sufficient water to prevent overflow. The final digestate should be a clear yellow liquid with black or dark reddish-brown particulates.

l. Filter the digestate through Whatman 41 filter paper and collect filtrate in a volumetric flask or beaker.

m. Wash the digestion beaker and filter paper, while still in the funnel, with no more than 5 mL of hot HCl.

NOTE: The purpose of this next step is to recover antimony, barium, and silver that may not have been completely solubilized. If the sample is not being prepared for these analytes, the next step may be skipped.

n. (Optional) After having washed the filter paper, remove the filter and residue from the funnel and place it back in the beaker. Add 5 mL of conc. HCl and place the beaker back on the heating source until the filter paper dissolves (temperature should not exceed 150 °C ±5 °C to prevent volatilization). Remove the beaker from the heating source and wash the cover and sides with reagent grade water and then filter the residue and collect the filtrate in the same flask or beaker as in sections f. and g. above. Allow the filtrate to cool and quantitatively transfer to a volumetric flask. Bring to volume.

o. (Optional) If the filtrate is collected in a beaker, the filtrate can be heated again to drive off excess HC1. This can reduce matrix effects in sample introduction (temperature should not exceed 150 °C ± 5 °C to prevent volatilization). When sufficient HCl has been removed, remove the beaker from the heating source, allow to cool, and then transfer the contents to a volumetric flask and bring to volume. However, if too much HCl is removed, barium, silver and antimony can be lost.

p. Analyze the flitrate by ICP-AES. Depending on the final volume selected, the total solids in the digestate may be high enough to cause nebulization problems. Problems due to high dissolved solids may be corrected by 1) following optional Section i., 2) using internal standards, 3) using flow injection analysis, or 4) using other matrix correction procedures.

Manganese Removal Steps

NOTE: The purpose of these next steps is to remove the manganese in the digest by precipitating it as manganese ammonium phosphate

under alkaline conditions. Elements that do not form insoluble phosphates, such as arsenic, are filtered out and can be analyzed at lower concentrations.

q. Take the digestate, or portion of digestate and reduce the volume to remove as much HCl as possible without going below 10 mL. Then add conc. NH_4OH until pH is 7 or greater. For most matrices, the digestate will change colors (often from yellow to brown) at pH 7. A mild exothermic reaction will occur immediately.

r. Add at least 2 g ammonium phosphate for each 1 g of potassium permanganate used in the digestion and stir. An excess of phosphate is needed for good analyte recovery. Then add enough water and mix to ensure maxium precipitation. A pink or yellow silky amorphous precipitate, manganese ammounium phosphate, will form. If too much NH_4OH is used some of the manganese ammonium phosphate can be solubilized. Stir until precipitation is complete. Some ammonium phosphate may remain unreacted at the bottom of the beaker.

s. Filter the digestate through Whatman 41 filter paper (or equivalent) and collect filtrate in a volumetric flask or beaker.

t. Heat the filtrate to volatilize the ammonia (temperature should not exceed 150 °C ± 5 °C to prevent volatilization). The volume of filtrate can be reduced by heating to no less thatn 10 mL. If too much water is removed ay ammonium chloride formed will solidify. If this occurs, either add enough water to dissolve the solids or filter out the solids and wash the residue with deionized water. The filtrate can be analyzed by ICP-AES.

u. The digestion log must contain the date, analyst, sample number, client, sample mass/volume, final volume of digestate, lot # of acids used and the preparation and ID of standards.

X. CALCULATIONS

A. The analyst must be supplied with both beginning sample masses/volumes and final digestate volumes. This information must be recorded in the digestion log.

XI. QUALITY CONTROL

A. Digestion

1. Temperature blank

   a. The temperature of the hot plate/hot block must be monitored for temperature during the digestion process.

   b. The thermometer must be tagged with annual calibration information. Record the thermometer reading, correction factor and the corrected temperature in the digestion log.

2. Blanks

   a. Digest a blank with every batch of samples digested (20 sample maximum). The blank is prepared by adding all the same reagents added to the samples to a clean dry beaker and taking it through the same process as the samples. **NOTE: The blank for OILs MUST include an analyte-free oil or explosive reactions can occur.**

   b. Also, there must be a blank for every different method of digestion that is set up that day, every 20 samples.

   c. There must also be a blank for every different matrix of samples that is to be digested, every 20 samples.

   d. Sample is given a unique identifier in the digestion log.

3. Laboratory Control Samples

   a. For water samples, one LCS is digested with every batch of samples digested (20 sample maximum).

   b. For water samples, a LCS is digested every day for each type of digestion, every 20 samples.

   c. For soil/sediment samples, a soil matrix standard reference material (SRM) must be digested per batch (20 samples maximum) or alternatively a spiked teflon chip sample.

   d. Sample is given a unique identifier in the digestion log.

   e. Recoveries of standard reference materials or laboratory control samples spiked with organo-metallic standards recoveries should be **±25% of their true values for OILS.**

4. Duplicates

   a. A duplicate is prepared every 20 samples. This usually takes the form of a matrix spike duplicate.

      NOTE: Certain projects require a sample duplicate and a matrix spike duplicate with each set of twenty samples.

5. Blank Spike

   a. This is required for certain projects.

B. Sample Matrix

NOTE: Field blanks/duplicates, trip blanks, or equipment blanks are not to be used for sample matrix QC samples.

1. Matrix spike

   a. Digest a spike and spike duplicate every 20 samples where sample volume is adequate to do so. Choose a sample (if possible) that has a lot of metals requested to be analyzed.

      NOTE: For some projects, a sample duplicate and sample spike may be required instead of a spike and spike duplicate. Your supervisor should make you aware of these projects.

   b. The following metals do not get digested spikes when using CLP spike.

      Calcium
      Magnesium
      Sodium
      Potassium

   v. For TCLP samples, a spike must be digested for every matrix. You should inspect the sample (original sample prior to extraction) or check the log book to determine matrix type. (Also the matrix spike aliquot must be added to the extract after filtration but before preservation.)

   d. The CLH project requires that a high and a low spike be prepared and analyzed. Spikes shoud be prepared at 40 mg/Kg and 400 mg/Kg for soil samples and 200 ug/L and 2000 ug/L for aqueous samples.

XII. CORRECTIVE ACTIONS

A. Sample boils during digestion.

1. Redigest another sample aliquot.

B. Sample goes dry or portion of beaker bottom is exposed due to excess evaporation during digestion.

1. Redigest another sample aliquot.
2. Glass beaker dry for an extended period of time? Discard beaker.

XIII. SPECIAL NOTES

A. **Never** take for granted how a sample should be digested. If the sample looks strange or unusual, or if you are not sure what metals the sample gets, what detection limits are required, whether the sample is total or dissolved, or even what method of digestion should be used, always ask your supervisor or the person who is to analyze the sample. How metals need to be digested changes too often to take it for granted.

B. **Antimony (Sb) soils** should be analyzed within 48 hours of digestion whenever possible. When a soil requesting Antimony analysis is received, you must coordinate with the person who will be analyzing it to be sure that they can analyze it on the same day that it is digested.

C. Labels for the digested sample must be written in a neat and legible manner. The labels must include such information as sample number, client name, the date digested, and the volume or mass digested.

D. There are several precautions that must be taken to minimize the possibility of contamination.

1. All metals glassware must be kept separate from all other laboratory glassware.

2. Metals glassware must be washed as soon as possible after being used. **Dirty metals beakers must not be left overnight.**

3. Acid to be used for metals digestions must be kept separate from all other laboratory acid.

E. Samples must be digested in a timely manner to ensure ICP analysis remains on schedule for data generation. Samples received on or before Wednesday of week X must be prepared for ICP digestion by the end of week X. Your supervisor must be consulted if this schedule can not be met at a particular time.

F. Please consult Waste Disposal SOP-405, for information concerning disposal of waste generated from this area. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

Addendum for USEPA CLPILM 05.2 AQUEOUS &SOIL/SEDIMENT

The following is a list of changes for sample preparation when the 5.2 statement of work is required:

1. Soluble samples are required to be digested unless the chain of custody specifically states that digestion is not required. An MDL study must be done on the unprepared MDL solution in order to provide MDL levels for samples that are not digested. When digestion is not required an LCSW and post digestion spike are not required.

2. Digestates must be stored until 365 days after delivery of a complete, reconciled data package.

3. Preparation codes are used on form 13's. They are found in the 5.2 statement of work page B-39 3.4.12.2.4.

DEFINITIONS – Refer to SOP-431 for common environmental laboratory definitions.

METALS ANALYSIS

BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY (ICP-AES) TECHNIQUE

METHODS 200.7, (SW846) 6010B, (SW846) 6010C, (SM 19th Edition 2340B) Hardness Calculation, (USEPA CLP) ILMO 4.1 (NJDEP does not accept CLPILM 04.1 after June, 2003) Addendum for USEPA CLPILM 05.2

SOP NUMBER: SOP-105

REVISION NUMBER: 15

APPROVED BY:

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SECTION MANAGER

Randy D. Ward
TECHNICAL DIRECTOR

EFFECTIVE DATE: 02/22/09
DATE OF LAST REVIEW: 05/08/09

ICP METHOD
SOP
References: SW-846, Method 6010B, December 1996; SW-846, Method 6010C, Revision 3 February 2007; USEPA, Method 200.7, June 1991; Standard Methods 19th Edition 2340B; 1995 USEPA CLP, ILM 04.1. See Addendum for USEPA CLPILM 05.2

I. SCOPE AND APPLICATION

A. Inductively Coupled Argon Plasma (ICAP) determines trace elements in solution. **We use the ICP to determine the concentration of the following metals: Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V and Zn.** All matrices, including ground water, aqueous samples, TCLP, SPLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

B. **Detection limits, sensitivity, and optimum ranges of the metals may be found in the ICP method file.** Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

II. SUMMARY OF METHOD

A. Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods (e.g., Methods 3005-3050 and SOW ILM 04.1/05.2). When analyzing for dissolved constituents, acid digestion is not always necessary if the samples are filtered and acid preserved prior to analysis. If particulates form after filtration and preservation the sample must be digested prior to analysis.

NOTE: When selenium is required soluble samples must always be digested.

B. This method describes the simultaneous multi-elemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the large droplets are removed by a spray chamber and the small droplets then pass through to the plasma. The solvent is evaporated. The residual sample decomposed to atoms and ions that become excited and emit characteristic light which is measured, giving a measurement of the concentration of each element type in the the original sample. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analytic wavelength measured.

Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. Control of the spectrometer is provided by PC based iTEVA software.

C. ICP's primary advantage is that it allows simultaneous determination of any elements in a short time. The primary disadvantage of ICP is background radiation from other elements and the plasma gases. Although all ICP instruments utilize high-resolution optics and background correction to minimize these interferences, analysis for traces of metals in the presence of a large excess of a single metal is difficult. Examples would be traces of metals in an alloy or traces of metals in a limed (high calcium) waste. ICP and Flame AA have comparable detection limits (within a factor of 4) except that ICP exhibits greater sensitivity for refractories (Al, Ba, etc.). Furnace AA, in general, will exhibit lower detection limits than either ICP or FAA.

D. It is standard procedure to use an internal standard (scandium) with samples to increase the stability of the instrument as recommended by the manufacturer (Thermo Fisher). (When samples are suspected of containing scandium internal standard cannot be used.)

III. SAMPLE HANDLING AND PRESERVATION

A. Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Water samples which have been prefiltered and acidified will not need acid digestion as long as the samples and standards are matrix matched and particulates do not form after the filtration and preservation take place. Solubilization and digestion procedures are presented in Sample Preparation Methods (Methods 3005A-3050A).

B. Sample digestates are stored at room temperature for at least 2 months unless a longer time is requested by the client. The samples contain an acid matrix of 3:1. Since the most concentrated acid matrix allowed for direct disposal down an acid sink is a ratio of 20:1, the samples must be diluted with 1 part water to 2 parts sample prior to pouring down the sink while the tap water is running.

C. **The appropriate SOPs should be consulted regarding sample preparation.** The following is a brief summary of the methods we use for metals preparation.

- <u>Method 3005A</u> prepares groundwater and surface water samples for total recoverable and dissolved metals determination by ICP. The unfiltered or filtered sample is heated with dilute HCl and HNO_3 prior to metal determination.

- Method 3010A prepares waste samples for total metal determination by ICP. The samples are vigorously digested with a mixture of nitric acid and hydrochloric acid followed by dilution with laboratory water. The method is applicable to aqueous samples, TCLP and mobility-procedure extracts.

- Standard Methods 19th Edition Method 3030C prepares groundwaters and suface water samples for acid extractable metals: (lead and chromium.) This preparation has a holding time of 72 hours. The samples are preserved at collection with 5mL/L of HNO3, in the laboratory 5 mL/100mL of 1+1 HCl is added and the sample is heated for 15 minutes in a block digester. The sample is filtered through a membrane filter and the filtrate is carefully transferred to a volumetric flask and brought back to 100 mLs.

- Method 3050B prepares wastes samples for total metals determination by ICP. The samples are vigorously digested in nitric acid and hydrogen peroxide followed by dilution with either laboratory water or hydrochloric acid and laboratory water. The method is applicable to soils, sludges, and solid waste samples.

IV. INTERFERENCES

A. Spectral interferences are caused by background contribution from continuum or recombination phenomena, stray light from the line emission of high-concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

1. Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be included in the correction algorithm. Off-line interferences are handled by including spectra on interfering species in the algorithm.

2. To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral intereference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequtetely describe the interference. Normally, 100 mg/L single element solutions are sufficient; however, for analytes such as iron that may be found at high concentration, a more appropriate test would be to use a concentration near the upper analytical range limit.

3. Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction require the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive determinations and be reported as analyte concentrations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users may apply interelement correction equations determined on their instruments with tested concentration ranges to compensate (off line or on line) for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelength are listed in the method in table 2. For multivariate methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

4. When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2 from the method, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximatley 0.13 mg/L. The user is cautioned that other instruments

may exhibit somewhat different levels of interferences than that shown in Table 2 from the method. The interference effects must be evaluated for each individual instrument since the intensities will vary.

5. Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an intefering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences.

6. The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and agron flow rate). When using the recommended wavelengths, the anlaylst is required to determine and document for each wavelength the effect from referenced interferences as well as any other suspected interferences that may be specific to the instrument of matrix. The analyst is encouraged to utilize a computer routine for automatic correction on all analyses.

7. If the correction routine is operating properly, the determined, apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and divided by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

8. When interelement corrections are applied, their accuracy should be verified, daily, by analyzing spectral interference check solutions. If the correction factors or multivariate correction matrices tested on a daily basis are found to be within 20% criteria for 5 consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples

analyzed is such they do not contain concentrations of the interfering elements at ± one reporting limit from zero, daily verification is not required. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrumentation change, such as in the torch, nebulizer, injector, or plasma conditions occurs. Standard solution should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

B. Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump, by using an internal standard or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, using a high solids nebulizer or diluting the sample. Also it is has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance: this may be accomplished with the use of mass flow controllers.

C. Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the elements and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit should be noted. Until the required rinse time is established, this method suggests a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst based upon their DQOs.

D. Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration

accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

V. SAFETY

A. Normal accepted laboratory safety practices should be followed while performing this analysis.

1. Care should be used in handling all samples. Safety glasses must be worn in the lab at all times. The use of appropriate safety gloves and lab coats is highly recommended.
2. Research into expected sample content and concentration should be done in order to be prepared for additional safety considerations. Generally, any samples that need special consideration have applicable notes on the sample logs.
3. MSDS sheets are available for all reagents and standards that have been purchased. These are located in the bookshelves in the Quality Assurance Officers office.

VI. EQUIPMENT/APPARATUS

A. Inductively coupled argon plasma emission spectrometer: Thermo Scientific 6500 DUO.

B. Computer-controlled emission spectrometer with background correction: Thermo Scientific 6500 DUO or equivalent.

C. Radio frequency generator compliant with FCC regulations: Thermo Scientific or equivalent.

D. Argon gas supply – Liquid Argon

E. Class A volumetric flasks

F. Class A volumetric pipettes

G. Analytical balance - capable of accurate measurement to a minimum of three significant figures (.001gm): Mettler model AE100

H. Variable Eppendorf Pipettes 1000µL; 5000µL

VII. REAGENTS AND STANDARD PREPARATION

A. Notes

1. Reagent Water. All references to water in the method refer to reagent grade water unless otherwise specified. Reagent water will be interference free.

2. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question analyze for contamination. If the concentration is less than the MDL then the reagent is acceptable.

B. REAGENTS

1. Hydrochloric acid (concentrated), HCl.
2. Nitric acid (concentrated), HNO_3.

C. STANDARDS

1. Matrix

a. All standards contain 2% HNO_3 and 5% HCl.

2. Storage

a. The standards are stored at room temperature in 500 mL Teflon bottles.

3. Traceability

a. All records shall be maintained on all reference materials within Element. The record shall include date of receipt, source, purity, all compositional information, storage conditions and expiration date. These materials/solutions are to be identified by a unique Element number that is recorded on the container's label.

b. All working standards made from reference materials shall be labeled with a unique Element ID number with complete information on preparation date, concentration of each compound, solvent, preparer's name, expiration date in Element. Reagents shall be labeled with date received and expiration date, if applicable. All of the information described above shall also be recorded in Element. Measurements made during standards preparation (e.g., from weighing operations,

volume diluted to, etc.) shall also be recorded. There should be no container with sample, sample extract, standard solution, etc. that is not correctly labeled and properly stored.

4. Calibration standards

a. All standards have an acid matrix of 2% HNO_3 and 5% HCl and should be prepared using class A volumetric flasks, class A volumetric pipettes (or calibrated Eppendorfs).

b. STD-1 is the calibration blank: Reagent grade water **matrix matched as in (a) above. Note: when this standard is analyzed the intensities should be compared to a previous run to make sure that no contamination has occurred. Prepare this solution fresh daily.**

c. Stock QC21 solution: (100 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element and includes the following metals - Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, Se, Sr, Tl, Ti, V, and Zn.

e. Stock QC7 solution: Order from the manufacturer already prepared. This solution is given a unique identifier within Element and includes the following metals- (50 ug/mL)- silver; (100 ug/mL)- aluminum, boron, barium and sodium; (1000 ug/mL)- potassium; (500 ug/mL or 100 ug/mL note we use two sources of this standard and each have different concentrations for Si) –Silica.

f. Boron solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

g. Stock Tin solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

h. Stock Silver solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

i. Stock Aluminum solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

j. Stock Calcium solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

k Stock Magnesium solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

l. Stock Iron solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

m. Stock Potassium solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

n Stock Barium solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

o Stock Sodium solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

p. Stock Arsenic solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

q. Stock Cobalt solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

r. Stock Chromium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

s Stock Copper solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

t. Stock Manganese solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

u Stock Nickel solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

v. Stock Lead solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

w. Stock Selenium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

x. Stock Thallium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

y. Stock Beryllium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

z. Stock Cadmium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

aa. Stock Antimony solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

bb. Stock Molybdenum solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

cc. Stock Strontium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifie within Element.

dd. Stock Titanium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifie Element.

ee. Stock Vanadium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

ff. Stock Zinc solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

gg. Stock Scandium solution (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier within Element.

5. Calibration and Calibration Verification standards

a. The calibration standards and calibration verification standards preparations are recorded in Element. Please find method of preparation in Appendix I.

b. The CRI solution is analyzed to check the accuracy of the instrument down near the contract required detection limits (CRDL). It is analyzed in conjunction with the interference check sample. The sample is prepared from a purchased solution which contains 120 µg/mL Sb, 100 µg/mL Co and V, 80 µg/mL Ni, 50 µg/mL Cu, 40 µg/mL Zn, 30 µg/mL Mn, 20 µg/mL As, Cr, Ag and Tl, 10 µg/mL Be, Cd and Se along with 6 µg/mL Pb. 500 µ/L of the solution is diluted to 500 mL. This solution is stable for 6 months.

hh. The interference check solutions (ICSA and ICSAB) are prepared to contain known concentrations of interfering elements that will provide an adequate test of the IECs. A solution containing 500 ug/mL Al, Ca, Mg and 200 ug/mL Fe is diluted 10x to prepare the ICSA. The ICSAB is prepared by diluting 100x a solution containing 10 ug/mL of As and Tl; 20 ug/mL Ag; 50 ug/mL Ba, Be, Cr, Co, Cu, Mn, and V; 100 ug/mL Cd, Ni and Zn; 5 ug/mL Pb and Se; and 60 ug/L Sb. Add to this a solution containing 500 ug/mL Al, Ca, Mg and 200 ug/mL Fe diluted 10x. These solutions are prepared as needed or monthly.

d. Reporting Limit Standard- Prepared 1.0 ml of RL Stock solution A and 1.0 ml of RL Stock Solution B diluted to 100 ml with 2% HNO3 and 5% HCL matrix , mix well. Solution stable for 3 months

6. Digestion standards

a. The Laboratory control sample (LCS) is prepared from High Purity solutions CLP-CAL-1 solution A and B; CLP-CAL-2 and CLP-CAL-3. 0.50 mL of CLP-CAL-1 A and B is diluted to 500 mL with 0.125 mL of CLP-CAL-2 and CLP-CAL-3. 25 mL of HCl and 10 mL of HNO3 are added for preservation. This solution is stored in a Teflon bottle. A portion is reserved in case of a problem with digestion. When there is a problem with the analysis of the LCS the solution is checked first before action is taken to make sure that it was made properly and has not deteriorated since it was made up. This solution is given a unique identifier. The LCS is prepared from a source independent from that used in the calibration standards. This solution is prepared daily or as needed. Note: The analysis of Molybdenum is not a routine procedure but a project-specific requirement. A customized LCSW mix must be prepared to contain this target analyte.

b. The solid Laboratory Control Sample (Soil) (LCSS) is prepared by weighing up 1.0 g of teflon chips and spiking using the same spiking

solutions used to spike the sample matrix. This standard is given a unique identifier i.e. LCSS(date prepared)A,B,C etc.

c. The spiking solutions are prepared as follows:

1. Stock Multi-element Spiking Solutions: High Purity CLP-CAL-1 solution A: 2000 ug/mL Al and Ba; 50 ug/mL Be; 200 ug/mL Cr; 500 ug/mL Co, Mn, Ni, V and Zn; 250 ug/mL Cu; 1000 ug/mL Fe; 5000 ug/mL Ca, Mg, K and Na; solution B: 250 ug/mL Ag; CLP-CAL-2: 1000 ug/L Sb; CLP-CAL-3: 1000 ug/mL As, Pb, Se, Tl; 500 ug/mL Cd. Order from the manufacturer already prepared. These solutions are given a unique identifier. Add 0.050 mL (0.20 mL for soil samples) of CLP-CAL-1 solutions A and B, and 0.0125 mL (0.05 mL for soil samples) of CLP-CAL-2 and 3 to 50 mL of sample (1gram of sample for soils) for the following spike values: 2000 ug/L Al and Ba; 50 ug/L Be; 200 ug/L Cr; 500 ug/L Co, Mn, Ni, V and Zn; 250 ug/L Cu; 1000 ug/L Fe; 5.0 mg/L Ca, Mg, K and Na, 250 ug/L Ag, Sb, As, Pb, Se and Tl; 125 ug/L Cd. A blank spike should be prepared at the time the samples are spiked to check the actual spike value and accuracy.

2. TCLP Spiking Solution: Use 0.50 mL diluted to 50 mL for digestion:
2.5 mL 10000 mg/L Ba stock standard diluted to 100 mL; 2.5 mL Cr, Pb and As 1000 mg/L stock standard diluted to 100 mL; 0.50 mL Cd and Se diluted to 100 mL . Store in a Teflon bottle. A blank spike should always be prepared at the same time a sample is being spiked. This solution should produce a spike value of 2500 ug/L Ba; 250 ug/L Cr, Pb and As; and 50 ug/L of Cd and Se. Note: Since the samples are diluted 10x when digested the spike value will appear to be 10x greater when analyzed.

3. TCLP Silver Spiking Solution: Use 5.0 mL diluted to 50 mL for digestion:
0.40 mL of 1000 mg/L stock Ag solution diluted to 200 mL. Store in a Teflon bottle. A blank spike should always be prepared at the same time a sample is being spiked. This solution should produce a spike value of 200 ug/L. . Note: Since the samples are diluted 10x when digested the spike value will appear to be 10x greater when analyzed. Also this solution is not very stable and may require fresh preparation at least weekly.

VIII. CALIBRATION AND ASSOCIATED QA/QC

A. Set up the instrument with proper operating parameters. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration).

B. Operating conditions - **The instrument settings can be found in method file.** For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

C. Autopeak when some change has been made to the introductory system and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions. **(See SOP-106, *ICP Instrument Operation*)** Flush the system with 2% HNO_3 / 5% HCl between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve consists of a blank and three standards ($r \geq 0.998$). If a three point calibration curve is not required for the client samples being analyzed Empirical Laboratories may use a blank and one standard as referenced in USEPA - CLP protocols.

D. Before beginning the sample run, analyze the Iron and Aluminum standards at their linear range to check for IEC drifts. Analyze these standards first as QC samples with an IEC check table and action taken should be to calculate IECs using the iTEVA software. Make sure to rinse thoroughly after running these linear range standards, they can cause carry over into the initial QC samples which are analyzed next. The analysis order follows as: ICV ($\pm$ 10%) for 200.7 ($\pm$ 5%) and ICB (< ±MDL or ±RL/CRDL for others or CLP, **for CCB, DOD QSM Ver. 3 no analytes detected >2xMDL**) first, then analyze a reporting limit standard (a standard at the concentration of the reporting limit). This standard should be within ±20% for DOD projects and ±30% for samples analyzed for 6010C. Then reanalyze the highest mixed calibration standard(s) as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5%. If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

E. For CLP projects, verify the validity of the curve in the region of 2x the contract required detection limit (CRDL) before and after each batch of 20 samples in the specific order of CRI, ICSA, ICSAB, CCV and CCB(CCB

criteria: < ±MDL or ±RL/CRDL for others or CLP, **for CCB, DOD QSM Ver. 3 no analytes detected >2xMDL, beginning and end of sequence and after every 10 samples**) or twice during every 8-hour work shift, whichever is more frequent. Results should be within ±20%. Supervisor must be notified if the control limit is not met. Supervisor will dictate corrective action if required. The final analytical report must document this situation. (For Internal QC)

F. Verify the interelement and background correction factors at the beginning and after each batch of 20 samples in the specific order of CRI, ICSA, ICSAB, CCV and CCB(CCB criteria: < ±MDL or ±RL/CRDL for others or CLP, **for CCB, DOD QSM Ver. 3 no analytes detected >2xMDL, beginning and end of sequence and after every 10 samples**) or twice during every 8-hour work shift, whichever is more frequent. Do this by analyzing the interference check solution A and AB. Results should be within ±20% of the true value for ICSAB. **For ICSA DOD QSM Ver 3. , absolute value of concentration for all non-spiked analytes < 2xMDL**.(CRI, ICSA and ICSAB required at the end for CLP projects only).

G. *When analyzing samples associated with North Carolina or with DOD QSM Ver. 3 work, a solution containing analytes at their reporting limit must be analyzed prior to sample analysis. The concentrations must be within 20% DOD(20 or 30% depending on project) of their true values to be acceptable.*

Note: Supervisor must be notified if the control limit is not met. Supervisor will dictate corrective action if required. The final analytical report must document this situation.

H. The instrument must be calibrated once every 24 hours if performing straight CLP work.

I. Instrument Autosampler Report example:

Calibration Rack(used by instrument software to insert QC)

1) STD 1-blank
2) Low Cal
3) Mid Cal
4) Ba @ 5000 ppb
5) QC5
6) QC 21
7) NAK 100
8) QC3

Sample Sequence RACK 1

1) Al IEC-(readback)

2) Fe IEC-(readback)
3) ICV
4) ICB-initial
5) RL-reporting limit standard
6) Ba@ 5000 ppb (readback)
7) QC5
8) NAK High-(readback)
9) QC 21 High-(readback)
10) Salt Cal at 500 ppm (readback)
11) Rinse
12) CRI-0
13) ICAS-0
14) ICASB-0
15) Rinse
16) CCV 1A
17) CCB 1A
18) Preparation Blank (*Batch #* BLK-1)
19) Laboratory Control Sample (*Batch #* BS-1)
20) Sample 1
21) Sample 2
22) Sample 3
23) Sample 4
24) Sample 5
25) Sample 6
26) Sample 7
27) Sample 8
28) CCV 1B
29) CCB 1B
30) Sample 9
31) Sample 10
32) Sample 11
33) Sample 12
34) Sample 13
35) Sample 14
36) Sample 15
37) Sample 16
38) Sample 17
39) Sample 18
40) CCV 2A
41) CCB 2A
42) Sample 19
43) Sample 20
44) Sample matrix spike (*batch#* MS-1)
45) Sample matrix spike duplicate (*batch#* MSD-1)
46) Sample post digestion spike (*batch#* PS-1)
47) Sample serial dilution (*batch#* SRD-1)
48) CRI-1

49) ICSA-1
50) ICSAB-1
51) Rinse
52) CCV 2B
53) CCB 2B
54) Preparation Blank (*batch#* BLK-1)
55) Laboratory Control Sample (*batch#* BS-1)
56) Sample 1
57) Sample 2
58) Sample 3
59) Sample 4
60) Sample 5

RACK 2

1) Sample 6
2) Sample 7

Etcetera…

Each rack holds 60 samples and there are 4 racks that are used for samples, CCVs and CCBs and run QC.

IX. PROCEDURE

A. Once the instrument has been calibrated, begin the analysis of samples.

B. If particulates are visible in the digestate, the sample must be filtered prior to analysis. If filtration is required, a filter blank must be prepared by filtering reagent grade water which has been properly acidified. **In the event USACE samples are filtered, all USACE samples and the QC samples in that QC batch must be filtered. All USACE solid samples and their associated batch QC samples must be filtered prior to analysis.**

C. Flush the system with 2% HNO_3 / 5% HCl for at least 1 minute before the analysis of each sample.

D. Dilute and reanalyze samples that are more concentrated than the linear calibration limit or, for 200.7, $\pm$ 10% of the linear range standard. **In the case of USACE samples, the criterion changes and requires dilution and reanalysis of all samples which produce a concentration that exceeds the highest calibration standard. Sample results detected between the MDL and RL are flagged as estimated with a ”B” flag.**

E. Verify calibration every 10 samples or every 2 hours, whichever is more frequent and at the end of the analytical run, using a continuing calibration verification (CCV) sample and a continuing calibration blank (CCB) sample.

- The results of the CCV are to agree within 10% for 6010 (5% for 200.7) on initial verification of the expected value, with relative standard deviation (RSD) < 5% from replicate (minimum of two integrations). If not, terminate the analysis, correct the problem, and reanalyze the previous ten samples. The analyst may continue the analytical run, and after conferring with the section manager it may be necessary to reanalyze a group of samples. The analyst must notify the section manager within 24 hours.

- The results of the calibration blank (this is not the method/preparation blank) are to agree within < ±MDL(SW-846 Method 6010B), and 3 x IDL or CRDL for CLP, for **DOD QSM Ver. 3 no analytes detected >2xMDL**. If the calibration blank is not in control, evaluate the impact upon the previous 10 samples. Reanalysis may be required after an evaluation of the data. If the blank < 1/10 the concentration of the action level of interest, and no sample is within 10% of the action limit, samples need not be reanalyzed. One must also evaluate the reporting limit (RL) as it relates to 3X the IDL/MDL. If the RL is significantly above 3X IDL or MDL then reanalysis may not be required (Na, K, Mg and Ca are good examples of this situation).

- Total hardness is reported from HNO_3 preserved sample. The final concentration is calculated from the calcium and magnesium results as follows:

$$\text{Ca mg/L} \times 2.5 + \text{Mg mg/L} \times 4.1 = \text{total Hardness in mg/L as } CaCO_3$$

F. Documentation of Capability (DOC) – Each analyst must perform a DOC to demonstrate proficiency with this method. Refer to SOP-413 for guidance.

X. CALCULATIONS

A. The instrument will generate data results in mg/L or µg/L (labeled appropriately). Each result represents an average of three individual readings per metal channel.

B. For aqueous samples, if a post/predigestion dilution is performed, the result must be multiplied by this factor or the dilution factor must be entered into the instrument data table in which case the instrument will generate data corrected for the dilution.

C. For solid samples, if a postdigestion dilution is performed , the result must be multiplied by this factor or the dilution factor must be entered into the instrument data table in which case the instrument will generate data corrected for the dilution. Also, the result must be converted to reporting units which are usually mg/kg.

SR (ug/g or mg/kg) = IR*DF*FED/SM

SR = Sample result
IR = Instrument result (µg/L)
DF = Dilution factor (post digestion)
FED = Final volume of digestate (L)
SM = Sample mass digested(g)

XI. QUALITY CONTROL

A. Daily

1. See sections VIII and IX above.

B. Quarterly

1. Linear range standards must be analyzed at a frequency no less than once every three months. The linear range standard represents the second standard required for verification that samples are actually linear to the degree claimed. The analyst is responsible for completing this task in a timely manner. The linear range standard must be within +/-5% of true value.

2. The interelement correction factors (IEC) should be verified at the time the linear range standards are analyzed.

3. IDL's if CLP work required.

C. Digestion

1. All quality control data should be maintained and available for easy reference or inspection.

2. Employ a minimum of one method blank per sample batch to determine if contamination or any memory effects are occurring. A method blank, sometimes referred to as the preparation blank is a volume of reagent water acidified with the same amounts of acids as were the standards and samples. These blanks are taken through the same digestion/preparation steps as the sample being tested. The result for the method blank should not indicate contamination greater than ± ½ RL (USACE) or ±RL/CRDL for other or CLP. If exceeded, the impact upon the data should be evaluated and the associated sample(s) should be either redigested or the data should be qualified.

3. Employ a minimum of one laboratory control sample (LCS) for aqueous samples or one teflon chip spiked sample per sample batch to verify the digestion procedure. These LCSs are taken through the same digestion/preparation steps as the sample being tested. The control limits

are ±15% method 200.7 - aqueous and soil samples or ±20% for all other methods aqueous and soil samples. If the LCS is not in control, the impact upon the client data should be evaluated and the associated sample(s) should be redigested. Consult your supervisor for further action. Qualifying the associated data may not be permissable for some clients.

D. Sample

1. Analyze one replicate sample for every twenty samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the whole sample preparation and analytical process in duplicate. It is acceptable to substitute a matrix spike duplicate for the sample replicate. Project specific requirements will take precedence in these situations. NJDEP demands that this requirement be met with a client specific duplicate rather than a spike duplicate. The control limits are 20% RPD (if both are >5x CRDL) or ± the CRDL (if either are <5X CRDL).

2. Analyze one spiked sample and spiked sample duplicate for every twenty samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the whole sample preparation and analytical process in duplicate. Project specific requirements will take precedence in these situations. If the analyte level in the sample is not greater than 4X the spiking level, the spike recoveries should be within ±25% of the true value (**± 20% for DOD projects**). If not, a post digestion spike should be analyzed.

3. The relative percent difference (RPD) between replicate determinations is to be calculated as referenced in the laboratory QA manual. (A control limit of ± 20% RPD (non-aqueous samples may routinely exceed this amount) shall be used for sample values greater than five times the contract required detection limit.) Supervisor must be notified if the control limit is not met. Supervisor will dictate corrective action if required. The final analytical report must document this situation.

4. *The following should be analyzed with each preparation batch containing a matrix spike.*

   - Serial dilution: If the analyte concentration is sufficiently high (minimally, a factor of 50 above the instrumental detection limit after dilution), an analysis of a 1:4 dilution (volumetric glassware must be used) should agree within ±10% of the original determination. If not, a chemical or physical interference effect should be suspected. The analyst and or section manager must note this situation on the final analytical report.

   - Post digestion spike addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 85% to 115% of the known value and is required if the pre-digestion matrix

spike (low-level only for CLH) is outside of control limits. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected. The analyst and or section manager must note this situation on the final analytical report.

E. Method Detection Limit (MDL), Empirical Laboratories Reporting Limit (ERL), Contract Required Quantitation Limit (CRQL) and Analyte Wavelength:

TABLE I

Aqueous and Soil Method Detection Limits(MDL), Empirical Laboratories Reporting Limits(ERL), CLP OLM04.1 & OLM05.2 Contract Required Quantitation Limits (CRQL)

Analytes by EPA 200.7,3005A/3050A- 6010B SOW 4.1 & 5.2	AQUEOUS MDL (ug/L)	AQUEOUS ERL (ug/L)	AQUEOUS CRQL ILMO 4.1 (ug/L)	AQUEOUS CRQL ILMO 5.2 (ug/L)	SOLID/SOIL MDL (mg/Kg)	SOLID/SOIL ERL (mg/Kg)	SOLID/SOIL CRQL ILMO 4.1 (mg/Kg)	SOLID/SOIL CRQL ILMO 5.2 (mg/Kg
Silver	**1.0**	**10**	**10**	**10**	**0.20**	**2.0**	**2**	**2**
Aluminum	**50**	**200**	**200**	**200**	**10**	**40**	**40**	**40**
Arsenic	**3.0**	**10**	**10**	**15**	**0.6**	**2.0**	**2**	**3**
Barium	**5.0**	**200**	**200**	**200**	**1.0**	**40**	**40**	**40**
Beryllium	**1.0**	**5.0**	**5**	**5**	**0.20**	**1.0**	**1**	**1**
Calcium	**1000**	**5000**	**5000**	**5000**	**20**	**1000**	**1000**	**1000**
Cadmium	**1.0**	**5.0**	**5**	**5**	**0.20**	**1.0**	**1**	**1**
Cobalt	**5.0**	**50**	**50**	**50**	**1.0**	**10**	**10**	**10**
Chromium	**2.0**	**10**	**10**	**10**	**0.40**	**2.0**	**2**	**2**
Copper	**4.0**	**25**	**25**	**25**	**0.40**	**5.0**	**5**	**5**
Iron	**30**	**100**	**100**	**100**	**1.0**	**20**	**20**	**20**
Potassium	**1000**	**5000**	**5000**	**5000**	**40**	**1000**	**1000**	**1000**
Magnesium	**1000**	**5000**	**5000**	**5000**	**40**	**1000**	**1000**	**1000**
Manganese	**1.0**	**15**	**15**	**15**	**0.20**	**3.0**	**3**	**3**
Sodium	**1000**	**5000**	**5000**	**5000**	**40**	**1000**	**1000**	**1000**
Nickel	**3.0**	**40**	**40**	**40**	**1.0**	**8.0**	**8**	**8**
Lead	**1.5**	**5.0**	**3**	**10**	**0.60**	**2.0**	**0.6**	**2**
Selenium	**3.0**	**10**	**5**	**35**	**0.60**	**2.0**	**1**	**7**
Antimony	**5.0**	**60**	**60**	**60**	**1.0**	**12**	**12**	**12**
Thallium	**3.0**	**10**	**10**	**25**	**0.60**	**2.0**	**2**	**5**
Vanadium	**5.0**	**50**	**50**	**50**	**1.0**	**10**	**10**	**10**
Zinc	**5.0**	**20**	**20**	**60**	**1.0**	**4.0**	**4**	**12**

TABLE 2

METAL	WAVELENGTH
Aluminum	396.1
Antimony	206.8
Arsenic	189.0
Barium	233.5
Beryllium	313.0
Cadmium	228.8
Calcium	317.9
Chromium	267.7
Cobalt	228.6
Copper	324.7
Iron	261.1
Lead	220.3
Magnesium	279.0
Manganese	257.6
Molybdenum	202.0
Nickel	231.6
Potassium	766.4
Selenium	196.0
Silver	328.0
Sodium	589.5
Thallium	190.8
Tin	189.9
Titanium	334.9
Vanadium	292.4
Zinc	206.2

XII. CORRECTIVE ACTIONS

A. INSTRUMENT RELATED

1. ICV not within ± 10% or ± 5% for 200.7
   a. Is the problem with the solution?
      i. Reprepare or obtain new stock.
   b. Is the problem with the calibration?
      i. Recalibrate through analysis of appropriate standards and recheck ICV.

2. ICB not ±MDL or within ± 3X IDL or CRDL for CLP, **DOD QSM Ver. 3 no analytes detected >2xMDL**

   a. Is the problem with the solution?
      i. Reprepare
   b. Is the problem with the calibration?
      i. Recalibrate with the blank solution or the low level standard. Restart analysis with the ICV.

3. Check standards not within ± 5%
   a. Is the problem with the solution?
      i. Repour, reprepare or obtain new stock.
   b. Is the problem with the calibration?
      i. Recalibrate thru analysis of appropriate standards. Restart analysis with the ICV.

4. CRI not within ± 20% (Internal QC, only required for CLP work).
   a. Is the problem with the solution?
      i. Reprepare or obtain new stock.
   b. Is the problem with the calibration?
      i. Recalibrate thru analysis of appropriate standards. Restart analysis with the ICV.
5. ICSA metals not present are not less than the CRDL for that metal, **for ICSA DOD QSM Ver 3. , absolute value of concentration for all non-spiked analytes < 2xMDL.**
   a. Is the problem with the solution?
      i. Reprepare or obtain new stock.
   b. Is the problem with the calibration?
      i. Recalibrate thru analysis of appropriate standards. Restart analysis with the ICV.

6. ICSAB not within ± 20%
   a. Is the problem with the solution?
      i. Reprepare or obtain new stock.
   b. Is the problem with the calibration?
      i. Recalibrate thru analysis of appropriate standards. Restart analysis with the ICV.

7. CCV not within ± 10%
   a. Is the problem with the solution?
      i. Reprepare or obtain new stock.
   b. Is the problem with the calibration?
      i. If appropriate, continue the analysis. Discuss effect of the out of control situation with your supervisor. The samples will be reanalyzed or the data will be qualified. Note: CLH data must

always be reanalyzed back to the last compliant CCV and not qualified.

8. CCB not ±MDL or within ± 3X IDL or CRDL for CLP, **DOD QSM Ver. 3 no analytes detected >2xMDL**
   a. Is the problem with the solution?
      i. Reprepare
   b. Is the problem with the calibration?
      i. Apply SW846 guidance. (See Section IX-E for additional guidance). Note: CLH data must always be reanalyzed back to the last compliant CCB and not qualified.

B. DIGESTION RELATED

1. Preparation blank not within ± ½ RL and ± RL for common contaminants USACE or RL/CRDL for other or CLP
   a. Is the problem with the instrument?
      i. Evaluate with respect to instrumental bias or reanalyze when instrument is in control.
   b. Is the problem with the digestion?
      i. If associated samples are less than 10X the level of the preparation blank but above the RL, the sample must be redigested or the data must be qualified on the final report.

2. LCS not within control limits
   a. Is the problem with the instrument?
      i. Evaluate with respect to instrumental bias or reanalyze when instrument is in control.
   b. Is the problem with the digestion?
      i. If biased low, associated samples must be redigested.
      ii. If biased high, the impact upon the data user must be evaluated. The samples will be redigested or the data will be qualified on the final report.

C. SAMPLE MATRIX RELATED

1. Replicate analysis RPD not within ±20% (if both are >5X CRDL) or ± the CRDL (if either are <5X CRDL).
   a. The associated sample data must be qualified on the final report.

2. Spike analysis recovery not within ±25%(**± 20% for DOD projects**)
   a. Is the analyte level in the sample greater than 4X the spiking level?
      i. If yes, the spike recovery is not evaluated.
      ii. If no, a post digestion spike must be analyzed and the associated sample data must be qualified on the final report.

3. When required, post digestion spike analysis recovery not within ±15%.

a. The associated sample data must be qualified on the final report.
b. For USACE analysis by MSA is required.

4. Serial dilution analysis percent difference not within ±10%
   a. Is the analyte concentration a factor of 50 above the instrumental detection limit after dilution?
      i. If no, the serial dilution data can not be evaluated.
      iii. If yes, a chemical or physical interference effect should be suspected. The analyst and or section manager must note this situation on the final analytical report.

XIII. WASTE DISPOSAL and POLLUTION PREVENTION

Please see Waste Disposal SOP-405 fot instruction of proper disposal of waste generated from this area.

Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

XIV. REFERENCES

1. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846; Third Edition (Update III)*; Method 6010B and Method 6010C

2. USEPA *Code of Federal Requlations, 40, CH 1,PT 136;* Method 200.7; APX-B

3. USEPA *Contract Laboratory Program(CLP) for Inorganics ILM04.1; ILM05.2*

Refer to SOP-431 for common environmental laboratory definitions.

Addendum for USEPA CLPILM 05.2

1. The control limit for the ICSA is at 20% or ±CRQL whichever is greater.
2. Preparation codes are required in the digestion log See SOW Exhibit B for a listing of these codes with definitions.
3. The CRQL check standard is run at the concentration of the respective CRQLs. For a listing of CRQL for this SOW see Exhibit C. Several of the metals concentration levels have changed.
4. The spiking level for CLP ILM 05.2 is at 50 ug/L for selenium. All other spike levels remain the same as in SOW ILM 04.1.
5. The CCV shall be analyzed at a different concentration then the ICV (at or near one-half of the calibration standard concentration.
6. The post digestion spike must be analyzed at 2x the indigenous level of the sample or two times the CRQL whichever is greater.
7. A Non-prepared MDL study must be analyzed and the results of this study used for MDL reporting when sample volumes are not digested.

CHANGES TO FORMS for SOWCLPILM 05.2

1. Forms must be double-sided
2. A photocopy of the instrument's direct sequential readout shall be included.
3. Undiluted samples must be reported as well as diluted samples.
4. J flags are used in place of B flags when a sample has a concentration less the CRQL but greater then or equal to the MDL.
5. A D flag is used for samples reported from a dilution.
6. All results are reported down to the MDL not the IDL.
7. Preparation codes are used on form 13.

   The form for method of standard additions (MSA) has been removed and all subsequent QC has move up one form number in other words form 8 is now serial dilution when it used to be the MSA form,etcetera.

ANALYST DATA REVIEW CHECKLIST Sample Number(s):

Batch Number(s):

Method: 6010B (ICP)

QA/QC Item	Yes	No	NA	Second Level Review
1. Were samples analyzed within USACE holding times?				
2. Was initial calibration curve QC criteria met?				
3. Was all continuing calibration criteria in control?				
4. Did any sample exceed the highest calibration standard? (If yes, were appropriate dilutions made to generate samples concentration within calibration range?)				
5. Did LCS or blank spike meet control limits?				
6. Did MS/MSD meet control limits?				
7. Was the preparation (Method) Blank below the project required detection limits?				
8. Did you return samples back to cold storage immediately after use?				
9. Was hot plate temperature monitored/documented and did you apply the thermometer correction factor?				
10. Sample preparation information is correct and complete.				
11. Analytical results are correct and complete.				
12. The appropriate SOP's have been used and followed.				
14. "Raw data" including all manual integration's have been correctly interpreted.				
15. "Special" sample preparation and analytical requirements have been met.				
16. Documentation complete (e.g., all anomalies in the analytical sequence have been documented, corrective action forms are complete.				

Comments on any "No" response:

_____

_____

_____

_____

_____

_____

Analyst: _____ Date: _____

Second-Level Review: _____ Date: _____

APPENDIX I

Preparation Method for Calibration Standards

Empirical Laboratories, LLC

SULFIDE
METHOD 376.1 and STANDARD METHODS SM4500S F(19th ED) (TITRIMETRIC, IODINE) WITH SAMPLE PRETREATMENT TO REMOVE INTERFERING SUBSTANCES OR TO CONCENTRATE THE SULFIDE

SOP NUMBER: SOP-153

REVISION NUMBER: 3

APPROVED BY:

Betty DeVille
SECTION MANAGER

Randy Dillard
TECHNICAL DIRECTOR

EFFECTIVE DATE: 06/24/08

DATE OF LAST REVIEW: 05/27/09

Empirical Laboratories, LLC

SULFIDE
METHOD 376.1 and STANDARD METHODS SM4500S F(19th ED)
(TITRIMETRIC, IODINE)
WITH SAMPLE PRETREATMENT TO REMOVE INTERFERING SUBSTANCES OR TO CONCENTRATE THE SULFIDE

I. SCOPE OF APPLICATION:

A. This method is applicable to the measurement of total and dissolved sulfides in drinking, surface and saline waters, domestic and industrial wastes.

B. Acid insoluble sulfides are not measured by the use of this test. (Copper sulfide is the only common sulfide in this class.)

C. This method is suitable for the measurement of sulfide in concentrations above 1 mg/L.

II. SUMMARY OF METHOD:

Excess iodine is added to a sample which has been treated with zinc acetate to produce zinc sulfide. The iodine oxidizes the sulfide to sulfur under acidic conditions. The excess iodine is backtitrated with sodium thiosulfate.

III. SAMPLE HANDLING AND PRESERVATION

A. Samples must be taken with a minimum of aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an unmeasurable form.

B. Samples are taken in glass bottles with stopper; preferably 500 to 1000 mL. Usually we use 300 mL (BOD bottle). Preserve with zinc acetate 2N and 6N NaOH. There should be no air-space in the container.

C. The holding time for sulfides preserved in this manner is 7 days.

IV. INTERFERENCES:

The iodometric method suffers interferences from reducing substances that react with iodine, including thiosulfate, sulfite and various organic compounds, both solid and dissolved. Interferences due to sulfite, thiosulfate, iodide and many

other soluble substances are eliminated by first precipitating ZnS in the samples, removing the supernatant, and replacing it with distilled water.

V. EQUIPMENT/APPARATUS:

A. 10 mL burette
B. Glass, stoppered bottle of 500 to 1000 mL (300 mL BOD bottles)
C. Vacuum pump
D. Magnetic stirrer with Teflon coated stirring bars
E. Buchner funnel
F. 500 mL Erlenmeyer flask

VI. REAGENTS:

A. Zinc acetate, 2N: dissolve 220 grams Zn $(C_2H_3O_2)_2 \cdot 2\ H_2O$ in 870 mL D.I. water; this makes 1 liter solution.

B. Sodium Hydroxide, 6N: dissolve 240 grams of NaOH in about 600 mL of D.I. water. Dilute to 1 liter.

C. Hydrochloric acid, 6N: add 250 mL concentrated HCl to 250 mL D.I. water, mix well.

D. Standard iodine solution, 0.025N: dissolve 20 to 25 grams KI in a little water and add 3.2 grams iodine. After iodine has dissolved, dilute to 1000 mL in a volumetric flask. Standardize against 0.0250N Na_2S0_3, using thyodene as indicator. **(Purchased commercially)**

E. Standard sodium thiosulfate titrant solution, 0.025N: dissolve 6.205 grams $Na_2S_20_3 \cdot 5H_20$ in distilled water. Add 1.5 mL 6N NaOH or 0.4 grams solid NaOH and dilute to 1000 mL. Standardize with bi-iodate solution. (May be purchased commercially.)

F. Standard potassium bi-iodate solution, 0.025ON: dissolve 812.4 mg $KH(IO_3)_2$ in distilled water and dilute to 1000 mL. Standardization of thiosulfate--dissolve approximately 2 grams KI, free from iodate, in an Erlenmeyer flask with 100 to 150 mL distilled water. Add 1 mL 6N H_2SO_4 or a few drops of concentrated H_2SO_4 and 20.00 mL standard bi-iodate solution. Dilute to 200 mL and titrate liberated iodine with thiosulfate titrant, adding 1 scoop thyodene toward end of titration, when a pale straw color is reached. When the solutions are of equal strength, 20.00 mL 0.0250N $Na_2S_20_2$ should

be required. If not, adjust the $Na_2S_2O_3$ solution to 0.025ON using N1V1 = N2V2 equation.

G. Thyodene.

VII. PROCEDURE

A. Pretreatment:

1. If sample has not been preserved with zinc acetate and NaOH, place 3 to 5 pasteur pipettes of 2N zinc acetate solution into a 500 mL glass bottle, fill with sample, and add 10 drops 6N NaOH solution. Stopper with no air bubbles under stopper and mix by rotating back and forth vigorously about a transverse axis. Vary volume of reagents added according to sample so that the resulting precipitate is not excessively bulky and settles readily. Add enough NaOH to produce a pH above 9.

2. Let precipitate settle for 30 minutes. The treated sample is relatively stable and can be held for several hours However, if much iron is present, oxidation may be fairly rapid. Holding time for this sample is 7 days.

B. Preparation and Titration of Sample:

1. Mark meniscus of sample volume on side of bottle so you can measure sample volume. Filter precipitate through glass fiber filter paper 11.0 to 12.5 cm in a Buchner funnel. Save the filter and all precipitate and discard filtered sample.

2. Measure exactly, amount of standard iodine solution (estimated to be an excess over the amount of sulfide present in the sample--usually 2 to 10 mL) into a 500 mL Erlenmeyer flask. Add distilled water, if necessary, to bring volume and iodine solution to 20 mL.

3. Add 2 mL 6N HCl.

4. Place filter with precipitate, making sure you wipe sides of Buchner funnel to get any precipitate clinging to the sides, into bottle with iodine solution and acid. Add 200 mL D.I. water.

5. Fill a 50 mL Burette with 0.0250 N sodium thiosulfate solution.

6. Put a small stirring bar in sample and place on magnetic stirrer. Stir bar turning slowly.

7. Titrate slowly with sodium thiosulfate titrant adding 1 scoop thyodene reagent toward the end of the titration, when a pale straw color is reached. The sample will go from straw yellow to a dark blue when thyodene is added. It should take only 2 or 3 drops of titrant to bring sample to the endpoint of clear at this point. Record mL of titrant used. Sample will turn back blue but the first change from blue to clear is the endpoint.

8. Do a blank with each set of samples taken D.I. water through the entire procedure the same as the samples including pretreatment. D.I. water is usually ~1.0 mg/L sulfide.

9. Discard titrated sample. Rinse out bottle and measure volume of sample used by filling bottle to the calibration mark on the side of bottle with water and pouring water into a graduate cylinder.

VIII. CALCULATIONS:

One milliliter 0.0250N iodine solution reacts with 0.4 mg S2-:

$$\text{Mg S2-/L} = \frac{(AXB) - (CXD)}{\text{Sample}} \times 16000 \times (\text{Ratio of final to mL initial volume})$$

where:

A = mL standard iodine solution
B = normality of iodine solution
C = mL $Na_2S_2O_3$ solution
D = normality of $Na_2S_2O_3$ solution
Final volume = 200 mL
Initial volume = measured volume of original sample

IX. QUALITY CONTROL:

A. Analyze a duplicate and second source check with each analytical batch. The second source check standard can be purchased commercially.

X. CORRECTIVE ACTIONS

A. If the LCS fails (exceeds 80-120 %). Contact Lab supervisor.

XI. HEALTH AND SAFETY

A. Care should be used in handling all samples. Safety glasses must be worn in the lab at all times. The use of gloves and lab coats is highly recommended.

B. Research into expected sample content and concentration should be done in order to be prepared for additional safety considerations. Generally, any samples which need special consideration have applicable notes on the sample logs.

B. MSDS sheets are available for all reagents and standards which have been purchased. These are located on the bookshelf outside the office supply storage room.

XII. POLLUTION PREVENTION

A. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

B. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

C. For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202) 872-4477.

XIII. WASTE MANAGEMENT

A. The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any waste discharge permit and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel," available from the American Chemical Society at the address listed in Section 14.3 from method 300.1.

XIV. METHOD PERFORMANCE

See Methods 376.1 and Standard Methods SM4500S F.

EMPIRICAL LABORATORIES, LLC
STANDARD OPERATING PROCEDURE

ORGANICS: SOP 202 **REVISION #: 22** **EFFECTIVE DATE: 093009**

GC/MS VOLATILES BY EPA METHOD E624 & SW846 METHOD 8260B INCLUDING APPENDIX IX COMPOUNDS

APPROVALS:

Lab Director: _____ Date: 10/5/09

Data Quality Manager: _____ Date: 10/5/09

Section Supervisor: _____ Date: 10/7/09

Changes Summary

Revision 22, 9/30/09

- The SOP is an update from Revision 21 dated 09/11/08
- The SOP is formatted to include all 22-elements required per the NELAC standards
- The laboratory's revision of all technical SOPs now includes a Table of Contents that provides the map of the technical information contained within the SOP.
- Additional requirements, based upon the DoD QSM 4.1, have been integrated into the routine sample flow; however, if the requirement is different from routine sample flow, then the requirement is outlined and documented as such to be followed only when DoD samples are analyzed.

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21. References
22. Tables, Diagrams, Flowcharts and Validation Data

1. Identification of the Test Method

1.1 This SOP is compliant with methods – EPA Method 624 and SW-846 Method 8260B

2. Applicable Matrix or Matrices

2.1 This SOP is applicable to – The analysis of volatile organic compounds in a variety of matrices including but not limited to soils, sediments, ground and surface waters, aqueous sludge, oily wastes, etc.

3. Detection Limit: See Table 1 of this SOP.

4. Scope of Application, Including components to be Analyzed

4.1 This SOP is based primarily on SW-846 Method 8260B. Methods SW-846 Method 8000B; *Federal Register* Method 624; and CLP Method for Volatiles have also been used in the development of this SOP. The analyses by these various methods are clearly defined in the respective regulatory manuals. A good understanding of these different methods is essential to the performance of each method. Each parameter that is analyzed and reported under the scope of this SOP is listed in **Table 1** of this SOP. This table also lists the associated Reporting Limit (also defined as the LOD) and the lowest Calibration level for each analyte. When applicable, surrogate and Internal Standard Analytes are listed and indicated as such within this table.

5. Summary of the Test Method

5.1 After sample preparation, the sample is introduced into the GC/MS generally using purge and trap but sometimes using direct injection (see SW-846 Methods 5030B, 5035 and 3585 for preparation). In purge and trap, the analytes are stripped from the sample using helium and trapped on an adsorbent tube. The tube is heated while being backflushed with helium to carry the analytes to the GC/MS system. The analytes are separated in the gas chromatograph by a combination of the temperature program and the capillary column. The analytes are then detected by the mass spectrometer. Analytes are identified by comparing the mass spectra of known standards with the mass spectra of the sample. Analytes are quantitated relative to known standards using the internal standard method.

6. Definitions

6.1 Laboratory Quality System SOP QS08 "Technical / Operational Definitions, Minimum Essential Quality Control Elements, and Laboratory Calibration Procedures" provides information on the commonly used definitions.

6.2 Additional definitions specific to this SOP are listed below:

amu	atomic mass unit
BFB	Bromofluorobenzene

°C	degrees Centigrade
CLP	Contract Laboratory Program
DOD	Department of Defense
EICP	extracted ion current profile
G	gram or grams
GC/MS	Gas Chromatograph/Mass Spectrometer
I.D.	inner diameter
ISTD	internal standard
µm	micometer
µL	microliter
mL	milliliter
mm	millimeter
ng	nanogram
P&T	purge and trap
SURR	surrogate
SPCC	System Performance Check Compound
TCLP	Toxicity Characteristic Leaching Procedure
USACE	United States Army Corps Of Engineers
VOA	volatile organic analysis

7. Interferences

7.1 Section 3.0 of SW-846 Method 8260B details interferences and potential problems which may be encountered when dealing with volatile analyses.

8. Safety

8.1 Laboratory SOP QS13 "Safety Program & Chemical Hygiene Plan" discusses the safety program that is to be followed labwide.

9. Equipment & Supplies

9.1 GC : HP 5890 or 6890, temperature programmable, suitable for split or splitless injection.

9.2 Column: DB-VRX 60 meter x 0.25 mm I.D. 1.4 µm film thickness or 20 meter x 0.18 mm ID 1.0 µm film thickness silicon coated fused silica capillary column or equivalent.

9.3 M.S. : HP 5971, 5972 or 5973 capable of scanning 35 to 500 amu every one second or less, using 70 volts electron energy in electron impact ionization mode. The MS is capable of producing a mass spectrum for p-Bromofluorobenzene, BFB, which meets all tuning criteria for EPA methods [when 1 µL (50 ng) of the GC/MS tuning standard is introduced to the GC.]

9.4 Purge and Trap Unit

9.4.1 Concentrators: Tekmar LSC 2000 or Tekmar/Dohrmann 3000/3100 Sample Concentrator equipped with Supelco trap number 2-1066-U or 2-4920-U VOCARB 3000 providing good delivery for all target compounds.

9.4.2 Autosamplers: Varian Archon 51 position programmable autosampler with 5ml to 25ml water and heated soil capability.

9.5 Acquisition Software: HP chemstation system interfaced to the GC/MS. The system acquires and stores data throughout the chromatographic programs.

9.6 Data Processing Software: TargetDB on Windows NT data system interfaced to the HP Chemstation. The system accepts and stores acquired data. It plots by extracted ion current profile (EICP). The system is also capable of integrating the abundances of any EICP between specified time or scan-number limits. NBS75K mass spectral library is installed.

9.7 Microsyringes – 1.0, 5.0,10, 25, 100, 250, 500 and 1000 µL.

9.8 Syringes – 5, 25 and 50 mL, gas-tight with Luer end.

9.9 Balance - analytical, 0.0001 g; top-loading, 0.01 g.

9.10 Disposable pasteur pipets.

9.11 Volumetric flasks, Class A - 2 mL, 5 mL, 10 mL, 50 mL, 100 mL and 250 mL with ground-glass stoppers.

9.12 Spatula - stainless steel.

9.13 Glass scintillation vials - 20mL with screw caps.

9.14 Nitrile Gloves

9.15 pH paper (measures pH from 0-14).

10. Reagents and Standards

10.1 The laboratory's LIMS system allows for complete documentation and for the traceability of reagents and standards used within the laboratory. The following information relates to the specific reagents and standards used for the performance of the method:

10.2 Organic-free reagent water - obtained from a modulab system.

10.3 Methanol - Purge and trap grade (EM-Omnisolv EM-0482-6 or equivalent)

10.4 Methanol - suitable for use in gas chromatography (B&J Omnisolv MX0484-1, or equivalent)

10.5 Sodium bisulfate, $NaHSO_4$ – ACS reagent grade, or equivalent. Available from Aldrich (Part No. 30,782-3).

10.6 Stock standards are purchased in mixtures from reputable vendors. The date they are received is noted on the label. The date they are opened is noted on the label and recorded in the LIMS system along with their lot number and vendor and given a sequential number. Each standard label is completed with the standard number, name, preparation date, expiration date, solvent and analyst initials. Stock standards, when opened, have an expiration date of 6 months, **except for gas standards for South Carolina samples which have a one week expiration date**. All stocks and standards are stored in the freezer at a temperature of -15°C $\pm$ 5°C or less from the date they are received/prepared. The freezer

temperature is monitored daily with an annually calibrated thermometer and recorded with calibration correction in the VOA refrigerator/freezer logbook. Makeup of common standards is detailed below. See standard ID in LIMS system for makeup of other standards.

10.6.1 The Bromofluorobenzene (BFB) tuning standard is prepared as follows: Using a 50µL syringe, 40µL of standard (BFB @ 2500ng/µL) is injected into a 2mL volumetric flask containing approximately 1.0mL P&T methanol (Vendor,Lot) and diluted to volume with same making a 50ng/µL standard. After capping and inverting 3 times, the solution is transferred to a labeled 2ml, teflon-lined, screw-capped vial and stored in the freezer at -15°C ± 5°C or less for up to 6 months **(1 week for South Carolina samples)**. A direct injection of 1µL (or equivalent purge) is used to tune the instrument.

10.6.2 The internal and surrogate standards are prepared as follows: Using the indicated syringe, the indicated amount of standard is injected into a 50 mL volumetric flask containing P&T methanol (Vendor,Lot) and diluted to volume with same making a 150ng/µL standard. After capping and inverting 3 times, the solution is transferred to the Archon standard vial and stored under helium for 1 month or less. Each 8260/624 sample is automatically injected with 1µL of this standard. The internal standard/surrogate solution will be replaced if the –50%-200% criteria fails in the CCV when calculated against the previous CCV.

Standard	Conc. (ng/µL)	Syringe (µL)	Amount (µL)
8260 ISTD Mix	2500	1000	3000
Surr. Mix	2500	1000	3000

10.6.3 Calibration standards are prepared from the vendor stock standards at appropriate concentrations as follows. Occasionally unusual compounds are added to the mix so it is best to check the VOA standards log book for exact standard makeup. Note: for laboratory control spikes (LCS), alternate sources or lot numbers from the main calibration standard are used to make the LCS standard. See the appendix for analytes in the main mixes.

10.6.3.1 Primary Standard: Using the indicated syringe, the indicated amount of standard is injected into a 2mL volumetric flask containing approximately 1.0mL P&T methanol (Vendor,Lot) and diluted to volume with same to make a 100-500ng/µL standard. After capping and inverting 3 times, the solution is transferred into 2ml amber vial w/mini-inert valve and stored in the freezer at -15°C ± 5°C for 1 week. A 50µg/L (5mL purge) standard is made using 25µL of this standard to 50mLof reagent water.

Stock Standard(CCV)	Conc (ng/µL)	Syringe(µL)	Amount(µL)	Final Conc (ng/µL)
2-CEVE **(Cat#30265)**	20000	25	20	200
Vinyl Acetate **(#3766)**	5000	100	80	200
Ketones **(cat#30006)**	5000	100	80	200
Liquid mix **(C-349H-07)**	2000	100	100	100
Custom mix **(CCS-1037)**	5000	50	40	100
Gases **(cat#30042)**	2000	100	100	100
Acrolein/Acrylonitrile **(CC2098.10)**	20,000	50	50	500

Additional compounds may be added such as Appendix IX. Refer to standard ID in LIMS system.

10.6.4 ICV/LCS/Matrix Spike Mix: A second source standard is used to check the validity of the gas and primary calibration standards used in analyzing the calibration curve. Using the indicated syringe, the indicated amount of standard is injected into a 2mL volumetric flask containing approximately 1.0mL P&T methanol (Vendor,Lot) and diluted to volume with same to make a 100-500ng/µL standard. After capping and inverting 3 times, the solution is transferred into 2ml amber vial w/mini-inert valve and stored in the freezer at -15°C ± 5°C for 1 week. A 50µg/L ICV/LCS/Matrix Spike is made using 25µL of this standard to 50mL of reagent water/Sample Matrix.

Stock Standard(ICV/LCS)	Conc (ng/µL)	Syringe(µL)	Amount(µL)	Final Conc (ng/µL)
2-CEVE	20,000	25	20	200
Vinyl Acetate	5000	100	80	200
Ketones	5000	100	80	200
Liquid mix	2000	100	100	100
Custom Mix	5000	50	40	100
Gases	2000	100	100	100
Acrolein/Acrylonitrile	50,000	50	50	500

11. Sample Collection, Preservation, Shipment, and Storage

11.1 Quality Systems SOP QS10 related to Sample Receipt, Handling, & Processing provides details for collection, preservation, shipment, and storage. All water samples are stored in the BlueIce refrigerator in the VOA lab at a temperature of 4°C. All unpreserved soil samples in TerraCore or encores are stored in the freezer in the VOA lab. All soil samples in bulk jars or chemically preserved TerraCore are stored in the soil walk-in refrigerator at a temperature of 4°C. Non-preserved water volatile samples have a holding time of 7 days from date of sampling. Preserved water samples and soil volatile samples have a holding time of 14 days from date of sampling (unless otherwise specified for the project).

12. Quality Control

12.1 Quality Systems SOP QS08 “Technical / Operational Definitions, Minimum Essential Quality Control Elements, and Laboratory Calibration Procedures” outlines details related to laboratory wide protocols on quality control.

12.1 Internal Standards - All samples and QC are spiked with internals. See **Table 2** for criteria and corrective action.

12.2 Surrogates - All samples and QC are spiked with surrogates. The surrogate recoveries from method blanks and LCS are used to generate control limits. See section 14.5.2 of this SOP for criteria and corrective action. **When analyzing samples for DOD QSM Version 4.1, DOD limits will be used.**

12.3 LCS Sample - An LCS is analyzed every 12 hour tune. To prepare the LCS, a blank is spiked with standards prepared from an alternate vendor or lot number from the calibration standards. Note: the concentration of the LCS will be 20 µg/L when analyzing 624 samples (QC Check Sample). The recoveries are used to generate control limits. The limits are in-house generated matrix spike limits or client specified limits for matrix spike analytes and 70-130% (or client specified limits) recovery for waters or soils for all other analytes if limits have not been generated. Limits for 624 LCSs are taken from table 5 of method 624. If the LCS compound has a recovery above the upper limit, but the same compound is not detected in any of the batch samples, no corrective action is required. For all other situations, the LCS should be reanalyzed for the failed analytes only. If the second analysis fails, all associated samples should be reanalyzed for the failed analytes only. **When analyzing samples for DOD QSM Version 4.1, DOD limits will be used. South Carolina limits are 70-130% except for poor purgers which are 60-140%.**

12.4 Method Blanks - The concentration for method target analytes must be < ½ the Reporting Limit (also defined as the Limit of Quantitation). The first step of corrective action is to assess the affect on the samples. If an analyte is found only in the method blank, but not in any batch samples, no further corrective action may be necessary. Steps should be taken to find/reduce/eliminate the source of this contamination in the method blank. If an analyte is found in the method blank and some, or all, of the other batch samples, then corrective action is required. The source of contamination must be investigated and appropriate action taken and documented to find/reduce/eliminate the source of this contamination. The method blank, and any samples containing the same contaminant, would likely be reanalyzed. For the common laboratory contaminants, meeting the above requirements is not practical. Random cases of contamination are difficult to control, however, daily contamination is not acceptable and corrective action is essential. If a contaminant is found in the method blank and the samples, the compound concentration must be flagged with a 'B' on the final report unless the concentration is greater than 10x that found in the method blank. A method blank is analyzed every 12 hour tune.

12.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Sample - 1 in 20 samples are spiked for an MS/MSD with the LCS standard. Criteria for the MS/MSD recoveries are the same as the LCS limits. Limits for the RPDs are 30% RPD for water and soil.. Samples that do not meet these criteria due to matrix must be flagged on the final report for QC problems. Generally, batch control is not based on MS/MSD results unless general method failure is determined to be the problem. In that case, the samples and associated QC would be reanalyzed for the

failed analytes only. MS data evaluation must include the consideration of the following factors. **When analyzing samples for DOD QSM Version 4.1, DOD limits will be used.**

12.5.1 Sample matrix - If the sample is a soil, grab sample or sequentially collected water sample it may affect the %R and RPD of the MS/MSD. A water sample which was taken from the same VOA vial for the original sample and the MS/MSD should have very good RPDs unless there has been a method problem. Corrective action must be taken in the form of reanalysis if a method problem is indicated.

12.5.2 Original sample concentration - If a spiked compound has a problem and the concentration of that compound in the original sample was four or more times the concentration of the spike, no further corrective action may be necessary other than the generation of a corrective action report to document the problem.

12.5.3 MS vs. MSD - If a spiked compound has a problem in both the MS and MSD, review the LCS and if acceptable no further action may be necessary since it is attributable to matrix effect.

12.5.4 Non-target Interference - The presence of significant non-target interference should be brought to the immediate attention of your supervisor who should discuss the problem with the client/project manager to determine the action to be taken.

13. Calibration and Standardization

13.1 Quality Systems **SOP QS08 "**Technical / Operational Definitions, Minimum Essential Quality Control Elements, and Laboratory Calibration Procedures" related to Calibration Procedures provides laboratory wide protocols for calibration and standardization.

13.2 Chromatographic conditions – Refer to corresponding instrument maintenance log for current gas chromatograph, mass spectrometer, and concentrator conditions.

13.3 System Bakeout - Prior to analysis an instrument blank is analyzed.

NOTE: Further cleaning may be accomplished by backflushing the lines with methanol and then analyzing blanks overnight.

13.4 Tuning - Prior to any calibration or analysis, BFB tuning criteria must be met for a 1.0µL injection of the tuning standard [see below]. Tune must be met every 12 hours sample analysis is to be performed **(every 24 hours for *Federal Register* Method 624 except for South Carolina which only allows 12 hours).** The mass spectrum of BFB is acquired as follows: by using the BFB method in Target (which uses three scans with backround subtraction) to process the BFB data file. If the BFB tune does not pass criteria corrective action should be taken

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

13.5 **Calibration:** Calibration standards are made up in water using the appropriate amount of the methanol standard. **Calibration for soils for South Carolina requires that 5mL of sodium bisulfate solution is added to each calibration standard made if the samples will be preserved with sodium bisulfate.** All calibration standard manual integrations must be approved by for acceptability.

13.5.1 Initial Calibration - An initial calibration curve at no less than five (six if using a quadratic curve fit) concentration levels must be analyzed and shown to meet the initial calibration criteria before any sample analysis may be performed. **For Arizona samples the surrogates must also be calibrated at a minimum of five concentrations.** Method 624 requires that the %RSD be less than 35% to use the average response factor for quantitation, the curve is to be used otherwise and should have a correlation coefficient (***r***) of $\geq$0.995. Method 8260B requires that the %RSD be less than 15% to use the average response factor for quantitation, the curve is to be used otherwise as long as ***r*** is $\geq$0.995 linear or $\geq$ 0.99 quadratic. In addition, there are calibration check compounds (CCCs) listed below which must have a %RSD less than 30% and five system performance check compounds (SPCCs) which must meet the average response factor criteria listed below. The lowest standard must be less than or equal to the reported quantitation limit and the highest standard must not exceed the linear range of the detector. Any manual integrations are documented by inclusion of the integrated signals (**before and after manual integration**) initialed, dated, and reason with the quantitation report and chromatograms. All calibration manual integrations must be approved by management. Any response factors less than 0.050 must be supported by the mass spectrum of the lowest standard. **No quadratic curves for South Carolina.**

CCCs:	1,1-Dichloroethene	Toluene
	Chloroform	Ethylbenzene
	1,2-Dichloropropane	Vinyl chloride

SPCCs:	Chloromethane	0.10
	1,1-Dichloroethane	0.10
	Bromoform	0.10
	Chlorobenzene	0.30

1,1,2,2-Tetrachloroethane 0.30

13.5.2 Initial Calibration Verification - A second source standard at the 50 µg/L (5mL purge) level is used to check the validity of the curve. The standard recovery for all analytes must be between 75 and 125%. **When analyzing samples for DOD QSM Version 4.1, DOD limits (80-120%) will be used.** If the second source recovery is above 125%, the main standard has probably deteriorated for that compound. That standard must be replaced and a new curve generated. If the second source recovery is below 75%, the second source standard has probably deteriorated for that compound and must be replaced. Any manual integrations are documented by inclusion of the integrated signals (**before and after manual integration**) initialed, dated, and reason with the quantitation report and chromatograms. All calibration manual integrations must be approved by management

13.5.3 Continuing Calibration Verification (every 12 hours) - A midpoint calibration standard (generally 50 µg/L - 5mL purge) must be analyzed and calculated against the initial calibration curve, then shown to meet the calibration check criteria before any sample analysis may be performed. Acceptance criteria for method 8260B consists of the same SPCC criteria as above and ≤20% drift or difference (calculations given in section 7.10) for the CCCs as listed above. The internal standards must also be evaluated as listed below. Any manual integrations are documented by inclusion of the integrated signals (**before and after manual integration**) initialed, dated, and reason with the quantitation report and chromatograms. All calibration manual integrations must be approved by management. Samples are then quantitated against the initial calibration curve. Note: If any compound in the continuing calibration not subject to the criteria above exceeds 30% D, it must be evaluated following the guidelines outlined in SOP QS05. If deemed acceptable, the analyst may continue analysis. **When analyzing samples for DOD QSM Version 4.1, DOD acceptance criteria of ≤ 20% drift or difference for all analytes will be used.**
NOTE: Acceptance criteria for method 624 consists of meeting recovery limits found in table 5 of the method for a QC check sample. This QC check sample is made from a separate source or lot number than the calibration standard at a concentration of 20 µg/L.

Internal standard checks

13.5.3.1 Retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

13.5.3.2 Response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to +

100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

14. **Procedure**

14.1 LCS - An LCS is analyzed every 12 hour tune.Using standards prepared from an alternate vendor or lot number, blank water is spiked at the 50 µg/L (5mL/soil) or 10 µg/L (25mL) level. See section 12 above for criteria and corrective action. **Note: the concentration of the LCS will be 20 µg/L when analyzing 624 samples (QC Check Sample). When analyzing samples for DOD QSM Version 4.1, DOD limits will be used.**

14.2 Method Blank - Prior to sample analysis, the system must be shown to be free of contamination through analysis of a method blank. See **Table 2** for criteria and corrective action.

14.3 Sample Analysis - Prior to analysis, the samples are prepared for chromatography using the appropriate sample preparation method (5mL water, 25mL water, low soil, high soil, etc.) See SOP 225 for preparation of a 5035 soil sample. For a 5mL/25mL water sample, use the following procedure:

14.3.1 Load the vial into the Archon autosampler in the expected position.

14.3.2 Program the Archon for the loaded vial range and necessary dilutions, making sure the programmed method is set for the same volume as the purge vessel on the front of the LSC 2000 or 3000/3100 and that the Chemstation sequence matches the Archon sequence. Note: TCLP samples are analyzed at a 10x dilution. One TCLP sample is spiked per batch at receipt of leachates.

14.3.3 After analysis of the sample has been completed, check the pH of the sample using pH paper and verify it to be less than a pH of 2 (recorded on the sequence log). If it is not, record the pH on the sequence log and generate a corrective action report. The sample report will have to be qualified for preservation if the analysis is being performed more than 7 days after sampling. [Note: TCLP samples do not require a pH check.]

14.4 **Instrument sequence**

An example of a typical instrument sequence log follows:

1-BFB Tune (12:00 am)
2-CCV
3-LCS
4-Method Blank
5-Sample
6-Sample
7-Sample
8-Sample
9-Sample
10-Sample
11-Sample
12-Sample
13-Sample
14-Sample
15-Sample
16-Sample
17-Sample MS
18-Sample MSD
19-BFB (12:00pm - 12 hours since last BFB/CCV)
20-CCV
21-LCS
22-Method Blank
23-Sample
24-Sample

14.5 Data Reduction/Evaluation - Each sample analysis sequence is documented using the computer run log generated on the chemstation. This run log is signed, dated and paginated then placed in a 3 ring binder for that instrument. After the sample has been analyzed, the data is processed through the TargetDB on Windows NT data system. Quantitative measurements are performed using the calculations found in section 15.2 of this SOP. The following must be checked to determine if the sample will need any reanalysis or dilution. Formal data evaluation is detailed in SOP QS05. **See SOP QS07 for guidance on manual integrations.**

14.5.1 Internal Standards - Areas should be within 50 to 200 percent of the area of the continuing calibration. Retention time should be within 30 seconds of the retention time of the continuing calibration. Note: criteria applies to the continuing calibration, not samples, but is used as an indication of the sample analysis validity. If not, the sample and historical data should be evaluated to determine the cause of the problem. Reanalysis is expected if it appears to be from a leak. If matrix effect is confirmed by reanalysis or historical data, complete a corrective action report and flag the affected compounds on the final report for matrix effect.

14.5.2 Surrogates – Control limits are determined by charting LCSs and method blanks. All of the surrogates must be within these limits in order for the analysis to be in control. If not, the reason for the malfunction must be determined and reanalysis may be necessary. If historical data indicates matrix, the sample would be flagged appropriately. When the surrogates exceed either the control limits, a corrective action report must be completed.
Federal Register **Method 624 contains no criteria for surrogate recovery. When analyzing samples for DOD QSM Version 4.1, DOD limits will be used.**

Surrogate	**WATER**	**SOIL/SEDIMENT**
Dibromofluoromethane	85-120	80-125
1,2-Dichloroethane-d4	85-135	75-140
Toluene-d8	85-115	80-120
Bromofluorobenzene	80-120	80-125

14.5.3 Analyte concentration must be within the range of the calibration curve after rounding to 2 significant figures. If an analyte exceeds the curve, a dilution must be performed, the next sample must be checked for carryover and the sparge position must be checked for contamination through the analysis of a system blank. Any dilution should keep the concentration of the analyte in question within the mid-range of the curve.

14.5.4 Qualitative identification is made as indicated below.

14.5.4.1 The mass spectra are compared to reference spectra in a user-created data base especially compiled to contain relatively uncontaminated mass spectra of each target compound. Note: Such a file cannot be obtained from the daily calibrations during each 12 hour analytical period due to overlapping peaks in the mixes.

14.5.4.2 The GC/MS analyst uses intelligence guided by experience to make the identifications.In uncontaminated spectra where ions are missing due to low concentration, if the major ions are present in the correct ratios at the correct retention time, the identification will be considered positive. In contaminated spectra, special emphasis will be placed upon higher mass ions, and the major ions will usually need to be present as major components of the spectrum (either unsubtracted or subtracted) for the identification to be positive. All assessments of relative intensities of ions will be made by visual estimates from the spectra.

15. Data Analysis and Calculations

15.1 Quality Systems SOP QS09 "General and Commonly used Laboratory Calculations" provides details on general calculations used throughout the laboratory.

15.2 Calculations:

15.2.1 The RF is calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.

A_{is} = Peak area (or height) of the internal standard.

C_s = Concentration of the analyte or surrogate.

C_{is} = Concentration of the internal standard.

15.2.2 Calibration verification involves the calculation of the percent drift (linear) or the percent difference (average) of the instrument response between the initial calibration and each subsequent analysis of the verification standard. Use the equations below to calculate % Drift or % Difference, depending on the calibration procedure used.

$$\% \text{ Drift} = \frac{(\text{Calculated concentration} - \text{Theoretical concentration}) * 100}{\text{Theoretical Concentration}}$$

where the calculated concentration is determined from the initial calibration and the theoretical concentration is the concentration at which the standard was prepared.

$$\% \text{ Difference} = \frac{(\text{CCV RF} - \text{Average RF}) * 100}{\text{Average RF}}$$

where CCV RF is the response factor from the analysis of the verification standard and Average RF is the average response factor from the initial calibration. The % difference or % drift calculated for the calibration verification standard must be within ±20% for each CCC analyte, or for all target analytes if the CCCs are not target analytes, before any sample analyses may take place.

15.2.3 Concentration in water samples is calculated as follows: [Note: Using the units specified here for these terms will result in a concentration in units of ng/mL, which is equivalent to ug/L.]

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(C_{is})(D)(V_i)}{(A_{is})(\overline{RF})(V_s)(1000)}$$

where:

A_s = Area (or height) of the peak for the analyte in the sample.

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

C_{is} = Concentration of the internal standard in the volume purged in ug/L.

D = Dilution factor, if the sample was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.

V_i = For purge-and-trap analysis, V_i is not applicable and is set at 1.

$\overline{RF}$ = Mean response factor from the initial calibration.

V_s = Volume of the aqueous sample purged (mL). If units of liters are used for this term, multiply the results by 1000.

15.2.4 Concentration in non-aqueous samples is calculated as follows: [Note: Using the units specified here for these terms will result in a concentration in units of ng/g, which is equivalent to ug/kg.]

$$\text{Concentration } (\mu\text{g/kg}) = \frac{(A_s)(C_{is})(D)(V_i)}{(A_{is})(\overline{RF})(W_s)(1000)}$$

where: A_s, A_{is}, C_{is}, D, and $\overline{RF}$ are the same as for aqueous samples.

W_s = Weight of sample extracted (g). Either a dry weight or wet weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term, multiply the results by 1000.

16. Method Performance

16.1 Demonstration of Capability (DOC): Each analyst must perform a DOC prior to reporting data. The analyst must prepare (for prep technicians) and analyze (analysts reviewing and reporting data) 4-LCS samples. The data is calculated for accuracy and precision requirements. The DOC form is completed by each analyst and then provided to the supervisor for further processing and approval. See **Table 2** for acceptance criteria. **When analyzing DOCs for DOD QSM Version 4.1, DOD limits will be used.**

17. Pollution Prevention

17.1 Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

18. **Data Assessment and Acceptance Criteria for Quality Control Measures**

18.1 Quality Control SOP QS05, "Data Deviations / Interpretations / Exceptions: Laboratory Non-Conformance / Corrective Action Procedures, Decision Making Guidelines for Evaluating Laboratory Analytical Sample and Quality Control Results", provides details on data assessment and acceptance criteria for Quality Control Measures. **Table 2** of this SOP provides information on QC samples, frequency, and the associated criteria specific to the performance of this method.

19. **Contingencies for Handling out-of-control or unacceptable data**

19.1 Quality Control SOP QS05, "Data Deviations / Interpretations / Exceptions: Laboratory Non-Conformance / Corrective Action Procedures, Decision Making Guidelines for Evaluating Laboratory Analytical Sample and Quality Control Results", provides details on handling out of control data. Table 2 within this SOP also lists corrective actions associated with the failure of the various QC samples employed for the performance of this method.

20. **Waste Management.**

20.1 Laboratory SOP QS14 on Waste Handling discusses general guidelines for the appropriate handling of wastes and the laboratory program on waste management.

21. **References**

21.1 40 CFR, Part 136; Appendix A
21.2 Test Methods for Evaluating Solid Waste, SW-846, Third Edition and updates
21.3 National Environmental Laboratory Accreditation Conference; CH. 5, 2001
21.4 USACE, EM 200-1-3; Appendix 1; Shell, 2/2001
21.5 DOD Quality Systems Manual for Environmental Laboratories version 3, 3/2005
21.6 DOD Quality Systems Manual for Environmental Laboratories version 4.1, 4/2009

22. Tables, Diagrams, Flowcharts and Validation Data

TABLE 1 – Analytes, Reporting Limit (RL), & Low Calibration Standard				
Parameter	**RL Water ug/L**	**LowCal Water ug/L**	**RL Soil ug/KG**	**LowCal Soil ug/KG**
1,1,1 Trichloroethane	1.0	1.0	5.0	2.0
1,1,1,2-Tetrachlorethane	1.0	1.0	5.0	2.0
1,1,2,2-Tetrachloroethane	1.0	1.0	5.0	2.0
1,1,2-Trichloroethane	1.0	1.0	5.0	2.0
1,1-Dichloroethane	1.0	1.0	5.0	2.0
1,1-Dichloroethene	1.0	1.0	5.0	2.0
1,2,4 Trichlorobenzene	1.0	1.0	5.0	2.0
1,2-Dibromo-3-chloropropane	1.0	1.0	5.0	2.0
1,2-Dibromoethane	1.0	1.0	5.0	2.0
1,2-Dichlorobenzene	1.0	1.0	5.0	2.0
1,2-Dichloroethane	1.0	1.0	5.0	2.0
1,2-Dichloropropane	1.0	1.0	5.0	2.0
1,3-Dichlorobenzene	1.0	1.0	5.0	2.0
1,4-Dichlorobenzene	1.0	1.0	5.0	2.0
2-Butanone	10	2.0	50	4.0
2-Hexanone	5.0	2.0	10	4.0
4-Methyl-2-pentanone	5.0	2.0	10	4.0
Acetone	10	2.0	50	4.0
Benzene	1.0	1.0	5.0	2.0
Bromochloromethane	1.0	1.0	5.0	2.0
Bromodichloromethane	1.0	1.0	5.0	2.0
Bromoform	1.0	1.0	5.0	2.0
Bromomethane	2.0	1.0	10	2.0
Carbon disulfide	1.0	1.0	5.0	2.0
Carbon tetrachloride	1.0	1.0	5.0	2.0
Chlorobenzene	1.0	1.0	5.0	2.0
Chloroethane	2.0	1.0	10	2.0
Chloroform	1.0	1.0	5.0	2.0
Chloromethane	2.0	1.0	10	2.0
Cis-1,2-Dichloroethene	1.0	1.0	5.0	2.0
Cis-1,3-Dichloropropene	1.0	1.0	5.0	2.0
Dibromochloromethane	1.0	1.0	5.0	2.0
Dibromomethane	1.0	1.0	5.0	2.0
Dichlorodifluoromethane	2.0	1.0	10	2.0
Ethylbenzene	1.0	1.0	5.0	2.0
Methylene chloride	2.0	1.0	10	2.0
M,p-Xylene	1.0	2.0	5.0	4.0
o-Xylene	1.0	1.0	5.0	2.0
Styrene	1.0	1.0	5.0	2.0

TABLE 1 – Analytes, Reporting Limit (RL), & Low Calibration Standard				
Parameter	**RL Water ug/L**	**LowCal Water ug/L**	**RL Soil ug/KG**	**LowCal Soil ug/KG**
Tetrachloroethene	1.0	1.0	5.0	2.0
Toluene	1.0	1.0	5.0	2.0
Trans-1-2 Dichlorethene	1.0	1.0	5.0	2.0
Trans-1-3-Dichloropropene	1.0	1.0	5.0	2.0
Trichloroethene	1.0	1.0	5.0	2.0
Trichloroflurorometh ane	2.0	1.0	10	4.0
Vinyl chloride	2.0	1.0	10	4.0
MTBE	1.0	1.0	5.0	2.0
Naphthalene	1.0	1.0	5.0	2.0

Table 2 - Method Quality Control Requirements Summary			
QC Check	**Minimum Frequency / Requirements**	**Acceptance Criteria**	**Corrective Action for Failures / Data Useability**
Tune	At the beginning of sequence and every 12 hours	See section 13.4 for criteria.	• Follow guidelines from SOP QS05
Calibration Curve	• Prior to analyzing any samples • A minimum of 5-points for linear fits • A minimum of 6-points for quadratic fits • Low standard at or below the RL/LOQ level	• For Linear or Quadratic calibration fits a RF of 0.995 • Average RSD for CCCs $\leq$ 30%, to use avg. RF $\leq$ 15%, Min. RF for SPCCs per method • Manual integrations on curve standards must have supervisory approval • Must follow curve processing requirements from SOP QS08	• Re-evaluate curve mix and makeup • Re-run curve • Check instrument for maintenance needs • Re-prep the curve standards Samples cannot be analyzed until there is a passing calibration
ICV	Alternate source standard to be analyzed after every calibration curve	75-125% for 8260B, 80-120% for DOD QSM 4.1	• Re-analyze an ICV from a different source • Re-prep and re-analyze the ICV • Re-calibrate and verify standard preps and sources
CCV	• At the beginning of every sequence • Every 12 hours	See section 13.5.3 for criteria.	• Follow guidelines from SOP QS05
MB	One per prep batch	• Must be < ½ the RL/LOQ	• Re-analysis to confirm the positive value • Ascertain if there are any samples within the batch that meet the MB criteria and provide the information for the decision makers • If results are between the LOD or RL/LOQ, then assess the data and notify the PM for further action • Re-prep of samples associated with the MB • NCR will be required for data reported • Final Report data flagging will be required
LCS	One per prep batch	Most stringent criteria listed within the LIMS.	• Follow guidelines from SOP QS05
LCSD	One per prep batch, when MS/MSD not included.	Criteria listed within LIMS or specified by client.	• Follow guidelines from SOP QS05

Table 2 - Method Quality Control Requirements Summary			
QC Check	**Minimum Frequency / Requirements**	**Acceptance Criteria**	**Corrective Action for Failures / Data Useability**
MS	One per prep batch, if sample volume available.	Criteria listed within LIMS or specified by client.	• Follow guidelines from SOP QS05
MSD	One per prep batch, if sample volume available.	Criteria listed within LIMS or specified by client.	• Follow guidelines from SOP QS05
Internal Standard	• A mix is used per sample post - prep	• 50 – 150 % of the IS from CCV	• If holding time is expired, fill out a NCR and follow directions from PM • Evaluate sample matrix and other applicable results to determine if re-analysis is required at a dilution • Re-injection or analysis • Re-prep followed by re-analysis • Follow guidelines from SOP QS05
Surrogates	• A mix is used per sample prior to sample prep	Criteria listed within LIMS or specified by client.	• If holding time is expired, fill out a NCR and follow directions from PM • Evaluate sample matrix and other applicable results to determine if re-analysis is required at a dilution • Re-injection or analysis • Re-prep followed by re-analysis • Follow guidelines from SOP QS05
DOC Study	• Initially per analyst prior to reporting data • Annually • Follow specific guidelines from section 16 for the preparation and analysis of DOC samples	• Must meet the criteria of the LCS for average accuracy	• Re-prep and /or re-analysis
MDL Study	Once per year	○ Calculated value must be greater than 10% of the Spike Level ○ Calculated value must be less than the Spike level	• Re-prep and /or re-analysis • Follow guidelines from SOP QS05
LOD Verification	Every quarter	○ Parameter must be detected ○ Check for Ion Abundance on MS methods ○ the response must be 3-times the noise level	• Re-prep and /or re-analysis • Follow guidelines from SOP QS05

Table 2 - Method Quality Control Requirements Summary			
QC Check	**Minimum Frequency / Requirements**	**Acceptance Criteria**	**Corrective Action for Failures / Data Useability**
LOQ Verification	Every quarter	○ Bias Requirement: Inorganics 50-150% Organics 10-150% ○ The LOQ value must be greater than the LOD value	• Re-prep and /or re-analysis • Follow guidelines from SOP QS05

Table 3, Technical Completeness / Accuracy Checklist

1. Were all the QC check elements analyzed – refer to Table 2 of the SOP
2. Were the QC criteria met
3. In cases of failures, was there an NCR written
4. Were all manual integrations signed
5. Were dilution factors applied correctly
6. Was there supervisory approval for manual integrations on standards and QC samples
7. Was the data uploaded into LIMS via direct upload – if yes, then was a cross check subset of the uploaded values performed
8. If the data was entered into LIMS manually, was a check of all entered values performed
9. Was the red marked data in LIMS checked for accuracy and the corresponding hard copy data documented appropriately
10. Were proper data qualifiers applied to the data in LIMS
11. Was the hard copy package checked for completeness to include all data for the sequence such that the data reviewer could reconstruct sample analyses and validate / approve the data

Table 4, Data Reviewers Checklist (Prior to approving data)

1. Does the hard copy raw data (or electronic raw data) package look complete and include all data points
2. Were QA objectives met and for failures were the appropriate actions taken
3. For direct uploads to LIMS, did a subset cross check match the raw data
4. Did all the manual entries into LIMS match the raw data
5. Were there appropriate signatures and documentation on the raw data
6. Were appropriate LIMS flags used
7. Were manual integrations signed
8. Were manual integrations for calibration and QC samples approved by supervisor
9. Were manual calculations verified

TOTAL ORGANIC CARBON (TOC)

SM5310C, SW846 METHOD 9060/9060A AND LLOYD KAHN METHOD

SOP NUMBER: SOP-221

REVISION NUMBER: 8

APPROVED BY:

Betty DeVille
SECTION MANAGER

Randy D. Ward
TECHNICAL DIRECTOR

EFFECTIVE DATE: 04/28/09

DATE OF LAST REVIEW: 04/28/09

TOTAL ORGANIC CARBON (TOC)
BY SM5310C, SW846 METHOD 9060/9060A AND Lloyd KAHN
METHOD "*DETERMINATION OF TOC IN SEDIMENT*"

I. SCOPE AND APPLICATION

This SOP describes the measurement of TOC by SM5310C, SW-846 Method 9060/9060A and Lloyd Kahn Method for determination in soil /sediment matrix.

SM5310C is used to determine the concentration of organic carbon in source and drinking water, SW-846 Method 9060/9060A is used to determine concentrations of carbon in saline waters, domestic and industrial wastes and SW846 Method 9060 is modified for soil determination and the L1oyd Kahn Method is used for determination of TOC in soil/sediment and solid matrices.SW846 Method 9060/9060A and the Lloyd Kahn Method require quadruplicate analysis of samples, where as SM5310C requires a minimum of two analyses. These methods should be read over carefully by the analyst and any restrictions should be noted.

II. SUMMARY OF METHOD

The organic carbon is measured using an Shimadzu Total Organic Carbon Analyzer (aqueous samples) and an OI Analytical Solids TOC Analyzer model 1010 (soil/sediment samples). The Shimadzu instrument converts the organic carbon in a sample using wet chemical oxidation. The CO_2 formed is then measured by an infrared detector (replaces ultraviolet detector in SM 5310C). With the model 1010 Solids TOC analyzer, TOC is determined by acidifying a sample and heating it to 250°C to remove the TIC. The sample is then heated to 900°C to combust the remaining TOC. The resulting carbon dioxide from the TOC is detected by a non-disperse infrared (NDIR) detector that has been calibrated to directly display the mass of carbon dioxide detected. This mass is proportional to the mass of TOC in the sample.

The limit of detection for the water method is 0.50 mg carbon/L and the Limit of quantitation is 1.0 mg carbon/L. The limits of detection and quantitation with the soil method depends on the how many grams of sample is used for the analysis. For a 250 mg sample the limit of detection is 460 mg/kg and the limit of quantitation is 1600 mg/kg.

III. SAMPLING HANDLING AND PRESERVATION

3.1 Sampling and storage in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples. NOTE 1: A brief study performed in the EPA Laboratory

indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

3.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. The holding time is 28 days for waters and soils with the exception of the Lloyd Kahn method soils, which requires a 14 day holding time. Also, samples must be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

3.3 When water samples cannot be analyzed immediately, the sample is preserved by acidification to (pH </= 2) with HCl or H_2SO_4. Both water and soil samples are stored at 4°C.

IV. INTERFERENCES

4.1 WATER METHOD

4.1.1 Removal or carbonate and bicarbonate carbon by acidification and purging with purified gas results in the loss of volatile organic substances. The volatiles also can be lost during sample blending, particularly if the temperature is allowed to rise. Another important loss can occur if large carbon-containing particles fail to enter the needle used for injection. Filtration although necessary to eliminate particulate organic matter when only DOC is to be determined, can result in loss or gain of DOC, depending on the physical properties of the carbon-containing compounds and the adsorption of carbonaceous material on the filter, or its desorption from it. Check filters for their contribution to DOC by analyzing a filtered blank. Note that any contact with organic material may contaminate a sample. Avoid contaminated glassware, plastic containers, and rubber tubing. Analyze treatment, system, and reagent blanks.

4.1.2 This procedure is applicable only to homogenous samples which can be injected into the apparatus reproducibly by means of a pipette. The openings of the pipette limit the maximum size of particles which may be included in the sample.

4.2 SOIL METHOD

4.2.1 All materials must be routinely demonstrated to be interference –free under the analysis conditions by running blanks. Use high purity or purified reagents and gases to help minimize interference problems.

4.2.2 The infrared detector is sensitized to CO_2 and accomplishes virtually complete rejection of response from other gases that absorb energy in the infrared region.

V. DEFINITIONS

5.1 ANALYTICAL BATCH-The set of samples extracted /distilled/ or digested at the same time to a maximum of 20 samples.

5.2 CALIBRATION BLANK (CB)- A volume of reagent water in the same matrix as the calibration standards, but without the analyte.

5.3 CALIBRATION STANDARD (CAL)- A solution prepared from the primary dilution standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

5.4 FIELD BLANK (FMB)- An aliquot of reagent water or equivalent neutral reference material treated as a sample in all aspects, including exposure to a sample bottle holding time, preservatives, and all preanalysis treatments. The purpose is to determine if the field or sample transporting procedures and environments have contaminated the sample.

5.5 FIELD DUPLICATE (FD)- Two samples taken at the same time and place under identical circumstances which are treated identically throughout field and laboratory procedures. Analysis of field duplicates indicates the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

5.6 LABORATORY BLANK (LRB)- An aliquot of reagent water or equivalent neutral reference material treated as a sample in all aspects, except that it is not taken to the sampling site. The purpose is to determine if the analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

5.7 LABORATORY CONTROL SAMPLE (LCS)- A solution prepared in the laboratory by dissolving a known amount of one or more pure compounds in a known amount of reagent water. Its purpose is to assure that the results produced by the laboratory remain within the acceptable limits for precision and accuracy. (This should not be confused with a calibrating standard, it must be prepared from a source other than the same source as the calibration standards).

5.8 LABORATORY DUPLICATE (LD)- Two aliquots of the same environmental sample treated identically throughout a laboratory analytical procedure. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.

5.9 QUALITY CONTROL CHECK SAMPLE (QCS)- A sample containing analytes of interest at known concentrations (true value) of analytes. The QCS is obtained from a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory

performance using test materials that have been prepared independently from the normal preparation process.

5.10 METHOD DETECTION LIMIT (MDL)- The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero.

VI. REAGENTS/STANDARDS

Store all reagents and standards according to recommendations. All standards should be stored away from light and at 4°C (± 2°C).

6.1 The laboratory reagent blank water used for TOC analysis is obtained from the Modulab Analytical water purification system in the analytical laboratory. **Boiling the water is not necessary as the method states.**

6.2 Potassium hydrogen phthalate, primary stock solution, 1000 mg/L: Dissolve 0.2128g of potassium hydrogen phthalate (primary standard grade) in 100.0 mL water.

6.3. Potassium hydrogen phthalate, standard solutions : A 100 mg/L standard is prepared by transferring 10 mL of the stock solution to a 100 mL volumetric flask and diluting to the mark with water. This solution is prepared on a daily basis.

6.4. The carbonate-bicarbonate solutions are not needed for this instrument.

6.5 Calibration Standards

1. For the water method, calibration standard is Potassium Hydrogen Phthalate. Standards are made from dilutions of the stock 1000 mg/L standard as follows:

   1.0 mg/L = 0.10 mL of 1000 mg/L -> 100 mL
   2.5 mg/L = 0.25 mL of 1000 mg/L -> 100 mL
   5.0 mg/L = 0.50 mL of 1000 mg/L -> 100 mL
   10.0 mg/L = 1.0 mL of 1000 mg/L -> 100 mL
   25.0 mg/L = 5.0 mL of 1000 mg/L -> 200 mL
   50.0 mg/L = 10.0 mL of 1000 mg/L -> 200 mL
   100 mg/L = 10.0 mL of 1000 mg/L -> 100 mL

   A low level standard curve must be run for drinking water samples with the standards made as follows:

   0.25 mg/L = 0.025 mL of 1000 mg/L -> 100 mL

0.50 mg/L = 0.050 mL of 1000 mg/L -> 100 mL
1.0 mg/L = 0.10 mL of 1000 mg/L -> 100 mL
1.5 mg/L = 0.15 mL of 1000 mg/L -> 100 mL
2.5 mg/L = 0.25 mL of 1000 mg/L -> 100 mL
5.0 mg/L = 0.50 mL of 1000 mg/L -> 100 mL
10.0 mg/L = 1.0 mL of 1000 mg/L -> 100 mL

2. The soil method the calibration standard is prepared by using an OI commercially prepared 30% carbon sucrose solution.

6.6 Laboratory Control Sample:

1. For the water method, the Laboratory Control Sample is normally made from a performance evaluation solution of which the true value is known. This solution is given a unique identifier.

2. For the soil method, the Laboratory Control Sample is made from a 30% sucrose solution which is made by weighing up 7.125 grams of EM Reagent Grade Sucrose and diluting to 10 mL with deionized water volumetrically.

6.7. Persulfate oxidation solution: This solution is made by dissolving 60g of sodium persulfate in DI water, adding 15 ml of phosphoric acid and diluting to 500 ml.

6.8 Phosphoric acid solution: Dilute 100 mL of concentrated 85% phosphoric acid in 500 mL of water. This is used for water.

6.9 Phosphoric acid solution 5%: Dilute 59 mL of concentrated 85% phosphoric acid in 1000 mL of water. This is used for soil.

VII. INSTRUMENTATION

7.1 The instrument used for the Water TOC analysis is a Shimadzu Total Carbon Analyzer. An OIC 1010 soil/sediment carbon analyzer is used for soil samples.

7.2 There is a Shimadzu autosampler which will hold 68 samples.

7.3 The corresponding data for each sample is obtained from the Shimadzu software for the water samples. The soil/sediment data are printed out at the organic GC printer.

VIII. AQUEOUS SAMPLE PROCEDURE

8.1 Wearing labcoat, gloves and safety glasses, the standards and check solutions should be taken out of the refrigerator and allowed to warm to room temperature. Also, remove samples from sample storage signing them out appropriately on the internal chain of custody form. Fresh acid and oxidation solutions should be poured into the appropriate containers on the front of the instrument.

8.2 Follow the instructions for operation of the instrument in Chapter 4, section 4.3 of the Shimadzu Model TOC-VWS User Manual. **See Appendix I. for Basic TOC start-up notes for analysis.**

8.3 **Following is a list outlining the order in which the samples should be run.** Each sample VOA vial should be numbered and its identity entered into the TOC schedule. Note: All blanks should be acidified to pH 2 to match the matrix of the samples analyzed.

1. 100 ppm
2. 50 ppm
3. 25 ppm
4. 10 ppm
5. 5.0 ppm
6. 2.5 ppm
7. 1.0 ppm
8. Method blank
9. LCS + 9 samples (including any sample QC
10. 25 ppm
11. 10 samples (including any sample QC)
12. 50 ppm

8.8 Insrument printouts are generated from the software. Normal procedure is followed for preparing reports and the data is second checked before being given to the supervisor.

IX. SOIL/SEDIMENT SAMPLE PROCEDURE

A sample is introduced into the Solid Module via a conditioned sample cup. Once the sample has been introduced the entire analysis sequence is automatic. Please reference Chapter 4 of the OI 1010 Solid Module instrument manual for instrument states and configuration when initially setting the instrument methods up.

TC Mode Instrument Settings:

Analysis Temp:900°C
Analysis Time: 6.5 minutes
Nitrogen Gas Flow: 60-100 psi (external regulator regulator)
Oxygen Gas Flow: 40-60 psi (external regulator)

This is a step by step description of a routine soil TOC analysis.

9.1 The standards and check solutions should be taken out of the refrigerator and allowed to warm to room temperature. The nitrogen and oxygen (internal regulator should be set at 50-60 psi) turned on allowing a nitrogen flow of 350-400mL/minute and an oxygen flow of 180 mL/minute (± 3 mL/minute).

NOTE: DO NOT TURN THE ANALYZER ON BEFORE TURNING THE GAS ON!

9.2 Let the gas flow through the instrument for a few minutes. The instrument should now be turned on and let to stabilize for 30 minutes.

9.3 Condition the cups (with quartz wool in them) using Diagnostics under Instrument Menu commands, (don't condition too many cups at a time since setting in contact with the air can cause contamination).

9.4 Set up the subdirectory (using the current date to ID it) under WinTOC output.

9.5 If doing an initial calibration curve use an appropriate µL syringe to make the following measurements of the sucrose standard in order to achieve the indicated concentrations. Make sure that there are no air bubbles in the syringe. Turn the syringe with the needle pointed up and vibrate the barrel and disperse any air from the syringe. To enter the calibration information on the instrument go to Instrument Cal Menu, type in the calibration standard values and save the file as the cal.. date analyzed.

µL 30% Sucrose STD	Concentration (mg)
0	0
2.0 (1:6 solution)	0.10
3.0	0.90
50	15
100	30

Note: The 1:6 solution of the 30% Sucrose standard is prepared by mixing 100µL of the 30% Sucrose standard with 500µL of water.

9.6 Enter the sequence to be analyzed as listed below:

1. CCV(CCV1+ date analyzed for ID) or Initial calibration – single analyses
2. Method Blank(MB + date analyzed for ID) – single analyses
3. LCS, 15 mg dextrose (LCS + date analyzed for ID) – single analyses
4. NY Cert – 4 replicates
5. Sample – 4 replicates
6. Sample – 4 replicates
7. Sample – 4 replicates
8. Sample – 4 replicates
9. Sample – 4 replicates
10. CCV(CCV1+ date analyzed for ID)2 – single analyses
11. Sample – 4 replicates
12. Sample – 4 replicates
13. Sample – 4 replicates
14. Sample – 4 replicates
15. Sample – 4 replicates
16. CCV (CCV2+ date analyzed for ID) – single analyses
17. Sample – 4 replicates
18. Sample – 4 replicates
19. Sample – 4 replicates
20. Sample – 4 replicates
21. Sample – 4 replicates
22. CCV(CCV3+ date analyzed for ID) – single analyses
23. Sample – 4 replicates
24. Sample – 4 replicates
25. Sample – 4 replicates
26. Sample – 4 replicates
27. Sample – 4 replicates
28. CCV(CCV4+ date analyzed for ID) – single analyses
29. SampleMS – 4 replicates
30. SampleDUP – 4 replicates
31. FCV(CCV4+ date analyzed for ID) – single analyses
32. FCB(FCB4+ date analyzed for ID) – single analyses

9.7 Samples should be stored away from light and at 4°C (± 2°C). Wearing labcoat, gloves and safety glasses remove samples from sample storage signing them out appropriately on the internal chain of custody form.

9.8 Transfer a homogeneous aliquot(~5 g) of the sample into a small pre-labeled aluminum weighing pan. Label each pan with the appropriate sample ID then add enough phosphoric acid (1-2 ml) to remove the Total inorganic carbon (TIC) when the sample is placed in an oven at 250°C. Place the samples in the 250°C oven for 10 minute and begin prepping the sample cups to weigh 0.2g-1.0g of each sample(in quadruplicate). Limit the time that the cups are

exposed to the atmosphere as to reduce potential contamination. **Note: Since the samples are dried in this manner, before the sample aliquot it taken, a % solids determination and calculation is NOT necessary to report the sample concentrations in dry weight.**

9.9 Set the OI 1010 to the TC Mode and start running the sequence beginning with the initial calibration or calibration verification standard as illustrated above. Weigh each sample in quadruplicate making sure to limit the time that samples are exposed to the atmosphere.

9.10 The Excel file for calculations is located in "V:\WCM\TESTS\TOC soil\". The sample identity, its corresponding mgC reading, and the sample weight are entered into the appropriate columns. The Excel worksheet is self explanatory. Normal procedure is followed for preparing reports and the data is second checked before being given to the supervisor.

X. QC REQUIREMENTS

10.1 Analyze a laboratory control sample (LCS) for each batch of samples **(maximum of 10 samples per day).** If the LCS does not fall within the control limits of 80 to 120%, corrective action must be taken to find and correct the problem.

10.2 Run a method blank (PB) for each batch of samples (maximum of 20 samples per day). The PB should be less than 1/2 the reporting limit.

10.3 One matrix spike and matrix spike duplicate must be run per set of 20 samples. For water analysis, a spike and spike duplicate are made by mixing 20 mLs of sample with 0.30 mLs of stock 1000 mg/L standard using an ependorf pipette. The true value is 15 mg/L. The percent recoveries on a MS and a MSD should be within 75 and 125%. Relative percent difference (RPD) on duplicates should be less than 20%. If not, a corrective action (CAR) must be approved by your supervisor.

10.4 Analyze an initial calibration verification (ICV) immediately after the calibration curve. Analyze a calibration check verification (CCV) standard every tenth sample and at the end or after every fifth sample when analyzing samples in quadruplicate. Analyze a CCV after every 5th sample when analyzing soil/sediment samples. The percent recoveries should be in the range of 90 to 110%. The CCV %RSD warning limits are $\leq$15% for aqueous samples and $\leq$20% for soil/sediment samples. If the CCV % RSD exceeds 15%(aqueous) or $\leq$30% (soil/sediment) and the correlation coefficient is less than 0.990 correct the problem and re-analyze the CCV.

10.5 When analyzing water samples, all water blanks before samples and standards must be below the detection limit, otherwise the samples must be rerun.

10.6 Analyze an initial calibration blank (ICB) following the ICV. Analyze a continuing calibration blank (CCB) following each CCV. The ICB and CCB should be less than ± the MDL.

10.7 Calculate all percent recoveries and relative percent differences on duplicates and show calculations on data.

10.8 Calculate all percent recoveries and relative percent differences on duplicates and show calculations on data.

Calculate spikes as follows where everything is in concentration.

$$\% \text{ Recovery} = \frac{\text{Spike} - \text{Sample}}{\text{True Value}} \times 100$$

. Relative percent difference is calculated as follows, with everything in concentration:

$$\text{RPD} = \frac{\text{Higher Concentration} - \text{Lower Concentration}}{\text{Average of Concentrations}} \times 100$$

10.9 SM5310B requires that the analyst repeat injection until consecutive measurements are obtained that are reproducible to within ±10%. A minimum of two injections is required for water samples with three replicates preferred. SW-846 Method 9060/9060A requires quadruplicate analysis of each sample. The Loyd Kahn soil method suggests 1 sample per 20 be run in quadruplicate. Some clients may request that all samples to be done in quadruplicate. Please check with your supervisor if you have any questions about the required numbered of sample replications.

10.10 **For aqueous samples check an acidified 20mg/L inorganic carbon standard quarterly, to assure that purge gas flow is adequate to remove inorganic carbon. The result should be below the reported quantitation limit.**

XI. CORRECTIVE ACTIONS

11.1 INSTRUMENT RELATED

1. ICV not within ± 20% (Soil) or ± 10% (SM 5310C0
a. If the problem is with the solution.

i. Re-prepare, obtain new stock if necessary.
b. If the problem is with the calibration.
i. Recalibrate through analysis of appropriate standards and recheck ICV.
2. CCV not within ± 30% (Soil) or ±15% (SM 5310C)
a. If the problem is with the solution.
i. Re-prepare, obtain new stock if necessary.
b. If the problem is with the calibration.
i. Recalibrate through analysis of appropriate standards and re-prepare /reanalyze the previous ten sample according the following guidelines.
a. If the CCV was biased high, any of the previous ten samples which were below the minimum detection limit do not require reanalysis.
b. If the CCV was biased low, the previous ten samples must be reanalyzed.

*** Incorrectly set gas flow is a common instrument related problem which requires corrective action. Verify that all gas flows are adjusted properly.**

11.2 SAMPLE MATRIX RELATED

1. Replicate analysis RPD not within ±20% aqueous or ±50% soil/sediment
i. The associated sample data must be qualified on the final report.
2. Spike analysis recovery not within ±25% aqueous or ±50% soil/sediment
i. If the analyte level in the sample is greater than 4X the spiking level, the %recovery can not be evaluated and no action is taken.
ii. If the analyte level in the sample is not greater than 4X the spiking level, the associated sample data must be qualified on the final report. A corrective action report must accompany the data and be emailed or given to the supervisor.

XII. HEALTH AND SAFETY

A. Care should be used in handling all samples. Safety glasses must be worn in the lab at all times. The use of blue nitrile gloves and lab coats is highly recommended.

B. Research into expected sample content and concentration should be done in order to be prepared for additional safety considerations. Generally, any samples which need special consideration have applicable notes on the sample logs.

C. MSDS are available for all reagents and standards, which have been purchased. These are located in the administrative section next to the break room.

D. Please see *Waste Disposal; SOP-405* for proper disposal of the waste generated from this area.

XIII. WASTE DISPOSAL and POLLUTION PREVENTION

Please see Waste Disposal SOP-405, for instruction of proper disposal of waste generated from this area. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

XIV. METHOD PERFORMANCE

14.1 Precision and Bias for Total Organic Carbon (TOC) by Persulfate-Ultraviolet Oxidation. (Water samples)

Characteristic Of Analysis Concentration determined, mg/L:	Spring Water	Spring Water +0.15 mg/L KHP*	Tap Water	Tap Water +10 mg/L KHP*	Municipal Wastewater Effluent
Replicate 1	0.402	0.559	2.47	11.70	5.88
Replicate 2	0.336	0.491	2.49	11.53	5.31
Replicate 3	0.340	0.505	2.47	11.70	5.21
Replicate 4	0.341	0.523	2.47	11.64	5.17
Replicate 5	0.355	0.542	2.46	11.55	5.10
Replicate 6	0.366	0.546	2.46	11.68	5.33
Replicate 7	0.361	0.548	2.42	11.55	5.35
Mean, mg/L	0.35	0.53	2.46	11.53	5.32
Std. Deviation: mg/L	0.02	0.03	0.02	0.21	0.23
%	6	6	1	2	4
Actual Value, mg/L	-	0.50	-	12.46	-
Recovery, %	-	106	-	93	-
Error, %	-	6	-	7	-

***KHP = potassium acid phthalate.**

14.2 There was no method performance data available for the soil procedure.

XV. REFERENCES

1. Annual Book of ASTM Standards, Part 31, "Water," Standard D 2574-79, p. 469 (1976).

2. Standard Methods for the Examination of Water and Wastewater, 19th ED., Method 5310C (1999).

3. EPA SW-846, Method 9060/9060A.

4. Lloyd Kahn Method, *"Determination of Total Organic Carbon in Sediment"*

APPENDIX I.

1. Power up the lamp for warm –up, check reagents inside instrument cavity to make sure all are filled before starting the run.
2. Fill Fresh DI water in 1 gallon jug; DI squirt bottle and 1 L plastic
3. Label and load VOA vials with standards and samples into round tray.
4. Place round tray onto autosampler, get a final sample count for end point and replace lid.
5. Make sure that round tray fits down flush onto the autosampler.
6. On computer screen, select "TOC-Control V" icon.
7. Then select "Sample Table Editor"
8. Enter user name: "analyst initials" select OK.
9. Under "File" select "calibration curve" "OK".
10. Under system select Shimadzu TOC-BWS Enter/next
11. Select Edit Calibration points manually Enter/next
12. Under "Analysis" select "NPOC" then make up your file name (use today's date) Enter/next.
13. Calibration Measurement Parameters are default: Just hit "next"
14. Select "ADD" and enter calibration points starting at (1) 100 mg/L (2) 50 mg/L (3) 25 mg/L (4) 10 mg/L (5) 5.0 mg/L (6) 2.5 mg/L (7) 1.0 mg/L (8) 0.0 mg/L. After 8 points it should show 0.00 mg/L first and 100 mg/L eigth if so "next"
15. Put a check mark in "Correlation Coefficient" check box "next"
16. "next"
17. "finish"
18. Go to file and select "new", "sample run" "ok" "ok" enter file name: user date "save"
19. Now go to insert and select "calibration curve" then scroll till you find your file name/date should have .cal after date "select" the "open"
20. You should now see the sparging /acid addition page which shows a picture of the round sample tray. Under vial manually enter "1"beside 0.00 mg/L.
21. manually enter "2" beside 1.0 mg/L and "3" beside 2.5 mg/L and so on and so forth all the way to "8" this shows what order they ar loaded on the tray. "Enter/OK"
22. Then a screen with your filename/date and all info should be in row 1 only with vial column showing. 1,2,3,4, etc.
23. Select the lightening bolt symbol then enter "use PC settings" this will start initializing wait till screen goes away then you will see the stop light symbol appear with green light showing, select that icon select "keep running" select "standby"
24. Sparging/acid addition page will re-appear just hit "OK"
25. Start ASI tray screen will appear hit "Start"
26. The instrument should start establishing the baseline and move auto tray into position – Lid must be on and samples loaded into corret position will take almost

3 hours to finish. Can view data as its coming off by selecting "view" "sample window". After calibration is done review.

27. Select "File" then "New" then "sample run" "ok"
28. General information screen: No change select "ok"
29. Save as screen: Select today's date for file name example 00month/00day/00year
30. Select "save"
31. Sample Table Screen: Select "insert" then select " auto generate" enter
32. **Page 1** sample group wizard sample source: select "calibration curve" then double click on box with 3 dots …
33. Open latest curve from calibration curves file
34. Highlight latest curve and select "open"
35. Should send you back to page 1 with calibration curve info submitted. Select "next"
36. **Page 2** Sample Parameter: Enter final sample count for "number of samples" select "next"
37. **Page 3** Calibration Curves: No changes Select "Next"
38. **Page 4** Calibration Checks: No changes Select "Next"
39. **Page 5** Controls: No changes select "finish", Select "ok" on "Sparging/ Acid page.
40. Type sequence as they are loaded on tray: ICV, ICB, LCSW, Sample #, client,etc.
41. Once everything is typed in double check that it matches the way samples and QC are loaded..
42. Click or select the lightening bolt symbol then select "use settings on PC". Wait for initializing. When screen goes awy the traffic light symbol should appear next to the lightning bolt symbol. Click on the traffic light symbol.
43. Click or select "shut down Instructions". Then select "standby" Sparging/ Acid addition screen will appear so you can confirm your tray is loaded the wax things are highlighted in blue. Select "OK" if it looks the same.
44. Start ASI measurement: External acid addition should have a check mark click on "start" analysis should begin to start.
45. Click on view and chose "sample window" to watch curves come off and to see beginning values.

Methane, Ethane, Ethene in Aqueous Samples by Modified RSK-175 (Automated Headspace)

SOP NUMBER: SOP-236

REVISION NUMBER: 1

APPROVED BY:

SECTION MANAGER

QUALITY ASSURANCE MANAGER

EFFECTIVE DATE: 05/23/08

DATE OF LAST REVIEW: 04/28/09

Methane, Ethane, Ethene in Aqueous Samples by Modified RSK-175 (Automated Headspace)

I. SUMMARY

The GC/FID/Headspace system is used to analyze methane, ethane, and ethane in aqueous samples . Reporting limits for these are methane 2.0 ug/L, ethane 1.4 ug/L, and ethene 1.1 ug/L.

II. SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Section 3.0 and tables 3-1 and 3-2 of the Empirical Laboratories, LLC Quality Assurance Manual include details concerning sample preservation, containers and handling of volatile samples. Samples are collected in 40 ml VOA vials and shipped to the lab in coolers with ice. Water samples are stored in the Hobart in the sample storage room at a temperature of 4°C.

III. INTERFERENCES AND POTENTIAL PROBLEMS

Methane found in the lab environment can be a source of contamination. The blank value is subtracted from the sample results.

IV. INSTRUMENTATION AND EQUIPMENT

A. Gas Chromatograph
1. HP 5890 Series II (temperature programmable).

B. Autosampler
1. Tekmar 7000 Headspace autosampler

C. Columns-Capillary columns.

1. Carboxen 1006 PLOT column–30 meter x 0.53mm ID

D. Data Acquisition and Processing Software.

1. HP Chemstation system is interfaced to the HP-GC for data acquisition and storage.
2. TARGET data system is interfaced to the acquisition systems. The system accepts, processes and stores acquired data.

E. Glassware

1. 25ml Graduated cylinder
2. 20ml headspace vials with crimp tops(National Scientific)

3. Gastight syringes- 25, 50, 100, and 250uL

V. STANDARDS

Gas standards are purchased from Restek and Supelco. The date they are received is noted on the container they are received in. The standards are given a sequential number the day they are opened and this is noted in the GC standards logbook. Standards for MEE are Scotty gases purchased in pressurized tanks. Calibration standards at a minimum of five levels are prepared by injecting the gas from a Scotty gas standard tank into capped 20 ml headspace vials with 15 ml of D.I. water using a gas-tight syringe.Usually 5,10,20,25,50,100,150,200ul and up to 5ml are used.

VI. PROCEDURE

The following information describes the instrument and QC requirements to analyze the compounds that we do by this method.

A. Instrumentation

1. GC
   - Initial Temperature: 35 ° C hold for 3.0 minutes.
   - Ramp: 25 °C / minute to 225 ° C.
   - Final Temperature 225 ° C hold for 3.08 minutes.
   - Detector Temperature 230 ° C.

2. Headspace Autosampler
   - Platen: 80 °C./ Platen Equil.: 0.50 min.
   - Sample Equil.: 2.0 min.
   - Pressurization: 0.50 min./ Pressure Equil.: 0.25 min.
   - Loop Equil.: 0.30 min.
   - Injection Time: 1.0 min.
   - Valve and Line Temp.: 95°C.

B. Calibration and Quality Control

1. Refer to SW-846 Method 8000B for proper calibration techniques.

   a. Five point minimum calibration curve must be introduced into the GC and analyzed for each analyte of interest using the appropriate instrument parameters. If the percent relative standard deviation (% RSD) of the calibration factor is less than 20 percent over the working

range, linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve(linear curve corr. ≥0.995, quadratic ≥0.99 with six points). The curve is then verified using a second source standard(**75-125% criteria**).

b. The calibration curve must be verified every day through the analysis of a mid-level standard at the beginning and end of the sequence and after every 10 field samples. The percent difference back to the curve must not exceed ± 20 percent. If this criteria is not met, corrective action must be taken before sample analyses continues. Usually this involves recalibration or checking the gastight syringes.

c. Calculations:

$$\text{Calibration Factor (CF)} = \frac{\text{Response}}{\text{Dec Equiv} \times 1000}$$

Decimal equivalents are taken from the sample quant reports and entered into an Excel spreadsheet to calculate final concentration in ug/L.

2. Retention Time (RT) Windows - RT criteria set forth in SW-846 method 8000C are used to set retention time windows. New in-house retention time windows are established after every major change to the system (new column or temperature program) and at initial calibration with midpoint standard. If the established retention time window is less than +/-0.03 minutes, the window defaults to +/-0.03 minutes. Retention times are updated with the first CCV of the day or the mid-level standard of the curve if samples are analyzed directly after a curve.

1. Quality control for this method can be referenced in SW-846 Method 8000C.

   a. A method blank is required before analyzing samples.The contamination level should not exceed the CRDL.

   b. An MS/MSD pair are required every 20 samples per matrix. Limits 75-125%.

   c. A Laboratory Control Sample (LCS) is required every 20 samples. Limits 75-125%.

   d. MDLs are either performed annually or by analyzing an MDL check according to SOP-414.

C. Sample analysis includes the following steps: 15 ml of sample are transferred to 20ml headspace vials capped and loaded onto the autosampler along with a method blank with 15 ml of D.I. water.

1. A mid-level standard must be run at the beginning and end of the sequence and after every 10 field sample and cannot exceed ±20 percent difference from the initial calibration. A mid-level standard must also be analyzed at the end of the analysis sequence.

2. The retention times are updated with the first midpoint check of the day or from the midpoint of the calibration curve if analyzed before the samples.

D. Following sample analysis, the data is reduced using the TARGET data system. The following must be checked to see if the samples will require re-analyses or dilution.

1. The analyte concentration must be within the range of the calibration curve. If an analyte exceeds the curve, a dilution must be performed and the next sample must be checked for carryover. Any dilution should keep the concentration of the analyte in question within the top half of the curve.

E. Demonstration of Capability (DOC) – Each analyst must perform a DOC to demonstrate proficiency with these methods. See SOP-413 for guidance.

VII. HEALTH AND SAFETY

A. Care should be used in handling all samples.

1. Safety glasses must be worn in the lab at all times. The use of blue nitrile gloves and lab coats is highly recommended.
2. Research into expected sample content and concentration should be done in order to be prepared for additional safety considerations. Generally, any samples that need special consideration have applicable notes on the sample logs.
3. MSDS sheets are available for all reagents and standards that have been purchased. These are located in the bookshelves across from the Quality Assurance Officers cube.

VIII. WASTE MANAGEMENT AND POLLUTION PREVENTION

A. Please see Waste Disposal, SOP-210 and SOP-405 for proper disposal of waste coming from this area within our laboratory.

B. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

IX. REFERENCES

A. Newell, Bryan, RSKSOP-175, Rev.0, August 1994.
B. Newell, Bryan, RSKSOP-147, Rev.0, January 1993.
C. Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846; Third Edition (Update III); Method 8000C.

DEFINITIONS

°C - degrees centigrade
CF - calibration factor
CRDL - contract required detection limit
%D - percent difference
FID - flame ionization detector
GC - gas chromatograph
LCS - laboratory control sample
MDL - method detection limit
µL - microliter
µm - micrometer
ml - milliliter
mm - millimeter
MS - matrix spike
MSD - matrix spike duplicate
%RSD - percent relative standard deviation
RT - retention time
SOP - standard operating procedure

Refer to SOP-431 for further definitions.

LABORATORY SAMPLE RECEIVING, LOG IN AND STORAGE STANDARD OPERATING PROCEDURES

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APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

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LABORATORY SAMPLE RECEIVING, LOG IN AND STORAGE

This SOP lists in as much detail as possible our daily procedures for sample receiving, log in and storage of laboratory samples. Keep in mind that there may be project specific requirements that are more strict or different than our routine procedures. In these instances, the project specific requirements must be met and followed. Although a few project specific requirements are detailed in this SOP, i.e. USACE certification issues, not every situation can be addressed. If there is ever any uncertainty on what procedures must be followed, please see the Testing Coordinator immediately. If ever in doubt, always go with the more stringent requirements. This document will constantly be reviewed and revised as necessary.

SAMPLE ACCEPTANCE CRITERIA

A sample may be rejected for compliance purposes if it does not meet the following criteria. Analyses may only proceed after notification and approval to proceed from the client or from the laboratory manager.

1. Sample must be properly preserved and in the proper container for the requested analysis.
2. Sample integrity must be maintained. The container shall be intact without cracks, leaks, or broken seals.
3. Adequate sample volume must be received for the requested analysis, including volume for any requested QA/QC (MS/MSD).
4. The sample ID on the bottle label must match the sample ID listed on the chain of custody.
5. The sample container label and the chain of custody must be completed with indelible ink. The sample label must be intact and list all necessary information; to include: sample date, sample time, sampler, and sample ID/location. The chain of custody shall also indicate sample date and time, requested analyses, and all necessary client information.
6. Sample temperature must be less than 6°C or received on ice.
7. Sample must be within holding time for the requested analysis.

These issues are discussed in more detail below under the "Sample Receiving" section of this document.

I. Sample Receiving

A. Samples are received at the Empirical Laboratories on 621 Mainstream Drive, Suite 270 Nashville, TN 37228.

1. The majority of samples are shipped in coolers by couriers such as Federal Express and UPS. All couriers are generally received in the Empirical Laboratories Sample Receiving (SR) area loading dock in back of the laboratory. The laboratory is located close to the Federal Express (FedEx) distribution station, therefore we do pick up our

coolers at the FedEx location and transport them back directly to the laboratory. Some coolers and/or samples are delivered directly to the SR area by the sampler and/or client.

2. Some coolers and/or samples may be received directly by Empirical Laboratories Sample Receiving personnel. If samples are hand delivered by the client make sure that necessary paperwork is included and that you sign and date the chain of custody, as well as record the temperature of the samples on the chain of custody as well. If the *Empirical Laboratories* ***Chain of Custody [Attachment II]*** is used the white and yellow copy of the chain of custody is retained and the pink copy must be given to the client.

B. When going through the required steps for Sample Receiving and Sample Log In, keep in mind that a ***Corrective Action Report (CAR) for Sample Receiving [Attachment III]*** must be completed to document any problems, discrepancies, project changes, etc. encountered during the process. This includes but is not limited to incorrect sample containers, improper preservatives [chemical and temperature], chain of custody discrepancies, sample descriptions, etc. A CAR may be completed just to keep a record of a situation, which is not actually "out of compliance."

1. Make sure that all information on the CAR is stated clearly and very detailed. Many times it is necessary to refer to these documents a year or more after they were completed. Document all correspondence including name, date, company and response.

2. The CAR forms must be numbered starting with No. 001 at the beginning of the year (e.g. 01-001). No two forms should have the same number. All CARs must be forwarded to the Project Manager and/or receiving manager for approval and distribution. THIS MUST BE DONE ASAP OF WHEN THE PROBLEM/SITUATION IS DISCOVERED.

C. Visually inspect all coolers for tampering, custody seals present and intact (if applicable) leakage, etc. If a cooler has been damaged beyond repair, unpack the samples and discard the cooler as to not reuse it. If you suspect a cooler may be damaged or is extremely dirty this cooler must not be reused. If coolers were sent by Federal Express, examine the Federal Express airbills for the number of packages in the shipment and make sure that all the packages (coolers, boxes etc.) in a group have been received. If there are any problems the Project Manager must be contacted immediately. If anything looks unusual, take the time to check it out and document the situation and findings.

D. Open each cooler in order to quickly inspect the contents and to locate the chain of custody. Sample Receiving personnel should wear the following personal protection equipment: gloves, safety glasses and a laboratory coat. All coolers received from projects with the **US Army Corps of Engineering (USACE) and AFCEE** projects should be opened under the hood in the sample storage room. Sign then list the date and time received on the chain of custody. The time received <u>must</u> reflect the actual time the samples were received even though they may be logged into the system at a later time. Samples received on Saturday may be processed on the following Monday morning, or samples received late in the day during the week may be processed the next morning. All cooler(s) <u>must</u> be opened, examined for