Global Operations, Environment, Health & Safety

159 Plastics Avenue
Pittsfield, MA 01201

April 27, 2017

Dean Tagliaferro
EPA Project Coordinator
U.S. Environmental Protection Agency
c/o Avatar
10 Lyman Street
Pittsfield, MA 01201

Re: GE-Pittsfield/Housatonic River Site
1½-Mile Reach of Housatonic River (GECD820)
2017 Sediment Sampling Plan

Dear Mr. Tagliaferro:

The U.S. Environmental Protection Agency (EPA) performed sediment and riverbank soil remediation activities in the 1½-Mile Reach of the Housatonic River (1½ Mile) from 2002 through 2006. This reach extends from the Lyman Street Bridge downstream to the confluence of the East and West Branches of the river in Pittsfield, Massachusetts (Figure 1). EPA performed these activities, known as the 1½-Mile Reach Removal Action, under the terms of the Consent Decree (CD) for the GE-Pittsfield/Housatonic River Site. Following the completion of remediation and associated restoration activities associated with the first portion of the 1½-Mile Reach Removal Action in 2004, EPA performed a number of post-remediation monitoring activities through 2007, including sediment and aquatic invertebrate sampling.

In 2008, pursuant to the CD, General Electric Company (GE) assumed responsibility for performing the post-remediation monitoring and maintenance activities, known as Post-Removal Site Control activities, associated with the 1½ Mile. These activities are currently governed by the *Final Post-Removal Site Control Plan: 1½-Mile Reach Removal Action* (Final PRSC Plan) prepared and issued by Weston Solutions (Weston) on behalf of EPA in March 2011 as part of the *Final Completion Report for the 1½-Mile Reach Removal Action*.

The Final PRSC Plan requires that a sediment sampling event be conducted every 5 years for a 15-year period to document polychlorinated biphenyl (PCB) concentrations in sediment in the 1½ Mile over time. The first sampling event of this program was conducted by EPA in 2007. The performance and results of this first of three 5-year sediment sampling events were summarized in the *Post-Remediation Sediment Sampling Report: 1.5-Mile Reach Removal Action*, prepared by Weston on behalf of EPA in August 2007. The second sampling event of this program was conducted by GE in 2012 in accordance with the *2012 Sediment Sampling Plan*, which was conditionally approved by EPA on May 22, 2012. The performance and results of the second of three 5-year sediment sampling events were summarized in the *2012 Sediment Sampling Report* (Sampling Report), prepared by Arcadis on behalf of GE in October 2012. The Sampling Report was conditionally approved by EPA on November 26, 2012.

This *2017 Sediment Sampling Plan* (Sampling Plan) describes the proposed sample collection activities and the associated laboratory analyses that will be performed by GE in 2017 to meet the requirements of the Final PRSC Plan. Following EPA approval of this Sampling Plan, GE will conduct the next sampling event (third round) for the 1½ Mile sediment sampling program during low flow conditions in the 1½ Mile, tentatively scheduled for June or July 2017.

Sediment Sampling and Analysis

The sediment sampling and analysis activities to be conducted by GE in 2017 in the 1½ Mile will be performed in accordance with the applicable requirements in the Final PRSC Plan and will be consistent with the activities

conducted by EPA in 2007 and by GE in 2012. These activities will follow the pertinent procedures described in GE's *2013 Field Sampling Plan/Quality Assurance Project Plan* (FSP/QAPP). The remainder of this plan provides additional detail about the procedures and methods that will be implemented to perform sediment sampling.

As part of pre-remediation activities, reference transects, the same used for the 2007 and 2012 sampling activities, were established at approximately 50-foot intervals for the length of the 1½ Mile. Sediment sample collection will be performed within the channel as close as possible to the locations sampled during the 2007 and 2012 monitoring activities,[1] with samples collected along every fourth transect (i.e., at 200-foot intervals along the length of the 1½ Mile). The sampling transects will be staked by a survey crew prior to sampling. To the extent practicable, sediment cores will be collected from the center, right, and left sides of the river channel at each transect (i.e., three collection locations per transect). In total, the 37 transects illustrated on Figure 1 will be targeted for sampling, starting downstream at T210 (at the confluence of the East and West Branches of the Housatonic River) and proceeding upstream to T066 (at the Lyman Street Bridge), resulting in 111 total sampling locations within the 1½ Mile. A summary of the sediment sampling program is provided in Table 1.

The sampling will be performed during low flow conditions, as measured at the U.S. Geological Survey river gage in Coltsville. At each of the 111 collection locations, the channel bottom will be probed in an effort to locate fine-grained sediment (i.e., sands or silts, rather than the underlying gravel/riprap). If a minimum of 6 inches of sediment is not present overlying the gravel/riprap, GE will attempt to identify a suitable nearby area (within approximately 10 feet) with adequate sediment depth. A tape measure will be used in the field to confirm that the proposed sample location is within approximately 10 feet of the surveyed transect.

If an area with a minimum of 6 inches of sediment cannot be located, an adequate volume will be collected from the area of the original sampling location, if possible, to meet analytical requirements (i.e., a minimum of 25 grams [approximately 1 ounce] for each analysis required). If sufficient volume of sediment cannot be obtained to meet analytical requirements, no sample will be collected and the omission of that sampling location and or transect will be documented in the field notebook.[2]

Sediment will be collected by physically pushing 2-inch diameter Lexan® tubes to the interface between the fine-grained sediment and the underlying riprap. To the extent practicable, a minimum of 1 foot of material will be collected in each core. Care will be taken to minimize material disturbance and/or loss during sediment collection activities. Recovered cores will be maintained upright in near *in-situ* conditions and will be measured for approximate recovery length. For each sample location, the average sediment depth, water depth, type of depositional environment, and any other pertinent comments about the sample location will be recorded in the field notebook. Wherever samples are successfully collected, actual sample locations will be surveyed at the time of sampling by field personnel using a hand-held GPS unit, with the location coordinates recorded in the field notebook.

The collected samples will be processed by sectioning each core into two specific layers: the upper 6-inch layer and the remaining fine-grained materials (i.e., from the bottom of the 6-inch layer to the bottom of the recovered core), resulting in a targeted total of 222 samples. For each core, the general sediment characteristics will be recorded in the field notebook, and a bulk sample will be taken from the homogenized sediments from both the upper interval (the top 6-inch interval) and the remaining materials. Quality assurance samples will be collected in accordance with the FSP/QAPP. If additional sample volume is needed beyond what is attained from one core, multiple cores will be collected in the vicinity of the original location and the material from corresponding depth interval(s) will be composited (and homogenized) for sample collection.

---

[1] Those locations were selected by EPA to be as close as feasible to the original pre-remediation sample locations established by EPA.

[2] During EPA's 2007 sampling effort, two transects (T-118 and T-122) were omitted from sampling due to the lack of depositional sediment present at the time of sampling. During GE's 2012 sampling effort, one transect (T-110) was omitted from sampling due to lack of depositional sediment present at the time of sampling. In addition, during GE's 2012 sampling effort no sample was collected at T-106-L due to lack of sufficient available sediment at location at the time of sampling.

Samples will be shipped on ice to the selected laboratory under standard chain-of-custody procedures and will be analyzed for PCBs (as Aroclors) and total organic carbon in general accordance with the procedures in the FSP/QAPP. However, the Pace Schenectady laboratory that provided analysis in 2012 and the standard operating procedures (SOPs) included in the FSP/QAPP is no longer in operation, and as such SGS has been selected to perform the analyses of samples collected in 2017. The SOPs specific to SGS are provided as Attachment 1.

Schedule and Reporting

Following receipt of the initial analytical results, the PCB data will be validated in accordance with the pertinent data validation procedures specified in the FSP/QAPP. This will include validation of all data to a Tier I level and validation of a minimum of 25% of the data to a Tier II level.

In accordance with the Final PRSC Plan, a summary report that includes the validated data will be prepared and submitted to EPA for review and approval within 90 days of completion of the sampling event. The summary report will also include a comparison of the 2017 sampling results with the 2007 and 2012 sampling results, including summary statistics such as mean, median, minimum, maximum PCB concentrations for both the upper six-inch interval and the remaining material interval.

In addition, GE will include a summary of the results from this sampling event in the 2017 Annual Monitoring Report for the 1½ Mile, to be submitted for EPA review and approval in February 2018.

Future Activities

This 2017 event represents the third round of the sediment sampling program, as outlined in the Final PRSC Plan. After completion of the 2017 event, GE will submit a proposal to EPA regarding the need for and scope of further long-term monitoring of the sediments in the 1½ Mile.

Please contact me if you have any questions regarding the information presented in this letter.

Sincerely,

Lauren Putnam /for
Kevin G. Mooney
Remediation Project Manager

Enclosures:
Table 1 – Summary of Proposed Sampling Program
Figure 1 – Sediment Sample Transect Locations
Attachment 1 – Standard Operating Procedures for SGS Laboratory Analyses

cc: John Kilborn, EPA*
Chris Ferry, ASRC Primus*
Robert Leitch, USACE*
Scott Campbell, Avatar* (plus 2 hard copies)
Izabela Zapisek, Avatar*
Michael Gorski, MDEP*
John Ziegler, MDEP*
Eva Tor, MDEP* (cover letter only)
Karen Pelto, MDEP* (Lead Administrative Trustee)
Nancy E. Harper, MA AG* (cover letter only)
Susan Peterson, CT DEP*
Nate Joyner, Pittsfield Dept. of Community Development*
Rod McLaren, GE* (cover letter only)
Andrew Silfer, GE*
James Bieke, Sidley Austin
Todd Cridge and Lauren Putnam, Arcadis*
Public Information Repositories
GE Internal Repositories

* *electronic copy*

TABLE

Table 1
Summary of Proposed Sampling Program

2017 Sediment Sampling Plan
1 1/2-Mile Reach of the Housatonic River
General Electric Company - Pittsfield, Massachusetts

Number of Transects to be Sampled	Quantity of Locations to be Cored at Each Transect	Number of Depth Intervals per Sample Core[1]	Total Quantity of Samples to be Collected[2]	Laboratory Analysis
37	3	2	222	- Total PCB (USEPA SW-846 8082) - Total Organic Carbon (Lloyd Kahn)

General Notes:

1. Sampling to be performed in low flow conditions from Transects T066 to T210.
2. A summary report of sampling activities will be submitted within 90 days of receipt of validated data.
3. GE will notify EPA of all scheduled monitoring, inspections, and maintenance activities a minumum of 14 days in advance to allow for arrangement of oversight.

Superscript Notes:

[1] To the extent practicable, a minimum of 1 foot of material will be collected in each core. Collected cores will be processed by sectioning each core into two specific samples: the upper 6 inches, and the remaining materials (i.e., from the bottom of the 6-inch layer to the bottom of the recovered core).

[2] Total quantity does not include quality assurance samples. One field duplicate sample will be collected for every 20 sediment samples collected. Similarly, one matrix spike sample and one matrix spike duplicate sample will be collected for every 20 sediment samples collected. Finally, if designated equipment is not used, one equipment blank will be collected in the field for every 20 sediment samples collected.

FIGURE

CITY: SYRACUSE, NY DIV/GROUP: ENVCAD DB: L.JPOSENAUER, K.SARTORI PIC:(Opt) PM:D.KNUTSEN TM:L.PUTNAM LYR:(Opt)ON=*;OFF=*REF*
G:\GE\PRJ\ENVCAD\SYRACUSE\ACT\C\ALL30144\4000\4000A\2017SSPLAN\31044G01.dwg LAYOUT: 1 SAVED: 3/28/2017 10:04 AM ACADVER: 19.1S (LMS TECH) PAGESETUP: C-PD2B-PDF-CONV PLOTSTYLETABLE: PLTFULL.CTB PLOTTED: 3/28/2017 10:05 AM BY: SARTORI, KATHERINE

XREFS: IMAGES: PROJECTNAME: ----
31044X00 31044X01.sid
31044X02.sid

LEGEND:

T-210 ———— SEDIMENT SAMPLING TRANSECT

0 250' 500'
GRAPHIC SCALE

NOTES:

1. THE BASEMAP IMAGES PRESENTED ON THIS FIGURE WERE OBTAINED FROM THE OFFICE OF GEOGRAPHIC AND ENVIRONMENTAL INFORMATION (MassGIS) COMMONWEALTH OF MASSACHUSETTS EXECUTIVE OFFICE OF ENERGY AND ENVIRONMENTAL AFFAIRS 1:5000 COLOR ORTHO IMAGERY, 2005. NAD27 STATE PLANE MA FT.
2. NOT ALL PHYSICAL FEATURES SHOWN.

GENERAL ELECTRIC COMPANY
PITTSFIELD, MASSACHUSETTS

2017 SEDIMENT SAMPLING PLAN
1 1/2-MILE REACH OF THE HOUSATONIC RIVER

SEDIMENT SAMPLE TRANSECT LOCATIONS

ARCADIS Design & Consultancy for natural and built assets

FIGURE 1

ATTACHMENT 1

STANDARD OPERATING PROCEDURE FOR DETERMINATION OF POLYCHLORINATED BIPHENYLS

LAB MANAGER: _____

QA MANAGER: _____

EFFECTIVE DATE: 3/14/2017

TITLE: SW846 8082A: DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY

METHOD REFERENCE SW846 8082A (Revision 1, February 2007)

Revised Sections: ***SOP Format, 2.1, 4.0, 6.1, 7.1.1, 7.1.2, 10.12.1, 11.6, 11.7, 11.8.3, Table 1, Table 2, Table 6B, Renumbered section 8.0, 9.0 and 10.0***

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the analytical procedures, which are utilized by SGS to acquire samples for analysis of polychlorinated biphenyls (PCBs) as Aroclors, using dual open-tubular, capillary columns with electron capture detectors (ECD).

1.2 This gas chromatographic (GC) method applicable to the determination of the PCB Aroclors listed in Table 1 in extracts from solid and aqueous matrices.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (from 250 mL to 1 L for liquids, 15 g for solids) is extracted using the appropriate matrix-specific sample extraction technique. Petroleum Products and organic wastes are diluted with an organic solvent and follow SW 846 Method 3580A. Aqueous samples are extracted at neutral pH with methylene chloride using Method 3510 (separatory funnel). Solid samples are extracted with using Method 3546, Microwave Extraction. Wipes are extracted using Method 3550C, Sonication.

2.2 Extracts for PCB analysis may be subjected to a sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for these analytes. This cleanup technique will remove (destroy) many single component organochlorine or organophosphorus pesticides.

2.3 After cleanup, the extract is analyzed by injecting a 1 or 2-µL aliquot into a gas chromatograph with dual narrow bore fused silica capillary columns and electron capture detectors (GC/ECD). The chromatographic data may be used to determine the seven Aroclors in Table 1.

2.4 The peaks detected are qualitatively identified by comparison to retention times specific to the known target list of PCBs on two different column types (primary and confirmation).

2.5 Once identified, the Aroclor is quantitated by external standard techniques with an average calibration factor generated from a calibration curve.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve. RL's may vary depending on matrix difficulties and sample volumes or weight and percent moisture. Refer to Table 1 for current reporting limits.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study. Forward the processed data to the QA group for archiving.

4.0 DEFINITIONS

BLANK - an analytical sample designed to assess specific sources of laboratory contamination. The types of blanks are Method Blank; Instrument Blank, Storage Blank, and Sulfur Blank.

CALIBRATION FACTOR (CF) - a measure of the gas chromatographic response of a target analyte to the mass injected. The calibration factor is analogous to the Relative Response Factor (RRF) used in the Volatile and Semivolatile fractions.

CONTINUING CALIBRATION - analytical standard run every 12 hours and at the end of analytical sequence to verify the initial calibration of the system.

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the electron capture detector to the target compounds.

MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOP, a sample matrix is either water or soil/sediment. Matrix is not synonymous with phase (liquid or solid).

MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents, internal standards and surrogate standards (or SMCs for VOA), that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background and reagent contamination.

METHOD DETECTION LIMITS (MDLs) - The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs must be determined approximately once per year for frequently analyzed parameters.

PERCENT DIFFERENCE (%D) - As used in this SOP and elsewhere to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference.)

PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105^{o}C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at or below 105^{o} C, including water. Percent moisture may be determined from decanted samples and from samples that are not decanted.

REAGENT WATER - water in which an interferant is not observed at or above the minimum detection limit of the parameters of interest.

RELATIVE PERCENT DIFFERENCE (RPD) - As used in this SOP and elsewhere to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. (In contrast, see percent difference.)

RELATIVE RESPONSE FACTOR (RRF) - a measure of the instrument response of an analyte. Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

RETENTION TIME (RT) - the time required (in minutes) for a standard compound to elute from a chromatographic column.

SURROGATES - for semivolatiles and pesticides/Aroclors, compounds added to every blank, sample, matrix spike, matrix spike duplicate, and standard; used to evaluate analytical efficiency by measuring recoveries. Surrogate are brominated, fluorinated, or isotopically labeled compounds not expected to be detected in environmental media.

INSTRUMENT BLANK - a system evaluation sample containing solvent and surrogate standards added. An instrument blank is used to remove and/or evaluate residual carryover from high level standards, spike samples and field samples.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the SGS Health and Safety Plan and Personal Protection Policy, which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 Polychlorinated biphenyls have been classified as known or suspected human or mammalian carcinogens. Primary standards of these toxic compounds must be prepared in a hood. A NIOSH/Mass approved toxic gas respirator must be worn when the analyst handles high concentrations of these toxic compounds.

6.0 SAMPLE PRESERVATION AND HOLDING TIME

6.1 PRESERVATION

6.1.1 Water Samples

6.1.1.1 Samples are collected in 300mL or 1000mL glass amber bottles without preservatives.

6.1.1.2 A minimum of 250mL of an unpreserved sample is required for extraction. Additional sample volume is necessary for any samples used for matrix spike and matrix spike duplicates. Therefore, 1 liter of at least one sample in every group of 20 field samples are required for analysis to accommodate all quality control requirements.

6.1.2 Soil Samples

6.1.2.1 Samples are collected in a glass containers . No preservative is required.

6.1.3 Sample must be taken with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing possible phthalate contamination.

6.1.4 The samples must be protected from light and refrigerated at $\leq$ 6 °C from the time of receipt until extraction and analysis.

6.2 HOLDING TIME

6.2.1 Aqueous sample must be extracted within 1 year of sampling.

6.2.2 Soil sample must be extracted within 1 year of sampling.

6.2.3 Extracts must be analyzed within 40 days following extraction.

7.0 APPARATUS AND MATERIALS

7.1 GAS CHROMATOGRAPH SYSTEM

7.1.1 Gas Chromatograph-Agilent or Hewlett Packard Model 5890, 6890, and/or 7890. The analytical system comes complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port is designed for split or splitless injection with capillary columns. The capillary columns are directly coupled to the detectors.

7.1.2 Columns

7.1.2.1 Column pair 1

7.1.2.1.1 30 m x 0.32 mm fused silica (0.32 μm film thickness) ZBCLP-1 narrow-bore capillary column or equivalent.

7.1.2.1.2 30 m x 0.32 mm fused silica (0.25μm film thickness) ZBCLP-2 narrow-bore capillary column or equivalent.

7.1.2.2 Column pair 2

7.1.2.2.1 30 m x 0.32 mm fused silica (0.5 μm film thickness) RTX CLPI narrow-bore capillary column or equivalent.

7.1.2.2.2 30 m x 0.32 mm fused silica (0.25 μm film thickness) RTX CLPII narrow-bore capillary column or equivalent.

7.1.3 Detectors

7.1.3.1 Electron Capture Detectors (HP).

7.1.3.2 Micro Electron Capture Detectors (HP).

7.2 AUTOSAMPLER

7.2.1 Agilent or Hewlett Packard Model 7673A, 7683, 7643A capable of holding 100 of 2-ml crimp vials.

7.3 DATA SYSTEM

7.3.1 MSD interfaced to the gas chromatograph which allows the continuous acquisition and storage on machine readable media (disc) of all chromatographic data obtained throughout the duration of the analysis.

7.3.2 The ENVIROQUANT data system is capable of quantitation using multi-point calibration.

7.3.3 Lagato Networker with lookup database on 4mm DAT tape for long term, off line magnetic storage of data.

7.4 SYRINGE

7.4.1 Manually held ul-syringes, various volumes (Hamilton or equiv.).

7.4.2 10 μl graduated, auto sampler (Hamilton or equiv.).

8.0 REAGENTS AND STANDARDS

8.1 Refer to SGS Sample Preparation SOPs EOP001 and EOP3546 for reagents and standards used for sample extraction.

8.2 Solvents - Ultra pure, chromatography grade Hexane.

8.3 Stock standard solutions.

8.3.1 Two separate sources of commercially prepared standards with traceability documentation are used. The standards contain Aroclors 1016, 1221, 1232, 1242, 1248, 1254 and 1260. Separate calibrations are prepared and performed for Aroclors 1262 and 1268 when needed for identification of the compounds in client samples.

8.4 Working Solutions

8.4.1 Prepare working solutions, using stock solution, in hexane, as needed, that contain the compounds of interest, either singly or mixed together. Refer to Table 3A, 3B for details.

8.5 Calibration Standards

8.5.1 Initial Calibration Standards

8.5.1.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks in the other five Aroclor mixtures. As a result, a multi-point calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing initial calibration for each of the seven Aroclors. Prepare a minimum of five calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260, including surrogates, by dilution of the above working solutions (Section 9.4) with hexane. Suggested levels and preparations are shown in Table 4A.

8.5.1.2 Separate calibration standards are required for the other five Aroclors. Unless otherwise necessary for a specific project, a single calibration standard near the mid-point of the expected calibration range of each remaining Aroclor is employed to determine its calibration factor and for pattern recognition. Refer to Table 4B for preparation scheme. Optional curves as shown on Table 4C may also be used for a multi-point calibration per project's specification.

8.5.2 Continuing Calibration Verification (CCV)

8.5.2.1 For Aroclor analyses, the continuing calibration checks must be a mixture of Aroclor 1016 and Aroclor 1260. Two standards at 500 μg/l and 1,000 μg/l are prepared as described in Table 5A. During the analysis, these two solutions are alternated to check the initial calibration.

8.5.2.2 In situations where only a few Aroclors are of interest for a specific project, the calibration checks of each Aroclor of interest may be prepared (Table 5B) and analyzed as the 1016/1260 mixture throughout the analytical sequence.

8.6 Initial Calibration Verification (ICV) - Second Source Calibration Check Standard

8.6.1 Prepare the ICV check standards from separate sources of stock standards from the calibration curve following the procedures in Table 6A, and 6B.

8.6.2 The ICV is prepared at 1,000 μg/l for each Aroclor and is analyzed immediately after the initial calibration.

8.7 Surrogates

8.7.1 Tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) are used as surrogate standards for this method.

8.7.2 A calibration range must be constructed for the surrogate compounds. Accordingly, appropriate amounts of surrogates are mixed with each calibration solution to define a range similar to the target compounds.

8.7.3 Surrogate compounds are also contained in continuing calibration checks, and second source calibration check standard.

8.7.4 Spike each sample, QC sample and blank with an appropriate amount of corresponding surrogate spiking solution, prior to extraction, for a final concentration in the extract of 40 μg/l of each surrogate compound.

8.8 Instrument Blank

8.8.1 An instrument blank is run after each Continuing Calibration Check. Spike hexane with an appropriate amount of surrogate spiking solution for a final concentration of 20 μg/l of each surrogate compound.

8.9 Storage of Standards

8.9.1 Store unopened stock standard solutions according to the manufacturer's documented holding time and storage temperature recommendations. Protect from light.

8.9.2 Store all other working standard solutions in glass vials with Teflon lined screw caps at $\leq$ 6°C in the dark.

8.9.3 Opened stock standard solutions must be replaced after 6 months or sooner if manufacturer's expiration date comes first or comparison with quality control check samples indicates a problem.

8.9.4 All other standards must be replaced after six months or sooner if routine QC indicates a problem or manufacturer's expiration date comes first.

9.0 INTERFERENCES

9.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

9.2 Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Glassware must be scrupulously cleaned. Refer to "The Preparation of Glassware for Extraction of organic contaminants" SOP for practices utilized in the extraction department.

9.3 Interferences may be caused by contaminants that are co-extracted from the sample. The extent of the interferences will vary from source to source, which can be grouped into three broad categories.

9.3.1 Contaminated solvents, reagents, or sample processing hardware.

9.3.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

9.3.3 Compounds extracted from the sample matrix to which the detector will respond**.**

9.4 Interferences by phthalate esters introduced during sample preparation can pose a major problem in PCB determination.

9.4.1 Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination can best minimize interference from phthalate esters.

9.4.2 Exhaustive cleanup of solvents, reagent and glassware may be required to eliminate background phthalate ester contamination.

9.4.3 These materials can be removed through the use of Method 3665 (sulfuric acid/permanganate cleanup).

9.5 Elemental sulfur is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Method 3660 is suggested for removal of sulfur.

9.6 To reduce carryover when high-concentration samples are sequentially analyzed, the syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of an instrument blank to check for cross contamination.

10.0 Procedure

10.1 INITIAL CALIBRATION

10.1.1 The method reporting limit is established by the concentration of the lowest standard analyzed during the initial calibration. Lower concentration standard may be needed to meet the reporting limit requirements of state specific regulatory program. The linear range covered by this calibration is the highest concentration standard.

10.1.2 The initial calibration for this method consists of two parts, described below.

10.1.2.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. Thus, such a standard may be used to demonstrate the linearity of the detectors and that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. The calibration range

covered for Aroclor 1016 and Aroclor 1260 employs standards of 50, 250, 500, 1,000, 2,000, and 3,000 µg/l.

10.1.2.2 Standards of the other five Aroclors are necessary for pattern recognition. These standards are also used to determine a single-point calibration factor for each Aroclor, assuming that the Aroclor 1016/1260 mixture in Section 10.1.2.1 has been used to describe the detector response. The concentration of each Aroclor standard is near the mid-point of the linear range of the detector, usually at 1,000 µg/l. The standards for these five Aroclors must be analyzed before the analysis of any samples, and may be analyzed before or after the analysis of those 1016/1260 standards.

10.1.2.3 In situations where only a few Aroclors are of interest for a specific project, an initial calibration of a minimum of five standards of each Aroclors of interest instead of the 1016/1260 mixture may be performed.

10.1.3 A calibration range must be constructed for each surrogate compound. Accordingly, add appropriate amounts of each surrogate compound to the calibration solution to define a range similar to the target compounds.

10.1.4 Aliquot proper amount of each calibration standard into a 2 ml crimp top vial.

10.1.5 PCBs are quantitatively determined as Aroclors by the external standard technique. The Calibration Factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards is calculated using the equation in Section 14.1.

10.1.5.1 Use at least five peaks for the Aroclor 1016/1260 mixture, none of which are found in both of these Aroclors. At least five sets of calibration factors will be generated, each set consisting of the calibration factors for each of the five (or more) peaks chosen for this mixture.

10.1.5.2 A minimum of 3 characteristic peaks must be chosen for each of the other Aroclors, and preferably 5 peaks. The peaks must be characteristic of the Aroclor in question. Thus, each single standard will generate at least three calibration factors, one for each selected peak.

10.1.5.3 Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 6 peaks must include at least one peak that is unique to that Aroclor.

10.1.5.4 The calibration factors from the initial calibration are used to evaluate the linearity of the initial calibration. When the Aroclor 1016/1260 mixture is used to demonstrate the detector response, the calibration model chosen for this mixture must be applied to the other five Aroclors for which only single standards are analyzed. If multi-point calibration is performed for individual Aroclors, use the calibration factors from those standards to evaluate linearity.

10.1.6 For the initial calibration to be valid, the percent relative standard deviation (% RSD) (see Section 14.2) must be less than 20 % for each Aroclor of interest on each column. If any analyte exceeds the 20% acceptance limit for a given calibration, corrective action must be taken.

10.1.6.1 If the problem is associated with specific standards, reanalyze the standard and recalculate the RSD.

10.1.6.2 Alternatively, narrow the calibration range by replacing one or more of the calibration standards that cover a narrow range.

10.1.6.2.1 The changes to the upper end of the calibration range will affect the need to dilute samples above the range. If the instrument response indicates signs of detector saturation, the concentration of the standard at the upper limit will be reduced. The changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end of the range.

10.2 INITIAL CALIBRATION VERIFICATION (ICV) - SECOND SOURCE CALIBRATION CHECK STANDARD

10.2.1 The initial calibration is verified with an ICV, a second source calibration check standard from an external source (Section 9.6). It must be performed right after the initial calibration.

10.2.2 The percent difference (%D) (Section 14.3) for this standard must meet the %D criteria of 20% used for calibration verification on each column.

10.2.2.1 If %D is greater than 20%, reanalyze the second source check. If the limit cannot be met upon re-injection, re-prepare the second source solution using a fresh ampoule and repeat the process.

10.2.2.2 If the %D criteria cannot be achieved after re-preparation of the second source, prepare a third source and repeat the process. Make fresh calibration standards using one of the two standard sources that match each other.

10.3 CONTINUING CALIBRATION VERIFICATION (CCV)

10.3.1 Continuing calibration verification (CCV) standards (Section 9.5.2) must be acquired at the beginning of each 12-hour shift, after every 10 injections not to exceed 12 hours and at the end of the analysis sequence. The 500 µg/l check standard is alternated with 1,000 µg/l standard for calibration verification.

10.3.2 For Aroclor analyses, the calibration verification standard must be a mixture of Aroclor 1016 and Aroclor 1260. The calibration verification process does not require analysis of the other Aroclor standards used for pattern recognition, but the analyst may wish to include a standard for one of these Aroclors after the 1016/1260 mixture used for calibration verification throughout the analytical sequence.

10.3.3 The percent difference (%D) (see section 14.3) must be less than 20**%** for each Aroclor of interest on each column.

10.3.4 Each sample analysis must be bracketed by periodic analyses of acceptable calibration verification standards every 10 injections not to exceed 12 hours. If %D criteria fails during a mid sequence calibration check or at the end of the analysis sequence, a continuing calibration check is allowed to be repeated only once; if the second trial fails, a new initial calibration must be performed. In situations where the first check fails to meet the criteria, the instrument logbook must have clear documented notations as to what the problem was and what corrective action was implemented to enable the second check to pass.

10.3.5 A continuing calibration standard is analyzed whenever the analyst suspects that the analytical system is out of calibration. If the calibration cannot be verified, corrective action is performed to bring the system into control. Analysis may not continue until the system is under control.

10.3.6 When a calibration verification standard fails to meet the QC criteria at the end of the analysis sequence, all samples injected after the last standard that met the QC criteria must be evaluated to prevent mis-quantitations, and re-injection of the sample extracts may be required.

10.3.6.1 If the analyte was not detected in the specific samples analyzed during the analytical shift or sequence, the extracts for those samples do not need to be reanalyzed when the calibration standard response is above the initial calibration response.

10.3.6.2 If the analyte was detected in the specific samples analyzed during the analytical shift or sequence, or the calibration standard response is below the initial calibration response, then the extracts for those samples need to be reanalyzed.

10.3.7 Each subsequent injection of a continuing calibration standard during the 12-hour analytical shift must be checked against the retention time windows established in Section 11.0. If any of these subsequent standards fall outside their absolute retention time windows, the GC system is out of control. Determine the cause of the problem and correct it. If the problem cannot be corrected, a new initial calibration must be performed.

10.4 RETENTION TIME WINDOWS

10.4.1 Absolute retention times are used for the identification of PCBs as Aroclors. Retention time windows must be calculated for each surrogate and at least 3 to 5 characteristic peaks of each Aroclor on each GC column, when a new initial calibration is run and whenever a new chromatographic column is installed, or when there are significant changes in the operating conditions. The retention time windows must be reported with the analysis results in support of the identifications made.

10.4.2 Employ the following approach to establish retention time windows:

10.4.2.1 Make three injections of each Aroclor at approximately equal intervals during the 72-hr period.

10.4.2.2 For each Aroclor, choose three or five major peaks and calculate the mean and standard deviation of the three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in the

samples. Record the retention time to three decimal places (e.g. 10.015 min) for each Aroclor.

10.4.2.3 In those cases where the standard deviations of the retention time window for a particular Aroclor is 0.01 minutes or less, the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes.

10.4.2.4 Apply plus or minus three times the standard deviations to retention time of each Aroclor standard (continuing calibration or middle level of initial calibration). This will be used to define the retention time window for the sample.

10.4.2.4.1 If default standard deviation of 0.01 minutes is employed, the width of the window will be 0.03 minutes.

10.4.2.5 Establish the center of the retention time window for each Aroclor and surrogate by using the absolute retention time for each Aroclor and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

10.4.2.6 When retention time windows are to be determined, analyze a standard containing DDT analogs to ensure that they do not elute at the same retention time as the last major Aroclor 1254 peak. The analyst must either adjust the GC conditions for better resolution, or choose another peak that is characteristic of the Aroclor and which does not elute at the same time as of the DDT analogs.

10.5 SAMPLE EXTRACTION

10.5.1 In general, water samples are extracted at a neutral pH with methylene chloride using a separate funnel (Method 3510) (Refer to SOP: EOP001 and EOP004). Solid samples are extracted using Method 3546, Microwave Extraction (Refer to SOP: EOP3546).

10.6 SAMPLE CLEANUP

10.6.1 Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. Refer to appropriate SOPs for details.

10.6.1.1 Interferences by phthalate esters can be removed through the use of a sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for PCBs. This method must be used whenever elevated baselines or overly complex chromatograms prevent accurate quantitation of PCBs.

10.6.1.2 Element sulfur, which may be present in certain sediments and industrial wastes, interfere with the electron capture gas chromatography of certain Aroclors. Sulfur must be removed by the technique described in Method 3660.

10.7 INSTRUMENT CONDITIONS.

10.7.1 Recommended instrument conditions are listed in Table 2. Modifications of parameters specified with an asterisk are allowed as long as criteria of calibration are met. Any modification must be approved by team leader/manager.

10.8 Initial calibration

10.8.1 Refer to Section 10.1.

10.9 Initial calibration Verification (ICV) -Second source calibration check standard

10.9.1 Refer to Section 10.2.

10.10 Continuing calibration Verifications (CCV)

10.10.1 Refer to Section 10.3.

10.11 Sample analysis (Primary)

10.11.1 All samples and quality control samples are injected into the Gas Chromatograph using the autosampler. Program the sampler for an appropriate number of syringe rinses and a 1ul or 2 μl injection size. A split or splitless injection technology is used.

10.11.2 Sample concentrations are calculated by comparing sample responses with the initial calibration of the system (Section 14.4). If sample response exceeds the limits of the initial calibration range, dilute the extract and reanalyze. Extracts must be diluted so that all peaks are on scale, as overlapping peaks are not always evident when peaks are off scale.

10.11.3 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the sample meet instrument QC requirements. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

10.11.4 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst must consult with the source of the sample to determine whether further concentration of the sample is warranted.

10.11.5 If compound identification or quantitation is precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract or replacement of the capillary column or detector is warranted. Rerun the sample on another instrument to determine if the problem results from analytical hardware or the sample matrix.

10.12 Confirmation analysis.

10.12.1 Confirmation analysis is to confirm the presence of Aroclors tentatively identified in the primary analysis.

10.12.1.1 All instrument performance quality control criteria for calibration and retention time must be satisfied on the confirmation analysis.

10.12.2 Each tentative identification must be confirmed: using a second GC column of dissimilar stationary phase (as in the dual-column analysis), based on a clearly identifiable Aroclor pattern, or using another technique such as GC/MS.

10.12.2.1 The primary and secondary analysis is conducted simultaneously in the dual-column analysis.

10.12.2.2 GC/MS confirmation may be used in conjunction with dual-column analysis if the concentration is sufficient for detection in GC/MS, normally a concentration of approximately 10 ng/μl in the final extract for each Aroclor is required. Method 8270 is recommended as a confirmation technique when sensitivity permits.

10.12.3 Once the identification has been confirmed, the agreement between the quantitative results on both columns must be checked.

10.13 Sample Dilution

10.13.1 Establish dilution of sample in order to fall within calibration range or to minimize the matrix interference.

- Utilize screen data (specific project only).
- Utilize acquired sample data.
- Utilize the history program or approval from client/project.
- Sample characteristics (appearance, odor).

10.13.2 If no lower dilution has been reported, the dilution factor chosen must keep the response of the largest peak for a target analyte in the upper half of the initial calibration range of the instrument.

10.13.3 Preparing Dilutions.

10.13.3.1 Prepare sample dilutions quantitatively. Dilute the stored sample extract if available with hexane using logical volume to volume ratios, i.e., 1:5, 1:10, 1:50, etc.

10.13.3.2 Syringe Dilutions - A calibrated 1ml syringe must be used to prepare dilutions. Gently shake to disperse the extract throughout the solvent prior to loading on the auto-sampler tray for further analysis.

10.13.3.3 Volumetric Flask Dilutions – Dilutions can also be made with a Class A volumetric flask. Measure appropriate sample extract volume in a calibrated syringe and bring to a final volume with dilution solvent in a Class A volumetric flask. Gently shake to disperse the extract throughout the solvent prior to loading on the auto-sampler tray for further analysis.

10.14 Data interpretation

10.14.1 Qualitative identification

10.14.1.1 Analyst shall identify the target analytes with competent knowledge interpreting retention time and/or chromatographic pattern by comparison of the sample to the standard of the suspected Aroclor. The criteria required for a positive identification are:

10.14.1.1.1 The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

10.14.1.1.2 The target analytes must elute within the daily absolute retention time window on both primary and confirmation column.

10.14.1.1.3 For PCBs, at least five major peaks are selected. The retention time window for each peak is determined from the initial calibration analysis. This identification of PCBs as Aroclors is based on agreement between the retention times of peaks in the sample chromatogram with the retention time windows established through the analysis of standards of multi-component target analytes. Tentative identification of an analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte.

10.14.1.1.4 Be aware of matrix interfering effects on peak shape and relative peak ratios which could distort the pattern. Interpretation of this phenomenon may require a highly experienced chromatographer or at least a second opinion.

10.14.2 Quantitative analysis

10.14.2.1 Once the Aroclor pattern has been identified, compare the responses of at least 3 major peaks in the single-point calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each corresponding peak and the linear calibration established from the multi-point calibration of the 1016/1260 mixture. A concentration (see section 14.4) based on the integrated area/or height of each of the characteristic peaks is determined and then those resulting concentrations are averaged to provide the final result for the sample.

10.14.2.2 Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. The quantitation may then be performed by measuring the total area of the PCB pattern and quantitating on the basis of the Aroclor standard that is most similar to the sample. Any peaks that are not identifiable as PCBs on the basis of retention times must be subtracted from the total area. When quantitation is performed in this manner, the problems must be fully described for the data user and the specific procedures employed by the analyst must be thoroughly documented.

10.14.2.3 When sample results are confirmed using two dissimilar columns or with two dissimilar detectors, the agreement between the quantitative results must be evaluated after the identification has been confirmed. Calculate the relative percent difference (RPD) between the two results using the formula in Section 14.6. The lower result is reported.

10.14.2.3.1 If one result is significantly higher (e.g., >40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are noted, examine the baseline parameters established by the instrument data system (or operator) during peak integration.

10.14.2.3.2 If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the lower result with the footnote (remark) indicating "More than 40% RPD for detected concentrations between two GC columns".

11.0 QUALITY CONTROL

11.1 QC Requirements Summary

Initial Calibration	Whenever needed
Initial Calibration Verification (ICV)	Following initial calibration
Continuing Calibration Verifications (CCV)	Every 12-hour shift , after every 10 samples and at the end of analysis sequence
Instrument Blank	After each CCV
Method blank	One per extraction batch*
Blank Spike	one per extraction batch*
Matrix Spike	one per extraction batch*
Matrix Spike Duplicate	one per extraction batch*
Surrogates	every sample and standard

*The maximum number of samples per batch is twenty or per project specification.

11.2 Initial Calibration.

11.2.1 Refer to Section 10.1.

11.3 Initial Calibration Verification (ICV) -Second Source Calibration Check.

11.3.1 Refer to Section 10.2.

11.4 Continuing Calibration Verifications (CCV)

11.4.1 Refer to Section 10.3.

11.5 Instrument Blank

11.5.1 If the instrument blank contains a target analyte above its MDL, the source of the contamination must be identified and corrected before proceeding with the analysis.

11.6 Method Blank.

11.6.1 The method blank is either DI water or ottawa sand (depending upon the sample matrix) which must be extracted with each set of 20 or less samples. For a running batch, a new method blank is required for each different extraction day. The method blank must be carried through all stages of the sample preparation and measurement.

11.6.2 If the method blank contains a target analyte above its MDL established by the laboratory, the entire batch must be re-extracted and reanalyzed.

11.6.3 Surrogate compounds are added to the method blank prior to extraction and analysis. If the surrogate accuracy in the blank does not meet criteria established by the laboratory, the entire batch must be re-extracted and reanalyzed.

11.7 Blank Spike (Laboratory Control Sample)

11.7.1 A blank spike must be extracted with each set of 20 or less samples. For a running batch, a new blank spike is required for each different day. The blank spike consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. It is spiked with the same analyte at the same concentration as matrix spike. When the presence of specific Aroclors is not anticipated, the Aroclor 1016/1260 mixture may be appropriate choice for spiking. In situations where the other Aroclors are of interest for a specific project, the analyst may employ different spiking mixtures. The blank spike is prepared at a concentration of 2 μg/l or 133.3 μg/kg (on a dry weight basis) for each Aroclor.

11.7.2 The blank spike recoveries must be assessed using in house limits established by the laboratory.

11.7.3 If a blank spike is out of control, the following corrective actions must be taken. In the case where the blank spike recovery is high and no hits reported in associated samples and QC batch the sample results can be reported with footnote (remark) and no further action is required.

11.7.3.1 Check to be sure that there are no errors in the calculations, or spike solutions. If errors are found, recalculate the data accordingly.
11.7.3.2 Check the instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the batch.
11.7.3.3 If no problem is found, re-extract and reanalyze the batch.

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

11.8.1 One sample is randomly selected from each extraction batch and spiked in duplicate with select Aroclors to assess the performance of the method as applied to a particular matrix and to provide information on the homogeneity of the matrix. Both the MS and MSD are carried through the complete sample preparation, cleanup, and determinative procedures.

11.8.2 The MS and MSD must be spiked with the Aroclors of interest. If samples are not expected to contain target analytes, a matrix spike and matrix spike duplicate pair must be

spiked with Aroclor 1016/1260 mixture. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclor must be used for spiking.

11.8.3 Matrix spikes are prepared by spiking an actual sample at a concentration 2 μg/l or 133.3μg/kg on a dry weight basis.

11.8.4 Assess the matrix spike recoveries and relative percent difference (RPD) against the control limits established by the laboratory.

11.8.5 If the matrix spike accuracy of any individual Aroclor is out of control, the accuracy for that Aroclor in the blank spike must be within control. Matrix interference is assumed and the data is reportable. No further corrective action is required.

11.9 Surrogates.

11.9.1 Tetrachloro-m-xylene (TCMX) and Decachlorobiphenyl (DCB) are used as surrogate standards. All blanks, samples, matrix spikes, and calibration standards contain surrogate compounds which are used to monitor performance of the extraction, cleanup (when used), and analytical system.

11.9.2 The recoveries (Section 14.5) of the surrogates must be evaluated versus the surrogate control limits developed by the laboratory annually.

11.9.3 If surrogate recoveries are not within established control limits, corrective action must be performed if surrogate recoveries indicate that a procedural error may have occurred during the analysis of the sample.

11.9.3.1 Check the surrogate calculations for calculation or integration errors and perform corrections if detected.

11.9.3.2 Reanalyze the extract if no calculation errors are detected. If the surrogate recoveries for the reanalyzed extract are in control, report the data from the reanalysis only.

11.9.3.3 If the data from the reanalysis is also out of control, re-extract and reanalyze the samples

11.9.3.4 If, upon reanalysis, the surrogate recoveries are acceptable, report the reanalysis data. If the holding time has expired prior to the reanalysis, report both the original and the reanalysis results and note the holding time problem.

11.9.3.5 If recovery is again not within limits, the problem is considered to be matrix interference. Submit both data sets with the original analysis being reported.

11.9.4 The retention time shift for surrogate must be evaluated after the analysis of each sample. The sample must be reanalyzed when the retention times for both surrogates are outside the retention time window.

11.9.4.1 Reanalyses are not required for samples having visible matrix interference, defined as excessive signal levels from target or non-target interfering peaks. This judgment must be approved by a team leader or a supervisor.

11.10 Refer to Project Specific Bench Notes (GC8082) for additional program or client specific QC requirements.

11.11 Calculations

11.11.1 Calibration Factor (CF).

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

where:
A_s = Area of the peak for the compound being measured.
C_s = Concentration of the compound being measured (µg/l).

11.11.2 Percent Relative Standard Deviation (% RSD).

$$\%RSD = \frac{SD}{CF_{av}} \times 100$$

where:
SD = Standard Deviation.
CF_{av} = Average calibration factor from initial calibration.

11.11.3 Percent Difference (% D).

$$\% D = \frac{|CF_{av} - CF_c|}{CF_{av}} X\ 100$$

where:
CF_c = CF from continuing calibration (CBCHK).

11.11.4 Concentration (Conc.).

For water:

$$Conc.\ (\mu g/l) = \frac{A_c \times M}{CF_{av}}$$

$$M = \frac{V_f \times D}{V_i}$$

For soil/sediment (on a dry weight basis, see SOP EGN007):

$$Conc.\ (\mu g/kg) = \frac{A_c \times M}{CF_{av}}$$

$$M = \frac{V_f \times D}{W_s \times S}$$

where:
A_c = Area of peak for compound being measured.
V_f = Final Volume of total extract (ml).
D = Secondary dilution factor.
V_i = Initial volume of water extracted (ml).
W_s = Weight of sample extracted (g).
S = (100 - % moisture in sample) / 100 or % solid/100.
M = Multiplier.

11.11.5 Percent Recovery (% R).

$$\%\ R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

11.11.6 Relative Percent Difference (RPD).

$$RPD = \frac{|C_1 - C_2|}{(1/2)(C_1 + C_2)} \times 100$$

where:
C_1 = Matrix Spike Concentration or the result on column 1.
C_2 = Matrix Spike Duplicate Concentration or the result on column 2.

12.0 DOCUMENTATION

12.1 The Analytical Logbook is a record of the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

12.1.2 If samples require reanalysis, a brief explanation of the reason must be documented in this log. For consistency, if surrogates are high or low indicate it as (↑) for high and (↓) for low.

12.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed, the page must be signed and dated by the respective person.

12.2.2 The SGS Lot Number must be cross-reference on the standard vial.

12.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument will have a separate log.

12.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

12.5 Unused blocks of any form must be X'ed and Z'ed by the analyst before submitting the data for review.

12.6 Supervisory (or peer) personnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information must also be verified during this review.

13.0 DATA REVIEW AND REPORTING

13.1 Initial and continuing calibration check. Verify that all calibration and continuing calibration criteria have been achieved. If the criteria had not been achieved, corrective action must be performed to bring the system in control before analyzing any samples.

13.1.1 If samples had been analyzed under non-compliant calibration criteria, all sample extracts must be re-analyzed once the system is brought into control.

13.2 Quality Control Data Review. Review all QC data. If QC criteria were not achieved, perform corrective action before proceeding with analysis.

13.2.1 In some situation, corrective action may demand that the entire sample batch be re-extracted and re-analyzed before processing data.

13.3 Chromatogram Review. The chromatogram of each sample is evaluated for target analytes.

13.3.1 Check specific retention time windows for each target compound for the presence of the target compound in each chromatogram.

13.3.1.1 Each sample may require the reporting of different target analytes. Review the login to assure that the correct target compounds are identified.

13.3.2 The Aroclor must be identified on the primary and confirmatory column before assigning a qualitative identification.

13.3.3 Manual integration of chromatographic peaks must be identified by the analysts. An electronic signature is applied upon data review.

13.4 Transfer to LIMS. Following the initial screen review, transfer the processed data to the LIMS.

14.0 POLLUTION PREVENTION & WASTE MANAGEMENT

14.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 17.2.

14.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

14.2.1 Non hazardous aqueous wastes.

14.2.2 Hazardous aqueous wastes

14.2.3 Chlorinated organic solvents

14.2.4 Non-chlorinated organic solvents

14.2.5 Hazardous solid wastes

14.2.6 Non-hazardous solid wastes

Table 1. PCB Aroclors and Reporting Limits				
Compound	**CAS Number**	**Water (µg/l)**	**Soil (µg/kg)**	**Oil (µg/kg)**
Arochlor – 1016	12674-11-2	0.5	33	500
Arochlor – 1221	11104-28-2	0.5	33	500
Arochlor – 1232	11141-16-5	0.5	33	500
Arochlor – 1242	53469-21-9	0.5	33	500
Arochlor – 1248	12672-29-6	0.5	33	500
Arochlor – 1254	11097-69-1	0.5	33	500
Arochlor – 1260	11096-82-5	0.5	33	500
Arochlor – 1262	37324-23-5	0.5	33	500
Arochlor – 1268	11100-14-4	0.5	33	500

Table 2. RECOMMENDED OPERATING CONDITION	
Gas Chromatograph/Electron Capture Detectors	
Carrier Gas	Helium
Make-up gas	5 % Methane/ 95 % Argon
Make-up gas flow	*30 ml/min
Injection port temperature	*****235 °C
Injection type	Split / Splitless
Detector temperature	*****320 °C
Column flow	*5 ml/min
Gas Chromatograph Temperature Program*	
Initial temperature	*170 °C
Time 1	*2 min
Column temperature rate 1	*30 degrees/min
Temperature 1	*180 °C
Column temperature rate 2	*3.5 degrees/min
Temperature 2	*240 °C
Column temperature rate 3	*10 degrees/min
Final temperature	*280 °C
Time 3	*5 min
Total run time	30-40 min

* Parameter modification allowed for performance optimization as long as QC criteria are achieved.

Table 3A. Aroclors 1016/1260 Mixture and Surrogates Working Solution	
Stock Solution	**Volume Added**
Aroclor 1016/1260 (1,000 µg/ml)	500 µl
Pesticides Surrogate Std Spiking Solution (200 µg/ml)	100 µl
Hexane	fill to volume
Total	25.0 ml

- Aroclors 1016/1260 (20 µg/ml) and Surrogates (0.8 µg/ml) Working Solution: Prepared by measuring 500 µl of 1,000 µg/ml Aroclor 101/1260 and 100µ of 200 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 3B. Individual Aroclor* and Surrogates Working Solution	
Stock Solution	**Volume Added**
Individual Aroclor* (1,000 μg/ml)	500 μl
Pesticides Surrogate Std Spiking Solution (200 μg/ml)	100 μl
Hexane	24.4 ml
Total	25 ml

*Aroclor: 1221, 1232, 1242, 1248, 1254, 1262 & 1268

- Individual Aroclor (20 μg/ml) and Surrogates (0.8 μg/ml) Working Solution: Prepared by measuring 500 μl of 1,000 μg/ml each individual Aroclor, 100 μl of 200 μg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 4A. Aroclors 1016/1260 Calibration Standard Solutions					
Standard	**Working Solution**	**Concentration (μg/ml)**	**Volume Added (μl)**	**Final Volume in Hexane (ml)**	**Final Concentration (μg/l)**
Standard A	Aroclors 1016/1260	20	62.5	25	50
	Surrogates	0.8			2
Standard B	Aroclors 1016/1260	20	312.5	25	250
	Surrogates	0.8			10
Standard C	Aroclors 1016/1260	20	625	25	500
	Surrogates	0.8			20
Standard D	Aroclors 1016/1260	20	1250	25	1,000
	Surrogates	0.8			40
Standard E	Aroclors 1016/1260	20	2,500	25	2,000
	Surrogates	0.8			80
Standard F	Aroclors 1016/1260	20	3,750	25	3,000
	Surrogates	0.8			120

- Standard A: Prepared by measuring 62.5 μl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.

- Standard B: Prepared by measuring 312.5 μl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.

- Standard C: Prepared by measuring 625 μl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.

- Standard D: Prepared by measuring 1,250 μl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.

- Standard E: Prepared by measuring 2,500 μl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.

- Standard F: Prepared by measuring 3,750 μl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.

Table 4B. Single-Point Calibration Standard (1,000 µg/l) for Individual Aroclor*	
Stock Solution	**Volume Added**
Individual Aroclor*/Surrogate Working Solution (20 µg/ml/0.80µg/ml) (Table 3B)	1,250 µl
Hexane	23.75 ml
Total	25 ml

* Aroclor: 1221, 1232, 1242, 1248, 1254, 1262, & 1268.

- Individual Aroclor Calibration Standard (1,000 µg/l) and Surrogates (40 µg/l) Solution: Prepared by measuring 1,250 µl of individual Aroclor and surrogates working solution, containing 20 µg/ml of each corresponding Aroclor and 0.80 µg/ml of both surrogate compounds, and bringing to 25 ml with hexane.

Table 4C. Multi-point Calibration Standards for Individual Aroclor* (optional)					
Standard	**Stock Solution**	**Concentration (µg/ml)**	**Volume Added (µl)**	**Final Volume in Hexane (ml)**	**Final Concentration(µg/l)**
Standard A	Aroclor*	20	62.5	25	50
	Surrogates	0.8			2
Standard B	Aroclor*	20	312.5	25	250
	Surrogates	0.8			10
Standard C	Aroclor*	20	625	25	500
	Surrogates	0.8			20
Standard D	Aroclor*	20	1250	25	1,000
	Surrogates	0.8			40
Standard E	Aroclor*	20	2,500	25	2,000
	Surrogates	0.8			80
Standard F	Aroclor*	20	3,750	25	3,000
	Surrogates	0.8			120

*Aroclor: 1221, 1232, 1242, 1248, 1254, 1262, & 1268.

- Standard A: Prepared by measuring 62.5 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

- Standard B: Prepared by measuring 312.5 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

- Standard C: Prepared by measuring 625 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

- Standard D: Prepared by measuring 1,250 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

- Standard E: Prepared by measuring 2,500 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

- Standard F: Prepared by measuring 3,750 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

Table 5A. Continuing Calibration Check Solutions for Aroclors 1016/1260					
Checks	**Working Solution**	**Concentration (µg/ml)**	**Volume Added (µl)**	**Final Volume in Hexane (ml)**	**Final Concentration (µg/l)**
Solution 1	Aroclors 1016/1260	20	625	25	500
	Surrogates	0.8			20
Solution 2	Aroclors 1016/1260	20	1250	25	1,000
	Surrogates	0.8			40

- Solution 1: Prepared by measuring 625 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.

- Solution 2: Prepared by measuring 1,250 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A), and bringing to 25 ml with hexane.

Table 5B. Continuing Calibration Check Solutions for Individual Aroclor*					
Checks	**Working Solution**	**Concentration (µg/ml)**	**Volume Added (µl)**	**Final Volume in Hexane (ml)**	**Final Concentration (µg/l)**
Solution 1	Aroclor*	20	625	25	500
	Surrogates	0.8			20
Solution 2	Aroclor*	20	1250	25	1,000
	Surrogates	0.8			40

* Aroclor: 1221, 1232, 1242, 1248, 12541262, & 1268

- Solution 1: Prepared by measuring 625 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

- Solution 2: Prepared by measuring 1,250 µl of Individual Aroclor and Surrogates Working Solution (Table 3B), and bringing to 25 ml with hexane.

Table 6A. Second Source Calibration Check Standard for Aroclors 1016/1260 (1,000 µg/l)		
	Stock Solution	**Volume Added**
Aroclors 1016/1260 (25 µg/ml) and Surrogates (2.5 µg/ml) Working Solution		1,000 µl
Hexane		24 ml
Total		25 ml

- Aroclors 1016/1260 (25 µg/ml) and Surrogates (2.5 µg/ml) Working Solution: Prepared by measuring 250 µl of 1,000 µg/ml Aroclors 1016/1260 mix solution (2nd source), 125 µl of 200 µg/ml pesticides surrogate std spiking solution and bringing to 10 ml with hexane.

- Aroclors 1016/1260 (1,000 µg/l) and Surrogates (100 µg/l) Solution: Prepared by measuring 1,000 µl of Aroclors 1016/1260 (25 µg/ml) and surrogates (2.5 µg/ml) working solution and bringing to 25 ml with hexane.

Table 6B. Second Source Calibration Check Standard for Individual Aroclor* (1,000 μg/l)	
Stock Solution	**Volume Added**
Individual Aroclor* (100μg/ml)	250uL
Surrogates (200 μg/ml)	5uL
Hexane	Add to bring to 25mL volume
Total	25 ml

*Aroclor: 1221, 1232, 1242, 1248, 1254, 1262 & 1268

- ICV preparation: Using Individual Aroclor (100 μg/ml) and Surrogates (200 μg/ml) Stock Solutions : Measure 250 μl of 1,00 μg/ml each individual Aroclor stock solution 2nd source and 5μl of 200 μg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

STANDARD OPERATING PROCEDURE FOR DETERMINATION OF TOTAL ORGANIC CARBON

LAB MANAGER: Stony Brook

QA MANAGER: Ryan Gaines

EFFECTIVE DATE: 12-21-2016

TITLE: TOTAL ORGANIC CARBON IN SOILS SAMPLES
REFERENCES: "PROCEDURES FOR HANDLING AND CHEMICAL ANALYSIS OF SEDIMENT AND WATER SAMPLES" PREPARED FOR THE US EPA CORPS OF ENGINEERS, MAY 1981, MODIFIED, AND EPA REGION 2 LLOYD KAHN METHOD JULY 1988, MODIFIED.
REVISED SECTIONS: Method reference, 1.2, 6.2
DELETED SECTIONS: 1.3

1.0 SCOPE AND APPLICATION

1.1 This method can be used to determine total organic carbon in any solid matrix. It may also be used for liquid matrices containing a high level of total organic carbon. Samples that are primarily aqueous may also be analyzed using this method, but sample sizes must be limited to $\leq$ 0.10 g.

1.2 The product code for total organic carbon is TOC by the Corp. of Engineers method. The product code is TOCLK for total organic carbon run by the Lloyd Kahn EPA Region 2 method, modified to use sucrose and glucose for the calibration standards and checks as per the manufacturer's instructions. The manufacturer specifically states that Potassium Hydrogen Phthalate (KHP) must not be used as a standard on the SSM. The potassium combining with the carbon will form an ionic bond that will not be broken completely with the 900° temperature.

2.0 SUMMARY OF METHOD

2.1 Total organic carbon is determined by combusting an acidified sample and quantitating the carbon dioxide released using infrared analysis. Total carbon is similarly determined, exception samples are not acidified nor combusted prior to analysis. The quantitation is done by comparison to a linear calibration curve.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 The normal reporting limit for TOC in soils is 1000 mg/kg. This is based on a 0.1 g sample size. A minimum reporting limit of 100 mg/kg can be obtained by using a 1.0 g sample size. A reporting limit of 100 mg/kg is required for samples being analyzed for Lloyd Kahn TOC. A low level calibration standard is run at the level of this reporting limit.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an

individual compound that meets the method qualitative identification criteria. Experimental MDLs must be determined annually for this method.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD: The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent. (For some methods this is mandatory and for some it is a recommendation only. Refer to individual method SOP's). For most methods, the mid-level calibration check standard criteria is ± 10 percent of the true value.

EXTERNAL CHECK STANDARD: The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. The laboratory must initially assess laboratory performance of a check standard using the control limits generated by the external check supplier or limits defined in the SOP. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK SAMPLE: Digest and analyze a high and a low standard with each batch of samples. These standards must have a recovery of 90 to 110 %. If the spike blank is outside of the control limits for a parameter, all samples must be redistilled and reanalyzed for that parameter. The exception is if the spike blank recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with qualification.

LAB CONTROL SAMPLE: A solid lab control sample from an external source may be distilled with a batch, depending on individual client requirements. The solid lab control is evaluated using manufacturer's limits. If the lab control is outside of the control limits for a parameter, all samples must be redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with qualification.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample must be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. If a matrix spike is out of control, then the results must be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and must be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent must be used.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{Matrix Spike Recovery}$$

‘

METHOD BLANK: The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMIT (MDL): The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs must be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard

solution to produce working standards which cover the working range of the instrument. Standards must be prepared at the frequency specified in the appropriate section. The calibration standards must be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The furnace operates at high temperature and the furnace must be allowed to cool down before doing any system maintenance or troubleshooting. If there are any signs of a system blockage, open the sample introduction port and turn off the furnace to prevent build up of back pressure.

5.3 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 Soil samples must be kept under refrigeration at 0-6^0 C until they are analyzed.

6.2 No holding time is outlined in the Corp. of Engineers method for TOC. Unless otherwise specified, a 28-day holding time will be applied to solid samples analyzed with that method.

6.3 A 14-day holding time must be followed when analyzing TOC soils following the EPA Region II, Lloyd Kahn method.

7.0 INTERFERENCES

7.1 High results may be obtained if the inorganic carbon is not completely removed from the sample before analysis. To ensure that all of the inorganic carbon is removed, heat an acidified sample at least 10 minutes at 75°C before starting the analysis. Some volatile organics may be lost in this heating step, resulting in a low bias in the TOC result.

8.0 APPARATUS

The following items are needed for the analysis of samples following the method outlined below:

8.1 Shimadzu 5000 TOC analyzer or TOC-V or TOC-L analyzer with soil analysis module or equivalent.

8.1.1 Each day of analysis, the humidifier must be checked to ensure that the water level is within 1 inch of the top of the humidifier.

8.1.2 Each day of analysis, the baseline must be checked to make sure that it is stable and near zero.

8.1.3 Whenever calibration check recoveries or blanks are out of compliance, the flow and the condition of the catalyst must be checked. If the catalyst appears bad (contains many small fines), it must be cleaned and replaced. Refer to the instrument manuals for additional information on system maintenance.

8.2 Syringes, 0.100 ml size.

8.3 Analytical balance, capable or weighing to 0.1 mg. The calibration of the analytical balance must be verified each day before use.

8.4 Volumetric glassware, class A, for standards preparation.

8.5 Ceramic boats.

8.6 Drying oven, capable of being set to 75°C

9.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Deionized water taken from the DI tap with the carbon filter must be used whenever water is required. Make sure to properly label all reagents and record the reagent preparation in the reagent logbook.

9.1 Sucrose Stock Solution, 200000 mgC/l (20% C from sucrose): Dry sucrose in dissector. Weigh out 47.5 grams into a 100 ml volumetric flask containing approximately 80 ml of DI water. Add concentrated hydrochloric acid to bring the pH to less than 2. Mix well and bring to a final volume of 100 ml. Note: This stock must be replaced whenever crystallization of the sucrose is apparent. It can be held for a maximum of 3 months. Refrigeration is not required.

9.2 Sucrose Standard Solutions: Dilute the above stock solution (200000 mC/l) as shown below to make the suggested calibration standards. Add concentrated hydrochloric acid to bring the pH to less than 2 before diluting each standard to the final volume.

9.2.1 Different standards may be used, but a minimum of 5 standards and a blank are required for the initial calibration. The top standards shown below are close to the top of the linear range of the instrument and sometimes will not work at these levels.

9.2.2 Suggested curve levels are shown below. These standards must be held for no longer than one month.

9.2.3 Either the 50000 mgC/l or the 40000 mgC/l may be used as the highest standard. Both are not required.

Standard Level	ml of stock	Final volume (ml)

50000 mgC/l	25.0	100
40000 mgC/l	20.0	100
25000 mgC/l	12.5	100
10000 mgC/l	10.0	200
5000 mgC/l	5.00	200
1000 mgC/l	1.00	200
Blank	0.000	100

9.3 Glucose Stock solution, 50000 mgC/l (5% C from glucose): Dry glucose in dessicator. Weigh out 12.5 grams into a 100 ml volumetric flask containing approximately 80 ml of DI water. Add concentrated hydrochloric acid to bring the pH to less than 2. Mix well and bring to a final volume of 100 ml. Note: This stock must be replaced whenever crystallization of the glucose is apparent. It can be held for a maximum of 1 month. Refrigeration is not required.

9.4 Glucose Check Solution, 25000 mgC/l (2.5% C from glucose): Dilute 50.00 ml of the glucose stock solution (50000 mgC/l) to approximately 80 ml with DI water. Add concentrated hydrochloric acid to bring the pH to less than 2 and then dilute to a final volume of 100 ml with DI water. This solution must be made up monthly.

9.4.1 A different concentration of this check solution will be needed if a lower curve is run.

9.5 Nitric Acid, reagent grade. Used for acidifying samples to remove inorganic carbon.

9.5.1 Dohrman Instruments recommends that phosphoric acid not be used for this purpose. Dohrman found that the phosphoric acid tended to coat both the boat and the catalyst in the furnace with a layer of polyphosphoric acid and that, possibly as a consequence of this, the release of inorganic carbon as carbon dioxide was slower than with nitric acid and possibly incomplete.

9.6 Oxygen Gas, high purity.

9.7 Silica sand.

10.0 PROCEDURE

10.1 Below is the procedure to be followed for the analysis of soil samples for total organic carbon using the Shimadzu TOC soil analyzer. For the procedure with the newer Shimadzu TOC-V and TOC-L soil analyzers, refer to step 10.2. (More details for use of the software can be found in the TOC-V and TOC-L user's manual.)

10.1.1 Turn on the oxygen. The pressure in the soil module must be set at 2 and the carrier gas must be set as marked on the dial (0.5 l/min). The oxygen pressure at the tank must be at least 60 psi to maintain sufficient pressure at the instrument. Check to make sure that the humidifier contains sufficient water. It must be filled to within approximately 1 inch of the top of the humidifier. (The humidifier is located under the magnetic plate on the right side of the instrument.)

10.1.2 If the power is off, then turn on the power at the side of the soil and water modules and for the computer.

10.1.3 Go into the TOC software on the TOC. Select measure and then connect. Wait for the software to connect with the TOC analyzer. Proceed to options and then instrument conditions. Under TOC, there must be no check next to Furnace on. Under ASI, there must be no check next to ASI used. Under SSM, the TOC furnace must be turned on.

10.1.4 Go to view and click on the background monitor. A graph will appear on screen showing the position of the baseline and the status of the furnace temperature. Wait for the baseline to stabilize and for the furnace temperature to indicate that it is OK. Make sure that the hatch on the boat sampler is tightly closed and that there are no leaks in the system. If the baseline is not within $\pm$ 10 of zero, then the zero of the instrument may need to be adjusted. Check with the lab supervisor or manager for further instructions.

10.1.5 If the instrument has not been calibrated within the last month, then it is recommended that it be calibrated at this point. (A new calibration is required at least once per quarter.)

10.1.5.1 Select a new file and insert standards. A minimum of 2 injections must be used for each standard. Five standards and a blank are required for the calibration. The lowest standard must be at 1000 mgC/l or lower. A 100 ul injection size must be used for all standards.

10.1.5.2 After the standard file is created and inserted into the run file, then save the run file using the save as command. The file must be named with the instrument ID (A or B), the last digit of the year, the month, the day, and a designation for the matrix and the run number for that matrix. For example, the first soil run on instrument A from 3/28/01 would be named A10328s1.

10.1.5.3 Press start in the software and follow the prompts. Place a clean boat filled with a small tuft of glass wool in the boat sampler. When indicated by the software, inject 100 ul of standard into the boat. Close the hatch and push the boat all the way forward. Enter OK at the software.

10.1.5.4 After the sample has finished running, the software will prompt you to pull the boat back to the cool position. Pull the boat only to the cool line at this point. When indicated by the software, then pull the boat back to the starting position.

10.1.5.5 Select the option to repeat the injection and repeat the steps outlined above.

10.1.5.6 When all of the standards have been completed, then review the curve using the view, calibration option.

10.1.5.6.1 If a correlation coefficient of greater than 0.995 is obtained, then save the curve using the file, save option. Check to make sure that the intercept, calculated using a weight of 1.0 g for Lloyd Kahn or using a weight of 0.1 g for other TOC analyses, is less than the reporting limit for each method (100 mg/kg for Lloyd Kahn or 1000 mg/kg for other TOC soils.)

10.1.5.6.2 If either the correlation coefficient or the intercept does not meet the above criteria, than recalibrate before proceeding with the samples.

10.1.5.7 If a previous calibration is being used, then it must be verified with a low and a high standard and a blank before proceeding on each analysis day. The low standard must be within 30 percent of the true value. All other check standards must be within 10 percent of the true value. The blank must contain less than the reporting limit for TOC. Make sure to use duplicate injections for all analyses. Note: The method blank may be used as the calibration blank check.

10.2 Below is the procedure to be followed for the analysis of soil samples for total organic carbon using the Shimadzu TOC-V or TOC-L soil analyzer.

10.2.1 Turn on the oxygen. Set the bench-top gauge to 29 psi. Check to make sure that the humidifier contains sufficient water. It must be filled to within the two white lines on the side of the humidifier. (The humidifier is located inside the water analyzer at the right side of the instrument.) For the TOC-L, the oxygen gauge on the bench must be set to 29 psi.

10.2.2 If the power is off, then turn on the power. For the TOC-V, it is turned on at the side of the soil modules and at the front panel of the water module and for the computer. For the TOC-L, it is turned on at the side of the soil module, and the back and the front of the water module.

10.2.3 Go into the TOC software on the TOC. In the TOC-Control V main window, double click on the sample table editor and click OK on the user name box.

10.2.4 Before starting the run, open the background monitor to make sure that the baseline is stable and the furnace is up to temperature. If there are problems at this point, check with the lab supervisor or manager for further instructions.

10.2.5 For the TOC-V, generate the file using the following instructions.

10.2.5.1 Click File, New, and choose Calibration Curve and click OK. Follow the directions on each screen. For the system, pick TOC-V with SSM. Click on the calibration points. Then enter the file name. The file must be named with the instrument identifier (B, C, or D), year (1 digit), the month (2 digits), the day, and a designation for the matrix and the run number for that matrix. For example, the first soil run on instrument C from 3/12/07 would be named C70312s1. Enter the file name and then go to the volume. Enter the concentration and number of points. Edit the points to correct the concentrations. Enter next until the last screen is reached and then click on finish.

10.2.5.1.1 If using a previously generated calibration, then this step can be omitted. A new calibration is required at least once per quarter, but it is recommended that this be run once per month.

10.2.5.2 Go back to the TOC-Control V main window and double click the sample table editor. Click File and New to open the sample run icon. Click the system tab and select the TOC-SSM system. Click on the new file and follow the prompts on the screen. Name the file using the convention as described above.

10.2.5.3 Connect to the instrument using the connect toolbar button or from the instrument menu. Insert the calibration file created above into the sample table. You must load the new curve into the method before running the samples.

10.2.5.4 To start running the calibration, press start in the software and follow the prompts. Place a clean boat in the boat sampler. When indicated by the software, inject 100 ul of standard into the boat. Close the hatch. Enter 100 ul into the volume prompt and then hit start. Wait for the prompt and then push the boat forward.

10.2.5.5 After the sample has finished running, the software will prompt you to pull the boat back to the cool position. Pull the boat only to the cool line at this point. When indicated by the software, then pull the boat back to the starting position.

10.2.6 For the TOC-L, generate the file using the following instructions.

10.2.6.1 Click File, New, and sample table. Then pick the instrument and connect. Then choose Calibration Curve and click OK. Follow the directions on each screen. Click on the calibration points. Then enter the file name. The file must be named with the instrument identifier (B, C, or D), year (1 digit), the month (2 digits), the day, and a designation for the matrix and the run number for that matrix. For example, the first soil run on instrument C from 3/12/07 would be named C70312s1. Enter the file name and then go to the volume. Enter the concentration and number of points. Edit the points to correct the concentrations. Enter next until the last screen is reached and then click on finish.

10.2.6.1.1 If using a previously generated calibration, then this step can be omitted. A new calibration is required at least once per quarter, but it is recommended that this be run once per month.

10.2.6.2 Go back to the TOC-Control L main window and click the sample table editor. Click File and New, and select the TOC-SSM system. Highlight the first row, click insert, select multiple samples, select choose method, and select number of samples. Name the file using the convention as described above.

10.2.6.3 Connect to the instrument using the connect button. Insert the calibration file created above into the sample table. You must load the new curve into the method before running the samples.

10.2.6.4 To start running the calibration, press start in the software and follow the prompts. Place a clean boat in the boat sampler. When indicated by the software, inject 100 ul of standard into the boat. Close the hatch. Enter 100 ul into the volume prompt and then hit start. Wait for the prompt and then push the boat forward.

10.2.6.5 After the sample has finished running, the software will prompt you to pull the boat back to the cool position. Pull the boat only to the cool line at this point. When indicated by the software, then pull the boat back to the starting position.

10.2.7 When all of the standards have been completed, then review the curve using the view, calibration option. If a correlation coefficient of greater than 0.995 is obtained and the intercept is less than the RDL, then save the curve and put it into the method(s) that you are running. Then you can proceed to add samples.

10.3 After the calibration or calibration checks are completed, then analyze the external check standard made from the secondary source. This standard must agree within 10 percent of the true value. If it is not within this range, determine the source of the problem before proceeding. Note: The spike blank may be used as the external calibration check, but then the results must be within 10 percent of the true value.

10.4 After every 10 samples, a continuing calibration check (CCV) sample must be analyzed. The continuing calibration check must be a standard near the mid-range of the curve. The continuing calibration check must agree within 10 percent of the true value. If the CCV is not within 10% of the true value, then no samples can be reported in the area bracketed by this CCV unless the CCV is biased high (110 to 150%) and the sample results to be reported are less than the reporting limit.

10.5 For some clients, a continuing calibration blank (CCB) may be required. This is not required as part of the normal TOC protocol. If it is required, than it must be run after each CCV check. The results of the CCB must be less than the reporting limit for TOC. If the CCB is not less than the reporting limit, then no samples can be reported in the area bracketed by this CCB unless the samples results to be reported are less than the reporting limit.

10.6 Begin analyzing the samples following the procedure outlined below.

10.6.1 Measure four 100 to 1000 mg sample aliquots into four ceramic boats using a 4-place analytical balance. For samples that contain high levels of TOC smaller sample sizes may be needed. For unknown samples, start with a sample size of 100 mg. (All method blanks and spike blanks must be calculated assuming a 100 mg sample size and must be set up using silica sand.) Samples that contain non-homogeneous particulates must be homogenized with a mortar and pestle before weighing out the sample aliquot.

10.6.1.1 If a client is requiring a detection limit lower than 1000 mg/kg, then larger sample sizes are required. A detection limit of 100 mg/kg (TOCLK) requires a weight of 1 gram. A smaller sample size may be used only to bring the sample to within the range of the calibration curve.

10.6.1.2 If less than 50 mg is used for a sample to bring it within linear range, then 4 replicates must be analyzed at that weight.

10.6.2 Add nitric acid dropwise to the sample until no additional effervescence is observed and the surface of the sample is covered with the acid. Heat the acidified sample in an oven at 75°C for a minimum of 10 minutes or until dry.

10.6.2.1 To analyze samples for total carbon (TCAR) omit step 10.6.2, and proceed from 10.6.1 to 10.6.3.

10.6.3 If the duplicate sample injections have a coefficient of variation (CV) of greater than15 percent or an RPD of greater than 20%, then repeat the analysis with 2 additional duplicate injections. If, on the repeated analysis, a high CV or RPD is still obtained, then the sample results must be reported with a flag due to possible sample non- homogeneity. This 15% CV or 20% RPD criteria does not apply if the sample results are low and the results are within plus or minus the reporting limit of each other.

$$CV = (\text{Std Dev}_{n-1} / \text{mean}) \times 100$$

$$RPD = (\text{Result1} - \text{Result 2})) \times 100/\text{mean}$$

10.6.4 With each batch of 10 samples or less, a matrix spike and a duplicate must be analyzed. On each analysis day, a method blank and spike blank must be analyzed. All of these quality control points must be analyzed in duplicate.

10.6.4.1 Prepare two method blanks by treating a small amount (approximately 100 mg) of silica sand with nitric acid and heating at 75 ºC for a minimum of 10 minutes or until dry.

10.6.4.2 Prepare two spike blanks in the same manner as the method blanks, but spike it with 100 ul of a 20000 mgC/l standard or external solution before adding the acid. Note: The spike blank can be used in place of the external check, but then must be prepared from the external source and must meet the 10% check criterion.

10.6.4.3 Prepare the duplicate in the same manner as a sample, but prepare a minimum of 4 boats. Quadruplicate injections are required for the duplicate sample.

10.6.4.4 Prepare four matrix spikes by adding 100 ul of a 20000 mgC/l standard or external solution to each sample aliquot before adding the acid and heating the sample.

10.6.5 At the end of the analysis, a continuing calibration check must be analyzed. If the calibration check is not within 10 percent of the true value then all samples bracketed by the out of compliance CCV must be reanalyzed. (If the CCV is within 110 to 150%, then samples with results <RDL may be reported.)

10.6.6 If required, a CCB must be analyzed after the final CCV check of the analysis. Refer to Section 10.5.

10.7 The final sample results are calculated using the equation shown below. The calculation is done automatically in the Shimadzu TOC software except for the percent solids correction. The percent solids correction is added when the data is transferred in the LIMS system. See area supervisor or manager for further details.

Organic Carbon, Total (mg/kg) =

$$\frac{\text{Conc. from curve (ug)}}{\text{Sample weight in g x \%sol/100}}$$

11.0 QUALITY CONTROL

Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

11.1 Method Detection Limits (MDLs). MDLs must be established using a blank sample spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.14, which is the student's t value for a 99% confidence level. MDLs must be determined approximately once per year.

11.2 Calibration Curve. The instrument must be calibrated a minimum of once per quarter. It is recommended that the instrument be calibrated at least once per month. The calibration curve must have a correlation coefficient of at least 0.995 and the intercept must be less than the reporting limit. If the instrument is not calibrated on a given day, then the curve must be verified using a low and a high standard and a blank before proceeding on each analysis day. The low standard must be within 30 percent of the true value. All other check standards must be within 10 percent of the true value. The blank must contain less than the reporting limit for TOC.

11.3 Method Blank. The laboratory must prepare and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different analysis day. The method blank must contain the analyte at less that the reporting limit. If the method blank contains over that limit, the samples must reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

11.4 Spike Blank. The laboratory must prepare and analyze a spike blank with each set of 20 or less samples. For a running batch, a new spike blank is required for each different analysis day. The laboratory must assess laboratory performance of the spike blank against recovery limits of 80 to 120 percent. (If the spike blank is used in place of the external, then it must be within recovery limits of 90 to 110 percent.) If the lab control recovery is high and the results of the samples to be reported are less than the reporting limit, then the sample results can be reported with qualification. In all other situations, all samples associated with a spike blank outside of recovery limits must be reanalyzed.

11.5 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. (Note: For Florida samples, spikes must be prepared for 1 in 10 samples.)

11.5.1 The spike recovery must be assessed using in house limits. Until these limits can be generated, then default limits of 75 to 125 percent recovery must be applied. If a matrix spike is out of control, then the results must be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount,

then the sample cannot be assessed against the control limits and must be footnoted to that effect.

11.5.2 The matrix spike recovery must be calculated as shown below.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{MS Recovery}$$

11.6 Matrix Duplicate. The laboratory must prepare and analyze a duplicate sample for a minimum of 1 in 20 samples. The duplicate must always be analyzed using a minimum of 4 injections to meet the quadruplicate injection requirement for the Lloyd Kahn method. The relative percent difference (rpd) between the duplicate and the sample must be assessed. Matrix spike duplicates may be used in place of matrix duplicates. The duplicate rpd is calculated as shown below.

11.6.1 The duplicate RPD must be assessed using in house limits. Until these limits can be generated, then default limits of 20 percent RPD must be applied. If a duplicate is out of control, then the results must be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control.

11.6.2 This duplicate fills the requirement for quadruplicate injections for one sample in 20 for the TOCLK method.

11.6.3 The duplicate RPD must be calculated as shown below.

$$\frac{\text{(Sample Result - Duplicate Result)} \times 100}{\text{(Sample Result + Duplicate Result)} \times 0.5} = \%\ \text{RPD}$$

11.7 Quality Control Sample (also referred to as Initial Calibration Verification Standard, (ICV)). A standard from a separate source than the calibration must be run at the beginning of each run. This ICV must be within 10 percent of the true value. If it is not, the problem must be resolved before any samples can be analyzed. Note: The spike blank may be used in place of the ICV as long as a separate source standard is used and the 10 percent criterion is met.

11.8 Continuing Calibration Verification (CCV). Analyze the continuing calibration verification solution after every tenth sample and at the end of the sample run. If the CCV solution is not within 10 percent of the true value, then no samples can be reported in the area bracketed by that CCV. (Note: the exception is if the CCV is biased high (111 to 150%) and the samples are less than the detection limit. In that case, the samples can be reported with no flag.) The CCV concentration must be at or near the mid-range of the calibration curve.

11.9 Continuing Calibration Blank (CCB). For some clients, a continuing calibration blank (CCB) may be required. This is not required as part of the normal TOC protocol. If it is required, than it must be run after each CCV check. The results of the CCB must be less than the reporting limit for TOC. If the CCB is not less than the reporting limit, then no samples can be reported in the area bracketed by this CCB unless the sample results to be reported are less than the reporting limit.

12.0 DOCUMENTATION REQUIREMENTS

12.1 Each analyst must review all data and assemble a data package consisting of the following information. This data package must be turned into the supervisor for review after the analysts complete their LIMS review (see 12.3 below).

- Results report, showing dilutions, replicate injection results, and CV or RPD results.
- Preparation/run log showing weights taken at the balance for each injection.
- Standards prep sheet.
- Reagent information sheet.
- QC Summary sheet with calculations

12.2 In addition, all reagent information such as lot numbers must also be recorded in the reagent log book. Any unusual characteristics of the samples must be noted on the raw data or on the preparation log. Make sure that all sample ID's and dilutions are labeled on the data.

12.3 An ASCI format file must be generated and copied over to the LIMS. The analyst is responsible for reviewing the data in the LIMS and adding appropriate spike amounts and true values before sending the data for supervisor approval.

13.0 POLLUTION PREVENTION & WASTE MANAGEMENT

13.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 13.2.

13.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

13.2.1 Non hazardous aqueous wastes.

13.2.2 Hazardous aqueous wastes

13.2.3 Chlorinated organic solvents

13.2.4 Non-chlorinated organic solvents

13.2.5 Hazardous solid wastes

13.2.6 Non-hazardous solid wastes

14.0 ADDITIONAL REFERENCES

14.1 Shimadzu Instrument Manuals

STANDARD OPERATING PROCEDURE FOR GRAIN SIZE AND SIEVE TESTING

LAB MANAGER: Stonybrook

QA MANAGER: Olga Gaidaen

EFFECTIVE DATE: 10-21-2016

TITLE: GRAIN SIZE AND SIEVE TESTING
REFERENCES: ASTM D422-63 (07)
REVISED SECTIONS: 6.1

1.0 SCOPE AND APPLICATION

1.1 This method is used as a quantitative determination of the distribution of particle size in soils. The distribution of particle sizes larger than 75µm (retained on the number 200 sieve) is determined by sieving, while the distribution of particle sizes smaller than 75µm is determined by a sedimentation process, using a hydrometer.

2.0 SUMMARY OF METHOD

2.1 An air-dried sample is divided into two portions; one portion is retained on a number 10 sieve and the second portion contains only particles that pass the number 10 sieve. The portion retained on the number 10 is separated into a series of fractions using as many sieves as needed depending on the sample. The portion passing the number 10 sieve is soaked in a dispersing agent for 16 hours, vigorously stirred, transferred to a sedimentation cylinder, and allowed to settle for a period of up to 24 hours with hydrometer readings taken at specific intervals.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit is not application for this method. Results are reported as a percent of the total sample weight.

3.2 Method Detection Limit. Method Detection limits studies are not required for this method.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is analyzed at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is

available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 All samples should be kept under refrigeration at 0-6^0 C(not frozen) until they are analyzed.

6.2 No specific holding time is listed in this method.

7.0 INTERFERENCES

7.1 No interferences are specified in this method.

8.0 APPARATUS

The following items are needed for the analysis of samples following the method outlined below:

8.1 Sieves, a series of sieves, of square-mesh woven wire cloth giving uniform spacing of data points for graph. The series of sieves listed below is recommended. An alternate series of sieves is also allowed in the method.

Sieve Name	Particle size
3 in	75.0 mm
1.5 in	37.5 mm
¾ in	19.0 mm
3/8 inch	9.5 mm
No. 4	4.75 mm
No. 8	2.36 mm
No. 10	2.00 mm
No. 16	1.18 mm
No. 30	0.600 mm
No. 50	0.300 mm
No. 100	0.150 mm
No. 200	0.075 mm

8.2 Four decimal place analytical balance. The balance must have its calibration verified with Class S weights

8.3 Stirring apparatus. A mechanically operated stirring device in which a suitably mounted electric motor turns a vertical shaft at a speed of not less than 10000 rom without a load. The shaft shall be equipped with a replaceable stirring paddle made of metal, plastic, or hard rubber. Humboldt model 936 stirrer or equivalent should be used in the lab.

8.4 Dispersion cup equipped with baffle rods. Humboldt model H-2465 or equivalent should be used in the lab.

8.5 Hydrometer, 152H, meeting ASTM specifications. (Hydrometer 151H may also be used as described in the method, but this SOP describes the use of hydrometer 152H.)

8.6 Sedimentation cylinder marked for a volume of 1000 ml and an inside diameter such that the 1000-ml mark is 36 ± 2 cm from the bottom on the inside.

8.7 Thermometer accurate to 1°F (0.5°C)

8.8 Timing device, watch or clock with a second hand

8.9 Beakers, at least 250-ml capacity

8.10 Drying Closet, forced air at approximately 80 deg F.

9.0 REAGENTS

9.1 All chemicals listed below are reagent grade unless otherwise specified. Deionized water should be used whenever water is required. Make sure to properly label all reagents and record the reagent preparation in the reagent log book. All chemicals must be low in silica.

9.2 Dispersing Agent, dissolve 40 gm of sodium metaphosphate (sometimes called sodium hexametaphosphate) in DI water with stirring and dilute to 1 liter. **NOTE:** If acidic, solutions of this salt will slowly hydrolyze back to the orthophosphate form with a decrease in dispersive action. New solutions should be made at least once a month or be adjusted to pH of 8 or 9 by means of sodium carbonate.

10.0 SAMPLE PREPARATION PROCEDURE FOR GRAINS

(Note – refer to Figure 1 for a summary of the steps in Sections 10 and 11.)

10.1 Weigh out a sample aliquot of approximately 100 to 200 g. Enough dried sample must be obtained to have 65 g of clay or silt or 115 g of sand that passes through the number 10 sieve. Spread the sample aliquot out evenly on a piece of aluminum foil or other clean surface. Let the sample air dry until dry in appearance. If the sample forms a crust during the drying processing, use a spatula to break up the crust and prevent water from being trapped below the crust. Mix the dried sample well. Note: The air drying may be done in a drying closet at a temperature of approximately 80 deg F.

10.2 Place an aliquot of the dried sample in the mortar and break it into small pieces with a rubber covered pestle. All clay clumps, etc. should be broken apart. Weigh out enough sample to have approximately 65 g of clay or silt sample passing through the Number 10 sieve or 115 g of sandy sample passing through the Number 10 sieve. Record the final weight.

10.3 Sieve the sample through the number 10 sieve. Shake the sieve stack laterally and vertically, accompanied by a jarring action in order to keep the sample moving continuously over the surface of the sieve. In no case turn or manipulate fragments of the sample through the sieve by hand. Continue shaking until not more than 1% of the mass remaining on the sieve passes that sieve during 1 minute of shaking. NOTE: Do not overload the sieve to the extent that the soil that would normally be retained on that sieve interferes with the soil that would normally pass through the sieve).

10.4 Pour the sample remaining on the top of the Number 10 sieve back into the mortar and use the pestle to again break up any clumps of clay or dirt.

10.5 Pour this sample back into the number 10 sieve and repeat the sieving process outlined in step 10.3.

10.6 Combine all sample going through the number 10 sieve into a separate container and save for additional sieve testing, moisture testing, and hydrometer testing as outlined below.

10.7 Take the sample remaining on the number 10 sieve and wash it with a small amount of water to remove any dust, etc. still adhering to the particulate. If insignificant dust remains on the sample, then this step may be omitted. Air dry the sample and record the final weight.

10.8 Separate the sample portion retained on the number 10 sieve into a series of fractions using as many sieves as needed depending on the sample or upon the specifications for the material being tested. The normal series of sieves used include the 3 inch sieve, the 1.5 inch sieve, the ¾ inch sieve, the 3/8 inch sieve, the number 4 sieve, and the number 8 sieve. Follow the following protocol for each sieve.

10.8.1 Shake the sieve stack laterally and vertically, accompanied by a jarring action in order to keep the sample moving continuously over the surface of the sieve. In no case turn or manipulate fragments of the sample through the sieve by hand. Continue shaking until not more than 1% of the mass remaining on the sieve passes that sieve during 1 minute of shaking.

10.8.2 When the step 10.8.1 is complete for a given sieve, then weigh the portion of sample remaining on the sieve and record the weight.

10.9 Weigh out an aliquot of approximately 10 g of the sample portion passing through the number 10 sieve (from section 10.6) and record the weight. Dry the aliquot to constant mass at 110 ± 5°C. Constant mass is defined as a change of less than 0.01 in the hygroscopic moisture correction factor. Calculate the hygroscopic moisture correction factor by dividing the mass of the oven dried sample by the mass of the air dried sample. (This correction factor will be used to correct the remaining test material mass to determine an accurate dry mass for the sample in the hydrometer testing).

10.10 Perform the hydrometer testing as outlined in Section 11 using the air dried sample that passed through the number 10 sieve. After the hydrometer testing is complete, pour the suspended sample through a number 200 sieve and wash well with DI water. Then dry the sample in an oven at 110 ± 5°C until completely dry.

10.11 Separate the oven-dried aliquot into a series of fractions using as many sieves as needed depending on the samples or upon the specifications for the material being tested. The normal series of sieves used include the number 16 sieve, the number 30 sieve, the number 50 sieve, the number 100 sieve, and the number 200 sieve. Follow the steps outlined above in 10.8.1 and 10.8.2 for the sieving process. The weight that passes through the 100 sieve will be equivalent to the weight retained on the 200 sieve since the fines that pass through the 200 sieve have already been removed at this point.

10.11.1 If hydrometer testing is not performed, then oven dry the whole aliquot of sample to be used for the sieves smaller than number 10.

10.12 Calculate the percentage of sample passing through each sieve. This can be done using the calculation template or it can be calculated by hand.

10.12.1 The equation to be used to calculate the percentage of the sample passing through the number 10 or larger sieve is shown below.

% of sample passing through the sieve (number 10 and larger) =

$$\frac{100 \times (\text{tot. sample wt} - (\text{wt retained on sieve of interest} + \text{wt retained on all larger sieves}))}{\text{tot. sample wt}}$$

10.12.2 The equations to be used to calculate the percentage of the sample passing through a sieve smaller than number 10 are shown below. These calculations include a correction factor to take into account the size of the aliquot used. Note that the weight of the aliquot is the weight of sample put into the hydrometer when hydrometer testing is done as the sample is poured through the number 200 sieve when it is first removed from the hydrometer.

A = (wt retained on sieve of interest + wt retained on all larger sieves under 10)

$$\text{Fraction of aliquot} = \frac{\text{(wt. of aliquot} - A)}{\text{wt. of aliquot}}$$

$$\%\ \text{passing through sieve} = \frac{\text{Fraction of aliquot x air dry weight passing through 10}}{\text{total air dry weight sieved}}$$

10.13 Calculate the percentage in the sample of gravel, sand, and silt, clay, and colloids. Gravel is defined as the sample passing through the 3 inch sieve and retained on the No. 4 sieve. Sand is defined as the sample passing through the No. 4 sieve and retained on the No. 200 sieve. Silt, clay, and colloids are defined as sample passing through the No. 200 sieve.

11.0 HYDROMETER ANALYSIS PROCEDURE FOR GRAINS

11.1 Determine hygroscopic moisture correction factor as described in section 10.9 above.

11.2 Determine the Composite Correction for Hydrometer – In a sedimentation cylinder, add 125 ml of the dispersing agent and dilute with DI water to 1000 ml (control sample).

11.2.1 Adjust the temperature of the control sample to 20 deg. C.(or to the lowest temperature expected during the measuring process.) Place the thermometer and the hydrometer into the control sample. Record the hydrometer and thermometer readings. Record the composite correction faction which is the difference between the hydrometer reading and zero.

11.2.1.1 The hydrometer should be read at the top of the meniscus formed on the stem.

11.2.2 Adjust the temperature of the control sample to 24 deg. C.(or to the highest temperature expected during the measuring process.) Place the thermometer and the hydrometer into the control sample. Record the hydrometer and thermometer readings. Record the composite correction faction which is the difference between the hydrometer reading and zero.

11.2.3 Use the known composite correction factors and temperatures to determine composite correction factors at different temperatures in the range tested.

11.3 When the soil is mostly clay and silt sizes, weigh out approximately 50 g of air-dried soil. When the soil is mostly sand, weigh out approximately 100 g. Record the weight used. Place

the sample aliquot into a beaker and cover with 125 ml of the sodium metaphosphate solution (5.1). Stir until the soil is thoroughly wetted. Allow it to soak for at least 16 hours.

11.4 After soaking, pour the sample into the dispersion cup, making sure to wash any sediment remaining in the original sample container into the dispersion cup with deionized water. Add deionized water so that the cup is more than half full and stirr for a period of 1 minute. Immediately after dispersion, transfer the slurry to the sedimentation cylinder, making sure all of the sample is removed from the beaker by using a wash bottle. Dilute to the 1000-ml mark on the cylinder with DI water.

11.5 Using Parafilm and the palm of the hand over the open end of the cylinder (or a robber stopper), turn the cylinder upside down and back for a period of 1 minute to complete the agitation of the slurry. Any soil remaining at the bottom of the cylinder during the first few turns, should be loosened by vigorous shaking while the cylinder is in the inverted position. The number of turns should be about 30, counting the turn upside down and back as one turn.

11.6 Set the sample cylinder next to the control cylinder and take hydrometer readings for the sample and the control at the following time intervals: 2, 5, 15, 30, 60, 250 (4 hours and 10 minutes), and 1440 minutes (24 hours).

11.6.1 When it is time to take a reading, record the temperature and the uncorrected hydrometer reading of the control sample on the data sheet. Then insert the hydrometer into the soil sample cylinder at the approximate depth it will have when the reading is taken (insert hydrometer 20 to 25 seconds before scheduled reading time). Record the uncorrected hydrometer reading for the sample on data sheet. The hydrometer should be read at the top of the meniscus formed on the stem

11.6.2 Clean the hydrometer after each reading in deionized water and store in deionized water between readings. They hydrometer should not be left in the sample after the reading.

11.7 Calculate the final particle sizes and percent smaller than a given diameter using the following equations. These calculations may be done manually or may be done in a spreadsheet.

11.7.1 Percentage of soil in suspension (percent smaller than a given diameter of soil) = (R x a)/W

where R = hydrometer reading with composite correction applied
a = correction factor from Table 1
W = 100 x (air dried mass used for hydrometer x hygroscopic moisture correction factor)/% passing through No. 10 sieve)

Note: Specific gravity of the soil is needed for Table 1. If the specific gravity is not listed on the table, extrapolate to an appropriate correction factor.

11.7.2 Diameter of soil particles = $K (L/T)^{1/2}$

Where K = constant taken from Table 3
L = effective depth taken from Table 2
T = time interval in minutes

Note: Specific gravity of the soil is needed for Table 3. If the specific gravity is not listed on the table, extrapolate to an appropriate K value.

11.7.3 Plot the diameters of the particles on a logarithmic scale as the abscissa and the percentages smaller than the corresponding diameters to an arithmetic scale as the ordinate. Read back the percentage of particles smaller than 0.075 mm, 0.005 mm, and 0.001 mm from the graph and record on the data sheet for entry into the LIMS. Note: depending on the conditions of the experiment, there may not be data for the percentage of particles at 0.001. In that case, report the percentage of particles at the lowest diameter available and footnote the result with the actual diameter.

12.0 SAMPLE PREPARATION PROCEDURE FOR SIEVE

12.1 Weigh out a sample aliquot of approximately 100 to 200 g. Enough dried sample must be obtained to have 65 g of clay or silt or 115 g of sand that passes through the number 10 sieve. Spread the sample aliquot out evenly on a piece of aluminum foil or other clean surface. Let the sample air dry until dry in appearance. If the sample forms a crust during the drying processing, use a spatula to break up the crust and prevent water from being trapped below the crust. Mix the dried sample well. Note: The air drying may be done in a drying closet at a temperature of approximately 80 deg F.

12.2 Place an aliquot of the dried sample in the mortar and break it into small pieces with a rubber covered pestle. All clay clumps, etc. should be broken apart. Weigh out enough sample to have approximately 65 g of clay or silt sample passing through the Number 10 sieve or 115 g of sandy sample passing through the Number 10 sieve. Record the final weight.

12.3 Sieve the sample through the number 10 sieve. Shake the sieve stack laterally and vertically, accompanied by a jarring action in order to keep the sample moving continuously over the surface of the sieve. In no case turn or manipulate fragments of the sample through the sieve by hand. Continue shaking until not more than 1% of the mass remaining on the sieve passes that sieve during 1 minute of shaking. NOTE: Do not overload the sieve to the extent that the soil that would normally be retained on that sieve interferes with the soil that would normally pass through the sieve).

12.4 Pour the sample remaining on the top of the Number 10 sieve back into the mortar and use the pestle to again break up any clumps of clay or dirt.

12.5 Pour this sample back into the number 10 sieve and repeat the sieving process outlined in step 12.3.

12.6 Combine all sample going through the number 10 sieve into a separate container and save for additional sieve testing testing as outlined below.

12.7 Take the sample remaining on the number 10 sieve and wash it with a small amount of water to remove any dust, etc. still adhering to the particulate. If insignificant dust remains on the sample, then this step may be omitted. Air dry the sample and record the final weight.

12.8 Separate the sample portion retained on the number 10 sieve into a series of fractions using as many sieves as needed depending on the sample or upon the specifications for the material being tested. The normal series of sieves used include the 3 inch sieve, the 1.5 inch sieve, the ¾ inch sieve, the 3/8 inch sieve, the number 4 sieve, and the number 8 sieve. Follow the following protocol for each sieve.

12.8.1 Shake the sieve stack laterally and vertically, accompanied by a jarring action in order to keep the sample moving continuously over the surface of the sieve. In no case turn or manipulate fragments of the sample through the sieve by hand. Continue shaking until not more than 1% of the mass remaining on the sieve passes that sieve during 1 minute of shaking.

12.8.2 When the step 12.8.1 is complete for a given sieve, then weigh the portion of sample remaining on the sieve and record the weight.

12.9 Weigh out an aliquot of approximately 10 g of the sample portion passing through the number 10 sieve (from section 12.6) and record the weight. Dry the aliquot to constant mass at 110 ± 5°C. Constant mass is defined as a change of less than 0.01 in the hygroscopic moisture correction factor. Calculate the hygroscopic moisture correction factor by dividing the mass of the oven dried sample by the mass of the air dried sample. (This correction factor will be used to correct the remaining test material mass to determine an accurate dry mass for the sample in the bottom sieves).

12.10 Weigh out 50 g of the air dried sample portion passing through the number 10 sieve (from 12.6) and place it into a sludge cup or small bottle and cover with DI water and let soak for approximately 15 to 30 minutes. Then shake well and pour through a 200 sieve. Rinse well with DI water until no more particulate is coming through the sieve. Then dry the sample in an oven at 110 ± 5°C until completely dry.

12.11 Start with the oven dried sample generated in 12.10 above. Separate this oven-dried aliquot into a series of fractions using as many sieves as needed depending on the samples or upon the specifications for the material being tested. The normal series of sieves used include the number 16 sieve, the number 30 sieve, the number 50 sieve, the number 100 sieve, and the number 200 sieve. Follow the steps outlined above in 12.8.1 and 12.8.2 for the sieving process. The weight that passes through the 100 sieve will be equivalent to the weight retained on the 200 sieve since the fines that pass through the 200 sieve have already been removed at this point.

12.12 Calculate the percentage of sample passing through each sieve. This can be done using the calculation template or it can be calculated by hand.

12.12.1 The equation to be used to calculate the percentage of the sample passing through the number 10 or larger sieve is shown below.

% of sample passing through the sieve (number 10 and larger) =

$$\frac{100 \times (\text{tot. sample wt} - (\text{wt retained on sieve of interest} + \text{wt retained on all larger sieves}))}{\text{tot. sample wt}}$$

12.12.2 The equations to be used to calculate the percentage of the sample passing through a sieve smaller than number 10 are shown below. These calculations include a correction factor to take into account the size of the aliquot used.

A = (wt retained on sieve of interest + wt retained on all larger sieves under 10)

$$\text{Fraction of aliquot} = \frac{\text{(wt. of aliquot – A)}}{\text{wt. of aliquot}}$$

$$\%\text{ passing through sieve} = 100 \times \text{Fraction of aliquot} \times \frac{\text{air dry weight passing through 10}}{\text{total air dry weight sieved}}$$

12.14 Calculate the percentage in the sample of gravel, sand, and silt, clay, and colloids. Gravel is defined as the sample passing through the 3 inch sieve and retained on the No. 4 sieve. Sand is defined as the sample passing through the No. 4 sieve and retained on the No. 200 sieve. Silt, clay, and colloids are defined as sample passing through the No. 200 sieve.

12.15 Sieve Screen Procedure. Product code for this process is SIEVESCREEN. Note: This process is only for client-specified procedures and is excluded from GRAINS or SIEVE analysis. Do not perform unless directed by a manager or supervisor.

12.15.1 Dry 100-200 g of well-mixed sample (use more mass for moist samples) for at least 12 h at 104 °C.

12.15.2 Gently break apart the dried sample using mortar and pestle.

12.15.3 Measure and record a mass between 50-75 g. Sieve using a No. 4 sieve stacked on a No. 200 sieve. Separately collect the portions retained on both sieves, and record the mass of each portion.

12.15.4 Calculate percent gravel, sand, and silt as follows (spreadsheet is available):

Gravel, % = [(mass retained on No. 4 sieve, g) ÷ (total mass sieved), g] × 100

Sand, % = [(mass retained on No. 200 sieve, g) ÷ (total mass sieved), g] × 100

Silt, % = 100% - (gravel, %) - (sand, %)

13.0 QC REQUIREMENTS

13.1 A summary of the main quality control requirements are given below. Other requirements specific to a given client or matrix may also be required. Check with the supervisor or manager to determine if there are additional quality control requirements.

13.2 A hydrometer control should be analyzed periodically or whenever a new hydrometer is used.

13.3 A duplicate should be analyzed with each batch of 20 samples or less. Control limits are compiled by Accutest annually and should be used to determine if matrix problems are present. If the duplicate is outside of the control limits, and all other quality control is within limits, then no

reanalysis is necessary, but the QC results must be footnoted to indicate possible sample non-homogeneity or matrix interferences. Until control limits can be generated, default control limits of 20% RPD should be applied.

14.0 DOCUMENTATION REQUIREMENTS

14.1 The analyst should document all relevant information, including all sample weights, all sample and control analysis results, and any relevant comments.

14.2 All reagent identification numbers should be recorded on the sample worksheets. In addition, all reagent information such as lot numbers should also be recorded in the reagent log book.

15.0 DATA REVIEW AND REPORTING

15.1 All samples should be updated to QC batches in the LIMS system. The analyst should calculate all sample results and all duplicate RPD's. They should verify that all calculations are complete and that all reagents are documented and traceable.

15.2 After the analyst review is completed, the supervisor or a designated reviewer shall review the run for technical compliance to the SOP. The supervisor is also responsible for making sure that the QC calculations are done correctly and responsible for reviewing the data entry into the LIMS. No LIMS entry review is necessary when the data is electronically transferred.

15.3 After the supervisor or designated reviewer completes their review, the data is released for client access in the LIMS. The raw data is submitted to the area manager. The department manager does an additional periodic review on the sample data as appropriate. The raw data is then filed electronically in the report generation department.

16.0 POLLUTION PREVENTION & WASTE MANAGEMENT

16.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 16.2.

16.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

16.2.1 Non-hazardous aqueous wastes.

16.2.2 Hazardous aqueous wastes

16.2.3 Chlorinated organic solvents

16.2.4 Non-chlorinated organic solvents

16.2.5 Hazardous solid wastes

16.2.6 Non-hazardous solid wastes

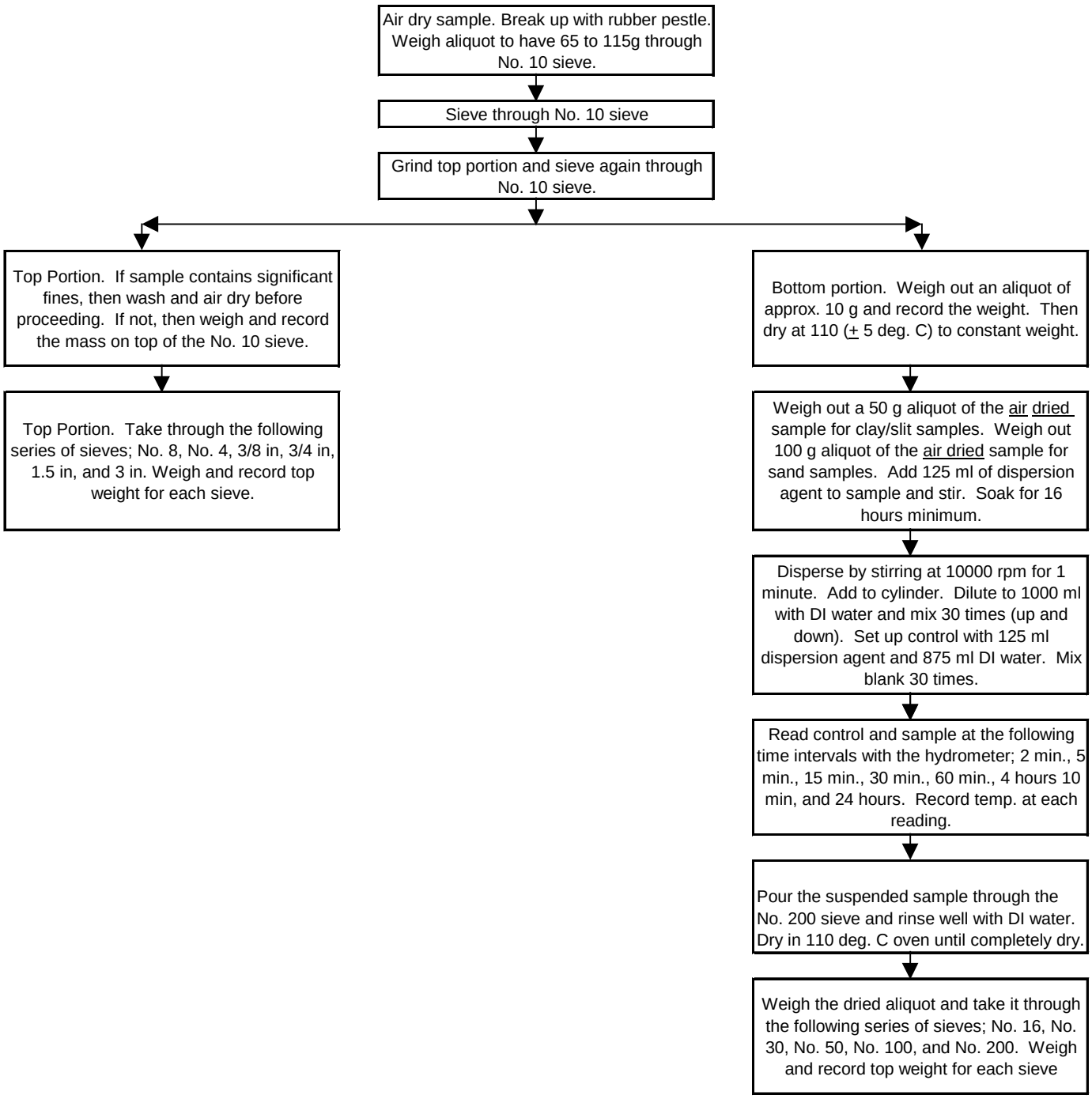
17.0 ADDITIONAL REFERENCES

17.1 Refer also to ASTM D421-85 for additional details on preparation of the soil samples.

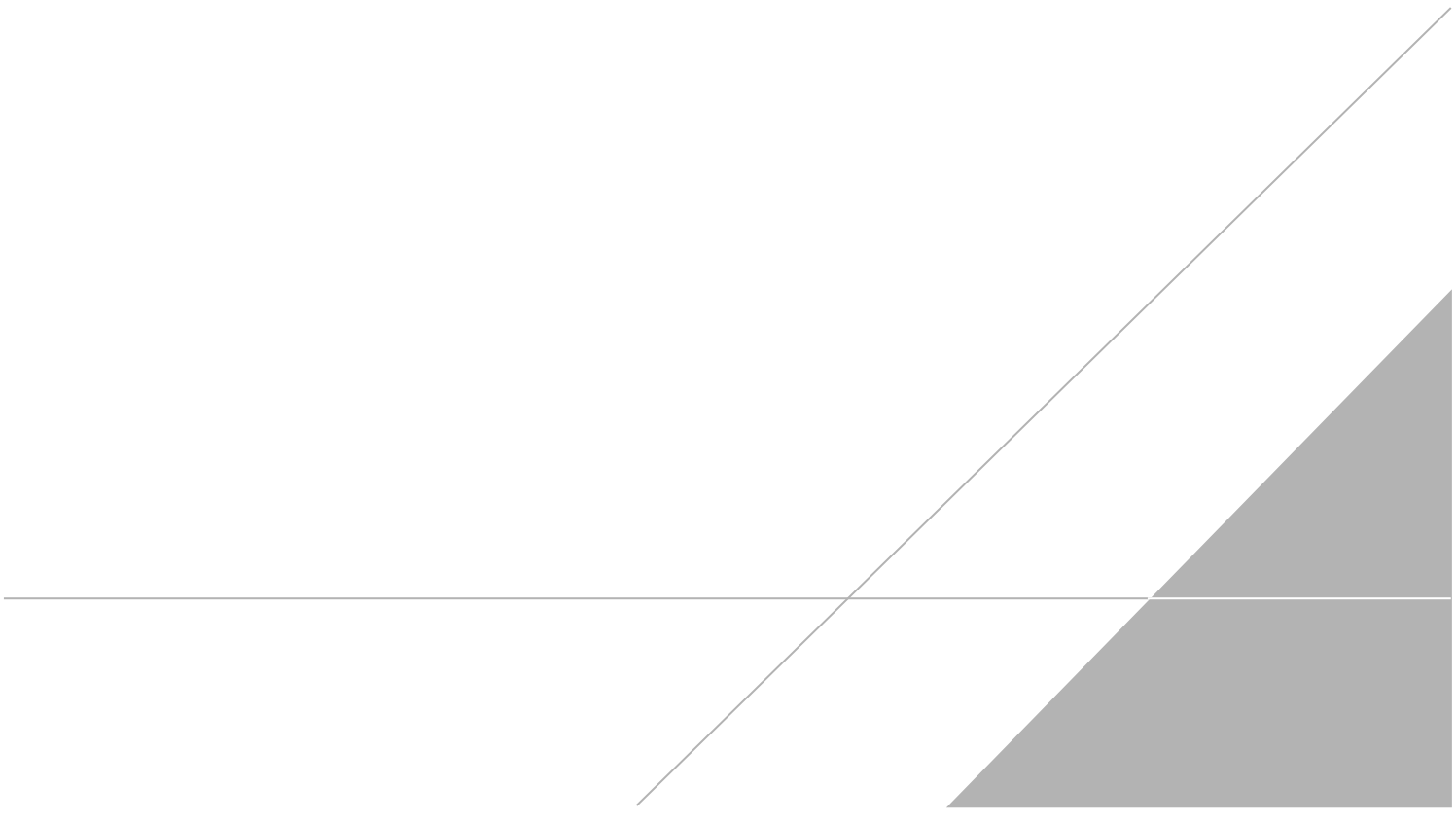
17.2 Refer to ASTM D422-63 for Tables 1, 2, and 3

17.3 Refer to SOP EGN247 for the process to use to determine soil specific gravities.

FIGURE 1: SIEVE AND HYDROMETER PROCESS FLOW CHART



STANDARD OPERATING PROCEDURE FOR PERCENT SOLIDS



LAB MANAGER: _____

QA MANAGER: _____

EFFECTIVE DATE: 8-9-2016

TITLE: PERCENT SOLIDS and TOTAL SOLIDS in SOIL/SOLID MATRICES
REFERENCES: SM2540G 18th Ed, ASTM Method D4643-00, 1.1
REVISED SECTIONS: 6.1, 11.0, 12.0, 13.0

1.0 SCOPE AND APPLICATION

1.1 This method is for the measurement of the percent solids or total solids in samples of soil, sludge, or other solid material. This method is based on a method SM2540G 18th Ed. and on ASTM method 4643-93.

1.2 The oven drying techniques for percent solids as described in this SOP can be applied to any sample type where percent solids can be determined. The microwave drying technique for percent solids described in this SOP can only be applied to samples which do not fall into the categories listed: lower percent solids (<50%), sludges or any other sample with a high organic content, samples containing high amounts of hydrated materials or larger clumps or particles, and samples with high TDS in the pore water (i.e. marine deposits). In addition, samples designated for hexavalent chromium analysis or NYASPB reporting cannot be dried in the microwave.

1.3 Sludge samples for regulatory reporting must follow the sludge procedure outlined in this SOP. These samples are tracked using the product code SLDGSOL

2.0 SUMMARY OF METHOD

2.1 A homogeneous aliquot of sample is placed in a tared dish and weighed. The wet sample is then dried to constant weight. The difference between the initial and final weight indicates the amount of water in the sample. Percent solids are calculated using the dry weight of the sample divided by the total weight of the sample. Percent moisture is calculated using the weight of water in the sample divided by the total weight of the sample.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Not applicable.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a

separate batch.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE (DUP): A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample must be assessed.

5.0 HEALTH AND SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Chemical Hygiene Plan. Always wear a lab coat and glasses and the appropriate gloves when analyzing samples for percent solids.

6.0 COLLECTION, PRESERVATION, AND HOLDING TIME

6.1 No specific holding time is in place for the calculation of percent solids in soil samples. Refrigerate samples at 0 to 6 °C (but not frozen) until analysis.

6.2 Sludge samples for regulatory reporting must be analyzed within 7 days from time of collection.

7.0 APPARATUS AND MATERIALS

The items listed below are needed for the sample analysis.

7.1 Crucibles. Capable of heating to 105°C and capable of being heated in a microwave.

7.2 Two or three place balance. All balances must have their calibration verified with Class S weights daily before the analysis of each batch of samples. Note: A 3 place balance is required for CLP samples.

7.3 Stainless Steel or Teflon coated Spatulas

7.4 Drying oven capable of maintaining a constant temperature at 103 to 105°C.

7.5 Variable temperature microwave oven.

7.6 Dessicator with dessicant.

8.0 STANDARDS AND REAGENTS

8.1 No special standards or reagents are required for this method.

9.0 INTERFERENCES

9.1 When heated at 103 to 105°C, samples will lose moisture, but can also lose certain volatile components and ammonium carbonate. When heated in the microwave, there is a possibility that the soil is overheated if the microwave is not cycled properly. Microwave heating must not be used for any samples with high organic content (black or oily appearance), with low percent solids (50% or less), or on soils containing significant amounts of hydrated materials or soils in which the pore water contains high dissolved solids (for example, marine deposits).

10.0 SAMPLE CLASSIFICATION PROCEDURE.

10.1 Each sample must first be classified as one of the following three types; a) a soil or solid that can be analyzed using the microwave method, b) a soil or solid that can be analyzed using the oven %solids method, or c) a sludge being analyzed for regulatory purposes that must use the sludge method. Classify the sample for analysis by microwave or oven. Certain sample types and certain protocols do not allow for the use of the microwave method. Samples which fall into any of the categories listed below must not be analyzed using the microwave.

10.1.1 Soils or solids to be analyzed by the microwave method must not be in any of the following categories.

10.1.1.1 Any NYASPB samples.

10.1.1.2 Any samples requiring analysis for hexavalent chromium (XCr).

10.1.1.3 Any samples with high organic content.

10.1.1.4 Any samples containing significant amounts of hydrated materials or with larger clumps or particles.

10.1.1.5 Any samples with low percent solids (< 50%).

10.1.1.6 Any samples in which the pore water contains high dissolved solids (for example marine deposits.)

10.1.1.7 Any sludge samples being reported for regulatory purposes.

10.1.2 Soils or solids to be analyzed by the oven %solids method can be any soils or solids that are not sludge samples being reported for regulatory purposes.

10.1.3 Sludges to be reported for regulatory purposes must be analyzed following the sludge %solids/total solids method.

11.0 MICROWAVE ANALYSIS METHOD FOR PERCENT SOLIDS/PERCENT MOISTURE (%SOL)

11.1 Dry the crucibles to be used at 103 to 105°C for a minimum of 1 hour or for 20 minutes at 50 to 70 percent power in the microwave. Allow to cool in a dessicator.

11.2 Tare the balance to zero. Before weighing any samples, make sure that the balance calibration has been checked with at least 2 class S weights covering the range of use before calibration and meets the specifications listed in front of the balance log. Normally 3 weights are used.

11.3 After the balance has been tared, weight the crucible(s) and record the weights. This may be done electronically or manually.

11.4 Mix the sample well using a stainless steel or teflon coated spatula. Do not just mix the top of the sample, but make sure that the whole sample is well mixed. Remove any stones, twigs, etc. from the sample.

11.4.1 If the sample jar is too full or the sample is difficult to mix, then empty the sample into a large stainless steel or ceramic bowl and stir well there before taking a sample aliquot.

11.5 Remove approximately a 5 to 20 g aliquot from the mixed sample and place it in the tared crucible. For at least one sample of every 20, set up a sample duplicate.

11.5.1 For any samples where it is difficult to obtain a representative sample aliquot, increase the sample aliquot size to 25 to 50 g.

11.5.2 If limited sample is available, smaller weights may be used if the aliquots are well homogenized.

11.5.3 Using the spatula, crush any large lumps in the aliquot to be weighed and dried.

11.6 Place a batch of 20 samples in the microwave and dry them for approximately 30 minutes at 50 to 70 percent power.

11.6.1 Power levels and times will need to be adjusted for smaller batches of samples. Check with area supervisors for assistance.

11.7 Remove the samples and let cool for 5 minutes. If they are going to be out for longer than 10 minutes, place them in a dessicator before weighing.

11.8 Weigh the samples on the balance and record the final weights. This can be done manually or electronically. Take at least 2 samples and stir them with a spatula, making sure not to retain any sample particles on the spatula. The 2 samples used for this check must be the 2 that have the highest moisture content (lowest percent solids) in the batch. Any samples with < 50% solids must be submitted for redo using the oven drying method.

11.9 Place these 2 samples back in the microwave and microwave for 3 to 5 minutes at 50 percent power. Remove the samples and let cool for 5 minutes.

11.10 Weigh the samples on the balance and record the final weights. Again, this can be done either manually or electronically.

11.10.1 If the sample weights on the re-dry differ by more than 0.05 g or 4%, whichever is less, from the previous weights, then then the whole batch must be stirred and re-dried until all percent solids agree within this criteria.

12.0 OVEN ANALYSIS METHOD FOR PERCENT SOLIDS/PERCENT MOISTURE (NOT TO BE USED FOR SLUDGES). (SOL104)

12.1 Dry the crucibles to be used at 103 to 105°C for a minimum of 1 hour. Allow to cool in a dessicator.

12.2 Tare the balance to zero. Before weighing any samples, make sure that the balance calibration has been checked with at least 2 class S weights covering the range of use before calibration and meets the specifications listed in front of the balance log. Normally 3 weights are used.

12.3 After the balance has been tared, weight the crucible(s) and record the weights. This may be done electronically or manually.

12.4 Mix the sample well using a stainless steel or teflon coated spatula. Do not just mix the top of the sample, but make sure that the whole sample is well mixed. Remove any stones, twigs, etc. from the sample.

12.4.1 If the sample jar is too full or the sample is difficult to mix, then empty the sample into a large stainless steel or ceramic bowl and stir well there before taking a sample aliquot.

12.5 Remove approximately a 5 to 20 g aliquot from the mixed sample and place it in the tared crucible. For at least one sample of every 20, set up a sample duplicate.

12.5.1 For any samples where it is difficult to obtain a representative sample aliquot, increase the sample aliquot size to 25 to 50 g.

12.5.2 If limited sample is available, smaller weights may be used if the aliquots are well homogenized.

12.5.3 Using the spatula, crush any large lumps in the aliquot to be weighed and dried.

12.6 Place a batch of samples in the oven at 103 to 105°C. The samples must remain in the oven for a minimum of 1 hour and up to 24 hours. Drying times must not exceed 24 hours unless specific project instructions are being followed. .Record the drying time.

12.6.1 Samples with high organic content must stay in the oven for a minimum of 8 to 12 hours.

12.6.2 Remove the samples and let cool for 5 minutes. If they are going to be out for longer than 10 minutes, place them in a dessicator before weighing.

12.6.3 Weigh the samples on the balance and record the final weights. This can be done manually or electronically.

12.6.3.1 If the samples are in the oven less than 12 hours, then place all of the samples back in the oven for a minimum of 1 hour at 103 to 105°C.

12.6.3.2 If the sample weights on the re-dry differ by more than 0.05 g or 4%, whichever is less, from the previous weights, then then the whole batch must be stirred and re-dried until all percent solids agree within this criteria.

12.7 Percent solids are calculated using the equation shown below.

Percent moisture = 100 – percent solids.

Percent solids = 100 x $\frac{\text{(final dry weight + crucible) - crucible tare weight}}{\text{(wet weight + crucible) – crucible tare weight}}$

13.0 ANALYSIS METHOD FOR PERCENT SOLIDS/PERCENT MOISTURE/TOTAL SOLIDS FOR SLUDGE MATRICES. (SLDGSOL)

Below is a step-by-step procedure for the analysis of sludge samples for percent solids and percent moisture and total solids.

13.1 Dry the crucibles to be used at 103 to 105°C for a minimum of 1 hour. Allow to cool in a dessicator.

13.2 Tare the balance to zero. Before weighing any samples, make sure that the balance calibration has been checked with at least 2 class S weights covering the range of use before calibration and meets the specifications listed in front of the balance log. Normally 3 weights are used.

13.3 After the balance has been tared, weight the crucible(s) and record the weights. This may be done electronically or manually.

13.4 Mix the sample well using a stainless steel or teflon coated spatula. Do not just mix the top of the sample, but make sure that the whole sample is well mixed. Remove any stones, twigs, etc. from the sample.

13.4.1 If the sample jar is too full or the sample is difficult to mix, then empty the sample into a large stainless steel or ceramic bowl and stir well there before taking a sample aliquot.

13.5 Remove approximately a 25 to 50 g aliquot from the mixed sample and place it in the tared crucible. For at least one sample of every 10, set up a sample duplicate.

13.5.1 If limited sample is available, smaller weights may be used if the aliquots are well homogenized.

13.5.2 Using the spatula, crush any large lumps in the aliquot to be weighed and dried.

13.6 Place a batch of samples in the oven at 103 to 105°C. The samples must remain in the oven for a minimum of 8 hours and up to 24 hours. Drying times must not exceed 24 hours unless specific project instructions are being followed. .Record the drying time.

13.6.1 Remove the samples and place them in a dessicator to cool.

13.6.2 Once the samples are cool, weigh them on the balance and record the final weights. This can be done manually or electronically.

13.6.3 Then place all of the samples back in the oven for a minimum of 1 hour at 103 to 105°C. Repeat steps 13.6.1 and 13.6.2.

13.6.4 If the sample weights on the re-dry differ by more than 0.05 g or 4%, whichever is less, from the previous weights, then the affected sample(s) must be stirred and re-dried until all percent solids agree within this criteria.

13.7 Percent solids are calculated using the equation shown below.

Percent moisture = 100 – percent solids.

$$\text{Percent solids} = 100 \times \frac{\text{(final dry weight + crucible) - crucible tare weight}}{\text{(wet weight + crucible) – crucible tare weight}}$$

14.0 QC REQUIREMENTS

14.1 Each batch of 20 samples will include a duplicate sample. The exception is for sludge samples where a duplicate is required for one in 10 samples.

14.2 The limit for duplicate samples is 5 % RPD. If the RPD values are outside of this range, and all other method quality control is within limits, then sample non-homogeneity must be suspected. A description of the duplicate sample appearance must be provided for all batches where the 5% RPD is not met. In general, it is recommended that batches with samples with high RPD's be reanalyzed to confirm the original results.

$$\text{The calculation for \%RPD} = \frac{100 \times \text{(Sample result – Duplicate result)}}{\text{(Sample result + Duplicate result)/2}}$$

14.3 The balance calibration must be verified at a minimum of 2 levels bracketing the range of weights measured each day before use. The calibration must meet the specifications listed in the balance logbook. If they do not, the balance must be recalibrated and rechecked before any samples can be analyzed.

14.4 For samples dried in the microwave, a minimum of 2 re-dries is required for every 20 samples. For solid or soil samples dried in the oven, all samples must be re-dried if the original drying time is less than 12 hours. For sludge samples, all samples must be re-dried. Re-dries must match within 0.05 g or 4% of the original weight, whichever is less.

15.0 DOCUMENTATION REQUIREMENTS

15.1 All data regarding the analysis must be recorded on the data worksheet. Make sure that all sample information is included on these sheets. Any unusual characteristics of the samples must be noted in the comment section. This can be done electronically or manually. Make sure to double check crucible and sample ID's when they are recorded.

15.2 Initial balance calibrations must be recorded in the balance calibration check log for each balance.

16.0 DATA REVIEW AND REPORTING

16.1 All samples must be updated to QC batches in the LIMS system. The analyst is responsible for reviewing all data for compliance with the QC outlined in this SOP. They are responsible

for making sure that the raw data is fully documented.

16.2 After the analyst review is completed, the supervisor or a designated reviewer shall review the run for technical compliance to the SOP. The supervisor is also responsible for making sure that the QC calculations are done correctly and responsible for reviewing the data entry into the LIMS. No LIMS entry review is necessary when the data is electronically transferred.

16.3 After the supervisor or designated reviewer completes their review, the data is released for client access in the LIMS. The raw data is submitted to the area manager. The manager will periodically review data for technical completeness. The raw data is then transferred to the report generation department.

17.0 POLLUTION PREVENTION & WASTE MANAGEMENT

17.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in the waste management SOP.

17.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

17.2.1 Non hazardous aqueous wastes.

17.2.2 Hazardous aqueous wastes

17.2.3 Chlorinated organic solvents

17.2.4 Non-chlorinated organic solvents

17.2.5 Hazardous solid wastes

17.2.6 Non-hazardous solid wastes