates are added to the MB and the MB is carried through the entire analytical procedure. The MB must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank 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. If surrogate recoveries are high, and the samples are non-detect, the data may be reported with proper narration.

**Note:** For Ohio VAP samples, all MB surrogates must meet criteria or the samples must be re-extracted if sufficient volume of sample remains. The exceptions are as follows: (a) insufficient sample for re-extraction (b) expired holding times, or (c) the surrogates are biased high and the samples have no detections above the RL.

9.5.3. LCS

9.5.3.1. The LCS must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the LCS has served the purpose of demonstrating effectiveness of the extraction process. If surrogate recoveries are low, re-extraction of the LCS and affected samples will normally be required. None of the surrogate recoveries can fall below 10% in the LCS. If surrogate recoveries are high, and the samples have no detections above the RL, the data may be reported with proper narration.

**Note:** For Ohio VAP samples, all LCS surrogates must meet criteria or the samples must be re-extracted if sufficient volume of sample remains. The exceptions are as follows: (a) insufficient sample for re-extraction (b) expired holding times, or (c) the surrogates are biased high and the samples have no detections above the RL.

9.5.4. Instrument QC

9.5.4.1. Surrogates in the 1016/1260 calibration standards must meet the same criteria as the ICAL. See section 10 for ICAL criteria.

9.5.4.2. Surrogates in the CCVs must have a %D of <15% for Method 8082, and <20% for Method 8082A.

9.5.4.3. Corrective actions for failing surrogates in the instrument QC are discussed in section 10.

9.5.5. Samples

9.5.5.1. If either surrogate is outside limits, the following corrective actions must take place (except for dilutions greater than 5X):

9.5.5.1.1. Check all calculations for error.

9.5.5.1.2. Ensure instrument performance is acceptable.

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

9.5.5.2. It is only necessary to re-prepare / re-analyze a sample once to demonstrate 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:** For Ohio VAP Projects, all surrogates must meet criteria unless the surrogates are out high and the samples have no detections above the RL. Otherwise, the analyst should re-analyze the sample, re-prep and re-analyze the sample, or a dilution may be performed if the analyst believes it will solve the issue. When there is an obvious interference causing the surrogate outlier that the analyst knows a corrective action would not resolve, it is permissible to flag the data with a qualifier indicating matrix interference.

9.5.5.3. If the surrogates are out of control for the sample and MS/MSD, then matrix effect has been demonstrated for that sample and re-preparation is not necessary. If the sample is out of control and the MS/MSD is in control, then re-preparation or flagging of the data is required. Re-preparation includes the parent sample and the MS/MSD.

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

9.6. Internal Standard (IS)

9.6.1. This procedure is an IS procedure. 1-Bromo-2-nitrobenzene (BNB) is the internal standard used.

9.6.2. Prior to analysis, the IS must be added to all standards, field sample extracts, and QC sample extracts. The concentration of the IS must be the same in all calibration standards, field sample extracts, and QC sample extracts. A concentration of 0.05 ug/mL is used.

9.6.3. The response of the IS in the ICV/CCV must be within 50-200% of the response of the IS in the CCV-level standard in the initial calibration sequence. If the response is outside of this range, the analysis of the ICV/CCV must be repeated and any samples associated with the ICV/CCV must also be re-analyzed. Repeated failure of the IS response will require recalibration.

9.6.4. The response of the IS in the samples and batch QC items must be within 50-200% of the response of the previous CCV. If the response is outside of the range, corrective action must be taken which may include re-analysis of the extract, re-spiking the extract with IS and re-analysis, or re-calibration of the analytical system. Obvious matrix interferences are qualified and noted in an NCM.

**Note:** OVAP samples with failing internal standards must be re-analyzed unless matrix interference is apparent. In cases where matrix interference is not obvious, spike a fresh aliquot of sample with IS solution and re-analyze. If the IS fails to meet criteria again, and the IS meets criteria in batch and instrument QC, the re-analysis serves to confirm matrix interference and the sample will be re-analyzed at a dilution as described below. If matrix interference is apparent, dilute the sample with hexane for re-analysis. When, in the analyst's professional judgment, there is obvious interference causing the IS failure that corrective action will not remedy, data must be flagged with a qualifier to indicate the effect of matrix interference. If the batch QC (MB and/or LCS) has failing internal standards, re-spike a fresh aliquot of the applicable QC sample with internal standard solution and re-analyze. If there is continuing failure, the batch may require re-preparation of the IS solution, and/or recalibration. If the ICV and/or CCV have failing internal standards, the batch must be re-analyzed. Continued failure may necessitate re-preparation of the IS solution and/or recalibration.

9.7. Control Limits

9.7.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.7.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMs.

## 10. CALIBRATION AND STANDARDIZATION

10.1. Internal or external calibration may be used. Prepare standards containing each analyte of interest at a minimum of five concentration levels. The low-level standard must be at, or below, the reporting limit. The other standards define the working range of the detector.

10.2. The initial PCB calibration must include at least one level with 1016 analyzed separately for pattern recognition purposes. This run does not have to be part of the calibration.

10.3. A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include new columns or replacing the ECD detector. A new calibration is not required after clipping the column, replacing the septum or syringe, or other minor maintenance, unless CCV criteria cannot be met.

10.4. With the exception of section 10.5 below, it is not acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or

lowest on the curve and the reporting limit and/or linear range is adjusted accordingly. In any event, at least five points must be included in the calibration curve. Quadratic (second order) calibrations require at least six points.

**Note:** Quadratic calibrations are not acceptable for PCB analysis for OVAP projects.

10.5. A level may be removed from the calibration if the reason can be clearly documented (for example, a broken vial or no purge run). A minimum of five levels must remain in the calibration. The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be re-analyzed and the re-analysis used for the calibration. All initial calibration points in a single calibration curve must be analyzed without any changes to instrument conditions, and all points in a single calibration curve must be analyzed within 24 hours.

10.6. Internal Standard Calibration

10.6.1. Internal standard calibration involves the comparison of instrument responses from the target compounds in the sample extract to the response of a specific standard added to the r sample extract prior to injection. This specific standard is referred to as the internal standard (IS) because it is contained within the aliquot of the sample extract and is actually injected into the instrumentation. The ratio of the peak area (or height) of the target compound in the sample extract to peak area (or height) of the IS in the sample extract is compared to a similar ratio derived for each calibration standard. The ratio is termed the response factor (RF), or relative response factor (RRF).

10.6.2. When preparing calibration standards for use with internal standard calibration, add the same amount of internal standard solution to each calibration standard, such that the concentration of each internal standard is constant across all of the calibration standards, whereas the concentrations of the target analytes will vary. The mass of the internal standard added to each sample extract immediately prior to injection into the instrument must be the same as the mass of the internal standard in each calibration standard. The volume of the solution spiked into sample extracts should be such that minimal dilution of the extract occurs.

10.6.3. Prepare calibration standards at a minimum of five concentration levels for each parameter of interest and each surrogate. Six standards must be used for a quadratic least squares calibration. Add the appropriate amount of the IS mixture to result in a 0.05 ug/mL concentration. The low standard must be at or below the reporting limit

10.6.4. Calculate response factors (RF), average response factors, and the percent RSD of the response factors for each compound and surrogate using the equations in Section 12.

10.7. External standard calibration

10.7.1. Quantitation by the external standard method assumes a proportional relationship between the analyte or surrogate response and the concentration

that is the same in all of the calibration standards and the samples. To use this approach, introduce each calibration standard into the GC using the technique that will be used for samples. The ratio of the peak height or area response to the mass or concentration injected is used to prepare a calibration curve.

10.8. Calibration Curve Fits

10.8.1. The calculations for all calibration curve fits are found in section 12.

10.8.2. Weighted linear regression, average calibration factor, non-weighted linear regression, or quadratic curves may be used to fit the data. - Average calibration factor is the preferred calibration model used for PCB.

10.9. Average calibration factor (CF) / response factor (RF)

10.9.1. The average CF (external calibration) or RF (internal standard) may be used if the average percent relative standard deviation (% RSD) of all the CFs / RFs taken together is $\leq$ 20%. The average % RSD is calculated by summing the %RSD value for each peak and dividing by the total number of peaks.

10.10. Linear Regression / Weighted Linear Regression

10.10.1. Linear / weighted linear regressions must have a minimum of 5 calibration levels with the lowest being at or below the reporting limit. The correlation coefficient (r) must be >0.990. The ICV %D must be <20%, and the CCV %D must be <15% for Method 8082. For Method 8082A, the criteria for both ICV and CCV are < 20% % D.

10.11. Quadratic Curve

10.11.1. A quadratic calibration curve must only be used if the analyst has reason to believe that a linear or average model does not fit the normal concentration-to-response behavior of the detector. A quadratic curve fit may be used only if the compounds have historically exhibited a non-linear response and cannot be used to extend the calibration range for compounds that normally exhibit a linear response, but within a narrower calibration range.

10.11.2. A quadratic calibration curve must have a minimum of 6 calibration levels with the lowest being at or below the reporting limit. The coefficient of determination ($r^2$) must be > 0.990.

10.12. Evaluation of Calibration Curves

10.12.1. The percent relative standard error (% RSE) from the calibration curve is used to evaluate the initial calibration. This provides a measure of how much error is associated with using the calibration curve for quantitation.

10.12.2. The least squares regression line is calculated and used to calculate the predicted concentration for each level.

**Note:** When average calibration factors are used, %RSE is equivalent to %RSD.

10.13. The following requirements must be met for any calibration to be used.

10.13.1. Response must increase with increasing concentration.

10.13.2. If a curve is used, the calculated intercept of the curve at zero response must be less than ± the reporting limit for the analyte.

10.13.3. The average Relative Standard Error (RSD for average response factors) of the calibration points from the curve used must be ≤ 20%.

10.13.4. Some data systems will not measure the %RSE from a linear or quadratic fit. For the linear case, the correlation coefficient may be used as an alternative to the %RSE, and must be greater than or equal to 0.990. For the quadratic case the Coefficient of Determination (COD) may be used, and must be greater or equal to 0.990.

**Note**: The Relative Standard Error (RSE) is superior to the Correlation Coefficient (*r*) and Coefficient of Determination ($r^2$) for testing the fit of a set of calibration points to a line. The lower points on a curve have little effect on *r.* As a result, a curve may have a very good correlation coefficient (>0.990) while also having > 100% error at the low point.

**Note**: The surrogates must be judged against these same criteria.

10.14. Weighting of Data Points

10.14.1. In linear and quadratic calibration fits, the points at the lower end of the calibration curve have less absolute variance than points at the high concentration end of the curve. This can cause severe errors in quantitation at the low end of the calibration. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason, it is preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and must be used when an average calibration factor is not appropriate, as long as the data system has this capability.

10.15. Initial Calibration

10.15.1. A minimum five-point calibration of all Aroclors is generated. The low-level standard must be at or below the reporting limit. The other standards define the working range of the detector.

10.15.2. If any Aroclor is determined above the calibration range, the extract must be diluted and re-analyzed.

10.15.3. The surrogate calibration curve is included in the calibration from the Aroclor 1016/1260 mix.

10.16. Initial Calibration Verification (ICV)

10.16.1. The ICVs are analyzed immediately after an initial calibration. The acceptance criterion is ± 20%.

10.16.2. If the overall average percent drift of all analytes is greater than ±20%, corrective action must be taken. This may include clipping the column, changing the liner, or other minor instrument adjustments, followed by re-analyzing the standard. If the overall average percent drift still varies by more than ±20%, a new calibration curve may be required.

10.17. Continuing Calibration Verification (CCV)

10.17.1. It is not necessary to run a calibration verification standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.

10.17.2. Mid-level standards covering all Aroclors of interest are used for the calibration verifications.

10.17.3. CCVs are analyzed for all Aroclors at the beginning of each day, and at the beginning of each 12 hour shift.

10.17.4. Retention times windows are updated daily from the opening CCVs.

10.17.5. Evaluate the resolution of the triplet towards the end of the 1260 chromatogram in the opening CCV. There must be at least 25% resolution on one of the two columns used.

10.17.6. The Aroclor 1016/1260 CCV is analyzed after every 20 injections. Depending on the type of samples, it may be advisable to analyze verifications more frequently in order to minimize reruns.

**Note:** Various programs require a CCV every 10 injections. Analysts are responsible for checking the program requirements.

10.17.7. For Method 8082A, the CCV acceptance criterion is ± 20%. For Method 8082, the CCV acceptance criterion is ±15%.

10.17.8. A bracketing CCV is not required for IS calibrations.

10.17.9. Samples quantitated against an external standard calibration must be bracketed by a 1016/1260 CCV.

10.17.10. Corrective Actions for Continuing Calibration Failures

10.17.10.1. If a CCV fails to meet criteria, corrective action must be taken. This may include clipping the column, changing the liner, or other minor

instrument adjustments, followed by re-analyzing the standard. If the re-analysis still fails to meet criteria, a new calibration curve may be required.

10.17.10.2. Samples quantitated against an external standard calibration must be bracketed with passing CCVs. All samples analyzed immediately prior to, and immediately following the failing CCV must be re-analyzed.

10.17.10.3. Sample results that are below the reporting limit may be reported when a CCV is biased high. Such action must be addressed in the case narrative.

10.18. Retention Time Windows

10.18.1. Retention time (RT) windows must be determined for all analytes.

10.18.2. Initial determination of Retention time windows

10.18.2.1. The center of the retention time (RT) window shall be updated based on the middle level in the initial calibration or the first CCV in the daily analytical sequence, whichever is more recent.

10.18.2.2. Evaluate the deviation from expected retention time for each analyte in at least three CCV and/or LCS samples spread over at least 72 hours. Calculate the standard deviation of these retention times.

10.18.2.3. If three days of analytical data are not available, use a default RT window of 0.01 minutes. At the end of the batch evaluate all CCVs and LCS in the batch. If necessary, widen the window such that all analytes fall within the RT window. Reprocess the batch using the new RT windows.

10.18.2.4. Multiply the standard deviation by 3. This is the retention time window, unless the result is less than 0.01 min, in which case the window is set at 0.01 min.

10.18.2.5. An alternative method to determine the retention time window is to multiply the maximum deviation of all points by 1.5. The minimum retention time window is 0.01 minutes. For example, if the maximum RT deviation for a specific analyte is 0.008 min, then the RT window is set at ± 0.012 min.

**Note:** For multi-component analytes, like Aroclors, the maximum deviation must be evaluated for each of the 3 to 6 major peaks used for sample calculations.

10.18.2.6. If the retention time windows for analytes of interest overlap, the analyte must be confirmed on a dissimilar column.

10.18.3. Ongoing evaluation of retention time windows

10.18.3.1. Evaluate the retention time windows on an ongoing basis. The center of the RT window is updated on the first CCV of the day and verified every 12 hours. All analytes for all subsequent CCVs, LCS and matrix spikes must fall within the retention time window (except as discussed below).

10.18.3.2. Matrix spike analytes may fall outside the retention time window if there is a large non-target peak coeluting with the analyte in the matrix spike.

10.18.3.3. If any analytes fall outside the retention time window in CCVs, LCS or matrix spikes (except as discussed above for matrix spikes) then the RT windows for those analytes shall be widened to the minimum degree required for the analyte to fall within the RT window. All samples in the batch shall be reprocessed with the new RT window, and the wider RT window shall remain in place for subsequent batches.

10.18.3.4. Retention time windows should be reliably narrower than +/- 0.03 min. If RT windows wider than this are necessary, the instrument should be evaluated and maintenance performed as needed. Subsequent to maintenance, RT windows shall be narrowed to the extent that is consistent with the data obtained.

## 11. PROCEDURE

11.1. 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. The Nonconformance Memo must be filed in the project file. The nonconformance is also addressed in the case narrative. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

**Note:** Procedural deviations are not allowed for Ohio VAP Projects.

11.2. Extraction

11.2.1. Extraction procedures are referenced in the SOPs NC-OP-037, NC-OP-038, NC-OP-039, and NC-OP-040, current revisions.

11.3. Suggested gas chromatographic conditions are given in Table 2.

11.4. Allow extracts to warm to ambient temperature before injection.

11.5. Sample Analysis

11.5.1. For samples analyzed by IS calibration models, transfer 100 µL of the extract to an autosampler vial and add 5 µL of the IS solution or equivalent volumes to give an IS concentration of 0.05 ug/mL. The concentration of the internal standard must be the same in all calibration samples, field samples, and QC samples. -.

11.5.2. For samples analyzed by external calibration models, transfer an adequate amount of extract into an autosampler vial and load the vials onto the instrument.

11.5.3. The sample extract must be injected using the same injection volume used for the calibration standards.

11.5.4. If highly contaminated samples are expected, it is acceptable to analyze solvent blanks or primers at any point in the run. Solvent blanks may not be routinely analyzed prior to QC samples.

11.6. Identification of Aroclors

11.6.1. The laboratory performs Update IV's recommended analysis of DDT and analogs DDD and DDE daily to assure there is no interference with major 1254 peaks.

11.6.2. Retention time windows are used for the identification of Aroclor peaks, but the "fingerprint" produced by major peaks of those analytes in the standard is used to differentiate the identity of any Aroclor that may be present. The ratios of the areas of the major peaks are also taken into consideration. Analyst judgement must weigh heavily in the identification of Aroclor patterns. Identification may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

11.7. Quantitation of Aroclors

11.7.1. For PCB analysis, the preferred reporting approach is the primary column approach. Dependent upon client program, the higher or lower result may be used for quantitation. Results may be report from the confirmation column when matrix interference is present and impacts either the IS or specific compounds and the RPD between columns.

11.7.2. Use 3-5 major peaks for quantitation

11.7.3. If the analyst believes that a combination of Aroclor 1254 and 1260 or a combination of 1242, 1248 and 1232 is present, then only the predominant

Aroclor is quantitated and reported, but the suspicion of multiple Aroclors is discussed in the narrative. If well-separated Aroclor patterns are present, then multiple Aroclors may be quantitated and reported.

11.7.4. Every sample undergoes dual column analysis; however, reporting the second column results will only be performed when requested by the client or regulatory program. The appearance of the multiple characteristic peaks in the sample usually serves as a confirmation of the presence of an Aroclor.

11.8. Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX). Corrective action is necessary if either DCB or TCMX are outside of acceptance limits. Samples may be reported when there is obvious matrix interference present; however, such action must be included in the case narrative.

**Note:** For Ohio VAP samples all surrogates must meet acceptance limits, unless the surrogate is biased high and the sample has no detections above the RL.

11.9. Dilutions

11.9.1. Samples may be screened to determine the appropriate dilution for the initial run.

11.9.2. If concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and re-analyzed.

11.9.3. Dilutions must target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range when allowed by sample matrix.

11.9.4. It may be necessary to dilute samples due to matrix. Analyst judgment is required to determine the most concentrated dilution that will not result in instrument contamination.

11.9.5. If the sample is run at a dilution and only minor matrix interferences are observed, then the sample should be re-analyzed at a more concentrated dilution in an attempt to target the upper half of the calibration range.

11.9.6. The most concentrated dilution with no target compounds above the calibration range should be reported. Other dilutions may be reported at client request if the lower dilutions will not cause detector saturation, column overload, or carryover. Analyst judgment and client site history will be factors in the reporting of multiple dilutions.

11.10. Interferences

11.10.1. If peak detection is prevented by interferences, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

11.11. Reporting of Data

11.11.1. The preferred reporting approach is the primary column approach, where the analyst evaluates the opening CCVs and designates a primary column to report data from. All data is reported from the primary column in an analytical run, as long as the RPD between columns is less than 40%.

11.11.2. When the RPD between the primary and confirmation column exceeds 40%, it is an indication of likely matrix interference. Every situation is different and the analyst must rely on their experience in choosing which data to report. Two common issues are addressed below:

11.11.2.1. When there is interference with an analyte of interest, the higher result is likely biased due to matrix; therefore, the lower result is reported.

11.11.2.2. When there is interference with the IS, the results on the entire column are biased; therefore, the column without interference in the IS may be the better result. Dilution and reanalysis may be required when there is interference with the IS.

11.12. Analytical Documentation

11.12.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.12.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

**Note:** When making new standards, it is required that all information entered into TALS is reviewed by another analyst.

11.12.3. Record sample and associated QC information in the LIMs. Level I and Level II technical reviews are performed in LIMS.

## 12. DATA ANALYSIS AND CALCULATIONS

12.1. Calibration Calculations

12.1.1. Calibration Factor (CF) for external calibration and Response Factor (RF) internal standard calibration

$$CF = \frac{A_s}{C_s}$$

Where $A_s$ = Peak area (or height) in standard

$C_s$ = Concentration of standard injected

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

Where: $A_x$ = Peak Area (or height) of the analyte or surrogate

$A_{is}$ = Peak Area (or height) of the internal standard

$C_x$ = Concentration of the analyte or surrogate (µg/L)

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

12.1.2. Evaluating the linearity of the initial calibration using an Average Calibration fit:

$$Mean\ CF = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$ (external calibration)

$$Mean\ RF = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$ (internal standard calibration)

Where n = the number of calibration standards

$$Standard\ Deviation\ (SD) = \sqrt{\frac{\sum_{i=1}^{n}(CF_i - \overline{CF})^2}{n-1}}$$ (external calibration)

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(RF_i - \overline{RF})^2}{n-1}}$$ (internal standard calibration)

Where n = the number of calibration standards

$$\%RSD = \frac{SD}{\overline{CF}} \times 100$$ (external)

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$ (internal standard)

**Note:** If the RSD of the calibration or response factors is less than or equal to 20%, the average calibration or response factor may be used to determine sample concentrations.

12.1.3. Percent Difference (%D)

$$\%D = \frac{CF_c - \overline{CF}}{\overline{CF}} \times 100$$

Where $CF_c$ = The calibration factor from the CCV or ICV

$\overline{CF}$ = The average calibration factors from the initial calibration

$$\%D = \frac{RF_c - \overline{RF}}{\overline{RF}} \times 100$$

Where $RF_c$ = The response factor from the CCV or ICV

$\overline{RF}$ = The average response factors from the initial calibration

12.2. Linear regressions

y = ax + b

Where y = Instrument response (area or height)

a = Slope of the line

x = Concentration of the calibration standard

b = The intercept

12.2.1. For internal standard the equation for weighted or non-weighted linear regression is:

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

Where $A_s$ = Area (or height) of the peak for the target analyte in the sample

$A_{is}$ = Area (or height) of the peak for the internal standard

$C_s$ = Concentration of the target analyte in the calibration standard

$C_{is}$ = Concentration of the internal standard

a = Slope of the line

b = The intercept

12.2.2. Correlation Coefficient

$$r = \frac{\sum d_x d_y}{\sqrt{\sum d_x^2 \sum d_y^2}}$$

Where:

$d_x$ = deviation of x from the mean

$d_y$ = deviation of y from the mean

12.2.3. Relative Standard Error (%RSE)

$$\%RSE = 100\% \times \sqrt{\frac{\sum_{i=1}^{n} \left[\frac{C_i - PC_i}{C_i}\right]^2}{(n-p)}}$$

Where: n = Number of points in the curve
p = Number of parameters in the curve (= 1 for average response factor, 2 for linear, 3 for quadratic)
$C_i$ = True concentration for level i
$PC_i$ = Predicted concentration for level i

12.2.4. Percent Drift for CCV and ICV

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

Where: $C_{actaul}$ = Known concentration in standard

$C_{found}$ = Measured concentration in CCV or ICV

12.2.5. Curve weighting may be beneficial for linear regressions. Curve weighting improves the linearity at the low end of the calibration curve. Weighted curve calculations are similar to the unweighted calculations above, but use 1/x or $1/x^2$ (where x = concentration) to determine the regression instead of the concentration.

12.3. Quadratic calibration fit (only to be used if applicable)

$y = ax^2 + bx + c$

Where: y = Response

x = Concentration

a = Curvature

b = Slope

c = Intercept

12.3.1. Coefficient of Determination (COD)

$$COD = r^2 = \frac{\sum_{i=1}^{n}(y_{obs} - \bar{y})^2 - \left(\frac{n-1}{n-p}\right)\sum_{i=1}^{n}(y_{obs} - y_i)^2}{\sum_{i=1}^{n}(y_{obs} - \bar{y})^2}$$

Where: $y_{obs}$ = Observed response (area) for each concentration from each initial calibration standard

$\bar{y}$ = Mean observed response from the initial calibration

$y_i$ = Calculated response at each concentration from the initial calibration

n = Total number of calibration points

p = Number of adjustable parameters in the polynomial equation (2 for second order polynomial)

12.4. Concentration

12.4.1. Aqueous

$$Concentration\ \left(\frac{\mu g}{L}\right)\frac{C_{ex}V_t}{V_o}$$

Where $C_{ex}$ = On-column concentration as determined in sections 12.1-12.3. (ng/µL)

$V_t$ = Final extract volume (µL)

$V_o$ = Initial sample volume (mL)

12.4.2. Non-aqueous

$$Concentration\ \left(\frac{\mu g}{Kg}\right) = \frac{C_{ex}V_t}{W_s D}$$

Where $C_{ex}$ = On-column concentration as determined in sections 12.1-12.3. (ng/µL)

$V_t$ = Final extract volume (µL)

$W_s$ = Initial sample mass (g)

D = (100-%moisture in sample) / 100 for dry weight basis

or

D = 1 for a wet weight basis

## 13. METHOD PERFORMANCE

13.1. Method Detection Limit

13.1.1. Each laboratory must generate a valid method detection limit 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 SOP CA-Q-S-006.

13.2. Training Qualification

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

## 14. POLLUTION PREVENTION

14.1. 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 Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

## 15. WASTE MANAGEMENT

15.1. All waste must 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 must 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. Vials containing sample extracts. These vials are placed in the vial waste located in the GC/MS laboratory.

15.2.2. **Tubes containing sample extracts, for PCBs:** these are capped and placed in the PCB/flammable waste located the GC prep laboratory.

15.2.3. Samples, standards, and all extraction materials contaminated with high levels (>50ppm) of PCB's must be segregated into their own waste stream. PCB wastes are collected in one of three waste streams, solid PCB, liquid PCB and PCB vial waste. PCB containing samples are located through a LIMS query and disposed of as PCB containing.

15.2.4. **Extracted solid samples contaminated with methylene chloride/acetone or acetone/hexane:** These materials are disposed of in the solid waste and debris in a red container located in the Extractions Lab.

15.2.5. **Discarded samples:** These samples are collected in the solid debris drum.

## 16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, and Section 8000B

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

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

16.4. Corporate Quality Management Plan (CQMP), current versions

16.5. SW846, Update III, December 1996, Method 8082

16.6. SW846, Update IV, Revision 1, February 2007, Method 8082A

16.7. Reporting Results for Methods that Require Dual Column, CA-Q-P-004

16.8. Policy for Determining RT Windows for GC/ECD Tests, CA-T-P-005

16.9. Revision History

| | | | | |
|---|---|---|---|---|
| Historical File: | | | | |
| Revision 0: 03/17/14 | | | | |
| Revision 1: 01/14/16 | | | | |
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**4/17/19: Changed logo and copyright information. No change made to revision number or effective date.*

16.10. Associated SOPs and Policies, current version

16.10.1. QA Policy, QA-003

16.10.2. Glassware Washing, NC-QA-014

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

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

16.10.5. Standards and Reagents, NC-QA-017

16.10.6. Cleanup Procedures for Organic Extractable Samples, NC-OP-025

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

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

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

16.10.10. Continuous Liquid / Liquid Extraction of Organic Compounds from Waters Based on Methods SW846 3520C and 600 Series and Waste Dilution Based on Method 3580A, NC-OP-037

16.10.11. Separatory Funnel Extraction of Organic Compounds from Waters Based on Methods SW846 3510C and 600 Series and Waste Dilution Based on Method, NC-OP-038

16.10.12. Sonication Extraction of Organic Compounds from Soils Based on Method SW846 3550C and Waste Dilution Based on Method 3580A, NC-OP-039

16.10.13. Soxhlet (Traditional) Extraction of Organic Compounds from Soils Based on Method SW846 3540C and Waste Dilution Based on Method 3580A, NC-OP-040

## 17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Chapter 1 of SW-846 states the method blank must not contain any analyte of interest at, or above, the Method Detection Limit. This SOP states the Method

Blank must not contain any analyte of interest at, or above, the reporting limit.

17.1.2. The extended hold time for PCBs can be applied to 8082 as per SW846 Update IV. State requirements should be consulted as applicable.

17.2. Tables

| Table 1 | |
|---|---|
| **Standard Analyte List and CAS Numbers** | |
| **Compound** | **CAS #** |
| Aroclor 1016 | 12674-11-2 |
| Aroclor 1221 | 11104-28-2 |
| Aroclor 1232 | 11141-16-5 |
| Aroclor 1242 | 53469-21-9 |
| Aroclor 1248 | 12672-29-6 |
| Aroclor 1254 | 11097-69-1 |
| Aroclor 1260 | 11096-82-5 |

| **TABLE 2**<br>**Suggested Instrumental Conditions for Methods 8082 and 8082A** | |
|---|---|
| **Parameter** | **Recommended Conditions** |
| Injection port temp | 220°C |
| Detector temp | 325°C |
| Temperature program | 70°C for 0.5min, 30°C/min to 190°C, 2.5°C/min to 225, 18°C/min to 280°C, 3 min hold |
| Column 1 | CLPesticide I, 30m, 0.53mm ID, 0.5µm |
| Column 2 | CLPesticide II, 30m, 0.53 mm ID, 0.5µm |
| | |
| Injection | 1-2 µL, - |
| Carrier gas | Hydrogen |
| Make up gas | Nitrogen |
| Y splitter | Glass, Restek or equivalent |

# Title: Total Organic Carbon
# Lloyd Kahn Method

**Approval Signatures:**

Don Dawicki
Laboratory Director

Luke Orchard
Quality Assurance Manager

Matt Kirk
Department Manager

Ben Kirchner
EHS Coordinator/CLP-SVOA Dept. Manager

**Approval Date: January 17, 2017**



**Facility Distribution No. Electronic** **Distributed To: Facility Intranet**

**The controlled copy of this SOP is the PDF copy of the SOP that is posted to the laboratory's SOP Directory. Printed copies of this SOP or electronic copies of this SOP distributed outside the facility are considered uncontrolled.**

## 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.

## 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℃ for 30-60 minutes to se parate 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

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. The table does not include all materials used in the procedure. A complete list of materials used can be found in section 7.0. 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. Any questions regarding the safe handling of these materials should be directed to the laboratory's Environmental Health and Safety Coordinator.

## 6.0 Equipment and Supplies

- Drying Oven: Capable of maintaining a temperature of 105 ±2℃.
- 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. Listed below are the recommended minimum sample size, preservation and holding time requirements:

| Matrix | Sample Container | Minimum Sample Size | Preservation | Holding Time | Reference |
|---|---|---|---|---|---|
| Solids | Amber glass | 10 g | Chilled to ≤ 4℃ | 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°C for 60 minutes. Fold the capsules. A blank (empty) tin must be dropped for the calibration blank. Proceed to Section 10.6 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.
- 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 Calculations / Data Reduction

### 11.1 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.

### 11.2 Data Review

#### 11.2.1 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.

#### 11.2.2 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.

#### 11.2.3 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.

## 12.0 Method Performance

### 12.1 Detection Limit (DL), Limit of Detection (LOD) and Limit of Quantitation (LOQ)

Establish a DL, LOD and LOQ for the method. Verify the LOQ at initial method set up following the procedures specified in laboratory SOP BR-QA-005. Verify the LOD and LOQ at the frequency established for the method using the procedures specified in BR-QA-005. The frequency of LOD and LOQ verification depends on the strictest frequency of the regulatory program for which the method supports. The frequency requirement is documented in a spreadsheet maintained by the QA Department.

### 12.2 Annual Precision and Accuracy Study

It is recommended by the laboratory that a P&A study be performed for each project site. In the absence of a site specific P&A study the laboratory will analyze the LCS in quadruplicate for comparison to an annual P&A study on historical LCS recoveries of at least 15 data points. Perform a precision and accuracy study annually or as directed in project setup by analyzing 15 replicates of a representative sample (LCS). Create a control chart of the results, calculate the standard deviation and generate an upper and lower limit at 3X the standard deviation. Use the results of the appropriate P&A study for evaluation of the quadruplicate LCS or sample included in each batch.

## 13.0 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."

## 14.0 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.

## 15.0 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)

## 16.0 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. |

## 17.0 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

## 18.0 Revision History

BR-WC-008, Revision 16.0

- Added Appendix D for Marine Sediment Process.
- Added Appendix E for Black Carbon Process.
- Combined BR-ME-008 and BR-ME-024 .
- Section 2: Added 30-60 minute requirement
- Section 10.1: Clarified a blank tin must be analyzed for calibration blank.
- Section 10.3: Clarified acidification-added verbiage “until reaction ceases.”; Added sample size requirement is due to instrumentation
- Section 10.3: Clarified MB is an acidified tin, and calibration blanks must analyze a blank tin.
- Section 10.4: Clarified calibration blanks must analyze a blank tin.

- Section 10.5: added sequence clarification for Routine & Dixon analysis, as well as clarification for blank analysis.
- Section 11.12.1: Added when to perform additional reps for Dixon analysis and to fill out Dixon Outlier Template FWC200.

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

---

### 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℃ oven. Grind the sample with the pink mor tar 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: SOXHLET (TRADITIONAL) EXTRACTION OF ORGANIC COMPOUNDS FROM SOILS BASED ON METHOD SW846 3540C**

**[Method: SW846 3540C]**

**Approvals (Signature/Date):**

| | | | |
|---|---|---|---|
| Technology Specialist | 05/14/18 Date | Health & Safety Coordinator | 05/14/18 Date |
| Quality Assurance Manager | 05/16/18 Date | Technical Director | 05/14/18 Date |

**This SOP was previously identified as SOP No. NC-OP-040, Rev 5a, dated 5/25/17**



**Facility Distribution No. _____** **Distributed To:_____**

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## 1. SCOPE AND APPLICATION

1.1. This SOP describes procedures for preparation (extraction) of semivolatile organic analytes in soil, sediment, waste and wipe matrices for analysis by Gas Chromatography (GC) and Gas Chromatography/Mass Spectrometry (GC/MS) using Soxhlet Extraction. The procedures are based on SW846 series methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.1.1. Extraction procedures for the following determinative methods are covered: 8081A, 8081B, 8082, 8082A, 8270C, 8270D, 8015B, 8015C, and 8015D.

1.1.2. The extraction procedures herein may be appropriate for other determinative methods when appropriate spiking mixtures are used.

## 2. SUMMARY OF METHOD

2.1. Soxhlet Extraction (Traditional)

2.1.1 A 30 g sample (10 g for Pesticides and PCBs) is mixed with anhydrous sodium sulfate until free flowing, or a 1 wipe sample is placed in an extraction thimble. They are extracted by refluxing with solvent.

2.2. Concentration

2.2.1 Procedures are presented for drying the extract and concentration of the extract to final volume for analysis.

## 3. DEFINITIONS

3.1. Definitions of terms and acronyms used in this SOP may be found in the glossary of the 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. 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. Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented.

## 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. 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 become contaminated must be removed and discarded; other gloves must be cleaned immediately.

5.3. The following analytes have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'dichlorobenzindine, benzo(a)pyrene, alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, dibenz(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyl compounds. Primary standards of these toxic compounds must be prepared in the hood.

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 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. |
| Acetone | Flammable | 1000 ppm-TWA | Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache. |
| Hexane | Flammable Irritant | 500 ppm-TWA | Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes. |
| **Note:** Always add acid to water to prevent violent reactions. | | | |
| 1 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

5.5. Exposure to hazardous 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.

5.6. The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride must be conducted in a fume hood with the sash closed as far as the operations will permit. If more than 500 mL of

methylene chloride is spilled, evacuate the area until the area has been cleaned by EH&S.

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

5.8. During Kuderna-Danish (KD) concentration, do not allow the extract to boil to dryness. The solvent vapors remaining in the KD apparatus may superheat and create an explosion or fire hazard. The KD apparatus and glass separatory funnels have ground glass joints that can become stuck. Technicians must use Kevlar or other cut/puncture-resistant gloves when separating stuck joints.

## 6. EQUIPMENT AND SUPPLIES

6.1. Glassware must be cleaned per Glassware Washing, SOP NC-QA-014.

6.2. Equipment and supplies for extraction procedures:

| EQUIPMENT AND SUPPLIES | Sox | Conc |
|---|---|---|
| Graduated cylinder: 1 liter. (other sizes may be used as needed) | | √ |
| Erlenmeyer flask: 250 mL (other sizes optional) | | √ |
| Solvent dispenser pump or 100 mL graduated cylinder | √ | √ |
| Round or flat bottom: 250 mL | √ | |
| Boiling chips: contaminant free, approximately 10/40 mesh (Teflon® PTFE, carbide or equivalent) | √ | √ |
| Cooling condensers | √ | |
| Heating mantle: rheostat controlled or equivalent | √ | |
| Auto-timer for heating mantle | √ | |
| Soxgriddle or equivalent | √ | |
| Beakers: 450mL wide-mouth glass jars | | √ |
| Balance: >100 g capacity, accurate to ±1.00 g | √ | √ |
| Soxhlet extractor | √ | |
| Cellulose and glass thimbles | √ | |
| Kuderna-Danish (K-D) apparatus: 500 mL | | √ |
| Concentrator tube: 10 mL, attached to K-D with clips | | √ |
| Snyder column: three-ball macro | | √ |
| Water bath: heated, with concentric ring cover, capable of temperature control (± 5°C) up to 95°C. The bath must be used in a hood or with a solvent recovery system. | | √ |
| Vials: glass, 2 mL and 40 mL capacity with Teflon®-lined screw-cap | | √ |
| Clean wipes for wipe matrix method blanks and laboratory control samples | | |
| Nitrogen blowdown apparatus | | √ |

| EQUIPMENT AND SUPPLIES | Sox | Conc |
|---|---|---|
| Nitrogen: reagent grade. | | √ |
| Culture Tubes: 10 mL, 16 x100 mm | | √ |
| Microliter pipette and/or syringe 1 mL | √ | |
| Glass wool | √ | |
| Glass funnel: 75 X 75 mm | √ | √ |
| Disposable pipettes, 5 ¾ in, and 9in. | √ | √ |

## 7. REAGENTS AND STANDARDS

7.1. Reagents for Extraction Procedures

7.2. All reagents must be ACS reagent grade or better, unless otherwise specified.

| REAGENTS | Sox | Conc |
|---|---|---|
| Sodium sulfate ($Na_2SO_4$), Granular, Anhydrous: Purify by heating at 800°C a minimum of one hour. | √ | √ |
| Magnesium sulfate | √ | |
| Extraction Solvents (pesticide quality or equivalent): Methylene chloride, Methylene Chloride/acetone hexane/acetone, | √ | √ |
| Hexane/Acetone:, reagent grade: Used for cleaning glassware. | √ | √ |

7.3. Standards

7.3.1. Stock Standards

7.3.1.1. Stock standards are purchased as certified solutions. S tock 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 (from the time of preparation, if prepared in house, or from the time the ampoule is opened, if purchased). Standards that are cold stored must be allowed to come to room temperature before use.

7.3.2. Surrogate Spiking Standards

7.3.2.1. Prepare or purchase surrogate spiking standards at the concentrations listed in Table 2. Surrogate spiking standards are purchased or prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light, or stored according to manufacturer's instructions. The standards must be replaced every six months at a minimum, or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.3. Matrix Spiking and Laboratory Control Spiking Standards

7.3.3.1. The same spiking solution is used for the matrix spike and the Laboratory Control Sample. Prepare MS/LCS spiking standards at the concentrations listed in Table 3. Spiking standards are purchased or prepared as dilutions of the stock standards.

7.3.3.2. Spiking solutions must be refrigerated and protected from light, or stored according to manufacturer's instructions. The standards must be replaced every six months at a minimum, or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.4. See SOP NC-QA-017 for additional information on Standards and Reagents.

## 8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored at 4°C ± 2°C in glass containers with Teflon®-lined caps.

8.3. Holding Times

8.3.1. The holding time for solid and waste samples is 14 days from sampling to extraction.

8.3.2. Analysis of the extracts is completed within 40 days of extraction.

## 9. QUALITY CONTROL

9.1. Quality Control Batch

9.1.1. The batch is a set of up to 20 client samples and appropriate QC that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank (MB), an LCS, and a matrix spike/matrix spike duplicate (MS/MSD). (In some cases, at client request, it may be appropriate to process a matrix spike and un-spiked sample duplicate in place of the MS/MSD). If clients designate specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs. See Policy QA-003 for further definition of the batch.

9.2. Method Blank (MB)

9.2.1. An MB consisting of all reagents added to the samples must be prepared and analyzed with each batch of samples. Surrogates are spiked into the MB at the same level as the samples. See Table 2 for the appropriate amount of surrogate to use for each analytical method. The MB is used to identify any background interference or contamination of the analytical system which may lead to the reporting of elevated concentration levels or false positive data.

9.2.2. For a solid MB, use approximately 30 g of sodium sulfate spiked with the surrogates. For PCB and Pesticides, use approximately 10 g ± 0.5 g of sodium sulfate. See Table 2 for the appropriate amount of surrogate to use for each analytical method. The MB goes through the entire analytical procedure.

9.2.3. For a wipe MB, use 1 clean wipe spiked with the surrogates. See Table 2 for the appropriate amount of surrogate to use for each analytical method. The MB goes through the entire analytical procedure.

9.3. Laboratory Control Sample (LCS)

9.3.1. LCSs are well-characterized laboratory-generated samples used to monitor the laboratory's day-to-day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision. The LCS goes through the entire analytical procedure.

9.3.2. The LCS is made up in the same way as the MB (see Sections 9.2.1 through 9.2.3), but spiked with the LCS standard and the surrogates. See Table 3 for the appropriate amount of spike to use for each analytical method.

9.4. Surrogates

9.4.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.4.2. Each applicable sample, MB, LCS, and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits of the applicable determinative method. See Table 2 for the appropriate amount of surrogate spike to use for each analytical method.

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

9.5.1. An MS is an environmental sample to which known concentrations of target analytes have been added. An MSD is a second spiked aliquot of the same sample, which is prepared and analyzed along with the sample and MS. See Table 3 for the appropriate amount of spike to use for each analytical method.

9.6. QC requirements can be found in the various associated analytical SOPs.

9.7. Control Limits

9.7.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.7.2. Laboratory control limits are internally generated and updated periodically, unless method specified. Control limits are easily accessible via the LIMs.

9.8. Method Detection Limits (MDLs) and MDL Checks

9.8.1. MDLs and MDL Checks are established and performed by the laboratory as described in SOPs CA-Q-S-006.

9.8.2. MDLs are easily accessible via the LIMs.

9.9. Nonconformance and Corrective Action

9.9.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

## 10. CALIBRATION AND STANDARDIZATION

10.1. On a weekly basis, measure the appropriate volumes of solvents into the appropriate sized glass culture tubes gravimetrically. The “standard” glass culture tubes are sealed, and the meniscus is noted by marking a line on the tubes. The glass culture tubes containing the sample final extracts are then compared against the “standard” glass culture tubes of the appropriate volume and solvent to ensure the volumes are consistent. (See Table 1 for final volumes)The bottle top dispenser is calibrated quarterly and must be within ±5% of the target volume with an RSD ≤ 1%.

10.2. All labware, pipettes, and balances are calibrated according to SOPs NC-QA-004 and NC-QA-015.

## 11. PROCEDURE

11.1. Procedural Variations

11.1.1. 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 and approved by a supervisor. The Nonconformance memo will be filed in the project file. Procedural variations are not allowed for Ohio VAP projects.

11.2. Soxhlet

11.2.1. Remove surrogate and matrix spiking solutions from refrigerator if cold stored, and allow to warm to room temperature.

11.2.2. If sample can be mixed easily in the sample jar, mix thoroughly by stirring with a clean plastic or wooden spoon or spatula. If the sample cannot be easily mixed (i.e., clay samples or samples of various and very different particle sizes), use the spoon or spatula to select enough separate portions from locations within the jar to produce a representative sample. Analyst judgment is important in determining how many portions and which locations are used to produce a representative aliquot. If the sample is uniform clay, at least 3 portions should be selected from different locations in the sample jar, if particle sizes or materials indicate a very non-homogenous sample, selection should be made carefully to collect an aliquot that represents the relative percentages of the various particle sizes and types in the sample jar.

11.2.3. Do not decant the water layer from sediment samples. The entire sample is used. A higher weight of sample portion must be weighed for sediment samples to account for the dry weight correction (see 11.2.3). Record and document in the LIMS if a water layer was present in the sample.

11.2.4. If the sample cannot be prepared using a Soxhlet due to matrix issues, a waste dilution may be required. Refer to SOP NC-OP-043 for the waste dilution procedure.

11.2.5. Place approximately 200mL of solvent into a 250 mL flat bottom flask containing one or two clean boiling chips. Weigh 30g ± 0.5 g of sample into a thimble or in a jar, recording the weight to the nearest 0.01g in LIMS. For PCB or Pesticides Extraction, weigh approximately 10 g of sample ± 0.5 g. Sample weights less than 30g, but over 1g, may be used if the appropriate reporting limits can be met. For sediment samples that contain excessive moisture, weigh 50 g ±0.5 g. For wipe samples, the wipe is placed in an extraction thimble. For concrete samples, weigh 5 g of sample ± 0.5g.

**Note:** Waste samples with difficult matrices (such as caulk) are extracted at 1g.

**Note:** Alternate sample volumes can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the sample to reagent ration. All samples and standards must be processed similarly.

11.2.6. Prepare an MB, LCS, and MS/MSD for each batch as specified in Section 9 of this SOP, using sodium sulfate or a clean wipe as the matrix for the LCS and MB. The parent sample is used for the MS/MSD. The weight of sodium sulfate used must be approximately the weight of soil used for samples.

11.2.7. Add anhydrous sodium sulfate to each solid, sediment or waste sample and mix well. The mixture must have a free-flowing texture. If not, add more sodium sulfate. Add the sample/sodium sulfate mixture to a soxhlet extractor thimble, but do not pack the thimble tightly. The soxhlet extractor or extraction thimble must drain freely for the duration of the extraction period. Thimbles are only used for PCB and Pesticide extraction. A glass wool plug below the sample in the soxhlet extractor is used for other extractions.

11.2.8. Add the appropriate amount of surrogate and matrix spiking solution as indicated in Tables 2 and 3.

11.2.9. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles per hour. Check the system for leaks at the ground glass joints after it has warmed up.

**Note**: If a reduced quantity of sample is extracted, it is usually necessary to increase the amount of sodium sulfate added or increase the solvent boiling rate to properly set the cycling rate.

Solvents:

| | |
|---|---|
| Semivolatile GC/MS and TPH | 1:1 v/v Methylene Chloride / Acetone |
| 8270 (MS) Concrete | Methylene Chloride |
| PCB and Pesticides | 1:1 v/v Hexane / Acetone |
| 8082 Concrete | 1:1 v/v Methylene Chloride/Acetone |

11.2.10. Allow the extract to cool after the extraction is complete then disassemble by gently twisting the soxhlet from the flask.

11.2.11. The sample is now ready for the concentration step (Section 11.3).

11.2.12. Cover the extracts with aluminum foil and store at 4°C ± 2°C if the extract will not be concentrated immediately. Refer to Section 11.3 for concentration.

11.3. Concentration: According to the type of sample, different solvents and final volumes will be required. Refer to Table 1 for the appropriate final volumes and concentrations.

11.3.1. Kuderna-Danish (KD) Method:

11.3.1.1. Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube (CT) to the 500 mL KD flask. Label the CT and KD. Transfer the sample to the labeled K-D flask filtering the extracts through funnels filled with sodium sulfate. Rinse the sample flasks from the soxhlet setups with approximately 10 – 20 mL of methylene chloride Transfer the rinsate through the funnel and rinse

the funnel with 20-30 mL of methylene chloride to complete the quantitative transfer.

11.3.1.2. Add one or two clean boiling chips to the KD flask and attach a three-ball Snyder Column. Add approximately 1 mL of clean methylene chloride to the top of the Snyder column. **Note:** It is important to wet with MeCl to ensure that the balls in the Snyder column do not stick, and the column will work properly.

11.3.1.3. Place the KD apparatus on a water bath (90-98$^{o}$C) so the tip of the concentrator tube is submerged. The water level must not reach the joint between the concentrator and the KD flask. At the proper rate of distillation, the balls will actively chatter; but the chambers should not flood.

11.3.1.4. Concentrate to 15-20 mL. If the determinative method requires a solvent exchange, add the appropriate exchange solvent to the top of the Snyder Column, and then continue the water bath concentration back down to 5-8 mL. Refer to Table 1 for details of exchange solvents and final volumes. The Snyder column may be insulated if necessary to maintain the correct rate of distillation.

**Note:** It is very important not to concentrate to dryness as analytes will be lost.

11.3.1.5. Remove the KD apparatus from the water bath and allow to cool for a minimum of 10 minutes. If the level of the extract is above the level of the CT joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.

11.4. Nitrogen Evaporation to Final Concentration

11.4.1. Transfer the CT to the evaporation apparatus.

11.4.2. Place the tube in a warm water bath that is at least 5$^{o}$C below the boiling temperature of the solvent being evaporated and evaporate the solvent using a gentle stream of nitrogen. The nitrogen flow will form a slight depression on the surface of the solvent, but must not create splattering of the extract.

Boiling points of commonly used solvents are:

| | |
|---|---|
| Methylene chloride | 40$^{o}$C |
| Acetone | 56$^{o}$C |
| Hexane | 69$^{o}$C |
| Acetonitrile | 82$^{o}$C |

**Note:** It is very important not to concentrate to dryness as analytes will be lost.

11.4.3. Refer to Table 1 to determine the final volume needed for a specific test method. Evaporate to slightly less than the required final volume.

11.4.4. Rinse the CT and quantitatively transfer the extract with the rinsate to the appropriate final container, rinse the CT and transfer the rinsate to the final container and dilute to the appropriate final volume using the "standard" glass vial noted in Section 10.1. Cap the sample and affix the appropriate label. The sample is now ready for analysis.

**Note:** The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

11.5. Analytical Documentation

11.5.1. Record all analytical information in 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. Record sample and associated QC information into LIMs. Level I and Level II technical reviews are performed in LIMS.

## 12. DATA ANALYSIS AND CALCULATIONS

12.1. Not applicable

## 13. METHOD PERFORMANCE

13.1. Initial Demonstration

13.1.1. Each analyst must make an initial demonstration of capability (IDOC) for each individual method. This requires analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance, which must contain all of the analytes of interest. The spiking level must be equivalent to a mid-level calibration. (For certain tests, more than one set of QC check samples may be necessary in order to demonstrate capability for the full analyte list.)

13.1.2. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.1.3. Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs. See SOPs NC-GC-038, NC-MS-018, NC-MS-003, and NC-GC-007 for detailed information on the determinative methods.

13.1.4. Method validation information (where applicable) in the form of analyst demonstrations of capabilities is maintained for this method in the analyst's training files

13.2. Training Qualification

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

## 14. POLLUTION PREVENTION

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

15.2.1. Used sodium sulfate and glass wool or filter paper contaminated with methylene chloride/acetone or acetone/hexane from the extract drying step. These materials are disposed of in the solid waste and debris in a red container located in the Extractions Lab.

15.2.2. **Assorted flammable solvent waste from various rinses**: These wastes are put into the halogenated/non-halogenated 25 gallon solvent waste container located under the fume hood in extractions.

15.2.3. **Methylene chloride waste from various rinses:** These wastes are disposed of in the liquid-liquid separation unit.

15.2.4. **Hexane-Hexane waste:** These samples are to be disposed in the flammable waste.

15.2.5. **Waste Hexane in vials:** These vials are placed in the vial waste located in the GC prep laboratory.

15.2.6. **Waste Methylene Chloride sample vials**: These vials are placed in the vial waste located in the GC prep laboratory.

15.2.7. **Extracted solid samples contaminated with methylene chloride/acetone or acetone/hexane:** These materials are disposed of in the solid waste and debris in a red container located in the Extractions Lab.

15.2.8. Samples, standards, and all extraction materials contaminated with high levels (>50ppm) of PCBs must be segregated into their own waste stream. PCB wastes are collected in one of three waste streams, solid PCB, liquid PCB, and PCB vial waste.

15.2.9. Solvent Recovery System Waste: Methylene Chloride waste from the Solvent Recovery System is collected and disposed of in the liquid-liquid separation unit. Acetone/Methylene Chloride waste from this system is disposed of in the flammable waste containers located in the laboratory.

## 16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, Sections 3500B, 3540C, and 3580A, current version

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

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

16.1.4. Corporate Quality Management Plan (CQMP), current version16.1.5 Federal Register - Environmental Protection Agency, 40 CFR, Part 136, Volume 49, No. 209, October 26, 1984, Method 625

16.1.5. EPA 600, Methods for Chemical Analysis of Water and Wastes, Method 608

16.1.6. Revision History

| | | | | |
|---|---|---|---|---|
| Historical File: | | Revision 3.4: 10/16/98 | | Revision 0: 03/12/08 (NC-OP-032) |
| (formerly CORP-OP-0001NC) | | Revision 3.5: 04/22/99 | | Revision 1: 01/07/09 (NC-OP-032) |
| | | Revision 3.6: 05/13/99 | | Revision 0: 03/24/11 (NC-OP-040) |
| | | Revision 3.7: 03/20/01 | | Revision 1-A: 01/24/12 |
| | | Revision 3.8: 05/23/01 | | Revision 2: 08/28/13 |
| | | Revision 3.9: 04/22/02 | | Revision 3: 08/25/14 |
| | | Revision 4.0: 02/04/03 | | Revision 4: 01/18/16 |
| | | Revision 4.1: 10/07/03 | | Revision 5a: 05/25/17 |
| | | Revision 4.2: 01/30/06 | | |

**4/19/19: Changed logo and copyright information. No changes made to revision number or effective date.*

16.2. Associated SOPs and Policies, current 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. Gas Chromatographic Analysis of Pesticides Based on Methods 8081A and 8081B, NC-GC-042

16.2.6. Gas Chromatographic Analysis of Diesel Range Organics Based on Methods 8015B, 8015C, and 8015D, NC-GC-043

16.2.7. Gas Chromatographic Analysis of PCBs Based on Methods 8082 and 8082A, NC-GC-045

16.2.8. GC/MS Analysis based on Method 8270C and 8270D, NC-MS-018

16.2.9. Analysis of Pesticides and PCBs by EPA Method 608, NC-GC-007

16.2.10. Analysis of Pesticides and PCBs by EPA Method 608.3, NC-GC-046

16.2.11. GC/MS Semivolatile Organic Compounds Capillary Column Technique Based on EPA Methods 625 and 625.1, NC-MS-003

16.2.12. Standards and Reagents, NC-QA-017

## 17. MISCELLANEOUS

17.1. Modifications from Reference method

17.1.1. Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

17.1.2. Sodium sulfate is heated for 1 hour at 800°C to purify. The reference method lists a minimum of 4 hours at 400°C.

17.2. Tables

**TABLE 1**

**Final Volumes and Exchange Solvents**

| Type | Exchange Solvent for Analysis* | Final Volume for Analysis in mL |
|---|---|---|
| Semivolatiles | N/A | 2.0 mL |
| PCB | Approximately 36 mL Hexane | 10.0 |
| Pesticides | Approximately 18 mL Hexane | 10.0 |
| BNA – SIM | N/A | 2.0 mL |
| TPH | N/A | 5.0 |

***Note:*** *PCBs and Pesticides only need the solvent exchange step when they are extracted in methylene chloride / acetone. If they are extracted in hexane / acetone, no solvent exchange is necessary.*
***Note:*** *Different final volumes may be necessary to meet special client reporting limit requirements.*

**TABLE 2**

**Surrogate Spiking Solutions**

| Analyte Group | Surrogate Spike Solution ID | Volume (mL) |
|---|---|---|
| BNA | 20 ppm BNA | 1.0 |
| BNA / SIM | 20 ppm BNA | 0.1 |
| PEST | 0.2 ppm DCB/TCX | 1.0 |
| TPH | o-Terphenyl | 1.0 |
| PCB | 0.2 ppm DCB/TCX | 1.0 |

**TABLE 3**
**Matrix Spike and LCS Solutions**

| Analyte Group | Matrix Spike Solution ID | Volume (mL) |
|---|---|---|
| BNA | 20 ppm BNA All-Analyte Spike | 1.0 |
| BNA / SIM | 20 ppm BNA All-Analyte Spike | 0.1 |
| PEST | Pest NPDES Spike | 1.0 |
| PCB | 10 ppm PCB Spike | 1.0 |
| TPH | Diesel Spike | 1.0 |

# 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**



**Facility Distribution No. _____ Distributed To:_____**

The controlled copies of this SOP are the PDF copy that is posted to the laboratory's SOP Directory and, where applicable, the copy that is printed and placed in the General Chemistry SOP binder. Printed or electronic copies of this SOP that are distributed outside of the facility are considered uncontrolled.

## 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 |

# Attachment C
# Work Plan Approval Form

**USEPA ID Number:** MID 005 356 621
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**Prepared by:** **GHD**
**Prepared for:** **RACER Trust Site**

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