Standard Operating Procedure for the Determination of Organic Acids Benzenesulfonic Acid, 4-Chlorobenzenesulfonic Acid, Dimethyl Phosphorodithioic Acid, Diethyl Phosphorodithioic Acid and Phthalic Acid by Reverse-Phase HPLC and UV Detection

1.0 Identification of the Test Method

1.1 Confidential Business Information (CBI)

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1.2 References

1.2.1 Method RRC-83-16: Determination of Benzenesulfonic Acid, 4-Chlorobenzenesulfonic Acid, Dimethyl Phosphorodithioic Acid, Diethyl Phosphorodithioic Acid and Phthalic Acid in Natural Water and Waste Brines by Reverse-Phase HPLC and UV Detection, Stauffer Chemicals, Richmond Research Center, March 1983.

1.2.2 Method 8000B: Determinative Chromatographic Separations, Revision 2, December 1996, Test Methods for Evaluating Solid Waste, Physical and Chemical Methods, SW-846, 3rd Edition, Final Update III, 1996.

Note: The instrumental procedures described in this SOP are a modification of the Stauffer Chemical procedures, and the quality control procedures described in this SOP are modeled after the EPA Method 8000B procedures.

2.0 Applicable Matrix or Matrices

2.1 This method is applicable to the determination of organic acids in drinking water, surface water, wastewater, groundwater, brines and solids.

3.0 Method Detection Limit

3.1 Method Detection Limits (MDLs) and compound sensitivity may vary with the sample matrix. However, in reagent water MDLs for organic acids typically range from a calculated concentration of 0.005 mg/L to 0.02 mg/L and in a soil matrix MDLs for organic acids range from a calculated concentration of 0.05 to 0.2 mg/Kg. The typical reporting limits for these analytes are as follows:

Target Analyte Table
Table E.64-1

Analyte	CAS	Acronym	Reporting Limit Water	Reporting Limit Soil
Dimethyl phosphorodithioic acid		DMPT	0.25 mg/L	2.5 mg/kg
Benzenesulfonic acid	98-11-3	BSA	0.05 mg/L	0.5 mg/kg
Phthalic acid	88-99-3	PA	0.05 mg/L	0.5 mg/kg
Diethyl phosphorodithioic acid	52857-42-8	DEPT	0.05 mg/L	0.5 mg/kg
4-Chlorobenzenesulfonic acid	98-66-8	pCBSA/MCBSA	0.05 mg/L	0.5 mg/kg

4.0 Scope and Application

4.1 The BMI complex (approximately 5000 acres) was originally known as the Basic Magnesium Inc., facility which was constructed by the U.S. Government primarily to produce magnesium metal for wartime use in the early 1940's. It has changed names to Black Mountain Inc, and is now known as the Basic Management Incorporated (BMI) complex in Henderson Nevada. The BMI complex included a chlorine-caustic plant which was necessary to support the U.S. government's production of magnesium.

The BMI complex houses several major chemical production companies to include Pioneer America, Inc. (now known as the Olin Corporation), Kerr-McGee Chemical Corporation (now known as Tronox LLC), Titanium Metals Corporation of America (TIMET), Combined Metals Reduction Company, US Lime (ChemStar) and Saguaro Power Company.

4.2 Well over 900 chemical compounds have been known to be used or produced at this complex to include the following classes of compounds: aldehydes, asbestos, dioxins, furans, herbicides, metals, organic acids, organochlorine pesticides, organophosphate pesticides, perchlorate, PCB's, radionuclides, SVOCs, and VOC's. In order to synthesize these types of organic compounds, a number of key starting and intermediate compounds are required for their production. As a result, organic acids included as target analytes in this procedure are some of those compounds used, consumed, or produced as a final product or byproduct at the BMI complex.

4.3 This analytical procedure was not developed by the EPA nor are the specific targets analytes regulated by the EPA. The organic acids listed as target analytes are quantitated against their salt equivalents (sodium, potassium and ammonium salts) all of which are commercially available except for dimethyl phosphorodithioic acid. This compound was synthesized by the Stauffer Chemical Company at a purity of 99%.

5.0 Summary of Method

5.1 A small volume of sample is introduced into a High Performance Liquid Chromatograph (HPLC) to flush and fill a fixed volume sample loop. The sample is then injected into a mobile phase eluent. The organic acids are separated and measured using an HPLC system comprised of a analytical column and a UV detector. Acids are identified based on their retention times and compared to known standards. Quantitation is accomplished by measuring peak area and comparing it to a calibration curve generated from known standards. An extraction procedure is performed on soil and/or solid samples prior to sample analysis.

6.0 Definitions

6.1 Analytical Batch - A set of up to 20 samples prepared and analyzed together. Each batch must be accompanied with a method blank, laboratory control sample and a matrix spike.

6.2 Calibration Standard (CAL) - A solution prepared from the stock standard solutions or primary dilution standards. The calibration standard solutions are used to calibrate the instrument response with respect to known analyte concentrations.

6.3 Calibration Verification (CV)- A solution typically prepared from the same stock standard solution as the calibration standards, used to assure calibration accuracy during each analytical sequence. At a minimum, it should be analyzed at the beginning of the sequence, after every 20 samples and after the last analytical sample.

6.4 Initial Calibration Verification (ICV) - A solution of a known concentration used to check laboratory performance with externally prepared test materials. The ICV is prepared from a source different then the source of calibration standards, and is analyzed each time a new calibration curve is generated.

6.5 Laboratory Control Sample (LCS) - An aliquot of a blank matrix, free from the analytes of interest, to which a known quantity of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the method is in control, and whether the laboratory is capable of making accurate and precise measurements.

6.6 Matrix Spike (MS) - An aliquot of a field sample to which a known quantity of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the method analytes in the sample matrix are determined in a separate aliquot and the measured values in the MS are corrected for background concentrations.

6.7 Method Blank (MB) - A sample of a matrix similar to the batch of associated samples that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedure, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.8 Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

6.9 Primary Dilution Standard - A solution prepared in the laboratory from the stock standard solution and diluted as needed to prepare more dilute working standards.

6.10 Reagent Water- Water, free of the analytes of interest or other analytes which may interfere with the determination of the target analytes.

6.11 Reporting Limit (RL) - The minimum concentration that can be reported as a quantitated value in a sample following analysis.

6.12 Stock Standard Solution (SSS) - A concentrated solution containing the target analytes prepared using reference material or purchased from a commercial source.

7.0 Interferences

7.1 Raw chromatographic data from all blanks, samples, and spikes must be evaluated for potential interferences. If interferences are found, the analyst should determine the source of the interference and take corrective actions to eliminate the problem.

7.2 There are four broad categories of potential interferences with this method.

7.2.1 Contaminated solvents, reagents, or sample processing hardware.

7.2.2 Contaminated HPLC mobile phase, parts, column or detector surfaces.

7.2.3 Target and non-target compounds which co-elute from the sample matrix to which the detector will respond.

7.2.4 Contamination by carryover can occur whenever high-concentration and low-

concentration samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it may be necessary to follow it with the analysis of a solvent or reagent blank to check for possible carryover contamination.

7.3 Target and Non-target Co-elution Interferences

7.3.1 Any species with retention times that are similar to and overlap the analytes of interest will interfere. These types of interferences can generally be divided into three different categories as follows:

- Direct Chromatographic Co-elution - A non-target analyte response is observed at very nearly the same retention time as a target analyte,
- Concentration Dependent Co-elution - Observed when the response of higher than typical concentrations of the neighboring peak (target and/or non-target analyte) overlaps into the retention time window of a target analyte, and
- pH Displacement - Retention times may significantly shift due to the influence of pH, caused primarily by a modification of the active sites in the column thus changing the retention times.

7.4 Most interference problems associated with retention time can be chromatographically improved by:

- Sample dilution,
- Adjusting mobile phase concentration,
- Adjusting mobile phase pH and/or,
- Adjusting flow-rate

7.5 Samples that contain particles larger than 0.45 µm and reagent solutions that contain particles larger than 0.20 µm require filtration to prevent damage to instrument columns and flow systems.

7.6 Known Interferences

7.6.1 Benzoic acid at concentration of 5 mg/L or higher can cause potential interference for the quantitation of pCBSA.

7.6.2 Perchlorate is observed as a non-retained analyte that can potentially interfere with the quantitation and reporting of DMPT. Perchlorate does not interfere directly with any of the 5 target analytes; however, as an un-retained peak, it elutes with the "water dip." This potential interference is essentially classified as a concentration dependent co-elution problem, meaning when

the response of this un-retained peak has a high concentration, it starts to overlap into the retention time window of its neighboring peak (DMPT) and may cause problems with compound resolution and absolute sample quantitation.

8.0 Safety

8.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals should be reduced to the lowest possible extent. A reference file of material safety data sheets is available. See Alpha's Laboratory Safety/Hazardous Communications Manual and Chemical Hygiene Plan for additional information and details.

8.2 Personal Protective Equipment (PPE) should be worn during sample preparation and during the preparation and disposal of reagents. PPE should include a lab coat, safety glasses, and safety gloves. Preparation of reagents should be carried out under a hood.

8.3 The following chemicals and reagents may be highly toxic or hazardous:

8.3.1 Concentrated phosphoric acid (H_3PO_4) can cause severe burns and react violently with water. Add cautiously and always work with phosphoric acid under a fume hood to avoid inhalation. If spills occur, neutralize immediately by dilution with copious amounts of water.

8.3.2 Sodium hydroxide is corrosive and may cause skin, eye and respiratory tract irritation. If spills occur, neutralize immediately by dilution with water.

8.3.3 Organic solvents, such as methanol may cause skin, eye and respiratory tract irritation. Wear all PPE when working with solvents.

8.4 Monitor all extraction apparatus, to ensure proper performance at all times.

8.5 Ensure that the fume hood is operating within specified guidelines. A fume hood should be used to prepare standards and sample extracts.

9.0 Equipment and Supplies

9.1 Instrument

Hewlett Packard HP 1050 HPLC System to include the following:

- Hewlett Packard titanium quaternary pump,
- Hewlett Packard 79853C Variable Wavelength Detector
- Hewlett Packard 79855A Auto-sampler,

- Column heater
- C_{18} Analytical column (4.6 x 250mm) 5*u*m
- Dionex AI-450 Data Acquisition Software

10.0 Reagents and Standards

10.1 Reagents

10.1.1 Ultra high-purity grade reagents and standards are used in this procedure to preclude any potential contamination.

10.1.2 Reagent Water - Water, free of the analytes of interest or other analytes which may interfere with the determination of the target analytes.

10.1.3 Dilution Water

Prepare by adding 200 ul or approximately ten drops of phosphoric acid to a volume of 250 m reagent water.

Note: Standards are diluted using pH adjusted dilution water.

10.1.4 Mobile Phase

10.1.4.1 [redacted]

Note: It is important to adjust the pH of the mobile phase. The relative retention time of phthtalic acid in the chromatogram has been shown to be highly pH dependent. If the LC column is changed, it may be necessary to re-adjust the pH of the mobile phase in order to chromatographically re-optimize the phthalic acid separation (resolution) from the other closely eluting analytes.

10.1.4.2 Store the mobile phase no longer than one month.

10.2 Standards

10.2.1 Stability of Standards

10.2.1.1 Stock standards are stable for a minimum of two years when stored at ≤6°C.

10.2.1.2 Primary dilution and working standards are prepared using the same storage conditions as described for the stock standards.

1) Clarification: A two year expiration date is a suggested expiration date used for all standards, unless they appear to have degraded.

10.2.2 Stock Standard Solutions (SSS)

10.2.2.1 The SSS used in the preparation of the initial calibration and QC check standards are typically purchased as certified pure "Neat" material, commercial stock standards are not available.

10.2.2.2 Preparation of Neat Standards

10.2.2.2.1 The preparation of stock standard solutions from neat material is prepared by weighing a determined amount of neat material into a volumetric flask and calculating the concentration as w/v and adjusting for purity.

10.2.2.2.2 Tare the volumetric flask containing, approximately one half full volume, reagent grade dilution water and add the neat material to the flask. Ensure the neat material falls directly into the dilution water without contacting the neck of the flask or container holding the standard.

10.2.2.2.3 Reweigh the container and dilute to volume with dilution water, cap the volumetric flask and mix by inverting the container several times. Calculate the actual stock concentration as follows:

$$Stock,\ mg/mL = \frac{(final\ wt,\ mg) - (tare\ wt,\ mg)}{Final\ volume\ mL}$$

10.3 Surrogate Standard

10.3.1 Stock Standard Solution - The SSS used int preparation of the surrogate standard is typically purchased in the neat form as follows:

Surrogate Stock Standard Solution
Purchase Table
Table E.64-2

Stock Standard Solution (SSS)	Manufacturer	Part Number	Concentration
[redacted]	Alfa Aesar	[redacted]	Neat

10.3.2 Stock Standard Solution - The SSS used in the preparation of the surrogate standard is generally prepared from the neat material as follows:

Surrogate Stock Standard Solution
Preparation Table
Table E.64-3

Stock Standard Solution (SSS)	Initial Concentration	Aliquot mg	Final Volume ml	Volume H_2O, pH <3 ml	Final Concentration ug/ml
[redacted]	Neat	200	20	Dilute to volume	10,000

10.3.3 Primary Dilution Standard - A primary dilution standard made prior to the preparation of the working standards is generally prepared as follows:

Surrogate Primary Dilution Standard
Preparation Table
Table E.64-4

Primary Dilution Standard	Initial Concentration ug/ml	Aliquot ul	Final Volume ml	Volume H_2O, pH <3 ml	Final Concentration ug/ml
[redacted]	10,000	800	8.0	7.20	1000

10.4 Calibration Standards (CAL)

10.4.1 Stock Standard Solution - The SSSs used in the preparation of the initial calibration standards are generally purchased as follows:

Initial Calibration Stock Standard Solution
Purchase Table
Table E.64-5

Stock Standard Solution (SSS)	Manufacturer	Part Number	Concentration
benzenesulfonic acid, sodium salt	[redacted]	[redacted]	Neat
dimethyl phosphorodithioic acid, ammonium salt	[redacted]	[redacted]	Neat
potassium hydrogen phthalate	[redacted]	[redacted]	Neat
diethyl phosphorodithioic acid, ammonium salt	[redacted]	[redacted]	Neat

Stock Standard Solution (SSS)	Manufacturer	Part Number	Concentration
4-chlorobenzenesulfonic acid	[redacted]	[redacted]	Neat

10.4.2 Standards are prepared from their salt equivalent with the exception of 4-Chlorobenzenesulfonic acid. Since these acids are analyzed and reported as the parent acid, their salt equivalent may be used as long as the standards are prepared stoichiometrically against the parent acid.

10.4.2.1 Benzenesulfonic Acid ($C_6H_5SO_3H$)

10.4.2.1.1 [redacted]

10.4.2.1.2 [redacted]

10.4.2.1.3 [redacted]

BSA Stock Standard Solution
Preparation Table
Table E.64-6

Stock Standard Solution (SSS)	Initial Concentration	Aliquot mg	Final Volume ml	Volume H_2O, pH <3 ml	Final Concentration ug/ml
Benzenesulfonic Acid	Neat	28.5	25	dilute to volume	1000

10.4.2.2 4-Chlorobenzenesulfonic acid ($ClC_6H_4SO_3H$)

10.4.2.2.1 [redacted]

10.4.2.2.2 [redacted]

10.4.2.2.3 [redacted]

[redacted]

pCBSA Stock Standard Solution
Preparation Table
Table E.64-7

Stock Standard Solution (SSS)	Initial Concentration	Aliquot mg	Final Volume ml	Volume H_2O, pH <3 ml	Final Concentration ug/ml
p-chlorobezene sulfonic Acid	Neat	27.8	25	dilute to volume	1000

10.4.2.3 Phthalic acid $C_6H_4(COOH)_2$

10.4.2.3.1 [redacted]

10.4.2.3.2 [redacted]

10.4.2.3.3 [redacted]

PA Stock Standard Solution
Preparation Table
Table E.64-8

Stock Standard Solution (SSS)	Initial Concentration	Aliquot mg	Final Volume ml	Volume H_2O, pH<3 ml	Final Concentration ug/ml
Phthalic Acid	Neat	30.8	25	dilute to volume	1000

10.4.2.4 Dimethyl phosphorodithioic acid $(CH_3O)_2P(S)SH$

10.4.2.4.1 [redacted]

10.4.2.4.2 [redacted]

[redacted]

10.4.2.4.3 [redacted]

DMPT Stock Standard Solution
Preparation Table
Table E.64-9

Stock Standard Solution (SSS)	Initial Concentration	Aliquot mg	Final Volume mL	Volume H_2O, pH<3 mL	Final Concentration ug/ml
Dimethyl phosphorodithioic Acid	Neat	27.8	25	dilute to volume	1000

10.4.2.5 Diethyl phosphorodithioic acid $(C_2H_5O)_2P(S)SH$

10.4.2.5.1 [redacted]

10.4.2.5.2 [redacted]

10.4.2.5.3 [redacted]

DEPT Stock Standard Solution
Preparation Table
Table E.64-10

Stock Standard Solution (SSS)	Initial Concentration	Aliquot mg	Final Volume ml	Volume H_2O, pH<3 ml	Final Concentration ug/ml
Diethyl phosphorodithioic Acid	Neat	28.7	25	dilute to volume	1000

Note: These stock standards are generally prepared at a concentration of 1000 mg/L but may vary because this standard is prepared from the neat form.

10.4.3 Primary Dilution Standard - A primary dilution standard made prior to the preparation of the working standard is generally prepared as follows:

Initial Calibration Primary Dilution Standard Preparation Table
Table E.64-11

Primary Dilution Standard	Initial Concentration ug/ml	Aliquot ml	Final Volume ml	Volume H_2O, pH<3 ml	Final Concentration ug/ml
BSA	1000	2.5	25	6.25 (dilute to volume)	100
DMPT	1000	6.25			250
PA	1000	2.5			100
DEPT	1000	2.5			100
pCBSA	1000	2.5			100
d-panthenol (surr)	10,000	2.5			1000

10.4.4 Working Standards - A minimum of five calibration standards are required to calibrate the instrument. The intent of this section of the SOP is not to detail a prescriptive approach to the number and concentration points of the initial calibration, but is written as a general guideline to produce an acceptable initial calibration standard. One of the standards is prepared at or below the reporting limit while the remaining standards define the working range of the instrument. Working calibration standards are generally prepared as follows:

Initial Calibration Working Standard Preparation Table
Table E.64-12

Initial Calibration Working Standard	Initial Concentration ug/ml	Aliquot ul	Final Volume ml	Volume H_2O, pH<3 ml	Final Concentration ug/ml
Mix 1	1000/250/100	2.0	8.0	7.998	0.25/0.0625/0.025
Mix 2	1000/250/100	4.0	8.0	7.996	0.50/0.125/0.05
Mix 3	1000/250/100	8.0	8.0	7.992	1.0/0.25/0.10
Mix 4	1000/250/100	20	8.0	7.98	2.5/0.625/0.25
Mix 5	1000/250/100	40	8.0	7.96	5.0/1.25/0.50
Mix 6	1000/250/100	80	8.0	7.92	10/2.5/1.0
Mix 7	1000/250/100	120	8.0	7.88	15/3.75/1.5
Mix 8	1000/250/100	160	8.0	7.84	20/5.0/2.0

10.5 Calibration Verification (CV)

10.5.1 Working standards - Working standards used in the preparation of the initial calibration are also used as the CV and are generally prepared as follows:

Calibration Verification Working Standard Preparation Table
Table E.64-13

CV Working Standard	Initial Concentration ug/ml	Aliquot ul	Final Volume ml	Volume H_2O, pH<3 ml	Final Concentration ug/ml
CV-1	1000/250/100	5.0	1.0	0.995	5.0/1.25/0.50
CV-2	1000/250/100	10	1.0	0.990	10/2.5/1.0

10.6 Second Source Standard

10.6.1 Stock Standard Solution - The SSS used in the preparation of the ICV, LCS and MS, standards independent from the calibration standard, are prepared as described above. Since no other source of standards exist, they are prepared from the same neat source as stated above, but are prepared independently from those primary standards used to prepare the calibration standards.

10.6.2 Initial Calibration Verification (ICV)

10.6.2.1 Primary Dilution Standard - A primary dilution standard made prior to the final preparation of the working standard is generally prepared as follows:

Second Source Primary Dilution Standard Preparation Table
Table E.64-14

Primary Dilution Standard	Initial Concentration ug/ml	Aliquot ml	Final Volume ml	Volume H_2O, pH<3 ml	Final Concentration ug/ml
BSA	1000	2.5	25	10 (dilute to volume)	100
DMPT	1000	5.0			200
PA	1000	2.5			100
DEPT	1000	2.5			100
pCBSA	1000	2.5			100

10.6.2.2 Working Standards - The ICV working standard is typically prepared from the second source primary dilution standard as follows:

Second Source Working Standard
Preparation Table
Table E.64-15

ICV Working Standard	Initial Concentration ug/ml	Aliquot ul	Final Volume ml	Volume H_2O, pH<3 ml	Final Concentration ug/ml
ICV	200/100	40	8.0	7.96	1.0/0.5

Note: The surrogate is typically added independently at a final concentration of 10 ug/ml. This is because this working standard is also used as the LCS and MS spike solution.

10.6.3 LCS/MS Spike Solution

The LCS and MS spike solution is generally prepared with the same secondary source of standard used in the preparation of the ICV. The ICV and LCS may be used interchangeably for aqueous samples and is typically prepared using the 200/100 ug/ml primary dilution standard.

10.6.4 Second Source Check

Prior to spiking samples, the second source standard should be analyzed to determine the recovery of target analytes. It is recommended that this check be done whenever a new source of LCS/MS or surrogate solution is prepared.

11.0 Sample Collection, Preservation, and Storage

11.1 Sample Collection

11.1.1 The volume or weight collected should be sufficient to ensure a representative sample, and allow for replicate analyses such as the MS.

11.1.1.1 Aqueous samples typically require a minimum sample volume of 2 x 40 ml VOA vials.

11.1.1.2 Soil samples typically require a 4 to 8 oz sample container to ensure a minimum sample weight was collected.

11.1.2 Samples may be collected in either glass or plastic containers.

11.2 Sample Preservation

11.2.1 Samples should not be chemically preserved for this procedure.

11.3 Sample Storage

11.3.1 Samples should be refrigerated to ≤6°C to minimize sample decomposition during transportation and storage.

11.4 Sample Holding Tim

11.4.1 Samples must be analyzed within 28 days of sample collection.

Sample Preservation, Storage and Holding Time Table
Table E.64-16

Analyte	Matrix	Collection Volume	Preservation	Holding Time
Organic Acids	Water	2 x 40mL VOA vial	Cool ≤6°C	28 days
	Soil	4 or 8 oz soil jar	Cool ≤6°C	28 days to extract and analyze

12.0 Quality Control

12.1 Initial Demonstration of Capability (IDC)

12.1.1 Definition - An IDC study is conducted and used to characterize instrument and sample preparation performance.

12.1.2 Purpose - An IDC study is conducted by the analytical chemist, analyzing samples to demonstrate the generation of acceptable accuracy and precision with each combination of sample preparation and determinative method.

12.1.3 Frequency - The IDC is conduced annually and repeated when new staff is trained or a significant change in instrumentation is made.

12.1.4 Procedure - A QC standard, independent of the initial calibration standard, is used to spike four replicate LCSs in a clean matrix. Since the IDC is used to evaluate the performance of the total analytical process, the reference samples must be handled in the same manner as actual samples.

12.1.5 Acceptance Criteria - The average recovery, standard deviation, and relative standard deviation determined from these four replicates are used to evaluate accuracy and precision of this analytical and sample preparation procedure. IDC spike recoveries are compared to established acceptance criteria.

2) Clarification: Statistically derived laboratory criteria are used to evaluate the IDC.

12.1.6 Corrective Action

12.1.6.1 If accuracy meets the acceptance criteria, system performance is acceptable and sample analysis may begin.

12.1.6.2 If it fails, the system performance is unacceptable. In this event, correct the problem and repeat the test. Repeated failure, however, will confirm a general problem with the measurement system.

12.2 Method Blank (MB)

12.2.1 Definition - A sample of a matrix similar to the batch of associated samples that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the preparation and analytical procedures, and in which no target analytes or interferences are present at concentrations that may impact the analytical sample results.

12.2.2 Purpose - The method blank is typically analyzed immediately following the calibration verification standard to ensure there is no carryover from the standard and to ensure target analytes or other potentially interfering analytes are not introduced through the sample preparation procedure.

12.2.3 Frequency

12.2.3.1 A MB is prepared and analyzed with each batch of up to 20 samples prepared at the same time, by the same procedure.

12.2.3.2 When new reagents or chemicals are received, a method blank should be prepared and monitored for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation if the source shows no prior problems. However, if reagents are changed during a preparatory batch, separate blanks should be prepared and monitored for each set of reagents.

12.2.4 Procedure

12.2.4.1 Aqueous - The MB is prepared by measuring [redacted]

12.2.4.2 Solid - The MB is prepared by weighing a [redacted].

12.2.5 Acceptance Criteria - The method blank should be less than the reporting limit to be acceptable.

12.2.6 Corrective Action - If the target analytes or interfering non-target analytes are detected above the reporting limit, the method blank is judged to be out-of-control and the source of the problem is identified and corrected. Samples analyzed along with a method blank determined to be out-of-control are considered suspect for that particular analyte. The following actions may be helpful in assessing this situation.

12.2.6.1 If the method blank does not meet the acceptance criteria, reanalyze the method blank.

12.2.6.2 If the method blank still does not meet the acceptance criteria, locate and correct the problem. Once the problem has been corrected, reprepare and reanalyze all samples associated with that blank.

12.2.6.3 If the method blank exceeds the criteria, but the samples are all below the reporting limit, the sample data may be used despite the contamination in the method blank.

12.2.6.4 If the repreparation or reanalysis is not practical, the data user should be provided with the method blank results and the data footnoted appropriately.

12.3 Laboratory Control Sample (LCS)

12.3.1 Definition - A sample matrix, free from the analytes of interest, spiked with a verified known amount of the target analytes or a material containing a known and verified amount of the target analytes.

12.3.2 Purpose - The laboratory control sample is used to evaluate the performance of the total analytical system, including all preparation and analysis steps.

12.3.3 Frequency - The laboratory control sample is prepared and analyzed with each batch of up to 20 samples or 5% of the total number of samples prepared at the same time, by the same procedure.

12.3.4 Procedure

12.3.4.1 Aqueous - The LCS is typically prepared by measuring a [redacted]

[redacted]

12.3.4.2 Solid - The LCS is typically prepared by weighing a [redacted]

12.3.5 Acceptance Criteria - The result of the laboratory control sample is evaluated to assess accuracy and is expressed as percent recovery (%R) which allows for the comparison to established acceptance criteria. These calculations are documented on method worksheets and/or on LIMs generated summary LCS reports. LCS results are compared to acceptance criteria.

3) Clarification: Statistically derived laboratory criteria are used to evaluate the LCS.

12.3.6 Corrective Action - An LCS that is determined to be within the criteria effectively establishes the analytical system is in control and validates system performance for the samples in the associated batch. If the recovery falls outside of the acceptance window, that analyte is judged to be out-of-control and the source of the problem is identified and corrected. Samples analyzed along with a laboratory control sample determined to be out-of-control are considered suspect for that particular analyte. The following actions may be helpful in assessing this situation.

12.3.6.1 If the laboratory control sample does not meet the acceptance criteria, reanalyze the laboratory control sample.

12.3.6.2 If the LCS still does not meet the acceptance criteria, than locate and correct the problem. Once the problem has been corrected, reprepare and reanalyze the samples associated with that spike.

12.3.6.3 If the repreparation or reanalysis is not practical, the data user should be provided with the laboratory control sample results and the data footnoted appropriately.

12.4 Matrix Spike (MS)

12.4.1 Definition - Matrix spike samples are prepared by adding a known mass of the target analytes to a specified amount of a field sample for which an independent estimate of the target analyte concentration is available.

12.4.2 Purpose - Matrix specific samples indicate the effect of the sample matrix on the precision and accuracy of the results generated using this procedure. The information from this control is sample and matrix specific and is not normally used to determine the validity of the entire batch.

12.4.3 Frequency - One sample is prepared and analyzed on a 10% frequency or one MS per 10 samples.

12.4.4 Procedure - Client samples are used as the matrix spike and are randomly chosen to ensure spiked samples are rotated through the client sample stream.

12.4.4.1 Aqueous - The MS is typically prepared by measuring a [redacted]

12.4.4.2 Solid - The MS is typically prepared by weighing a [redacted]

12.4.4.3 The MS is spiked with the same secondary source of standards and typically at the same concentration as the LCS.

12.4.5 Acceptance Criteria - The result from the matrix spike sample is evaluated to assess the accuracy in a given matrix and is expressed as percent recovery (%R) which allows for the comparison to established acceptance criteria. This calculation is documented on method worksheets and/or on LIMs generated summary MS reports. MS results are compared to acceptance criteria.

4) Clarification: Statistically derived laboratory criteria are used to evaluate the MS.

12.4.5.1 If the concentration of fortification is less than 25% of the background concentration determined in the native sample, the matrix spike recovery may be questionable and should not be used to evaluate the matrix spike.

12.4.5.2 The background concentration is first determined in a separate non-spiked sample, and the measured value in the spiked MS

is then corrected for the background concentration. Percent recovery is calculated as follows:

$$R = \frac{C_s - C}{S} X100$$

Where:

R = Percent recovery
C_s = Fortified sample concentration
C = Sample background concentration
S = Concentration of analyte spiked into the sample

12.4.6 Corrective Action

12.4.6.1 If matrix spike accuracy results are outside of the established criteria, corrective action is documented or the results are reported with the appropriate footnotes.

12.4.6.2 If the MS recoveries exhibit matrix interference and are outside the range of acceptability, the LCS is used to qualify the analytical data, i.e., the recovery problem encountered with the spiked sample is judged to be a matrix-related problem, not a system-related problem, provided both the LCS and MS were prepared in the same batch.

12.5 Matrix Spike Duplicate (MSD) and Sample Duplicate

12.5.1 Definition - A replicate intra-laboratory sample aliquot, that is either spiked in the identical fashion as the matrix spike or a non-spiked replicate split, treated and processed through the entire preparation and analytical procedure as its original sample counterpart.

12.5.2 Purpose - The result form this analysis indicates the precision of the results when compared to the original spiked or non-spiked sample counterpart for the specific sample using the selected method.

12.5.3 Frequency - Either a field duplicate, a laboratory duplicate or a duplicate MS should be prepared and analyzed at a minimum frequency of 5% of the total number of samples prepared in the batch.

12.5.3.1 If the field duplicate or laboratory duplicate is chosen for this procedure, it must contain measurable target analytes in order to establish the precision of the analytical batch.

12.5.3.2 If no samples have measurable concentrations, a second matrix spike should be employed as the duplicate.

5) Clarification: The measurement of precision is predicated on the presence of target analytes; therefore, to ensure precision can be determined, an MSD is prepared as the batch duplicate.

12.5.4 Procedure - The concentrations determined in the MS and MSD, corrected for the concentration measured in the unfortified sample, are used to assess method precision. Precision is estimated from the Relative Percent Difference (RPD) of the concentrations, not recoveries, measured in the MS/MSD pair. Relative percent difference is calculated as follows:

$$RPD = \frac{|MS - MSD|}{\left(\frac{MS + MSD}{2}\right)} X100$$

Where MS and MSD are the corrected spike concentrations.

12.5.5 Acceptance Criteria - The duplicate precision data results are compared to acceptance criteria.

6) Clarification: Statistically derived laboratory criteria are used to evaluate the RPD.

12.5.6 Corrective Action

12.5.6.1 If the duplicate precision results are outside of the established criteria, corrective action is documented or the results are reported with the appropriate footnotes.

12.5.6.2 In the event of insufficient sample being available for the MSD or duplicate preparation, precision may be determined using the LCS/LCSD.

12.6 Surrogates

12.6.1 Definition - A substance with the properties that mimics the analyte of interest and is unlikely to be found in the environmental samples.

12.6.2 Purpose - To assess the ability of the method to successfully recover specific non-target analytes from an actual sample.

12.6.2.1 Because surrogates are added to each sample in a batch, they are used to monitor recovery on a sample-specific, rather than a batch-specific basis.

12.6.2.2 Surrogates are used in conjunction with the MS/MSD to assess accuracy by measuring both surrogate and analyte recovery.

12.6.3 Frequency - Surrogate is added to all samples, method blanks, laboratory control samples and matrix spike samples. The surrogate is added directly to the calibration standards and does not need to be independently fortified. However, for the ICV, MB, LCS, MS and samples, independent surrogate fortification is required.

12.6.4 Procedure - The surrogate is typically spiked as follows:

12.6.4.1 Aqueous - The sample is prepared by [redacted]

12.6.4.2 Soil - The sample is prepared by spiking a [redacted]

12.6.5 Acceptance Criteria - Whereas the laboratory control sample is normally evaluated on a batch-specific basis, the surrogate spike is evaluated on a sample-specific basis. Surrogate recovery data taken with the information derived from the other spikes such as the LCS, MS and MSD are used to determine the bias in the analytical system. These calculations are documented on method worksheets and/or LIMS generated summary surrogate reports. Surrogate recovery results are compared to acceptance criteria. Surrogate recovery is calculated as follows:

$$\text{Recovery (\%)} = \frac{\text{Concentration found}}{\text{Concentration added}} \times 100$$

7) Clarification: Statistically derived laboratory criteria are used to evaluate the surrogate.

12.6.6 Corrective Action

12.6.6.1 If the surrogate recovery is outside the established criteria, corrective action is documented such as reextraction and/or reanalysis or the results are reported with the appropriate footnotes.

13.0 Calibration and Standardization

13.1 Initial Calibration

13.1.1 Definition - Analysis of analytical standards at different concentration points that are used to determine and calibrate the working range of the response of the analytical instrument. The graphical depiction of this relationship is often referred to as the calibration curve.

13.1.2 Purpose - To establish a calibration curve for the quantitation of the target analytes. The IC defines the working range of the instrument.

13.1.3 Frequency - In order to perform quantitative measurements, the relationship between the response of the instrument and the concentration of the target analytes must be established prior to sample analysis.

13.1.4 Procedure

13.1.4.1 Calibration Standards

13.1.4.1.1 An external calibration procedure is used for this method of analysis.

13.1.4.1.2 The IC is prepared by analyzing a minimum of five calibration standards.

13.1.4.1.3 Calibration Concentrations - See section 10 above.

13.1.4.2 Calibration Factors (CF)

13.1.4.2.1 An external standard calibration involves comparison of instrument responses from the sample to the responses from the target compounds in the calibration standards. The ratio of the detector response to the concentration of analyte in the calibration standard is defined as the calibration factor and is the slope of the curve. A constant injection volume of each calibration standard is used to calibrate the instrument. Calibration factors are determined as follows:

$$CF = \frac{\text{Concentration of the compound injected}}{\text{Peak Area of the compound in the standard}}$$

13.1.4.3 Calculate the calibration factor for each analyte at each

concentration, the average CF, the standard deviation and the Relative Standard Deviation (RSD).

13.1.4.4 Retention Time (RT) - Determine the retention time for each analyte using the retention times recorded during the IC.

13.1.4.5 Calibration Models

13.1.4.5.1 All calibration models must be continuous. A curve is continuous when it has consecutive numerical values along the function, whether increasing or decreasing without having breaks, i.e., standards cannot be randomly removed from the IC. In addition, the calibration model must also be monotonic, such that all tangent lines of the points on the calibration curve have either only positive or negative slopes, i.e. parabolic curves are not allowed.

13.1.4.5.2 The choice of choosing a specific calibration model should be made in one of two ways.

13.1.4.5.2.1 The first is to begin with the simplest approach, the linear model through zero, i.e., average calibration factor, and progress through the other calibration models until the calibration acceptance criteria are met.

13.1.4.5.2.2 The second approach is to use *priori knowledge* of the detector response to choose the calibration model.

13.1.4.5.3 Linear (non-forced zero) and non-linear calibrations cannot force the line through the origin, i.e., do not set the intercept as 0, and do not include the origin (0,0) as a calibration point.

13.1.4.5.4 The option for a non-linear calibration may be necessary to achieve low detection limits or to address specific instrumental techniques. However, it is not EPA's intent to allow non-linear calibrations to be used to compensate for detector saturation at higher concentrations or to avoid proper instrument maintenance.

13.1.4.5.5 Linear Calibrations Through Zero (Average CF)

As described above, the calibration factor is a measure of the slope of the calibration curve and assumes that the curve passes through the origin. Under ideal conditions, the calibration factors will not vary with the concentration of the standard that is injected into the instrument. In practice, some variation is to be expected. This variation is measured as the relative standard deviation.

13.1.4.5.5.1 If the RSD calculated from the CF of each IC standard is ≤20%, then the response of the instrument is considered linear and the average calibration factor can be used to determine sample results.

13.1.4.5.5.2 Linearity through zero is a statistical assumption and is not a rationale for reporting results below the calibration range demonstrated by the analysis of standards.

13.1.4.5.6 Linear Calibration Not Forced Through Zero (Least Squared (LS) Regression)

13.1.4.5.6.1 If the RSD is greater than 20%, linearity through the origin cannot be assumed. However, a linear calibration not forced through zero can be generated by using a linear regression model.

Note: At the discretion of the analyst, this approach may be used for analytes that do meet the minimum RSD limits where an average CF model could be used.

13.1.4.5.6.2 Weighting

The regression calculations attempt to minimize the sum of squares, hence the name least squared regression.

Weighting the sum of the squares may significantly improve the ability of the least

squared regression to fit the linear model of the data. The mathematics employed in least squared regression has a tendency to favor numbers of larger values over numbers of smaller values. Thus the regression curves that are generated will tend to fit points that are at the upper calibration levels better than those points at the lower calibration. To compensate for this, a weighting factor which reduces this tendency can be used such as: a) inverse concentration, or b) inverse squared concentration.

13.1.4.5.6.3 Linear Correlation Coefficient

The linear regression calculation will generate a weighted correlation coefficient (r) that is a measure of the "goodness of fit." A value of 1.00 indicates a perfect fit.

13.1.4.5.7 Non-Linear Calibration (Quadratic)

13.1.4.5.7.1 In situations where the instrument response does not follow a linear model over a sufficiently wide working range, or when the other calibration models have not met the acceptance criteria, a non-linear calibration model may be used.

13.1.4.5.7.2 Weighting

Weighting in this type of calibration model may significantly improve its accuracy.

13.1.4.5.7.3 Non-linear Coefficient of Determination

The curve fitting mathematics uses a form of least squares to minimize the coefficients of the polynomial to obtain the polynomial that best fits the data. The "goodness of fit" of curve fitting equations is evaluated by calculating the weighted Coefficient of Determination (COD). Under ideal conditions, with a "perfect fit" of the model to the data,

the coefficient of determination will equal 1.00

13.1.5 Acceptance Criteria

13.1.5.1 Number of Calibration Points

A minimum of five calibration points is required to construct a calibration curve. However, the statistical consideration in developing a nonlinear calibration model requires more data than the linear model. Whereas Method 8000B requires a minimum of five standards for a linear (first order) calibration model, a quadratic (second order) model requires six standards and a third order polynomial requires seven standards.

13.1.5.2 Reporting Limit Standard

The lowest concentration standard that is analyzed during the IC must be at or below the established reporting limit. The concentration of this standard is related back to the sample concentration using sample size, dilution, and final volume. Therefore, the IC must contain at least one standard at or below the calculated reporting limit.

13.1.5.3 Working Range

13.1.5.3.1 The other concentration points define the working range of the instrument. In order to produce acceptable sample results, the response of the instrument must be within the working range established by the initial calibration.

13.1.5.3.2 Extrapolation of the calibration concentrations above or below those of the actual IC is not appropriate and may lead to significant quantitative errors regardless of calibration model chosen.

13.1.5.4 Relative Standard Deviation (RSD)

If the RSD is $\leq$20%, then the response of the instrument is considered linear and the average calibration factor can be used to determine sample results. If not than a least squared regression or a quadratic curve model must be used to construct a calibration curve.

13.1.5.5 Correlation Coefficient and Coefficient of Determination

If a linear least squared or non-linear quadratic curve model is used, the correlation coefficient or the COD must be ≥ 0.99.

13.1.6 Corrective Action

13.1.6.1 Corrective Actions Requiring No Instrument Maintenance

13.1.6.1.1 If the RSD exceeds 20%, then the following steps are recommended but not required:

13.1.6.1.1.1 If the RSD appears to be associated with a single standard, that one standard may be re-analyzed and the RSD recalculated. Replacing the standard may be necessary in some cases.

13.1.6.1.1.2 Narrow the calibration range by eliminating one or more of the calibration standards producing a narrower calibration range. If linearity can be achieved using a narrower calibration range, document the calibration linearity, and proceed with sample analysis.

Note Changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the overall sensitivity of the method.

Note: As previously noted, the method reporting limit is established by the concentration of the lowest standard analyzed during the initial calibration. Hence, if the low level standard is at the reporting limit, then narrowing the calibration range by changing the concentration of the lowest standard will, by definition, change the method reporting limit.

8) Clarification: If linearity can be achieved by either replacing an aberrant standard, or by using a narrower calibration range, then that decision must be clearly documented. If a standard is replaced, then the entire standard and all CF associated with that standard must be replaced.

13.1.6.2 Corrective Actions Requiring Instrument Maintenance

13.1.6.2.1 If the minimum RSD, correlation coefficient or coefficient of determination is not met, the system must be evaluated and corrective action taken before sample analysis begins. Possible problems include standard degradation, rotor valve contamination, contamination at the front end of the analytical column, active sites in the column or chromatographic system or degradation and/or system contamination.

13.1.6.2.2 Possible corrective actions include replacing the UV lamp or analytical column, rebuilding the pump and/or injector assembly and then repeat the initial calibration. If no source of the problem can be determined after corrective actions have been taken, a new initial calibration curve must be generated. These criteria must be met before sample analysis begins.

13.2 Initial Calibration Verification (ICV)

13.2.1 Definition - A standard obtained or prepared from a source independent of the source of standards used in the preparation of the initial calibration.

13.2.2 Purpose - To verify the accuracy of the initial calibration.

13.2.3 Frequency - Immediately after the initial calibration has been established or as required to meet data-quality needs.

13.2.4 Procedure

13.2.4.1 The ICV is prepared from a source, independent of the source of standards used for the initial calibration, at or near the middle of the calibration range.

Note: Since neat standards are used and only a single source is available, the second source must be prepared using a second set of independently prepared primary dilution standards.

13.2.5 Acceptance Criteria - If the responses are within the lab prescribed criteria of ± 30%, the initial calibration is considered valid.

13.2.6 Corrective Action - If the response is not within ±30% of the expected

response, correct the problem and rerun the second source standard. If that fails take corrective action and recalibrate the instrument or footnote the data appropriately.

13.3 Calibration Verification (CV)

13.3.1 Definition - A standard solution used to evaluate the performance of the instrument system with respect to a defined set of criteria.

13.3.2 Purpose - To verify the instrument response is reliable, and has not changed significantly from the current initial calibration curve.

13.3.3 Frequency - The initial calibration is verified at the beginning, once every 20 samples, recommended after every 10 samples, and at the end of the analytical sequence.

13.3.4 Procedure - Prepare CV standards, using the same source of standards used to prepare the IC, at varying concentrations.

13.3.5 Acceptance Criteria - If the responses are within the lab prescribed criteria of ± 20%, the initial calibration is considered valid.

13.3.6 Corrective Action

13.3.6.1 Response Check

13.3.6.1.1 If a CV fails to meet the QC criteria, then analyze a second CV. If the response is still not within the acceptance criteria, then a new IC must be prepared or the data flagged appropriately.

13.3.6.1.2 The results of these bracketing standards must meet the CV criteria to be completely acceptable. When a CV standard fails to meet the QC criteria, all samples that were injected after the last standard that last met the QC criteria may be evaluated as follows:

13.3.6.1.2.1 If the standard exhibits a response that is above the acceptance limit and the analyte was not detected in any of the samples in that set of bracketed samples, then the samples do not need to be reanalyzed, as the standard has demonstrated that the analyte would have been detected if it were present.

13.3.6.1.2.2 In contrast, if the standard exhibits a response for an analyte that is above the acceptance limits, and the analyte was detected in a sample extract, then reanalysis is necessary to ensure adequate sample quantitation.

13.3.6.1.2.3 If an analyte was not detected in the sample and the standard response is greater than the acceptance limit below the initial calibration then reanalysis is necessary to ensure the detector response has not deteriorated to a point where it would not have been detected if the analyte was present. If samples cannot be reanalyzed, flag the data appropriately.

14.0 Procedure

14.1 HPLC Pump Start Up

14.1.1 [redacted]

14.1.1.1 [redacted]

14.1.1.2 [redacted]

Note: Ensure the stop time of the auto-sampler is exactly the same stop time established on the quaternary pump.

Note: These are suggested instrument conditions and may be modified to enhance analyte or instrument conditions.

14.1.2 [redacted]

14.1.3 [redacted]

14.1.4 [redacted]

14.1.5 [redacted]

14.2 UV Start-up

14.2.1 [redacted]

14.2.2 [redacted]

14.3 Sample Preparation

14.3.1 Water

14.3.1.1 [redacted]

14.3.1.2 [redacted]

14.3.1.3 [redacted]

14.3.2 Soil

14.3.2.1 [redacted]

14.3.2.2 [redacted]

14.3.2.3 [redacted]

14.3.2.4 [redacted]

14.3.2.5 [redacted]

14.4 Analyze and evaluate the IC as described in section 13.1.

14.5 Analyze and evaluate the ICV as described in section 13.2.

14.6 Analyze and evaluate the MB as described in section 12.2.

14.7 Analyze and evaluate the LCS as described in section 12.3.

14.8 Analyze and evaluate the MS as described in section 12.4.

14.9 Analyze and evaluate the MSD as described in section 12.5.

14.10 Analyze and evaluate sample results.

14.11 Dilute and re-analyze samples that are beyond the upper calibration range.

14.12 Analyze and evaluate the ending CV as described in Section 13.3

15.0 Calculations

15.1 The quantitated values are reported in mg/L for aqueous samples and mg/kg for solid samples.

15.2 Quantitation

15.2.1 Water Samples - Procedural standards are used for standards; therefore, data calculations for water samples require no additional data manipulation other than for those samples which require sample dilutions.

15.2.2 Soil Samples - Soil samples need to be corrected for concentration using the same procedural calibration standards as used for water samples.

For example: 0.50mg/L procedural concentration

$$= \frac{0.50ug}{mL} \times \frac{20mL\ extract}{10g\ sample} = \frac{1.0\ ug}{g} \text{ or } \frac{1.0mg}{Kg}$$

15.3 Compound Identification

Tentative identification of an analyte occurs when a peak from a sample extract falls within the calculated retention time window of a target analyte. The tentative identification should be confirmed by sample spiking.

15.3.1 Retention Time (RT)

15.3.1.1 Retention time windows are crucial to the identification of target analytes. Calibration verification standards that bracket the samples are used in the determination of a retention time window.

15.3.1.2 Record the retention time for each analyte in the initial calibration to three decimal places (e.g., 0.003). Calculate the average and standard deviation for each analytes.

15.3.1.3 If the standard deviation is 0.000, then use the standard deviation of an analyte close in RT or use a suggest default window of ±0.05 to 0.25 minutes. The retention time defaults vary by analyte, e.g., DMPT should have a default of 0.05 and MCBSA should have a default of 0.25 minutes. The width of the RT window of each analyte is typically defined as ±3 times the SD from the mean absolute retention time established during that sequence.

15.4 Confirmation

15.4.1 Most established EPA methods require the use of a confirmation column or other confirmatory technique when reporting data from a non-selective detector. The UV detector would generally be considered as a non-selective detector, however, it is selective [redacted] wavelength for these compounds, but does not completely satisfy the confirmation requirements of most methods.

15.4.2 There are essentially five possible confirmation techniques when using HPLC methods of analysis: 1) a confirmation column, 2) changing the column flow rate, 3) changing the mobile phase eluent strength and/or changing the gradient proportioning sequence, 4) the use of an alternate detector and 5) sample spiking.

15.4.2.1 These have all been evaluated with varying degrees of success and drawbacks for each one. The most promising is the use of an alternate detector. The obvious choice would be the HPLC-DAD (Diode Array Detector). Essentially the DAD can simultaneously scan the UV/VIS spectra from approximately 160nm to 800nms. Compounds which have a chromophoric absorbing electron system may exhibit a number of wavelengths with maxima and minima absorption frequencies which can be measured. Therefore, compounds have somewhat unique UV spectra and can be positively identified in the presence of other interfering compounds which do not exhibit the same unique spectra. The drawback

with this detector is its absolute sensitivity. Generally speaking, this detector is 1 to 2 orders of magnitude less sensitive than the single wavelength scanning UV detector.

15.4.3 Our established confirmation procedure is sample spiking. Samples are spiked with target analytes at the typical MS spike level and evaluated for confirmation.

Note: There should be no observable peak broadening or peak shouldering on the matrix spike sample. Peak shouldering would indicate the compound in the original native sample was not a target analyte and if reported would more than likely be reported as a false positive.

16.0 Method Performance

16.1 In-house derived method performance data is used to calculate accuracy and precision. No other data exists for the evaluation of this procedure.

17.0 Pollution Prevention

17.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice.

17.1 A minor amount of reagents, phosphoric acid and methanol, are used in this method. The only other chemicals used in this method are the occasional use of neat materials used in the preparation of standards and the mobile phase. All are used in extremely small amounts and pose no threat to the environment.

18.0 Data Assessment and Acceptance Criteria for Quality Control Measures

18.1 Table E.64-17, Summary of Calibration Procedures.

18.2 Table E.64-18, Summary of QC Procedures.

19.0 Corrective Actions for Out-of-Control Data

19.1 Failed Instrument Parameters

Repeat the test. If repeat failure occurs, locate and correct the source of the problem and repeat the test. For specifics see Table E.64-17.

19.2 Failed QC Parameters

Repeat the test. If repeat failure occurs, locate and correct the source of the problem. Reprocess and analyze any samples during the out-of-control condition or footnote the data appropriately. For specifics see Table E.64-18.

20.0 Contingencies for Handling Out-of-Control or Unacceptable Data

20.1 Failed Instrument/QC Parameters

If upon reprocessing and reanalysis, the corrective action fails to solve the problem perform the following:

- Footnote the data accordingly,
- Resample and/or reanalyze samples after the instrument has been corrected,
- Send samples to another accredited laboratory for analysis, and/or,
- Upgrade the instrument failure to a field engineer for service.

21.0 Waste Management

21.1 Reference Alpha Analytical's Sample Waste SOP.

Approved By: _____ Date: May, 2013

Walter J. Hinchman
QA Officer

SUMMARY OF CALIBRATION PROCEDURES FOR ORGANIC ACIDS
TABLE E.64-17

METHOD	PARAMETER	MINIMUM FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Organic Acids	Initial Demonstration of Capability (IDC)	Once per analyst and annually.	Prepare and analyze four replicate LCSs. IDCs are evaluated against in-house established criteria.	If the analyte fails, correct the source of the problem and repeat the test.
	Initial Calibration (IC)	A minimum of five calibration points. Prepare ICprior to analysis.	If RSD is ≤20% linearity through the origin is assumed and average CF is used. If the RSD is >20% and correlation coefficient is ≥ 0.99 then linear calibration (LS) not forced through zero is acceptable. Alternatively, prepare a calibration curve with a coefficient of determination ≥0.99.	Correct the problem and repeat the initial calibration.
	Initial Calibration Verification (ICV)	Immediately after the IC has been established.	Response of the ICVstandard should be ± 30% of the expected value.	Repeat the test. If repeat failure occurs correct the problem and reanalyze the ICV or recalibrate.
	Calibration Verification (CV)	Verify the IC at the beginning, after every 20 (10 recommended) and at the end of the analytical sequence.	Response of the CV standard should be ±20% of the expected value.	Repeat the test. If repeat failure occurs recalibrate. Samples analyzed after the criteria was exceeded should be reanalyzed or footnote the data accordingly.
	Retention Time (RT)	Each IC and CV over the course of the day.	RT window established at ± 3 times the standard deviation centered around the mean.	If analytes are outside the window recheck and/or recalculate window
	Stock Standard Expiration	Two years when stored at ≤6°C.	Not specified.	If comparison to second source standard indicates degradation, replace standards.
	Working Standard Expiration	Two years when stored at ≤6°C.	Not specified.	If comparison to second source standard indicates degradation, replace standards.

SUMMARY OF QC PROCEDURES FOR ORGANIC ACIDS
TABLE E.64-18

METHOD	PARAMETER	MINIMUM FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Organic Acids	Method Blank (MB)	One MB with each batch of 20 samples or less.	No analytes above the reporting limit.	Determine the source of the contamination and eliminate interferences before proceeding or footnote the data accordingly.
	Laboratory Control Sample (LCS)	Analyze one LCS with each batch of 20 saples or a 5% frequency. Note: Aqueous LCS and ICV may be used interchangeably.	Compare results to laboratory established limits.	Repeat the test. If repeat failure occurs, locate and correct the source of the problem and/or footnote the data accordingly.
	Matrix Spike (MS)	Analyze one MS with each batch of 10 samples or a MS/MSD pair at a 5% frequency.	Compare results to laboratory established limits.	If % recovery fails and the LCS is acceptable, problem is judged to be matrix related. Footnote the data accordingly.
	Surrogate	Add surrogate to all standards, QC samples and field samples.	Compare results to laboratory established limits.	Check for errors. If necessary, rerun extract. If extract still exceeds limits, footnote the data accordingly.
	Preservation and Storage Conditions	All samples and soil extracts.	Cool to ≤6° C.	If samples are not correctly stored footnote the data accordingly.
	Holding Time	All samples and soil extracts.	28 days.	If samples are received or analyzed outside of hold time footnote the data accordingly.

Corrective Action Report
Organic Acids by HPLC

Batch: _____ Analyst: _____ Date: _____ Instrument ID: _____

Directions: Items are checked if a corrective action or footnotes are required.

QC Checks	Acceptance Criteria	Typical Review Procedures	QC Review	CA closure
Initial Calibration	Method acceptance criteria	Review prep logs for errors		
ICV Standard	± 30% of true value	Determine if PM is required		
CV Standard	± 20% of true value	Review for the use of expired standards		

Corrective Actions:
1) Recalculate IC; 2) Prepare fresh standards; 3) Re-calibrate the instrument; 4) Perform PM; 5) Re-analyze samples; 6) Take measures to eliminate sources of contamination.

QC Checks	Acceptance Criteria	Typical Review Procedures	QC Review	CA closure
Method Blank	Less than R.L.	Verify Reagent / water source		

Corrective Actions:
1) Review data with respect to the reported contamination levels. If sample concentrations are near the reported blank levels, then re-extract associated samples or resample if possible;
2) If sample concentrations are significantly higher than blanks, or contaminants are not detected in the sample, then footnote and report the sample data and concentrations in the blank "B",
3) Take measures to eliminate future problems such as discarding reagents, revising protocols, performing preventative maintenance, or changing the use of interfering chemicals.

QC Checks	Acceptance Criteria	Typical Review Procedures	QC Review	CA closure
LCS	Lab derived limits	Review prep log and recheck calculations		
LCS Dup	Lab derived limits	Review prep log and recheck calculations		
Matrix Spike	Lab derived limits	Review prep log and recheck calculations		
Matrix Spike Dup	Lab derived limits	Review prep log and recheck calculations		

Corrective Actions:
1) Take measures to eliminate contamination problems; reprocess or re-extract samples, and re-analyze as necessary;
2) Perform required maintenance and/or revise PM schedule;
3) Review preparation, calculations, and record keeping to determine if additional training or more stringent protocols are required; and,
4) If the sample matrix produces consistently unacceptable recoveries, and none of the sources discussed above are responsible for the problem, then the sample should be re-extracted and re-analyzed. If re-analysis produces the same results, then the associated samples should be reported with a footnote to qualify the results.

QC Checks	Acceptance Criteria	Typical Review Procedures	QC Review	CA closure
Sample re-extraction	Lab limits	review prep and ext. logs for errors		

Comment: _____

Appendix A Data Quality Objectives

A1 Generation of Control Limits

A1.1 LCS, MS and surrogate recovery data was compiled for both water and soil matrtices. Statistical analysis was performed on those data sets to generate control limits.

A1.2 Control limits were set at three standard deviations around the mean for all compounds.

Note: EPA MICE has established the use of a ±30% window eliminating the need to statistically calculate these values.

A1.2.1 LCS Control Limits

Limits tighter than ±30% were raised to ±30% from the true value. The lower control limit was then raised to10% for those analytes in which three standard deviations fall below that level.

A1.2.2 MS Control Limits

Limits tighter than ±30% were raised to ±30% from the true value. The lower control limit was then raised to5% for those analytes in which three standard deviations fall below that level.

A1.2.3 Surrogate Control Limits

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A2 In-house Method Organic Acids E.64

A2.1 Accuracy limits of acceptability are laboratory defined.

A2.2 Precision limits of acceptability are laboratory defined. This window may be established at ≤20% RPD.

Note: EPA MICE has established the use of a ≤20% RPD as a default window eliminating the need to statistically calculate this value.

Method Organic Acids E.64
Water Matrix

Analyte	LCS	MS	
	3 SD Window %	3 SD Window %	RPD %
DMPT	70-132	20-166	39
BSA	70-130	51-150	27
PA	70-130	50-154	25
DEPT	70-130	29-150	33
pCBSA	70-130	60-134	20
d-Panthenol (surrogate)	58-130		

Method Organic Acids E.64
Solid Matrix

Analyte	LCS	MS	
	3 SD Window %	3 SD Window %	RPD %
DMPT	63-134	27-151	33
BSA	70-135	60-135	20
PA	61-130	35-143	20
DEPT	63-130	51-130	20
pCBSA	70-130	56-139	20
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