Quality Assurance Project Plan for

Comparison of VOC Recoveries from Fortified Soils Using
SW-846 Methods 5021, 5032, and 5035

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by
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for
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J. Zimmerman, LM Chemistry Lead

A. Project Management

1. Project Organization

The project organization and names of responsible individuals are given in Figure 1. The Work Assignment Manager (WAM), Dr. Brian Schumacher, of the Environmental Protection Agency (EPA) Environmental Sciences Division-Las Vegas (ESD-LV), is accountable for direction and oversight of the project. He will coordinate all laboratory analytical work for this project. Lee Riddick and Mike Hiatt, both of EPA ESD-LV, will be responsible for analytical procedures, including all applicable quality control (QC) procedures, recording and reporting of laboratory activities, and observations of samples under their supervision. George Brilis, ESD-LV Quality Assurance Manager, will ensure that the project description conforms to the quality standards set by the EPA.

The Lockheed Martin (LM) Quality Assurance (QA) Representative, Vicki Ecker, will verify that the Quality Assurance Project Plan (QAPP) is comprehensively developed and implemented.

The Technical Task Lead, Dr. Marti Minnich, will be responsible for ensuring that the QAPP is implemented, that procedural documentation is regularly reviewed, that the project schedule is followed, and that deliverables meet the goals of the project. Dr. Minnich will make decisions for any necessary adjustments or clarifications to procedures during implementation. She will be responsible for all communications with the WAM, including reports of any major problems, required modifications to the QAPP, and draft and final written reports.

The LM Chemistry Lead, John Zimmerman, will be responsible for sample preparation procedures in accordance with this QAPP. He will be also responsible for providing technical input on the required laboratory procedures as specified in this QAPP. He will assist in data

management and report preparation, as needed. Mr. Zimmerman will communicate progress to the Task Lead on a weekly basis.

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│      B.A. Schumacher        │              │      G.M. Brilis         │
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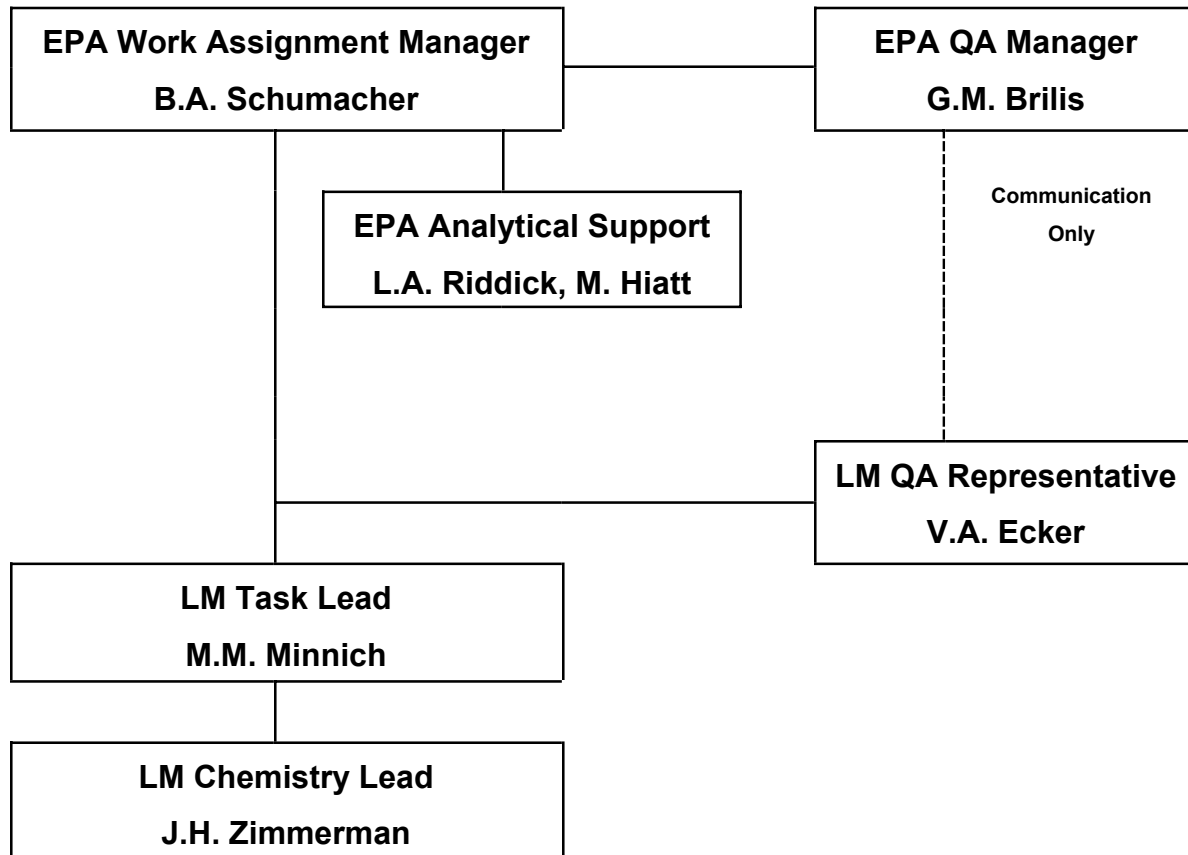
Figure 1. Project Organizational Chart

2. Problem Definition

Soils contaminated with volatile organic compounds (VOCs) can be a source of groundwater contamination if the release rate (or flux) of VOCs from the soils causes groundwater concentrations to exceed regulatory levels. Surface soil contamination may cause additional

problems by affecting plant growth, exposing children who play in the soil, or resulting in high volatile emissions from the site. It is necessary to measure the total soil-sorbed VOC concentration in addition to potential flux rates (e.g., migration to the groundwater, plant uptake, and volatile emissions) to fully evaluate the impact of VOC contamination and the remediation alternatives.

The bias, precision, and comparability of soil VOC concentrations measured using the purge-and-trap procedures of SW-846 Method 5030 (USEPA, 1992) were challenged by many researchers (Siegrist and Jenssen, 1990; Lewis et al., 1991; West et al., 1995). Four problems affecting interpretation of soil VOC measurements were identified: (1) sample homogenization in the field or laboratory promotes loss of VOCs (Lewis et al., 1991); (2) soil samples lose VOCs during shipping and storage at 4 °C (King, 1993; Hewitt, 1994; West et al., 1995); (3) laboratory subsampling procedures generate VOC losses (Siegrist and Jenssen, 1990); (4) the low-level purge-and-trap protocol is less effective than the high-level or methanol extraction protocol for numerous VOCs and certain soil types (Sawhney et al., 1988; Askari et al., 1996; Minnich et al., 1996).

The USEPA Office of Solid Waste responded to these studies by promulgating three new methods for analysis of VOCs in Update III of SW-846 (USEPA, 1997):

1)   Method 5021, "Volatile Organic Compounds in Solid Matrices Using Equilibrium Headspace Analysis";

2)   Method 5032, "Volatile Organic Compounds by Closed Vacuum Distillation with Cryogenic Condensation"; and

3)   Method 5035, "Closed-System Purge-and-Trap and Extraction for Volatile Organic Compounds in Soil and Waste Samples."

These methods are all used for extracting VOCs from the soil and introducing the analytes into a gas chromatograph (GC). Method 5035 has replaced Method 5030 for the purge-and-trap introduction of volatiles from solid matrices into a GC. The methods are commonly used in

conjunction with analysis via gas chromatography/ mass spectrometry (GC/MS) as described in SW-846 Method 8260B, although other detectors are an option.

Method 5035 (low-level) reduces VOC losses by sealing samples in VOA vials in the field; the samples are then analyzed on a purge-and-trap instrument designed to stir the samples and add water, surrogates, and internal standards without reopening the vials. Method 5035 (high-level) is a methanol extraction, followed by the laboratory step of opening the vial and transferring an aliquot of the methanol into another vial to be analyzed by purge-and-trap. As an alternative choice, EPA has issued Method 5021, a static headspace method for introduction of VOCs into a GC. This method also accepts vials that are sealed in the field and not opened prior to analysis, although it allows the option of reopening the vials in the laboratory for the addition of water before analysis.

Method 5032 is yet another option for extraction of soil VOCs. It is designed to extract not only nonpolar VOC analytes, but also the more water-soluble, polar analytes (such as ketones and methyl terbutyl ether, MTBE). Furthermore, the method is designed to extract VOCs from "messy" soils or sediments, such as soil contaminated with PCBs or an oily phase. Method 5032 has received only limited testing to date, because the vacuum distillation instrument is not readily available from a commercial source. Another limitation is that the method requires the transfer of contaminated soil into a round bottom flask as part of the procedure, a container that is not suited for field use. No data are available which compare Method 5032 with the methanol extraction of Method 5035 (high-level).

All of the methods specify instrument calibration using water-based standards. While this is probably the most practical procedure for calibration, it should be noted that the VOCs originating in soil must partition from the soil matrix to the water to simulate the water-based standards. For soils or sediments with a propensity to retain VOCs, the soil-to-water partitioning step (as in Methods 5021 and 5035 [low-level]) is likely to be incomplete, generating data biased below the true concentration. Method 5035 (low-level) is expected to offer a somewhat more thorough extraction than Method 5021 because it utilizes an agitated, 11-minute, continuous

sweep of the headspace rather a static headspace observation. A more nearly complete extraction is expected with either Method 5035 (high-level) or Method 5032 because the partitioning involves a solvent extraction (methanol) or is driven by vacuum distillation (soil-to-air), respectively. None of the methods measures the retention of VOCs by soils directly, but soils that retain VOCs would exhibit the greatest difference in concentration between replicate samples analyzed by a water extraction method versus one of the more rigorous extraction methods.

To conduct a tenable comparison, procedural differences that might produce artifacts in the study must be resolved. The methods have a number of differences in the sample collection, transfer, and handling procedures. For example,

1. Methods 5021 and 5035 (low-level) recommend acid preservation. The acid preservation step is now understood to be unusable if the sample is calcareous or of high pH; formal discussion of this problem has been issued with respect to Method 5035 (USEPA, 1998).

2. The method-specific requirements for opening vials prior to analysis vary, creating unpredictable additional vapor losses. Samples collected for Method 5021 may be opened in the laboratory for addition of the matrix modifying solution (MMS). Method 5032 includes a mandatory soil transfer step in the laboratory. Low-level Method 5035 soils remain sealed until analysis unless the option of an EnCore® sampler is selected, which results in a simple, plug-push laboratory transfer step. Samples collected for high-level Method 5035 include a transfer of the methanol extract prior to analysis, and may also have the additional plug-push soil transfer in the laboratory if an EnCore® sampler is selected.

Given these differences, a variety of soil types and compounds must to tested to insure an equitable and complete comparison. Uniform laboratory replicates, both with respect to contaminant concentrations and sample homogeneity, are critical to the endeavor. The sample handling steps are integral to the methods and must be carried out as described, but as quickly as possible to minimize the potential for VOC losses. The laboratory test will not take into account all factors that could affect field samples, but will be influenced most by differences in

extractability and laboratory handling steps among the methods. The results are intended to demonstrate which methods are best suited for each of the soil types and classes of compounds.

3. Project Description

The objective of this study is to compare the recoveries of VOCs from soils by SW-846 Methods 5021, 5032, and 5035. All samples will be analyzed by SW-846 Method 8260 to isolate the effect of each sample introduction method. Two modifications of Method 5035 will also be included in the study, the high-level procedure (methanol extraction) and the low-level procedure without the stirring bar. Soil batches will be fortified at two concentrations, 40 ng/g and 400 ng/g, to test for an effect of VOC concentration on the recoveries. The Method 5035 low-level, unstirred procedure will be included at the 40 ng/g concentration only and the Method 5035 high-level procedure will be included with only the 400 ng/g concentration. Seven replicates of five soils at each concentration will be prepared for analysis by each of the methods. This will generate 70 samples per VOC method plus 35 samples for analysis by high-level Method 5035 and 35 samples for low-level Method 5035 unstirred, totaling 280 samples in all.

Dry, fortified soil will be used in the study to provide uniform laboratory replicates (Minnich et al, 1996). The inclusion of five soils, of varying pH and residual contamination levels, will survey the effect of soil factors on compound extractability and recovery. One of the soils will have a high back-ground contamination of petroleum residues (Bunker C oil).

Three types of VOCs will be included in the study to examine the effect of each extraction technique on the recovery of chemically/physically dissimilar compounds. The fortification compounds will include two chlorinated solvents, two gasoline contaminates, and two polar solvents. The number of target analytes will be limited to insure adequate sorption of all compounds on the dry soil.

Preparation of the fortified soil samples will be the responsibility of LM, and sample analysis will be conducted by the EPA. Critical measurements include the concentrations of soil VOCs as determined by each of the methods. Ancillary data to characterize soil properties (i.e., pH, organic carbon content, and particle size distribution) have been measured during previous studies or will be determined under the direction of the WAM. These data will be used in the interpretation of results.

The schedule for initiating this project will be set by the WAM. Initiation is contingent upon the availability of the analytical instruments and analysts. Once the study is underway, each soil, fortified at two levels, will be sampled and analyzed before the next soil is prepared, constituting one "batch". Using 7 replicates for each soil/fortification level, 14 samples are to be analyzed by each method in a single batch. Ideally, five batches will require no more than 5 weeks to prepare and analyze. However the three analytical systems must be running simultaneously, and any instrument difficulties in one system will delay sample throughput for the experiment as a whole. A draft report of the study will be completed by LM within 4 weeks of receipt of all data, or as requested by the WAM.

4. Data Quality Objectives

To meet the project objectives, the performance of the GC/MS analytical systems must be stable and comparable so that the sample extraction/introduction techniques may be fairly evaluated. Quality objectives for the overall project are discussed below, while instrument/measurement quality objectives (MQOs) for the analyses of VOC concentrations in soil are addressed in Section 4.2. Quality control samples, calculation of QC results, and acceptance criteria are discussed in Section 8.

4.1 Project Quality Objectives

The VOC concentration data produced by each of the sample introduction methods will be measured using GC/MS systems and conditions which are as close to identical as practical. Quality control analyses are included in many forms to insure that inconsistencies originating from instrument drift, contamination, or other laboratory problems are identified, and in so far as possible, to quantify the overall uncertainty in the data sets.

In each of the methods under study, surrogate and internal standard compounds are added to the sample just prior to analysis. Recoveries will be used to identify anomalous problems in each sample extraction/introduction/analytical system which could impact the soil VOC results. The stability (i.e, precision) of each sample introduction system can also be monitored by calculating the relative standard deviation (%RSD) of compound recoveries on the analytical system.

Representativeness is defined as "the degree to which the data accurately and precisely represent a characteristic of a parameter, variation of a property, a process characteristic, or an operation condition" (Stanley and Verner, 1985). Representativeness in this set of experiments is the degree to which the data accurately and precisely represent the fortified soil concentrations. Replicate samples within a method will reflect the method precision and the sampling representativeness. Any differences in concentration that emerge among the sample introduction methods will not be taken as inherent differences in representativeness or bias in the methods.

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another (Stanley and Verner, 1985). The objective of this project is to provide a data set that directly compares the sample extraction/introduction methods for soil VOC analysis. The data comparability between these procedures will be maximized because: (1) highly reproducible soil replicates will be run by each method, and (2) there will be strict adherence to analytical QC procedures, including the use of blanks, internal standards, surrogates, and continuing calibration standards. The data reporting units for these studies will be ng on-column for raw data and ng/g dry soil for report data.

4.2 Measurement Quality Objectives

Precision for each VOC on each extraction/introduction system (purge-and-trap, static headspace, and vacuum distillation) will be expressed as the percent difference (%D) between ongoing calibration standard responses and the initial calibration response. The MQO for precision will be to achieve an %D ≤ 15% between initial and ongoing calibration standards.

The instrument detection limit (IDL) is the lowest concentration of an analyte that the measurement system can consistently detect and/or measure. The IDL is an expression of the precision of the analytical systems in detecting each analyte in seven samples identically spiked at a low concentration. The project MQO is an IDL of 20 ng on-column for each analyte on all analytical systems.

Bias in each analytical system will be determined by comparing the VOC concentrations from the analysis of a QC check standard (a certified, second-source standard) relative to the initial calibration curve compound values. A second-source standard will be analyzed for each initial calibration curve. An initial calibration curve will be analyzed at the beginning of the project and repeated as needed based on continuing calibration standard results. The MQO for bias will be a %R of 100 ± 20% of the QC standard nominal concentration.

Completeness relates the proportion of valid data collected to the total number of anticipated analyses. A valid datum will be a measurement of any analyte in this study that is within the acceptable criteria for instrument calibration, detection limits, internal standard and surrogate recovery, and blanks for that analyte. The completeness goal is 90% of all expected measurements as valid measurements.

5. Documentation and Records

All soil VOC concentration data will be generated in electronic and hard copy formats via the instrument-associated software. All data will be transferred to electronic spreadsheets for analysis and presentation. If the WAM directs LM to prepare a QA report and/or draft manuscript, the WAM will provide all project analytical data in electronic and hard copy formats. The records of the study will be maintained by LM for two years after the final report is accepted and then transferred to the WAM for storage. If the WAM prepares the draft manuscript, copies of all records of the study in the custody of LM will be supplied to the WAM.

B. Data Acquisition

6. Experimental Design

6.1 Materials

Five soils of varying properties have been selected for this study (Table 1). Data missing in Table 1 will be determined under the direction of the WAM during the course of this study. All soils will be air-dried and sieved to retain the 2-mm or less size fractions. Each soil will be dried in a desiccator for a minimum of 2 days just prior to fortification.

Six target analytes will be included in this study: toluene, ethylbenzene, trichloroethene (TCE), tetrachloroethene (PCE), 2-butanone (also known as methyl ethyl ketone or MEK), and methyl terbutyl ether (MTBE). Selected physicochemical parameters of the target compounds are listed in Table 2.

Table 1. Characteristics of the Study Soils

Soil Designation	horizon	sand(%)	silt (%)	clay (%)	organic carbon (%)	pH (0.01 M CaCl$_2$)
Hayesville	B	46	22	32	0.2	4.4
Charleston	A	61	31	8	3.8	7.3
New England A	A	47	48	5	4.2	4.4
New England C	C	96	3.5	0.5	0.12	4.8
Bunker C contaminated	na[a]	TBD[b]	TBD	TBD	TBD	TBD

a– not applicable; b–to be determined

Table 2. Chemical Properties of Study VOCs

Compound	m.w. (g/mole)	density (g/mL)	solubility (mg/L, 25 ºC)	vapor pressure (mm Hg, 25 ºC)	Henry's law constant atm-m^3/mole	log K$_{ow}$[a]
toluene	92.13	0.867	534.8[c]	28.4[c]	5.94 x 10^{-3}	2.73[c]
ethylbenzene	106.16	0.867	161[b]	9.5[b]	8.44 x 10^{-3}	3.15[b]
tetrachloroethene (PCE)	165.82	1.623	150.3[c]	18.5[c]	1.49 x 10^{-2}	3.40[c]
trichloroethene (TCE)	131.40	1.464	1100[c]	69.0[c]	1.02 x 10^{-2}	2.42[c]
methyl ethyl ketone (MEK)	72.10	0.805	239,000	90.6	1.05 x 10^{-5}	0.29
Methyl tertiary butyl ether (MTBE)	88.14	0.74	48,000	313 torr @ 30 ºC	5.5 x 10^{-4d}	1.24[d]

a- log octanol water partition coefficient; b- Howard, 1989;   c- Howard, 1990;
d-www.epa.gov/opptintr/chemfact/s_mtbe.txt

6.2 Sample Preparation Procedures

Desiccator-dried soil will be divided into two batches for fortification with neat standards at two concentrations, 40 and 400 ng/g. Soil (500 g) will be placed in unused 1-gal paint cans and standards will be added as shown in Table 3. The can of fortified soil will then be sealed and tumbled end-over-end for 24 hr. After tumbling the cans will be chilled at 4 °C for at least 24 hr prior to sampling.

Precleaned 40-mL glass vials with Teflon®-lined, septum-sealed screw tops (VOA vials) will be used for Methods 5035 and 5032, and clean 22-mL headspace vials with crimp-sealed, Teflon®-lined, butyl rubber septa will be used for Method 5021. Vials will be labeled and the solutions added into the vials (MMS or methanol, as appropriate) prior to the addition of soil. The acid preservation recommended in Method 5035 (1 g of $NaHSO_4$ per 5 g soil) will not be used because: a) sample analysis is expected to be completed within 5 days, and b) acid cannot be added to calcareous soils. The MMS for Method 5021 will be customized to include only the salt (180 g NaCl per 500 mL) without the acid for the same reasons given for the variation in Method 5035.

Table 3. Preparation of Fortified Soil

Compound	μL of neat compound added to 500 g soil	
	40 ng/g	400 ng/g
toluene	0.02	0.23
ethylbenzene	0.02	0.23
PCE	0.01	0.12
TCE	0.01	0.14
MEK	0.02	0.25
MTBE	0.03	0.27

The fortified soil will be dispensed using glass weighing funnels to quickly parcel out an approximate 5-g or 2-g quantity. Replicate vials for each method will be prepared in rounds to minimize potential bias caused by volatilization during the transfer of the fortified soil. Round 1 starts with the addition of the fortified soil samples to a Method 5021 vial, followed by the addition of fortified soil samples to the other method vials in the order given below. Round 2 starts with a Method 5032 vial, and so on until all seven replicates have been prepared. The procedures for preparing the samples for each method are as follows:

Method 5021 - An aliquot (10 mL) of MMS is added to a 22-mL headspace vial and the vial weight is recorded. A sample of the fortified soil (5 g of 40 ng/g or 2 g of 400 ng/g) is placed into the vial. The vial is crimp-sealed, weighed, and the weight recorded.

Method 5032 - A sample of the fortified soil (5 g of 40 ng/g or 2 g of 400 ng/g) is added to a 40-mL VOA vial. The vial is then sealed, weighed, and the weight recorded.

Method 5035 - A stir bar is added to a 40-mL VOA vial and the vial weight is recorded. A sample of fortified soil (5 g from the 40 ng/g or 2 g from the 400 ng/g) is added to the vial. The vial is sealed, weighed, and the weight recorded.

Method 5035 unstirred - The same as above except that no stir bar is added and no samples are prepared from the 400 ng/g soil.

Method 5035 high-level - An aliquot (2-mL) of methanol is added to a 40-mL VOA vial. A sample of fortified soil (2 g of 400 ng/g) is added to the vial. The vial is then sealed, weighed, and the weight recorded. A 100-μL subsample is removed and placed in a clean 40-mL vial just prior to analysis.

All weights will be determined to the nearest 0.01 g. Fortified soil replicates will be stored at 4ºC until analysis.

6.3 Sample Tracking

Samples will be identified by a six digit code. The soil will be designated by a two letter code, i.e., "HA" --Hayesville, "CH" --Charleston, "EA" --New England A, "EC" --New England C, and "BC" --Bunker C. The VOC concentration will be designated as "L" for 40 ng/g and "H" for 400 ng/g. Next, the preparation method will be given two (or three) digits: "21" for 5021, "32" for 5032, "35" for 5035, "35U" for 5035 unstirred, and "35M" for the high-level or methanol extraction of 5035. Finally, the replicate number will be assigned. For instance, "HAH353" would represent Hayesville soil, fortified at 400 ng/g, to be extracted by Method 5035, replicate 3 and "NCH35M2" would be the New England C soil, fortified at 400 ng/g, extracted by Method 5035 high-level, replicate 2.

6.4 Experimental Assumptions

The analytical system will be held as consistent as possible to isolate the effect of the extraction procedures. There is likely to be no one "best" sample extraction/introduction method for all compounds and soil types. Variations in compound activity and soil parameters may affect the performance of the methods and some of the variability in VOC recoveries may arise from differences in sample handling factors among the methods. The "best" method(s) will be defined as the method(s) giving a statistically significant mean analyte concentration (across all matrices) that is closest to the nominal spike concentration. A multiple regression technique may be applied to determine the degree to which the soil characterization parameters are useful for predicting the appropriate method of analysis for different soil types. The limitation of this experiment is collecting a sufficient amount of data to properly evaluate the effects of soil characterization parameters on each extraction procedure.

7. Analytical Methods

Three extraction/sample introduction methods for analysis of soil VOCs will be followed: Methods 5021, 5032, and 5035 as per SW-846 (USEPA, 1997). All samples will be stored at 4 °C and analyzed within 5 days of preparation. As written, the methods allow optional steps in the procedures at many points. Specifications on the steps to be used for this study where the methods offer flexibility are given below.

Method 5021– Internal standards and surrogate compounds will be manually injected though the septum of each headspace vial just prior to analysis.

Method 5032– Dry soil will be chilled to 4°C, held for 12, hours and then quickly transferred into a round-bottom flask for analysis. Surrogates and internal standards will be added just prior to analysis as recommended in the method.

Method 5035– Water (10 mL), internal standards, and surrogate compounds will be added by the autosampler just prior to analysis. For the high-level analysis, a 100-µL aliquot of the methanol extract will be analyzed using the Method 5035 low-level soil procedure.

Samples introduced by the above methods will be analyzed by GC/MS following the procedures in EPA SW-846 Method 8260B, "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Technique" (USEPA, 1997). Instruments will be calibrated for the analytes and surrogates in the study, without regard to the other compounds listed in the method. Quality assurance/quality control (QA/QC) will follow the guidelines listed in Section 8.

8. Analytical Quality Control

The laboratory must adhere to the quality control (QC) procedures specified in SW-846 Methods 5021, 5032, 5035 and 8260 and the project-specific acceptance criteria described in this section. The method QC components are summarized in Table 4.

8.1 GC/MS Mass Calibration

A mass calibration or tune of the analytical system is performed when the system is initially set up, after the mass spectrometer has been shut down, or whenever there is a mass misassignment. Mass calibration is performed to ensure the accurate assignment of masses to ions generated in the ion volume of the mass spectrometer. Perflurotributylamine (FC43) is the compound which is used to perform the mass calibration of the instrument. The FC43 spectrum must meet the criteria presented in Appendix A. If the criteria are not met the system must be retuned or instrument maintenance must be performed until the system can meet the criteria.

Table 4. QC Sample Procedures, Acceptance Criteria, and Corrective Actions

QC Sample	Frequency	Acceptance Criteria	Corrective Action
Mass Calibration (Tune/FC43)	Initial system startup, after system shutdown, if mass misassignment occurs	See Appendix A	Perform autotune, instrument maintenance
Tune Check Standard (BFB)	Beginning of 12-hr analytical period	Ion abundance ratio, see Appendix B	Perform instrument maintenance, reanalyze, retune
Initial Calibration (IC)	Prior to initial sample analysis, and if OCCS fails	%RSD ≤ 20%	Determine problem, correct, reanalyze
Quality Control Check Standard (QCCS)	Each time a new IC is analyzed	%D ≤ 20% of IC responses	Reanalyze, check all calculations, obtain new lot or manufacturer's QCCS
Instrument Detection Limit (IDL)	Prior to sample analysis	Meet IS %R and surrogate %R. %D ≤ 20% from MQL of 20ng	Perform instrument maintenance, and/or reanalyze
Ongoing Calibration Check Standard (OCCS)	Beginning and end of each 12- hr analytical period	%D ≤ 15% of mid-point IC standard response	Reanalyze std., perform instrument maintenance, new IC, reanalyze, flag data "D"
Instrument Blank (IB)	Beginning and end of each 12- hr analytical period	Below analyte IDL or sample values ≥ 5x IB concentration	Reanalyze, perform instrument maintenance, flag data "B"
Internal Standard (IS) Recovery	Each sample, blank, and standard	%R = 50% to 200%	Reanalyze if blank, standard, or methanol trt; flag data "I"
Surrogate Recovery	Each sample, blank, and standard	%R= 100% ± 25%	Reanalyze if blank, standard, or methanol trt; flag data "S"

8.2 Tune Check Standard

Prior to the start of sample analysis and at the beginning of each 12-hr analytical period a GC/MS tune check standard is to be analyzed. The tune check standard is a solution containing the compound 4-Bromofluorobenzene (BFB) at a concentration of 25 ng. Proper tuning of the mass spectrometer is necessary to produce standardized fragmentation patterns of target and non-

target compounds. The mass spectrum produced for the BFB must meet all of the criteria in Appendix B. If the criteria are not met, maintenance must be performed and the instrument must be retuned.

8.3 Initial Calibration

An initial five-point calibration (IC) curve is generated before any samples are analyzed (Section 9). The acceptance limit of the IC curve is a %RSD of the response factors ≤ 20. If the IC curve or ongoing calibration check data are outside of the method QC requirements, the analyst must determine the source of the problem, make any necessary adjustments (to instrument, software, or standards), and recalibrate the instrument.

8.4 Quality Control Check Standard

The quality control check standard (QCCS) is analyzed immediately following every initial calibration of the instrument. The QCCS is a second-source-certified methanolic standard containing all the target analytes at a concentration of 300 ng each. The QC acceptance criteria are a %D ≤ 20% of the nominal analyte concentrations. The corrective action if the QC acceptance criteria are not achieved is to analyze a second aliquot of the QCCS; if the results still do not meet criteria, the source of the problem must be determined, corrected, the system recalibrated (if necessary), and another aliquot of the QCCS analyzed. Samples may not be analyzed until the QCCS meets the acceptance criteria.

8.5 Instrument Detection Limit

The instrument detection limit (IDL) will be determined using the standard deviation of seven replicate standards, spiked at a low concentration (≤20 ng). Each of the replicate samples are expected to meet the criteria for IS and surrogate recoveries. The anticipated IDL is 20 ng on-column for each of the target analytes.   If the actual IDL has a %D > 20% from the anticipated IDL, the analyst must determine the source of the problem, make any necessary adjustments (to

instrument, software, or standards), and rerun the IDL study. Samples can not be analyzed until the IDL study results meet the acceptance criteria.

8.6 Ongoing Calibration Check Standard

The ongoing calibration check standard (OCCS) is analyzed several times each day: 1) following the BFB and instrument blank; 2) at the end of each 12-hr analytical time period; or 3) at the end of the analysis sequence within a 12-hr analytical time period. The results of the OCCS are used to verify the stability of the instrument response. The OCCS is prepared using the same stock standard used to prepare the initial calibration standards. The QC acceptance criteria are %D ≤ 15% of the nominal values of the initial midpoint calibration standard (300ng). The corrective actions for a OCCS outside the QC acceptance criteria are: 1) analyze a second aliquot of the OCCS; 2) if the QC criteria are still not met, the reason must be determined and corrected prior to sample analysis; or 3) if one or more of the final OCCS results are out of QC acceptance limits, the corresponding analyte results for the associated batch of samples are to be flagged "D".

8.7 Instrument Blanks

Instrument blanks (IBs) consists of IS and surrogate spiked reagent water and are used to monitor sample extraction/introduction/analysis system contamination. An IB will be included at the beginning and end of each 12-hr analytical period or more often if the analyst deems necessary. If the IB at the beginning of the analysis sequence is contaminated with target analyte(s) above the analyte IDL(s), samples should not be analyzed until corrective action has been taken. If the blank at the end of an analysis sequence is contaminated with target analytes, data will be considered acceptable if the sample target analyte concentration(s) are at least five times greater than the blank concentration(s) for the offending analyte(s). If contamination can not be eliminated or the sample concentrations do not meet the aforementioned criteria, results for all samples analyzed within the same analytical batch as the contaminated blank must be flagged "B."

8.8 Internal Standards

The internal standards (IS) pentafluorobenzene, chlorobenzene-d5, and 1,4-difluorobenzene are added to every standard, blank, and sample. These compounds are used in the quantification of detected compounds to take into account changes in the mass spectrometer response during the analyses. The QC acceptance criteria are %R = 50% to 200% of the mean IC values. The corrective actions for standards and QC samples with IS recovery outside the QC acceptance criteria are: 1) analyze a second aliquot of the standard or QC sample; 2) if the QC criteria are still not met the cause must determined and corrected prior to further sample analysis. All sample data with IS recoveries outside the QC criteria are to be flagged with an "I."

8.9 Surrogates

The surrogate compounds toluene-d8, 4-bromofluorobenzene, and dibromofluoromethane are added to every standard, blank and sample. The surrogate recoveries are used to monitor the purge and GC components of the analysis system. The QC acceptance criteria are %R of 100% ± 25% of the spiked values. The corrective actions for standards or QC samples with surrogate recoveries outside of the criteria are: 1) analyze a second aliquot of the standard or QC sample; 2) if the QC criteria are still not met the cause must determined and corrected prior to further sample analysis. All sample data with surrogate recoveries outside the QC criteria are to be flagged with an "S."

8.10 QC Calculations

Precision - Precision represents the reproducibility of measurements under a given set of conditions and provides an estimate of random error (Taylor, 1987). Instrument precision will

be monitored by analyzing ongoing calibration check standards. The percent difference (%D) between an OCCS and the IC response will be calculated as follows:

$$\%D = (R1 - R2)/R1 \times 100$$

where R1 is the initial midpoint calibration standard peak area count and R2 is the subsequent or daily peak area count.

The precision of the laboratory preparation and subsampling of VOC- fortified soils is confounded with the analytical precision. It will be calculated as the relative standard deviation (RSD) of the seven replicate measurements of each soil.

$$RSD = \frac{SD_{n-1}}{mean} \times 100$$

where SD_{n-1} = standard deviation of the replicate measurements. RSDs will be calculated for each VOC in each soil by treatment. These replicates will be used to determine the sum of the analytical and soil sample preparation precision. Consistent differences (for more than one compound) in RSD values among the methods will indicate differences in method handling and analytical precision. The consistency among samples is not a QC issue, but may offer information on differences among the extraction/sample introduction methods.

Bias - Laboratory bias will be estimated by (1) the %D of the target analytes measured in the QCCS versus the midpoint standard of the IC curve, and (2) %R of the surrogates. Percent recovery (%R) of the surrogates will be calculated as follows:

$$\%R = 100\ (S/C_{sa})$$

where S is the measured concentration and C_{sa} is the nominal concentration of a given analyte in the standard or sample.

IDL - The IDL will be defined as follows:

$$IDL = 3.14 * sd$$

where *sd* is the standard deviation (n-1 degrees of freedom) for the analytical results from seven replicate low-level standards, and 3.14 is the Student's t-value for a one-sided 99% confidence level (USEPA, 1992).

9. Instrument Calibration and Frequency

The instruments will be calibrated as specified in U.S. EPA Method 8260B in conjunction with the internal standards and surrogates recommended in the preparatory methods. A five-point calibration curve consisting of study analytes at the nominal concentrations of 30, 90, 300, 600, and 900 total ng on-column will be prepared. If the ongoing calibration check standard data for one or more of the target analytes are outside of the method QA/QC requirements, the analyst must determine the source of the problem, complete preventive maintenance, and recalibrate the instrument. The data for the corresponding analytes from any samples analyzed while the instrument was out of calibration will be flagged with a "D."

10. Data Management

Lockheed Martin will be responsible for tracking samples sent to the EPA laboratory for analysis. The WAM will be responsible for the coordination of all laboratory-generated data. If the WAM tasks LM to prepare a draft report, the WAM will provide copies of all laboratory data. Lockheed Martin will assume data management responsibility while analyzing the data and writing the report. If the WAM prepares the final report, LM will transfer data management responsibilities to the WAM. The task of data management for this study includes: (1) generating unique data labels, (2) tracking QC data with sample data, (3) tracking sample dilutions and replicates, (4) creating spreadsheet macros to transfer the electronic data from one

software environment to another, minimizing errors that can accumulate from transferring large amounts of data, and (5) maintaining electronic backup of data.

C. Assessment/Oversight

11. Assessment and Response Actions

Problems that arise beyond those discussed in this QAPP may be caused by uncontrolled laboratory factors such as spurious contamination, instrument problems, or unanticipated data analysis problems. Corrective actions for non-routine problems generally require an assessment of the problem with respect to project objectives, time, and cost considerations. Lockheed Martin management and the WAM will be notified of any problems encountered during project implementation and will be directly involved if corrective actions require additional resources. The WAM will be consulted if there are any modifications to, or significant deviations from this QAPP.

12. Reports to Management

The Task Lead will be responsible for monthly progress reports to the WAM. Separate written communications will be forwarded to the WAM regarding any modifications to this QAPP. If the WAM requests a draft report, it will include a project summary, a description of the methods, results, and a discussion of the results. Appendices will include: (1) a copy of all raw data, and (2) a QA/QC report which outlines the results of QC procedures and discusses these results with respect to the initial QA objectives.

D. Data Validation and Usability

13. Data Review, Validation, and Verification Requirements

A datum will be considered valid if all applicable QC parameters are within method- or QAPP-specified windows. The analyst is expected to provide an initial review of the data with respect to QC acceptance criteria, and if QC samples fall outside of the windows, to halt analysis until corrective measures resolve the discrepancy. Any data generated with corresponding QC samples outside of the expected range will be flagged and discussed in the QA/QC report. Justification for the inclusion or exclusion of qualified data in the data analysis steps will be based in context with the entire data set as described below.

14. Reconciliation of Data Quality Objectives

A Data Quality Assessment process will be used for reconciliation of MQOs. This process will consist of the following steps:

(1)   A review of all data will be conducted to assess the quality with respect to the QC parameters. Data with QA/QC parameters out of the windows will be flagged. Inclusion of qualified data in the data analysis steps will be based on a thorough review of the data for a particular VOC within the context of other compounds in that sample and other samples within the same analytical batch.

(2)   Data that have been verified to be of acceptable quality will be used in a preliminary review of the results. Basic statistical quantities will be calculated, that is, means and standard deviations for each method/soil/compound combination at each concentration. This information will be used to identify patterns, relationships, or potential anomalies.

(3)   Appropriate statistical procedures for analyzing and summarizing the data will be identified on the basis of the preliminary review. All assumptions for the statistical procedures to be used will be identified and verified as acceptable.

(4)   The applicable statistical procedures will be performed, interpreted, and any conclusions will be documented. The data completeness and performance of the experimental design will be assessed to determine whether or not the project objectives were met.

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Appendix A

Mass Calibration Criteria

Mass Ratio

Mass (m/z)	Target Percent of Mass 69
69	100
131	25.0 - 60.0
219	25.0 - 60.0
414	1.4 - 4.0
502	0.8 - 4.0

Isotope Ratio

Mass Ratio	Target Percent
70/69	0.8 - 1.3
132/131	2.0 - 3.4
220/219	3.5 - 5.2
415/414	7.2 - 10.8
503/502	8.1 - 12.1

Appendix B

BFB Ion Abundance Ratio Criteria

Mass (m/z)	Relative Ion Abundance Criteria
50	8.0 - 40.0 percent of mass 95
75	30.0 - 66.0 percent of mass 95
95	Base Peak, 100 percent relative abundance
96	5.0 - 9.0 percent of mass 95
173	less than 2 percent of mass 174
174*	50.0 - 120.0 percent of mass 95
175	4.0 - 9.0 percent of mass 174
176	93.0 - 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

* All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.