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Naval Facilities Engineering Command
Naval Surface Warfare Center
Crane, Indiana

Mine Fill A Battery Site Cleanup
Final Work Plan
NSWC Crane
Crane, Indiana

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Supplemental SOP Binder

TOLTEST, INC.

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Quanterra Environmental Services

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*OPERATION-SPECIFIC STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF CYANIDES (ALL TYPES) USING MANUAL DISTILLATION, FOLLOWED BY AUTOMATED COLORIMETRY

(METHODS EPA 335.4, REVISION 1.0; SW-9010B/9012A,UPDATE III; CARB 426; SM 4500-CN.I)

(SUPERSEDES: ALL VERSIONS OF LM-CAL-1034, 1053, 1101 AND 1102; CARB 426 DRAFT)

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1. SCOPE AND APPLICATION

1.1. This SOP is based on EPA 600/Method 335.4, Revision 1.0, August 1993; SW-846 9010B/9012A, update III, Standard Method 4500-CN.I, 19th edition, 1995 and CARB Method 426, January 1987.

1.2. Reduced volume versions of the above methods applied to this SOP are acceptable as long as the same volume - ratio of samples and reagents were used and they meet the quality control performance requirements stated in the methods.

1.3. This procedure is applicable to the determination of:

Analyte	CAS Number
Total Cyanide	57-12-5
Cyanide amenable to chlorination	10-87-7
Weak acid dissociable cyanide	10-71-9

1.4. Applicable Matrices

1.4.1. This procedure is applicable to the determination of Total Cyanide, cyanide amenable to chlorination, and weak and dissociable cyanide for drinking, ground, surface and saline water, domestic and industrial wastes, leachates, soil, and other nonaqueous matrices.

1.4.2. Also applicable to aerosol and gas emissions from stationary sources.

1.4.3. This procedure is ***not*** applicable to oily matrices.

1.5. Reporting Limits:

Parameter	Waters	Soil/Waste
Total cyanide	0.01 mg/L	0.5 mg/kg
Amenable to chlorination	0.01 mg/L	0.5 mg/kg
Weak acid dissociable	0.01 mg/L	0.5 mg/kg
Total cyanide, low (specific client requests)	0.005 mg/L	NA

1.6. Dynamic Range

1.6.1. The applicable range is 0.01 mg/L to 0.50 mg/L. Higher concentrations are analyzed by dilution of the sample.

1.6.2. A low level range is also used when requested to meet client requirements or for special projects. The low level range is from 0.005 mg/L to 0.20 mg/L.

1.7. The analysis portion of this method is restricted to use by, or under supervision of, analysts experienced in the operation of Lachat Auto-Analyzer and the interpretation of its results. The prep portion is restricted to analysts experienced in cyanide reflux-distillation procedure.

2. SUMMARY OF METHOD

2.1. The cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by automated colorimetry.

2.1.1. In the automated colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction with Chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. The CNCl then forms a red-blue dye by reacting with pyridine-barbituric acid reagent. The color is read at 570 nm.

2.1.2. The concentration of NaOH must be the same in the standards, the scrubber solutions, and any dilution of the original scrubber solution, in order to obtain colors of comparable intensity.

2.2. Cyanide amenable to chlorination - The method is designed to measure the amount of cyanide that can be removed from the samples by alkaline chlorination treatment processes.

2.2.1. Two sample aliqouts are required to determine cyanides amenable to chlorination especially when the total cyanide is found to be greater than the reporting limit. One portion of sample is chlorinated, which destroys some dissociable forms of cyanide prior to the reflux-distillation process. A second portion of sample is not treated . Both portion are distilled and analyzed for cyanide as outlined in section 2.1.

2.2.2. The difference between the two results is reported as cyanide amenable to chlorination.

2.3. Weak acid dissociable cyanide - The method is designed to measure free and potentially dissociable forms of cyanide.

2.3.1. It exclude CN- from tight complexes that would be amenable to oxidation by chlorine. It is particularly useful for samples that produce negative amenable results.

2.3.2. The sample is slightly acidified, (pH 4.5 to 6.0) then distilled rigoruosly as described in section 2.1

3. DEFINITIONS

3.1. Cyanide - The term "cyanide" refers to all of the CN groups in cyanide compounds that can be determined as the cyanide ion, CN- by the various chemical methods. These compounds include both simple and complex cyanides.

3.2. Dissociable cyanide - The degree of dissociation of the various metallocyanide complexes at equilibrium, which may not be attained for a long time, increases with decreased concentration and decreased pH, and is inversely related to their stability, which varies greatly by compound. For example, the zinc and cadmium cyanide complexes are easily dissociated, whereas the iron and cobalt cyanides are very stable. Due to the differences in toxicity and treatment abilities among these complexes, environmental regulations specify chemical methods that can distinguish at least broad categories of these complexes.

3.3. Definitions of terms in this SOP maybe found in the glossary of the Quality Assurance Management Plan (QAMP).

4. INTERFERENCES

4.1. Interferences are eliminated or reduced by using the distillation procedure, however, some specific testing and treatments of interferences are discussed in detail under section 10.

4.2. Oxidizing agents such as chlorine decompose most cyanides. Chlorine interferences can be removed by adding excess sodium arsenite to the sample prior to preservation and storage of the sample to reduce chlorine to chloride which does not interfere with cyanide. Recommended to be done at the time of sampling.

4.2.1. For cyanide amenable to chlorination, the extent to which some metal-cyanide complexes are destroyed by chlorination depends on the amount of chlorine present and the time allowed for reaction. This is monitored by chlorine tests during chlorination. Chlorine added to the sample must be completely destroyed before distillation.

4.3. Samples that contain sulfide compounds may produce hydrogen sulfide during the distillation and interfere with color development causing false positive results. Sulfide interferences can be removed by adding an excess bismuth nitrate to the sample to precipitate the sulfide before distillation. Note: Lead Carbonate can be used instead of bismuth nitrate or cadmium carbonate. This will eliminate nitrate interference from bismuth nitrate and to minimize handling of hazard from $CdCO_3$.

4.4. High results may be obtained for samples containing nitrate and/or nitrite which may react with organic compounds during distillation to form oximes. These compounds once formed will decompose under test conditions to generate HCN. Sulfamic acid is added prior to the distillation process to remove the nitrate and/or nitrite interference. Nitrate and nitrite interfere when present at levels higher than 10 mg/L and in conjuction with certain organic compounds.

4.5. Fatty acids, detergents, surfactants, and other compounds may cause foaming during the distillation when they are present in high concentrations. If encountered this may be remedied by sample dilution or by addition of anti-foaming agent.

4.6. Thiocyanate is reported to be an interference when present at level greater than 10 mg/L.

4.7. High carbonate concentrations may react violently when sulfuric acid is added to the samples during distillation. It may also interfere with the automated colorimetric analysis by forming bubbles in the flow cell thus giving false positives and a noisy baseline. If this is encountered dilute distillate and reanalyze.

4.8. Aldehydes, glucose, and other sugars may convert cyanide to cyanohydrin, which form nitrile under the distillation conditions. These sample types are not normally encountered in our lab. Only direct titration without distillation can be used, which reveals only non-complex cyanides.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all Quanterra associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded.

5.2.1. Neoprene, natural rubber, and vinyl gloves provide varying degrees of protection against those chemicals listed. Refer to permeation/degradation charts for the actual data.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.3.1. Staff must follow EHS030 safety procedures to reduce any potential for exposure. See Appendix V.

5.3.2. Acute poisons (e.g. cyanide, barbiturates, azides) shall be kept in locked cabinets. Access to the cabinet shall be controlled.

5.4. The following specific hazards are known:

5.4.1. Chemicals known to be **flammable** are: Pyridine, acetone, and acetic acid.

5.4.2. The following materials are known to be **corrosive** are: Sulfuric Acid, Sodium hydroxide, hydrochloric acid, acetic acid, and potassium hydroxide, ascorbic acid.

5.4.3. The following materials are known to be **oxidizing agents** are: Chloramine-T and calcium hypochlorite, sodium arsenite.

5.4.4. The following materials are known to be **toxic** are: Barbituric acid, pyridine, chloramine-T, Brij-35, zinc acetate, methyl red, lead acetate, lead carbonate, sulfamic acid, p-dimethylaminobenzalrhodanine, silver nitrate, and disodium ethylenediamine tetraacetate, sodium arsenite.

5.4.5. **Pyridine** and chloramine-T are eye/skin'membrane irritants and should be handled only in a fume hood. The pyridine-barbituric acid **reagent must be kept covered.**

5.4.6. **Cyanide** and its salts are extremely toxic. Handle only in a hood. Do not pour concentrated cyanide solutions down the drain. Do not allow acids to come in

contact with cyanide salts or concentrated solutions. Do not breathe dust or vapors.

5.4.7. The waste from the analysis is slightly acidic. The waste must be capped at all times and stored under the vented waste analytical station. Rotate out any full containers to the Hazardous Waste disposal area.

5.4.8. Vapors from **glacial acetic acid** are extremely irritating. This material should be handled only in a fume hood.

5.5. Build-up of pressure in the distillation apparatus will cause the hot, acidic solution to spray out of the thistle tube. Ensure that the distillation set-up is enclosed at all times. Extra care is needed when adding the sulfuric acid into the sample during the distillation procedure (**Faceshields must be worn during this process**). In case vacuum is lost, the condensers must be opened to prevent build-up of pressure. If the solution overflows onto the heating mantle, turn it off. Unplug and replace the heating mantle when it cools. Ensure that the cooling system is on and working at all times during the distillation process.

5.6. All distillations are to be performed in an enclosed fume hood.

5.7. Distillates with concencentration of 10 mg/L or higher must be separated from the rest of the distillates and rotated to the Hazardous Waste disposal area for lab packing.

5.8. Exposure to chemicals must be maintained **as low as reasonable achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.9. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit. For cyanide ammenable to chlorination, the chlorination step will also be performed in a fume hood.

5.10. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor and the Health and Safety Officer.

6. EQUIPMENT AND SUPPLIES

6.1. LACHAT System:

6.1.1. LACHAT QuikChem Automated Flow Injection Ion Analyzer system, consisting of:

6.1.1.1. Autosampler.

6.1.1.2. Proportioning pump.

6.1.1.3. Injection module equipped with 150 cm, 0.8 mm i.d., sample loop.

6.1.1.4. Colorimeter with 570 nm filter and 10 mm, 80 uL flow cell.

6.1.1.5. Reaction module 10-204-00-1-A

6.1.1.6. Heating bath with temperature controller and a circulating cell: 4" coil, 0.81 mm i.d., double wrapped. Setting 45°C

6.1.1.7. Recorder or QuikCalc II Software System

6.1.1.8. Approximate injection timing:

6.1.1.8.1. Pump speed - 35

6.1.1.8.2. Cycle period - 40 sec

6.1.1.8.3. Sample loop length - 150 cm

6.1.1.8.4. Load period - 20 sec

6.1.1.8.5. Inject period - 20 sec

6.1.1.8.6. Inject to start of peak period - 25 sec

6.1.1.8.7. Inject to end of peak period - 61 sec

6.1.2. Disposable autosampler vials or test tubes for samples.

6.1.3. Volumetric flasks, class A, various sizes.

6.1.4. Volumetric pipettes, class A, various sizes.

6.2. Midi-distillation apparatus consisting of:

6.2.1. 125 mL round-bottom flasks

6.2.2. cold-finger condensers

6.2.3. absorption tubes (25-50 mL capacitty

6.2.4. and other associated apparatus.

6.3. Heating mantles for 125 mL round-bottom flasks and associated control module.

6.4. Vacuum pump.

6.5. Recirculating chiller.

6.6. Magnetic stirrer and bars.

6.7. 100 mL plastic bottle

6.8. 10 mL glass burrette

6.9. Erlenmeyer flask - 125-500 mL and

6.10. other miscellaneous laboratory galssware.

7. REAGENTS AND STANDARDS

7.1. 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 the 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 permits its use without lessening the accuracy of the determination.

7.2. Reagent water: Distilled or deionized water, free of analyte of interest. Water should contain particles no larger than 0.20 micron and have a resistance of at least 18 megohms.

7.3. Reagents for sample collection , preservation and handling:

7.3.1. Sodium hydroxide (50%), NaOH. Dissolve 50gm of NaOH pellets into a 100mL volumetric flask containing at least 25 mL of reagent water. Cool to room temperature, fill volume to the 100 mL mark. Also commercially available. Good for at least 1 year.

7.3.2. Sodium arsenite, 0.1N, $NaAsO_2$. Dissolve 3.2 gm of $NaAsO_2$ in 250 mL water. Good for at least 1 year.

7.4. Reagents for preliminary sample treatment:

7.4.1. pH paper strips capable of reading pH 2-12.

7.4.2. Lead acetate paper to spot check for presence of Sulfide in the sample. If color turns blue, means that sulfide is present in the sample, while clear color indicates absence of sulfide.

7.4.3. Potassium Iodide starch paper (KI). If color turns blue indicates presence of chlorine in the sample, while clear color indicates absence of chlorine.

7.5. Reagents for CN reflux-distillation procedure:

7.5.1. Sodium hydroxide solution, 5% (1.25N). Dissolve 50 gm of NaOH pellets in 1liter volumetric flask containing at least 500mL reagent water. Cool to room temperature, fill volume to the 1L mark. Store in plastic bottle. Good for at least 1 year.

7.5.2. Sodium Hydroxide, 1% (0.25N) NaOH, wash receptacle/carrier solution, dilution water: Dissolve 10 gm sodium hydroxide in a 1 liter volumetric flask containing at least 500 mL reagent water. Cool to room temperature, dilute to 1000 mL mark. Mix well and store in a plastic bottle. Good for one year from preparation.

7.5.3. Glacial acetic acid (concentrated), CH_3COOH. Commecially available.

7.5.4. Bismuth Nitrate (0.062M), $Bi(NO)_3 \bullet 5H_2O$. Dissolve 30 gm $Bi(NO)_3 \bullet 5H_2O$ in a 1 liter volumetric flask containing 100 mL of water. While stirring, add 250 ml glacial acetic acid, CH_3COOH. Stir gently until dissolved, cool to room temperature and dilute to the 1L mark with water. Good for at least 1 year.

7.5.5. Sulfamic acid (0.4N), H_2NSO_3H. Dissolve 40 gm of H_2NSO_3H in 1 liter volumetric flask containing at least 500 mL of water. Dilute to the mark 1L mark. Good for at least 1 year.

7.5.6. Sulfuric acid concentrated. Commercially available.

7.5.7. Sulfuric acid (50%) 18N H_2SO_4. Slowly and carefully add 500 mL of concentrated H_2SO_4 to 500 ml of water. Mix gently, cool to room temperature before using. ***Note: Wear a faceshield when mixing this solution.*** Good for at least 1 year.

7.5.8. Magnesium chloride solution (2.5M), $MgCl_2 \bullet 6H_2O$. Dissolve 510 gm of $MgCl_2 \bullet 6H_2O$ in 1 liter volumetric flask containing at least 500 mL water. Dilute to 1 liter mark. Good for at least 1 year.

7.6. Reagents for cyanide amenable to chlorination treatment prior to distillation:

7.6.1. Calcium hypochlorite solution (0.35M), $Ca(OCl)_2$. Add 5 gm of calcium hypochlorite into 100 mL of water. Warming the solution can expedite dissooving the $Ca(OCl)_2$ salts. Shake well before using - do not refrigerate. Good for at least 1 month.

7.6.2. Sodium hydroxide, 5% (1.25N) and 1% (0.25N). See sections 7.5.1. and 7.5.2.

7.6.3. Sodium arsenite (0.1N). See section 7.3.2.

7.6.4. Ascorbic acid (crystals), $C_6H_8O_6$. Can be used as an alternative for sodium arsenite solution but is not as effective as arsenite.

7.6.5. Potassium Iodide starch paper (KI).

7.7. Reagents for the distillation of Weak and Dissociable cyanide:

7.7.1. Acetate buffer: Dissolve 410 gm sodium acetate trihydrate ($NaC_2H_3O_2 \bullet 3H_2O$ in approximately 450 mL reagent water . Using a pH meter, adjust the pH to 4.5 with glacial acetic acid and dilute to final volume of 1000 mL with deionized water. Good for one year from preparation.

7.7.2. Zinc Acetate solution: Dissolve 100 gm zinc acetate monohydrate in a 1 liter volumetric flask with approximately 500 mL reagent water. Dilute to final volume of 1000 mL. Good for one year from preparation.

7.7.3. Methyl Red Indicator solution: Dissolve 0.1 gm methyl red in 100 mL deionized water. Good for one year from preparation.

7.7.4. Acetic acid, 1 + 9, (10%): Carefully add 50 mL glacial acetic acid to about 300 mL reagent water, mix, cool, and dilute to 500 mL mark. Good for one year from preparation.

7.8. Reagents for analytical determination of Cyanide content using Automated Colorimetry (Lachat Quickem Method No. 10-204-00-1-A):

7.8.1. Pyridine-Barbituric: **(Must be prepared under the hood!):** Place 15 gm of barbituric acid in a 1000 mL volumetric flask, add just enough water to wash the sides of the flask and wet the barbituric acid (approximately 50-100ml). Gently add 75 mL pyridine and mix until the barbituric acid is 90% dissolved. Carefully add 15 mL concentrated hydrochloric acid and stir until all the barbituric acid powder are completely dissolved. Dilute to volume with deionized water, store in an amber glass bottle and store at room temperature. This reagent is stable for approximately six months if stored in a cool, dark location.

7.8.2. Phosphate Buffer Solution, (0.71M): In a 1 L volumetric flask, dissolve 97 g anhydrous potassium dihydrogen phosphate (KH_2PO_4) in approximately 800 mL reagent water. Dilute to the mark and mix well. Good for at least one year.

7.8.3. Chloramine-T: Dissolve 1.0 gm chloramine-T in reagent water and dilute to 250 mL. Refrigerate and prepare fresh weekly.

7.8.4. Sodium Hydroxide, 1% (0.25N) NaOH, wash receptacle/carrier solution, dilution water: Dissolve 10 gm sodium hydroxide in a 1 liter volumetric flask containing at least 500 mL reagent water. Cool to room temperature, dilute to 1000 mL mark. Mix well and store in a plastic bottle. Good for one year from preparation.

7.9. Other Miscellaneous Reagents:

7.9.1. Lead carbonate powder or Cadmium carbonate powder, reagent grade. As an alternative for bismuth nitrate in precipitating sulfide interferences present in the sample.

7.10. Standards and standardization procedure:

NOTE: All expired standards must be rotated out of the laboratory to the Hazardous Waste storage area for disposal.

7.10.1. Cyanide Calibration Stock Standard, 1000 mg/L: Dissolve 2.51 gm potassium cyanide (KCN) and 2 g potassium hydroxide (KOH) in water and dilute to 1000 mL. Standardize with 0.0141N $AgNO_3$. Good for 1 year from preparation.

7.10.2. Reagents needed for standardization:

7.10.2.1. Indicator sol'n.: Dissolve 20 mg p-dimethylaminobenzalrhodanine in 100 mL acetone. Good for one year from preparation.

7.10.2.2. Silver nitrate standard titrant, (0.0141 N) $AgNO_3$: Dissolve 2.395 g $AgNO_3$ in reagent water and dilute to 1000 m. Standardized against 0.0141 M NaCl. 1.00 mL = 0.50 mg Cl^-. Good for at least 1 year. Also commercially available.

7.10.2.3. Standard sodium chloride, (0.0141 N) NaCl: Dissolve 0.824 gm NaCl (pre-dried at 140°C) in reagent water and dilute to 1000 mL; 1.0 mL = 0.50 mg Cl. Good for at least 1 year.

7.10.2.4. Potassium chromate indicator solution: Dissolve 5 gm of K_2CrO_4 in a 100 mL volumetric flask containing at least 10 mL of reagent water. Add $AgNO_3$ solution until a definite red precipitate is formed. Let stand for 12 hour, filter and dilute to 100 ml with reagent water. Good for at least 1 year.

7.10.3. Standardization of 0.0141 N $AgNO_3$ Standardized against 0.0141 N NaCl. (Perform duplicate analyses)

7.10.3.1. Pour 10 mL of 0.0141 N NaCl into a 125 mL erlenmeyer flask.

7.10.3.2. Add 1 mL K_2CrO_4 indicator, titrate with 0.0141 N $AgNO_3$ until a pinkish yellow end point is reach.

7.10.3.3. Establish a reagent blank value by the above titration method using 100 mL reagent water. A blank of 0.2 to 0.3 mL is usual.

7.10.4. Calculations:

$$N = [500 \text{ ug Cl/mL}) \times (10 \text{ mL})] \div [(A-B) \times (35450)]$$

where:

N = Normality of $AgNO_3$ (titrant)

A = mL of titrant used for 500 ug Cl/mL Std.

B = mL of titrant used for the blank

Reference: SM 4500 - Cl- B. Sections 3a-c; 4a-b and 5.

7.10.5. Cyanide Stock Standardization Procedure: Must be performed everytime a fresh stock solution is made.

7.10.5.1. Add 5 mL of the 1000 mg/L Cyanide Stock Standard solution to a 500 mL Erlenmeyer flask. Add 245 mL of 0.25 N NaOH. Prepare and titrate in triplicate.

7.10.5.2. Add 5-6 drops of p-dimethylaminobenzalrhodanine indicator solution. See section 7.10.2.1.

7.10.5.3. Titrate with standard silver nitrate, (0.0141N)$AgNO_3$, to the first change in color from a canary yellow to a salmon hue. Record volume of titrant used.

7.10.5.4. Prepare a blank in the same procedure by using 250 mL of 0.25 N NaOH solution.

7.10.6. Calculate the true stock cyanide concentration as follows:

$$\text{mg/L Stock Cyanide} = \frac{[(A - B) \times 1000]}{\text{mL of sample}} \times 0.734$$

where:

A = Volume of $AgNO_3$ for titration of sample, mL (average of 3 replicates)

B = Volume of $AgNO_3$ for titration of blank, mL

Note: At 0.0192 N AgNO3, 1 mL of titrant is equivalent to 1 mg cyanide *(Reference: SM 4500-CN⁻ D. Sections 3-5.)*
Therefore: 1 mL of 0.0141 N AgNO3 = 0.734 mg CN

Enter all titration informations into the standardization log book and default CN concentration into the standard preparation log.

7.10.6.1. Acceptance criteria = (+/– 5%) : 1000 mg/L concentration is to be used if the titrated value is between 950 mg/L and 1050 mg/L.

7.10.6.2. Corrective action : If stock solution is less than 950 mg/L, add more KCN crystals (record added mass). If the stock solution is greater than 1050 mg/L add more reagent water. Repeat standardization for both corrective actions. If after two adjustments have failed, prepare fresh batch of stock solution (see section 7.10) and repeat standardization procedure from section 7.10.5.

7.11. Intermediate Calibration Standard (ICS) , 10 mg/L: Pipette 1.0 mL of 1000 mg/L calibration stock standard into a 100 mL volumetric flask. Dilute to volume with 1% sodium hydroxide (same as 0.25 N NaOH). Prepare fresh daily.

7.11.1. Working Calibration Curve, (0.01-0.50 mg/L): NOTE: All standard solutions, sample dilutions and distillates must be have a final NaOH normality of 0.25N NaOH. Use 1 % NaOH solutions when preparing standards and diluting the samples/distillate. Prepare fresh daily.

Linear Working Calibration Standard Curve - prepare fresh daily:

Volume of ICS to add (mL of 10 ppm)	Final volume using 1 % NaOH (mL)	Final CN concentration, (mg/L)
0.0	100	0.0
0.10	100	0.01
0.50	100	0.05
2.0	100	0.20
4.0	100	0.40
5.0	100	0.50

7.11.2. For low-level curve, the linear range is 0.005-0.20 mg/L. Prepare a series of working standard curve following the above format using 0.05 mL, 0.10 mL, 0.50 mL, 1.0 mL and 2.0 mL of the ICS solution into 100 mL flask each using 1 % NaOH solutions to make the following concentrations - 0.005, 0.010, 0.05, 0.10 and 0.20 mg/L standards respectively. Prepare fresh daily.

7.12. It is recommended that at least two standards (a high and a low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. This requirement is only applicable when distilling for Total cyanide and/or when distilling a batch of samples that underwent the chlorination process for cyanide amenable to chlorination.

Using the ICS (10 mg/L), prepare and distill the following standards with every analytical prep batch:

Standards to Distill with every prep batch	Volume of ICS to add (mL of 10 ppm)	Volume of 1 % NaOH in a flask (mL)	Final CN conc. At the analytical stage (ppm)
HIGH	2.0	50	0.40
LOW (also used as LCS)	0.50	50	0.10

7.12.1. Acceptance criteria - The distilled standards should agree within ± 10% of the undistilled standard. If recovery is greater than 110%, and all the associated samples are ND, the sample results can be reported with an anomaly filed.

7.12.2. Corrective actions:

7.12.2.1. Reanalyze once, if pass, accept data.

7.12.2.2. If failed, find the cause of the apparent error, fix.

7.12.2.3. If no error found, redistill and reanalyze.

7.12.2.4. If reprep and reanalysis is not possible, a non conformance memo (anomaly) must be filed and the client contacted by the laboratory Program Manager.

7.13. Second-Source Stock Standard, (REF), 1000 mg/L: The second-source standard is prepared from a different lot or different manufacturer other than the source of the Calibration Stock Standard. Prepare and standardize a second-source standard using procedures as described in section 7.10.

7.14. Intermediate Reference Standard (IRS), 10 mg/L: Pipette 1.0 mL of the stock REF standard, 1000 mg/L into a 100 mL volumetric flask. Dilute to volume with 1% NaOH. Prepare fresh daily.

7.15. Working ICV (REF) standard, 0.20 mg/L: From IRS (10 mg/L), pipette 2 mL into a 100 mL volumetric flask. Dilute to volume with 1 % NaOH. This is used during the analytical procedure - distillation is not needed. Prepare fresh daily.

Note: For CLP only, this working ICV must be distilled along with the prep batch by adding 0.50 mL of the IRS into the distillation flask containing 50 mL of 1% NaOH prior to the distillation procedure. The %recovery must be $\pm$ 15% from the true value.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples should be collected in plastic or glass bottle. All bottles must be thoroughly cleaned and rinsed. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis (if required) and minimize waste disposal.

8.2. Samples must be preserved with 50% sodium hydroxide to pH $\geq$ 12 at the time of collection, approximately 2 mL per liter of sample.

8.3. All samples must be stored and refrigerated at 4° $\pm$ 2°C.

8.4. It is recommended that the samples are checked for chlorine content at the time of collection using KI-starch paper. If positive, add 0.1 N sodium arsenite solution a few mL at a time until presence of chlorine is no longer detected. Add additional 5 mL of 0.1 N sodium arsenite per liter of sample. If this is not added during collection time, then this check must be done prior to the reflux-distillation procedure. Document any positive interference in the benchsheets.

8.5. When properly preserved, cyanide samples can be stored for up to 14 days prior to sample preparation steps. For CLP samples, holding time is 12 days from sample receipt.

8.6. For holding time limitations, both CN forms must be done together, irregardless of the CN-T results. See section 10.7 and section 10.9.

9. QUALITY CONTROL

9.1. QC Batch - The QC batch is a set of up to 20 field samples plus associated QC samples that are similar in composition (matrix) and that are processed using the same procedures, reagents, and within the same time period.

9.2. Associated QC samples consistst of - Method blank (MB), Laboratory Control Sample (LCS), Matrix Spike and Matrix Spike Duplicate (MS/MSD). Sample Duplicate (DU) is also batched if the client specifically requested it.

9.3. Matrix type for MB and LCS:

9.3.1. For water samples, use 50 gm of 1% NaOH

9.3.2. For soil/solid samples, use 1 gm of Ottawa sand + 50 gm of 1% NaOH.

9.4. Method Blank, (MB) - One method blank must be prepared with every batch of similar matrix, not to exceed twenty (20) samples. A separate MB must be treated for each type of procedure.

9.4.1. Cyanide amenable to chlorination -

9.4.1.1. One MB is treated/chlorinated with the samples prior to the distillation process.

9.4.1.2. Another MB is not treated and distilled with the QC batch that underwent the treatment/chlorination process. This MB is treated and distilled as the MB for Total CN.

9.4.2. Total cyanide - One MB is distilled with prep QC batch.

NOTE: This MB can be shared by the QC prep batch described in 9.4.1.2 and from prep batch in section 9.4.4. as long as both batches have the same matrix and the total combined number of samples for both preps do not exceed 20 samples.

9.4.3. Weak and dissociable cyanide - One MB is treated and distilled with the each prep QC batch.

9.4.4. CARB 426 - One MB with similar matrix is distilled with prep QC batch. Prepared and treated like MB for Total CN.

NOTE: The matrix of the impinger solution and air sampling train is normally collected in 0.1N NaOH, however, since the final normality of the solution after distillation is in 1% NaOH, an MB and DCS in 1% NaOH should be used instead.

9.4.5. Acceptance Criteria - The concentration of cyanide in the method blanks must be less than the reporting limit. Verification, repreparation, and reanalysis of the blank and all associated samples are required unless the following conditions apply:

- The samples associated with the contaminated blank are "ND," i.e. no detectable analytes. Flag and narrate.

- The sample concentration is > 20X the blank concentration. Flag and narrate the appropriate samples.

9.4.6. Corrective actions:

9.4.6.1. Reanalyze once, if pass, accept data.

9.4.6.2. If failed, find the cause of the apparent error, fix.

9.4.6.3. If no error found, reprepare, redistill and reanalyze the entire batch.

9.4.6.4. If reprep and reanalysis is not possible, a non conformance memo (anomaly) must be filed and the client contacted.

9.5. Laboratory Control Sample (LCS) - An LCS of similar matrix is spiked with known amounts of KCN and is prepared the same way as the sample is treated with every QC batch. The concentration for each LCS is the same as the LOW distilled standard as described in Section 7.12.

9.5.1. Cyanide Amenable to Chlorination

9.5.1.1. One LCS is treated /chlorinated with the samples prior to distillation process.

9.5.1.2. Another LCS is not treated and distilled with the QC batch that underwent the treatment/chlorination process. This MB is treated and distilled as the MB for Total CN.

9.5.2. Total Cyanide - One LCS is distilled with prep QC batch.

NOTE: This LCS can be shared by the QC prep batch described in section 9.5.1.2 as long as both batches have the same matrix and the total combined number of samples for both preps do not exceed 20 samples.

9.5.3. Weak and dissociable cyanide - one LCS is treated and distilled with each prep QC batch.

9.5.4. For CARB 426 - same as in section 9.5.2 or for limited volume of sample, see section 9.6.

9.5.5. Acceptance Criteria - The LCS recovery for all types of CN except as noted below must be [true value] $\pm$ 10 % of the true value. Exception: if the LCS is

high and all of the associated samples are ND, the results can be reported with an anomaly filed.

9.5.5.1.For Cyanide amenable to chlorination only:

9.5.5.1.1.For treated/chlorinated/distilled LCS, the recovery is approximately between 0%-25% which is an indicative that the chlorination efficiency to drive CN by chlorination is about 75% to 100%.

9.5.5.1.2.For untreated/distilled LCS, the criteria is the same as for Total CN which is 90%-100% recovery.

9.5.6. Corrective actions:

9.5.6.1. Reanalyze once, if pass, accept data.

9.5.6.2. If failed, find the cause of the apparent error, fix.

9.5.6.3. If no error found, reprepare, redistill and reanalyze the entire batch.

9.5.6.4.If reprep and reanalysis is not possible, a non conformance memo (anomaly) must be filed and the client contacted.

9.5.7. **LCS for CLP samples only** - Add 0.5 mL of the 10 mg/L (IRS - see section 7.15), into the distillation flask containing the 50 mL of 1% NaOH prior to the distillation procedure. True value is 0.10 mg/L.

9.6. Duplicate Control Sample (DCS) - is an LCS pair or LCS duplicate. Same preparation, criteria, and corrective action as the LCS. Performed only when client required it or there is a volume limitations where an MS/SD or MS/DU cannot be performed in the same QC batch.

9.6.1. A DCS pair is normally use for CARB 426 due to sample volume limitations.

9.7. Matrix Spike and Matrix Spike Duplicate (MS/MSD) - A matrix spike (MS) is a replicate portion of one of the sample in the QC batch that is spiked with known amounts of KCN. A matrix spike duplicate (MSD) consists of an additional portion of the same sample used to prepare the MS. A pair of MS/SD is prepared with each QC batch for every type of extraction procedure that the samples/MB/LCS underwent. Both MS/SD are spiked the same way as the LCS.

9.7.1. Add 0.50 mL of the 10 mg/L standard (ICS) to MS/MSD sample aliqout of 50 gm or portion thereof, diluted to 50 gm with 1% NaOH. The spike level is 0.10 mg/L.

9.7.2. For Cyanide Amenable to chlorination, an MS/MSD will only be performed if the client specifically requested it, otherwise an MB/LCS/DU treated/distilled and an MB/LCS untreated/distilled will be the batch QC for this determination.

9.7.3. Acceptance Criteria - The MS/MSD recovery limit is 75-125% with an RPD limit of 20%. The batch is not controlled by the MS/SD recovery but with the MB and LCS. If the %RPD is acceptable, no further reanalysis needed but an electronic anomaly must be filed.

9.7.3.1. For MS/SD criteria for CN-AMEN, the recovery is calculated as in CN measured after chlorination process (with recovery of about 0% to 25%), subtracted from the true value of 100%, therefore the calculated MS/SD is about 75% to 100%. This percentage represents the % of spike added that was driven off by the chlorinaton process. Percent RPD is set at 50%. (There is no historical data for this matrix and also not required by the method source.

9.7.4. Corrective Actions, ONLY if both limits for MS/SD and %RPD criteria has failed:

9.7.4.1. Reanalyze once, narrate and file an anomaly.

9.7.4.2. If the %RPD is 50% or greater, evaluate data and impact of the MS/SD failure.

9.7.4.3. If there is no impact to the data, accept results and anomalized.

9.7.4.4. If there is a clear spiking error or distillation set-up failure, redistill and reanalyze the MS/SD and the sample that was spiked.

9.8. Sample Duplicate (DU) - a sample duplicate (DU) is a second aliqout sample taken from the same sample container whenever possible, that is processed with the first aliquot of that sample. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the preparation and analytical process. Sample duplicate (DU) are performed when requested by the client and for cyanide amenable to chlorination pre-treatment process only. Criteria - 20% RPD.

9.9. High and Low Concentration, Distilled Standards - It is recommended that at least two standards (a high and a low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. This requirement is only applicable when distilling for Total cyanide and/or when distilling a batch of samples that underwent the chlorination process for cyanide amenable to chlorination.

9.9.1. Acceptance criteria - The distilled standards should agree within ± 10% of the undistilled standard. If recovery is greater than 110%, and all the associated samples are ND, the sample results can be reported with an anomaly filed.

9.9.2. Corrective actions:

9.9.2.1. Reanalyze once, if pass, accept data.

9.9.2.2. If failed, find the cause of the apparent error, fix.

9.9.2.3. If no error found, redistill and reanalyze.

9.9.2.4. If reprep and reanalysis is not possible, a non conformance memo (anomaly) must be filed and the client contanted by the laboratory Program Manager.

9.10. Standard Curve for samples with sulfide only - It is recommended that at least five standards and a blank be treated and distilled the same way as the samples by method of standard additions (example: lead carbonate must be added to the standards also).

9.10.1. The correlation coefficient must be ≥ 0.995.

9.10.2. Corrective action:

9.10.2.1. Reanalyze once, if pass accept data.

9.10.2.2. If failed reprepare, redistill and reanalyze the entire batch.

9.11. Method specific criteria - For cyanide amenable to chlorination, if the chlorinated aliquot shows more cyanide than the unchlorinated aliquot, a corrective action and/or a discussion in the final report is required. Also see section 10.6.1.

9.11.1. Iron-cyanides can cause this to occur. Weak acid dissociable cyanide would be a better method for these types of samples and should be recommended to the client. Notify area leader or project manager.

9.12. Criteria for calibrations and analytical events are described in Section 11.

10. SAMPLE PREPARATION PROCEDURES

10.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. Depending on the severity of the change and prior arrangements, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

10.2. The different forms of cyanide are differentiated by either pretreatment steps ("Cyanide Amenable to Chlorination") or by different distillation procedures ("Weak and Dissociable Cyanide").

10.3. The preparation and distillation portion of this method is restricted to perform by, or under supervision of analyst experienced in the cyanide-reflux distillation procedure and associated preliminary treatments.

10.4. **Preliminary testing of all samples prior to any treatment and/or distillation:**

10.4.1. ***For aerosol and gas emissions only*** which are requesting CN determination by Method CARB 426, volumes of the entire samples and/or all fractions must be measured volumetrically first prior to any treatment or measurements that follow. Record the type of fraction and the measured volume to the prep benchsheets. The volume measurements will be used for final calculations after the CN determination.

10.4.2. Check pH of samples with pH test strips. Samples should have a pH of $\geq$ 12. File a non-comformance memo (anomaly) for improperly preserved samples. Soil pH determination is not applicable for soil samples.

10.4.3. Check for Sulfide content using lead acetate paper. Moisten the paper with 2-3 drops of acetate buffer, and then place 1 drop of water sample on the paper. A dark color indicates a positive test for Sulfide. For *soil samples*, weigh 1 gm of wet sample into the distillation flask, add 50 gm of 1% NaOH, swirl for 5 minutes and check Record the results a (+) positive or (-) negative on the bench sheet. See section 10.5.1 for removal of Sulfide interference.

10.4.4. Check for Chlorine content of the sample by placing a drop of water sample to the KI paper strips. For *soils samples*, weigh 1 gm of wet sample into the

distillation flask, add 50 ml of 1% NaOH, swirl for 5 minutes and check. A dark color indicates that chlorine is present in the sample. Record the results as (+) positivie and (-) negative) on the bench sheet. For removal of chlorine interfence, see section 10.5.

10.5. **Removal of interferences prior to distillation** (For CN-Total, CN-amenable, and CN by CARB 426):

10.5.1. For samples that contain Sulfide only - Samples that are tested "positive" for Sulfide must be treated and distilled in a separate QC batch. Per method, it is recommended that at least five CN standard curve points and a blank undergo the same treatment as with samples positive for sulfide. Treat these standards and blank the same way as the samples (example: addition of lead carbonate).

10.5.1.1. For *water samples*, pour a portion of the sample into a 500 mL erlenmeyer flask. Treat enough volume for replicates, MS/SD, etc.

10.5.1.2. Add a few scoopfull of lead carbonate, and swirl. Sulfide present in the sample will precipitate to form lead sulfide.

10.5.1.3. Keep adding lead carbonate powder until the lead acetate paper indicates that sulfide is no longer detected. Add an additional 0.5 gm of lead carbonate.

Note: Lead carbonate is used instead of bismuth nitrate to minimize interference from NO_3. It is used instead of cadmium carbonate, because the lead, although toxic itself, is less toxic than cadmium.

10.5.1.4.Decant and filter the solution using Whatman #40 filter paper. The clear liquid can be measured and used for treatment or distillation for CN determination. Discard the precipitate into the waste stream designed to collect sulfide.

10.5.1.5. For *soil samples*, the elimination of interferences are done after the sample is placed in the distillation flask and prior to the treatment or distillation procedure. Treat the sulfides in the sample by following section 10.5.1.2 to 10.5.1.3. Filtration is not needed.

10.5.2. For samples that are positive for chlorine interference - Oxidixing agents such as chlorine decompose most cyanides and must be eliminated prior to the treatment or distillation procedure.

10.5.2.1. *For water*, weigh 50 gm of sample or a portion of the sample diluted to 50 gm with 1 % NaOH into the distillation flask. Samples positive for sulfide must be treated for sulfide first before treating the treated samples for chlorine interference.

10.5.2.2. *For soils*, weigh 1 gm of soil into the flask then add 50 mL of 1% NaOH.

10.5.2.3. Add 0.1 N sodium arsenite solution a few mL at a time until a drop of the sample or the solution no longer indicates the presence of chlorine using KI-starch paper. Add an additional 0.5 mL of the 0.1N sodium arsenite.

10.6. For *cyanide amenable to chlorination*, two identical sample aliquot is needed to determine cyanide amenable to chlorination. One portion is treated by chlorination prior to the distillation procedure which is detailed in section 10.7. The CN detected after the chlorination process are tightly bind cyanides that did not decompose during the chlorination process. The other portion is not treated but is distilled the same manner as for total cyanide distillation, see section 10.7. The CN results that was detected after chlorination is subtracted from the total CN content of the sample. The difference between the two is termed as cyanide amenable to chlorination, which is the CN content of the sample driven off by the chlorination process.

10.6.1. For samples with no interference, CNAMEN (cyanide amenable to chlorination) is equal to or less than the CN-T (total cyanide). However, matrix interference present in the sample can affect the chlorination process, where the CN measured after chlorination comes out higher than the total CN. In cases such as this, the only corrective action is to reanalyze both distillate for confirmation. The result is reported as ND, footnoted and accompanied by an electronic non-conformance memo (anomaly).

10.6.2. If the distilled total cyanide is found to be ND "Not Detected" at the reporting limit, the cyanide amenable to chlorination may not need to be done. This must only be done with the consent of the area leader, the client project manager and the client. If this is done, the result should be entered as "NA" not applicable, an anomaly must be filed, and at no cost to the client.

10.6.3. If CN-T is above the reporting limit or above the client's action level, then the CNAMEN must be done. See section 10.7.

10.7. Cyanide Amenable To Chlorination only (Sample Pretreatment prior to Distillation)

Caution : The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride (CNCl); therefore it is necessary that this procedure be performed in a hood.

10.7.1. This treatment must be performed under amber light. $K_3[Fe^{-}(CN)_6]$ may decompose under UV light and may test positive for cyanide amenable to chlorination if exposed to fluorescent lighting or sunlight.

10.7.2. Pour 50 gm of water sample or portion diluted to 50 gm into a beaker. Add calcium hypochlorite solution dropwise while agitating and maintaining the pH between 11 and 12 with 5% (1.25N) NaOH until excess chlorine is present as indicated by KI-starch paper turning blue.

10.7.2.1. *For soil samples*, weigh 1 gm of soil into the flask, add 50 gm of 1% NaOH then add the sodium hypochlorite solution.

10.7.3. Agitate the sample for 1 hour with constant mixing by using a magnetic stirrer. Monitor presence of chlorine by checking the solution every 10 minutes with KI-starch paper. A distinct blue color on the test paper indicates a sufficient chlorine level. If needed, add additional calcium hypochlorite solution. Maintain pH of the solution between pH 11-12 with 5% NaOH.

10.7.4. After one hour, add 0.1 mL portion of 0.1N sodium arsenite to the sample until the KI-starch paper no longer indicate presence of chlorine (must be clear). Add 0.5 mL excess sodium arsenite to ensure presence of excess reducing agent.

10.7.5. If water samples tested positive for Sulfide, add one small scoop full of lead carbonate to the beaker. Mix for 3 minutes. Use lead paper to check for presence of sulfide. Keep adding lead carbonate until all traces of sulfide are no longer detected.

10.7.5.1. For soils samples tested for sulfide, treat the solution that was previously chlorinated/dechlorinated by adding lead carbonate powder until all traces of sulfide are no longer detected in the solution. Filtration is not recommended. The treated content is now ready for distillation. See section 10.9.

10.7.6. Filter out the precipitate prior to transferring the contents into distillation flask quantitatively, rinsing with reagent water. See section 10.9 for distillation procedure.

10.8. All associated prep QC samples required for each determination must be batch and treated the same way as the samples see section 9.

10.9. Distillation Procedure for CN-total, CN by CARB 426 and CN Amenable After the Chlorination Process:

10.9.1. The procedure described here utilizes a midi-distillation apparatus requires a sample aliquot of 50 mL or less for aqueous samples and one (1) gram for solid materials.

10.9.2. For samples already treated for interferences and chlorinated for CNAMEN, add 2-3 boiling chips and proceed to section 10.8.6.

10.9.3. For water samples: Pour 50 mL of sample, or an aliquot diluted to 50 mL with 1% NaOH, into the distillation flask along with 2-3 boiling chips.

10.9.4. For solid samples: Weigh 1.0 gm of sample (to the nearest 0.01 gm) into the distillation flask and add 50 mL of 1% NaOH

10.9.5. Place 10 mL of (1.25N) sodium hydroxide and 10 mL of deionized water into the gas absorption tubes.

10.9.6. Connect the boiling flask, condenser and absorber tubes. Ensure that all connections and joints are tightly held together, this can be done by dripping a few mL of reagent water to each joint. Ensure that the fume hood is on.

10.9.7. Turn on the vacuum pump and chiller. Adjust the individual vacuum flow rate of approximately 2-4 bubbles per second in each distillation flask. Verify that there are no leaks in the system by looking onto each joints (must be wet) for bubbles or listening to sucking noises. The flow rate may not remain constant during the distillation, readjust as needed.

10.9.8. Add 2 mL sulfamic acid solution (7.5.5) through the inlet tube. Allow to mix for 3 minutes.

10.9.9. Slowly and carefully, add 5 mL of 50% H_2SO_4 through the inlet tube. Rinse the tube with reagent water and allow to mix for 3 minutes.

NOTE: The volume of acid added must be sufficient to bring the sample/solution pH to below 2. Check the pH of the acidified solution by dipping the tip of a glass transfer pipet into the solution through the inlet tube. CAUTION: The system must

be intact during this process, once the H_2SO_4 is added into the solution, generation of HCN gas starts.

10.9.10. Add 2 mL of 2.5M $MgCl_2$ solution and mix. If excessive foaming is observed, add additional magnesium chloride. Rinse down the inlet tube with a few mL of reagent water.

10.9.11. Turn on the heating mantle. Heat the solution to boiling, adjust the vacuum flow to prevent solution back up. Ensure that the water chiller is working and flowing freely through the system by touching individual condenser (it must be cool to touch).

10.9.12. Distill-reflux the solution for 1.5 hour. Turn off the heat and continue the vacuum for additional 15 minutes. The flasks should be cool at this time. NOTE: Do not turn off the vacuum if the flasks are still hot or warm to prevent back pressure that can result to sample spilling through the thistle tube.

10.9.13. Remove the absorber solution and transfer the solution into a 100 mL plastic distillate container previously placed at the top loading balance. Rinse with reagent water the inside and outside of the bubbler into the absorber tube, add the rinsate into the plastic container. Dilute the content to 50 gm with reagent water. Record the final weight on the prep bencsheets.

10.9.14. Place each batch of distillates in a tray or box labeled with the QC lot number. Store the distillates at 4°C until they are analyzed.

10.9.15. Distillation clean up.

10.9.15.1. Raise the cold-finger condensers and rinse into the distillation flasks with deionized water. then remove the flask and rinse their contents into the carboy labelled "Cyanide Waste". Residue not removed by this method must be scrubbed out.

10.9.15.2. Rinse absorber tubes with deionized water.

10.9.16. The distillate is ready for analysis using automated colorimetric determination, see section 12.

10.10. Distillation Procedure for Weak and Dissociable Cyanide

10.10.1. The distillation procedure is the same as in section 10.9 with minor differences. For weak and dissociable cyanide, the samples are slightly acidified to pH 4.5 to 6.0 to liberate free and weak hydrogen cyanide (HCN) while for total cyanide and cyanide amenable to chlorination, the samples and/or treated samples are acidified to less than pH 2 to liberate free, complex and tightly bound HCN.

10.10.2. Follow section 10.9.1 to 10.9.8 (Addition of Sulfamic acid is omitted since nitrate and nitrite do not interfere).

10.10.3. Instead of H_2SO_4 and $MgCl_2$ reagents, add:

10.10.3.1. Add 2 mL of each of the acetate buffer and zinc acetate solution through the inlet tube.

10.10.3.2. Add 2-3 drops of methyl red indicator. Rinse inlet tube with reagent water and let air mix the contents.

10.10.3.3. Add acetic acid (1 + 9) solution dropwise through the inlet tube until a pink color persists. If the color of the solution is already pink, addition of acetic acid in not necessary.

10.10.4. Follow steps from section 10.9.12 to 10.9.14.

11. CALIBRATION AND STANDARDIZATION

11.1. For instrument set-up, operation, and calibration of Lachat Ion Auto-analyzer, see Section 12.

11.2. Calibration must be performed daily or once every 24 hours or each time that the instrument is off or non-operational for more than two hours.

11.2.1. Working Calibration Curve, 0.01-0.50 mg/L: All standard solutions, samples dilutions and distillate must be in the final NaOH normality of 0.25N NaOH. Use 1 % NaOH solutions when preparing standards and diluting the samples/distillate. Prepare fresh daily. See section 7.11.1

11.3. For low-level curve, the linear range is 0.005-0.20 mg/L. See section 7.11.2.

11.4. Standard curve for samples with sulfide

11.4.1. It is imperative that all standards be distilled in the same manner as the samples using the method of standard additions (for example, lead carbonate must also be added to the standards). It is recommended that at least five standards be distilled (final concentration = 0.01 - 0.50 mg/L) See section 9.10 for criteria and acceptance.

11.4.2. Preferably in a separate analytical run, analyze the treated/distilled standard curve as the calibration curve, followed by the treated/distilled prep QC and samples.

11.4.3. As a convenience, the analyst may choose to analyze treated/distilled, untreated/distilled samples within the same analytical run sequence (autosampler tray). However, the analyst is required to quantitate the samples using a curve appropriate to the procedures used to process samples (Section 11.2).

11.4.3.1. After the analysis, recalculate the curve for the treated/distilled standards using the area counts of each standard points. Re-plot the curve.

11.4.3.2. Using the new curve, recalculate concentrations of samples tested with sulfide against the curve of the treated/distilled standards.

11.5. Initial Calibration Curve Acceptance Criteria - The correlation coefficient of the curve must be $\geq$ 0.995. Corrective action - reanalyze once, identify problems, correct, and/or remake the standards if needed, and recalibrate.

Note for Calibration standards of samples with sulfide only: If the standard curve for samples with sulfide (distilled in same manner as the samples) is not acceptable, the entire prep batch including the curve must be reprepared. If the second preparation does not give an acceptable calibration curve, the samples may be reanalyzed on an undistilled calibration curve with a discussion in the final report narrative.

11.6. Initial Calibration Checks - Immediately after the initial calibration, the calibration is verified using a second-source initial calibration verification (ICV/REF) standard (true value of 0.20 mg/L) and an initial calibration blank (ICB- a reagent blank, 1% NaOH). The measured result for the ICV must be within 10% of the expected value, and the ICB must be less than the reporting limit. See section 11.8 for corrective actions.

11.6.1. For CLP, the ICV/REF must be distilled with the batch as LCS low and analyzed as ICV. True value is 0.10 mg/L. Recovery acceptance criteria per CLP limit is within 15 % of the true value.

11.7. Continuing Calibration Checks - A continuing calibration verification (CCV) standard and a continuing calibration blank (CCB) are required after every 10 or fewer samples and at the end of the run. The CCV can be either the ICV or one of the mid level calibration standards such as the 0.2 mg/L standard. The CCV result must be within 10% of the expected value. The CCB must be less than the reporting limit. See corrective action on section 11.8

11.8. Corrective action for failed analytical QC (when applicable)

11.8.1. Reanalyze once, if failed proceed to 11.8.2. If pass, continue with the analysis.

11.8.2. Check for contamination in the reagents and standards.

11.8.3. Be sure all reagents and standards were made correctly and have not exceeded their expiration dates.

11.8.4. Check system for obvious problems such as plugs, leaks, and pump tubes.

11.8.5. Once the cause has been determined, the instrument must be recalibrated and all samples since the last successful calibration check must be reanalyzed.

11.9. Acceptance criteria and corrective action for prep QC batch is detailed in section 9.

12. ANALYSIS OF DISTILLATES

12.1. To obtain colors of comparable intensity, it is essential to have the same NaOH content in both the samples and the standards which is 0.25N NaOH or 1% NaOH.

12.2. Each QC lot should be analyzed together as a group. Dilute any samples that are greater than the high standard and reanalyze. All dilutions must be performed with 1% sodium hydroxide. See analytical sequence.

12.3. The analysis portion of this method is restricted to use by, or under supervision of, analysts experience in the operation of Lachat Auto-Analyzer and the interpretation of its results. Also see SOP for Lachat Operation (SOP #SAC-WC-0051).

12.4. Instrument Start-Up: The instrument is to be set up and operated in accordance to the manufacturer's instructions for Lachat Quickem Automated Flow Injection Analyzer. For complete list of apparatus and instrument spec, see section 6.1

12.4.1.1. Inspect manifold for proper connections. Be sure that there is sufficient volume for all reagents and that none is expired.

12.4.1.2. Turn on the power to all modules and the software system. Be sure that the lamp on the colorimeter is on. The heating bath control should be set at 45°C. Allow temperature to equilibrate before beginning analysis.

NOTE: All waste generated during the analysis must be collected in CN waste labelled containers.

12.4.1.3. Establish water baseline by placing all reagent lines into a 1 Liter erlenmeyer flask containing 500 mL of reagent water . Fasten down the pump tube cassettes. Pump reagent water at normal flow for at least 5 minutes until all air bubbles have been pumped out of the system. **Note**: This step is necessary but is not required, in most cases this is use as a preliminary assurance that the manifold is free of debris from prolonged storage. This is also a good comparison against reagent baseline. If this is not done, skip this step and proceed to section 12.4.1.4.

12.4.1.4. Establish reagent baseline by placing all reagent lines into the proper reagent containers. Fasten down the pump tube cassettes. Pump reagents at normal flow until all air bubbles have been pumped out of the system.

12.4.1.5. Load the CYANIDE method in the computer. It will automatically switch to background and display the output from the colorimeter.

12.4.1.6. Continue pumping at normal flow until a stable baseline is obtained. Adjust baseline and gain to proper position.

12.4.1.7. Maximize the instrument "gain" by using the highest standard point of the curve. Baseline may have to be adjusted again to compensate for this change.

12.4.2. LACHAT Analysis

12.4.2.1. Fill autosampler tray with sample cups containing either the distilled standards (batches with sulfide interference) or undistilled working standards. Arrange the standard cups in decreasing order and place them in the tray positions that are designated for standards only.

12.4.2.2. The samples can be loaded onto the autosampler at the beginning or as the calibration standards are being analyzed. Fill sample cup in the #1 position with an ICV and the rest with all the associated prep QC batch and analytical standards that correspond to the instrument log or entry.

12.4.2.3. Start the analysis. The instrument will analyze the standards first, automatically calculate the "*r*" value and then will allow you to accept or reject the calibration curve. If the curve is acceptable, the instrument will proceed to analyze the samples in the tray.

12.4.2.4. Results will be automatically calculated. The instrument should be monitored periodically to make sure that standard checks are in control and no other problems arise. Otherwise, the instrument will run unattended and signal with a beep at the end of the run.

12.4.2.5. Check the printout for any off-scale samples. If dilutions are necessary, they must be made with 1% NaOH.

12.4.2.6. If additional samples are to be analyzed, reload the autosampler and enter the new tray information. Since the instrument is already calibrated, you may proceed directly to analysis of the new samples and corresponding QC requirements.

12.4.3. Instrument Shut-Down

12.4.3.1. Place all reagent lines in deionized water and pump at normal speed for 5 to 10 minutes. Then remove the lines from the water and pump the system dry (another 5-10 minutes).

12.4.3.2. Drain the water out of the wash vessel/receptacle.

12.4.3.3. Turn off all modules and unfasten the pump tube cassettes from the pump.

12.4.3.4. Remove the CN manifold and tubings for storage.

12.4.3.5. Clean up the work area and replace any reagents that have been depleted.

13. DATA ANALYSIS AND CALCULATIONS

13.1. All routine CN calculations are performed by either the LACHAT software, provided dilutions and other information have been correctly entered.

13.2. Results for samples treated for sulfide are subject to calculation by the method of additions based on the single-point addition.

13.3. Cyanide amenable to chlorination:

Unchlorinated Aliquot result - Chlorinated Aliquot result = Amenable Cyanide.

13.4. Total Cyanide for CARB 426 (Gas emissions from stationary sources):

Other information needed - volume measurements as received from the client and taken prior to the distillation procedure.

CN, in mg/S (sample) = CN found * (mg/L) × total volume of the sample (in L)

where:

* CN found, from the instrument print out.

Volume = total sum of all the individual fractions combined and converted to liter (L)

13.5. Reporting.

13.5.1. Reporting units are mg/L for aqueous samples and mg/kg for nonaqueous samples.

13.5.2. For CARB 426, the unit is in mg/sample.

13.5.3. Samples less than the reporting limit are reported as ND.

13.5.4. Report print out should include standard tracking number for both standard curve and reference standards, date and initial of the analyst and other manual calculations performed.

13.5.5. Data package for Level 2 review should include all the necessary preparation information, analytical results, instrument run log, level 1&2 review checklist, and applicable narrative or anomalies. All results must be entered in lims.

14. METHOD PERFORMANCE

14.1. Training Qualifications

14.1.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and had the required experience.

14.1.2. Both prep and analytical chemists must passed the analyst certification training and acceptance criteria prior to performing actual sample preparation and analysis.

15. POLLUTION PREVENTION AND WASTE MANAGEMENT

15.1. Lead carbonate is added for sulfide removal instead of cadmium carbonate in order to minimize the use of pollutants.

16. WASTE MANAGEMENT

Waste generated in this procedure must be segregated and disposed of according to the wastestreams detailed in the facility hazardous waste management procedures, Attachment B, Chemical Hygiene Plan, Section WS002, Table 1, current edition..

16.1. All sample waste generated during and after the distillation procedure including analyzed distillates are collected in designated carboys and rotated to the Hazardous Waste disposal area.

16.2. Analytical waste are collected in designated CN waste stream and/or can be combined with other waste stream that are compatible with CN analytical waste.

17. REFERENCES

17.1. EPA Method 335.4, Revision 1.0, August 1993.

17.2. SW-846 Methods 9010B (distillation portion only) and 9012A, Update III, December 1996.

17.2.1. SW-846 Methods 9010, 9010A, and 9012.

17.3. Methods 4500 CN^- B, C, E, G, and I, Standard Methods for the Examination of Water and Wastewater, 19th Edition, 1995.

17.4. CLP SOW ILM0 3.0, Method 335.2 CLP-M. Description - Total Cyanide on Water and soils by MIDI-distillation followed by Semi-automated colorimetry.

17.5. State of California Air Resource Board, CARB 426, January 1987.

17.6. Lachat Quickem Method No. 10-204-00-1-A, October 1993.

17.6.1. EPA Method 335.3, March 1983.

17.6.2. SM 14th Editon, APHA-AWWA-WCPC, Part 413D, pp. 370-372.

18. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

18.1. Deviations from source method and rationale.

18.1.1. Cyanide amenable to chlorination is sometimes referred to as "Free Cyanide." The weak acid dissociable method also determines "Free Cyanide" and it is important to distinguish between the two due to the different sample preparation required.

18.1.2. The reflux time for Cyanide Amenable to Chlorination and Total Cyanide has been changed to 1.5 hours from 1.0 hours contained in Method 9012 of SW-846 to accommodate the reflux time for samples requiring distillation under the Clean Water Act (EPA Method 335.4).

18.1.3. The linear range and the distillation procedure in this SOP is adopted from EPA 335.4 with minor modifications as stated below.

18.1.3.1. Ten mL of 5% NaOH and 10 mL of reagent water was used in the adsorber tubes instead of 50 mL of 1% NaOH. The final volume of the solution is adjusted after the distillation procedure to 50 mL using reagent water as rinsate. The final content of NaOH in the distillate is the same which is 1% NaOH.

18.1.4. The sample/reagent ratio criteria during the distillation procedures of the other method sources are met, eventhough the distillation set-up in this SOP required a reduced sample volume. Other modifications made are:

18.1.4.1. The 2:1 concentration ratio from initial raw sample volume to final distillate collected is not adopted here. The raw sample to distillate collected in this SOP is 1:1. The reporting limit is achieved using 1:1 ratio.

18.1.4.2.Lead Carbonate is used to eliminate sulfide interference instead of using Bismuth Nitrate or Cadmium Carbonate. Lead Carbonate is less toxic than Cadmium Carbonate and Bismuth Nitrate can introduce Nitrate interference to the sample.

18.1.5. The analytical portion of this SOP is adopted from Lachat Quickem Automated Ion Analyzer Method which is compatible to automated colorimetric reaction recommended in Methods SW-848 9012A, Standard Methods, CLP 335.2, etc. All analytical reagents needed are prepared according to Quickem Method 10-204-00-1-A.

18.1.5.1.Analytical determination by Titrimetric procedure as stated in CARB 426 was not adopted, as well as the blank correction procedure.

18.1.6. Calibration is verified with an independently prepared check standard (ICV) with every analytical run and a CCV is run after every 10 samples, instead of for every 15 samples as given in SW-846 Method 9012.

18.2. Changes from the Previous Revisions:

18.2.1. All revisions for SOP No. LM-CAL-1034, LM-CAL-1053, LM-CAL-1101, LM-CAL-1102 and Draft CARB 426 are replaced and combined into this SOP.

18.2.2. Format is changed from Enseco to Quanterra format.

18.2.3. Contents were expanded, revised and updated to reflect the most current versions of method source and QA Policy 003.

18.2.4. Reagents preparations and strength were changed to reflect the most current source method recommendations. Example: 18 N Sulfuric Acid is used instead of concentrated H_2SO_4.

18.2.5. The LCS limits (non-CLP) are changed to 90-110% based on method requirements for high and low distilled standards. Future limits will be changed to reflect laboratory's performance of this method using historical data points.

18.3. Appendix I: Cyanide Preparation Example Bench Sheet

18.4. Appendix II: Cyanide Distillation Apparatus

18.5. Appendix III: Cyanide Manifold LACHAT Schematic

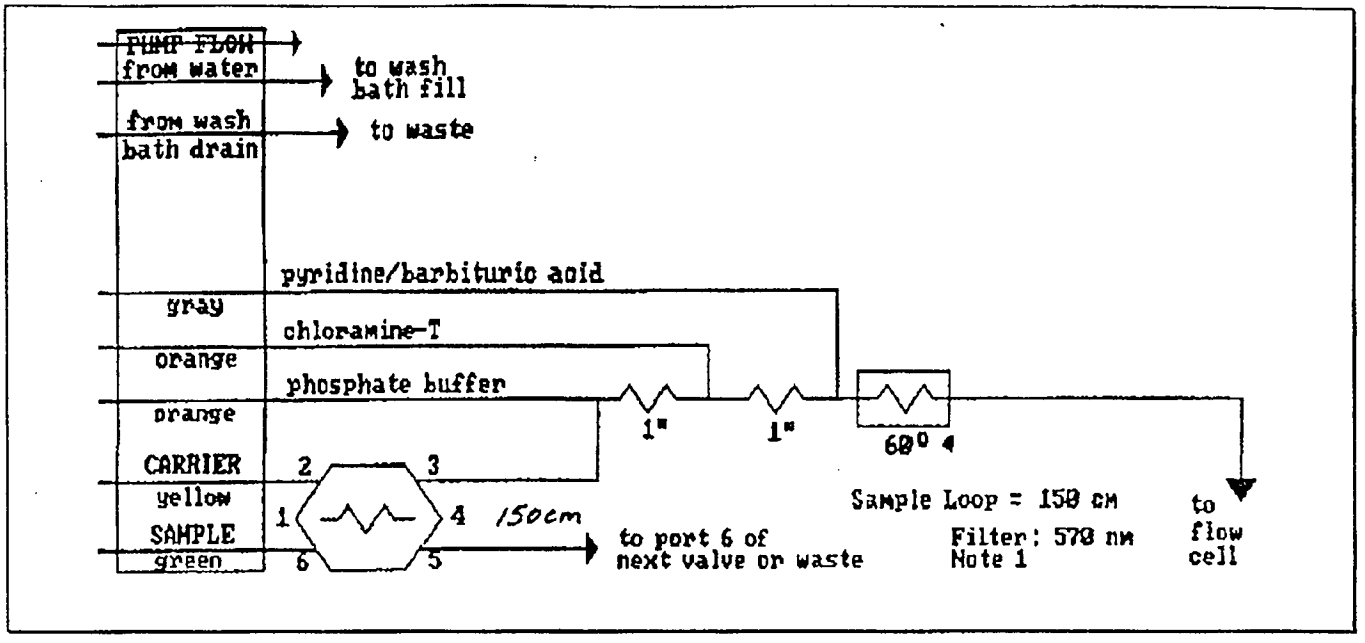
18.6. Appendix IV: LACHAT Flow Diagram

Appendix I: Cyanide Preparation Example Bench Sheet

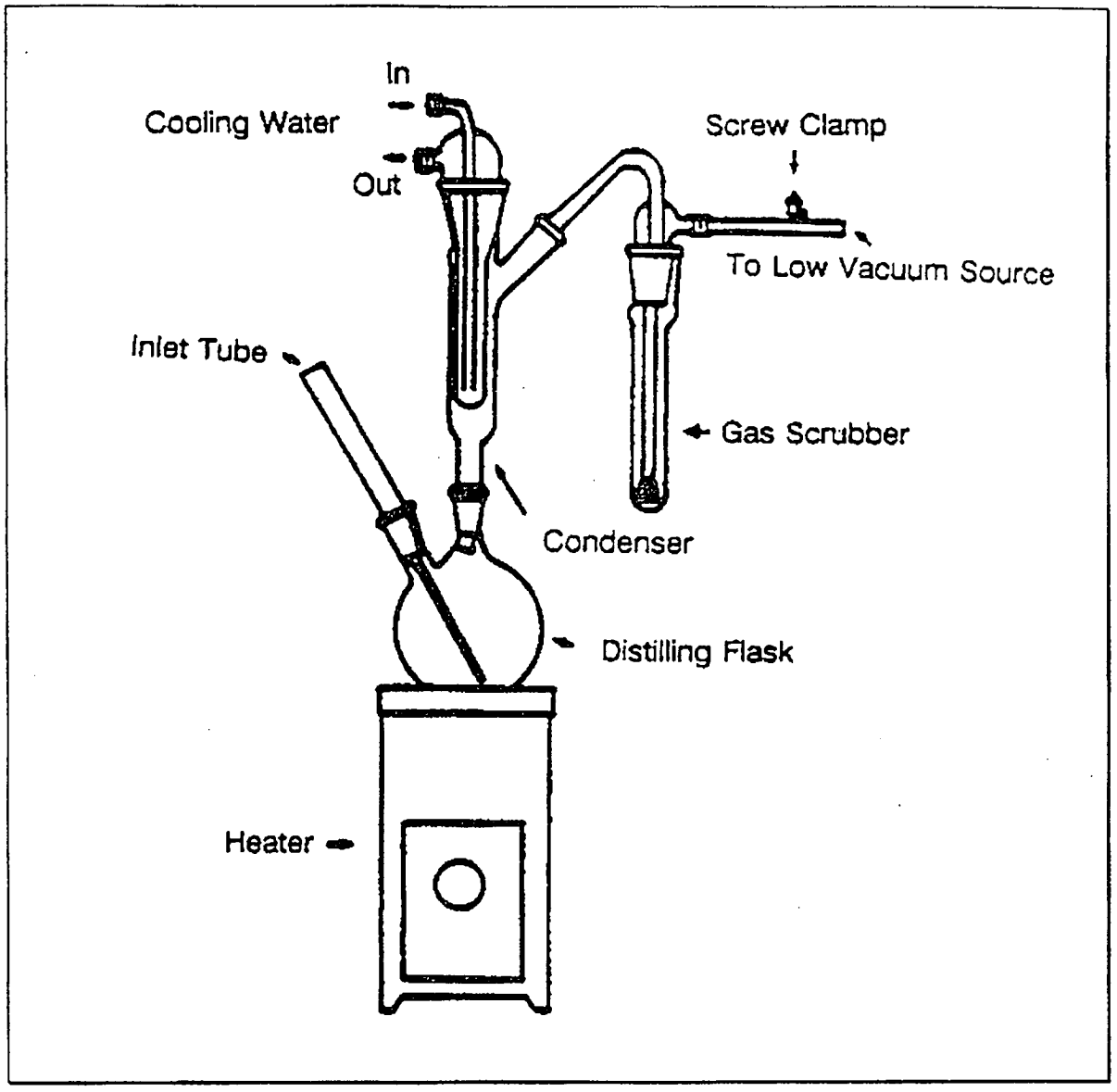
Laboratory Bench Sheet

Wet Chemistry Sample Preparation

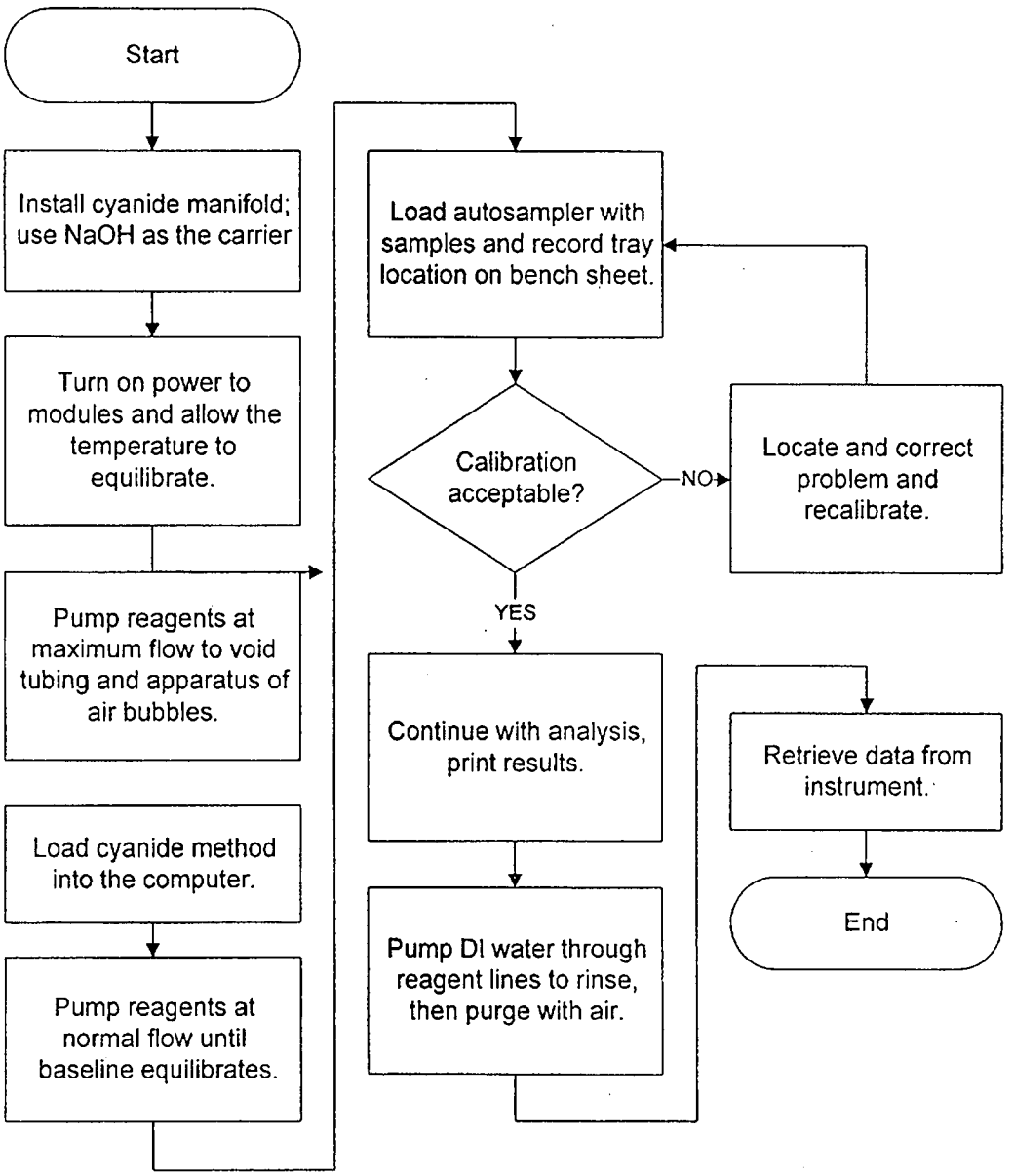
Appendix III: LACHAT Manifold Schematic



Appendix IV: Cyanide Distillation Apparatus



Appendix VI: LACHAT Flow Diagram



QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: SULFIDE

(SUPERSEDES: ENSECO SOP #LM-WALN-1330 (REVISION 1.0))

Prepared by: _____

Reviewed by: _____
Technology Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental Health and Safety Coordinator

Approved by: _____
Laboratory Director

Proprietary Information Statement:

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of the concentration of Sulfide in waters, liquids, solids, and sludges. It is based on SW846 Method 9030A and Methods for Chemical Analysis of Water and Wastes (MCAWW) 376.1. The working range is 1 to 30 mg/L for waters and 50 to 1500 mg/kg for solids and sludges.

1.2. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory QA department.

2. SUMMARY OF METHOD

2.1. An excess of iodine is added to a sample which oxidizes the Sulfide to sulfur under acidic conditions. The excess iodine is back titrated with sodium thiosulfate.

3. DEFINITIONS

3.1. Refer to the glossary in the Quality Assurance Management Plan (QAMP).

4. INTERFERENCES

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

4.2. Reducing substances such as thiosulfite, sulfites, and various organic compounds cause interferences, but treatment with zinc acetate solution will eliminate some of these interferences. (Use approximately 15 drops of 2 N zinc acetate per 500 mL of sample if not already preserved with it.)

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all Quanterra associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive: Hydrochloric Aicd, Sodium Hydroxide**

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

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

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Volumetric pipets: various

6.2. Buret: 25 mL Class A

6.3. Erlenmeyer flasks: 500 mL

6.4. Graduated cylinder: 250 mL

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

6.6. Volumetric flasks: various

6.7. Vacuum pump, filter and flask

6.8. Whatman 934-AH filters

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. (1:1) Hydrochloric Acid: Add 250 mL concentrated hydrochloric acid (HCl) to 250 mL of reagent water.

7.1.2. Starch Indicator: Add 10 mL of reagent water to 5 g starch (potato) and mix. Add starch mixture to 500 mL of boiling reagent water. Mix, cool, and store in a well-labeled squirt bottle. Alternately, use purchased starch solution.

7.1.3. 0.025 N Sodium Thiosulfate: Add 0.4 g NaOH and 6.205 g of sodium thiosulfate ($Na_2S_2O_3 \bullet 5H_2O$) to 500 mL of reagent water in a 1 liter volumetric. Dilute to volume with reagent water. Store in a dark container. Also available commercially.

7.1.3.1. Standardization of 0.025 N Sodium Thiosulfate Solution: To make 0.025N Biodate Solution, dissolve 0.462 g $KH(IO_3)_2$ in 500 mL with reagent water. Weigh 2 g KI in a 500 mL Erlenmeyer flask. Add 100 to 150 mL reagent water, 5 drops H_2SO_4 and 20 mL biodate solution using a volumetric pipet. Dilute to 200 mL with reagent water. Titrate with Sodium Thiosulfate. When a pale straw yellow color is reached, add 1-2 mL starch. Continue titrating from a blue to a clear end point.

Calculation

$$Na_xS_2O_3 \text{ Normality} = \frac{(a)\,(b)}{c}$$

a = *mLs Biodate (20 mL)*

b = *Normality Biodate (0.025N)*

c = *mLs of $Na_2S_2O_3$ used to titrate*

Repeat two more times

7.1.4. 0.025 N Iodine Solution: Add 20 g KI (potassium iodide) and 3.2 g iodine to a 1 liter volumetric flask. Add 500 - 700 mL of reagent water and dissolve. Dilute to volume with reagent water. Store in a dark container. Also available commercially.

7.1.4.1. Standardization 0.025 N Iodine Solution: Perform three method blanks. Refer to method blank section in SOP.

Calculation

$$\textit{Normality Iodine} = \frac{(\textit{Normality } Na_2S_2O_3)(\textit{mL of titrant } Na_2S_2O_3)}{\textit{20 mL Iodine}}$$

7.1.5. 2N Zinc Acetate: Dissolve 220 g of zinc acetate in 870 mL of reagent water and dilute to 1 liter with reagent water.

7.2. Standards

7.2.1. Laboratory Control Sample

7.2.1.1. 100 mg/L Sulfide: Add 0.35 g of sodium sulfide to 500 mL of reagent water in a 1 liter volumetric flask. Dilute to volume with reagent water. Store at 4°C ± 2°C. Stable for one week.

7.2.2. Matrix Spike Standard

7.2.2.1. Prepare a midrange matrix spike standard as described in 7.2.1 for use as a MS/MSD.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Waters are preserved to a pH > 9 with NaOH and zinc acetate. Non-water samples are unpreserved. All matrices are stored at 4°C ± 2°C in plastic or glass containers.

8.2. The holding time is seven days from sampling to analysis.

9. QUALITY CONTROL

9.1. Batch Definition

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

9.2. Method Blank

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

9.2.2. A reagent water blank consisting of 250 mL of reagent water must be analyzed with each analytical batch of samples.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. A midrange LCS consisting of 10.0 L of 100 mg/L sulfide standard and 240 mL of reagent water must be analyzed with each analytical batch of samples.

9.3.3. Corrective Action for LCS

9.3.3.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.3.2. Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

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

9.4.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. A MS/MSD consisting of 5 g or 250 mL of the sample and 50 mL of the 100 mg/L sulfide standard should be analyzed with every 20 samples.

9.4.3. Corrective action for MS/MSDs

9.4.3.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.4.3.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as DIL (diluted out).

9.4.3.3. If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The

RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

10. CALIBRATION AND STANDARDIZATION

10.1. Not Applicable

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. Water Samples

11.3.1.1. Using the vacuum apparatus, filter 250 mL (or a lesser aliquot) of well homogenized sample. Discard the filtrate and analyze the pad and solids following section 11.4. Record volume filtered on the analytical logsheet.

11.3.2. Non-Water Samples

11.3.2.1. No preparation necessary.

11.4. Sample Analysis

11.4.1. Summary

11.4.1.1. Excess iodine is added to a sample and under acidic conditions is back titrated with sodium thiosulfate from a blue to a clear color.

11.4.2. Sample Analysis Procedure

11.4.2.1. Place the pad from the filtered water sample (section 11.3.1) or 5 g of non-water sample in a 500 mL Erlenmeyer flask. At this time, add any spiking solutions if necessary. Add 20.0 mL .025 Iodine solution and 1-2 mL 1:1 HCl solution (watch for fumes). Add 250 mL reagent water and mix. Add 1 squirt (1-2 mL) of starch indicator and mix. Titrate from blue to clear with .025 N sodium thiosulfate titrant. Record the amount of titrant used on the analytical logsheet.

NOTE: Some matrices may be turbid or colored and the color change from blue to clear may not be easily seen. In this case, look for a shade change.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.5.2. All standards are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Sample results and associated QC are entered into the LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

$$\textit{Sulfide, mg / L or mg / kg} = \frac{[(A \times B) - (C \times D)] \times 16{,}000}{\textit{mL or g of sample used}}$$

Where:

A = *mL of iodine solution*

B = *Normality of iodine solution*

C = *mL of sodium thiosulfate titrant*

D = *Normality of sodium thiosulfate titrant*

NOTE: If the normality of both the iodine solution and sodium thiosulfate solution equal 0.025, the following calculation may be used

$$\textit{Sulfide, mg / L or mg / kg} = \frac{(20 - \textit{mL titrant}) \times 400}{\textit{mL or g of sample used}}$$

12.1.1.

$$\textit{LCS \% Recovery} = \frac{\textit{mg / L (from 12.1.1)}}{\textit{4.0 (true)}} \times 100$$

12.1.2.

$$\textit{MS / MSD \% Recovery} = \frac{A - B}{\textit{5000 (true)}} \times 100$$

Where:

A = *(20 - mL titrant for MS/MSD) x 400*

B = *Concentration from 12.1.1 x mL or g of sample used*

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. All aqueous sample preparations can be rinsed down the drain with copious amounts of water.

15.2. Solvent waste must be disposed of in clearly labeled waste cans.

15.3. Acid waste must be collected in clearly labeled acid waste containers.

15.4. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.5. Refer to the Laboratory Sample and Waste Disposal plan.

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

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods of Evaluating Solid Waste, Third Edition, Sulfide, Method 9030A, Update I, September 1994.

16.1.2. EPA 600, Methods for Chemical Analysis of Waters and Wastes, Sulfide (Titrimetric, Iodine), Method 376.1

16.1.3. Standard Methods Eighteenth Edition, Sulfide Method 4500-5^2-E

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The lower reporting limits (RL) are 1 mg/L for waters and 50 mg/kg for solids.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Troubleshooting guide

17.2.1. Samples that contain strong oxidizers or reducers will interfere with this method.

17.2.2. Samples that are not water miscible (oils, various solvents) cannot be analyzed using this method.

17.2.3. The iodine should turn a yellow-orange color when added to the sample after the addition of the reagent water. If it does not, the sample may be high in sulfide and less sample should be used.

OPERATION-SPECIFIC STANDARD OPERATING PROCEDURE

TITLE: IGNITABILITY

(SUPERSEDES: LM-CAL-1022, REVISION , 12/1/87)

Prepared by: Ensecco

Reviewed by: _____
Technical Specialist

Approved by: _____
Quality Assurance Manager, Pamela A. Schemmer

Approved by: _____
Environmental Health and Safety Coordinator

Approved by: _____
Laboratory Manager, Eric Redman

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1. SCOPE AND APPLICATION

1.1. The method determines the ignitability of a sample based upon its flash point. The flash point of the sample is determined using an automated closed cup flash point tester.

1.2. There is not reporting limit applicable for ignitability.

1.3. The method is applicable to non-aqueous liquids. Other matrices can also be tested although results are unreliable and should be carefully interpreted. See section 4.

1.4. The approximate test range for Ignitability is from 70^0F to 140^0F.

1.5. The appropriate analytical time is between 30 and 60 minutes per sample including preparation and clean-up.

2. SUMMARY OF METHOD

2.1. A representative sample aliquot is heated slowly from approximately 700F and depending upon the matrix.

2.2. An igniter is automatically introduced to the vapor above the heated sample at regular intervals until a flash is detected OR the sample temperature reaches approximately 140^0F, whichever occurs first.

3. DEFINITIONS

3.1. Definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Management Plan (QAMP).

4. INTERFERENCES

4.1. For samples other than non-aqueous liquids, the characteristic of Ignitability should ONLY be used to describe the sample under controlled laboratory conditions and should NOT be regarded as the sole factor in assessing risk or hazard under actual fire conditions.

4.1.1. Loss of volatiles due to improper storage or handling will yield erroneous results.

4.1.2. Erroneous results will be obtained if the igniter is damaged or not properly cleaned or connected.

4.1.3. Erroneous results will be obtained if the temperature probe is damaged.

4.1.4. Helpful hints:

4.1.4.1. The term "liquid" is used frequently in this SOP and does not necessarily mean "aqueous." Pay particular attention to such terminology to avoid misinterpretation.

4.1.4.2. The flashpoint of a sample may indicate the presence of materials possessing a different volatility or flammability. For example, an abnormally low flashpoint for kerosene sample may indicate gasoline contamination.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all Quanterra associates.

5.2. Eye protection that satisfied ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.2.1. Neoprene, natural rubber, and butyl gloves provide varying degrees of protection against those chemicals listed. Refer to permeation/degradation charts for the actual data.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

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

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

5.7. The flashpoint tester should be located and operated in a properly vented hood.

5.8. Extra caution should be taken during the initial application of the igniter since samples containing volatile material may give an abnormally strong flash.

6. EQUIPMENT AND SUPPLIES

6.1. Precision Scientific Group GCA Corp. #10AM/3 flashpoint tester.

6.2. Thermometer covering at least 50^0C - 150^0F.

7. REAGENTS AND STANDARDS

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are collected in glass jars with a minimum headspace and stored at 4^0C.

8.2. There is no holding time for Ignitability.

9. QUALITY CONTROL

9.1. One method blank must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The method blank is an aliquot of laboratory reagent water processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, then implemented when target analytes are detected in the method blank above the reporting limit or when surrogate recoveries are outside control limits. Re-extraction of the blank, other batch QC, and the affected samples are required when the method blank is deemed unacceptable. See Quanterra Inc. QA Policy 003 for specific acceptance criteria.

9.2. A Laboratory Control Sample (LCS) must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The LCS is an aliquot of laboratory matrix (e.g. water, Ottawa sand, sodium sulfate, etc.) spiked with analytes

of known identity and concentration. The LCS must be processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, then implemented when recoveries of any spiked analyte is outside control limits provided on the LIMS or by the client. Re-extraction of the blank, other batch QC and all associated samples are required if the LCS is deemed unacceptable. See Quanterra Inc. QA Policy 003 for specific acceptance criteria.

9.3. A Matrix Spike/Matrix Spike Duplicate (MS/MSD or MS/SD) pair must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. An MS/MSD pair are aliquots of a selected field sample spiked with analytes of known identity and concentration. The MS/MSD pair must be processed in the same manner and at the same time as the associated samples. Spiked analytes with recoveries or precision outside control limits must be within control limits in the LCS. Corrective actions must be documented on a Non-Conformance memo, then implemented when recoveries of any spike analyte is outside control limits provided on the LIMS or by the client. Re-extraction of the blank, an LCS, the selected field sample, the MS/MSD may be required after evaluation and review.

9.4. A duplicate control sample (LCSD or DCS) must be substituted when insufficient sample volume is provided to process an MS/MSD pair. The LCSD is evaluated in the same manner as the LCS. See Quanterra Inc. QA Policy 003 for specific acceptance criteria.

9.5. Spikes, DCS, and blanks are not applicable to Ignitability.

9.6. Duplicates may be required for project specific QC.

9.7. Acceptance criteria

9.7.1. Control limits for project specific QC have not been established.

9.8. Corrective Actions

9.8.1. Check to see that the igniter connections are tight and that it appears to be operating properly.

9.8.2. Check to be sure that the temperature probe is not damaged.

10. CALIBRATION AND STANDARDIZATION

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documents as a nonconformance, with a cause and corrective action described.

11.3. Preparation

11.3.1. Identify the samples and tests to be analyzed using the backlogs.

11.3.2. Obtain the samples to be analyzed from the refrigerator. Record the sample number in the logbook.

11.3.3. Check LIMS for Special Instruction for EVERY sample. Make copies when they apply, include them with data package.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Examine the sample container. If it is plastic or shows evidence of leaking, record and anomalized in the logbook.

12.2. After mixing, add sample to sample cup, filling it to approximately 2/3 level.

12.3. Place cover on cup and insert thermometer into sample.

12.4. NOTE: If the probe is not inserted into the port in the cup cover, ignition of vapors outside the instrument may occur resulting in a flame or explosion.

12.5. Place cup in heater unit.

12.6. Turn the thermometer fully counter clockwise.

12.7. Monitor thermometer and wait until temperature reaches 70^{0}F. Place a lit match over shutter and open shutter. Watch for flash.

12.8. If no flash, continue above procedure every 10 degrees to an upper limit of 140^{0}F.

12.9. Turn thermometer fully clockwise when the sample has reached 140^{0}F.

12.10. Allow to cool before sample is removed and discarded.

12.11. LIMS Data Entry

12.11.1. Results for samples which did not flash at or below approximately 140^{0}F are reported at > 140^{0}F.

12.12. Anomalies

12.12.1. Results from improperly stored samples are anomalized "Results of sample XX may be inaccurate-loss of volatiles may have occurred from improper storage and/or handling." See section 9.9.1.

13. METHOD PERFORMANCE

13.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required expertise.

14. POLLUTION PREVENTION

14.1. No solvents of any kind or in any amount are to be disposed of in the sinks or evaporated in the hoods.

15. WASTE MANAGEMENT

15.1. Waste management in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Coordinator or Hazardous Materials Technician should be contacted if additional information is required.

15.2. All waste must be disposed of according to the facility hazardous waste management procedures, Attachment C of the Chemical Hygiene Plan, Section WS002, Table 1.

15.3. Samples and other solutions containing high concentrations of toxic materials must be disposed of according to the facility hazardous waste management procedures, Attachment C of the Chemical Hygiene Plan, Section WS003, Disposal of Samples After Analysis.

16. REFERENCES

16.1. Source Method: Method 1010, SW-846- Test Methods for Evaluating Solid Waste, 3rd Edition, 1986.

16.2. Related documents

16.2.1. ASTM D 93-85, Section 4, Volume 04.09, "Test Method for Flashpoint by Pensky-Martens Closed Cup Tester," 1986.

16.2.2. 40 CFR Ch. 1, Part 261, Section 21, "Characteristic of Ignitability," 1987.

16.2.3. Operating Instruction Manual for Herzog Flashpoint Tester According. to Pensky Martens ASTM D 93 - Method A-B, PI 34, Model Electronic 328.

17.

18. MISCELLANEOUS

18.1. Deviations from reference method.

18.1.1. The source method provides little detail of the actual analysis and references ASTM D 93-80. An update to that method (ASTM D 93-85) was consulted for many of the details included in this document.

18.1.2. ASTM D 93-85 specifies various storage and analysis stipulations related to a samples "expected flashpoint." This information is seldom, if ever, available; samples will be stored at 4^0C and analysis will begin as soon as possible after removal from storage.

18.2. Summary of modifications to SOP from previous revisions.

18.2.1. Update format from Enseco to Quanterra Inc. only.

18.3. List of other SOPs cross-referenced in SOP.

18.4. Facility-specific information required to implement SOP.

18.5. Tables or figures referenced in body of SOP.

18.6. Record Management and Documentation. (Sample bench sheets, logbook pages, data review checklists, etc.).

18.7. Method appendices.

QUANTERRA INC. (West Sacramento)

STANDARD OPERATING PROCEDURE CHANGE FORM

SOP Number:	
SOP Title:	
SOP Sections Affected by Change:	
Reason for Addition or Change:	
Change Effective From [Date]:	
Change or Addition (Specific Section; use additional sheets if necessary.):	

Submitted by/Date:

Approved by:*

Technical Reviewer: *Date:*

EH&S Signature: *Date:*

QA Signature: *Date:*

Management Signature: *Date*

****Must be same signature authorities of SOP being revised.***

Controlled Copy
Copy No._____

Implementation Date: 7-9-99

OPERATION-SPECIFIC STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF ALKALINITY, CONDUCTIVITY AND PH

(SUPERSEDES: LM-CAL-1056)

Prepared by: Kuldip Hundal

Reviewed by: _____
Technical Specialist

Approved by: _____
Quality Assurance Manager, Pamela Schemmer

Approved by: _____
Environmental Health and Safety Coordinator

Approved by: _____
Laboratory Manager, Eric Redman

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1. SCOPE AND APPLICATION

1.1. This method is to be used for the determination of pH, specific conductance, and alkalinity. The different forms of alkalinity (total, bicarbonate, carbonate, and hydroxide) can be calculated.

1.2. The detection limits are:
pH --Detection limit not applicable
Specific conductance -- 2$^{\mu}$mho/cm
Alkalinity -- 5mg/L as calcium carbonate

1.3. This method is applicable to drinking, surface and saline waters, domestic and industrial wastes.

1.4. This method is applicable to all ranges likely to be encountered. As a practical matter, samples with alkalinities greater than 1500 mg/L as calcium carbonate should be analyzed manually using a stronger titrant. For lower detection limits, analyze the sample manually using 0.01N H_2SO_4 acid as the titrant.

1.5. The approximate analysis time is five minutes per sample. Samples with high alkalinity or undissolved solids may require longer titration times.

2. SUMMARY OF METHOD

2.1. Samples are analyzed on an automatic titrator.

2.2. The specific conductance is measured first by application of a voltage across the conductivity cell in series with a known reference resistance. The ratio of voltage across the cell and the known resistance is measured which allows the resistance of the cell to be calculated. This is then converted to the conductance of the cell. By calibrating against a solution of known conductance, the cell constant is determined and also the specific conductance of the sample in the cell. A thermocouple measures the temperature of the sample and electronically corrects the measurements to 25 $^{\circ}$C.

2.3. The pH is then determined electrometrically with a glass electrode in combination with a reference electrode. The special glass used in the electrode develops a voltage across it that depends on the pH of the solution being analyzed. The voltage is measured and converted to pH by calibration against buffers of known pH.

2.4. Alkalinity is determined by titrating the sample with a standardized acid to specified endpoints (pH 8.3 and 4.5). Alkalinity is calculated from the volume of acid required to reach the endpoints and is traditionally reported as Calcium carbonate.

3. DEFINITIONS

3.1. Definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Management Plan (QAMP).

4. INTERFERENCES

4.1. Sodium can interfere with pH determinations at pHs greater than 10. This is controlled by using a "low sodium error" electrode.

4.2. Oil and particulate matter in the samples may coat the pH electrode and conductivity cell causing erroneous readings. This will also affect the alkalinity results.

4.3. Temperature variations will affect both pH and conductance measurements. The conductance measurements are corrected for temperature automatically. The effect on pH is controlled by performing the measurements at the same (i.e. room) temperature. All samples must be within 2 °C.

4.4. Salts of weak organic and inorganic acids will contribute to alkalinity. If the alkalinity is intended to be a measure of carbonate and bicarbonate only, the presence of these substances will cause high results.

4.5. The alkalinity is titrated to pH 4.5. The endpoint may not be appropriate for all samples.

4.6. Specific conductance is extremely sensitive to contamination. The titration head, electrodes, and all glassware must be thoroughly rinsed with deionized water to remove all traces of salts.

4.7. Samples not in equilibrium with the atmosphere may exhibit changes in pH and in the distribution of the various forms of alkalinity when exposed to the atmosphere. The sample containers should be filled completely and kept closed until just prior to the analysis. The analysis should be performed as soon as possible.

4.8. The pH electrode may exhibit slow or noisy response with high purity waters due to the lack of ionic strength.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all Quanterra associates.

5.2. Eye protection that satisfied ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.2.1. Neoprene, natural rubber, and butyl gloves provide varying degrees of protection against those chemicals listed. Refer to permeation/degradation charts for the actual data.

5.2.2. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.2.3. The sulfuric acid is known to be **corrosive**.

5.3. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

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

5.5. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Radiometer Automatic Titration System, consisting of autosampler, burette, pH meter and electrodes, conductance meter and cell, temperature probe, stirrer, printer, etc.

6.2. Plastic beakers to fit autosampler. These must be thoroughly rinsed to remove all traces of salt.

6.3. Oxford pipette calibrated to 10.0 ml, and disposable tips.

6.4. Burette, 25 ml capacity, magnetic stirrer and stirrer bars, pH meter and electrode disposable plastic beakers, 100ml capacity (For manual alkalinity titration)

6.5. Miscellaneous laboratory apparatus and glassware.

7. REAGENTS AND STANDARDS

7.1. pH buffers, 4.0, 7.0, and 10.0. Obtained commercially.

7.2. 0.01 M potassium chloride (Conductance Standard)

Dry potassium chloride at 105 °C for two hours. Then dissolve 0.7456 g in deionized water and dilute to 1 liter. This solution has a conductance of 1417 μmhos/cm at 25 °C. Prepare monthly.

7.3. 0.05 N sodium carbonate

Dry anhydrous sodium carbonate at 250 °C for four hours and cool in a desiccator. Dissolve 2.6497 g in deionized water and dilute to 1 liter.

7.4. 0.02 N sulfuric acid (Alkalinity Titrant)

Very carefully add 3.0 ml concentrated sulfuric acid to approximately 500 ml deionized water and dilute to 1 liter. This solution must be standardized using the procedure given in section 10. Record standardization data and calculate the actual normality of the solution. This reagent can also be obtained commercially.

7.5. 0.1 N Sulfuric Acid (Manual Titration)

Very carefully add 3.0 ml concentrated sulfuric acid to approximately 500 ml deionized water and dilute to 5 liters with deionized water. Standardize the solution using the procedure given in section 10. Record standardization data and calculate the actual normality of the solution. This reagent can also be obtained commercially.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are to be collected in plastic bottles and refrigerated to 4 °C.

8.2. Samples for alkalinity must not be filtered, diluted, concentrated, or altered in any way.

8.3. The official holding times for these parameters are;

pH -- 24 hours

Conductance -- 28 days

Alkalinity -- 14 days

9. QUALITY CONTROL

9.1. QC Samples

9.1.1. Deionized water is to be analyzed at least once daily. The conductance of this to be recorded in the notebook provided for that purpose.

9.1.2. Check a 7.0 pH standard with each new calibration.

9.1.3. One blank and DCS samples must be analyzed in every batch of 20 or less samples. The blank is deionized water. The ICV and first CCV can be used as the DCS.

9.1.4. A CCB and CCV are to be performed after every 10 or fewer readings and at the end of the run. Use the DCS for standard checks. The CCB is deionized water.

9.1.5. Sample duplicates may be required as project specific QC for every batch of 20 or less samples.

9.1.6. A second source reference is to be performed after the ICB.

9.1.7. Check the project and sample instructions for program or project specific QC requirements.

9.2. Acceptance Criteria

9.2.1. Deionized water should have a conductance of 2 μmhos/cm or less. The alkalinity should be less than 5 mg/L. The pH is usually 5 - 6.

9.2.2. pH 7.0 standard should read within $\pm$ 2% of 7.0.

9.2.3. Control limits for accuracy and precision (RPD) on DCS samples are:

Parameter	Accuracy	Precision
pH	98-102%	2%
Conductance	90-110%	10%
Alkalinity	90-110%	10%

9.2.4. Standard check should be within 10% of the expected value.

9.2.5. Blanks should be less than the 2 times the reporting limits for conductance and alkalinity. pH blanks should be around 5 to 6.

9.2.6. There may be specific acceptance criteria for project specific QC. Check the project QAPjP or with the Project Manager.

9.3. Corrective Action Required

9.3.1. Follow the corrective actions outlined in the current Quanterra Incorporated QA Policy 003 or client QAPjP, whichever is applicable to the samples being analyzed.

9.3.2. If the deionized water has a conductance more than 2 μmhos/cm, repeat the reading. If it is still high, the deionized water system needs maintenance.

9.3.3. If the pH 7.0 standard is not within limits, recalibrate and check the standard again. If it is still out of limits, see your supervisor.

9.3.4. If the control limits for DCS samples are exceeded, the problem must be corrected and the samples reanalyzed. Check the calibration procedure and thoroughly clean the electrodes, titration head, and beakers. The most common problem is contamination, which causes high conductance readings.

10. CALIBRATION AND STANDARDIZATION

10.1. Standardization of Alkalinity Titrant

10.1.1. Accurately measure 0.05 N sodium carbonate solution into a 250 ml beaker. Use 40 ml if 0.1 N sulfuric acid is being standardized, or 15 ml if using 0.02 N sulfuric acid. Add deionized water to bring the total volume to 100 ml.

10.1.2. Titrate with the appropriate acid strength to a pH of about 5. Lift electrode and rinse into the beaker. Cover with a watch glass and boil the solution gently for 3 - 5 minutes. Cool to room temperature, rinse watch glass into beaker, and continue the titration to the pH inflection point. Calculate the acid normality using the formula in section 12.

10.1.3. Perform all titrations for standardization in duplicate.

10.2. Calibration for pH

10.2.1. Be sure that the reference electrode has been filled with saturated potassium chloride and that all electrodes and the titration heads are clean and dry (only use Kim Wipes to dry the electrodes).

10.2.2. Pour approximately 20 ml of pH 7 buffer into the beaker and lower the electrodes into it. Place the titrator in pH mode and press the **CAL** button when the reading has stabilized. Step through the calibration routine by pressing the **CAL** button. When **Buffer 2** is displayed, rinse the electrodes and immerse in pH 4 buffer. Allow the reading to stabilize and continue with the calibration routine. At each step, make sure that the displayed parameter is correct (e.g. buffer value, temperature, etc.). If you need to change an entry, press the **SHIFT** button and enter the correct value. When **Buffer 3** is displayed, press the pH button to exit the calibration routine (this part of the calibration routine is for a different application not used here). Rinse the electrodes.

10.2.3. For manual pH, calibrate the pH meter using pH buffers 4.0 and 10.0. Check calibration using pH buffer 7.0. Run check standard after every 10 samples and at the end of the run.

10.3. Calibration for Conductance

10.3.1. Be sure that the electrodes and titration head are clean and dry (only use Kim Wipes to dry the electrodes).

10.3.2. Pipette 20 ml Conductance Standard (0.01 M potassium chloride) into a clean beaker and immerse electrodes. Verify that the reference temperature is set to 25 °C and that the temperature compensation is 2% per degree C. Then adjust

the cell constant to give a reading of 1.42 mS/cm. Rinse the electrodes when done.

11. PROCEDURE

11.1. Obtain samples from sample receiving. Check each sample for special instruction. Fill out the benchsheet.

11.2. Thoroughly homogenize samples before taking an aliquot for analysis. Allow aliquots to equilibrate to room temperature before analyzing.

11.3. Turn on the power to the burette and autosampler. Be sure the titrant reservoir is full. The 0.02 N sulfuric Acid should be used. If new titrant has been prepared, rinse out the reservoir with it, refill, and flush out the burette and titrant delivery line. Be sure that there are no bubbles in the line.

11.4. Set the autosampler to 2 rinse and a delay of 0.4 minutes. Fill two beakers with deionized water (20 - 25 ml) and place them in positions 19 and 20. These are the rinse beakers.

11.5. Set the titrator to **EP** mode and be sure that **Method 1** is displayed.

11.6. Pipette 20 ml of ERA standard of known pH, EC, and Alkalinity in a clean beaker and place on position 1 on the autosampler, followed by ICB. Another ERA standard from different source should be run after ICB. Then similarly pipette 20 ml of each sample into a clean beaker and place on the turntable. A 10 ml Oxford pipette may be used to dispense two 10 ml aliquots of sample, if it has been calibrated previously to 10 ml. Record the sample ID and position on the titrator. Allow sample aliquots to equilibrate to room temperature.

11.7. Press **START NEW CYCLE** on the autosampler and the analysis will commence. Results will be automatically printed out and the sampler will stop when all samples have been titrated. At this point, additional samples can be placed on the titrator and analyzed starting at step 11.5. Be sure to keep the titrant reservoir filled and replace the water in the rinse beakers periodically (every two to three samples).

11.8. The titrator has been programmed to deliver a maximum volume of 30 ml titrant. Samples requiring more than this should be analyzed manually using stronger titrant (0.1 N Sulfuric acid).

11.9. To run alkalinity manually, calibrate the pH meter according to manufacturers instructions and also see section 10.2. Pipette 50.0mL sample into a beaker and place

on the magnetic stirrer. Measure and record the pH of the sample. If the pH is >8.3, titrate to pH 8.3 and record the volume of titrant used. Then titrate to pH 4.5 and record the total volume of the titrant used, including that used to reach pH 8.3. Calculate the alkalinity as shown in section 12.

11.10. Clean up the work area. Return the samples to sample control. Process the results using the alkalinity benchsheet program.

11.11. Complete the data package by including a copy of the data tape and of the run log. Submit the data package for approval.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Standardization of Alkalinity Titrant

Nacid = (Nbase x Vbase) / Vacid

Nacid = Normality of titrant

Nbase = Normality of sodium carbonate

Vbase = Volume of sodium carbonate used, ml

Vacid = Volume of titrant needed for titration, ml

12.2. Calculations of Alkalinity

12.2.1. P-Alkalinity (Phenolphthalein Alkalinity)

$^{P}alk = (^{V}1 \times {}^{N}acid \times 50000)/Vol.$

^{P}alk = P-Alkalinity, mg/L as $CaCO_3$
$^{V}1$ = Volume of titrant needed to reach pH 8.3, mL
$^{N}acid$ = Normality of titrant
Vol = Sample volume used, mL

12.2.2. T-Alkalinity (Total Alkalinity)

$^{T}alk = (^{V}2 \times {}^{N}acid \times 50000)/Vol.$

^{T}alk = T-Alkalinity, mg/L as $CaCO_3$
$^{V}2$ = Volume of titrant needed to reach pH 4.5, mL

^{N}acid = Normality of titrant
Vol. = Sample volume titrated, mL

12.3. pH values are recorded directly from the titrator printout.

12.4. Conductance values are taken as-is from the print out. If they are printed out in mS/cm, they must be multiplied by 1000. The units $^{\mu}$S/cm are equivalent to $^{\mu}$mhos/cm.

12.5. Three values for alkalinity will be printed if the pH is greater than 8.3. Record the values at pH 8.3 and 4.5 on the bench sheet. The third value is the difference and is ignored. Note that some results will be printed in scientific notation; be careful to check this when processing results.

If the pH is less than 8.3, only one value will be printed (at pH 4.5). Record this value on the benchsheet. P alkalinity is ND on these samples.

Calculate the individual forms of alkalinity:

T = Total Alkalinity = Alkalinity at pH 4.5

P = Phenolphthalein Alkalinity = Alkalinity at pH 8.3

	Hydroxide Alkalinity	Carbonate Alkalinity	Bicarbonate Alkalinity
P=ND	ND	ND	T
P<T/2	ND	2 x P	T-2 x P
P=T/2	ND	T	ND
P>T/2	2 x P – T	2(T – P)	ND
P = T	T	ND	ND

Record the values for Total, Bicarbonate, Carbonate, and Hydroxide Alkalinity.

13. METHOD PERFORMANCE

13.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required expertise.

14. POLLUTION PREVENTION

14.1. No solvents of any kind or in any amount are to be disposed of in the sinks or evaporated in the hoods.

15. WASTE MANAGEMENT

15.1. Waste management in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Coordinator or Hazardous Materials Technician should be contacted if additional information is required.

15.2. All waste must be disposed of according to the facility hazardous waste management procedures, Attachment C of the Chemical Hygiene Plan, Section WS002, Table 1, current edition.

15.3. Samples and other solutions containing high concentrations of toxic materials must be disposed of according to the facility hazardous waste management procedures, Attachment C of the Chemical Hygiene Plan, Section WS003, Disposal of Samples After Analysis, current edition.

16. REFERENCES

16.1. pH is EPA Method 150.1.

16.2. Conductance is EPA Method 120.1.

16.3. Alkalinity is EPA Method 310.1. Additional information was obtained from Standard Methods #403.

17. MISCELLANEOUS

17.1. Deviations from reference method.

17.1.1. Successive aliquots of samples are not analyzed for pH as in the reference methods.

17.1.2. Temperature is not reported with the pH measurement. All measurements are made at room temperature.

17.1.3. Alkalinity titrations are not performed at 25 °C as specified in the reference method.

17.1.4. Method 310.1 contains no provisions for determining the different forms of alkalinity. This part of the method was obtained from Standards Methods for the Examination of water and Wastewater, 14th. Edition.

17.1.5. A fixed endpoint of 4.5 is used for all alkalinity titrations.

17.2. Summary of modifications to SOP from previous revisions.

17.2.1. The SOP was converted to Quanterra format only.

17.3. Procedure flow diagram (mandatory last page(s)).

QUANTERRA INC. (West Sacramento)

STANDARD OPERATING PROCEDURE CHANGE FORM

SOP Number:	
SOP Title:	
SOP Sections Affected by Change:	
Reason for Addition or Change:	
Change Effective From [Date]:	
Change or Addition (Specific Section; use additional sheets if necessary.):	

Submitted by/Date:

Approved by:*

Technical Reviewer: *Date:*

EH&S Signature: *Date:*

QA Signature: *Date:*

Management Signature: *Date*

****Must be same signature authorities of SOP being revised.***

Procedure Flow Diagram

Standardize titrants, pH meter, and conductivity meter.

↓

Allow samples to equilibrate to room temperature.

↓

Turn on autotitrator.

↓

Fill reservoirs and flush lines.

↓

Place samples in the autosampler tray.

↓

Start analysis sequence.

↓

Review and retitrate samples that require more than 30 mls of titrant.

QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: REACTIVE CYANIDE

(SUPERSEDES: REVISION 0, 04/12/99)

Prepared by:	Melissa A. Fuller-Gustafson	3 June 1999
		Date
Approved by:		06-04-99
	Technology Specialist	Date
Approved by:		6/7/99
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Approved by:		6-18-99
	Environmental Health and Safety Coordinator	Date
Approved by:		6-22-99
	Laboratory Director	Date

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Reactive Cyanide in all wastes, with the condition that wastes combined with acids do not form explosive mixtures. It is based on SW846 Section 7.3.3.2 The working linear range is 10 to 1000 mg/kg.

1.2. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory QA department.

1.3. The applicable LIMs method code is GI. The preparation code for samples is 08.

2. SUMMARY OF METHOD

2.1. An aliquot of sample is acidified to a pH of 2 in a closed system. The gas generated is trapped in a sodium hydroxide solution and then analyzed using the titration method for Cyanide.

3. DEFINITIONS

3.1. Refer to the glossary in the Quality Assurance Management Plan (QAMP).

4. INTERFERENCES

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

4.2. Sulfide interferes with analysis and can be precipitated out using cadmium carbonate prior to titration.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all Quanterra associates.

5.2. Eye protection that satisfies ANSI Z87.1 (per the Chemical Hygiene Plan), Laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive: Sulfuric Acid, Sodium Hydroxide.**

5.4. Exposure to chemicals must be maintained **as low as reasonable achievable,** therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

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

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Reactivity flask: 3-neck, 500 mL minimum capacity

6.2. Separatory funnel: 250 mL pressure-equalizing

6.3. Stir plate and stir bars

6.4. Compressed Nitrogen and two-way regulator

6.5. Scrubber and absorber tube: 50 mL capacity

6.6. Buret: 10 mL Class A

6.7. Erlenmeyer flasks: various

6.8. Volumetric flasks: various

6.9. Graduated cylinders: various

6.10. Whatman filter paper #4

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Sulfuric Acid: (H_2SO_4), concentrated, reagent grade

7.1.2. 0.05 M H_2SO_4: Add 2.8 mL concentrated H_2SO_4 to 900 mL reagent water and dilute to 1 liter with reagent water.

7.1.3. 0.005 M H_2SO_4: Add 100 mL 0.05 M H_2SO_4 to 800 mL reagent water and dilute to 1 liter with reagent water.

7.1.4. Sodium Hydroxide: (NaOH), reagent grade

7.1.5. 1.25 N NaOH: Add 50 g NaOH to 900 mL reagent water and dilute to 1 liter with reagent water.

7.1.6. 0.25 N NaOH: Add 200 mL 1.25 N NaOH to 700 mL reagent water and dilute 1 liter with reagent water.

7.1.7. 0.0192 N Silver Nitrate Solution: reagent grade

7.1.8. Rhodanine Indicator: Dimethylaminobenzalrhodanine, reagent grade

7.1.9. Acetic acid: (CH_3COOH), concentrated, reagent grade

7.1.10. Methyl Red: reagent grade

7.1.11. Methyl Red Indicator: Add 0.02 g methyl red to 40 mL acetic acid and dilute to 100 mL with reagent water.

7.1.12. Kaolin: reagent grade

7.1.13. Cadmium Carbonate: ($CdCO_3$), reagent grade

8. SAMPLE PRESERVATION AND STORAGE

8.1. Samples are stored in plastic or glass containers at $4^\circ \pm 2^\circ$C.

8.2. Solid and water samples are not chemically preserved.

8.3. The holding time is fourteen days from sampling to analysis (based on the Total Cyanide holding time).

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, MS, MSD, Method Blanks) which are processed similarly, with respect to the procedure. All samples within the batch must be treated with the same lots of reagents and the same processes. All samples within the batch must be treated with the same processes.

9.2. Method Blank (MB)

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

9.2.2. A blank consisting of 10 g Kaolin or other inert solid must be reacted and analyzed with each analytical batch of samples.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be taken in consultation with the client and must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.3. Duplicate Sample

16.2.2. Reactive Sulfide, NC-WC-0061

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Troubleshooting Guide

17.1.1. If the sample turns black while titrating, sulfide is present. See Sample Analysis Procedure 11.4.1 for removal. Use the remaining aliquot.

9.3.1. A duplicate sample should be reacted and analyzed every 10 samples.

10. CALIBRATION AND STANDARDIZATION

10.1. Not Applicable.

11. PROCEDURE

11.1. Summary

11.1.1. The sample is acidified to a pH of 2 in a closed system and liberated Cyanide gas is trapped in 0.25 N NaOH.

11.2. Sample Preparation Procedure

11.2.1. Add 50 mL 0.25 N NaOH to the absorber tube and connect the scrubber.

11.2.2. Add 10 g of sample (waters and non-waters) to the reactivity flask and add 5 drops of methyl red indicator.

11.2.3. Add 200 mL of 0.005 M H_2SO_4 to the separatory funnel.

11.2.4. Close the entire system and begin the flow of nitrogen. The flow should be 60 mL/minute.

11.2.5. Begin sample stirring and start adding the acid by opening the stopcock on the separatory funnel. The sample will turn pink-red when the pH is 2 or less.

11.2.6. If the pH is not <2, make a note on the analytical logsheet. Allow the sample to react (while mixing) for thirty minutes.

11.2.7. After the thirty minute reacting period, disconnect the system and shut off the nitrogen.

11.2.8. Pour the scrubber contents into a 250 mL volumetric flask. Rinse the scrubber with reagent water and pour the rinsate into the 250 mL volumetric flask. Dilute to volume with reagent water.

11.3. Preparation Documentation

11.3.1. Record all the necessary information on the analytical logsheet.

11.4. Sample Analysis Procedure

11.4.1. After the 100 mL aliquot has been removed (and checked and/or analyzed) for sulfide, if necessary, add one scoop (1 - 2 g) of $CdCO_3$ powder to the volumetric flask and mix. If the precipitate turns yellow, add another scoop until white precipitate forms. This removes sulfide which interferes with the titration. If the results of the sulfide analysis are "ND", go to section 11.4.2. Filter 100 mLs of treated scrubber solution through a #4 Whatman filter paper into an Erlenmeyer flask.

11.4.2. Add 10-12 drops of rhodanine indicator to the Erlenmeyer flask. The solution should turn yellow. Titrate with 0.0192 N silver nitrate until a orange-peach color develops. Record the volume of titrant used on the analytical logsheet.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

*Reactive Cyanide, mg/Kg = mLs of titrant x 125**

Where:

* = *125 is a factor taking in consideration that 10 g of sample is used, it is reacted for 30 minutes and 100 mL of the scrubber contents are used. If any of these volumes or times change the calculations in 12.2.2 must be used.*

$$\frac{A(1000)}{B} \times \frac{250}{C} = mg / L \text{ Cyanide in scrubber solution}$$

Where:

A = mL of titrant used

B = Volume of sample titrated

C = mL of scrubber solution titrated (usually 100 mL)

$$\frac{(X)(L)}{(W)(S)} = \text{(R) Rate of release}$$

Where:

X = Conc. Cyanide from previous equation

L = Total volume of scrubber solution in liters (0.25 l)

W = Weight of original sample used in kg (10 g = 0.1 kg)

S = Time of reaction in seconds (30 minute = 1800 seconds)

R = Rate of release from second equation

12.2. Report Documentation

12.2.1. Record all analytical information on the analytical logsheet, including the analytical data from standards, blanks, and LCSs.

12.2.2. All standards are logged onto the departmental standard logsheet. All standards are assigned in an unique number for identification. Logbooks are reviewed by the supervisor or designee.

12.2.3. The documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, ect.) and daily calibration data corresponding to all final runs is available for each data file.

12.2.4. Sample results and associated QC are entered into the LIMS after final technical review.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Acid waste must be collected in the clearly labeled acid waste containers.

15.2. Solid materials (soil, gloves, soiled paper products) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Refer to the Laboratory Sample and Waste Disposal plan.

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

16. REFERENCES

16.1. References.

16.1.1. SW846, Test Methods for Evaluating Solid Waste, Reactivity, Method 7.3.3.2 for Cyanide Reactivity, and its Updates.

16.1.2. SW846, Test Methods for Evaluating Solid Wastes, Reactivity, Method 9010 and 9012 for Cyanide Analysis, and its Updates.

16.2. Associated SOPs

16.2.1. Cyanide, Total NC-WC-0031

LABORATORY-SPECIFIC

QUANTERRA® STANDARD OPERATING PROCEDURE

TITLE: REACTIVE SULFIDE

(SUPERSEDES: LM-WALN-1335 (REVISION 1.0, DATED 04/27/95))

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	Environmental Health and Safety Coordinator	Date
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17. MISCELLANEOUS (TABLES, APPENDICES, ETC...) *12*

1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Reactive Sulfide in all wastes, with the condition that wastes combined with acids do not form explosive mixtures. It is based on SW846 Section 7.3.4.2. The lower detection limit is 200 mg/kg.

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

2. SUMMARY OF METHOD

2.1. An aliquot of sample is acidified to a pH of 2 in a closed system. The gas is generated and trapped in a sodium hydroxide solution and then analyzed using the titration method for Sulfide.

3. DEFINITIONS

3.1. Refer to the glossary in the Quality Assurance Management Plan (QAMP), current version.

4. INTERFERENCES

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

4.2. Oxidizers and reducers interfere with Sulfide analysis.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all Quanterra associates.

5.2. Eye protection that satisfied ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive: Hydrochloric Acid, Sodium Hydroxide, and Sulfuric Acid**

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

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

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Reactivity flask: 3-neck, 500 mL

6.2. Separatory funnel: 250 mL pressure-equalizing

6.3. Stir plate and stir bars

6.4. Compressed nitrogen and Two-way regulator

6.5. Scrubber and absorber tube: 50 mL capacity

6.6. Burettes: 10 mL and 25 mL Class A

6.7. Erlenmeyer Flasks: various

6.8. Pipettes: various

6.9. Graduated cylinders: various

6.10. 250 mL volumetric flasks

7. REAGENTS AND STANDARDS

7.1.1. Sulfuric Acid, 0.05 M H_2SO_4: Add 2.8 mL concentrated sulfuric acid to a 1 liter volumetric flask containing 900 mL reagent water and bring to volume with reagent water.

7.1.2. Sulfuric Acid, 0.005 M H_2SO_4: Add 100 mL 0.05 M H_2SO_4 to a 1 liter volumetric flask and bring to volume with reagent water.

7.1.3. Sodium Hydroxide, 1.25 N NaOH: Add 50 g sodium hydroxide to a 1 liter volumetric flask and bring to volume with reagent water.

7.1.4. Sodium Hydroxide, 0.25 N NaOH: Add 200 mL 1.25 N NaOH to a 1 liter volumetric flask and bring to volume with reagent water.

7.1.5. Iodine Solution, 0.025 N: Manufactured, or add 20 g KI (potassium iodide) and 3.2 g iodine to a 1 liter volumetric flask. Add 500 - 700 mL of reagent water and dissolve. Dilute to volume with reagent water. Store in a dark container.

7.1.5.1. Standardization 0.025N Iodine Solution: Prepare three (3) method blanks using 250 mL of reagent water. Follow the analysis procedure and calculate an average normality.

$$\text{Normality Iodine} = \frac{(\text{Normality } Na_2S_2O_3)(\text{mL of titrant } Na_2S_2O_3)}{20 \text{ mL Iodine}}$$

7.1.6. Sodium Thiosulfate, 0.025 N: Manufactured, or add 0.4 g of NaOH and 6.205 g of sodium thiosulfate ($Na_2S_2O_3 \bullet 5H_2O$) to 500 mL of reagent water in a 1 liter volumetric flask. Dilute to volume with reagent water. Store in a dark container.

7.1.6.1. Standardization of 0.025 N Sodium Thiosulfate Solution: To make 0.025N Biodate Solution, dissolve 0.4062 g $KH(IO_3)_2$ in 500 mL reagent water. Weigh 2 g KI in a 500 mL Erlenmeyer flask. Add 100 to 150 mL reagent water, 5 drops H_2SO_4, and 20 mL biodate solution using a volumetric pipet. Dilute to 200 mL with reagent water. Titrate with Sodium Thiosulfate. When a pale straw yellow color is reached, add 1-2 mL starch. Continue titrating from a blue to a clear end point. Repeat two (2) more times. Calculate an average normality.

$$Na_2S_2O_3 \text{ Normality} = \frac{(a)(b)}{c}$$

where:

a = mLs Biodate (20mL)

b = Normality Biodate (0.025N)

c = mLs of $Na_2S_2O_3$ used to titrate

7.1.7. Starch Indicator: Add 10 mL reagent water to 5 g potato starch and mix. Add mixture to 500 mL boiling reagent water, mix, and cool.

7.1.8. Hydrochloric Acid, 6 N: Add 250 mL concentrated hydrochloric acid to 250 mL reagent water.

7.1.9. Methyl Red Indicator: Add 0.02 g methyl red in 40 mL acetic acid and dilute to 100 mL with reagent water.

7.1.10. Zinc Acetate Solution: Add 220 g Zinc Acetate to a 1000 mL volumetric flask and dilute to volume with reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Waters may be preserved to a pH > 12 with sodium hydroxide and zinc acetate. Solids are unpreserved.

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

8.3. There is no defined holding time.

9. QUALITY CONTROL

9.1. Batch Definition

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

samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank

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

9.2.2. A blank consisting of 10 g of Kaolin must be reacted and analyzed with each analytical batch of samples.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.3. Sample Duplicate

9.3.1. Sample duplicates are performed at a minimum frequency of one per analytical batch and must meet laboratory-specific limits for precision.

10. CALIBRATION AND STANDARDIZATION

10.1. Not Applicable

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documents as a nonconformance, with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. Summary

11.3.1.1. The sample is acidified to a pH of 2 in a closed system and liberated Sulfide gas is trapped in 0.25 N NaOH.

11.3.2. Sample Preparation Procedure

11.3.2.1. Add 50 mL 0.25 N NaOH to the absorber tube and connect the scrubber.

11.3.2.2. Add 10 g of sample to the reactivity flask and add 1 - 2 mL of methyl red indicator.

11.3.2.3. Fill 250 mL separatory funnel three-quarters full (200 mL) with 0.005M H_2SO_4.

11.3.2.4. Close the entire system and begin the flow of nitrogen. The flow should be 60 mL/minute.

11.3.2.5. Begin sample stirring and start the addition of acid to the flask. The sample will turn pink-red when the pH is 2 or less. If the solution does not turn pink-red, note it on the analytical logsheet.

11.3.2.6. Begin timing for thirty minutes.

11.3.2.7. After the thirty minute reacting period, disconnect the system and shut off the nitrogen.

11.3.2.8. Pour the scrubber contents into a 250 mL volumetric flask. Rinse the scrubber with reagent water and pour the rinsate into the 250 mL volumetric flask. Bring to volume with reagent water.

11.4. Sample Analysis

11.4.1. Pour 100 mL of scrubber into a 500 mL Erlenmeyer flask and add 150 mL of reagent water. Add 1-2 mL of zinc acetate solution, 20.0 mL of 0.025 N iodine, 2-3 mL of 1:1 HCl, and 2 - 3 mL of starch indicator to solution and mix. Titrate with 0.025 N sodium thiosulfate until blue color disappears. Record the volume of titrant used.

11.4.2. Preliminary Evaluation

11.4.2.1. The color of the scrubber solution should be a golden color after the addition of the iodine and HCl; if it is not, a lesser volume of sample (25 mL is recommended) is titrated.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.5.2. All standards are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Sample results and associated QC are entered into the LIMS after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ***Reactive Sulfide, mg / kg = 20 - mLs titrant x 50***

Where:

50 is a factor taking in consideration that 10 g of sample is used, the normalities are correct, it is reacted for 30 minutes, and 100 mL of the scrubber solution is titrated. If any of these factors are different, use the calculations in Section 12.2.

12.2. ***mg / L Sulfide in scrubber solution*** $= \dfrac{[(A \bullet a) - (B \bullet b)]16{,}000}{C}$

Where:

A = mL of iodine used

a = N of iodine

B = mL titrant used

b = N of titrant

C = mL of scrubber solution titrated

12.3. ***Rate of release (R)*** $= \dfrac{(X)(L)}{(W)(S)}$

Where:

X = Concentrated Sulfide from 12.1 or 12.2

L = Total volume of scrubber solution in liters (0.25 L)

W = Weight of original sample used in kg (10 g = 0.1 kg)

S = time of reaction in seconds (30 minute = 1800 seconds)

12.4. ***mg / kg Reactive Sulfide = R x 1800***

Where:

R = Rate of release from second equation

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Solvent waste must be disposed of in clearly labeled waste cans.

15.2. Acid waste must be collected in clearly labeled acid waste containers.

15.3. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.4. Refer to the Laboratory Sample and Waste Disposal plan.

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

16. REFERENCES

16.1. References

16.1.1. SW846, Test methods for Evaluating Solid Wastes, 3rd Edition, Reactivity, Method 7.3.4.2 for Sulfide.

16.1.2. SW846, Test Methods for Evaluating Solid Wastes, 3rd Edition, Reactivity, Method 9030A for Sulfide.

16.1.3. Quanterra® Quality Assurance Management Plan (QAMP), current version.

16.2. Associated SOPs

16.2.1. Sulfide, NC-WC-0060

16.2.2. Reactive Cyanide, NC-WC-0033

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The lower reporting limit (RL) is 200 mg/kg Reactive Sulfide.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

QUANTERRA® STANDARD OPERATING PROCEDURE

TITLE: TOXICITY CHARACTERISTIC LEACHING PROCEDURE AND SYNTHETIC PRECIPITATION LEACHING PROCEDURE

(SUPERSEDES: REVISION 0)

Prepared by: _____
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Reviewed by: _____
Technology Standardization Committee

Approved by: _____
Director, Quality Assurance

Approved by: _____
Director, Environmental Health and Safety

Approved by: _____
Management

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1. SCOPE AND APPLICATION

1.1. This SOP describes the application of the Toxicity Characteristic Leaching Procedure (TCLP), SW846 Method 1311. The Toxicity Characteristic (TC) of a waste material is established by determining the levels of 8 metals and 31 organic chemicals in the aqueous leachate of a waste. The TC is one of four criteria in 40 CFR Part 261 to determine whether a solid waste is classified as a hazardous waste. The other three are corrosivity, reactivity and ignitability. The TC Rule utilizes the TCLP method to generate the leachate under controlled conditions which were designed to simulate leaching through a landfill. EPA's "worst case" waste disposal model assumes mismanaged wastes will be exposed to leaching by the acidic fluids generated in municipal landfills. The EPA's model also assumes the acid/base characteristics of the waste will be dominated by the landfill fluids. The TCLP procedure directs the testing laboratory to use a more acidic leaching fluid if the sample is an alkaline waste, again in keeping with the model's assumption that the acid fluids will dominate leaching chemistry over time.

1.2. The specific list of TC analytes and regulatory limits may be found in Appendix A.

Note: The list in Appendix A does not include the December 1994 EPA rule for Universal Treatment Standards for Land Disposal Restrictions. Those requirements include 216 specific metallic and organic compounds and, in some cases, lower detection limit requirements (see 40 CFR 268.40). TCLP leachates are part of the new Universal Treatment Standards, but the conventional analytical methods will not necessarily meet the new regulatory limits. Consult with the client and with Quanterra® Technical Specialists before establishing the instrumental methods for these regulations.

1.3. This SOP also describes the application of the Synthetic Precipitation Leaching Procedure (SPLP) which was designed to simulate the leaching that would occur if a waste was disposed in a landfill and exposed only to percolating rain water. The procedure is based on SW846 Method 1312. The list of analytes for SPLP may extend beyond the toxicity characteristic compounds shown in Appendix A. With the exception of the use of a modified extraction fluid, the SPLP and TCLP protocols are essentially equivalent. Where slight differences may exist between the SPLP and TCLP they are distinguished within this SOP.

1.4. The procedure is applicable to liquid, solid, and multiphase wastes.

1.5. The results obtained are highly dependent on the pH of the extracting solution, the length of time that the sample is exposed to the extracting solution, the temperature

during extraction, and the particle size/surface area of the sample. These parameters must be carefully controlled.

1.6. The reporting limits are based on the individual samples as well as the individual analysis techniques. However, the sample is determined to be hazardous if it contains any analyte at levels greater than or equal to the regulatory limits.

1.7. If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the procedure need not be run. If the total analysis results indicate that TCLP is not required, the decision to cease TCLP analysis should be remanded to the client.

1.8. If an analysis of any one of the liquid fractions of the procedure leachate indicates that a regulated compound is present at such a high concentration that, even after accounting for dilution from the other fractions of the leachate, the concentration would be equal to or above the regulatory level for that compound, then the waste is hazardous and it may not be necessary to analyze the remaining fractions of the leachate. However, the remaining analyses should not be terminated without the approval of the client.

1.9. Volatile organic analysis of the leachate obtained using a bottle extraction, normally used for extractable organics and metals, can be used to demonstrate that a waste is hazardous, but only the ZHE option can be used to demonstrate that the concentration of volatile organic compounds is below regulatory limits.

2. SUMMARY OF METHOD

2.1. For liquid wastes that contain less than 0.5% dry solid material, the waste, after filtration through 0.6 to 0.8 µm glass fiber filter, is defined as the TCLP leachate.

2.2. For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solids and stored for later analysis. The particle size of the remaining solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. For TCLP, the extraction fluid employed for extraction of non-volatile analytes is a function of the alkalinity of the solid phase of the waste. For SPLP, the extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil. If the sample is a waste or wastewater the extraction fluid employed is a pH 4.2 solution. Two leachates may be generated: a) one for analysis of non-volatile constituents (semi-volatile organics, pesticides, herbicides and metals and/or b) one from a Zero Headspace Extractor (ZHE) for analysis of volatile organic constituents.

Following extraction, the liquid leachate is separated from the solid phase by filtration through a 0.6 to 0.8 µm fiber filter.

2.3. If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid leachate and these are prepared and analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3. DEFINITIONS

3.1. "Leachate" is used to refer to the TCLP solution generated from this procedure.

3.2. "Percent Wet Solids" is that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure.

4. INTERFERENCES

4.1. Oily wastes may present unusual filtration and drying problems. As recommended by EPA (see Figure 3), oily wastes will be assumed to be 100% liquid and analysis for total concentrations of contaminants will be performed. This applies specifically to samples containing viscous non-aqueous liquids that would be difficult to filter.

4.2. Wastes containing free organic liquids (i.e., those with separable non-aqueous liquid phases) will be assumed to be 100% liquid and totals analysis will be performed to determine if the oil exceeds TCLP limits.

4.3. Solvents, reagents, glassware and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks as described in the Section 9.0 and the individual determinative SOPs.

4.4. Glassware and equipment contamination may result in analyte degradation. Soap residue on glassware and equipment may contribute to this. All glassware and equipment should be rinsed very carefully to avoid this problem.

4.5. Phthalates may be eliminated by proper glassware cleanup and by avoiding plastics. Only glass, Teflon or Type 316 stainless steel tumblers may be used for leachates to be analyzed for organics. Plastic tumblers may be used for leachates to be analyzed for the metals.

4.6. Overexposure of the sample to the environment will result in the loss of volatile components.

4.7. Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all Quanterra® associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. Chemicals that have been classified as **carcinogens**, or **potential carcinogens**, under OSHA include:

Methylene chloride

5.3.2. Chemicals known to be **flammable** are:

Methanol

5.3.3. The following materials are known to be **corrosive**:

Hydrochloric acid, nitric acid, sulfuric acid, acetic acid, sodium hydroxide

The following materials are known to be **oxidizing agents**:

Nitric Acid.

5.4. Gas pressurized equipment is employed in this procedure. Be sure all valves and gauges are operating properly and that none of the equipment, especially tubing, is over-pressurized. CAUTION: Do not open equipment that has been pressurized until it has returned to ambient pressure.

5.5. A rotary agitation apparatus is used in this procedure. Certain samples may break the glass jars used in the procedure. For these samples, extra caution, including plastic or polyethylene overwraps of the glass jar, may be necessary.

5.6. Secure tumbler and extraction apparatus before starting rotary agitation apparatus.

5.7. During sample rotation, pressure may build up inside the bottle. Periodic venting of the bottle will relieve pressure.

5.8. Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.9. The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.10. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra® associate. The situation must be reported **immediately** to a laboratory supervisor.

5.11. Due to the potential for ignition and/or flammability, do not attempt to dry non-aqueous liquid samples in an oven.

6. EQUIPMENT AND SUPPLIES

6.1. Extraction vessels

6.1.1. For volatile analytes - zero-headspace extraction (ZHE) vessel, gas-pressure actuated, Millipore YT3009OHW or equivalent (see Figure 2).

6.1.2. For metals - either borosilicate glass jars (1/2 - 1 gallons, with Teflon lid inserts) or 1 L HDPE (Nalgene or equivalent) bottles may be used.

6.1.3. For non-volatile organics - only borosilicate glass may be used.

6.2. Vacuum filtration apparatus, capable of 0 - 50 psi and stainless steel pressure filtration apparatus (142 mm diameter), capable of 0 - 50 psi.

6.3. Borosilicate glass fiber filters, 0.6 - 0.8 µm (Whatman GF/F 14.2 cm, 0.7 µm or equivalent). When analyzing for metals, wash the filters with 1 N nitric acid and de-

ionized water prior to use. Glass fiber filters are fragile and should be handled with care.

6.4. Rotary agitation apparatus, multiple-vessel, Associated Design and Manufacturing Company 3740-6 or equivalent (see Figure 1). The apparatus must be capable of rotating the extraction vessel in an end-over-end fashion at 30 ± 2 rpm.

6.5. ZHE Extract Collection Devices are used to collect the initial liquid phase and the final extract of the waste from the ZHE device, either of the following may be used:

6.5.1. Gas-tight syringes, 100 mL capacity, Hamilton 0158330 or equivalent, or

6.5.2. Tedlar bags

6.6. Top loading balance, capable of 0 - 4000 ± 0.01g (all measurements are to be within ± 0.1 grams).

6.7. pH meter and probe capable of reading to the nearest 0.01 unit, and with automatic temperature compensation.

6.8. pH probes.

6.9. Magnetic stirrer/hotplate and stirring bars.

6.10. VOA vials, 20 mL, with caps and septa.

6.11. Glass jars, 1/2 - 1 gallon, with Teflon lid-inserts.

6.12. Nalgene plastic bottles, 1 liter.

6.13. Miscellaneous laboratory glassware and equipment.

7. REAGENTS AND STANDARDS

7.1. Reagent water for non-volatile constituents must be produced by a Millipore DI system or equivalent. For volatile constituents, water must be passed through an activated carbon filter bed (Milli-Q or tap water passed through activated carbon). Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Hydrochloric acid, 1 N: Carefully add 83 mL concentrated reagent grade HCl to 800 mL reagent water, cool and dilute to 1 liter with reagent water. Cap and shake to mix well.

7.3. Nitric acid, 1 N: Carefully add 64 mL concentrated reagent grade HNO_3 to 800 mL of reagent water, cool and dilute to 1 liter with reagent water. Cap and shake to mix well.

7.4. Sodium hydroxide, 1 N: Carefully add 40 g reagent grade NaOH pellets to 800 mL reagent water, stir until the pellets are completely dissolved, cool and dilute to 1 liter with reagent water.

CAUTION: Heat is generated during this process.

7.5. Acetic acid, glacial: concentrated, reagent grade liquid (HOAc).

7.6. pH calibration solutions: buffered to a pH of 4, 7, and 10. Commercially available. Fresh buffer solution must be used each day of analysis.

7.7. TCLP Leaching Fluids

7.7.1. General Comments

7.7.1.1. The pH of both solutions listed below should be monitored daily and the pH probes are to be calibrated prior to use.

7.7.1.2. The leaching fluids MUST be prepared correctly. If the desired pH range is not achieved and maintained, the TCLP may yield erroneous results due to improper leaching. If the pH is not within the specifications, the fluid must be discarded and fresh extraction fluid prepared.

7.7.1.3. Additional volumes of extraction fluids listed above may be prepared by multiplying the amounts of acetic acid and NaOH by the number of liters of extraction fluid required.

7.7.2. TCLP Fluid #1: Carefully add 5.7 mL glacial acetic acid and 64.3 mL of 1 N NaOH to 500 mL reagent water in a 1 liter volumetric flask. Dilute to a final volume of 1 L with reagent water, cap and shake to mix well. When correctly prepared, the pH of this solution is 4.93 ± 0.05.

7.7.3. TCLP Fluid #2: Carefully add 5.7 mL glacial acetic acid to 500 mL reagent water in a 1 liter volumetric flask. Dilute to a final volume of 1 L with

reagent water, cap and shake to mix well. When correctly prepared, the pH of this solution is 2.88 ± 0.05.

7.8. Nitric acid, 50% solution: Slowly and carefully add 500 mL concentrated HNO_3 to 500 mL reagent water. Cap and shake to mix well.

7.9. Sulfuric acid / nitric acid (60/40 weight percent mixture) H_2SO_4/HNO_3. Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid.

7.10. SPLP Leaching fluids

7.10.1. SPLP solutions are unbuffered and exact pH may not be attained. The pH of TCLP and SPLP fluids should be checked prior to use. If not within specifications, the fluid should be discarded and fresh fluid prepared.

7.10.2. SPLP fluid #1: Add 60/40 weight percent mixture of sulfuric and nitric acids to reagent water until the pH is 4.20 ± 0.05 This fluid is used for soils from a site that is east of the Mississippi River and for wastes and wastewaters.

7.10.3. SPLP fluid #2: Add 60/40 weight percent mixture of sulfuric and nitric acids to reagent water until the pH is 5.00 ± 0.05. This fluid is used for soils from a site that is west of the Mississippi River.

7.10.4. SPLP fluid #3: This fluid is reagent water and is used for leaching of volatiles. Additionally, any cyanide-containing waste or soil is leached with fluid #3 because leaching of cyanide containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

7.11. Methanol and methylene chloride - used to aid in cleaning oil contaminated equipment.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples being analyzed for non-volatile organic compounds should be collected and stored in glass containers with Teflon lid liners. Chemical preservatives shall NOT be added UNTIL AFTER leachate generation.

8.2. Samples being analyzed for metals only can be collected in either glass or polyethylene containers.

8.3. When the waste is to be evaluated for volatile analytes, care should be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in

Teflon lined septum capped vials with minimal headspace and stored at 4 ± 2 °C). Samples should be opened only immediately prior to extraction.

8.4. Samples should be refrigerated to 4 ± 2 °C unless refrigeration results in irreversible physical changes to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

8.5. The minimum TCLP sample collection size is determined by the physical state or states of the waste and the analytes of concern. The amount of waste required varies with the percent solids. The lower the percent solids, the more waste will be required for preliminary and final testing. For aqueous samples containing between 0.5 and 10% solids, several kilograms of sample are required to complete the analyses. The general minimal requirements when the samples are 100% solids include: 1 - 32 oz jar for semi-volatile organic analysis and metals, and 1 - 4 oz jar for volatile organic analysis. Low density sample materials, such as rags or vegetation, will require larger volumes of sample. For liquid samples (less than 50% solids), minimum requirements are 2 - 32 oz jars for semi-volatile organic analysis and metals, and 2 - 8 oz jars for volatile organic analysis. If volatile organic analysis is the only requested parameter, 2 separate jars are required. If matrix spike or duplicate control samples are requested, additional sample volume is required. If sufficient sample volumes were not received, analyses cannot be started and the client should be notified as soon as possible.

8.6. TCLP leachates should be prepared for analysis and analyzed as soon as possible following extraction. Leachates or portions of leachates for metallic analyte determinations must be acidified with nitric acid to a pH less than 2, unless precipitation occurs. If precipitation occurs upon addition of nitric acid to a small aliquot of the leachate, then the remaining portion of the leachate shall not be acidified and the leachate shall be analyzed as soon as possible. All other leachates should be stored under refrigeration (4 ± 2 °C) until analyzed. ZHE leachates must be stored in VOA vials filled to eliminate all headspace.

8.7. Samples are subject to appropriate treatment within the following time periods:

Table 1 - Holding Times (days)

Parameter	Collection to Start of TCLP Leach	End of TCLP Tumble to Preparation	Start of TCLP Leach or Semi- volatile Prep Extraction to Analysis	Total Elapsed Time
Volatiles:	14	N/A	14	28
Semi-volatiles:	14	7	40	61
Mercury:	28	N/A	28	56
Other Metals:	180	N/A	180	360

NOTE: The initial holding time is measured from date of collection to date TCLP extraction started. (This should be the TCLP extraction date in QuanTims.) Semi-volatile method prep holding time is measured from the day tumbling is complete to the start of method extraction. Subsequent analysis holding times are measured from the date extraction (TCLP or method prep) starts. If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding holding times is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory limit. The Total Elapsed Time is to be used as guidance. If preps are initiated at the last possible moment of a holding time, the elapsed times may be exceeded.

9. QUALITY CONTROL

9.1. Quality Control Batch (QC Batch) - QA-003 defines a QC Batch as a set of up to 20 field samples of similar matrix that behave similarly and are processed using the same procedures, reagents and standards within the same time period. The same lot of reagents must be used within a batch. A minimum of one TCLP extraction blank (Method Blank), one Laboratory Control Sample (LCS), one Matrix Spike (MS), and one Matrix Spike Duplicate (MSD) will be prepared with each TCLP leachate batch.

9.2. Batching Samples - Groups of samples with visibly different bulk matrices (e.g., petroleum sludge and soil samples) must be batched separately for QC testing purposes.

9.3. TCLP Extraction Blanks - A minimum of one blank (using the same extraction fluid as used for the samples) must be prepared and analyzed for every batch of samples extracted in a particular vessel type. The blanks are generated in the same way as the samples (i.e., blanks will be tumbled and filtered with the samples). Extraction vessels will be uniquely numbered. Each time a new batch is set up the blank should be rotated sequentially to the next vessel to ensure all vessels are periodically checked. Consult the Quanterra® QC Program and the individual analysis SOPs for blank acceptance criteria.

9.4. Laboratory Control Sample (LCS) - A LCS is required with each batch of 20 or fewer samples. The LCS shall be generated after a batch of TCLP leachates have been generated (i.e., at the time of the preparative digestion or extraction) by spiking an aliquot of the appropriate extraction fluid used for that batch. Consult the individual analysis SOPs for additional LCS guidance (i.e., spike amounts, spike levels, recovery criteria, etc.).

9.5. Matrix Spike (MS/MSD) - Matrix spikes are used to monitor the performance of the analytical methods on the matrix and to assess the presence of interferences. A MS/MSD pair are required with each batch of 20 or fewer samples.

9.5.1. Matrix spikes are to be added after filtration of the TCLP leachate. Spikes are not to be added prior to the TCLP leaching. <u>For metals, matrix spikes are to be added before preservation with nitric acid</u>.

9.5.2. The use of internal calibration or alternate methods may be needed when the recovery of the matrix spike is below the expected performance (see Section 9.6.2).

9.5.3. Consult the individual analysis SOPs for additional guidance on spike compounds and levels.

9.6. Corrective Actions

9.6.1. Consult the Quanterra® QC Program and individual analysis SOPs for corrective action for blanks and LCS

9.6.2. Method of Standard Additions (MSA) shall be used for metals if all of the following conditions are met:

- Recovery of the analyte in matrix spike is not at least 50%,
- the concentration of the analyte does not exceed the regulatory level, and
- the concentration of the analyte measured in the sample is within 20% of the appropriate regulatory level.

If the matrix spike recovery is 5% or less due to dilution or matrix interference, contact the project manager and client for guidance. The client should also be contacted prior to initiation of any MSA steps. Refer to the individual analysis SOPs for details on how to perform MSA analysis.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to appropriate analysis SOPs.

11. PROCEDURE

11.1. GENERAL COMMENTS

11.1.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented on a Nonconformance Memo kept in the project file and described in the final report. The variation must be approved by a project manager, Technical Specialist and QA Manager. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.2. PRELIMINARY SAMPLE EVALUATIONS (Refer to Flow Chart #1, Appendix D)

11.2.1. Preliminary TCLP evaluations (percent solids, particle size, selection of extraction fluid, and fluid/leachate compatibility) are required to be done using a minimum of a 100 gram aliquot of waste. This aliquot may also undergo the actual TCLP or SPLP extraction for Non-volatiles ONLY IF it has NOT been oven dried. If the solid portion is oven dried, a separate aliquot must be used for the actual leaching procedure.

11.2.2. Consult the holding times for the appropriate tests (Section 8.7) and prioritize extractions such that holding times are not exceeded.

11.2.3. Determine the total volume of TCLP leachate (solid phase leachate + liquid filtrate) that needs to be generated for analysis according to the following:

Table 2. Minimum Required Leachate Volume

Analysis	Required Volume (mL)
Volatiles	3 x 20
Semi-volatiles	400
Pesticides	200
Herbicides	200
Metals	300

11.2.3.1. SPLP - similar volumes are required for volatiles and metals. If semivolatiles, pesticides or herbicides are required, a full 1 L volume must be prepared for each test requested.

11.2.3.2. For TCLP and SPLP samples used for matrix spike and matrix spike duplicate analysis, three times the listed volumes are required.

11.2.4. **Sample Description** (enter data on Worksheet 1)

11.2.4.1. Record the number of phases observed in the sample. It is common that when more than one container of multi-phasic materials is received from the field, each container will show different amounts of each phase.

11.2.4.1.1. If the sample has multiple phases and is received in more than 1 bottle then the contents of each bottle

should be combined in a single larger container prior to processing the sample further. If this is not possible, then the alternate procedure described in the following section should be used.

11.2.4.1.2. Properly record the relative amounts of each phase by measuring the depth of the layers in each container after the contents have been allowed to settle. Determine the combined volume of each phase for all containers. Then mark the phase composition on a single container, mix thoroughly to obtain a representative subsample, and accurately measure the phase composition according to the following procedure. The two sets of values (combined volumes per phase and phase composition for one container) are used to determine the correct volume/mass adjustments on the final result. This procedure is not appropriate if testing will be done for volatile organic compounds.

11.2.4.2. Solid - record the visible presence of a solid material heavier than water. If the sample contains more than one solid phase (e.g., wood and sediment mixed with water), attach additional documentation to Worksheet 1, line A1.

11.2.4.3. Liquid - record the number of liquid phases observed in the sample according to apparent density. It may be impossible to distinguish apparent density if only one liquid phase is observed and there is no indication on the COC form. If this is the case, record it as aqueous material and let the subsequent analytical record show if the liquid is organic.

11.2.5. **Percent Solid Phase** (enter data on Worksheet No. 1)

11.2.5.1. Percent Solids and ZHE Extractions - The ZHE filtration apparatus cannot accurately determine percent solids less than 5%. If an extraction is to be performed solely for volatile organic compounds and the percent solids concentration is apparently greater than 5%, proceed to Section 11.4 (Procedure: ZHE Extraction Procedure, Volatile Constituents). Otherwise, continue with the steps in this section. The aliquot of sample used here cannot be used again for the ZHE extraction.

11.2.5.2. Determine Type of Filtration Apparatus Needed

11.2.5.2.1. If the waste will obviously yield no free liquid when subjected to pressure filtration (i.e., it is 100% solid), then proceed to Section 11.2.6 (Particle-size Reduction).

11.2.5.2.2. If the sample is mostly a non-viscous liquid (water or non-viscous organic liquid) of low solids content (<10%) or a highly granular, liquid containing waste vacuum filtration may be used.

11.2.5.2.3. If the sample is viscous (sludge or has high solids content), use pressure filtration.

11.2.5.3. Weight of filter - Measure and record this value before loading the filter into the filter holder (Worksheet 1, line B1).

11.2.5.4. Weight of subsample and filtrate for percent solids measurement

11.2.5.4.1. Assemble the filtration apparatus (use blunt forceps to handle the 0.6 to 0.8 µm filter membrane).

11.2.5.4.2. Homogenize the waste, transfer a minimum of a 100 g subsample to the weighing vessel. Measure and record the gross weight (Worksheet 1, line B2a).

11.2.5.4.3. Measure and record the tare weight of the filtration vessel (Worksheet 1, line B3b).

11.2.5.4.4. Transfer the sample to the filtration device attempting to spread the waste sample evenly over the surface of the filter. Measure and record the tare weight of the empty weighing vessel and any residual sample (Worksheet 1, line B2b).

11.2.5.4.5. Calculate and record the net weight of sample used for testing (Worksheet 1, line B2c).

11.2.5.5. Filtration for percent solids

11.2.5.5.1. Slowly apply gentle pressure or vacuum of 10 psi to the filtration apparatus. Allow the sample to filter until no SIGNIFICANT additional liquid has passed through the filter during a 2 minute period.

11.2.5.5.2. Repeat previous step by increasing the pressure in 10 psi increments until a maximum of 50 psi is reached. Stop the filtration when no additional filtrate is generated within a 2 minute period.

Note: Some samples will contain liquid material that does not filter (e.g., oil). Do not attempt to filter the sample again by exchanging filters. Viscous oils or any wastes which does not pass through the filter is classified as a solid.

11.2.5.5.3. Remove the filtrate collection vessel, weigh and record the gross weight (Worksheet 1, line B3a).

11.2.5.5.4. Calculate and record the net weight of filtrate (Worksheet 1, line B3c). This result will be used in the percent solids calculation.

11.2.5.5.5. Pour the filtrate into a graduated cylinder. Measure and record the volume of the aqueous phase (Worksheet 1, line B7). Measure and record the volume of any organic phase (Worksheet 1, line B8). If more than one organic phase is observed, enter "see below" and provide a description at the bottom of Worksheet 1. These results will be used in the final sample calculations (Worksheets 5 & 6).

11.2.5.5.6. Retain the filtrate for use in Section 11.2.8 (Determination of Filtrate/Extraction Fluid Compatibility), and for possible recombination with the filtrate obtained in Section 11.3.

11.2.5.6. Percent of Wet Solids

11.2.5.6.1. Calculate the total weight of wet solids using Equation 0 on Worksheet 1 and record the result on line B4.

11.2.5.6.2. Calculate the weight percent of wet solids using Equation 1 on Worksheet 1 and record the result on line B5.

11.2.5.6.3. If the percent wet solids result is $\geq 0.5\%$ and $< 5.0\%$, and it is noticed that a small amount of the aqueous filtrate is entrained in the wetting of the filter, proceed

to Section 11.2.5.7 to complete the percent solids measurement on a dry-weight basis.

Note: If obviously oily (non-aqueous) material is entrained on the filter, do not dry the filter; proceed to Section 11.2.6 (Particle-Size Reduction).

11.2.5.6.4. If the percent wet solids result is greater than 5.0%, proceed to Section 11.2.6 (Particle-Size Reduction) and mark "≥0.5%" on Worksheet 1, line B6c.

11.2.5.6.5. If the percent wet solids result is less than 0.5%, discard the solid phase. No leaching will be necessary; the filtrate is equivalent to the final leachate.

11.2.5.7. Weight percent of dry solids (skip this step for oily samples).

Note: These steps are required only if it is noticed that a small amount of the filtrate is entrained in wetting of the filter <u>and</u> the percent wet solids content is ≥ 0.5% and < 5.0 %.

11.2.5.7.1. Remove the filter with the wet solids from the filtration apparatus.

11.2.5.7.2. Dry the filter and solid phase at 100 ± 20 ° C.

11.2.5.7.3. Remove the filter from the oven and allow to cool in a desiccator.

11.2.5.7.4. Weigh and record the gross dry weight (Worksheet 1, line B6a).

11.2.5.7.5. Repeat the drying step. Weigh and record the second gross dry weight (Worksheet 1, line B6b). If the two weightings do not agree within 1%, perform additional drying and weighing until successive weighings agree within 1%.

11.2.5.7.6. Calculate the weight percent of dry solids using Equation 2 on Worksheet 1 and record the result on line B6c.

11.2.5.7.7. If the dry solids result is ≥ 0.5% and the sample will be extracted for non-volatile constituents, proceed to

Section 11.2.6 (Particle Size Reduction) using a fresh wet portion of waste.

11.2.5.7.8. If the percent solids result is less than 0.5%, discard the solid phase. No leaching will be necessary; the filtrate is the TCLP leachate. Proceed to Section 11.2.8 (Determination of Filtrate/Leachate Compatibility) to determine whether or not the material is a non-aqueous, immiscible liquid.

11.2.6. **Particle-size Reduction for Fluid Selection** (enter data on Worksheet 2)

11.2.6.1. The subsample used for fluid selection must consist of particles less than 1 mm in diameter (versus the less than 1 cm requirement for the material used for the actual extraction). The method requires a smaller particle size to partially compensate for the shorter duration of contact time with the leachate solution as compared to the full extraction. Inappropriate use of coarser materials could result in the selection of the wrong fluid type.

11.2.6.2. Surface area exclusion - size reduction is not required if the sample surface area is greater than or equal to 3.1 cm^2 per gram. Enter "No" on Worksheet 2, line C1.

11.2.6.3. If the sample contains particles greater than 1 mm in diameter, crush, cut, or grind the solids to the required size. Enter "Yes" on Worksheet 2, line C1.

11.2.6.4. Consult your supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick).

11.2.7. **Determination of Appropriate Extraction Fluid** (Worksheet 2)

11.2.7.1. If the solid content is greater than or equal to 0.5%, and if the sample is being analyzed for metals or nonvolatile organic compounds, the type of leaching solution must be determined.

11.2.7.2. Follow times, temperature, and particle size specified in this section as closely as possible. If reaction time between the acid solution and solid waste is too short or too long, the procedure may produce false pH readings.

11.2.7.3. For SPLP, refer to Section 7.10 for fluid selection. Matrix type must be specified by the client. Check special instructions or see

the project manager, then put a check mark by the fluid type selected (Worksheet 2, D).

11.2.7.4. The TCLP leaching fluid for all volatiles is Fluid #1.

11.2.7.5. For TCLP leach fluid determination for non-volatile analytes, continue with the following steps.

11.2.7.6. Calibrate the pH meter with fresh buffer solution in accordance with the pH SOP.

11.2.7.7. Weigh out a 5.0 ± 0.1 g subsample (less than 1 mm particle size) of the solid phase into a 250-mL beaker, and enter a "✔" on Worksheet 2, line C2. If 5.0 grams not used, enter the actual weight on line C2.

11.2.7.8. Add 96.5 ± 1.0 mL of reagent water, cover with a watchglass, and stir for 5 minutes on a stirrer, and enter a "✔" on Worksheet 2, line C3. If a different volume used, enter the actual volume on line C3.

11.2.7.9. Measure and record the sample pH (Worksheet 2, line C4).

Note: To avoid damaging the pH probe when organic liquid is present, use narrow range pH indicator paper.

11.2.7.10. If the pH is less than or equal to 5.0, use Fluid #1 and proceed to Section 11.2.8 (Fluid Compatibility).

11.2.7.11. If the fluid pH is greater than 5.0, add 3.5 mL 1 N HCl, cover with a watchglass. Slurry the sample briefly then heat at 50 °C for 10 minutes. Enter a "✔" on Worksheet 2, line C5 and C6).

Note: The heating cycle is a critical step. If the solid waste does not remain in contact with the acidic solution under specified time and temperature conditions, an erroneous pH may be measured.

11.2.7.12. Cool to room temperature.

11.2.7.13. Measure and record the pH immediately after the sample has reached room temperature (Worksheet 2, line C7).

11.2.7.13.1. If the pH is less than or equal to 5.0, use Fluid #1. Enter a "✔" on Worksheet 2, line D1.

11.2.7.13.2. If the pH is greater than 5.0, use Fluid #2. Enter a "✔" on Worksheet 2, line D2.

11.2.8. **Determination of Filtrate/Extraction Fluid Compatibility** (skip this step for SPLP extractions)

11.2.8.1. Place 5 mL of the appropriate leaching fluid (determined in the previous step) into a 20-25 mL vial.

Note: Use fluid type # 1 if simply testing the filtrate for a sample with less than 0.5% solids.

11.2.8.2. Add 5 mL of the initial filtrate, cap and shake.

11.2.8.3. If the phases are miscible, the initial filtrate and solid phase leachate will be physically recombined upon completion of the leachate generation. Enter a "✔" on Worksheet 2, line D3 for TCLP, or on line D1 for SPLP.

11.2.8.4. If the phases are NOT miscible, enter "No" on Worksheet 2, line D3. The initial filtrate and the solid phase leachate will be prepared and analyzed separately and the results mathematically combined (see Section 12.1.4).

11.2.9. For samples requiring analysis for semi-volatile organics, pesticides, herbicides or metals proceed to Section 11.3.

11.2.10. For samples requiring analysis for volatile organics (ZHE), proceed to Section 11.4.

11.3. **BOTTLE EXTRACTION PROCEDURE: NON-VOLATILE CONSTITUENTS: SEMI-VOLATILES, PESTICIDES, HERBICIDES, METALS** (Refer to Flow Chart #2, Appendix D)

11.3.1. All masses should be recorded to the nearest 0.1 g.

11.3.2. The aliquot used in the Preliminary Evaluation MAY be used for this procedure ONLY if it was not oven dried. If the sample is 100% solid or if the preliminary aliquot was not oven dried proceed directly to Section 11.3.7 (Particle Size Reduction). If the Preliminary Evaluation aliquot was oven dried then, using a fresh aliquot of sample, continue as described in Sections 11.3.3 through 11.3.6.

11.3.3. Examine the sample and determine the type of filtration to employ per Section 11.2.5.2.

11.3.4. Repeat the steps outlined in Sections 11.2.5.3 through 11.2.5.5.3.

11.3.5. Determine and record the volume (mass) of the initial filtrate. Cover with aluminum foil and retain for use as defined in Section 11.3.18.

11.3.6. Determine and record the "solid" phase mass by subtracting the mass of the liquid filtrate from the mass of the subsample.

11.3.7. Evaluate the solid portion of the waste for particle size. If it contains particles greater than 1 cm in size, prepare the solid portion of the waste for leaching by crushing, cutting, or grinding such that all particles are less than 1 cm in size (i.e., capable of passing through a 9.5 mm, 0.375 inch, standard sieve). Size reduction is not required if the sample surface area is greater than or equal to 3.1 cm^2 per gram. If particle size reduction was required, record this on Worksheet 3, line E1.

11.3.7.1. Consult your supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick). Scissors or shears may be used to cut cloth, plastic or sheet metal. Saws may be used for wood or solid metal. Bricks, rocks, or other solids amenable to grinding should be subcontracted out for particle size reduction. (Contact PA or PM.) Note that size reduction to fine powder is not appropriate, and could invalidate results. If necessary, consult client for guidance.

11.3.8. Determine the minimum total volume of solid phase leachate that needs to be generated. Refer to Section 11.2.3.

11.3.9. Divide the total volume of solid phase leachate required by 20 to determine the mass of solid phase required for leaching. Round this mass UP to the nearest 5g.

11.3.10. Weigh the required mass of solid phase into an appropriate bottle (plastic for metals only, glass for all others) and **slowly** add 20 times its mass of appropriate leaching fluid as determined under Section 11.2.7 (e.g., 20 g of sample would require 400 g of leaching fluid). Record the weight of the sample aliquoted for the extraction on Worksheet 3, line E2 and the amount of extraction fluid added on line F1.

11.3.11. Ensure any effervescence has stopped before capping the bottle tightly. Secure in a rotary agitator and rotate end-over-end at 28-32 rpm for 16-20

hours. The temperature of the room should be 23 ± 2°C. The room temperature and time should be checked at both the start and end of the extraction and recorded on Worksheet 3, lines G1 through G3.

NOTE: As agitation continues, pressure may build up within the bottle for some types of wastes. To relieve excessive pressure, the bottle may be removed and opened periodically in a properly vented hood to relieve any built-up pressure.

11.3.12. Remove the bottle and filter the sample using vacuum or pressure filtration by filtering through a new glass fiber filter as discussed in Sections 11.2.5.5.1 - 11.2.5.5.2. For final filtration of the TCLP leachate, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filters must be acid washed if metals are to be determined (see Section 6.3). The entire sample need not be filtered; however, sufficient volume should be generated to support the required analyses. Record the date and time the filtration is completed on Worksheet 3, Line G4.

11.3.13. If the waste contained no initial filtrate, this solution from 11.3.12 is defined as the TCLP leachate.

11.3.14. If the waste did yield an initial filtrate, consult the worksheet for initial filtrate/leachate compatibility. If they are compatible, they are to be combined in the correct proportions (see Section 12.1.4) and mixed well. This combined solution is defined as the TCLP leachate.

11.3.15. If the individual phases are NOT compatible, they are to be prepared and analyzed separately and the results combined mathematically. See Section 12.1.5.

11.3.16 Measure and record the pH of the TCLP leachate on Worksheet 3, Line 5. (Do not attempt to measure the pH of oily samples as the probe may be rendered inoperable.)

11.3.17. Prepare subsamples for metals for MS/MSD quality control testing using the appropriate TCLP spiking solution (do not spike for organics). Refer to the appropriate determinative SOPs for further guidance on the spike components, levels and action criteria.

11.3.18. Immediately preserve the leachate as follows:

Metals	pH < 2 w/50% HNO_3 for non-oils (do not acidify oils)
All others	Refrigerate to 4 ± 2 °C

Note: Refer to Section 8.6 if precipitation occurs upon preservation.

11.3.19. Label each sample with the appropriate information and submit to the appropriate analytical groups for prep and analysis with copies of the TCLP preparation worksheets.

11.4. **ZHE EXTRACTION PROCEDURE: VOLATILE CONSTITUENTS** (Refer to Flow Chart #3, Appendix D)

11.4.1. Use the ZHE device to obtain a TCLP leachate for analysis of volatile compounds only. Leachate resulting from the use of the ZHE shall NOT be used to evaluate the mobility of non-volatile analytes (e.g., metals, pesticides, etc...).

11.4.2. Due to some shortcomings of the method, losses of volatile compounds may occur. Extra care should be observed during the ZHE procedure to ensure that such losses are minimized. Charge the ZHE with sample only once and do not open the device until the final extract has been collected. Do not allow the waste, the initial liquid phase or the extract to be exposed to the atmosphere any longer than necessary.

11.4.3. If the TCLP extraction is for volatile components only, refer to Section 11.2.5.1 before proceeding.

11.4.4. All masses should be recorded to the nearest 0.1 g.

11.4.5. Assemble the ZHE apparatus. Test for leakage by closing all valves except the gas inlet/outlet valve and pressurizing to 50 psi. Allow to stand for 15 minutes and check the pressure on the built-in gauge to make sure it is not leaking. If the pressure is NOT 50 psi, consult your supervisor.

11.4.6. Adjust the ZHE piston in the ZHE body to the appropriate height (slightly moisten the O-rings with leaching fluid if necessary).

11.4.7. Consult the worksheet and examine the sample. If the sample appears to be different from the preliminary information found on the worksheet, consult your supervisor.

11.4.8. If the preliminary evaluations indicated the need for particle size reduction, homogenize the waste, weigh out a sufficient size subsample and prepare for leaching by crushing, cutting, or grinding such that all particles are less than 1 cm in size as measured with a ruler (Do NOT sieve the sample). Size reduction is not required if the sample surface area is greater than or equal to

3.1 cm^2 per gram If particle size reduction was required record this on Worksheet 4, Line H1.

Note: To minimize loss of volatiles, samples for volatiles that require particle size reduction should be kept in sample storage (at 4 °C) until immediately before size reduction. Aggressive reduction which would generate heat should be avoided and exposure of the waste to the atmosphere should be avoided to the extent possible. Size reduction to a fine powder is not appropriate. Also see Section 11.3.11.

11.4.8.1. Consult your supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick). Scissors or shears may be used to cut cloth, plastic or sheet metal. Saws may be used for wood or solid metal. Bricks, rocks, or other solids amenable to grinding should be subcontracted out for particle size reduction (Contact PA or PM).

11.4.9. Place the ZHE apparatus on the balance and tare the balance.

11.4.10. Determine the appropriate size subsample to weigh using the percent solids information from Section 11.2.5 and record the weight used on Worksheet 4, Line H2.

11.4.10.1. For wastes that are 100% solids, a 25 g sample is used.

11.4.10.2. For wastes containing < 0.5% solids the liquid portion of the waste, after filtration, is defined as the TCLP leachate. Filter enough of the sample to support all of the volatile analyses required.

11.4.10.3. For wastes containing ≥ 0.5% and < 5.0% solids, a 500 g subsample of waste is recommended.

11.4.10.4. If the sample has ≥ 5.0% solids, the appropriate sample size should be determined using the equation in Section 12.1.2.

Note: For wastes containing greater than 0.5% wet or dry solids (Section 11.2.5), the "solids" value from the ZHE filtration process may be used to determine the volume of fluid to load into the ZHE. This approach is recommended since the solids value from Section 11.2.5 may differ from the filtration solids due to sample variability or differences in the filtration apparatus.

11.4.11. Homogenize and transfer an appropriate size subsample of the waste into the ZHE and record the mass on Worksheet 4, Line I1.

11.4.12. Carefully place the glass fiber filter between the support screens and secure to the ZHE. Tighten all the fittings.

11.4.13. Place the ZHE in a vertical position; open both the gas AND liquid inlet/outlet valves. Attach a gas line to the gas inlet/outlet valve.

11.4.14. If the waste is 100% solid, slowly increase the pressure to a maximum of 50 psi to force out as much headspace as possible and proceed to Section 11.4.18.

11.4.15. If the waste is < 100% solids, carefully apply gentle pressure of 10 psi (or more, if necessary) to force all headspace slowly out of the ZHE. At the FIRST appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue gas pressure.

11.4.16. Assemble a syringe and place the plunger in all the way. Adjust the tension on the plunger to provide slight drag. Attach the pre-weighed syringe or Tedlar bag to the liquid inlet/outlet valve and open the valve. Record the tare weight of the collection device on Worksheet 4, Line 3b.

11.4.17. Carefully apply gas pressure of no more than 10 psi to force out the liquid phase. Allow the sample to filter until no SIGNIFICANT additional filtrate has passed in a 2 minute period.

Note: If the capacity of the syringe is reached, close the liquid inlet/outlet valve, discontinue gas pressure, remove the syringe and return to Section 11.4.15.

11.4.18. Repeat previous step increasing the pressure in 10 PSI increments until 50 psi is reached and no significant liquid has passed in a 2 minute period. Remove the collection device and record the total weight of the collection device with filtrate on Worksheet 4, Line 3a. Close the valve and discontinue gas pressure. Transfer the filtrate to VOA vials and label appropriately. Calculate the weight of filtrate collected and record on Worksheet 4, Line I3c.

Notes: If the original waste contained less than 0.5% solids (Section 11.2.5), this filtrate is defined as the TCLP leachate and you may proceed to Section 11.4.28. Otherwise, save the vials by storing at 4 C under minimal headspace conditions, for recombination as in Section 11.4.27.

The material remaining in the ZHE is defined to be the "solid" phase. Calculate the weight of the solid phase using Equation 4.

11.4.19. Based on the information from Sections 11.2.5 and 11.4.11 and using the formula in 12.1.3, determine the weight of fluid to load into the ZHE on the "solid" phase. The ZHE device has approximately a 500-mL capacity. Based on the need to add an amount of extraction fluid equal to 20 times the mass of the "solid" phase, the ZHE can therefore accommodate a maximum of 25 grams of "solid".

Note: The TCLP ZHE prep uses only TCLP fluid #1; the SPLP ZHE prep uses only SPLP fluid #1.

11.4.20. Load the fluid transfer reservoir with an excess of Fluid #1 and preflush the transfer line to eliminate air pockets. Be sure the required volume remains.

11.4.21. Attach the transfer line to the liquid inlet/outlet valve and open the valve. Carefully pump the required volume into the ZHE and close the valve. Disconnect the transfer line.

11.4.22. Check the ZHE to make sure all the valves are closed and manually rotate the ZHE (end-over-end) 2 or 3 times. Reposition the ZHE in the vertical position.

11.4.23. Pressurize the ZHE to 5-10 psi. Allow to stand for 10 minutes, and then recheck the pressure. If the ZHE appears to be leaking, follow the corrective action protocols recommended by the manufacturer and repeat the analysis.

11.4.24. Slowly open the liquid inlet/outlet valve to bleed out any headspace that may have been introduced during the introduction of the Fluid. Upon the first sign of liquid from the valve, close the valve.

11.4.25. Repressurize the ZHE to 5-10 psi and place in the rotary agitator. Rotate at 28-32 rpm for 16-20 hours. Room temperature should be 23 ± 2 °C. The room temperature and time should be checked at both the start and end of the extraction and recorded on Worksheet 4, lines J1, J3 and J4.

11.4.26. Confirm that the pressure of 5-10 psi was maintained throughout the leaching. If it was NOT maintained, return to Section 11.4.1 and repeat the leachate with a new aliquot of sample.

11.4.27. Attach a syringe or Tedlar bag and open the liquid inlet/outlet valve to collect the aqueous leachate and proceed as outlined in 11.4.19 - 11.4.20. Record the volume/mass of the leachate and any oil phase on Worksheet 4, Lines J7 and J7a. Record the date and time the filtration is completed on Worksheet 4, Line J6.

Notes: If the waste contained an initial liquid phase, the liquid may be filtered directly into the same collection device holding the initial liquid phase of the waste.

A separate filtrate collection container must be used if combination would create multiple phases or there is not enough volume left within the filtrate collection container.

11.4.28. If the waste contained an initial filtrate (Section 11.4.18) that is miscible with the solid phase leachate (as determined in Section 11.2.8), the solid phase leachate and the initial filtrate are directly recombined in the correct proportions (see Section 12.1.4). If the individual phases are NOT compatible, they are to be collected, prepped and analyzed separately.

Note: Chill the filtrate and receiving vessels before recombining.

11.4.29. Following collection, store the TCLP leachate in 3 20-mL VOA vials with minimal headspace at 4 ± 2 °C and prepare for analysis as soon as possible using the appropriate organic extraction procedure (see Section 16.3).

11.4.30. If the individual phases are analyzed separately, combine the results mathematically by using the recombination calculation in Section 12.1.5.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

12.1.1. Calculation of Percent Wet Solids:

$$Percent\ Wet\ Solids = 100\left|\frac{Mass,"solid"\ phase}{Mass, initial\ subsample}\right|$$

12.1.2. Calculation of weight of waste to charge to ZHE:

$$Weight\ of\ waste\ to\ charge\ to\ ZHE = 100\left|\frac{25}{\%wet\ solids}\right|$$

12.1.3. Calculation of weight of extraction fluid to use:

$$Weight\ of\ Extraction\ fluid = \frac{20\ x\ \%\ wet\ solids\ x\ weight\ of\ waste\ to\ be\ extracted}{100}$$

12.1.4. Calculation of volume of initial filtrate phase to recombine with solid phase leachate:

$$\text{Volume of filtrate for recombination} = \left[\frac{\textit{Weight of solids leached}}{\textit{Total weight of solids}}\right]\left[\left(\frac{\textit{Leachate recovered}}{\textit{Fluid added}}\right)\right]\left(\textit{Volume of initial aqueous filtrate}\right)$$

12.1.5. Mathematical recombination of analytical results:

$$\textit{Final Analyte Concentration} = \frac{(V_1 \times C_1) + (V_2 \times C_2)}{V_1 + V_2}$$

V_1 = total volume of the initial filtrate phase (L).
C_1 = analyte concentration in initial filtrate phase (mg/L).
V_2 = volume of the theoretical solid phase leachate (L).
C_2 = analyte concentration in solid phase leachate (mg/L).,

12.2. REPORTING REQUIREMENTS

12.2.1. Follow these reporting conventions for multi-phase samples:

12.2.1.1. If both phases have positive results, use the values from each phase to calculate the recombined result. Use the reporting limit for each phase to calculate the recombined reporting limit.

12.2.1.2. If both phases are "ND," not detected, the recombined result is "ND," and the reporting limit is calculated from the reporting limit for each phase.

12.2.1.3. If one phase is "ND" and the other phase has a positive result, use the reporting limit for the "ND" phase and the positive value for the other phase to calculate the combined result. The combined reporting limit is based on the reporting limit for both phases. If the combined result is less than the combined reporting limit, then supply a footnote to indicate that "a positive result was detected below the calculated detection limit."

12.2.2. Units - regardless of the nature of the sample, all TCLP and SPLP results are reported in units of mg/L.

12.2.3. For limits and significant figures, consult the appropriate analytical methods (Section 16.3).

12.2.4. Anomalies - all anomalies observed during the leach procedure must be noted on the worksheet or an anomaly form. Some examples of such anomalies are:

12.2.4.1. Sample was monolithic - subsample was obtained by crushing, cutting, grinding, sawing, etc.

12.2.4.2. Insufficient sample - less than the required 100 g minimum was available.

12.2.4.3. Multiple phases - "X" phases were present.

12.2.4.4. Sample was oil - single phase.

12.2.4.5. Sample contained liquid which did not filter under test conditions.

12.3. REVIEW REQUIREMENTS

12.3.1. Review all applicable holding times. If a holding time was exceeded, confirm that a holding time violation form was properly documented and routed.

12.3.2. If Total analysis results are available, those results may be compared with the TCLP analysis results according to the following:

$$Total \geq 20 \times TCLP$$

NOTE: Assumes the sample is 100% Solids.

12.3.3. Total constituent analysis results can be used to demonstrate the TCLP protocol is unnecessary. In performing a TCLP analysis, there is a 20:1 dilution of the original sample with the leaching solution. Thus, if the "total constituent" result is less than 20 times the TC level, it is impossible for the leachate to "fail" and the TCLP does not need to be performed. For example, the TC level for lead is 5.0 mg/L (ppm). Therefore, if a sample of lead-contaminated soil contains less than 100 ppm total lead, a TCLP test need not be run for lead.

13. METHOD PERFORMANCE

13.1. Refer to individual analysis SOPs.

13.2. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure must be segregated and disposed according to the facility's hazardous wastes procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. Method 1311, Toxicity Characteristic Leaching Procedure, Revision 0, July 1992, SW-846 Final Update I.

16.2. Method 1312, Synthetic Precipitation Leaching Procedure, Revision 0, November 1992, SW-846 Proposed Update II.

16.3. Related Documents

16.3.1. Toxicity Characteristic: Corrections to Final Rule. Method 1311, Federal Register, Vol. 55, No. 126, Friday, June 29, 1990.

16.3.2. Toxicity Characteristic: Final Rule. Method 1311, Federal Register, Vol. 55, No. 61, Thursday, March 29, 1990.

16.3.3. Technical Background Document and Response To Comments, Method 1311, Toxicity Characteristic Leaching Procedure, USEPA/OSW, April, 1989.

16.3.4. QA-003, Quanterra® QC Program

16.3.5. CORP-IP-0003: Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods.

16.3.6. CORP-MT-0001: Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis, Method 6010A and Method 200.7.

16.3.7. CORP-MT-0003: Graphite Furnace Atomic Absorption Spectroscopy, SW846 Method 7000A and MCAWW 200 Series Methods.

16.3.8. CORP-MT-0005: Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, SW-846 7470A and MCAWW 245.1.

16.3.9. CORP-IP-0003: Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods.

16.3.10. CORP-MS-0002: Determination of Volatile Organics by GC/MS based on Methods 8240B and 8260A.

16.3.11. CORP-MS-0001 : GC/MS Analysis Based on Method 8270B, SW846.

16.3.12. CORP-GC-0001: Gas Chromatographic Analysis Based on Methods 8000A, 8010B, 8020A, 8080A and 8150B, SW846.

16.3.13. CORP-OP-0001: Extraction and Cleanup of Organic Compounds from Waters and Soils, Based on SW846 3500 Series, 3600 Series, 8150 and 600 Series Methods.

17. MISCELLANEOUS

17.1. Modifications/Interpretations from Reference Methods

17.1.1. Section 8: Preliminary Evaluations. Section 7.1 of the source method states that the sample aliquot used for the preliminary evaluation "...may not actually undergo TCLP extraction." Section 7.1.5 of the source method indicates that the portion used for the preliminary evaluation may be used for either the ZHE or non-volatile extraction if the sample was 100% solid. Section 7.1.5 further indicates that if the sample was subjected to filtration (i.e., < 100% solid) that this aliquot may be used for the non-volatile extraction procedure only as long as sufficient sample is available (minimum 100 g). Samples which have been subjected to the oven drying step may not be used for TCLP extraction because solid phase degradation may result upon heating.

17.1.2. Section 11.2.5.6.3: Percent Solids Determination. Section 7.1.2 of the source method indicates that "if the percent wet solids is ≥ 0.5% and it is noticed that a small amount of the filtrate is entrained in wetting of the filter"

that the filter should be oven dried to determine percent dry solids ". Drying of oil or organic matrices can both be hazardous and inappropriate. Additionally, it may be impossible to achieve a constant weight when performing this step. Due to safety concerns, if obviously oily or heavy organic matrices are entrained on the filter, the filter is not oven dried.

17.1.3. Section 11.2.8: Preliminary Determination of Filtrate/Extraction Fluid Compatibility. Section 7.2.13 of the source method provides no guidance as to how to make this determination. As a result, the procedure herein was developed and incorporated into the Preliminary Determinations section.

17.1.4. Section 9.2: TCLP Extraction Blanks. Section 8.1 of the source method states that a minimum of one blank for every 20 extractions "...that have been conducted in an extraction vessel." Quanterra® has interpreted this to mean one blank per twenty samples leached per TYPE of leaching vessel (i.e., Bottle or ZHE) per leach fluid used.

17.1.5. Section 11.2.7.9: Determination of Appropriate Extraction Fluid. Method 1311 does not address the appropriate approach to take if the pH equals 5.0. This SOP requires that Fluid #1 must be used if the pH is less than or equal to 5.0.

17.1.6. Section 9.4: QA/QC - Matrix Spikes. Section 8.2 of the source method states "A matrix spike shall be performed for each waste type..." and "A minimum of one matrix spike must be analyzed for each analytical batch." Further, Section 8.2.3 of the source method also states "The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist." The standard Quanterra® QAPP is designed to address the performance monitoring of analytical methodology through the LCS program. A minimum of one MS and MSD will be prepared for each TCLP leachate batch. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, the MS/MSD results have immediate bearing only on the specific sample spiked and not all samples in the batch.

17.1.7. Section 8.2.2 of the source method states that "In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level." The method also states "If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration but may not be less than five times the method detection limit". For several analytes, spiking at the regulatory level is inappropriate to the range of analysis afforded by the determinative methods.

Due to the wide range in these levels, Quanterra® spikes at the levels specified in the determinative SOPs.

17.2. Modifications from Previous SOP

None

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

17.4. Documentation and Record Management

The following documentation comprises a complete TCLP preparation raw data package:

- Completed worksheets (Appendix C).
- Non-conformance summary (if applicable).
- Anomaly documentation (if applicable).

APPENDIX A

TABLES

Table 3 - Toxicity Characteristic Analytes and Regulatory Levels (Final Rule)

Contaminant	mg/L
Arsenic	5.0
Barium	100.0
Benzene	0.5
Cadmium	1.0
Carbon tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
Chromium	5.0
o-Cresols	200.0
m-Cresols	200.0
p-Cresols	200.0
Total Cresols (used if isomers not resolved)	200.0
2,4-D	10.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
2,4-Dinitrotoluene	0.13
1,1-Dichloroethylene	0.7
Endrin	0.02
Heptachlor (& epoxide)	0.008
Hexachlorobenzene	0.13
Hexachlorobutadiene	0.5
Hexachloroethane	3.0
Lead	5.0
Lindane	0.4
Mercury	0.2
Methoxychlor	10.0
Methyl ethyl ketone	200.0
Nitrobenzene	2.0
Pentachlorophenol	100.0
Pyridine	5.0
Selenium	1.0
Silver	5.0
Tetrachloroethylene	0.7
Toxaphene	0.5
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP (Silvex)	1.0
Vinyl chloride	0.2

APPENDIX B

FIGURES

Figure 1 & 2 - Rotary Agitation Apparatus and Zero Headspace Extraction Vessel (ZHE)

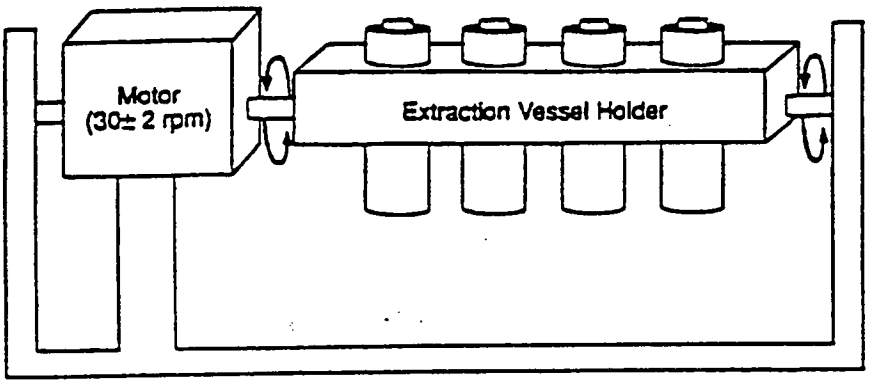

Figure 1. Rotary Agitation Apparatus

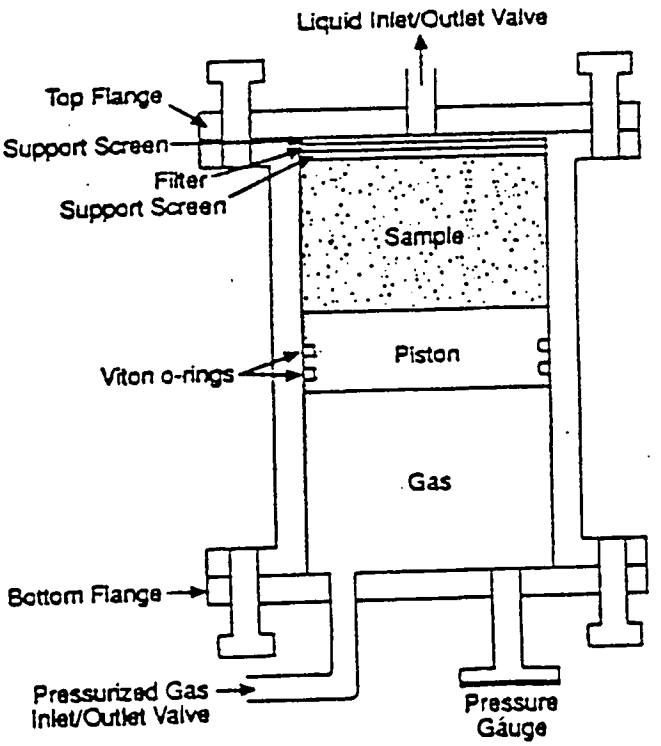

Figure 3 - US Environmental Protection Agency Memorandum #35, Page 1

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
SOLID WASTE AND EMERGENCY RESPONSE

MEMORANDUM # 35

DATE: June 12, 1992

SUBJECT: Notes on RCRA Methods and QA Activities

From: Gail Hansen, Chief Gail Hansen
Methods Section (OS-331)

This memo addresses the following topics:

- o 1992 Symposium on Waste Testing and Quality Assurance
- o SW-846 Update
  - Final Rule for January 23, 1989 Proposed Rule
  - Notice, Proposed Rulemaking for the Second Update to the Third Edition
- o Chlorofluorocarbon 113 (CFC-113) Solvent Replacement Update
- o Environmental Monitoring Methods Index (EMMI)
- o Sampling Work Group Formation
- o MICE Update
- o Oily Waste Analysis
- o Electronic SW-846 Availability.

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Figure 3 - US Environmental Protection Agency Memorandum #35, Page 10

Oily Waste Analysis

One of the most frequently asked questions on the MICE Service concerns the application of the TCLP, Method 1311, to oily wastes. Many callers request technical guidance on the extraction of oily wastes due to the difficulty in the filtration on these types of waste. In many cases, an oily waste does not filter completely due to premature clogging of the glass fiber filter. This can result in the retention of standing liquid on the glass fiber filter. Material that do not pass through the glass fiber filter at the conclusion of the filtration step is defined by the method as the solid phase of the waste. The solid phase is then subjected to the leaching procedure of the TCLP. For oily wastes, clogging of the glass fiber filter can result in an overestimation of the amount of solid material available for leaching.

To solve this problem, the Agency recommends a conservative approach, one that probably will overestimate the amount of leaching. Rather than performing the TCLP extraction on the unfiltered portion of the oily waste, assume the waste is 100% liquid (e.g., will pass through the glass fiber filter) and perform a totals analysis on the oily waste to determine if the oil exceeds the appropriate regulatory level.

Filterable waste oil generated during the TCLP must be analyzed for a variety of organic and inorganic analytes. The OSW recognizes the difficulty in achieving acceptable performance for the analysis of waste oil using methods currently provided in SW-846. As a result, the Agency will provide several new methods for the preparation and analysis of oil samples to the Organic Methods Workgroup in July. In addition, a microwave assisted digestion procedure should improve the analysis of metals and will be proposed as part of the Second Update of the Third Edition of SW-846. Brief descriptions of these techniques are provided below, for additional information on the organic procedures contact Barry Lesnik at (202) 260-7459. For additional information on microwave digestion contact Ollie Fordham (202) 260-4778.

The use of purge-and-trap (Method 5030) for volatiles in oil generally results in severe contamination of analytical instrumentation. Traps, transfer lines and chromatography columns may become contaminated with oil. This leads to elevated baselines, hydrocarbon background in subsequent analyses, and cross-contamination. Headspace (Method 3810) is currently allowed only as a screening procedure in SW-846. The Agency is evaluating the use of headspace in conjunction with isotope dilution mass spectrometry for the quantitative analysis of volatiles in oil. Headspace reduces interference problems encountered with purge-and-trap. However, headspace quantitation can be questionable because the distribution of analytes is not

APPENDIX C

WORKSHEETS

TCLP/SPLP Worksheet 1 - Sample Description

Lot Number					
Laboratory Sample No.					
A. Sample Description					
Number of phases					
1. Solid					
2. Liquid					
a. lighter than water					
b. water					
c. heavier than water					
B. Percent Solid Phase					
1. weight of filter (g)					
2. weight of subsample					
a. gross weight (g)					
b. tare weight (g)					
c. net weight (g)					
3. weight of filtrate					
a. gross weight (g)					
b. tare weight (g)					
c. net weight (g)					
4. total weight wet solids[0]					
5. weight percent wet solids[1] (%)					
6. weight percent dry solids (%)					
a. gross dry weight (g)					
b. final gross dry weight (g)					
c. percent dry solids[2] (%)					
7. volume of initial aqueous filtrate (mL)					
8. volume of initial organic filtrate (mL)					

[0] $Total\ Weight\ of\ wet\ solids = (B2c - B3c)$

[1] $\text{Weight percent wet solids} = 100\left|\frac{Total\ weight\ wet\ solids,\ B4}{Weight\ of\ subsample,\ B2c}\right|$

[2] $\text{Weight percent dry solids} = 100\left|\frac{(Gross\ dry\ weight,\ B6b) - (weight\ of\ filter,\ B1)}{Weight\ of\ subsample,\ B2c}\right|$

Comments: _____

Analyst: _____ Date: _____

TCLP/SPLP Worksheet 2 - Selection of Extraction Fluid

TCLP

Lot Number.					
Laboratory Sample No.					
C. Extraction Fluid Determination—does not apply to determination of volatile organic components.					
1. particle size reduction? yes/no (<1 mm)					
2. sample weight, ✓ if 5.0 ± 0.1 g					
3. volume of water, ✓ if 96.5 ± 1.0 mL					
4. initial pH (after 5 min. mixing time)					
5. if pH >5.0, ✓ if 3.5 mL 1N HCL					
6. ✓ if heated and held at 50^{0}C for ten minutes					
7. secondary pH (at room temperature)					
D. Selection of Extraction Fluid					
1. ✓ if pH from § C (4) or § C (7) is <5.0, use extraction fluid No. 1.					
2. ✓ if pH from § C (7) IS >5.0, use extraction fluid No. 2					
3. ✓ if filtrate and fluid are miscible					

SPLP

Laboratory Sample No.					
Field Sample No.					
D. Selection of Extraction Fluid (✓ one)					
Fluid 1: Soils—East of the Mississippi River; Wastes; or Wastewaters.					
Fluid 2: Soils—West of Mississippi River					
Fluid 3: If VOCs or Cyanide containing wastes.					
1. ✓ if filtrate and fluid are miscible					

Comments: _____

_____

Analyst: _____ Date: _____

TCLP/SPLP Worksheet 3 - Extraction for Metals, Semi-Volatile Organic Components and Pesticides/Herbicides

Lot Number					
Laboratory Sample No.					
E. Determination of Samples Size for Leach Testing—the method requires a minimum 100 gram sample size for extraction					
1. particle size reduction? yes/no (<9.5 mm)					
2. weight of wet solids after filtration (g)					
F. Determination of Amount of Extraction Fluid—the selection of the correct extraction fluid is found in Section D - Worksheet No. 2.					
1. Fluid weight = 20 x solids weight (g)					
G. Record of Extraction Test—the extraction period is specified as 18 ± 2.					
1. room temperature initial (°C) final (°C)					
2. vessel number					
3. extraction start time					
4. extraction stop time					
5. date and time filtration complete					
6. pH of leachate					
7. volume of leachate (for multiphase samples only) (mL)					
8. volume of initial aqueous filtrate for recombination[3] (mL)					
9. combined initial aqueous + leachate (mL)					

[3] $$\text{Volume of filtrate used for recombination} = \left(\frac{\text{Weight of solids leached, E2}}{\text{Total weight of solids, B4}}\right)\left(\frac{\text{Leachate recovered, G7}}{\text{Fluid added, F1}}\right)\left(\text{Volume of initial aqueous filtrate, B7}\right)$$

Comments: _____

_____

Analyst: _____ Date: _____

TCLP/SPLP Worksheet 4 - Zero Headspace Extraction (ZHE)

Lot Number					
Laboratory Sample No.					
H. Determination of Sample Size for Each Testing – maximum 25 grams					
1. particle size reduction? yes/no (<9.5 mm)					
2. weight of wet solid (g)					
I. Determination of Amount of Extraction Fluid No. 1					
1. weight of material added to ZHE (g)					
2. volume of filtrate in syringe (mL)					
3. weight of filtrate in syringe					
a. gross weight (g)					
b. tare weight (g)					
c. net weight (g)					
4. wet solids in ZHE[4] (g)					
5. weight of fluid to add[5] (g)					
J. Record of ZHE Extraction Text – the extraction period is as 18 ± 2 hours.					
1. room temperature initial (°C) final (°C)					
2. ZHE vessel number					
3. extraction start date & time					
4. extraction stop date & time					
5. ✓ if still under positive pressure					
6. filtration completed date & time					
7. volume of filtrate recovered after leaching (mL)					
a. volume of oil recovered after leaching (mL)					
8. volume of initial aqueous filtrate for recombination[6] (mL)					
9. combined initial aqueous + leachate (mL)					

[4] Solids remaining in ZHE = (*Material added, I1*) - (*Weight of filtrate in syringe, I3*)

[5] Weight of fluid to add = 20(*Wet solids in ZHE, I4*)

[6] Volume of filtrate used for recombination = $\left(\frac{\text{Weight of solids leached, I4}}{\text{Total weight of solids, B4}}\right)\left(\frac{\text{Leachate recovered, J7}}{\text{Fluid added, I5}}\right)$(*Volume initial aqueous filtrate, B7*)

Comments: _____

Analyst: _____ Date: _____

TCLP/SPLP Worksheet 5 - Organic Results

TCLP/SPLP ZHE Worksheet No. 5
Organic Results

Sample Number: _____

Organics Preparation		Volume	Units
Combined initial Aqueous/Leachate from § J9	V_A		mL
Oil phase Volume for Calculations[7]	V_O		mL

Analyte		Oil Phase			Combined Initial Aqueous/Leachate			Final Results	
Compound	Std. Reporting Limit (mg/L)	Dilution Factor	Result C_O	Reporting Limit	Dilution Factor	Results C_A	Reporting Limit	Result C_{Final}	Reporting Limit

$$C_{Final} = \frac{(C_A \times V_A) - (C_O \times V_O)}{V_A + V_O}$$

[7] Volume of oil phase for calculation $= \left[\frac{\text{Wet solids leached, I4}}{\text{Total solid, B4}}\right]\left[\left(\frac{\text{Leachate recovered, J7}}{\text{Fluid added, I5}}\right)(\text{Initial volume of oil, B8}) + (\text{Oil recovered from leaching, J7a})\right]$

Comments: _____

_____

Analyst: _____ Date: _____

TCLP/SPLP Worksheet 6 - Metals Results

Metals Results

Sample Number : _____

Metals Preparation		Volume	Units
Combined Initial Aqueous/Leachate from §G8	VA		mL
Oil phase volume for calculations[8]	VO		mL

Analyte		Oil Phase			Combined Initial Aqueous/Leachate			Final Results	
Element	Std. Reporting Limit (mg/L)	Dilution Factor	Result C_O	Reporting Limit	Dilution Factor	Results C_A	Reporting Limit	Result C_{Final}	Reporting Limit
Arsenic	0.5								
Barium	10								
Cadmium	0.1								
Chromium	0.5								
Lead	0.5								
Mercury	0.0002								
Selenium	0.25								
Silver	0.5								

$$C_{Final} = \frac{(C_A \times V_A) + (C_O \times V_O)}{V_A + V_O}$$

[8] $$\text{Volume of oil phase for calculation} = \left(\frac{\text{Wet solids leached, E2}}{\text{Total solid, B4}}\right)\left(\frac{\text{Leachate recovered, G7}}{\text{Fluid added, F1}}\right)(\text{Initial volume of oil, B8}) + (\text{Oil recovered from leaching, G7a})$$

Notes: If sample contains no solids, volume of oil phase (V_0) is the volume of the initial organic filtrate

In cases where analytes are detected in only one phase, a footnote indicating a result reported below the reporting limit should be included.

Comments: _____

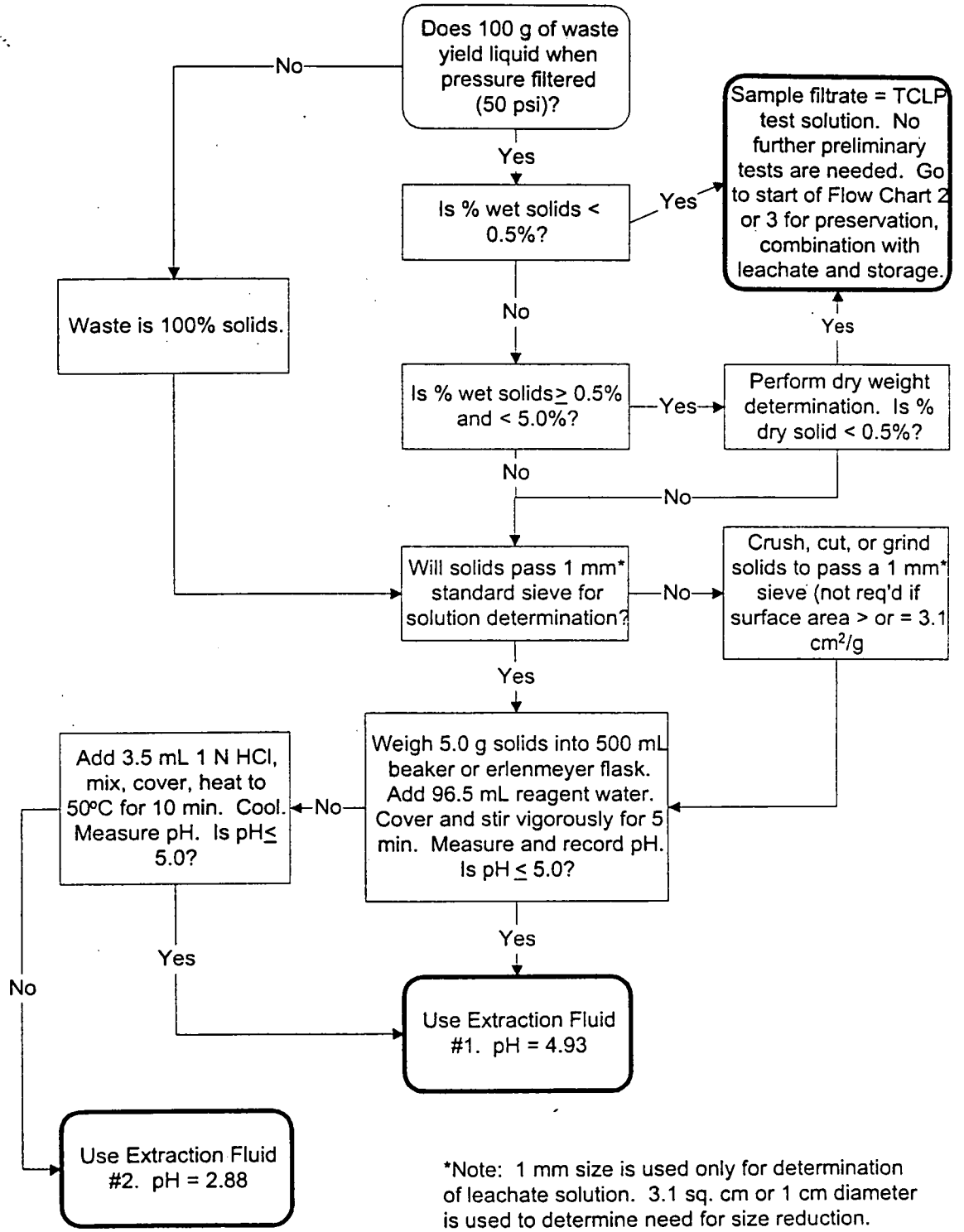
_____

Analyst: _____ Date: _____

APPENDIX D

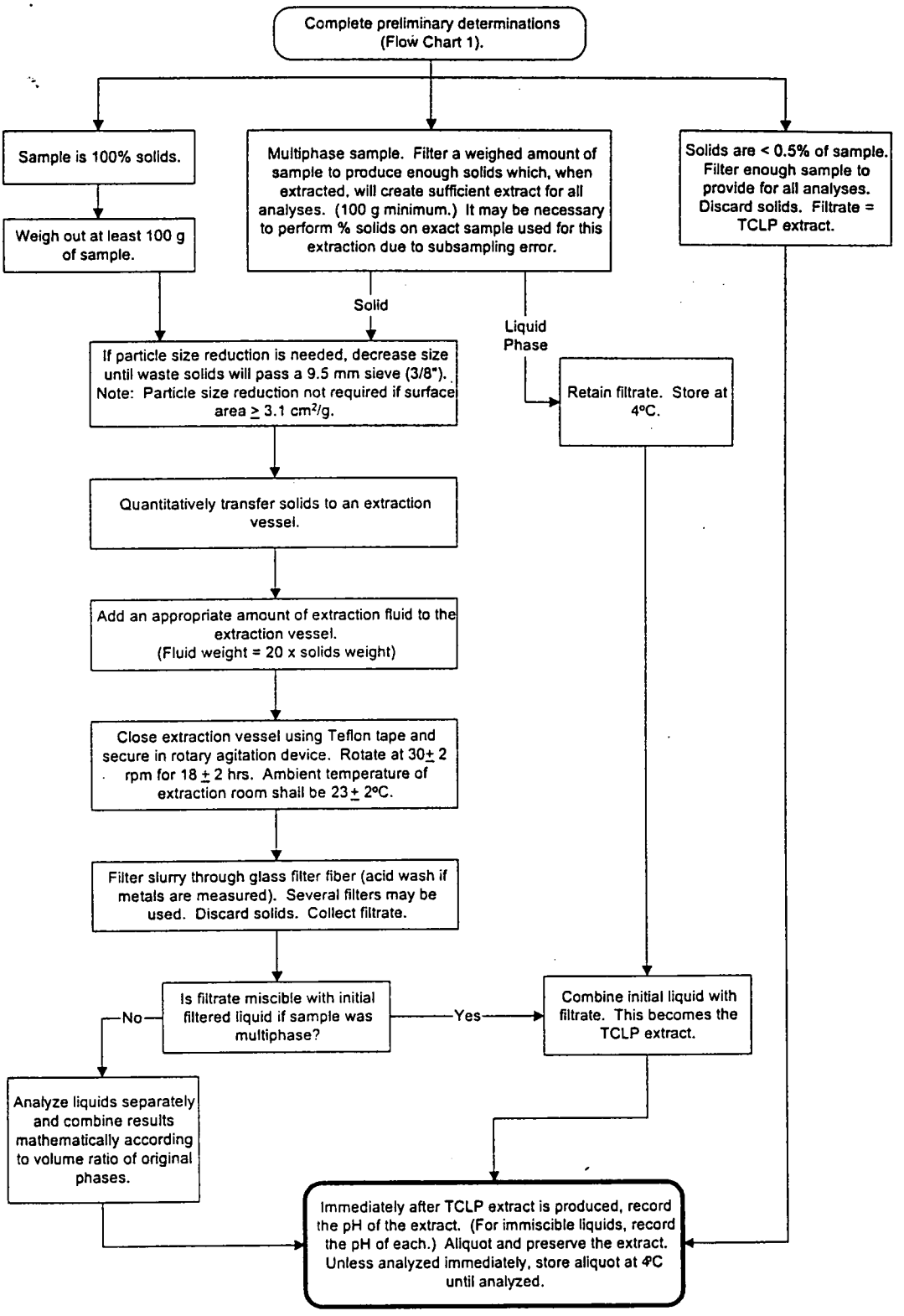
FLOW CHARTS

Flow Chart 1. Preliminary Sample Evaluation (Section 11.2)

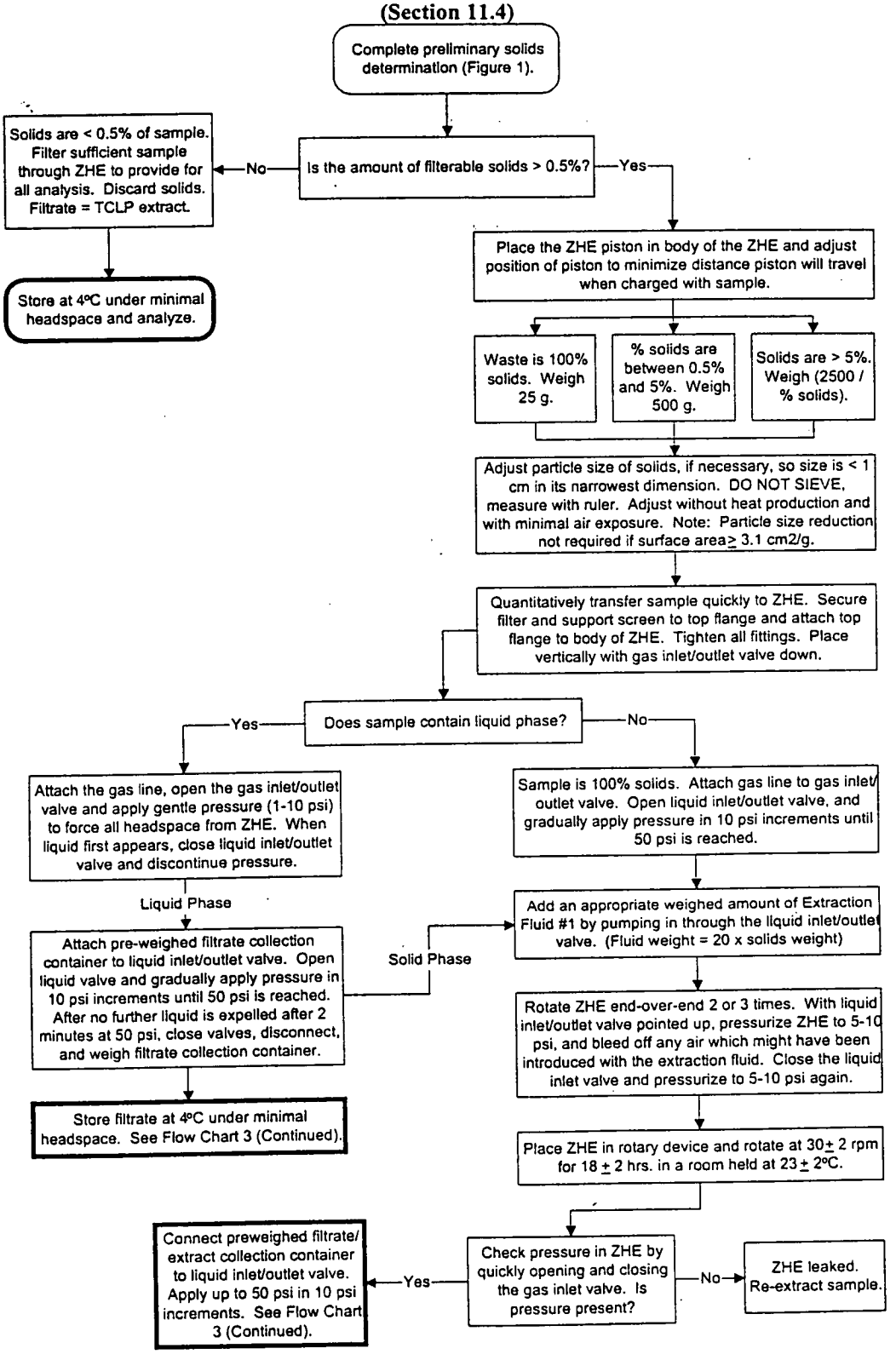


*Note: 1 mm size is used only for determination of leachate solution. 3.1 sq. cm or 1 cm diameter is used to determine need for size reduction.

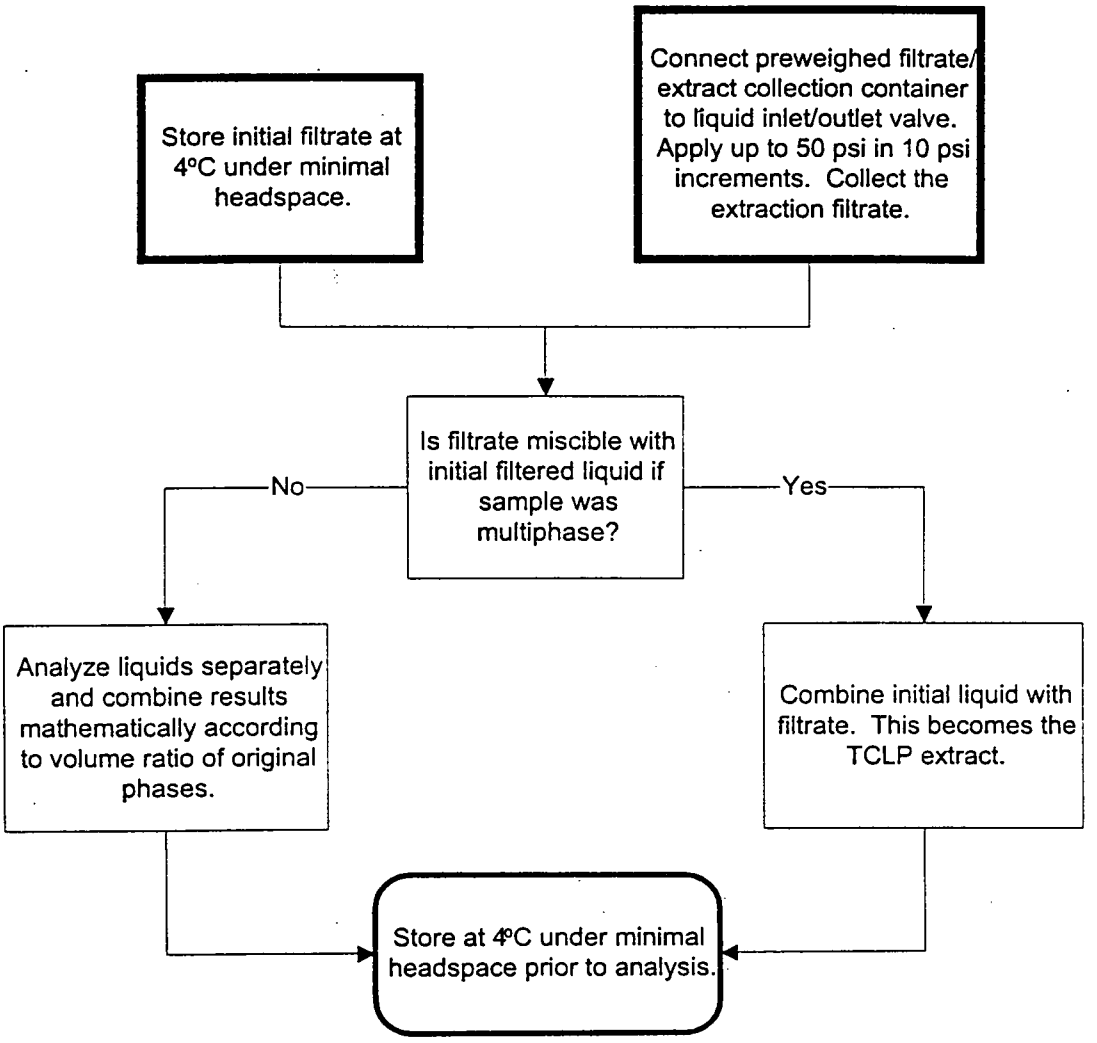
Flow Chart 2. Bottle Extraction, Non-Volatile Constituents (Section 11.3)



Flow Chart 3. ZHE Extraction, Volatile Constituents (Section 11.4)



Flow Chart 3. ZHE Extraction (Continued)



Quanterra
Environmental Services

Controlled Copy
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SOP No. CORP-MS-0002SAC
Revision No. 2.1
Revision Date: 9/1/98
Implementation Date:

QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF VOLATILE ORGANICS BY GC/MS BASED ON METHOD 8260B, 624 AND 524.2

(SUPERSEDES: REVISION 2)

Prepared by: Richard Burrows

Reviewed by: _____ 9.2.98
Technical Reviewer

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental Health and Safety Coordinator

Approved by: _____
Laboratory Manager

Approved by: _____ 9/1/98
Corporate Technology or Quality Assurance

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APPENDIX A

APPLICATION OF METHOD 524.2 AND METHOD 8260A TO THE DRINKING WATER ANALYTE LIST 56

APPENDIX B

ANALYSIS OF VOLATILE ORGANICS BY METHOD 624 64

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Table 2 Quanterra Primary Standard Calibration Levels

Table 3 Quanterra Appendix IX Standard and Reporting Limits

Table 4 Quanterra Appendix IX Standard Calibration Levels

Table 5 Reportable Analytes for Quanterra Standard Tests, Primary Standard

Table 6 Reportable Analytes for Quanterra Standard Tests, Appendix IX Standard

Table 7 Internal Standards

Table 8 Surrogate Standards

Table 9 Matrix Spike / LCS Standards

Table 10 BFB Tune Criteria

Table 11 SPCC Compounds and Minimum Response Factors

Table 12 CCC Compounds

Table 13 Characteristic Ions

Table A-1 Quanterra Drinking Water List Standard and Reporting Limits

Table A-2 Internal Standards, Drinking Water List

Table A-3 Surrogate Standards, Drinking Water List

Table A-4 Calibration Levels, Drinking Water List

Table B-1 Method 624 Analytes and Reporting Limits

Table B-2 Method 624 QC Acceptance Criteria

1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Volatile Organic Compounds in waters, wastewater, soils, sludges and other solid matrices. Standard analytes are listed in Tables 5 and 6.

1.2. This SOP is applicable to method 8260B. At client request, it may also be used for analysis following method 8240B. Appendices A and B present modifications to the procedures in the main SOP that are necessary for analysis of drinking water by method 524.2 and wastewater by method 624.

1.3. This method can be used to quantify most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile water soluble compounds can be included in this analytical technique; however, for more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency.

1.4. The method is based upon a purge and trap, gas chromatograph/mass spectrometric (GC/MS) procedure. The approximate working range is 5 to 200 µg/L for 5 mL waters, 1 to 60 µg/L for 25 mL purge waters, 5 to 200 µg/kg for low-level soils, and 250 to 25,000 µg/kg for medium-level soils. Reporting limits are listed in Tables 1 and 3.

1.5. Method performance is monitored through the use of surrogate compounds, matrix spike/matrix spike duplicates, and laboratory control spike samples.

2. SUMMARY OF METHOD

2.1. Volatile compounds are introduced into the gas chromatograph by the purge and trap method. The components are separated via the chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.2. Aqueous samples are purged directly. Generally, soils are preserved by extracting the volatile analytes into methanol. If especially low detection limits are required, soil samples may be preserved with sodium bisulfate and purged directly.

2.3. In the purge and trap process, an inert gas is bubbled through the solution at ambient temperature or at 40°C (40°C required for low level soils) and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbant column where the volatile components are trapped. After purging is completed, the sorbant column (trap) is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas

chromatographic column is then heated to elute the components which are detected with a mass spectrometer.

2.4. Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing the resultant mass spectra and GC retention times. Each identified component is quantified by relating the MS response for an appropriate selected ion produced by that compound to the MS response for another ion produced by an internal standard.

3. DEFINITIONS

3.1. Batch

The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. Using this method, each BFB analysis will normally start a new batch. Batches for medium level soils are defined at the sample preparation stage and may be analyzed on multiple instruments over multiple days, although reasonable effort should be made to keep the samples together.

3.1.1. The Quality Control batch must contain a matrix spike/spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. Refer to the Quanterra QC Program document (QA-003) for further details of the batch definition.

3.2. Method Blank

A method blank consisting of all reagents added to the samples must be analyzed with each batch of samples. The method blank is used to identify any background interference or contamination of the analytical system which may lead to the reporting of elevated concentration levels or false positive data.

3.3. Laboratory Control Sample (LCS)

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

3.4. Surrogates

Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples. Each sample, blank, LCS, and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

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

A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second aliquot of the same sample which is prepared and analyzed along with the sample and matrix spike. Matrix spikes and duplicates are used to evaluate accuracy and precision in the actual sample matrix.

3.6. Calibration Check Compound (CCC)

CCCs are a representative group of compounds which are used to evaluate initial calibrations and continuing calibrations. Relative percent difference for the initial calibration and % drift for the continuing calibration response factors are calculated and compared to the specified method criteria.

3.7. System Performance Check Compounds (SPCC)

SPCCs are compounds which are sensitive to system performance problems and are used to evaluate system performance and sensitivity. A response factor from the continuing calibration is calculated for the SPCC compounds and compared to the specified method criteria.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. The use of ultra high purity gases, pre-purged purified reagent water, and approved lots of purge and trap grade methanol will greatly reduce introduction of contaminants. In extreme cases the purging vessels may be pre-purged to isolate the instrument from laboratory air contaminated by solvents used in other parts of the laboratory.

4.2. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) into the sample through the septum seal during shipment and

storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

4.3. Matrix interferences may be caused by non-target contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature and diversity of the site being sampled.

4.4. Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially or in the same purge position on an autosampler. Whenever an unusually concentrated sample is analyzed, it should be followed by one or more blanks to check for cross-contamination. The purge and trap system may require extensive bake-out and cleaning after a high-level sample.

4.5. Some samples may foam when purged due to surfactants present in the sample. When this kind of sample is encountered an antifoaming agent (e.g., J.T. Baker's Antifoam B silicone emulsion) can be used. A blank spiked with this agent must be analyzed with the sample because of the non-target interferences associated with the agent.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all Quanterra associates.

5.2. The Chemical Hygiene Plan (CHP) gives details about the specific health and safety practices which are to be followed in the laboratory area. Personnel must receive training in *safety* prior to working in the laboratory. Consult the CHP, the Quanterra Health and Safety Policies and Procedures Manual, and available Material Safety Data Sheets (MSDS) prior to using the chemicals in the method.

5.3. Consult the Quanterra Health and Safety Policies and Procedures Manual for information on Personal Protective Equipment. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan) and a laboratory coat must be worn in the lab. *Chemically resistant* gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded. Disposable gloves shall not be reused.

5.3.1. *N-Dex nitrile gloves provide varying degrees of intermittant splash protection against those chemicals listed. Refer to permeation/degradation charts for actual data.*

5.4. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined, therefore each chemical compound should be treated as a potential

health hazard. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

5.4.1. Chemicals that have been classified as **carcinogens, or potential carcinogens**, under OSHA include: Acrylonitrile, benzene, carbon tetrachloride, chloroform, 1,2-dibromo-3-chloropropane, 1,4-dichlorobenzene, and vinyl chloride.

5.4.2. Chemicals known to be **flammable** are: Methanol. Methanol readily absorbs via the skin.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

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

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

5.8. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices outlined in Appendix B, Chemical Hygiene Plan, current edition. These employees must have training on the hazardous waste disposal practices initially upon assignment of these tasks, followed by an annual refresher training.

6. EQUIPMENT AND SUPPLIES

6.1. Microsyringes: 10 µL and larger, 0.006 inch ID needle.

6.2. Syringe: 5 or 25 mL glass with luerlok tip, if applicable to the purging device.

6.3. Balance: Analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.1 g

6.4. Glassware:

6.4.1. Vials: 20 mL with screw caps and Teflon liners.

6.4.2. Vials: 40 mL with screw caps and Teflon liners.

6.4.3. Volumetric flasks: 10 mL and 100 mL, class A with ground-glass stoppers.

6.5. Spatula: Stainless steel.

6.6. Disposable pipets: Pasteur.

6.7. pH paper: Wide range.

6.8. Gases:

6.8.1. Helium: Ultra high purity, gr. 5, 99.999%.

6.8.2. Nitrogen: Ultra high purity, from cylinders of gas generators, may be used as an alternative to helium for purge gas.

6.8.3. Compressed air: Used for instrument pneumatics.

6.8.4. Liquid nitrogen: Used for cryogenic cooling if necessary.

6.9. Purge and Trap Device: The purge and trap device consists of the sample purger, the trap, and the desorber.

6.9.1. Sample Purger: The recommended purging chamber is designed to accept 25 mL samples with a water column at least 12 cm deep. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. Alternative sample purge devices may be used provided equivalent performance is demonstrated. Low level soils are purged directly from a VOA vial.

6.9.2. Trap: A variety of traps may be used, depending on the target analytes required. For most purposes the Vocarb 3000 trap is suitable. Other traps, such as Vocarb 4000, or Tenax / Silica gel / Charcoal may be used if the Quality Control criteria are met.

6.9.3. Desorber: The desorber should be capable of rapidly heating the trap to 180°C. Many such devices are commercially available.

6.9.4. Sample Heater: A heater capable of maintaining the purge device at 40°C is necessary for low level soil analysis.

6.10. Gas Chromatograph/Mass Spectrometer System:

6.10.1. Gas Chromatograph: The gas chromatograph (GC) system must be capable of temperature programming.

6.10.2. Gas Chromatographic Columns: Capillary columns are used. Some typical columns are listed below:

6.10.2.1.Column 1: 105m x 0.53 ID Rtx-624 with 3 µm film thickness.

6.10.2.2.Column 2: 75 m x 0.53 ID DB-624 widebore with 3 µm film thickness.

6.10.2.3. Mass Spectrometer: The mass spectrometer must be capable of scanning 35-300 AMU every two seconds or less, using 70 volts electron energy in the electron impact mode and capable of producing a mass spectrum that meets the required criteria when 50 ng of 4-Bromofluorobenzene (BFB) are injected onto the gas chromatograph column inlet.

6.10.3. GC/MS interface: In general glass jet separators are used but any interface (including direct introduction to the mass spectrometer) that achieves all acceptance criteria may be used.

6.10.4. Data System: A computer system that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between the specified time or scan-number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The most recent release of the NIST/EPA mass spectral library should be used as the reference library. The computer system must also be capable of backing up data for long-term off-line storage.

6.10.5. Cryogenic Cooling: Some columns require the use of liquid nitrogen to achieve the subambient temperature required for the proper separation of the gases.

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Methanol: Purge and Trap Grade, High Purity

7.1.2. Reagent Water: High purity water that meets the requirements for a method blank when analyzed. (See section 9.4) Reagent water may be purchased as commercial distilled water and prepared by purging with an inert gas overnight. Other methods of preparing reagent water are acceptable.

7.2. Standards

7.2.1. Calibration Standard

7.2.1.1. Stock Solutions: Stock solutions may be purchased as certified solutions from commercial sources or prepared from pure standard materials as appropriate. These standards are prepared in methanol and stored in Teflon-sealed screw-cap bottles with minimal headspace at -10° to -20°C.

7.2.1.2. Working standards: A working solution containing the compounds of interest prepared from the stock solution(s) in methanol. These standards are stored in the freezer or as recommended by the manufacturer. Working standards are monitored by comparison to the initial calibration curve. If any of the calibration check compounds drift in response from the initial calibration by more than 20% then corrective action is necessary. This may include steps such as instrument maintenance, preparing a new calibration verification standard or tuning the instrument. If the corrective actions do not correct the problem then a new initial calibration must be performed.

7.2.1.3. Aqueous Calibration Standards are prepared in reagent water using the secondary dilution standards. These aqueous standards must be prepared daily.

7.2.1.4. If stock or secondary dilution standards are purchased in sealed ampoules they may be used up to the manufacturers expiration date.

7.2.1.5. Each multipoint calibration curve must be compared against a second source standard that is independant of the solution used for preparing the curve. This practice is to ensure that no adverse drift in response is occurring.

7.2.2. Internal Standards: Internal standards are added to all samples, standards, and blank analyses. Refer to Table 7 for internal standard components.

7.2.3. Surrogate Standards: Refer to Table 8 for surrogate standard components and spiking levels.

7.2.4. Laboratory Control Sample Spiking Solutions: Refer to Table 9 for LCS components and spiking levels.

7.2.5. Matrix Spiking Solutions: The matrix spike contains the same components as the LCS. Refer to Table 9.

7.2.6. Tuning Standard: A standard is made up that will deliver 50 ng on column upon injection. A recommended concentration of 25 ng/µL of 4-Bromofluorobenzene in methanol *should be prepared.*

7.2.7. *All expired standards must be rotated out of the lab to the Hazardous Waste storage area.*

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Holding times for all volatile analysis are 14 days from sample collection.

8.2. Water samples are normally preserved at pH $\leq$ 2 with 1:1 hydrochloric acid. If residual chlorine is present, 2 drops of 10% sodium thiosulfate are added.

8.3. Solid samples are field preserved with sodium bisulfate solution for low level analysis, or with methanol for medium level analysis. Soil samples can also be taken using the EnCore™ sampler and preserved in the lab within 48 hours of sampling. At specific client request, unpreserved soil samples may be accepted.

8.4. There are several methods of sampling soil. The recommended method, which provides the minimum of field difficulties, is to take an EnCore sample. (The 5 g or 25 g sampler can be used, depending on client preference). Following shipment back to the lab the soil is preserved in methanol. This is the medium level procedure. If very low detection limits are needed (< 50 µg/kg for most analytes) then it will be necessary to use two additional 5 g EnCore samplers or to use field preservation.

8.5. Sample collection for medium level analysis using EnCore samplers.

8.5.1. Ship one 5 g (or 25 g) EnCore sampler per field sample position.

8.5.2. An additional bottle must be shipped for percent moisture determination.

8.5.3. When the samples are returned to the lab, extrude the (nominal) 5g (or 25 g) sample into a tared VOA vial containing 5 mL methanol (25 mL methanol for the 25 g sampler). Obtain the weight of the soil added to the vial and note on the label.

8.5.4. Add the correct amount of surrogate spiking mixture. (Add 50 µL of 1250 µg/mL solution for a nominal 25 g sample, 10µL for a nominal 5 g sample.)

8.5.5. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 50 µL of 1250 µg/mL solution for a nominal 25 g sample, 10µL for a nominal 5 g sample.) The addition of spike introduces a slight error (0.4%), which can be neglected, into the calculations.

8.5.6. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (50 µL of spike to 25 mL methanol or 10 µL spike to 5 mL methanol).

8.5.7. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.5.8. Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at $4 \pm 2^{\circ}C$ until analysis.

8.6. Sample collection for medium level analysis using field methanol preservation

8.6.1. Prepare a 2 oz sample container by adding 25 mL purge and trap grade methanol. (If a 5 g sample is to be used, add 5 mL methanol to a 2 oz container or VOA vial).

8.6.2. Seal the bottle and attach a label.

8.6.3. Weigh the bottle to the nearest 0.01g and note the weight on the label.

8.6.4. Ship with appropriate sampling instructions.

8.6.5. Each sample will require an additional bottle with no preservative for percent moisture determination.

8.6.6. At client request, the methanol addition and weighing may also be performed in the field.

8.6.7. When the samples are returned to the lab, obtain the weight of the soil added to the vial and note on the label.

8.6.8. Add the correct amount of surrogate spiking mixture. (Add 50 µL of 1250 µg/mL solution for a nominal 25 g sample, 10µL for a nominal 5 g sample.)

8.6.9. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 50 µL of 1250 µg/mL solution for a nominal 25 g sample, 10µL for a nominal 5 g sample.) The addition of spike introduces a slight error, (0.2%) which can be neglected, into the calculations.

8.6.10. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (50 µL of spike to 25 mL methanol or 10 µL spike to 5 mL methanol).

8.6.11. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.6.12. Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4±2°C until analysis.

8.7. Low level procedure

8.7.1. If low detection limits are required (typically < 50 µg/kg) sodium bisulfate preservation must be used. However, it is also necessary to take a sample for the medium level (field methanol preserved or using the EnCore sampler) procedure, in case the concentration of analytes in the soil is above the calibration range of the low level procedure.

8.7.2. A purge and trap autosampler capable of sampling from a sealed vial is required for analysis of samples collected using this method. (Varian Archon or O.I. 4552).

8.7.3. The soil sample is taken using a 5g EnCore sampling device and returned to the lab. It is recommended that two EnCore samplers be used for each field sample position, to allow for any reruns than may be necessary. A separate sample for % moisture determination is also necessary.

8.7.4. Prepare VOA vials by adding a magnetic stir bar, approximately 1 g of sodium bisulfate and 5 mL of reagent water.

8.7.5. Seal and label the vial. It is strongly recommended that the vial is labeled with an indelible marker rather than a paper label, since paper labels may cause the autosampler to bind and malfunction. The label absolutely must not cover the neck of the vial or the autosampler will malfunction.

8.7.6. Weigh the vial to the nearest 0.1g and note the weight on the label.

8.7.7. Extrude the soil sample from the EnCore sampler into the prepared VOA vial. Reweigh the vial to obtain the weight of soil and note on the label.

8.7.8. **Note:** Soils containing carbonates may effervesce when added to the sodium bisulfate solution. If this is the case at a specific site, add 5 mL of water instead, and freeze at <10°C until analysis.

8.7.9. Alternatively the sodium bisulfate preservation may be performed in the field. This is not recommended because of the many problems that can occur in the field setting. Ship at least two vials per sample. The field samplers must determine the weight of soil sampled. Each sample will require an additional bottle with no preservative for percent moisture determination, and an additional bottle preserved with methanol for the medium level procedure. Depending on the type of soil it may also be necessary to ship vials with no or extra preservative.

8.8. Unpreserved soils

8.8.1. At specific client request unpreserved soils packed into glass jars or brass tubes may be accepted and subsampled in the lab. This is the old procedure based on method 5030A. It is no longer included and is likely to generate results that are biased low, possibly be more than an order of magnitude.

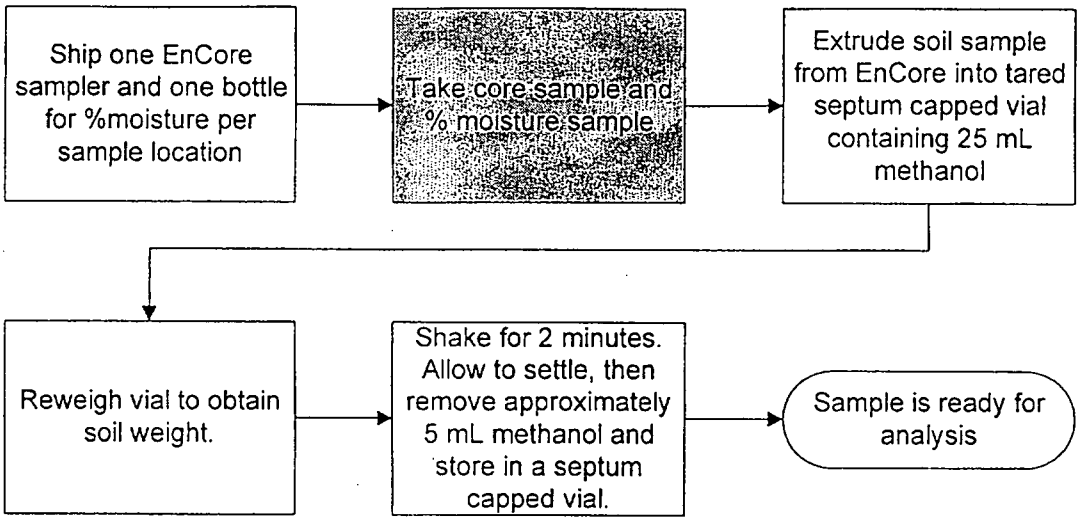
8.9. Aqueous samples are stored in glass containers with Teflon lined septa at 4°C +/- 2°C, with minimum headspace.

8.10. Medium level solid extracts are aliquoted into 2 - 5 mL glass vials with Teflon lined caps and stored at 4°C +/- 2°C. The extracts are stored with minimum headspace.

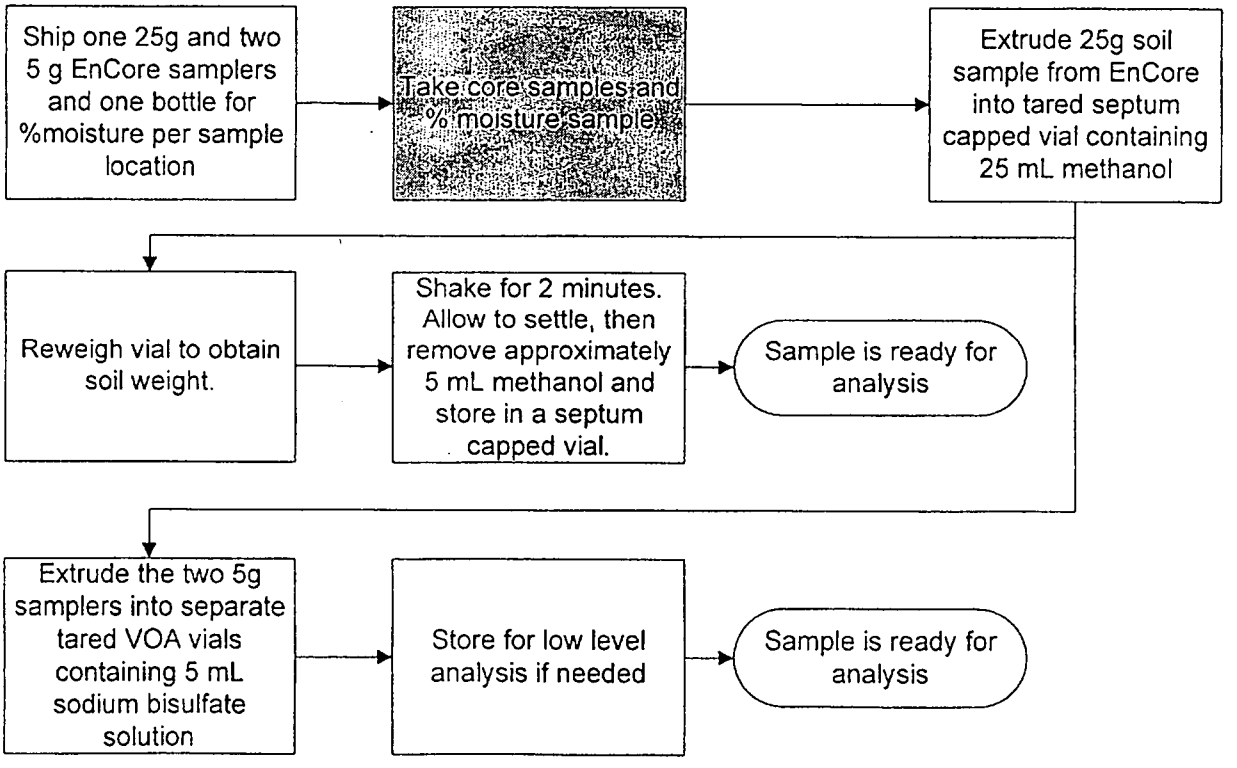
8.11. The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14 day holding time. However they should be analyzed as soon as possible. The lack of preservation should be addressed in the case narrative). Maximum holding time for the EnCore sampler (before the sample is added to methanol or sodium bisulfate) is 48 hours.

8.12. A holding blank is stored with the samples. This is analyzed and replaced if any of the trip blanks show any contamination. Otherwise it is replaced every 14 days.

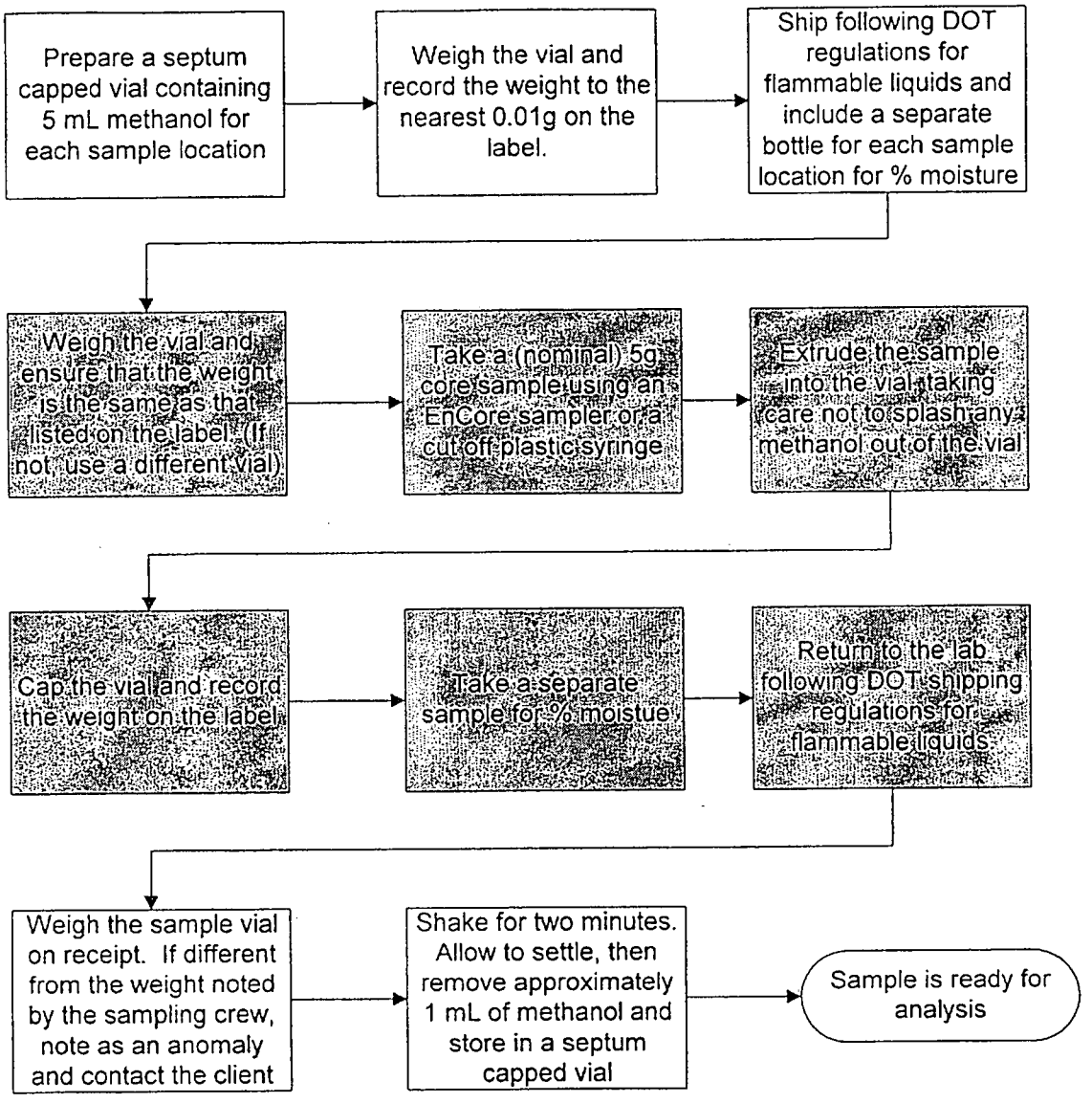
EnCore procedure when low level is not required (field steps in gray)



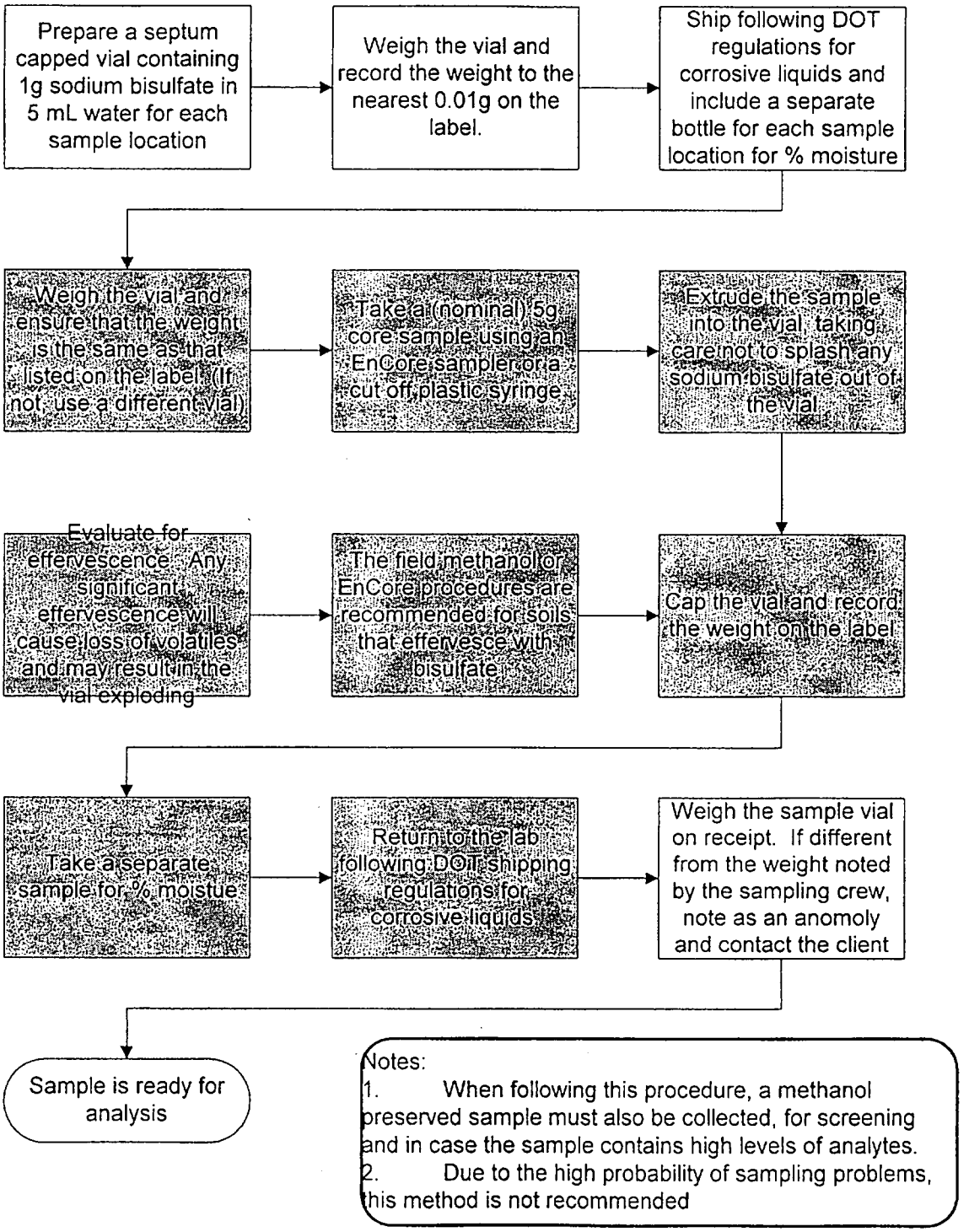
EnCore procedure when low level is required



Field methanol extraction procedure (field steps in gray)



Field bisulfate preservation procedure (field steps in gray)



9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.1.1. For the standard analyte list, the initial demonstration described in Section 13 and method detection limit (MDL) studies must be acceptable before analysis of samples may begin. MDLs should be analyzed for low and medium soils and aqueous samples. See section 17.4.1.

9.1.2. For non-standard analytes, a MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of a standard at the reporting limit and a single point calibration.

9.2. Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations for surrogates, matrix spikes and LCS. Precision limits for matrix spikes / matrix spike duplicates are 0 to mean relative percent difference + 3 standard deviations.

9.2.1. All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.2.2. Refer to the QC Program document (QA-003) for further details of control limits.

9.3. Surrogates

Every sample, blank, and QC sample is spiked with surrogates. Surrogate recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits. The compounds included in the surrogate spiking solutions are listed in Tables 8. If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.

- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.
- Reprepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem.

The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare/reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.3.1. If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and repreparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then reanalysis or flagging of the data is required.

9.3.2. Refer to the Quanterra QC Program document (QA-003) for further details of the corrective actions.

9.4. Method Blanks

For each batch of samples, analyze a method blank. The method blank is analyzed after the calibration standards, normally before any samples. For low-level volatiles, the method blank consists of reagent water. For medium-level volatiles, the method blank consists of 25.0 mL of methanol. Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

- If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone) the data may be reported with qualifiers if the concentration of the analyte is less than five times the reporting limit. Such action must be taken in consultation with the client.
- Reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.
- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be done in consultation with the client.

9.4.1. The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

9.4.2. If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B," and appropriate comments may be made in a narrative to provide further documentation.

9.4.3. Refer to the Quanterra QC Program document (QA-003) for further details of the corrective actions.

9.5. Laboratory Control Samples (LCS)

For each batch of samples, analyze a LCS. The LCS is analyzed after the calibration standard, and normally before any samples. The LCS contains a representative subset of the analytes of interest (See Table 9), and must contain the same analytes as the matrix spike. If any analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally be repreparation and reanalysis of the batch.

- If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. (Examples of acceptable reasons for not reanalyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS.)

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

9.5.1. Refer to the Quanterra QC Program document (QA-003) for further details of the corrective action.

9.5.2. If full analyte spike lists are used at client request, it will be necessary to allow a percentage of the components to be outside control limits as this would be expected statistically. These requirements should be negotiated with the client.

9.6. Matrix Spikes

For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in Table 9. Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

- If the recovery for any component is outside QC limits for both the matrix spike/ spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include reanalysis of the batch.

- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.

- The matrix spike/duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.7. Nonconformance and Corrective Action

Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

9.8. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.9. Quanterra QC Program

Further details of QC and corrective action guidelines are presented in the Quanterra QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. Prior to the analysis of samples and blanks, each GC/MS system must be tuned and calibrated. Hardware tuning is checked through the analysis of the 4-Bromofluorobenzene (BFB) to establish that a given GC/MS system meets the

standard mass spectral abundance criteria. The GC/MS system must be calibrated initially at a minimum of five concentrations (analyzed under the same BFB tune), to determine the linearity of the response utilizing target calibration standards. Once the system has been calibrated, the calibration must be verified each twelve hour time period for each GC/MS system. The use of separate calibrations is required for water and low soil matrices.

10.2. Recommended Instrument Conditions

10.2.1. General

Electron Energy: 70 volts (nominal)
Mass Range: 35–300 AMU
Scan Time: to give at least 5 scans/peak, but not to exceed 2 second/scan
Injector Temperature: 200–250°C
Source Temperature: According to manufacturer's specifications
Transfer Line Temperature: 250–300°C
Purge Flow: 40 mL/minute
Carrier Gas Flow: 15 mL/minute
Make-up Gas Flow: 25–30 mL/minute

10.2.2. Gas chromatograph suggested temperature program

10.2.2.1.BFB Analysis

Initial Temperature: 140°C
Temperature Program: 20°C/minute
Final Temperature: 210°C

10.2.2.2.Sample Analysis

Initial Temperature: 40°C
Initial Hold Time: 4 minutes
Temperature Program: 8°C/minute
Final Temperature: 184°C
Second Temperature Program: 40°C/minute
Final Temperature: 240°C
Final Hold Time: 2.6 minutes

10.3. Instrument Tuning

10.3.1. Each GC/MS system must be hardware-tuned to meet the abundance criteria listed in Table 10 for a maximum of a 50 ng injection or purging of BFB. Analysis must not begin until these criteria are met. These criteria must be met for each twelve-hour time period. The twelve-hour time period begins at the moment of injection of BFB.

10.4. Initial Calibration

10.4.1. A series of five initial calibration standards is prepared and analyzed for the target compounds and each surrogate compound. Typical calibration levels for a 5 mL purge are: 10, 20, 50, 100, and 200 µg/L. Certain analytes are prepared at higher concentrations due to poor purge performance. Typical calibration levels for a 25 mL purge are 0.5, 1, 4, 10, 20, and 40 µg/L. Again, some analytes are prepared at higher levels. Tables 2, 4, and 7 list the calibration levels for each analyte. Other calibration levels and purge volumes may be used depending on the capabilities of the specific instrument. However, the same purge volume must be used for calibration and sample analysis, and the low level standard must be at or below the reporting limit.

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10.4.1.1 ~~10.4.1~~. It may be necessary to analyze more than one set of calibration standards to encompass all of the analytes required for same tests. For example, the Appendix IX list requires the Primary standard (Table 5) and the Appendix IX standard (Table 6). If acceptable analytical performance can be obtained the primary and appendix IX standards may be analyzed together.

10.4.2. Internal standard calibration is used. The internal standards are listed in Table 7. Target compounds should reference the nearest internal standard. Each calibration standard is analyzed and the response factor (RF) for each compound is calculated using the area response of the characteristic ions against the concentration for each compound and internal standard. See equation 1, Section 12, for calculation of response factor.

10.4.3. The % RSD of the calibration check compounds (CCC) must be less than 30%. Refer to Table 12 for the CCCs.

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

10.4.4. The average RF must be calculated for each compound. A system performance check is made prior to using the calibration curve. The five system performance check compounds (SPCC) are checked for a minimum average response factor. Refer to Table 11 for the SPCC compounds and required minimum response factors.

10.4.5. If the average of all the %RSDs in the calibration is $\leq$ 15%, then all analytes may use average response factor for calibration.

10.4.5.1. If the software in use is capable of routinely reporting curve coefficients for data validation purposes, and the necessary calibration reports can be generated, then the analyst should evaluate analytes with %RSD > 15% for calibration on a curve. If it appears that substantially better accuracy would be obtained using quantitation from a curve then the appropriate curve should be used for quantitation. If Relative Standard Error (RSE) is used to evaluate the curve it must be better than 15%. Otherwise the correlation coefficient (coefficient of determination for non-linear curves) must be $\geq$ 0.990.

10.4.5.2. If the average of all the %RSDs in the calibration is > 15% then calibration on a curve must be used for all analytes with %RSD > 15%. The analyst should consider instrument maintenance to improve the linearity of response. If Relative Standard Error (RSE) is used to evaluate the curve it must be better than 15%. Otherwise the correlation coefficient, r (coefficient of determination, r^2 for non-linear curves) must be $\geq$ 0.990.

10.4.6. Weighting of data points

In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. $1/\text{Concentration}^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.4.7. If time remains in the 12-hour period initiated by the BFB injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.4.8. A separate five point calibration must be prepared for analysis of low level soils. Low level soils analysis requires the use of a closed vial autosampler such as the Varian Archon, O.I. 4552 or Tekmar Precept. Each standard is prepared by spiking the methanolic standard solution through the septum of a VOA vial containing 5 mL of water and 1 g sodium bisulfate. The standards are heated to 40°C for purging. All low-level soil samples, standards, and blanks must also be heated to 40°C for purging. Medium soil extracts should be analyzed using the water (unheated) calibration curve.

10.4.9. Non-standard analytes are sometimes requested. For these analytes, it is acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five point initial calibration. If the analyte is detected in any of the samples, a five point initial calibration must be generated and the sample(s) reanalyzed for quantitation. However, if the analyte is not detected, the non-detect may be reported and no further action is necessary.

10.5. Continuing Calibration: The initial calibration must be verified every twelve hours.

10.5.1. Continuing calibration begins with analysis of BFB as described in Section 10.3. If the system tune is acceptable, the continuing calibration standard(s) are analyzed. The level 3 calibration standard is used as the continuing calibration.

10.5.2. The RF data from the standards are compared with the average RF from the initial five-point calibration to determine the percent drift of the CCC compounds. The calculation is given in equation 4, Section 12.3.4.

10.5.3. The % drift of the CCCs must be $\leq$ 20% for the continuing calibration to be valid. The SPCCs are also monitored. The SPCCs must meet the criteria described in Table 11. In addition, the % drift of all non-CCC and non-SPCC analytes must be $\leq$ 50% with allowance for up to six target analytes to have % drift > 50%.

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

10.5.3.2. Cyclohexanone, one of the components of the Appendix IX standard, is unstable in the calibration solution, forming 1,1-dimethoxycyclohexane. No calibration criteria are applied to cyclohexanone and quantitation is tentative. Cyclohexanone is included on the Universal Treatment Standard and FO-39 regulatory lists (but not on Appendix IX).

10.5.4. If the CCCs and or the SPCCs do not meet the criteria in Section 10.5.3, the system must be evaluated and corrective action must be taken. The BFB tune and continuing calibration must be acceptable before analysis begins. Extensive corrective action such as a different type of column will require a new initial calibration.

10.5.5. Once the above criteria have been met, sample analysis may begin. Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs. Analysis may proceed until 12

hours from the injection of the BFB have passed. (A sample *desorbed* less than or equal to 12 hours after the BFB is acceptable.)

11. PROCEDURE

11.1. Procedural Variations

11.1.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation shall be completely documented using a Nonconformance Memo and approved by a Supervisor or group leader and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.1.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.2. Preliminary Evaluation

11.2.1. Where possible, samples are screened by headspace or GC/MS off-tune analysis to determine the correct aliquot for analysis. Alternatively, an appropriate aliquot can be determined from sample histories.

11.2.2. Dilutions should be done just prior to the GC/MS analysis of the sample. Dilutions are made in volumetric flasks or in a Luerlok syringe. Calculate the volume of reagent water required for the dilution. Fill the syringe with reagent water, compress the water to vent any residual air and adjust the water volume to the desired amount. Adjust the plunger to the mark and inject the proper aliquot of sample into the syringe. If the dilution required would use less than 1 µL of sample then serial dilutions must be made in volumetric flasks.

11.2.2.1. The diluted concentration is to be estimated to be in the upper half of the calibration range.

11.3. Sample Analysis Procedure

11.3.1. All analysis conditions for samples must be the same as for the continuing calibration standards (including purge time and flow, desorb time and temperature, column temperatures, multiplier setting etc.).

11.3.2. All samples must be analyzed as part of a batch. The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The batch also must contain a MS/MSD, a LCS, and a method blank.

11.3.2.1. *The 12-hour tune period defines the batch.* If any re-tuning of the instrument is necessary, or if a period of greater than 24 hours from the preceding BFB tune has passed, a new batch must be started. For medium level soils the batch is defined at the sample preparation stage.

11.3.2.2. Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

11.3.2.3. It is not necessary to reanalyze batch QC with reanalyses of samples. However, any reruns must be as part of a valid batch.

11.4. Water Samples

11.4.1. All samples and standard solutions must be at ambient temperature before analysis.

11.4.2. Fill a syringe with the sample. If a dilution is necessary it may be made in the syringe if the sample aliquot is $\geq$ 5 µL. Check and document the pH of the remaining sample.

11.4.3. Add 250 ng of each internal and surrogate standard (5 µL of a 50 µg/mL solution, refer to Table 7). The internal standards and the surrogate standards may be mixed and added as one spiking solution (this results in a 50 µg/L solution). Inject the sample into the purging chamber.

11.4.3.1. For TCLP samples use 0.5 mL of TCLP leachate with 4.5 mL reagent water and spike with 10 µL of the 25 µg/mL TCLP spiking solution. (Note that TCLP reporting limits will be 10 times higher than the corresponding aqueous limits).

11.4.4. Purge the sample for eleven minutes (the trap must be below 35°C).

11.4.5. After purging is complete, desorb the sample, start the GC temperature program, and begin data acquisition. After desorption, bake the trap for 5-10 minutes to condition it for the next analysis. When the trap is cool, it is ready for the next sample.

11.4.6. Desorb and bake time and temperature are optimized for the type of trap in use. The same conditions must be used for samples and standards.

11.5. Methanol Extract Soils

11.5.1. Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard (if used). Load the sample onto the purge and trap device and analyze as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe.

11.6. Liquid wastes that are soluble in methanol and insoluble in water.

11.6.1. Pipet 2 mL of the sample into a tared vial. Use a top-loading balance. Record the weight to the nearest 0.1 gram.

11.6.2. Quickly add 7 mL of methanol, then add 1 mL of surrogate spiking solution to bring the final volume to 10 mL. Cap the vial and shake for 2 minutes to mix thoroughly. For a MS/MSD or LCS, 6 mL of methanol, 1 mL of surrogate solution, and 1 mL of matrix spike solution is used.

11.6.3. Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard (if used). Load the sample onto the purge and trap device and analyze as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe.

11.7. Aqueous and Low level Soil Sample Analysis (Purge and Trap units that sample directly from the VOA vial)

11.7.1. Units which sample from the VOA vial should be equipped with a module which automatically adds surrogate and internal standard solution to the sample prior to purging the sample.

11.7.2. If the autosampler uses automatic IS/SS injection, no further preparation of the VOA vial is needed. Otherwise the internal and surrogate standards must be added to the vial. *Note:* Aqueous samples with high amounts of sediment present in the vial may not be suitable for analysis on this instrumentation, or they may need to analyzed as soils.

11.7.3. Soil samples must be quantitated against a curve prepared with standards containing about the same amount of sodium bisulfate as the samples (1 g in 5 mL).

11.7.4. Sample remaining in the vial after sampling with one of these mechanisms is no longer valid for further analysis. A fresh VOA vial must be used for further sample analysis.

11.7.5. For aqueous samples, check the pH of the sample remaining in the VOA vial after analysis is completed.

11.8. Low-Level Solids Analysis using discrete autosamplers

Note: This technique may seriously underestimate analyte concentration and must not be used except at specific client request for the purpose of comparability with previous data. It is no longer part of SW-846.

This method is based on purging a heated soil/sediment sample mixed with reagent water containing the surrogates and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples (e.g., heated). The calibration curve is also heated during analysis. Purge temperature is 40°C.

11.8.1. Do not discard any supernatant liquids. Mix the contents of the container with a narrow metal spatula.

11.8.2. Weigh out 5 g (or other appropriate aliquot) of sample into a disposable culture tube or other purge vessel. Record the weight to the nearest 0.1 g. If method sensitivity is demonstrated, a smaller aliquot may be used. Do not use aliquots less than 1.0 g. If the sample is contaminated with analytes such that a purge amount less than 1.0 g is appropriate, use the medium level method. For the medium level method, add 4g soil to 10 mL methanol containing the surrogates, mix for two minutes, allow to settle then remove a portion of the methanol and store in a clean Teflon capped vial at 4°C until analysis. Analyze as described in section 11.5.

11.8.3. Connect the purge vessel to the purge and trap device.

11.8.4. Rinse a 5 mL gas-tight syringe with organic free water, and fill. Compress to 5 mL. Add surrogate/internal standard (and matrix spike solutions if required.). Add directly to the sample from 11.5.2.

11.8.5. The above steps should be performed rapidly and without interruption to avoid loss of volatile organics.

11.8.6. Add the heater jacket or other heating device and start the purge and trap unit.

11.8.7. Soil samples that have low IS recovery when analyzed (<50%) should be reanalyzed once to confirm matrix effect.

11.9. Initial review and corrective actions

11.9.1. If the retention time for any internal standard in the continuing calibration changes by more than 0.5 minutes from the mid-level initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.9.2. If the internal standard response in the continuing calibration is more than 200% or less than 50% of the response in the mid-level of the initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.9.2.1. Any samples that do not meet the internal standard criteria for the continuing calibration must be evaluated for validity. If the change in sensitivity is a matrix effect confined to an individual sample reanalysis is not necessary. If the change in sensitivity is due to instrumental problems all affected samples must be reanalyzed after the problem is corrected.

11.9.3. The surrogate standard recoveries are evaluated to ensure that they are within limits. Corrective action for surrogates out of control will normally be to reanalyze the affected samples. However, if the surrogate standard response is out high and there are no target analytes or tentatively identified compounds, reanalysis may not be necessary. Out of control surrogate standard response may be a matrix effect. It is only necessary to reanalyze a sample once to demonstrate matrix effect, but reanalysis at a dilution should be considered.

11.10. Dilutions

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

11.10.1.Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than half the height of the internal standards, or if individual non target peaks are less than twice the height of the internal standards, then the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgement.

11.10.2.Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative identification

An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NIST Library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

- The sample component retention time must compare to within ± 0.2 min. of the retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.
- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.
- The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20 and 80 percent.)

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

12.2. Tentatively Identified Compounds (TICs)

12.2.1. If the client requests components not associated with the calibration standards, a search of the NIST library may be made for the purpose of tentative identification. Guidelines are:

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

12.2.1.2. The relative intensities of the major ions should agree to within 20%. (Example: If an ion shows an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%).

12.2.1.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

12.2.1.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

12.2.1.5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the spectrum because of background contamination or coeluting peaks. (Data system reduction programs can sometimes create these discrepancies.)

12.2.1.6. Computer-generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual inspection of the sample with the nearest library searches should the analyst assign a tentative identification.

12.3. Calculations.

12.3.1. Response factor (RF):

Equation 1

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

Where:

A_x = Area of the characteristic ion for the compound to be measured

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

C_{is} = Concentration of the specific internal standard, ng/L 12/12/98

C_x = Concentration of the compound being measured, ng/L 12/12/98

12.3.2. Standard deviation (SD):

Equation 2

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(Xi - X)^2}{N - 1}}$$

X_i = Value of X at i through N

N = Number of points

X = Average value of X_i

12.3.3. Percent relative standard deviation (%RSD):

Equation 3

$$\%RSD = \frac{\textbf{Standard Deviation}}{\overline{RF_i}} \times 100$$

$\overline{RF_i}$ = **Mean of RF values in the curve**

12.3.4. Percent drift between the initial calibration and the continuing calibration:

Equation 4

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

Where

$C_{expected}$ = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

12.3.5. Target compound and surrogate concentrations:

Concentrations in the sample may be determined from linear or second order (quadratic) curve fitted to the initial calibration points, or from the average response factor of the initial calibration points. Average response factor may only be used when the % RSD of the response factors in the initial calibration is $\leq$ 15%.

12.3.5.1.Calculation of concentration using Average Response Factors

Equation 5

$$\textbf{Concentration } \mu g / L = \frac{x}{RF}$$

12.3.5.2.Calculation of concentration using Linear fit

Equation 6

$$\textbf{Concentration } \mu g / L = A + Bx$$

12.3.5.3.Calculation of concentration using Quadratic fit

Equation 7

$$\textbf{Concentration } \mu g / L = A + Bx + Cx^2$$

x is defined in equations 8, 9 and 10
A is a constant defined by the intercept
B is the slope of the curve
C is the curvature

12.3.5.4.Calculation of x for Water and water-miscible waste:

Equation 8

$$x = \frac{(A_x)(I_s)(D_f)}{(A_{is})(V_o)}$$

Where:

A_x = Area of characteristic ion for the compound being measured (secondary ion quantitation is allowed only when there are sample interferences with the primary ion)

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

I_s = Amount of internal standard added in ng

$$\text{Dilution Factor} = D_f = \frac{\text{Total volume purged (mL)}}{\text{Volume of original sample used (mL)}}$$

V_o = Volume of water purged, mL

12.3.5.5.Calculation of x for Medium level soils:

Equation 9

$$x = \frac{(A_x)(I_s)(V_t)(1000)(D_f)}{(A_{is})(V_a)(W_s)(D)}$$

Where:

A_x, I_s, D_f, A_{is}, same as for water.

V_t = Volume of total extract, mL (Typically 25 mL)

V_a = Volume of extract added for purging, µL

W_s = Weight of sample extracted, g

$$D = \frac{100 - \%moisture}{100}$$

12.3.5.6.Calculation of x for Low level soils:

Equation 10

$$x = \frac{(A_x)(I_s)}{(A_{is})(W_s)(D)}$$

Where:

A_x, I_s, A_{is}, same as for water.

D is as for medium level soils

W_s = Weight of sample added to the purge vessel, g

12.3.5.7. Calculation of TICs: The calculation of TICs (tentatively identified compounds) is identical to the above calculations with the following exceptions:

A_x = Area in the total ion chromatogram for the compound being measured

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

RF = 1

In other words, the concentration is equal to x as defined in equations 8, 9 and 10.

12.3.6. MS/MSD Recovery

Equation 11

$$\textbf{Matrix Spike Recovery, } \% = \frac{SSR - SR}{SA} \times 100$$

SSR = Spike sample result
SR = Sample result
SA = Spike added

12.3.7. Relative % Difference calculation for the MS/MSD

Equation 12

$$\mathbf{RPD} = \frac{|\mathbf{MSR - MSDR}|}{\frac{1}{2}(\mathbf{MSR + MSDR})} \times \mathbf{100}$$

Where:

RPD = Relative percent difference

MSR = Matrix spike result

MSDR = Matrix spike duplicate result

13. METHOD PERFORMANCE

13.1. Method Detection Limit

Generally, each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005. When non-standard compounds are analyzed at client request, lesser requirements are possible with client agreement. At a minimum, a standard at the reporting limit must be analyzed to demonstrate the capability of the method.

13.2. Initial Demonstration

Each laboratory must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest. The QC check sample is made up at 20 µg/L. (Some compounds will be at higher levels, refer to the calibration standard levels for guidance.)

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

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. The %RSD should be $\leq$ 15% for each analyte, and the % recovery should be within 80-120%.

13.2.3. If any analyte does not meet the acceptance criteria, check the acceptance limits in the reference methods (Table 6 of method 8240B, paragraph 8.3.5 of method 8260A). If the recovery or precision is outside the limits in the reference methods, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the waste streams detailed in the facility hazardous waste management procedures, Attachment B, Chemical Hygiene Plan, Section WS002, Table 1, current edition.

16. REFERENCES

16.1. SW846, *Test Methods for Evaluating Solid Waste,* Third Edition, Gas Chromatography/Mass Spectrometry for Volatile Organics, Method 8260B, Update III, December 1996

17. MISCELLANEOUS

17.1. Modifications from the reference method

17.1.1. Ion 117 is used as the quantitation ion for chlorobenzene-d5 for 25 mL purge tests.

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

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

17.1.4. Method 8260A recommends that the purge vessel is run through an additional purge cycle after 25 mL sample analysis to remove carryover. Instead, purge vessels are oven baked between analyses or disposable vessels are used one time only.

17.1.5. SW-846 recommends that a curve be used for any analytes with %RSD of the response factors > 15%. However, some industry standard data systems and forms generation software cannot report this data with the necessary information for data validation. In addition most software available does not allow weighting of the curve. Unweighted curves may exhibit serious errors in

quantitation at the low end, resulting in possible false positives or false negatives. Therefore, this SOP allows used of average response factors if the average %RSD for all compounds is $\leq$ 15%.

17.2. Modifications from previous revision

This SOP has been substantially revised to reflect the changes included in Update III to SW-846. Directions for method 524.2 and method 624 have also been added.

17.3. Facility specific SOPs

Each facility shall attach a list of facility-specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.4. Flow diagrams

17.4.1. Initial Demonstration and MDL

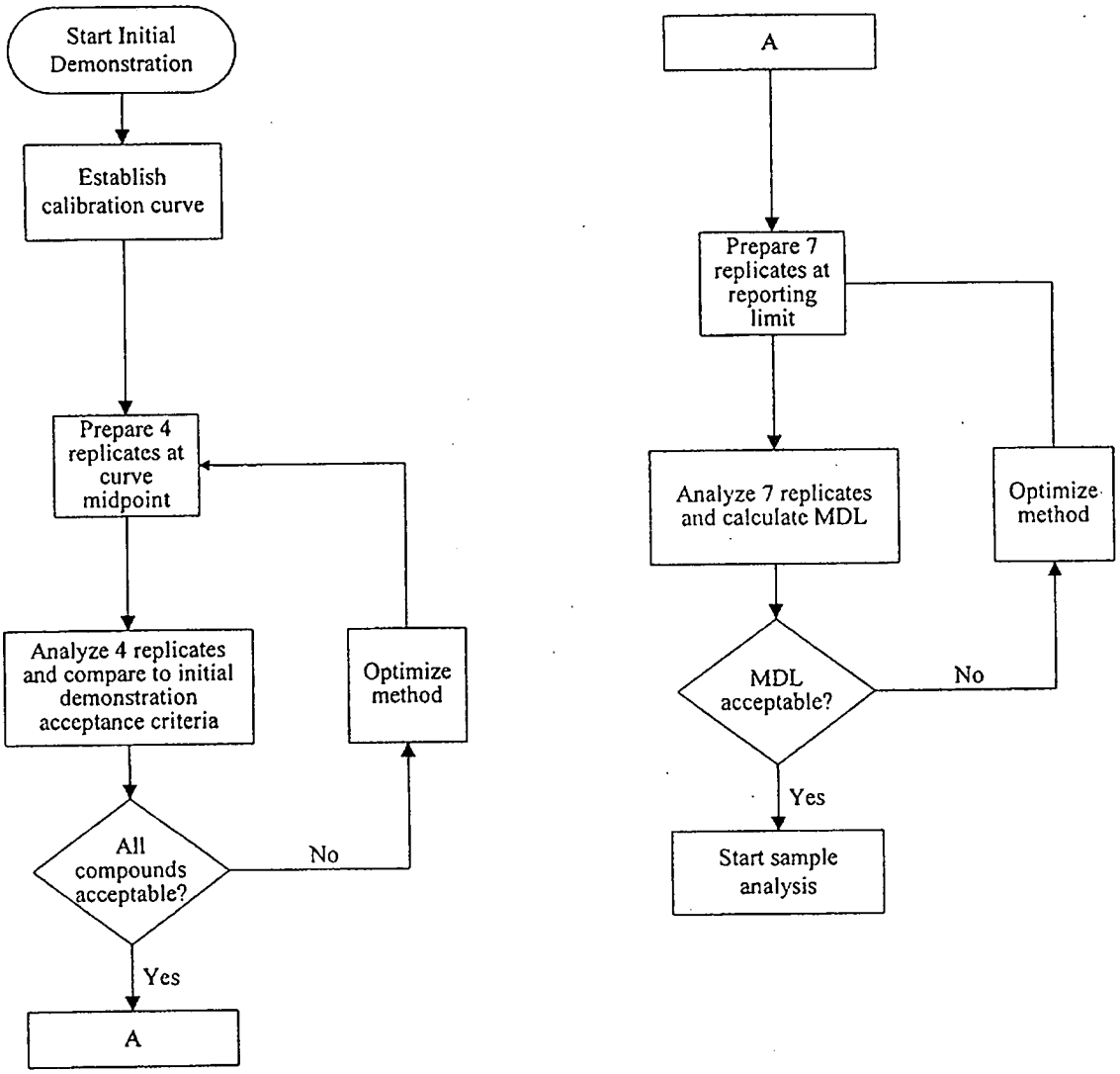

Table 1

Quanterra Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]			
		5 mL Water µg/L	25 mL water µg/L	Low soil µg/kg	Med. Soil µg/kg
Dichlorodifluoromethane	75-71-8	10	2	10	500
Chloromethane	74-87-3	10	2	10	500
Bromomethane	74-83-9	10	2	10	500
Vinyl chloride	75-01-4	10	2	10	500
Chloroethane	75-00-3	10	2	10	500
Trichlorofluoromethane	75-69-4	10	2	10	500
Acrolein	107-02-8	100	20	100	5000
Acetone	67-64-1	20	10	20	1000
Trichlorotrifluoroethane	76-13-1	5	1	5	250
Ethanol	64-17-5	500	200	500	25,000
Iodomethane	74-88-4	5	1	5	250
Carbon disulfide	75-15-0	5	1	5	250
Methylene chloride	75-09-2	5	1	5	250
tert-Butyl alcohol	75-65-0	200	50	200	10,000
1,1-Dichloroethene	75-35-4	5	1	5	250
1,1-Dichloroethane	75-34-3	5	1	5	250
trans-1,2-Dichloroethene	156-60-5	2.5	0.5	2.5	125
Acrylonitrile	107-13-1	100	20	100	5000
Methyl *tert*-butyl ether (MTBE)	1634-04-4	20	5	20	1000
Hexane	110-54-3	5	1	5	250
cis-1,2-Dichloroethene	156-59-2	2.5	0.5	2.5	125
1,2-Dichloroethene (Total)	540-59-0	5	1	5	250
Tetrahydrofuran	109-99-9	20	5	20	1000
Chloroform	67-66-3	5	1	5	250
1,2-Dichloroethane	107-06-2	5	1	5	250
Dibromomethane	74-95-3	5	1	5	250
2-Butanone	78-93-3	20	5	20	1000
1,4-Dioxane	123-91-1	500	200	500	25000
1,1,1-Trichloroethane	71-55-6	5	1	5	250
Carbon tetrachloride	56-23-5	5	1	5	250
Bromodichloromethane	75-27-4	5	1	5	250
1,2-Dichloropropane	78-87-5	5	1	5	250
cis-1,3-Dichloropropene	10061-01-5	5	1	5	250
Trichloroethene	79-01-6	5	1	5	250

Table 1

Quanterra Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]			
		5 mL Water µg/L	25 mL water µg/L	Low soil µg/kg	Med. Soil µg/kg
Dibromochloromethane	124-48-1	5	1	5	250
1,2-Dibromoethane	106-93-4	5	1	5	250
1,2,3-Trichloropropane	96-18-4	5	1	5	250
1,1,2-Trichloroethane	79-00-5	5	1	5	250
Benzene	71-43-2	5	1	5	250
Ethylmethacrylate	97-63-2	5	1	5	250
trans-1,3-Dichloropropene	10061-02-6	5	1	5	250
Bromoform	75-25-2	5	1	5	250
4-Methyl-2-pentanone	108-10-1	20	5	20	1000
2-Hexanone	591-78-6	20	5	20	1000
Tetrachloroethene	127-18-4	5	1	5	250
Toluene	108-88-3	5	1	5	250
1,1,2,2-Tetrachloroethane	79-34-5	5	1	5	250
2-Chloroethyl vinyl ether	110-75-8	N/A[2]	N/A	50	1000
Vinyl acetate	108-05-4	10	2	10	500
Chlorobenzene	108-90-7	5	1	5	250
Ethylbenzene	100-41-4	5	1	5	250
Styrene	100-42-5	5	1	5	250
t-1,4-Dichloro-2-butene	110-57-6	5	1	5	250
m and p Xylenes		2.5	0.5	2.5	125
o-xylene	95-47-6	2.5	0.5	2.5	125
Total xylenes	1330-20-7	5	1	5	250
1,3-Dichlorobenzene	541-73-1	5	1	5	250
1,4-Dichlorobenzene	106-46-7	5	1	5	250
1,2-Dichlorobenzene	95-50-1	5	1	5	250

[1] Reporting limits listed for soil/sediment are based on wet weight. The reporting limits calculated by the laboratory for soil/sedimei calculated on dry weight basis, will be higher.

[2] 2-Chloroethyl vinyl ether cannot be reliably recovered from acid preserved samples

Table 2

Quanterra Primary Standard Calibration Levels, 5 mL purge[1]

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,2-Dichloroethane-d4 (Surrogate)	5	20	50	100	200
Toluene-d8 (Surrogate)	5	20	50	100	200
4-Bromofluorobenzene (Surrogate)	5	20	50	100	200
Dichlorodifluoromethane	5	20	50	100	200
Chloromethane	5	20	50	100	200
Bromomethane	5	20	50	100	200
Vinyl chloride	5	20	50	100	200
Chloroethane	5	20	50	100	200
Trichlorofluoromethane	5	20	50	100	200
Acrolein	50	200	500	1000	2000
Acetone	5	20	50	100	200
Trichlorotrifluoroethane	5	20	50	100	200
Ethanol	500	2000	5000	10000	20000
Iodomethane	5	20	50	100	200
Carbon disulfide	5	20	50	100	200
Methylene chloride	5	20	50	100	200
tert-Butyl alcohol	100	400	1,000	2,000	4,000
1,1-Dichloroethene	5	20	50	100	200
1,1-Dichloroethane	5	20	50	100	200
trans-1,2-Dichloroethene	5	20	50	100	200
Acrylonitrile	50	200	500	1,000	2,000
Methyl *tert*-butyl ether (MTBE)	5	20	50	100	200
Hexane	5	20	50	100	200
cis-1,2-Dichloroethene	5	20	50	100	200
Tetrahydrofuran	5	20	50	100	200
Chloroform	5	20	50	100	200
1,2-Dichloroethane	5	20	50	100	200
Dibromomethane	5	20	50	100	200
2-Butanone	5	20	50	100	200
1,4-Dioxane	250	1000	2,500	5,000	10,000
1,1,1-Trichloroethane	5	20	50	100	200
Carbon tetrachloride	5	20	50	100	200
Bromodichloromethane	5	20	50	100	200
1,2-Dichloropropane	5	20	50	100	200
cis-1,3-Dichloropropene	5	20	50	100	200

Table 2

Quanterra Primary Standard Calibration Levels, 5 mL purge[1]

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
Trichloroethene	5	20	50	100	200
Dibromochloromethane	5	20	50	100	200
1,2-Dibromoethane	5	20	50	100	200
1,2,3-Trichloropropane	5	20	50	100	200
1,1,2-Trichloroethane	5	20	50	100	200
Benzene	5	20	50	100	200
Ethylmethacrylate	5	20	50	100	200
trans-1,3-Dichloropropene	5	20	50	100	200
Bromoform	5	20	50	100	200
4-Methyl-2-pentanone	5	20	50	100	200
2-Hexanone	5	20	50	100	200
Tetrachloroethene	5	20	50	100	200
Toluene	5	20	50	100	200
1,1,2,2-Tetrachloroethane	5	20	50	100	200
2-Chloroethyl vinyl ether	10	40	100	200	400
Vinyl acetate	5	20	50	100	200
Chlorobenzene	5	20	50	100	200
Ethylbenzene	5	20	50	100	200
Styrene	5	20	50	100	200
t-1,4-Dichloro-2-butene	5	20	50	100	200
m and p Xylenes	10	40	100	200	400
o-xylene	5	20	50	100	200
1,3-Dichlorobenzene	5	20	50	100	200
1,4-Dichlorobenzene	5	20	50	100	200
1,2-Dichlorobenzene	5	20	50	100	200

[1] **Levels for 25 mL purge are 5 times lower in all cases**

Table 3

Quanterra Appendix IX Standard and Reporting Limits, 5 mL purge[1]

Compound	CAS Number	Reporting Limits			
		5 mL Water µg/L	25 mL water µg/L	Low Soil µg/kg	Medium Soil µg/mL
Allyl Chloride	107-05-1	10	2	10	500
Acetonitrile	75-05-8	100	20	100	5000
Dichlorofluoromethane		10	2	10	500
Isopropyl ether	108-20-3	10	2	10	500
Chloroprene	126-99-8	5	1	5	250
n-Butanol	71-36-3	200	50	200	10,000
Propionitrile	107-12-0	20	4	20	1000
Methacrylonitrile	126-98-7	5	1	5	250
Isobutanol	78-83-1	200	50	200	10,000
Methyl methacrylate	80-62-6	5	1	5	250
1,1,1,2-Tetrachloroethane	630-20-6	5	1	5	250
1,2-Dibromo-3-chloropropane	96-12-8	10	2	10	500
Ethyl ether	60-29-7	10	2	10	500
Ethyl Acetate	141-78-6	20	4	20	1,000
2-Nitropropane	79-46-9	10	2	10	500
Cyclohexanone	108-94-1	N/A[2]	N/A[2]	N/A[2]	N/A[2]
Isopropylbenzene	98-82-8	5	1	5	250

[1] **Levels for 25 mL purge are 5 times lower in all cases**

[2] Cyclohexanone decomposes to 1,1-dimethoxycyclohexane in methanolic solution. Reporting limits cannot be accurately determined.

Table 4

Quanterra Appendix IX Standard Calibration Levels, µg/L

Compound	Level 1	Level 2	Level 3	Level 4	Level 5
Allyl Chloride	5	20	50	100	200
Acetonitrile	50	200	500	1,000	2,000
Dichlorofluoromethane	5	20	50	100	200
Isopropyl ether	5	20	50	100	200
Chloroprene	5	20	50	100	200
n-Butanol	100	400	1,000	2,000	4,000
Propionitrile	10	40	100	200	400
Methacrylonitrile	5	20	50	100	200
Isobutanol	100	400	1,000	2,000	4,000
Methyl methacrylate	5	20	50	100	200
1,1,1,2-Tetrachloroethane	5	20	50	100	200
1,2-Dibromo-3-chloropropane	10	40	100	200	400
Ethyl ether	5	20	50	100	200
Ethyl Acetate	10	40	100	200	400
2-Nitropropane	10	40	100	200	400
Cyclohexanone	50	200	500	1,000	2,000
Isopropylbenzene Mike wants this moved to primary standard	5	20	50	100	200

Table 5

Reportable Analytes for Quanterra Standard Tests, Primary Standard

Compound	CAS Number	Quanterra Standard List	TCLP	TCL	Appendix IX	UTS
Dichlorodifluoromethane	75-71-8				X	X
Chloromethane	74-87-3	X		X	X	X
Bromomethane	74-83-9	X		X	X	X
Vinyl chloride	75-01-4	X	X	X	X	X
Chloroethane	75-00-3	X		X	X	X
Trichlorofluoromethane	75-69-4				X	X
Acrolein	107-02-8				X	X
Acetone	67-64-1	X		X	X	X
Trichlorotrifluoroethane	76-13-1					X
Ethanol	64-17-5					
Iodomethane	74-88-4				X	X
Carbon disulfide	75-15-0	X		X	X	X
Methylene chloride	75-09-2	X		X	X	X
tert-Butly alcohol	75-65-0					
1,1-Dichloroethene	75-35-4	X	X	X	X	X
1,1-Dichloroethane	75-34-3	X		X	X	X
trans-1,2-Dichloroethene	156-60-5	X		X	X	X
Total dichloroethene		X		X	X	X
Acrylonitrile	107-13-1				X	X
Methyl *tert*-butyl ether (MTBE)	1634-04-4					
Hexane	110-54-3					
cis-1,2-Dichloroethene	156-59-2	X		X		
Tetrahydrofuran	109-99-9					
Chloroform	67-66-3	X	X	X	X	X
1,2-Dichloroethane	107-06-2	X	X	X	X	X
Dibromomethane	74-95-3				X	X
2-Butanone	78-93-3	X	X	X	X	X
1,4-Dioxane	123-91-1				X	X
1,1,1-Trichloroethane	71-55-6	X		X	X	X
Carbon tetrachloride	56-23-5	X	X	X	X	X
Bromodichloromethane	75-27-4	X		X	X	X
1,2-Dichloropropane	78-87-5	X		X	X	X
cis-1,3-Dichloropropene	10061-01-	X		X	X	X

Table 5

Reportable Analytes for Quanterra Standard Tests, Primary Standard

Compound	CAS Number	Quanterra Standard List	TCLP	TCL	Appendix IX	UTS
	5					
Trichloroethene	79-01-6	X	X	X	X	X
Dibromochloromethane	124-48-1	X		X	X	X
1,2-Dibromoethane	106-93-4				X	X
1,2,3-Trichloropropane	96-18-4				X	X
1,1,2-Trichloroethane	79-00-5	X		X	X	X
Benzene	71-43-2	X	X	X	X	X
Ethylmethacrylate	97-63-2				X	X
trans-1,3-Dichloropropene	10061-02-6	X		X	X	X
Bromoform	75-25-2	X		X	X	X
4-Methyl-2-pentanone	108-10-1	X		X	X	X
2-Hexanone	591-78-6	X		X	X	
Tetrachloroethene	127-18-4	X	X	X	X	X
Toluene	108-88-3	X		X	X	X
1,1,2,2-Tetrachloroethane	79-34-5	X		X	X	X
2-Chloroethyl vinyl ether	110-75-8					
Vinyl acetate	108-05-4				X	
Chlorobenzene	108-90-7	X	X	X	X	X
Ethylbenzene	100-41-4	X		X	X	X
Styrene	100-42-5	X		X	X	
t-1,4-Dichloro-2-butene	110-57-6				X	
m and p Xylenes		X		X	X	X
o-xylene	95-47-6	X		X	X	X
Total xylenes	1330-20-7	X		X	X	X
1,3-Dichlorobenzene	541-73-1					
1,4-Dichlorobenzene	106-46-7					
1,2-Dichlorobenzene	95-50-1					

Table 6

Reportable Analytes for Quanterra Standard Tests, Appendix IX standard

Compound	Number	Quanterra Standard List	TCLP	TCL	Appendix IX	UTS
Allyl Chloride	107-05-1				X	
Acetonitrile	75-05-8				X	X
Dichlorofluoromethane	75-43-4					
Isopropyl ether	108-20-3					
Chloroprene	126-99-8				X	
n-Butanol	71-36-3					
Propionitrile	107-12-0				X	
Methacrylonitrile	126-98-7				X	X
Isobutanol	78-83-1				X	X
Methyl methacrylate	80-62-6				X	X
1,1,1,2-Tetrachloroethane	630-20-6				X	X
1,2-Dibromo-3-chloropropane	96-12-8				X	X
Ethyl ether	60-29-7					X
Ethyl Acetate	141-78-6					X
2-Nitropropane	79-46-9					
Cyclohexanone	108-94-1					X
Isopropylbenzene	98-82-8					

Table 7

Internal Standards

	Standard Concentration µg/mL	Quantitation ion (5 mL purge)	Quantitation ion (25 mL purge)
1,4-Difluorobenzene	50	114	114
Chlorobenzene-d5	50	117	117
1,4-Dichlorobenzene-d4	50	152	152

Notes:

1) 5 µL of the internal standard is added to the sample. This results in a concentration of each internal in the sample of 50µg/L .

2) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

Table 8

Surrogate Standards

Surrogate Compounds	Standard Concentration µg/mL
1,2-Dichloroethane-d_4	50
Dibromofluoromethane	50
Toluene-d_8	50
4-Bromofluorobenzene	50

Notes:

1) 5 µL of the surrogate standard is added to the sample. This results in a concentration of each surrogate in the sample of 50µg/L .

2) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

3) Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

Table 9

Matrix Spike / LCS Compounds

Compound	Standard Concentration µg /mL
1,1-Dichloroethene	50
Trichloroethene	50
Toluene	50
Benzene	50
Chlorobenzene	50

Notes:

1) 5 µL of the standard is added to the LCS or matrix spiked sample. This results in a concentration of each spike analyte in the sample of 50µg/L .

2) Recovery and precision limits for LCS and MS/MSD are generated from historical data and are maintained by the QA dedartment.

3) Full analyte spikes may also be used at the laboratories option or at client request.

Table 10

BFB Key Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15% to 40% of Mass 95
75	30% to 60% of Mass 95
95	Base Peak, 100% Relative Abundance
96	5% to 9% of Mass 95
173	Less Than 2% of Mass 174
174	Greater Than 50% of Mass 95
175	5% to 9% of Mass 174
176	Greater Than 95%, But Less Than 101% of Mass 174
177	5% to 9% of Mass 176

Table 11

SPCC Compounds and Minimum Response Factors

Compound	8240B Min. RF	8260B Min. RF
Chloromethane	0.300	0.100
1,1-Dichloroethane	0.300	0.100
Bromoform	>0.100	>0.100
1,1,2,2-Tetrachloroethane	0.300	0.300
Chlorobenzene	0.300	0.300

Table 12

CCC compounds

Compound	Max. %RSD from Initial Calibration	Max. %D for continuing calibration
Vinyl Chloride	<30.0	<20.0
1,1-Dichloroethene	<30.0	<20.0
Chloroform	<30.0	<20.0
1,2-Dichloropropane	<30.0	<20.0
Toluene	<30.0	<20.0
Ethylbenzene	<30.0	<20.0

Table 13

Characteristic ions

Compound	Primary*	Secondary	Tertiary
1,2-Dichloroethane-d_4 (Surrogate)	65	102	
Dichlorodifluoromethane	85	87	50, 101,103
Chloromethane	50	52	49
Vinyl chloride	62	64	61
Bromomethane	94	96	79
Chloroethane	64	66	49
Trichlorofluoromethane	101	103	66
1,1-Dichloroethene	96	61	98
Acrolein	56	55	58
Iodomethane	142	127	141

Table 13

Characteristic ions

Compound	Primary*	Secondary	Tertiary
Carbon disulfide	76	78	
Trichlorotrifluoroethane	151	101	153
Ethanol	45	46	
Acetone	43	58	
Methylene chloride	84	49	51, 86
tert-Butyl alcohol	59	74	
trans-1,2-Dichloroethene	96	61	98
Acrylonitrile	53	52	51
Methyl *tert* butyl ether	73		
Hexane	57	43	
1,1-Dichloroethane	63	65	83
cis-1,2-Dichloroethene	96	61	98
2-Butanone	43	72**	
Tetrahydrofuran	42	71	
Chloroform	83	85	47
1,2-Dichloroethane	62	64	98
Dibromomethane	93	174	95, 172, 176
1,4-Dioxane	88	58	
Vinyl acetate	43	86	
1,1,1-Trichloroethane	97	99	117
Carbon tetrachloride	117	119	121
Benzene	78	52	77
Trichloroethene	130	95	97, 132
1,2-Dichloropropane	63	65	41
Bromodichloromethane	83	85	129
2-Chloroethyl vinyl ether	63	65	106
cis-1,3-Dichloropropene	75	77	39
trans-1,3-Dichloropropene	75	77	39
1,1,2-Trichloroethane	97	83	85, 99
Chlorodibromomethane	129	127	131
Bromoform	173	171	175, 252
1,2,3-Trichloropropane	75	110	77, 112, 97
Toluene-d_8 (Surrogate)	98	70	100
4-Bromofluorobenzene (Surrogate)	95	174	176
Toluene	91	92	65
4-Methyl-2-pentanone	43	58	57, 100
Tetrachloroethene	164	166	131
Ethyl methacrylate	69	41	99, 86, 114

Table 13

Characteristic ions

Compound	Primary*	Secondary	Tertiary
2-Hexanone	43	58	57, 100
Chlorobenzene	112	114	77
Ethylbenzene	106	91	
Xylenes	106	91	
Styrene	104	103	78, 51, 77
Dichlorobenzene (all isomers)	146	148	111
trans 1,4-Dichloro-2-butene	53	75	89, 77, 124
1,1,2,2-Tetrachloroethane	83	85	131, 133
Allyl Chloride	76	41	78
Acetonitrile	40	41	
Dichlorofluoromethane	67	69	
Isopropyl ether	87	59	45
Chloroprene	53	88	90
n-Butanol	56	41	42
Propionitrile	54	52	55
Methacrylonitrile	41	67	52
Isobutanol	41	43	74
Methyl methacrylate	41	69	100
1,1,1,2-Tetrachloroethane	131	133	119
1,2-Dibromo-3-chloropropane	157	155	75
Ethyl ether	59	74	
Ethyl Acetate	43	88	61
2-Nitropropane	41	43	46
Cyclohexanone	55	42	98
Isopropylbenzene	105	120	

* The primary ion should be used for quantitation unless interferences are present, in which case a secondary ion may be used.

** m/z 43 may be used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

18. SUMMARY

This appendix lists modifications to the main body of the SOP that are necessary for analysis of drinking water by method 524.2.

18.1. A target analyte list based on the list in method 524.2 is frequently requested for analysis by method 8260B. Quanterra's standard analyte list for this test, and the internal and surrogate standards used, are listed in Tables A-1 to A-4 below. In all other respects the method is as described in the main body of this SOP. Note that this without the modifications listed in Section 19, the method is ***not*** appropriate for drinking water analysis by method 524.2.

19. MODIFICATIONS REQUIRED FOR DRINKING WATER ANALYSIS BY METHOD 524.2

19.1. This method can be applied to surface water, ground water and drinking water.

19.2. Purge sample volume is normally 25 mL, but lesser volumes may be used if adequate sensitivity is obtained.

19.3. Sample concentrations are calculated using initial calibration curve.

19.4. Only one internal standard -- Fluorobenzene -- is used for this method, and therefore all target analytes are assigned to it.

19.5. A maximum of 25 ng of BFB is used for tuning for method 524.2

19.6. BFB tuning criteria for mass 75 are 30-80% of mass 95.

19.7. The recovery limits for the initial demonstration of capability are 80-120% with %RSD less than 20%.

19.8. Initial calibration curve requirements:

19.8.1. The number of calibration standards depends on the calibration range used. For a range of up to a factor of 20 (e.g. 1µg/L - 20µg/L) a minimum of three standards are necessary. For a factor of up to 50 four standards are necessary, and for a factor of up to 100 five standards are necessary.

19.8.2. All target compounds must have RSD ≤ 20%.

19.8.3. If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds. There is no correlation coefficient requirement for the regression curve.

19.9. Continuing calibration verification (CCV) requirements:

19.9.1. All target compounds must have %D ≤ 30%.

19.9.2. The internal standards in each CCV must be over 70% of the abundance found in the CCV analysis immediately preceding it *and* over 50% of the calibration point in the initial calibration curve whose concentration matches that of the CCV.

19.9.3. The same analysis run may be used to satisfy the requirements for an LCS (also known as a laboratory fortified blank, LFB) and a continuing calibration verification. The LCS/CCV does not need to be a second source standard.

19.10. Method clarifications, modifications and additions

19.10.1.19.10.1.Section 7.1 requires that the trap packing materials be Tenax GC, Methyl silicone, silica gel and coconut charcoal. Quanterra routinely employs the Supelco VOCARB 3000, which consists of Carbopack B and Carboxen 1000 and 1001.

19.10.2.19.10.2.Section 7.8.2 of the source method requires that each calibration standard be prepared by diluting the appropriate volume of the working standard with organic-free water adjusted to pH < 2 in a volumetric flask. Quanterra prepares calibration standards by diluting the the appropriate volume of the working standard with organic-free water in the gas-tight syringe that will be used to inject the sample into the purge and trap device.

19.10.3.19.10.3.Sections 9.8 and 9.9 of the source method require that duplicate spiked blanks and a second-source initial calibration verification standard be analyzed at least quarterly. Since some Quanterra do not normally analyze drinking waters samples, these QC samples will be analyzed only during the conduct of projects that require this method.

Table A-1

Quanterra 8260 Drinking Water List Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]			
		5 mL water µg/L	25 mL water µg/L	Low soil µg/kg	Med. Soil µg/kg
Dichlorodifluoromethane	75-71-8	10	2	10	500
Chloromethane	74-87-3	10	2	10	500
Bromomethane	74-83-9	10	2	10	500
Vinyl chloride	75-01-4	10	2	10	500
Chloroethane	75-00-3	10	2	10	500
Trichlorofluoromethane	75-69-4	10	2	10	500
Acetone[1]	67-64-1	20	10	20	1000
Methylene chloride	75-09-2	5	2	5	250
1,1-Dichloroethene	75-35-4	5	1	5	250
1,1-Dichloroethane	75-34-3	5	1	5	250
trans-1,2-Dichloroethene	156-60-5	2.5	0.5	2.5	125
Methyl *tert*-butyl ether (MTBE)[1]	1634-04-4	20	5	20	250
2,2-Dichloropropane	590-20-7	5	1	5	250
cis-1,2-Dichloroethene	156-59-2	2.5	0.5	2.5	125
1,2-Dichloroethene (Total)	540-59-0	5	1	5	250
Chloroform	67-66-3	5	1	5	250
Bromochloromethane	74-97-5	5	1	5	250
1,2-Dichloroethane	107-06-2	5	1	5	250
Dibromomethane	74-95-3	5	1	5	250
2-Butanone[1]	78-93-3	20	5	20	1000
1,1,1-Trichloroethane	71-55-6	5	1	5	250
Carbon tetrachloride	56-23-5	5	1	5	250
1,1-Dichloropropene	563-58-6	5	1	5	250
Bromodichloromethane	75-27-4	5	1	5	250
1,2-Dichloropropane	78-87-5	5	1	5	250
1,3-Dichloropropane	142-28-9	5	1	5	250
cis-1,3-Dichloropropene	10061-01-5	5	1	5	250
Trichloroethene	79-01-6	5	1	5	250
Dibromochloromethane	124-48-1	5	1	5	250
1,2-Dibromoethane	106-93-4	5	1	5	250
1,2,3-Trichloropropane	96-18-4	5	1	5	250
1,1,2-Trichloroethane	79-00-5	5	1	5	250
Benzene	71-43-2	5	1	5	250

Table A-1

Quanterra 8260 Drinking Water List Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]			
		5 mL water µg/L	25 mL water µg/L	Low soil µg/kg	Med. Soil µg/kg
trans-1,3-Dichloropropene	10061-02-6	5	1	5	250
Bromoform	75-25-2	5	1	5	250
4-Methyl-2-pentanone[1]	108-10-1	20	5	20	1000
2-Hexanone[1]	591-78-6	20	5	20	1000
Tetrachloroethene	127-18-4	5	1	5	250
Toluene	108-88-3	5	1	5	250
1,1,2,2-Tetrachloroethane	79-34-5	5	1	5	250
Chlorobenzene	108-90-7	5	1	5	250
1,1,1,2-Terrachloroethane	630-20-6	5	1	5	250
Ethylbenzene	100-41-4	5	1	5	250
Styrene	100-42-5	5	1	5	250
m and p Xylenes		2.5	0.5	2.5	125
o-xylene	95-47-6	2.5	0.5	2.5	125
Total xylenes	1330-20-7	5	1	5	250
Isopropylbenzene	98-82-8	5	1	5	250
Bromobenzene	108-86-1	5	1	5	250
n-Propylbenzene	103-65-1	5	1	5	250
2-Chlorotoluene	95-49-8	5	1	5	250
4-Chlorotoluene	106-43-4	5	1	5	250
1,3,5-Trimethylbenzene	108-67-8	5	1	5	250
tert-Butylbenzene	98-06-6	5	1	5	250
1,2,4-Trimethylbenzene	95-63-6	5	1	5	250
sec-butylbenzene	135-98-8	5	1	5	250
1,3-Dichlorobenzene	541-73-1	5	1	5	250
1,4-Dichlorobenzene	106-46-7	5	1	5	250
1,2-Dichlorobenzene	95-50-1	5	1	5	250
4-Isopropyltoluene	99-87-6	5	1	5	250
n-Butylbenzene	104-51-8	5	1	5	250
1,2-Dibromo-3-chloropropane	96-12-8	5	1	5	250
1,2,4-Trichlorobenzene	120-82-1	5	1	5	250
Napthalene	91-20-3	5	1	5	250
Hexachlorobutadiene	87-68-3	5	1	5	250
1,2,3-Trichlorobenzene	87-61-6	5	1	5	250

[1] Not included on the method 524.2 analyte list, but includes in the calibration standard as an add on frequently requested by method 8260B.

Table A-2

Internal Standards, Method 8260A Drinking water list

	Standard Concentration µg/mL	Quantitation ion
Fluorobenzene	50	96
1,4-Dichlorobenzene-d4	50	152

Notes:

1) Fluorobenzene only is used for method 524.2

2) 10 µL of the internal standard is added to the sample. This results in a concentration of each internal in the sample of 50µg/L.

3) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

Table A-3

Surrogate Standards, Drinking water list

Surrogate Compounds	Standard Concentration µg/mL
1,2-Dichloroethane-d_4[1]	50
Dibromofluoromethane[1]	50
Toluene-d_8[1]	50
1,2-Dichlorobenzene-d4[2]	50
4-Bromofluorobenzene[1,2]	50

[1] 8260B surrogate

[2] 524.2 surrogate

Notes:

1) 5 µL of the surrogate standard is added to the sample. This results in a concentration of each surrogate in the sample of 50µg/L.

2) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

Table A-4

Quanterra Drinking water list Standard: Calibration Levels

Compound	Level 1		Level 2		Level 3		Level 4		Level 5	
	5 mL	25 mL	5 mL	25 mL	5 mL	25 mL	5 mL	25 mL	5 mL	25 mL
Dichlorodifluoromethane	10	2	40	10	100	20	200	60	400	120
Chloromethane	10	2	40	10	100	20	200	60	400	120
Bromomethane	10	2	40	10	100	20	200	60	400	120
Vinyl chloride	10	2	40	10	100	20	200	60	400	120
Chloroethane	10	2	40	10	100	20	200	60	400	120
Trichlorofluoromethane	10	2	40	10	100	20	200	60	400	120
Acetone[1]	10		40	10	100	20	200	60	400	120
Methylene chloride	5	1	20	4	50	10	100	20	200	40
1,1-Dichloroethene	5	1	20	4	50	10	100	20	200	40
1,1-Dichloroethane	5	1	20	4	50	10	100	20	200	40
trans-1,2-Dichloroethene	5	1	20	45	50	10	100	20	200	40
Methyl *tert*-butyl ether (MTBE)	10		40	10	100	20	200	60	400	120
2,2-Dichloropropane	5	1	20	4	50	10	100	20	200	40
cis-1,2-Dichloroethene	5	1	20	4	50	10	100	20	200	40
Chloroform	5	1	20	4	50	10	100	20	200	40
Bromochloromethane	5	1	20	4	50	10	100	20	200	40
1,2-Dichloroethane	5	1	20	4	50	10	100	20	200	40
Dibromomethane	5	1	20	4	50	10	100	20	200	40
2-Butanone[1]	10		40	10	100	20	200	60	400	120
1,1,1-Trichloroethane	5	1	20	4	50	10	100	20	200	40
Carbon tetrachloride	5	1	20	4	50	10	100	20	200	40
Bromodichloromethane	5	1	20	4	50	10	100	20	200	40
1,2-Dichloropropane	5	1	20	4	50	10	100	20	200	40
cis-1,3-Dichloropropene	5	1	20	4	50	10	100	20	200	40
Trichloroethene	5	1	20	4	50	10	100	20	200	40

Table A-4

Quanterra Drinking water list Standard: Calibration Levels

Compound	Level 1		Level 2		Level 3		Level 4		Level 5	
Dibromochloromethane	5	1	20	4	50	10	100	20	200	40
1,2-Dibromoethane	5	1	20	4	50	10	100	20	200	40
1,2,3-Trichloropropane	5	1	20	4	50	10	100	20	200	40
1,1,2-Trichloroethane	5	1	20	4	50	10	100	20	200	40
Benzene	5	1	20	4	50	10	100	20	200	40
trans-1,3-Dichloropropene	5	1	20	4	50	10	100	20	200	40
Bromoform	5	1	20	4	50	10	100	20	200	40
4-Methyl-2-pentanone[1]	10		40	10	100	20	200	60	400	120
2-Hexanone[1]	10		40	10	100	20	200	60	400	120
Tetrachloroethene	5	1	20	4	50	10	100	20	200	40
Toluene	5	1	20	4	50	10	100	20	200	40
1,1,2,2-Tetrachloroethane	5	1	20	4	50	10	100	20	200	40
Chlorobenzene	5	1	20	4	50	10	100	20	200	40
Ethylbenzene	5	1	20	4	50	10	100	20	200	40
Styrene	5	1	20	4	50	10	100	20	200	40
m and p Xylenes	5	1	20	4	50	10	100	20	200	40
o-xylene	5	1	20	4	50	10	100	20	200	40
Isopropylbenzene	5	1	20	4	50	10	100	20	200	40
Bromobenzene	5	1	20	4	50	10	100	20	200	40
n-Propylbenzene	5	1	20	4	50	10	100	20	200	40
2-Chlorotoluene	5	1	20	4	50	10	100	20	200	40
4-Chlorotoluene	5	1	20	4	50	10	100	20	200	40
1,3,5-Trimethylbenzene	5	1	20	4	50	10	100	20	200	40
tert-Butylbenzene	5	1	20	4	50	10	100	20	200	40
1,2,4-Trimethylbenzene	5	1	20	4	50	10	100	20	200	40
sec-butylbenzene	5	1	20	4	50	10	100	20	200	40
1,3-Dichlorobenzene	5	1	20	4	50	10	100	20	200	40
1,4-Dichlorobenzene	5	1	20	4	50	10	100	20	200	40

Table A-4

Quanterra Drinking water list Standard: Calibration Levels

Compound	Level 1		Level 2		Level 3		Level 4		Level 5	
1,2-Dichlorobenzene	5	1	20	4	50	10	100	20	200	40
4-Isopropyltoluene	5	1	20	4	50	10	100	20	200	40
n-Butylbenzene	5	1	20	4	50	10	100	20	200	40
1,2-Dibromo-3-chloropropane	5	1	20	4	50	10	100	20	200	40
1,2,4-Trichlorobenzene	5	1	20	4	50	10	100	20	200	40
Napthalene	5	1	20	4	50	10	100	20	200	40
Hexachlorobutadiene	5	1	20	4	50	10	100	20	200	40
1,2,3-Trichlorobenzene	5	1	20	4	50	10	100	20	200	40

[1] Not included in the Quanterra Standard test, but included in the standard as a frequently requested add-on.

20. REQUIREMENTS FOR EPA 624

20.1. Method 624 is required for demonstration of compliance with NPDES wastewater discharge permits. This method can be applied only to aqueous matrices. The standard analyte list and reporting limits are listed in Table B-1.

20.2. The tune period for this method is defined as 24 hours.

20.3. The initial calibration curve for this method requires at least three points.

20.4. Sample concentrations are calculated using the average RRF from the initial calibration curve.

20.5. Each target analyte is assigned to the closest eluting internal standard.

20.6. Initial demonstration of Proficiency

20.6.1. The spiking level for the four replicate initial demonstration of proficiency is 20 µg/L. The acceptance criteria are listed in Table B-2

20.7. Initial calibration curve requirements:

20.7.1. Target compounds must have RSD ≤ 35%.

20.7.2. If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds. There is no correlation coefficient requirement for the regression curve.

20.8. Continuing calibration verification requirements:

20.8.1. The continuing calibration standard is from a different source than the initial calibration standard. The acceptance criteria are listed in Table B-2.

20.9. Matrix Spike and LCS requirements

20.9.1. The matrix spike and LCS are spiked at 20 µg/L. A matrix spike duplicate is not necessary for this method. The recovery limits for matrix spike and LCS recovery are listed in Table C-2.

20.10. Method clarifications, modifications and additions

20.10.1.1.20.10.1.Section 5.2.2 of the source method describes the trap packing materials as Tenax GC, Methyl silicone, silica gel and coconut charcoal. Quanterra routinely employs the Supelco VOCARB 3000, which consists of Carbopack B and Carboxen 1000 and 1001.

20.10.1.2.20.10.2.Section 5.3.2 of the source method describes a packed analytical column. Quanterra routinely employs capillary columns when performing this method.

20.10.1.3.20.10.3.The source method provides a suggested list of compounds for internal and surrogate standards. Quanterra uses the following two compounds which are not on the table: Chlorobenzene-d_5 (internal standard) and 1,2-Difluorobenzene-d_4 (surrogate).

Table B-1.

Method 624 Analytes and Reporting Limits

Analytes	µg/L
Benzene	5
Bromodichloromethane	5
Bromoform	5
Bromomethane	5
Carbon tetrachloride	5
Chlorobenzene	5
Chloroethane	5
2-Chloroethyl vinyl ether	5
Chloroform	5
Chloromethane	5
Dibromochloromethane	5
1,2-Dichlorobenzene	5
1,3-Dichlorobenzene	5
1,4-Dichlorobenzene	5
1,1-Dichloroethane	5
1,2-Dichloroethane	5
1,1-Dichloroethene	5
trans-1,2-Dichloroethene	5
1,2-Dichloropropane	5
cis-1,3-Dichloropropene	5
trans-1,3-Dichloropropene	5
Ethylbenzene	5
Methylene chloride	5
1,1,2,2-Tetrachloroethane	5
Tetrachloroethene	5
Toluene	5
1,1,1-Trichloroethane	5
1,1,2-Trichloroethane	5
Trichloroethene	5
Trichlorofluoromethane	5
Vinyl chloride	5

Table B-2.

Method 624 QC Acceptance Criteria

Analytes	Daily QC check acceptance criteria (20µg/L spike)	Mean recovery, 4 replicate initial demonstration acceptance criteria (20µg/L spike)	Standard deviation, 4 replicate initial demonstration acceptance criteria (20µg/L spike)	Matrix spike and LCS acceptance criteria (% recovery)
Benzene	12.8-27.2	15.2-26.0	6.9	37-151
Bromodichloromethane	13.1-26.9	10.1-28.0	6.4	35-155
Bromoform	14.2-25.8	11.4-31.1	5.4	45-169
Bromomethane	2.8-37.2	D-41.2	17.9	D-242
Carbon tetrachloride	14.6-25.4	17.2-23.5	5.2	70-140
Chlorobenzene	13.2-26.8	16.4-27.4	6.3	37-160
Chloroethane	7.6-32.4	8.4-40.4	11.4	14-230
2-Chloroethyl vinyl ether	D-44.8	D-50.4	25.9	D-305
Chloroform	13.5-26.5	13.7-24.2	6.1	51-138
Chloromethane	D-40.8	D-45.9	19.8	D-273
Dibromochloromethane	13.5-26.5	13.8-26.6	6.1	53-149
1,2-Dichlorobenzene	12.6-27.4	11.8-34.7	7.1	18-190
1,3-Dichlorobenzene	14.6-25.4	17.0-28.8	5.5	59-156
1,4-Dichlorobenzene	12.6-27.4	11.8-34.7	7.1	18-190
1,1-Dichloroethane	14.5-25.5	14.2-28.5	5.1	59-155
1,2-Dichloroethane	13.6-26.4	14.3-27.4	6.0	49-155
1,1-Dichloroethene	10.1-29.9	3.7-42.3	9.1	D-234
trans-1,2-Dichloroethene	13.9-26.1	13.6-28.5	5.7	54-156
1,2-Dichloropropane	6.8-33.2	3.8-36.2	13.8	D-210
cis-1,3-Dichloropropene	4.8-35.2	1.0-39.0	15.8	D-227
trans-1,3-Dichloropropene	10.0-30.0	7.6-32.4	10.4	17-183
Ethylbenzene	11.8-28.2	17.4-26.7	7.5	37-162
Methylene chloride	12.1-27.9	D-41.0	7.4	D-221
1,1,2,2-Tetrachloroethane	12.1-27.9	13.5-27.2	7.4	46-157
Tetrachloroethene	14.7-25.3	17.0-26.6	5.0	64-148
Toluene	14.9-25.1	16.6-26.7	4.8	47-150
1,1,1-Trichloroethane	15.0-25.0	13.7-30.1	4.6	52-162
1,1,2-Trichloroethane	14.2-25.8	14.3-27.1	5.5	52-150
Trichloroethene	13.3-26.7	18.6-27.6	6.6	71-157
Trichlorofluoromethane	9.6-30.4	8.9-31.5	10.0	17-181
Vinyl chloride	0.8-39.2	D-43.5	20.0	D-251

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QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: GC/MS ANALYSIS BASED ON METHODS 8270C AND 625

(SUPERSEDES: Revision 1)

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1. SCOPE AND APPLICATION

1.1. This method is based upon SW846 8270C, and is applicable to the determination of the concentration of semivolatile organic compounds in extracts prepared from solid and aqueous matrices. The modifications presented in Attachment A may be followed for analysis of wastewater following method 625. Direct injection of a sample may be used in limited applications. Refer to Tables 1, 2, 3 and 4 for the list of compounds applicable for this method. Note that the compounds are listed in approximate retention time order. Additional compounds may be amenable to this method. If non-standard analytes are required, they must be validated by the procedures described in section 13 before sample analysis.

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

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

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

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

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

- Hexachlorophene is not amenable to analysis by this method.

- 3-Methylphenol cannot be separated from 4-methylphenol by the conditions specified in this method, and is reported as 4-methylphenol.

1.3. The standard reporting limit (SRL) of this method for determining an individual compound is approximately 0.33 mg/kg (wet weight) for soil/sediment samples, 1 - 200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for groundwater samples. Some compounds have higher reporting limits.

Refer to Tables 1 and 2 for specific SRLs. Reporting limits will be proportionately higher for sample extracts that require dilution.

2. SUMMARY

2.1. Aqueous samples are extracted with methylene chloride using a separatory funnel, a continuous extractor or Accelerated One-Step™. Solid samples are extracted with methylene chloride / acetone using sonication, soxhlet, accelerated soxhlet or pressurized fluid extraction. Waste dilution is used for samples that are miscible with the solvent. The extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/MS. Extraction procedures are detailed in SOP# CORP-OP-0001. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of characteristic ions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

3. DEFINITIONS

3.1. CCC (Calibration Check Compounds) - A subset of target compounds used to evaluate the calibration stability of the GC/MS system. A maximum percent deviation of the CCC's is specified for calibration acceptance.

3.2. SPCC (System Performance Check Compounds) - Target compounds designated to monitor chromatographic performance, sensitivity, and compound instability or degradation on active sites. Minimum response factors are specified for acceptable performance.

3.3. Batch - The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process to the extent possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the Quanterra QC Program document (QA-003) for further details of the batch definition.

3.4. Method Blank - An analytical control consisting of all reagents, internal standards and surrogate standards, that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and reagent contamination.

3.5. LCS (Laboratory Control Sample) - A blank spiked with the parameters of interest that is carried through the entire analytical procedure. Analysis of this sample with acceptable recoveries of the spiked materials demonstrates that the laboratory techniques for this method are acceptable.

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

3.7. MSD (Matrix Spike Duplicate)- a second aliquot of the same sample as the matrix spike (above) that is spiked in order to determine the precision of the method.

3.8. DCS (Duplicate Control Sample) - A pair of blanks spiked with the parameters of interest that are carried through the entire analytical procedure. Analysis of these samples with acceptable recoveries of the spiked materials demonstrates that the laboratory techniques and precision for this method are acceptable.

4. INTERFERENCES

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

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

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

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

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

5. SAFETY PRECAUTIONS

5.1. Procedures shall be carried out in a manner that protects the health and safety of all Quanterra associates. The following requirements must be met:

5.1.1. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded.

5.1.2. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

- Chemicals that have been classified as **carcinogens, or potential carcinogens**, under OSHA include: Benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, n-nitrosodimethylamine, and methylene chloride. Primary standards should be purchased in solution. If neat materials must be obtained, they shall be handled in the standards preparation hood.

- Chemicals known to be **flammable** include: acetone

5.1.3. Quanterra associates must ensure that they have participated in an orientation on Embryo-Fetal toxins (EHS 016) BEFORE working with neat materials.

5.1.4. Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers should be kept closed unless transfers are being made.

5.1.5. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported immediately to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

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

6.2. Column: 30 m x 0.32 mm I.D. (or 0.25 mm I.D.) 0.25-µm film thickness silicon-coated fused-silica capillary column (J & W Scientific DB-5.625 or equivalent). Alternate columns are acceptable if they provide acceptable performance.

6.3. Mass Spectrometer: Capable of scanning from 35 to 500 AMU every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 6 when 50 ng of the GC/MS tuning standard is injected through the GC (ICOS 50 and/or HP5973).

6.4. GC/MS Interface: Any GC-to-MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used (GC used is HP6890).

6.5. Data System: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as the Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library is recommended (currently using TARGET).

6.6. Syringe: 10 µL Hamilton Laboratory grade syringes or equivalent.

6.7. Carrier gas: Ultra high purity helium.

7. REAGENTS AND STANDARDS

7.1. A minimum five point calibration curve is prepared. The low point should be at or below the reporting limit. Refer to Tables 12 and 13 for typical calibration levels for all analytes. Other calibration levels may be used, depending on instrument

capability, but the low standard must support the reporting limit and the high standard defines the range of the calibration.

7.2. An Internal Standard solution is prepared. Compounds in the I.S. Mix are: acenaphthene-d10, chrysene-d12, 1,4-dichlorobenzene-d4, naphthalene-d8, perylene-d12, and phenanthrene-d10.

7.2.1. Internal Standards are added to all standards and extracts to result in 40ng injected onto the column. For example, if the volume of an extract used was 200 µL, 20 µL of a 400 µg/mL internal standard solution would be added for a 1 µL injection.

7.3. Surrogate Standard Spiking Solution: Prepare as indicated in the preparative methods. See appropriate preparation SOP. Surrogate compounds and levels are listed in Table 11.

7.4. GC/MS Tuning Standard: A methylene chloride solution containing 50 µg/mL of decafluorotriphenylphosphine (DFTPP) is prepared. Pentachlorophenol, benzidine, and DDT, should also be included in the Tuning Standard at 50 µg/mL.

7.5. Laboratory Control Spiking Solution: Prepare as indicated in the preparative methods. See appropriate preparation SOP. LCS compounds and levels are listed in Tables 9 and 10.

7.6. Matrix Spike Solution: Prepare as indicated in the preparative methods. See preparation SOP. The matrix spike compounds and levels are the same as the LCS compounds.

7.7. The standards listed in 7.1 to 7.6 should be refrigerated at $\leq 6^{\circ}C$ when not in use. Refrigeration at $-10^{\circ}C$ to $-20^{\circ}C$ may be used if it can be demonstrated that analytes do not fall out of solution at this temperature. The continuing calibration standard must be replaced every week and is stored at $\leq 6^{\circ}C$.

7.8. The standards must be replaced at least once a year. Rotate them to the Hazardous Waste storage area for disposal.

8. SAMPLE PRESERVATION AND STORAGE

8.1. Reference appropriate facility SOP for sample bottle preservation and storage.

8.2. Samples are stored at $4 \pm 2^{\circ}C$. Samples and extracts should be stored in suitable glass containers with Teflon lined caps. (Extracts will normally be stored for 30

days after invoicing.)

8.3. Water samples are extracted within seven days of sampling and the extracts are analyzed within forty days of extraction. Solids, sludges, and organic liquids are extracted within fourteen days of sampling and the extracts are analyzed within forty days of extraction.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.1.1. For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in section 13 must be acceptable before analysis of samples may begin. Refer to the flow chart in section 17.4.1.

9.1.2. For non-standard analytes an MDL study should be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

9.2. Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations for surrogates, MS and LCS. Precision limits for matrix spikes / matrix spike duplicates are mean relative percent difference +/- 3 standard deviations.

9.2.1. These limits do not apply to dilutions (except for tests without a separate extraction), but surrogate and matrix spike recoveries will be reported unless the dilution is more than 5X.

9.2.2. All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.2.3. Refer to the QC program document (QA-003) for further details of control limits.

9.3. Method Blank

A method blank is prepared and analyzed with each batch of samples. The method blank consists of reagent water for aqueous samples, and sodium sulfate for soil samples (Refer to SOP No. CORP-OP-0001 for details). Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

- If the analyte is a common laboratory contaminant (phthalate esters), the data may be reported with qualifiers if the concentration of the analyte is less than five times the RL. Such action must be taken in consultation with the client.
- Reanalysis of any samples with reportable concentrations of analytes found in the method blank is required unless other actions are agreed with the client.
- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

9.3.1. The method blank must have acceptable surrogate recoveries. Re-extraction of the blank and affected samples will be required. Document all corrective actions in the anomaly.

9.3.2. If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B", and appropriate comments may be made in a narrative to provide further documentation.

9.3.3. Refer to the Quanterra QC Program document (QA-003) for further details of the corrective actions.

9.3.4. Sample results are NOT blank subtracted unless specific requests and arrangements have been made with a client or agency.

9.4. Instrument Blank

9.4.1. Instruments must be evaluated for contamination during each 12 hour analytical run. This may be accomplished by analysis of a method blank. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of methylene chloride with the internal standards added. It is evaluated in the same way as the method blank.

9.5. Laboratory Control Sample (LCS)

9.5.1. A laboratory control sample (LCS) is prepared and analyzed with every batch of samples. All analytes must be within established control limits. The LCS is spiked with the compounds listed in Tables 9 and 10 unless specified by a client or agency. The compounds must be spiked at a concentration equivalent to 50 or 75 ng on-column depending on the analyte.

9.5.2. If any analyte in the LCS is outside the laboratory established historical control limits, corrective action must occur. Corrective action may include re-extraction and reanalysis of the batch.

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

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

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

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

A matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every batch of samples. The MS/MSD is spiked with the same subset of analytes as the LCS (See Tables 9 and 10). Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

- If the recovery for any component is outside QC limits for both the Matrix spike / spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.

- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.

- The matrix spike / duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.7. Surrogates

9.7.1. Every sample, blank, and QC sample is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits. Surrogate compounds must be spiked at either 50 or 75 ng on-column, depending on the surrogate. The compounds routinely included in the surrogate spiking solution, along with recommended standard concentrations, are listed in Table 11.

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

- Check all calculations for error.

- Ensure that instrument performance is acceptable.

- Recalculate the data and/or reanalyze the extract if either of the above checks reveal a problem.

- Re-extract and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem.

The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare / reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.7.3. If the sample with surrogate recoveries outside the recovery limits was a sample used for an MS/MSD and the surrogate recoveries in the MS/MSD are also outside of the control limits, then the sample, the MS, and the

MSD do not require reanalysis as this phenomenon would indicate a possible matrix problem.

9.7.4. If the sample is reanalyzed and the surrogate recoveries in the reanalysis are acceptable, then the problem was within the analyst's control and only the reanalyzed data should be reported. (Unless the reanalysis was outside holding times, in which case reporting both sets of results may be appropriate.)

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

9.8. Nonconformance and Corrective Action

9.8.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

9.9. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.10. Quanterra QC Program

Further details of QC and corrective action guidelines are presented in the Quanterra QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. The instrument is tuned for DFTPP, calibrated initially with a five-point calibration curve, and verified each 12-hour shift with one or more continuing calibration standard(s). Recommended instrument conditions are listed in Table 5.

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

10.3. Instrument Tuning

At the beginning of every twelve hour shift when analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria (Table 6) is achieved for DFTPP (decafluorotriphenylphosphine).

10.3.1. Inject 50 ng of the GC/MS tuning standard (Section 7.4) into the GC/MS system. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 6 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed.

10.3.2. The GC/MS tuning standard should also be used to evaluate the inertness of the chromatographic system. Benzidine and pentachlorophenol should not exhibit excessive tailing. If DDT is an analyte of interest, it must be included in the tuning standard, and its breakdown must be < 20%. Refer to section 12 for the appropriate calculations.

10.4. Initial Calibration

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

10.4.2. Compounds should be assigned to the IS with the closest retention time.

*10.4.*3. Prepare calibration standards to generate a multipoint curve for each parameter of interest. *At the West Sacramento lab, six standards are used for average response factor quantitations, linear, or non-linear curves; five standards are used for selected compounds known to exhibit poor response or poor chromatography at low concentrations. Compounds using curves comprised of five standards are quantitated using the linear curve or the average response factor only. Compounds and the required calibration standards are identified in Tables 12 and 13.*

10.4.4. Analyze each calibration standard and tabulate the area of the primary characteristic m/z against concentration for each compound and internal standard. Calculate response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in section 12 and verify that the CCC and SPCC criteria in

section 10.4.5 and 10.4.6 are met. **No sample analysis may be performed unless these criteria are met.**

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

SPCC Compounds:

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

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

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

10.4.6.2.CCC Compounds:

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

10.4.7. If the average of all %RSDs in the initial calibration is $\leq$ 15%, then all analytes may use average response factor for calibration.

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

10.4.7.2. If the average of all the %RSDs in the initial calibration is > 15%, then calibration on a curve must be used for those analytes with %RSD > 15%. Linear or quadratic curve fits may be used. Use of 1/Concentration^2 weighting is recommended to improve the accuracy of quantitation at the low end of the curve. The analyst should consider instrument maintenance to improve the linearity of response. If Relative Standard Error (RSE) is used to evaluate the curve it must be better than 15%. Otherwise the correlation coefficient (coefficient of determination for non-linear curves) must be $\geq$ 0.990.

10.4.8. Weighting of data points

In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. 1/Concentration^2 weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.4.9. If time remains in the 12 hour period initiated by the DFTPP injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.4.10. **Quantitation is performed using the calibration curve or average response factor form the initial curve, not the continuing calibration**

10.5. Continuing Calibration

10.5.1. At the start of each 12-hour period, the GC/MS tuning standard must be analyzed. A 50 ng injection of DFTPP must result in a mass spectrum for

DFTPP which meets the criteria given in Table 6.

10.5.2. Following a successful DFTPP analysis the continuing calibration standard(s) are analyzed. The standards must contain all semivolatile analytes, including all required surrogates. A mid level calibration standard is used for the continuing calibration. *Note: use the 50 ng or 80 ng standard for the mid level standard.*

10.5.3. The following criteria must be met for the continuing calibration to be acceptable:

- The SPCC compounds must have a response factor of ≥ 0.05.
- The percent difference or drift of the CCC compounds from the initial calibration must be $\leq 20\%$. (see section 12 for calculations) In addition, other non-CCC compounds should have a percent difference or drift $\leq 50\%$, however, up to six target compounds are allowed to have percent drift greater than 50%.
- The internal standard response must be within 50-200% of the response in the mid level of the initial calibration.
- The internal standard retention times must be within 30 seconds of the retention times in the mid-level of the initial calibration.

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

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

11. PROCEDURE

11.1. Sample Preparation

Samples are prepared following SOP CORP-OP-0001.

11.2. Sample Analysis Procedure

11.2.1. Calibrate the instrument as described in section 10. Depending on the

target compounds required by the client, it may be necessary to use more than one calibration standard.

11.2.2. All samples must be analyzed using the same instrument conditions as the preceeding continuing calibration standard.

11.2.3. Add internal standard to the extract to result in 40 ng injected on column (for example, 50 µL internal standard solution in 0.5 mL of extract for a 1 µL injection). Mix thoroughly before injection into the instrument.

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

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

11.2.6. Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst or automatically by the data system.

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

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

11.3. Dilutions

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

11.3.1. Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than the

height of the internal standards, or if individual non-target peaks are less than two times the height of the internal standards, the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgement. For example, samples containing organic acids may need to be analyzed at a higher dilution to avoid destroying the column.

11.3.2. Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

11.4. Perform all qualitative and quantitative measurements. When the extracts are not being used for analyses, refrigerate them at -10 to -20°C, protected from light in screw cap vials equipped with unpierced Teflon lined septa.

11.5. Retention time criteria for samples

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

11.5.1. If the retention time of any internal standard in any sample varies by more than 0.1 minute from the preceeding continuing calibration standard, the data must be carefully evaluated to ensure that no analytes have shifted outside their retention time windows.

11.6. Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to the facility specific SOP for determination of percent moisture.

11.7. Procedural Variations

11.7.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file. Any unauthorized deviations from this procedure must also be documented as a

non-conformance, with a cause and corrective action described.

11.8. Troubleshooting Guide

11.8.1. Daily Instrument Maintenance

In addition to the checks listed in the instrument maintenance schedule in the Quanterra QAMP, the following daily maintenance should be performed.

- Clip Column as necessary.
- Install new or cleaned injection port liner as necessary.
- Install new septum as necessary.
- Perform mass calibration as necessary.

11.8.2. Major Maintenance

11.8.2.1.A new initial calibration is necessary following major maintenance. Major maintenance includes changing the column, cleaning the ion volume or repeller, cleaning the source, and replacing the multiplier. Refer to the manufacturer's manual for specific guidance.

NOTE: Follow the company lock out/tag out policy BEFORE servicing any equipment.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative identification

An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NBS library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

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

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

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

- The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%.)

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

12.2. Mass chromatogram searches.

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

12.2.1. Hexachlorophene

Display the mass chromatograms for mass 196 and mass 198 for the region of the chromatogram from at least 2 minutes before chrysene-d12 to at least 4 minutes after chrysene-d12. If peaks for both ions coincide then the analyst evaluates the spectrum for the presence of hexachlorophene. No quantitation is possible.

12.3. For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches shall the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

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

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

- Molecular ions present in the reference spectrum should be present in the sample spectrum.

- Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible background contamination or presence of coeluting compounds.

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

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

12.4. Anyone evaluating data is trained to know how to handle isomers with identical mass spectra and close elution times. These include:

Dichlorobenzenes
Methylphenols
Trichlorophenols
Phenanthrene, anthracene
Fluoranthene, pyrene
Benzo(b) and (k)fluoranthene
Chrysene, benzo(a)anthracene

Extra precautions concerning these compounds are to more closely scrutinize retention time vs. the calibration standard and also to check that all isomers have distinct retention times.

A second category of problem compounds would be the poor responders or compounds that chromatograph poorly. Included in this category would be:

Benzoic acid
Chloroanilines
Nitroanilines
2,4-Dinitrophenol
4-Nitrophenol
Pentachlorophenol
3,3'-Dichlorobenzidine

Benzyl alcohol
4,6-Dinitro-2-methylphenol

Manually checking the integrations would be appropriate for these compounds.

12.5. Calculations

12.5.1. Percent Relative Standard Deviation for Initial Calibration

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

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

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

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

$RFi =$ RF for each of the calibration levels

$N =$ Number of RF values

12.5.2. Continuing calibration percent drift

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

$C_{actual} =$ Known concentration in standard

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

12.5.3. Concentration in the extract

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

12.5.3.1.Average response factor

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

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

12.5.3.2.Linear fit

$$C_{ex} = A + B\frac{(R_x C_{is})}{R_{is}}$$

C_{ex}= Concentration in extract, µg/mL

R_x= Response for analyte

R_{is}= Response for internal standard

C_{is}= Concentration of internal standard

A= Intercept

B= Slope

12.5.3.3.Quadratic fit

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

C= Curvature

12.5.4. The concentration in the sample is then calculated.

12.5.4.1.Aqueous Calculation

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

Where:

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

V_O = Volume of water extracted (mL)

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

wet-weight basis:

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

W_S = Weight of sample extracted or diluted in grams

D = (100 - % moisture in sample)/100, for a dry weight basis or 1 for a wet weight basis

12.6. MS/MSD percent recovery calculation.

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

S_{SR} = Spike sample result

S_R=Sample result

S_A = Spike added

12.7. Relative % Difference calculation for the MS/MSD

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

RPD = Relative percent difference

MS_R = Matrix spike result

MSD_R = Matrix spike duplicate result

12.8. Relative response factor calculation.

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

A_x=Area of the characteristic ion for the compound being measured

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

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

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

12.9. Calculation of TICs: The calculation of TICs (tentatively identified compounds) is identical to the above calculations with the following exceptions:

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

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

RF=1

12.10. Percent DDT breakdown

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

The total ion current areas are used for this calculation

13. METHOD PERFORMANCE

13.1. Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005.

13.2. Initial Demonstration

Each laboratory must make an initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to the level 4 calibration standard.

13.2.2. Calculate the average recovery and standard deviation of the recovery for

each analyte of interest. Compare these results with the acceptance criteria given in table 14.

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

13.3. Non-standard analytes

For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

13.4. Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13.5. Data Quality Objectives (DQO). Refer to project-specific Quality Assurance plans for DQO information.

14. POLLUTION PREVENTION

14.1. This section is not applicable to this procedure.

15. WASTE MANAGEMENT

15.1. Waste generated during aliquotting and from used vials must be disposed of to the vial waste stream as defined in Attachment B of the Chemical Hygiene Plan, Section WS002, Table 1.

16. REFERENCES

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

16.2. J. W. Eichelberger, L. E. Harris, and W. L. Budde, "Reference Compound to

Calibrate Ion Abundance Measurement in Gas Chromatography/Mass Spectrometry," Analytical Chemistry, 47, 995 (1975)

17. MISCELLANEOUS

17.1. Modifications from Reference Method

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

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

17.2. Modifications from Previous Revision

17.2.1. This SOP has been substantially revised to meet the requirements of method 8270C.

17.2.2. Directions for analysis be method 625 have been added as an attachment.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.4 Tables

Table 1

Quanterra Primary Standard[1] and Standard Reporting Limits

Analytes	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Pyridine	110-86-1	20	660
N-nitrosodimethylamine	62-75-9	10	330
Aniline	62-53-3	10	330
Phenol	108-95-2	10	330
Bis(2-chloroethyl)ether	111-44-4	10	330
2-Chlorophenol	95-57-8	10	330
1,3-Dichlorobenzene	541-73-1	10	330
1,4-Dichlorobenzene	106-46-7	10	330
Benzyl alcohol	100-51-6	10	330
1,2-Dichlorobenzene	95-50-1	10	330
2-Methylphenol	95-48-7	10	330
2,2'-oxybis(1-chloropropane)[2]	108-60-1	10	330
4-Methylphenol	106-44-5	10	330
N-Nitroso-di-n-propylamine	621-64-7	10	330
Hexachloroethane	67-72-1	10	330
Nitrobenzene	98-95-3	10	330
Isophorone	78-59-1	10	330
2-Nitrophenol	88-75-5	10	330
2,4-Dimethylphenol	105-67-9	10	330
Benzoic acid	65-85-0	50	1600
Bis(2-chloroethoxy)methane	111-91-1	10	330
2,4-Dichlorophenol	120-83-2	10	330
1,2,4-Trichlorobenzene	120-82-1	10	330
Naphthalene	91-20-3	10	330
4-Chloroaniline	106-47-8	10	330
Hexachlorobutadiene	87-68-3	10	330
4-Chloro-3-methylphenol	59-50-7	10	330
2-Methylnaphthalene	91-57-6	10	330
Hexachlorocyclopentadiene	77-47-4	50	1600
2,4,6-Trichlorophenol	88-06-2	10	330
2,4,5-Trichlorophenol	95-95-4	10	330
2-Chloronaphthalene	91-58-7	10	330
2-Nitroaniline	88-74-4	50	1600
Dimethyl phthalate	131-11-3	10	330
Acenaphthylene	208-96-8	10	330
3-Nitroaniline	99-09-2	50	1600
Acenaphthene	83-32-9	10	330
2,4-Dinitrophenol	51-28-5	50	1600
4-Nitrophenol	100-02-7	50	1600

Table 1

Quanterra Primary Standard[1] and Standard Reporting Limits

Analytes	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Dibenzofuran	132-64-9	10	330
2,4-Dinitrotoluene	121-14-2	10	330
2,6-Dinitrotoluene	606-20-2	10	330
Diethylphthalate	84-66-2	10	330
4-Chlorophenyl phenyl ether	7005-72-3	10	330
Fluorene	86-73-7	10	330
4-Nitroaniline	100-01-6	50	1600
4,6-Dinitro-2-methylphenol	534-52-1	50	1600
N-Nitrosodiphenylamine	86-30-6	10	330
Azobenzene	103-33-3	10	330
4-Bromophenyl phenyl ether	101-55-3	10	330
Hexachlorobenzene	118-74-1	10	330
Pentachlorophenol	87-86-5	50	1600
Phenanthrene	85-01-8	10	330
Anthracene	120-12-7	10	330
Carbazole	86-74-8	10	330
Di-n-butyl phthalate	84-74-2	10	330
Fluoranthene	206-44-0	10	330
Benzidine	92-87-5	100	3300
Pyrene	129-00-0	10	330
Butyl benzyl phthalate	85-68-7	10	330
3,3'-Dichlorobenzidine	91-94-1	50	1600
Benzo(a)anthracene	56-55-3	10	330
Bis(2-ethylhexyl)phthalate	117-81-7	10	330
Chrysene	218-01-9	10	330
Di-n-octylphthalate	117-84-0	10	330
Benzo(b)fluoranthene	205-99-2	10	330
Benzo(k)fluoranthene	207-08-9	10	330
Benzo(a)pyrene	50-32-8	10	330
Indeno(1,2,3-cd)pyrene	193-39-5	10	330
Dibenz(a,h)anthracene	53-70-3	10	330
Benzo(g,h,i)perylene	191-24-2	10	330

[1] The Quanterra primary standard is the standard normally used at Quanterra. Additional standards, such as the Appendix IX standard may be necessary to include all target analytes required for some clients.

[2] 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

Table 2

Quanterra Appendix IX[1] Standard Reporting Limits

Semivolatiles	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
2-Picoline	109-06-8	20	660
N-Nitrosomethylethylamine	10595-95-6	10	330
Methyl methanesulfonate	66-27-3	10	330
N-Nitrosodiethylamine	55-18-5	10	330
Ethyl methanesulfonate	62-50-0	10	330
Pentachloroethane	76-01-7	50	1600
Acetophenone	98-86-2	10	330
N-Nitrosopyrrolidine	930-55-2	10	330
N-Nitrosomorpholine	59-89-2	10	330
o-Toluidine	95-53-4	20	660
3-Methylphenol	108-39-4	10	330
N-Nitrosopiperidine	100-75-4	10	330
o,o,o-Triethyl-Phosphorothioate[2]	126-68-1	50	1600
a,a-Dimethyl-phenethylamine	122-09-8	50	1600
2,6-Dichlorophenol	87-65-0	10	330
Hexachloropropene	1888-71-7	100	3300
p-Phenylenediamine	106-50-3	100	3300
n-Nitrosodi-n-butylamine	924-16-3	10	330
Safrole	94-59-7	20	660
1,2,4,5-Tetrachlorobenzene	95-94-3	10	330
Isosafrole	120-58-1	20	660
1,4-Dinitrobenzene	100-25-4	10	330
1,4-Naphthoquinone	130-15-4	50	1600
1,3-Dinitrobenzene	99-65-0	10	330
Pentachlorobenzene	608-93-5	10	330
1-Naphthylamine	134-32-7	10	330
2-Naphthylamine	91-59-8	10	330
2,3,4,6-Tetrachlorophenol	58-90-2	50	1600
5-Nitro-o-toluidine	99-55-8	20	660
Thionazin[2]	297-97-2	50	1600
1,3,5-Trinitrobenzene	99-35-4	50	1600
Sulfotepp[2]	3689-24-5	50	1600
Phorate[2]	298-02-2	50	1600
Phenacetin	62-44-2	20	660
Diallate[3]	2303-16-4	20	660
Dimethoate[2]	60-51-5	20	660
4-Aminobiphenyl	92-67-1	50	1600
Pentachloronitrobenzene	82-68-8	50	1600
Pronamide	23950-58-5	20	660
Disulfoton[2]	298-04-4	50	1600
2-secbutyl-4,6-dinitrophenol (Dinoseb)	88-85-7	20	660
Methyl Parathion[2]	298-00-0	50	1600

Table 2

Quanterra Appendix IX[1] Standard Reporting Limits

Semivolatiles	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
4-Nitroquinoline-1-oxide	56-57-5	100	3300
Parathion[2]	56-38-2	50	1600
Methapyrilene	91-80-5	50	1600
Aramite	140-57-8	20	660
Isodrin[3]	465-73-6	10	330
Kepone[2]	143-50-0	100	3300
Famphur[3]	52-85-7	100	3300
p-(Dimethylamino)azobenzene	60-11-7	20	660
p-Chlorobenzilate[3]	510-15-6	10	330
3,3'-Dimethylbenzidine	119-93-7	50	1600
2-Acetylaminofluorene	53-96-3	100	3300
Dibenz(a,j)acridine	224-42-0	20	660
7,12-Dimethylbenz(a)anthracene	57-97-6	20	660
3-Methylcholanthrene	56-49-5	20	660

1 The Appendix IX standard contains additional analytes required for the Appendix IX list. The Quanterra primary standard must also be analyzed to include all of the Appendix IX list.

2 May also be analyzed by method 8140 or 8141, which can achieve lower reporting limits.

3 May also be analyzed by method 8080 or 8081, which can achieve lower reporting limits

Table 3

Reportable Analytes for Quanterra Standard Tests, Primary Standard

Analyte	CAS Number	Quanterra Standard List	TCLP	TCL	Appendix IX
Pyridine	110-86-1		X		X
N-nitrosodimethylamine	62-75-9				X
Aniline	62-53-3				X
Phenol	108-95-2	X		X	X
Bis(2-chloroethyl)ether	111-44-4	X		X	X
2-Chlorophenol	95-57-8	X		X	X
1,3-Dichlorobenzene	541-73-1	X		X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X
Benzyl alcohol	100-51-6				X
1,2-Dichlorobenzene	95-50-1	X		X	X
2-Methylphenol	95-48-7	X	X	X	X
2,2'-oxybis(1-chloropropane)[1]	180-60-1	X		X	X
4-Methylphenol	106-44-5	X	X	X	X
N-Nitroso-di-n-propylamine	621-64-7	X		X	X
Hexachloroethane	67-72-1	X	X	X	X
Nitrobenzene	98-95-3	X	X	X	X
Isophorone	78-59-1	X		X	X
2-Nitrophenol	88-75-5	X		X	X
2,4-Dimethylphenol	105-67-9	X		X	X
Benzoic acid	65-85-0				
Bis(2-chloroethoxy)methane	111-91-1	X		X	X
2,4-Dichlorophenol	120-83-2	X		X	X
1,2,4-Trichlorobenzene	120-82-1	X		X	X
Naphthalene	91-20-3	X		X	X
4-Chloroaniline	106-47-8	X		X	X
Hexachlorobutadiene	87-68-3	X	X	X	X
4-Chloro-3-methylphenol	59-50-7	X		X	X
2-Methylnaphthalene	91-57-6	X		X	X
Hexachlorocyclopentadiene	77-47-4	X		X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	X	X
2-Chloronaphthalene	91-58-7	X		X	X
2-Nitroaniline	88-74-4	X		X	X
Dimethyl phthalate	131-11-3	X		X	X
Acenaphthylene	208-96-8	X		X	X
3-Nitroaniline	99-09-2	X		X	X
Acenaphthene	83-32-9	X		X	X
2,4-Dinitrophenol	51-28-5	X		X	X
4-Nitrophenol	100-02-7	X		X	X
Dibenzofuran	132-64-9	X		X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X		X	X
Diethylphthalate	84-66-2	X		X	X

Table 3

Reportable Analytes for Quanterra Standard Tests, Primary Standard

Analyte	CAS Number	Quanterra Standard List	TCLP	TCL	Appendix IX
4-Chlorophenyl phenyl ether	7005-72-3	X		X	X
Fluorene	86-73-7	X		X	X
4-Nitroaniline	100-01-6	X		X	X
4,6-Dinitro-2-methylphenol	534-52-1	X		X	X
N-Nitrosodiphenylamine	86-30-6	X		X	X
Azobenzene[4]	103-33-3				
4-Bromophenyl phenyl ether	101-55-3	X		X	X
Hexachlorobenzene	118-74-1	X	X	X	X
Pentachlorophenol	87-86-5	X	X	X	X
Phenanthrene	85-01-8	X		X	X
Anthracene	120-12-7	X		X	X
Carbazole	86-74-8	X		X	
Di-n-butyl phthalate	84-74-2	X		X	X
Fluoranthene	206-44-0	X		X	X
Benzidine	92-87-5				
Pyrene	129-00-0	X		X	X
Butyl benzyl phthalate	85-68-7	X		X	X
3,3'-Dichlorobenzidine	91-94-1	X		X	X
Benzo(a)anthracene	56-55-3	X		X	X
Bis(2-ethylhexyl)phthalate	117-81-7	X		X	X
Chrysene	218-01-9	X		X	X
Di-n-octylphthalate	117-84-0	X		X	X
Benzo(b)fluoranthene	205-99-2	X		X	X
Benzo(k)fluoranthene	207-08-9	X		X	X
Benzo(a)pyrene	50-32-8	X		X	X
Indeno(1,2,3-cd)pyrene	193-39-5	X		X	X
Dibenz(a,h)anthracene	53-70-3	X		X	X
Benzo(g,h,i)perylene	191-24-2	X		X	X

[1] 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

[2] Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

Table 4

Reportable analytes for Quanterra Standard Tests, Appendix IX Standard

Semivolatiles	CAS Number	Quanterra Standard List	TCLP	TCL	Appendix IX
2-Picoline	109-06-8				X
N-Nitrosomethylethylamine	10595-95-6				X
Methyl methanesulfonate	66-27-3				X
N-Nitrosodiethylamine	55-18-5				X
Ethyl methanesulfonate	62-50-0				X
Pentachloroethane	76-01-7				X
Acetophenone	98-86-2				X
N-Nitrosopyrrolidine	930-55-2				X
N-Nitrosomorpholine	59-89-2				X
o-Toluidine	95-53-4				X
3-Methylphenol	108-39-4				X
N-Nitrosopiperidine	100-75-4				X
o,o,o-Triethyl-Phosphorothioate[2]	126-68-1				X
a,a-Dimethyl-phenethylamine	122-09-8				X
2,6-Dichlorophenol	87-65-0				X
Hexachloropropene	1888-71-7				X
p-Phenylenediamine	106-50-3				X
n-Nitrosodi-n-butylamine	924-16-3				X
Safrole	94-59-7				X
1,2,4,5-Tetrachlorobenzene	95-94-3				X
Isosafrole	120-58-1				X
1,4-Dinitrobenzene	100-25-4				
1,4-Naphthoquinone	130-15-4				X
1,3-Dinitrobenzene	99-65-0				X
Pentachlorobenzene	608-93-5				X
1-Naphthylamine	134-32-7				X
2-Naphthylamine	91-59-8				X
2,3,4,6-Tetrachlorophenol	58-90-2				X
5-Nitro-o-toluidine	99-55-8				X
Thionazin[2]	297-97-2				X
1,3,5-Trinitrobenzene	99-35-4				X
Sulfotepp[2]	3689-24-5				X
Phorate[2]	298-02-2				X
Phenacetin	62-44-2				X
Diallate	2303-16-4				X
Dimethoate[2]	60-51-5				X
4-Aminobiphenyl	92-67-1				X
Pentachloronitrobenzene	82-68-8				X
Pronamide	23950-58-5				X
Disulfoton[2]	298-04-4				X
2-secbutyl-4,6-dinitrophenol (Dinoseb)[2]	88-85-7				X
Methyl parathion[2]	298-00-0				X

Table 4

Reportable analytes for Quanterra Standard Tests, Appendix IX Standard

Semivolatiles	CAS Number	Quanterra Standard List	TCLP	TCL	Appendix IX
4-Nitroquinoline-1-oxide	56-57-5				X
Parathion[2]	56-38-2				X
Isodrin[3]	465-73-6				X
Kepone [2]	143-50-0				X
Famphur[2]	52-85-7				X
Methapyrilene	91-80-5				X
Aramite	140-57-8				X
p-(Dimethylamino)azobenzene	60-11-7				X
p-Chlorobenzilate[3]	510-15-6				X
3,3'-Dimethylbenzidine	119-93-7				X
2-Acetylaminofluorene	53-96-3				X
Dibenz(a,j)acridine	224-42-0				
7,12-Dimethylbenz(a)anthracene	57-97-6				X
3-Methylcholanthrene	56-49-5				X
Hexachlorophene[4]	70-30-4				X
Diphenylamine[5]	122-39-4				X

[2] May also be analyzed by method 8140 or 8141, which can achieve lower reporting limits.

[3] May also be analyzed by method 8080 or 8081, which can achieve lower reporting limits

[4] Hexachlorophene is a required analyte for Appendix IX. This compound is not stable, and therefore not included in the calibration standard. The characteristic ions for hexachlorophene are searched for in the chromatogram. (See section 12.2.1)

[5] Diphenylamine is a required compound for Appendix IX. N-nitrosodiphenylamine decomposes in the injection port to form diphenylamine. Therefore these two compounds cannot be distinguished. Diphenylamine is not included in the calibration standard.

Table 5

Suggested Instrumental Conditions

Mass Range	35-500 amu
Scan Time	≤1 second/scan
Initial Column Temperature/Hold Time	40°C for 2 minutes
Column Temperature Program	40 - 320°C at 11.5°C/min
Final Column Temperature/Hold Time	320°C (until at least one minute after benzo(g,h,i)perylene has eluted)
Injector Temperature	250 - 300°C
Transfer Line Temperature	250 - 300°C
Source Temperature	According to manufacturer's specifications
Injector	Grob-type, split / splitless
Sample Volume	1 or 2 µl
Carrier Gas	Helium at 30 cm/sec

Table 6

DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30 - 60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40 - 60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5 - 9% of mass 198
275	10 - 30% of mass 198
365	>1% of mass 198
441	Present, but less than mass 443
442	>40% of mass 198
443	17 - 23% of mass 442

Table 7

Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard

Analyte	Primary	Secondary	Tertiary
N-nitrosodimethylamine	74	42	
Pyridine	79	52	
2-Fluorophenol (Surrogate Standard)	112	64	63
Phenol-d5 (Surrogate Standard)	99	42	71
Aniline	93	66	
Phenol	94	65	66
Bis(2-chloroethyl)ether	93	63	95
2-Chlorophenol	128	64	130
1,3-Dichlorobenzene	146	148	113
1,4-Dichlorobenzene-d4 (Internal Standard)	152	150	115
1,4-Dichlorobenzene	146	148	113
Benzyl Alcohol	108	79	77
1,2-Dichlorobenzene	146	148	113
2-Methylphenol	108	107	79
2,2'-oxybis(1-chloropropane)[1]	45	77	79
4-Methylphenol	108	107	79
N-Nitroso-di-n-propylamine	70	42	101,130
Hexachloroethane	117	201	199
Nitrobenzene-d5 (Surrogate Standard)	82	128	54
Nitrobenzene	77	123	65
Isophorone	82	95	138
2-Nitrophenol	139	65	109
2,4-Dimethylphenol	107	121	122
Benzoic Acid	122	105	77
Bis(2-chloroethoxy)methane	93	95	123
2,4-Dichlorophenol	162	164	98
1,2,4-Trichlorobenzene	180	182	145
Naphthalene-d8 (Internal Standard)	136	68	54
Naphthalene	128	129	127
4-Chloroaniline	127	129	65
Hexachlorobutadiene	225	223	227
4-Chloro-3-methylphenol	107	144	142
2-Methylnaphthalene	142	141	115
Hexachlorocyclopentadiene	237	235	272
2,4,6-Trichlorophenol	196	198	200
2,4,5-Trichlorophenol	196	198	200
2-Fluorobiphenyl (Surrogate Standard)	172	171	170
2-Chloronaphthalene	162	164	127
2-Nitroaniline	65	92	138
Dimethylphthalate	163	194	164
Acenaphthylene	152	151	153

Table 7

Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard

Analyte	Primary	Secondary	Tertiary
2,6-Dinitrotoluene	165	63	89
Acenaphthene-d10 (Internal Standard)	164	162	160
3-Nitroaniline	138	108	92
Acenaphthene	153	152	154
2,4-Dinitrophenol	184	63	154
Dibenzofuran	168	139	84
4-Nitrophenol	109	139	65
2,4-Dinitrotoluene	165	63	89
Diethylphthalate	149	177	150
Fluorene	166	165	167
4-Chlorophenylphenylether	204	206	141
4-Nitroaniline	138	92	108
4,6-Dinitro-2-methylphenol	198	182	77
N-Nitrosodiphenylamine	169	168	167
2,4,6-Tribromophenol (Surrogate Standard)	330	332	141
Azobenzene	77	182	105
4-Bromophenylphenylether	248	250	141
Hexachlorobenzene	284	142	249
Pentachlorophenol	266	264	268
Phenanthrene-d10 (Internal Standard)	188	94	80
Phenanthrene	178	179	176
Anthracene	178	179	176
Carbazole	167	166	139
Di-n-butylphthalate	149	150	104
Fluoranthene	202	101	100
Benzidine	184	92	185
Pyrene	202	101	100
Terphenyl-d14 (Surrogate Standard)	244	122	212
Butylbenzylphthalate	149	91	206
Benzo(a)Anthracene	228	229	226
Chrysene-d12 (Internal Standard)	240	120	236
3,3'-Dichlorobenzidine	252	254	126
Chrysene	228	226	229
Bis(2-ethylhexyl)phthalate	149	167	279
Di-n-octylphthalate	149	167	43
Benzo(b)fluoranthene	252	253	125
Benzo(k)fluoranthene	252	253	125
Benzo(a)pyrene	252	253	125
Perylene-d12 (Internal Standard)	264	260	265
Indeno(1,2,3-cd)pyrene	276	138	277
Dibenz(a,h)anthracene	278	139	279
Benzo(g,h,i)perylene	276	138	277

Table 8

Analytes in Approximate Retention Time Order and Characteristic Ions, Appendix IX Standard

Analyte	Primary	Secondary	Tertiary
2-Picoline	93	66	92
N-Nitrosomethylethylamine	88	42	43
Methyl methanesulfonate	80	79	65
N-Nitrosodiethylamine	102	44	57
Ethyl methanesulfonate	79	109	97
Pentachloroethane	117	119	167
Acetophenone	105	77	120
N-Nitrosopyrrolidine	100	41	42
N-Nitrosomorpholine	116	56	86
o-Toluidine	106	107	
3-Methylphenol	108	107	77
N-Nitrosopiperidine	114	42	55
o,o,o-Triethyl-Phosphorothioate	198	121	93
a,a-Dimethyl-phenethylamine	58	91	
2,6-Dichlorophenol	162	164	63
Hexachloropropene	213	215	211
p-Phenylenediamine	108	80	
n-Nitrosodi-n-butylamine	84	57	41
Safrole	162	104	77
1,2,4,5-Tetrachlorobenzene	216	214	218
Isosafrole 1	162	104	131
Isosafrole 2	162	104	131
1,4-Dinitrobenzene	168	75	122
1,4-Naphthoquinone	158	104	102
1,3-Dinitrobenzene	168	75	76
Pentachlorobenzene	250	248	252
1-Naphthylamine	143	115	
2-Naphthylamine	143	115	
2,3,4,6-Tetrachlorophenol	232	230	131
5-Nitro-o-toluidine	152	77	106
Thionazin	97	96	143
1,3,5-Trinitrobenzene	213	75	120
Sulfotepp	97	322	202
Phorate	75	97	121
Phenacetin	108	179	109
Diallate	86	234	
Dimethoate	87	93	125
4-Aminobiphenyl	169		
Pentachloronitrobenzene	237	142	214
Pronamide	173	175	255
Disulfoton	88	97	89
2-secbutyl-4,6-dinitrophenol (Dinoseb)	211	163	147
Methyl parathion	109	125	263
4-Nitroquinoline-1-oxide	190	128	160

Table 8

Analytes in Approximate Retention Time Order and Characteristic Ions, Appendix IX Standard

Analyte	Primary	Secondary	Tertiary
Parathion	109	97	291
Isodrin	193	66	195
Kepone	272	274	237
Famphur	218	125	93
Methapyrilene	97	58	
Aramite 1	185	319	
Aramite 2	185	319	
p-(Dimethylamino)azobenzene	120	225	77
p-Chlorobenzilate	251	139	253
3,3'-Dimethylbenzidine	212	106	
2-Acetylaminofluorene	181	180	223
Dibenz(a,j)acridine	279	280	
7,12-Dimethylbenz(a)anthracene	256	241	120
3-Methylcholanthrene	268	252	253

Table 9

8270C LCS Compounds

LCS Compounds	Spiking Level, ng/µL in extract[1]
1,2,4-Trichlorobenzene	100
Acenaphthene	100
2,4-Dinitrotoluene	100
Pyrene	100
N-Nitroso-di-n-propylamine	100
1,4-Dichlorobenzene	100
Pentachlorophenol	150
Phenol	150
2-Chlorophenol	150
4-Chloro-3-methylphenol	150
4-Nitrophenol	150

[1] Levels are 50 and 75 ng/µL if 2 µL injection is used

Table 10

TCLP LCS Compounds

LCS Compounds	Spiking Level, ng/µL in extract[1]
1,4-Dichlorobenzene	100
2,4-Dinitrotoluene	100
Hexachlorobenzene	100
Hexachlorobutadiene	100
Hexachloroethane	100
2-Methylphenol	100
3-Methylphenol	100
4-Methylphenol	100
Nitrobenzene	100
Pentachlorophenol	100
Pyridine	100
2,4,5-Trichlorophenol	100
2,4,6-Trichlorophenol	100

[1] Levels are 50 ng/µL if 2 µL injection is used

Recovery limits for the LCS and for matrix spikes are generated from historical data and are maintained by the QA department.

Table 11

8270C Surrogate Compounds

Surrogate Compounds	Spiking Level, ng/µL in extract[2]
Nitrobenzene-d5	100
2-Fluorobiphenyl	100
Terphenyl-d14	100
1,2-Dichlorobenzene-d4[1]	100
Phenol-d5	150
2-Fluorophenol	150
2,4,6-Tribromophenol	150
2-Chlorophenol-d4[1]	150

[1] Included in standard mix, but not routinely evaluated for method 8270B

[2] Levels are 50 and 75 ng/µL if 2 µL injection is used

Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

Table 12

Calibration Levels, Primary Standard, µg/mL

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
Pyridine	10	20	50	80	120	160
N-nitrosodimethylamine	10	20	50	80	120	160
Aniline	10	20	50	80	120	160
Phenol	10	20	50	80	120	160
Bis(2-chloroethyl)ether	10	20	50	80	120	160
2-Chlorophenol	10	20	50	80	120	160
1,3-Dichlorobenzene	10	20	50	80	120	160
1,4-Dichlorobenzene	10	20	50	80	120	160
Benzyl alcohol	10	20	50	80	120	160
1,2-Dichlorobenzene	10	20	50	80	120	160
2-Methylphenol	10	20	50	80	120	160
2,2'-oxybis(1-chloropropane)[1]	10	20	50	80	120	160
4-Methylphenol	10	20	50	80	120	160
N-Nitroso-di-n-propylamine	10	20	50	80	120	160
Hexachloroethane	10	20	50	80	120	160
Nitrobenzene	10	20	50	80	120	160
Isophorone	10	20	50	80	120	160
2-Nitrophenol	10	20	50	80	120	160
2,4-Dimethylphenol	10	20	50	80	120	160
Benzoic acid	---	20	50	80	120	160
Bis(2-chloroethoxy)methane	10	20	50	80	120	160
2,4-Dichlorophenol	10	20	50	80	120	160
1,2,4-Trichlorobenzene	10	20	50	80	120	160
Naphthalene	10	20	50	80	120	160
4-Chloroaniline	10	20	50	80	120	160
Hexachlorobutadiene	10	20	50	80	120	160
4-Chloro-3-methylphenol	10	20	50	80	120	160
2-Methylnaphthalene	10	20	50	80	120	160
Hexachlorocyclopentadiene	---	20	50	80	120	160
2,4,6-Trichlorophenol	10	20	50	80	120	160
2,4,5-Trichlorophenol	10	20	50	80	120	160
2-Chloronaphthalene	10	20	50	80	120	160
2-Nitroaniline	---	20	50	80	120	160
Dimethyl phthalate	10	20	50	80	120	160
Acenaphthylene	10	20	50	80	120	160
3-Nitroaniline	---	20	50	80	120	160
Acenaphthene	10	20	50	80	120	160
2,4-Dinitrophenol	---	20	50	80	120	160
4-Nitrophenol	---	20	50	80	120	160
Dibenzofuran	10	20	50	80	120	160
2,4-Dinitrotoluene	10	20	50	80	120	160
2,6-Dinitrotoluene	10	20	50	80	120	160
Diethylphthalate	10	20	50	80	120	160
4-Chlorophenyl phenyl ether	10	20	50	80	120	160

Table 12

Calibration Levels, Primary Standard, µg/mL

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
Fluorene	10	20	50	80	120	160
4-Nitroaniline	---	20	50	80	120	160
4,6-Dinitro-2-methylphenol	---	20	50	80	120	160
N-Nitrosodiphenylamine	10	20	50	80	120	160
Azobenzene[2]	10	20	50	80	120	160
4-Bromophenyl phenyl ether	10	20	50	80	120	160
Hexachlorobenzene	10	20	50	80	120	160
Pentachlorophenol	---	20	50	80	120	160
Phenanthrene	10	20	50	80	120	160
Anthracene	10	20	50	80	120	160
Carbazole	10	20	50	80	120	160
Di-n-butyl phthalate	10	20	50	80	120	160
Fluoranthene	10	20	50	80	120	160
Benzidine	---	50	100	80	120	160
Pyrene	10	20	50	80	120	160
Butyl benzyl phthalate	10	20	50	80	120	160
3,3'-Dichlorobenzidine	---	20	50	80	120	160
Benzo(a)anthracene	10	20	50	80	120	160
Bis(2-ethylhexyl)phthalate	10	20	50	80	120	160
Chrysene	10	20	50	80	120	160
Di-n-octylphthalate	10	20	50	80	120	160
Benzo(b)fluoranthene	10	20	50	80	120	160
Benzo(k)fluoranthene	10	20	50	80	120	160
Benzo(a)pyrene	10	20	50	80	120	160
Indeno(1,2,3-cd)pyrene	10	20	50	80	120	160
Dibenz(a,h)anthracene	10	20	50	80	120	160
Benzo(g,h,i)perylene	10	20	50	80	120	160

[1] 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

[2]Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

Table 13

Calibration Levels, Appendix IX Standard, µg/mL

Semivolatiles	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
2-Picoline	---	20	50	80	120	160
N-Nitrosomethylethylamine	10	20	50	80	120	160
Methyl methanesulfonate	10	20	50	80	120	160
N-Nitrosodiethylamine	10	20	50	80	120	160
Ethyl methanesulfonate	10	20	50	80	120	160
Pentachloroethane	---	20	50	80	120	160
Acetophenone	10	20	50	80	120	160
N-Nitrosopyrrolidine	10	20	50	80	120	160
N-Nitrosomorpholine	10	20	50	80	120	160
o-Toluidine	---	20	50	80	120	160
3-Methylphenol	10	20	50	80	120	160
N-Nitrosopiperidine	10	20	50	80	120	160
o,o,o-Triethyl-Phosphorothioate	---	20	50	80	120	160
a,a-Dimethyl-phenethylamine	---	20	50	80	120	160
2,6-Dichlorophenol	10	20	50	80	120	160
Hexachloropropene	---	20	50	80	120	160
p-Phenylenediamine	---	20	50	80	120	160
n-Nitrosodi-n-butylamine	10	20	50	80	120	160
Safrole	---	20	50	80	120	160
1,2,4,5-Tetrachlorobenzene	10	20	50	80	120	160
Isosafrole 1 + 2	---	20	50	80	120	160
1,4-Dinitrobenzene	10	20	50	80	120	160
1,4-Naphthoquinone	---	20	50	80	120	160
1,3-Dinitrobenzene	10	20	50	80	120	160
Pentachlorobenzene	10	20	50	80	120	160
1-Naphthylamine	10	20	50	80	120	160
2-Naphthylamine	10	20	50	80	120	160
2,3,4,6-Tetrachlorophenol	---	20	50	80	120	160
5-Nitro-o-toluidine	---	20	50	80	120	160
Thionazin	---	20	50	80	120	160
1,3,5-Trinitrobenzene	---	20	50	80	120	160
Sulfotepp	---	20	50	80	120	160
Phorate	---	20	50	80	120	160
Phenacetin	---	20	50	80	120	160
Diallate 1 + 2	---	20	50	80	120	160
Dimethoate	10	20	50	80	120	160
4-Aminobiphenyl	---	20	50	80	120	160
Pentachloronitrobenzene	---	20	50	80	120	160
Pronamide	---	20	50	80	120	160
Disulfoton	---	20	50	80	120	160
2-secbutyl-4,6-dinitrophenol (Dinoseb)	---	20	50	80	120	160
Methyl parathion	---	20	50	80	120	160
4-Nitroquinoline-1-oxide	---	20	50	80	120	160
Parathion	---	20	50	80	120	160

Table 13

Calibration Levels, Appendix IX Standard, µg/mL

Semivolatiles	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
Isodrin	10	20	50	80	120	160
Kepone	---	20	50	80	120	160
Famphur	---	20	50	80	120	160
Methapyrilene	---	20	50	80	120	160
Aramite 1 and 2	---	20	50	80	120	160
p-(Dimethylamino)azobenzene	---	20	50	80	120	160
p-Chlorobenzilate	10	20	50	80	120	160
3,3'-Dimethylbenzidine	---	20	50	80	120	160
2-Acetylaminofluorene	---	20	50	80	120	160
Dibenz (a,j)acridine	---	20	50	80	120	160
7,12-Dimethylbenz(a)anthracene	---	20	50	80	120	160
3-Methylcholanthrene	---	20	50	80	120	160

Table 14
Initial demonstration recovery and precision limits

Compound	Spiking concentration µg/L	Limit for Relative Standard Deviation	Limit for average recovery, %
Acenaphthene	60	27.6	60.1-132.3
Acenaphthylene	60	40.2	53.5-126.0
Aldrin[1]	60	39.0	7.2-152.2
Anthracene	60	32.0	43.4-118.0
Benz(a)anthracene	60	27.6	41.8-133.0
Benzo(b)fluoranthene	60	38.8	42.0-140.4
Benzo(k)fluoranthene	60	32.3	25.2-145.7
Benzo(a)pyrene	60	39.0	31.7-148.0
Benzo(ghi)perylene	60	58.9	D-195.0
Benzylbutyl phthalate	60	23.4	D-139.9
B-BHC[1]	60	31.5	41.5-130.6
d-BHC[1]	60	21.6	D-100.0
Bis(2-chloroethyl) ether	60	55.0	42.9-126.0
Bis(2-chloroethoxy)methane	60	34.5	49.2-164.7
Bis(2-chloroisopropyl) ether	60	46.3	62.8-138.6
Bis(2-ethylhexyl) phthalate	60	41.1	28.9-136.8
4-Bromophenyl phenyl ether	60	23.0	64.9-114.4
2-Chloronaphthalene	60	13.0	64.5-113.5
4-Chlorophenyl phenyl ether	60	33.4	38.4-144.7
Chrysene	60	48.3	44.1-139.9
4,4'-DDD[1]	60	31.0	D-134.5
4,4'-DDE[1]	60	32.0	19.2-119.7
4,4'-DDT[1]	60	61.6	D-170.6
Dibenzo(a,h)anthracene	60	70.0	D-199.7
Di-n-butyl phthalate	60	16.7	8.4-111.0

Table 14
Initial demonstration recovery and precision limits

Compound	Spiking concentration µg/L	Limit for Relative Standard Deviation	Limit for average recovery, %
1,2-Dichlorobenzene	60	30.9	48.6-112.0
1,3-Dichlorobenzene	60	41.7	16.7-153.9
1,4-Dichlorobenzene	60	32.1	37.3-105.7
3,3'-Dichlorobenzidine	60	71.4	8.2-212.5
Dieldrin[1]	60	30.7	44.3-119.3
Diethyl phthalate	60	26.5	D-100.0
Dimethyl phthalate	60	23.2	D-100.0
2,4-Dinitrotoluene	60	21.8	47.5-126.9
2,6-Dinitrotoluene	60	29.6	68.1-136.7
Di-n-octylphthalate	60	31.4	18.6-131.8
Endosulfan sulfate[1]	60	16.7	D-103.5
Endrin aldehyde	60	32.5	D-188.8
Fluoranthene	60	32.8	42.9-121.3
Fluorene	60	20.7	71.6-108.4
Heptachlor[1]	60	37.2	D-172.2
Heptachlor epoxide[1]	60	54.7	70.9-109.4
Hexachlorobenzene	60	24.9	7.8-141.5
Hexachlorobutadiene	60	26.3	37.8-102.2
Hexachloroethane	60	24.5	55.2-100.0
Indeno(1,2,3-cd)pyrene	60	44.6	D-150.9
Isophorone	60	63.3	46.6-180.2
Naphthalene	60	30.1	35.6-119.6
Nitrobenzene	60	39.3	54.3-157.6
N-Nitrosodi-n-propylamine	60	55.4	13.6-197.9
PCB-1260[1]	60	54.2	19.3-121.0
Phenanthrene	60	20.6	65.2-108.7
Pyrene	60	25.2	69.6-100.0
1,2,4-Trichlorobenzene	60	28.1	57.3-129.2
4-Chloro-3-methylphenol	60	37.2	40.8-127.9
2-Chlorophenol	60	28.7	36.2-120.4
2,4-Chlorophenol	60	26.4	52.5-121.7
2,4-Dimethylphenol	60	26.1	41.8-109.0
2,4-Dinitrophenol	60	49.8	D-172.9
2-Methyl-4,6-dinitrophenol	60	93.2	53.0-100.0
2-Nitrophenol	60	35.2	45.0-166.7
4-Nitrophenol	60	47.2	13.0-106.5
Pentachlorophenol	60	48.9	38.1-151.8
Phenol	60	22.6	16.6-100.0
2,4,6-Trichlorophenol	60	31.7	52.4-129.2

[1]Since the organochlorine pesticides and PCBs are normally determined by method 8080 at Quanterra, they will not be included in the initial demonstration of capability for method 8270B.

ATTACHMENT A

MODIFICATIONS REQUIRED FOR ANALYSIS OF WASTEWATER FOLLOWING METHOD 625

REQUIREMENTS FOR METHOD 625

- Method 625 is required for demonstration of compliance with NPDES wastewater discharge permits. The standard analyte list and reporting limits are listed in Table A-1.
- This method can be applied only to aqueous matrices.
- The tune period for this method is defined as 24 hours.
- Initial calibration curve requirements:
- The initial calibration curve for this method requires at least three points.
- Target compounds must have RSD ≤ 35%.
- If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds.
- Continuing calibration verification requirements: All target compounds must have %D ≤ 20%.
- Matrix Spike and LCS requirements:
- A full analyte spike is required for method 625. The spiking levels are given in Table A-2.

Table A-1. Quanterra Method 625 standard reporting list and reporting limits.

Analytes	CAS Number	Aqueous µg/L
Phenol	108-95-2	10
Bis(2-chloroethyl)ether	111-44-4	10
2-Chlorophenol	95-57-8	10
1,3-Dichlorobenzene	541-73-1	10
1,4-Dichlorobenzene	106-46-7	10
1,2-Dichlorobenzene	95-50-1	10
2,2'-oxybis(1-chloropropane)	108-60-1	10
N-Nitroso-di-n-propylamine	621-64-7	10
Hexachloroethane	67-72-1	10
Nitrobenzene	98-95-3	10
Isophorone	78-59-1	10
2-Nitrophenol	88-75-5	10
2,4-Dimethylphenol	105-67-9	10
Bis(2-chloroethoxy)methane	111-91-1	10
2,4-Dichlorophenol	120-83-2	10
1,2,4-Trichlorobenzene	120-82-1	10
Naphthalene	91-20-3	10
Hexachlorobutadiene	87-68-3	10
4-Chloro-3-methylphenol	59-50-7	10
Hexachlorocyclopentadiene	77-47-4	50
2,4,6-Trichlorophenol	88-06-2	10
2-Chloronaphthalene	91-58-7	10
Dimethyl phthalate	131-11-3	10
Acenaphthylene	208-96-8	10
Acenaphthene	83-32-9	10
2,4-Dinitrophenol	51-28-5	50
4-Nitrophenol	100-02-7	50
2,4-Dinitrotoluene	121-14-2	10
2,6-Dinitrotoluene	606-20-2	10
Diethylphthalate	84-66-2	10
4-Chlorophenyl phenyl ether	7005-72-3	10
Fluorene	86-73-7	10
4,6-Dinitro-2-methylphenol	534-52-1	50
N-Nitrosodiphenylamine	86-30-6	10
4-Bromophenyl phenyl ether	101-55-3	10
Hexachlorobenzene	118-74-1	10
Pentachlorophenol	87-86-5	50
Phenanthrene	85-01-8	10
Anthracene	120-12-7	10
Di-n-butyl phthalate	84-74-2	10
Fluoranthene	206-44-0	10
Benzidine	92-87-5	100
Pyrene	129-00-0	10

Analytes	CAS Number	Aqueous µg/L
Butyl benzyl phthalate	85-68-7	10
3,3'-Dichlorobenzidine	91-94-1	50
Benzo(a)anthracene	56-55-3	10
Bis(2-ethylhexyl)phthalate	117-81-7	10
Chrysene	218-01-9	10
Di-n-octylphthalate	117-84-0	10
Benzo(b)fluoranthene	205-99-2	10
Benzo(k)fluoranthene	207-08-9	10
Benzo(a)pyrene	50-32-8	10
Indeno(1,2,3-cd)pyrene	193-39-5	10
Dibenz(a,h)anthracene	53-70-3	10
Benzo(g,h,i)perylene	191-24-2	10

Table A-2. Method 625 LCS and MS compounds and spike concentrations.

LCS Compounds	Spiking Level, ng/µL in extract[1]
Phenol	100
Bis(2-chloroethyl)ether	100
2-Chlorophenol	100
1,3-Dichlorobenzene	100
1,4-Dichlorobenzene	100
1,2-Dichlorobenzene	100
2,2'-oxybis(1-chloropropane)	100
N-Nitroso-di-n-propylamine	100
Hexachloroethane	100
Nitrobenzene	100
Isophorone	100
2-Nitrophenol	100
2,4-Dimethylphenol	100
Bis(2-chloroethoxy)methane	100
2,4-Dichlorophenol	100
1,2,4-Trichlorobenzene	100
Naphthalene	100
Hexachlorobutadiene	100
4-Chloro-3-methylphenol	100
Hexachlorocyclopentadiene	100
2,4,6-Trichlorophenol	100
2-Chloronaphthalene	100
Dimethyl phthalate	100
Acenaphthylene	100
Acenaphthene	100
2,4-Dinitrophenol	100
4-Nitrophenol	100
2,4-Dinitrotoluene	100
2,6-Dinitrotoluene	100
Diethylphthalate	100
4-Chlorophenyl phenyl ether	100
Fluorene	100
4,6-Dinitro-2-methylphenol	100
N-Nitrosodiphenylamine	100
4-Bromophenyl phenyl ether	100
Hexachlorobenzene	100
Pentachlorophenol	100
Phenanthrene	100
Anthracene	100
Di-n-butyl phthalate	100
Fluoranthene	100
Benzidine	100
Pyrene	100
Butyl benzyl phthalate	100
3,3'-Dichlorobenzidine	100

LCS Compounds	Spiking Level, ng/µL in extract[1]
Benzo(a)anthracene	100
Bis(2-ethylhexyl)phthalate	100
Chrysene	100
Di-n-octylphthalate	100
Benzo(b)fluoranthene	100
Benzo(k)fluoranthene	100
Benzo(a)pyrene	100
Indeno(1,2,3-cd)pyrene	100
Dibenz(a,h)anthracene	100
Benzo(g,h,i)perylene	100

[1] **Levels are 50 and 75 ng/µL if 2 µL injection is used**

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QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN SOLID SAMPLES BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY, SW846 7471A AND MCAWW 245.5

(SUPERSEDES: REVISION 0)

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7471A and MCAWW Method 245.5.

1.2. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.3. Methods 7471A and 245.5 are applicable to the preparation and analysis of mercury in soils, sediments, bottom deposits and sludge-type materials. All matrices require sample preparation prior to analysis.

1.4. The Quanterra reporting limit for mercury in solid matrices is 0.1 mg/kg based a 0.2 g sample aliquot (wet weight).

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. Total Metals: The concentration determined on an unfiltered sample following digestion.

4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Potassium permanganate which is used to breakdown organic mercury compounds also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.2. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.3. Chlorides can cause a positive interference. Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample headspace before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.4. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.5. Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.6. The most common interference is laboratory contamination which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all Quanterra associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid, nitric acid and sulfuric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid, potassium permanganate, potassium persulfate and magnesium perchlorate.

5.3.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean-up techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as:

5.3.3.1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or

5.3.3.2. Iodine, 0.25%, in a 3% KI solution.

5.3.4. Magnesium sulfate is known to be a reproductive toxin (mutagen).

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

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

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

5.7. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.8. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory and the gas led to the instrument through approved lines.

5.9. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath (capable of maintaining temperature of 90- 95 °C) or autoclave capable of obtaining 15 lbs., 120 °C.

6.2. Atomic Absorption Spectrophotometer equipped with:

6.2.1. Absorption Cell with quartz end windows perpendicular to the longitudinal axis. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.2.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).

6.2.3. Peristaltic pump which can deliver 1 L/min air.

6.2.4. Flowmeter capable of measuring an airflow of 1 L/min.

6.2.5. Recorder or Printer.

6.2.6. Aeration Tubing: A straight glass frit having a course porosity and Tygon tubing is used for the transfer of mercury vapor from the sample bottle to the absorption cell and return.

6.2.7. Drying device (a drying tube containing magnesium perchlorate or magnesium sulfate and/or a lamp with a 60 W bulb) to prevent condensation in cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10 °C above room temperature. Other drying devices that acheive the same purpose are also acceptable (i.e., Gortex filter).

Note: Instruments designed specifically for the measurement of mercury using the cold vapor technique may be substituted for the atomic absorption spectrophotometer.

6.3. BOD bottles or equivalent.

6.4. Nitrogen or argon gas supply, welding grade or equivalent.

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Class A volumetric flasks.

6.7. Top-loading balance, capable of reading up to two decimal places.

6.8. Thermometer (capable of accurate readings at 95 °C).

6.9. Disposable cups or tubes.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (1000 ppm) mercury standards (in 10% HNO_3) are purchased as custom Quanterra solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Intermediate mercury standard (10 ppm): Take 1 mL of the stock mercury standard (7.2) and dilute to 100 mL with reagent water. The intermediate standard must be made monthly and must be prepared in a matrix of 2% HNO_3. This acid (2 mL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. Working mercury standard (0.1 ppm): Take 1 mL of the intermediate mercury standard (7.3) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.5. The calibration standards must be prepared fresh daily from the working standard (7.4) by transferring 0, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 mL aliquots of the working mercury standard into sample prep bottles and proceeding as specified in Section 11.1

Note: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained. For example, automated mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.6. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards.

7.7. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better.

Note: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

7.9. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better.

7.9.1. Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated H_2SO_4 to 1 liter with reagent water.

7.10. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.11. Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

7.12. Stannous sulfate solution: Add 25 g of stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should appear cloudy. This solution should be made daily and should be stirred continuously during use.

Note: Stannous chloride may be used in place of stannous sulfate. Prepare the stannous chloride solution according to the recommendations provided by the instrument manufacturer.

7.13. Sodium chloride-hydroxylamine hydrochloride solution: Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride to every 100 mL of reagent water.

Note: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.14. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

7.15. Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate for every 100 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of collection to the time of sample analysis.

8.2. Soil samples do not require preservation but must be stored at 4° C ± 2° C until the time of analysis.

9. QUALITY CONTROL

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to the analysis of any analyte using 7471A or the 245.5, the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the Quanterra reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well characterized laboratory generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS) are not included in the sample count for determining the size of a preparation batch. MS/MSD are not included in the sample count unless there are multiple sets of MS/MSD per batch. In other words, the first MS/MSD are not counted; all additional MS and MSDs are counted as samples.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20 times higher than the blank contamination level).

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. The CCV results can be reported as the LCS results since all CCVs (as well as all other standards) are processed through the sample preparation step with the field samples. No more than 20 samples can be associated with one CCV used for the purpose of reporting LCS data.

- If the LCS is outside established control limits the system is out of control and corrective action must occur. Until in-house control limits are established, a control limit of 80 - 120% recovery must be applied.

- In the instance where the LCS recovery is > 120% and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the case narrative."

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are

established, a control limit of 75 - 125 % recovery and 20% RPD must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.7. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 20% of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. (See Section 11.2.10 and Section 11.2.11 for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.8. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV must be a mid-range standard at a concentration other than that of the ICV. The CCV result must fall within 20% of the true value for that solution. A CCB is analyzed immediately following each CCV. (See Section 11.2.10 and 11.2.11 for required run sequence.) The CCB result must fall within +/- RL from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs. If a mid-run CCV or CCB fails, the analysis must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. If the cause of the CCV or CCB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.9. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. Refer to Section 11.2.12 for additional information on when full 4 point MSA is required as well as Appendix C for specific MSA requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the facility specific instrument SOP and CVAA instrument manual for detailed setup and operation protocols.

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the Quanterra reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.6. The calibration curve must have a correlation coefficient of ≥0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results can not be reported from a curve with an unacceptable correlation coefficient.

10.7. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corrective actions.

11. PROCEDURE

11.1. Standard and Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed through the digestion procedure as well as the field samples.

11.1.2. Transfer 0, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 mL aliquots of the working standard (7.5) into a series of sample digestion bottles.

Note: Alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained.

11.1.3. Add reagent water to each standard bottle to make a total volume of 10 mL. Continue preparation as described under 11.1.5 or 11.1.6 below.

11.1.4. Transfer triplicate 0.2 g portions of a well mixed sample into a clean sample digestion bottle. Continue preparation as described under 11.2.2 or 11.2.3 below.

11.1.5. Water Bath protocol:

11.1.5.1. To each **standard** bottle: Add 5 mL of aqua regia.
To each **sample** bottle: Add 5 mL of reagent water and 5 mL of aqua regia.

11.1.5.2. Heat for 2 minutes in a water bath at 90 - 95 ° C.

11.1.5.3. Cool.

11.1.5.4. Add 50 mL of distilled water.

11.1.5.5. Add 15 mL of potassium permanganate solution.

11.1.5.6. Add 8 mL of potassium persulfate solution, mix thoroughly

11.1.5.7. Heat for 30 minutes in the water bath at 90 - 95 °C.

11.1.5.8. Cool.

11.1.5.9. Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate.

11.1.5.10. To each **standard** bottle: Add 50 mL of reagent water.
To each **sample** bottle: Add 55 mL of reagent water.

11.1.5.11. Continue as described under Section 11.2.

11.1.6. Autoclave protocol:

11.1.6.1. Add 5 mL concentrated of H_2SO_4 and 2 mL of concentrated HNO_3.

11.1.6.2. Add 5 mL of saturated potassium permanganate solution.

11.1.6.3. Add 8 mL of potassium persulfate solution.

11.1.6.4. Cover digestion bottle with aluminum foil or screw cap loosely applied.

11.1.6.5. Heat samples at 121 °C and 15 lbs. pressure for 15 minutes.

11.1.6.6. Cool.

11.1.6.7. Make up to volume of 100 mL with reagent water.

Note: Alternate final volumes may be used as long as the standards and sample are treated the same way.

11.1.6.8. Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce excess permanganate.

11.1.6.9. Continue as described under Section 11.2 .

11.2. Sample Analysis:

11.2.1. Because of differences between various makes and models of CVAA instrumentation, no detailed operating instructions can be provided. Refer to the facility specific instrument operating SOP and the CVAA instrument manual for detailed setup and operation protocols.

11.2.2. All labs are required to detail the conditions/programs utilized for each instrument within the facility specific instrument operation SOP.

11.2.3. Manual determination:

11.2.3.1. Treating each sample individually, purge the head space of the sample bottle for at least one minute.

11.2.3.2. Add 5 mL of stannous chloride solution and immediately attach the bottle to the aeration apparatus.

11.2.3.3. Allow the sample to stand quietly without manual agitation while the sample is aerated (1 L/min flow). Monitor the sample absorbance during aeration. When the absorbance reaches a maximum and the signal levels off, open the bypass valve and continue aeration until the absorbance returns to its baseline level. Close the bypass valve and remove the aeration device.

11.2.3.4. Place the aeration device into 100 mLs of 1% HNO_3 and allow to bubble rinse until the next sample is analyzed.

11.2.4. Automated determination: Follow instructions provided by instrument manufacturer.

11.2.5. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. ug of mercury. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.2.6. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

11.2.7. If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

11.2.8. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.9. Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

11.2.10. The following analytical sequence must be used with 7471A and 245.5:

Instrument Calibration
ICV
ICB
Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

Refer to Quality Control Section 9.0 and Table II (Appendix A) for quality control criteria to apply to Methods 7471A and 245.5.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

11.2.11. The following run sequence is consistent with 7471A, CLP and 245.5 and may be used as an alternate to the sequence in 11.2.10. This run sequence is recommended if multiple method requirements must be accommodated in one analytical run:

Instrument Calibration
ICV
ICB
CRA*
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.
CCV
CCB

Refer to the appropriate CLP SOP (CORP-MT-0008) for quality control requirements for QC samples.

* Refer to the CLP SOP for information on the CRA.

11.2.12. For TCLP samples, full four point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

Appendix E provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sampe preparation.

11.3. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.4. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.5. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.6. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix spike recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.5. For automated determinations, the final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

mg/kg, dry weight = (C x V x D)/(W x S)

Where:
C = Concentration (ug/L) from instrument readout

V = Volume of digestate (L)
D = Instrument dilution factor
W = Weight in g of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the "S" factor should be omitted from the above equation.

12.6. For manual (total) determinations, the final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

$$mg/kg,\ dry\ weight = (C)/(W \times S)$$

Where:
C = Concentration (ug) from instrument readout
W = Weight in g of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the "S" factor should be omitted from the above equation.

12.7. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8. Sample results should be reported with up to three significant figures in accordance with the Quanterra significant figure policy.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2. Method performance is determined by the analysis of method blank, laboratory control sample, matrix spike and matrix spike duplicate samples. The matrix spike recovery should fall within +/- 25 % and the matrix spike duplicates should compare within 20% RPD. The method blanks must meet the criteria in Section 9.3. The

laboratory control sample should recover within 20% of the true value until in house limits are established.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7471A (Mercury).

16.2. "Methods for the Chemical Analysis of Water and Wastes", EPA-600/4-79-020, U.S.EPA, August 1983, Method 245.5.

16.3. U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0.

16.4. QA-003, Quanterra QC Program.

16.5. QA-004, Rounding and Significant Figures.

16.6. QA-005, Method Detection Limits.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference method.

17.1.1. Modifications from both 7471A and 245.5.

17.1.1.1. A potassium persulfate oxidation step has been included to facilitate the breakdown of organic mercurials which are not completely oxidized by potassium permanganate. Use of potassium persulfate in combination with the permanganate improves the recovery of mercury from organo-mercury compounds. The use of persulfate has been incorporated in several recent EPA mercury protocols.

17.1.1.2. The alternate run sequence presented in Section 11.2.11 is consistent with method requirements. An additional QC analysis (CRA) was added to accommodate the CLP protocol requirements.

17.1.2. Modifications from Method 7471A

17.1.2.1. Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.2.2. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.

17.1.2.3. Method 7471A does not state control criteria within the text of the method. The QC section of 7471A refers the analyst to Section 8.0 of Method 7000A, the generic atomic absorption method, which discusses flame and furnace methods. The ICV criteria stated in Method 7000A is ± 10%. This SOP requires ICV control limits of ± 20% based on the fact that the mercury ICV, unlike the ICV for the flame and furnace analytes, is digested and therefore is equivalent to a LCS. The CLP protocol 245.5 CLP-M recognizes this factor and requires control limits of ± 20%.

17.1.3. Modifications from 245.5

17.1.3.1. Method 245.5 Section 9.3 states concentrations should be reported as follows: Between 0.1 and 1 ug/g, to the nearest 0.01 ug; between 1 and 10 ug/g, to the nearest 0.1ug; above 10 ug/g, to the nearest ug. Quanterra reports all Hg results under this SOP to two significant figures.

17.2. Modifications from previous SOP

None.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

17.4. Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software where this option is available or manually generated run log. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.
- Non-conformance summary (if applicable).

Figure 1. Solid Sample Preparation for Mercury - Autoclave Procedure

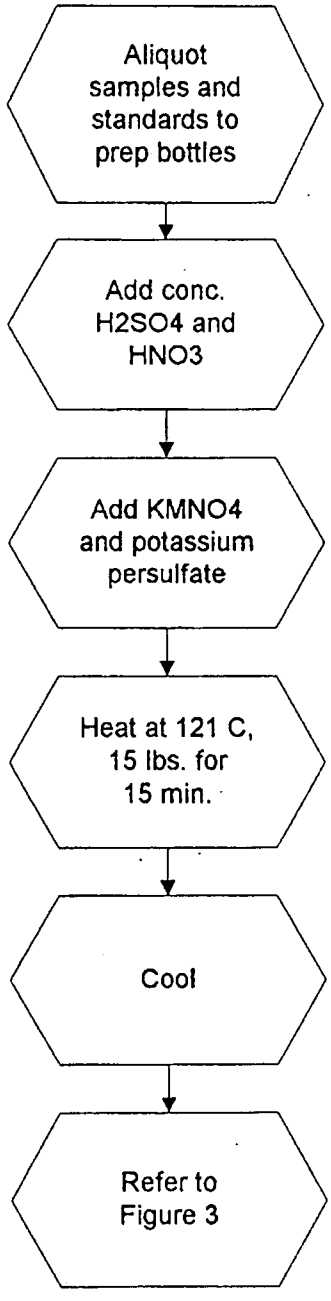


Figure 2. Solid Sample Preparation for Mercury - Water Bath Procedure

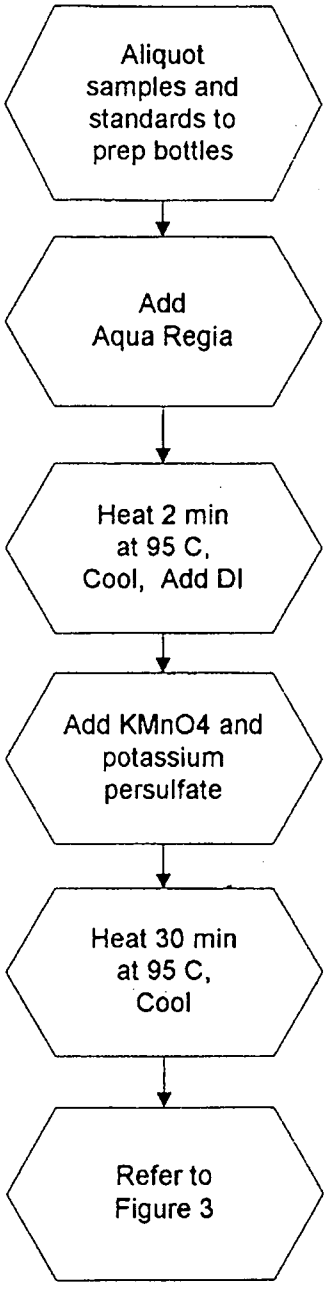
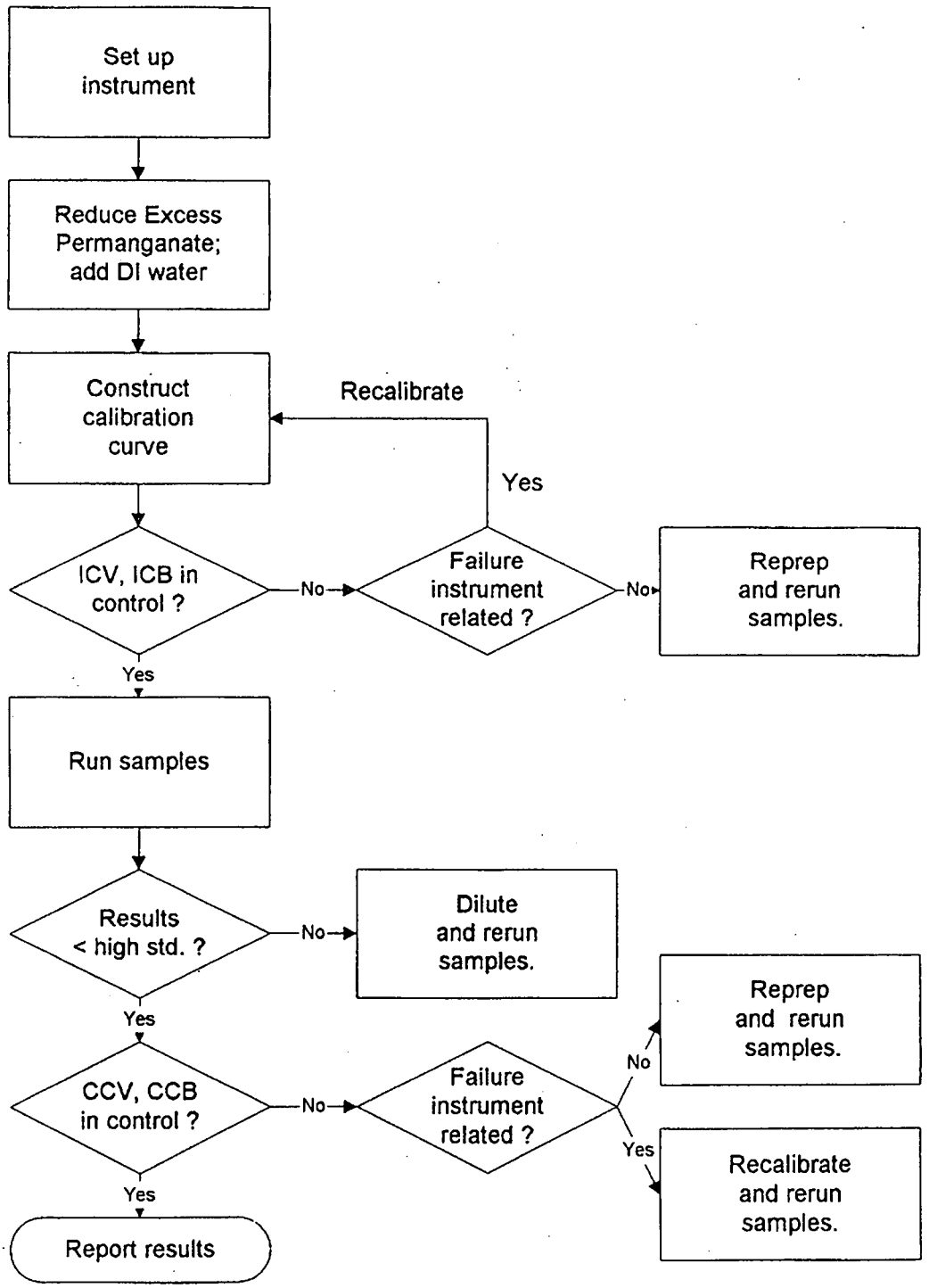


Figure 3. CVAA Mercury Analysis



APPENDIX A

TABLES

TABLE I. MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS

Soil RL (mg/kg)	0.1
Std 0 (mg/L)	0
Std 1 (mg/L)	0.0002
Std 2 (mg/L)	0.0005
Std 3 (mg/L)	0.001
Std 4 (mg/L)	0.002
Std 5 (mg/L)	0.005
Std 6 (mg/L) **	0.010
ICV (mg/L)	0.001 or 0.0025 ***
CCV/LCS (mg/L)	0.0025 or 0.005 ***
MS (mg/L)	0.001

* **SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements. Deviations from specified calibration levels must be documented in the facility specific instrument operation SOP and must be approved by the facility technical manager and Quality Assurance Manager.**

** **Optional standard which may be used to extend the calibration range as allowed by the instrument configuration. If the instrument configuration prevents the use of 6 standards, the 2 ppb standard may be eliminated in favor of the 10 ppb standard.**

*** **Concentration level dependent on high calibration standard used. CCV must be 50% of the high standard concentration and the ICV must be 20-25% of the high standard concentration.**

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
CCV	Every 10 samples and at the end of the run.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep batch (see Section 9.8).
CCB	Immediately following each CCV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep batch (see Section 9.8).
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require redigestion (See Section 9.4)	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.4 for additional requirements.

*See Sections 11.2.10 and 11.2.11 for exact run sequence to be followed.

TABLE II. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits.	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (see Section 9.5).
Matrix Spike	One per sample preparation batch of up to 20 samples.	75 - 125 % recovery or in-house control limits. If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.6) For TCLP see Section 11.3.12
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery or in-house control limits; RPD ≤ 20%. (See MS)	See Corrective Action for Matrix Spike.

APPENDIX B
QUANTERRA Hg DATA REVIEW CHECKLIST

Quanterra Hg Data Review Checklist

Run/Project Information

Run Date: _____ **Analyst:** _____ **Instrument:** _____
Prep Batches Run: _____

Circle Methods used: **7470A / 245.1** : CORP-MT-0005 Rev 1 **7471 / 245.5** : CORP-MT-0007 Rev 1
CLP - AQ : CORP-MT-0006 Rev 0 **CLP - SOL** : CORP-MT-0008 Rev 0

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2ndLevel
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels ?				
2. ICV/CCV analyzed at appropriate frequency and within control limits?				
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)?				
4. CRA run (CLP only)?				
B. Sample Results				
1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?				
2. All reported results bracketed by in control QC ?				
3. Sample analyses done within holding time?				
C. Preparation/Matrix QC				
1. LCS done per prep batch and within QC limits ?				
2. Method blank done per prep batch and < RL or CRDL (CLP) ?				
3. MS run at required frequency and within limits ?				
4. MSD or DU run at required frequency and RPD within SOP limits?				
D. Other				
1. Are all nonconformances documented appropriately ?				
2. Current IDL/MDL data on file?				
3. Calculations and Transcriptions checked for error ?				
4. All client/ project specific requirements met?				
5. Date of analysis verified as correct ?				

Analyst: _____ **Date:** _____
Comments:

_____

_____

2nd Level Reviewer : _____ **Date:** _____

_____

_____

APPENDIX C

MSA GUIDANCE

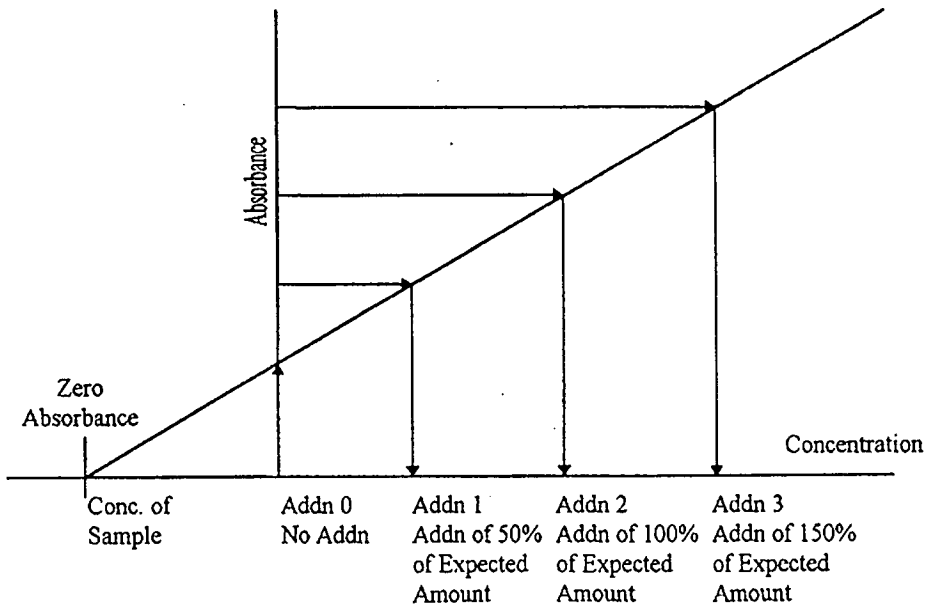
APPENDIX C. MSA GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. On the vertical axis the absorbance (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.
- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX D

TROUBLESHOOTING GUIDE

APPENDIX D. TROUBLESHOOTING GUIDE

Problem	Possible Cause
Poor or No Absorbance or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak EDL power supply set on "Continuous"
Erratic Readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL Won't Light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards reading twice or half normal absorbance or concentration	Incorrect standard used Incorrect dilution performed Dirty cell
Background Correction Light Blinking	Background screen or attenuator faulty

APPENDIX E

CONTAMINATION CONTROL GUIDELINES

APPENDIX E. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

APPENDIX F

PREVENTIVE MAINTENANCE

APPENDIX F. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman PS 200)[1]

Daily	Semi-annually	Annually
Clean lens.	Check Hg lamp intensity.	Change Hg lamp.
Check aperture.		Check liquid/gas separator.
Check argon flow.		
Check tubing.		
Check drain.		
Replace drying tube.		

Cold Vapor Atomic Absorption (PE 5000)[1]

Daily	Monthly
Clean aspirator by flushing with DI water.	Clean cell in aqua regia.
Check tubing and replace if needed.	Clean aspirator in aqua regia.
Clean windows with methanol.	
Change silica gel in drying tube.	
Check argon gas supply.	
Adjust lamp.	

Quanterra
Environmental Services

West Sacramento
SOP REVIEW FORM

SOP NUMBER: CORP-MT-0007
SOP TITLE: **Preparation and Analysis of Mercury in Solid Samples by Cold Vapor Atomic Absorption Spectroscopy, SW846 7471A and MCAWW 245.5**
The subject SOP has undergone the required peer/management review. No modifications are necessary at this time.
REVIEWED BY DATE: John Barnett
***APPROVED BY:**
Technical Review Signature John Barnett Date 9/23/98
Environmental Health and Safety Signature Cheryl Stto Date 9/23/98
Quality Assurance Manager Signature [illegible] Date 9/23/98
Management Signature Robert Dow Date 9/23/98

*Must be the same signature authorities as the SOP being reviewed.

Control Copy #_____

Quanterra Environmental Services

QUANTERRA ENVIRONMENTAL SERVICES (West Sacramento)
SOP CHANGE FORM

SOP Number:	Corp-MT-0007
SOP Title:	Prep & Analysis of Mercury on Solid samples
SOP Sections Affected by Change:	11.1.6.7
Reason for Addition or Change:	Clarify current procedure
Change Effective From [Date]:	8/96
Change or Addition (Specific Section; Use additional sheets if necessary):	We are using an alternate final volume of 44 ml for standards and samples before Hydroxylamine is added.

Submitted by/Date: Marilyn Toomey 7/9/96

Approved by:*

Technical Reviewer: [signature] Date 7/10/96

EH&S Signature: [signature] Date 7/10/96

QA Signature: [signature] Date 7/10/96

Management Signature: _____ Date _____

* Must be same signature authorities of SOP being revised.