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Revision 0

CCP Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry

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Mark Pearcy

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RECORD OF REVISION

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0	05/02/2007	Initial Issue.

1. ABSTRACT

This Central Characterization Project (CCP) procedure is used for analyzing volatile organic compounds (VOCs) by gas chromatography/mass spectrometry (GC/MS) in all types of soil and solid waste matrices.

VOCs are introduced into the gas chromatograph (GC) by purge-and-trap techniques. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and back-flushed with helium to desorb trapped sample components. The analytes are desorbed directly to a narrow bore capillary column for analysis. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the GC.

A portion of the sample is dispersed in solvent to dissolve the volatile organic constituents. A portion of the solution is combined with organic-free reagent water in a purge chamber.

Analytes eluted from the capillary column are introduced directly into the mass spectrometer. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard with a five-point or six-point calibration curve.

2. APPLICABILITY

This method implements SW-846 Methods 8260B, “Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS),” 5035A, “Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples,” and 8000B, “Determinative Chromatographic Separations.”This method is suitable for characterization of homogeneous solids and soil/gravel per the requirements of the Waste Isolation Pilot Plant (WIPP) Waste Analysis Plan (WAP).

Compounds that are routinely determined by this method are listed in Table 1.

This method can be used to quantitate most VOCs that have boiling points below 200 ^{o}C and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique. However, for the more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, alcohols, nitriles, acetates, acrylates, ethers, and sulfides.

This procedure functions as an Idaho Cleanup Project (ICP) Use Type 2 document for performing operations in the Analytical Laboratories Department (ALD) facilities.

Personnel performing this procedure will be trained and qualified in accordance with CCP-QP-002, *CCP Training and Qualification Plan,* prior to performing this procedure.

3. DISCUSSION

Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealant, plastic tubing, or flow controllers with rubber components must be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. Subtracting blank values from sample results is not permitted.

Interfering contamination may occur when a sample containing low concentrations of VOCs is analyzed immediately after a sample containing high concentrations of VOCs. After analysis of a sample containing high concentrations of VOCs, one or more blanks are analyzed to check for cross contamination.

Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area must be isolated from all atmospheric sources of methylene chloride; otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing must be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst must be clean since clothing previously exposed to methylene chloride fumes during extraction procedures can contribute to sample contamination.

Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank prepared from organic-free sand and carried through the sampling and handling process serves as a check on such contamination.

4. SAFETY PRECAUTIONS

4.1 Chemical Hazards

4.1.1 Handle all chemicals per MCP-3635, “Chemical Hygiene Plan.”

4.1.2 Wear the following standard laboratory PPE in the lab:

A. Lab coat

B. Safety glasses with side shields

C. Substantial footwear

D. Appropriate gloves.

4.1.3 Change gloves immediately upon chemical contact.

4.1.4 Handle all spills per ACLP-0.24, “Laboratory Spill Cleanup.”

4.2 Radiological Hazards

4.2.1 Perform all work under an applicable RWP per MCP-7, “Radiological Work Permit”.

4.2.2 Handle nonroutine samples per ACLP-0.21, "Work Control Procedure for the Analysis of Nonroutine Samples."

4.3 Compressed Gas Hazards

4.3.1 Handle compressed gases per MCP-3635.

4.3.2 Fill liquid nitrogen dewars per TPR-7590, "Filling Dewars with Liquid Nitrogen."

4.3.3 Wear safety shoes when moving compressed gas cylinders.

4.4 Physical Hazards

4.4.1 Use a holding device or a passive reshielding technique for recapping syringes.

4.4.2 Dispose of syringe needles in appropriate containers.

4.5 Thermal Hazards

4.5.1 Avoid contact with hot surfaces on drying ovens, purge and trap concentrators, and gas chromatographs.

4.6 Waste Disposition and Pollution Prevention

4.6.1 Manage all waste generated per ACLP-0.40, "Analytical Laboratories Waste Management."

5. APPARATUS AND REAGENTS

5.1 Apparatus

5.1.1 Gas Chromatograph/mass spectrometer/data system

5.1.1.1 Gas chromatograph, Agilent 6890N, or equivalent

5.1.1.2 Mass spectrometer, Agilent 5973, or equivalent

5.1.1.3 Analytical column, VOCOL (Supelco) capillary column, 60 m × 0.25 mm ID, 1.5 µm film thickness, or equivalent

5.1.1.4 Data system, Chemstation, or equivalent

5.1.1.5 Purge and Trap (P&T) system, Tekmar/Dohrmann 3100, Teledyne/Tekmar Velocity XPT, or equivalent

5.1.1.6 Autosampling system, Tekmar/Dohrmann SOLATek 72, Teledyne/Tekmar Aquatek, or equivalent

5.1.2 Sorbent Traps

Prior to use for calibration or analysis of samples, precondition the sorbent trap per manufacturer directions.

5.1.2.1 Supelco Vocarb (CarbopackB/Carboxen 1000 & 1001), or equivalent

5.1.2.2 Tekmar Carbopack B/Carbosieve S, or equivalent

5.1.3 Purge vessels, various sizes

5.1.4 Microsyringes, various sizes

5.1.5 Syringes, glass, gas-tight, various sizes.

5.1.6 Balance, analytical, 0.01 g (minimum) sensitivity

5.1.7 Disposable pipetes, Pasteur

5.1.8 Volumetric flasks, Class A, various sizes with ground glass stoppers

5.1.9 Spatula

5.1.10 Vials, 40-mL and 20-mL glass with Teflon-coated septa and open screw caps or equivalent

5.1.11 Vials, 2-mL with Teflon-coated screw caps or equivalent.

5.1.12 Gases

5.1.12.1 Nitrogen, ultra high purity (UHP) or better, compressed

5.1.12.2 Nitrogen, liquid

5.1.12.3 Helium, UHP, compressed

5.2 Reagents

Use reagent grade chemicals unless otherwise specified. Store all standard solutions at ≤-10 °C in vials with Teflon-lined screw caps with minimal headspace. Use all purchased standards within the manufacturer-specified shelf life, or within one year of opening the supplier's vial, whichever occurs first.

NOTE: *Volumes other than specified may be prepared by using the appropriate ratio of reagents.*

5.2.1 Organic-free reagent water. Prepare organic-free reagent water by boiling ASTM Type II conductivity or better water for at least 15 minutes while bubbling high purity nitrogen through the water. Continue nitrogen purge as water cools. Store in glass bottle with Teflon lined cap.

5.2.2 Reagent sand. Purchase sea sand, Fisher catalog # S25 or equivalent. Bake the sand for a minimum of 4 hours at 400 °C, cool, and store in a tightly closed glass container.

5.2.3 Methanol, (CH_3OH). Purge and trap quality grade or better, demonstrated to be free of analytes.

5.2.4 Stock Standard Solutions. Purchase certified stock standard solutions containing Table 1 analytes, certified stock standard solutions from a single source for internal standard stock solutions, and tuning stock standard solutions. Multiple stock standard solutions may be required to encompass all target analytes.

5.2.5 Secondary dilution standards (Items 5.2.6–5.2.10). Prepare secondary dilution standard solutions in methanol from the stock standard solutions. Store secondary dilution standards in vials with no headspace and check frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Use secondary dilution standards within six months of preparation.

5.2.6 Surrogate Spiking Standards. Surrogate compounds are toluene-d_8, 4-bromofluorobenzene, and 1,2-dichloroethane-d_4.

5.2.6.1 50 µg/mL Surrogate Spiking Standard. Prepare by diluting the stock standard solution in methanol.

5.2.7 Internal Standards. Internal standards are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5.

5.2.7.1 50 µg/mL Internal Standard Solution. Prepare by diluting the stock standard solution in methanol. This concentration is recommended for use with autosampler applications where 5-µL injection increments can be used.

5.2.7.2 125 µg/mL Internal Standard Solution. Prepare by diluting the stock standard solution in methanol. This concentration is recommended for use with the Velocity XPT where 2-µL injection increments are used.

5.2.8 4-Bromofluorobenzene (BFB) Tuning Standard. Prepare by diluting a certified stock standard solution of 4-BFB in methanol. Recommended concentration of the BFB Tuning Standard Solution is 50 µg/mL.

5.2.9 Matrix spike (MS)/laboratory control sample (LCS) Spiking Solution. MS/LCS compounds are 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. Prepare the MS/LCS Spiking Solution from a second-source stock standard solution in methanol. Recommended concentration of the MS/LCS Spiking Solution is 50 µg/mL. Do not prepare the MS/LCS Spiking Solution from the same stock standard solution source as the calibration standards.

5.2.10 Calibration standards. Prepare a secondary dilution calibration standard containing all target analytes and surrogates in methanol from the primary-source stock standard solutions. Recommended concentration of the secondary dilution calibration standard is 50 µg/mL for each analyte. Instructions are provided in Section 7 for preparing calibration standards from this secondary dilution standard.

6. SAMPLE HANDLING

6.1 Store all samples and extracts at 4 °C in areas free from organic contamination.

NOTE: *SW-846 allows a range of ±2 °C around the specified storage temperature.*

6.2 Extract samples within 14 days of collection.

6.3 Analyze the extracts within 40 days of extraction.

6.4 Analyze samples in analytical batches. An analytical batch consists of a suite of samples of similar matrix that is processed as a unit, using the same analytical method, within a specific time period. An analytical batch can contain up to 20 samples, excluding laboratory QC samples, all of which must be received by the laboratory within 14 days of validated time of sample receipt (VTSR) of the first sample in the batch.

7. PROCEDURES

NOTE: *Individual samples may be at different steps in the process at any given time. Instrument operation may occur concurrently with or independent from sample or standard preparation activities. The sequence of instrument and data station setup, QC sample preparations, data evaluation and interpretation tasks may vary.*

7.1 Instrument Set-Up

NOTE: *This section provides recommended operating parameters. Operating parameters may be optimized if necessary; however, actual operating parameters used for sample analysis must match those used for the associated ICAL.*

7.1.1 Chromatographic Conditions

WARNING

There are thermal burn hazards in some areas (e.g., GC injector port, sorbent trap heater). Injury can occur when touching areas with temperatures greater than 50 °C.

7.1.1.1 Noncryogenic Cooling Parameters

NOTE: *These conditions are used for direct injection tune verification analysis.*

Carrier gas (He) head pressure	~10 psi
Carrier gas (He) flow rate	0.5–2.0 mL/min
Split flow ratio	~50:1
Initial temperature	100 °C, hold for 1 minute
Injector temperature	200–225 °C
Transfer line temperature	250–300 °C
Temperature program	15 °C/min
Final temperature	200 °C, hold until all expected compounds have eluted

7.1.1.2 Cyrogenic Cooling Parameters

Carrier gas (He) flow rate	1 mL/min
Split flow ratio	10:1
Initial temperature	10 °C, hold for 0 minutes
Temperature program 1	10 °C/min to 220 °C
Final temperature	220 °C, hold until all expected compounds have eluted
Injector temperature	200–250 °C
Transfer line temperature	200–300 °C

7.1.2 MS Operating Conditions

7.1.2.1 General

Mass range	35–260 amu
Scan time	0.6–2 sec/scan
Source temperature	According to manufacturer specifications

7.1.2.2 Hardware Tuning

7.1.2.2.1 Hardware-tune each GC/MS system to meet the criteria in Table 2 for a 1 µL (50 ng) injection of 4-BFB per manufacturer guidance.

7.1.3 Purge and Trap Operating Conditions

	3100/SOLATek	XPT/Aquatek
Purge gas:	Helium, UHP	Helium, UHP
Purge gas flow rate (mL/min)	30	60
Purge time (min)	11.0 ± 0.1	11.0 ± 0.1
Purge temperature (°C)	35	35
Dry purge (min.)	6	0
Moisture control module (°C)	0	NA
Desorb preheat (°C)	230	245
Desorb temperature (°C)	250	250
Backflush inert gas flow (mL/min)	20–60	200
Desorb time (min):	6	1
Bake (°C)	260	270
Bake (min.)	15	4
Moisture control module bake (°C)	60	NA

7.1.4 Autosampler Operating Parameters

7.1.4.1 Autosampler Parameters

	3100/SOLATek	XPT/Aquatek
Method	VOA4	VOA5
Sample Type	Water	Water
Rinse Water Temp	90 °C	NA
Transfer Line Temp	20 °C	NA
Soil Valve Temp	12.5 °C	NA
Sample Cup Temp	30 °C	NA
Sample Needle Temp	30 °C	NA
Sample Sweep Time	0.5 minutes	0.25 minutes
Needle Rinse Volume	7 mL	NA
Needle Sweep Time	0.5 minutes	NA
Bake Rinse Volume	7 mL	NA
Bake Sweep Time	0.5 minutes	NA
Bake Drain Time	0.5 minutes	0.5 minutes
# Bake Rinses	3	2
GC Start	Start of Desorb	Start of Desorb
Valve Oven Temp	120 °C	110 °C
Transfer Line Temp	120 °C	110 °C
Sample Mount Temp	40 °C	NA
MCS Temp	40 °C	40 °C
MCS Bake Temp	310 °C	310 °C
Purge Ready Temp	40 °C	40 °C

7.2 Extraction of Solid Samples

7.2.1 Weigh aliquots of the appropriate matrix material (Item 5.2.2) into VOA vials for laboratory blanks (LBs) and laboratory control samples (LCSs).

7.2.1.1 Prepare one LB and one LCS with each set of samples extracted within an analytical batch.

7.2.1.1.1 Weigh 3 g aliquots into a 20-mL vial and record weight to 0.01 grams in the Sample Preparation Logbook.

NOTE: *Samples are preweighed.*

7.2.1.2 Cap the vials, and DO NOT remove the caps until the extraction process is complete.

7.2.2 Record sample weights to 0.01 g in the Sample Preparation Logbook.

7.2.3 Add 9.5 mL of methanol using a syringe through the septum to all vials except those designated as the LCS, MS, and MSD.

7.2.4 Add 9.0 mL of methanol using a syringe through the septum to the vials designated as the LCS, MS and MSD.

NOTE: *A minimum of one matrix spike (MS) and one matrix spike duplicate (MSD) are required per analytical batch.*

7.2.5 Add 0.5 mL of MS/LCS Spiking Solution to the vials designated as the LCS, MS and MSD, using an appropriate syringe through the septum.

7.2.6 Add 0.5 mL of Surrogate Spiking Solution (Item 5.2.6.1) to all vials, using an appropriate syringe through the septum.

7.2.7 Shake each vial for 2 minutes.

7.2.8 Allow the solid material to settle.

7.2.9 Transfer sufficient liquid into at least two 2-mL auto-sampler vials for each sample.

NOTE: *Some matrices of samples may absorb extract solvent to the extent that insufficient extract exists to fill two vials.*

7.2.9.1 Ensure the vials are labeled with either the prep number (from Sample Preparation Logbook) or lab sample ID.

7.2.9.2 Fill the vials completely with no headspace.

NOTE: *Steps 7.6.1, 7.7, and 7.8 may be performed concurrently with the previous step to begin analysis.*

7.2.10 IF extracts were prepared in a CA
AND samples will NOT be run in a CA,
THEN prepare an aliquot of the extract for radiological screening.

WARNING

Some sample extracts are potentially alpha contaminated.

7.2.10.1 Transfer 100 µL of the extract onto a stainless steel planchet.

7.2.10.2 Air-dry the planchet.

7.2.10.3 IF a heavy residue remains after drying,
THEN consult with the technical lead.

7.2.10.4 Place the planchet in a transfer container.

7.2.10.5 Request the RCT perform gross α/β counting of the planchet.

7.2.10.5.1 IF the contamination levels are ≤48 cpm α
AND ≤30 cpm β/γ,
THEN analyze the extracts outside of a CA if desired.

7.2.10.5.2 IF the contamination levels are >48 cpm α
OR >30 cpm β/γ,
THEN analyze the extracts in a CA.

7.2.11 Place the autosampler vials in a vial rack and transfer the rack to either a sample storage refrigerator or instrument autosampler, as needed.

7.3 System Tune Verification

7.3.1 Set up the data station to accept data for the specified solution.

7.3.1.1 Introduce 50 ng of 4-BFB standard (e.g., 1 µL of 50 µg/mL solution), either by direct injection or purging, at the beginning of each 12-hour shift.

7.3.1.2 Evaluate the analysis data using the data system quantitation routines.

7.3.2 Acquire the BFB mass spectrum by performing the "Auto Find" command.

NOTE: *Auto Find acquires the BFB mass spectrum by averaging the peak apex scan and the scans immediately preceding and following the apex, and background subtracting from the average.*

7.3.3 Compare the resultant mass spectra for the BFB to Table 2 acceptance criteria.

7.3.3.1 IF the BFB criteria are met,
THEN proceed with the analytical sequence.

7.3.3.2 IF the criteria in Table 2 are NOT met,
THEN repeat Step 7.3.1.

7.3.3.3 IF the second attempt to meet Table 2 criteria fails,
THEN perform any required instrument maintenance (e.g. a hardware tune) as necessary and repeat Step 7.3.1.

7.4 Initial Calibration

NOTE: *Step 7.4 is to be performed initially, then as needed based on instrumentation maintenance or QC check results.*

7.4.1 Standard Preparation

NOTE: *These steps do not have to be performed in sequence.*

7.4.1.1 Prepare a set of at least five calibration standards containing all method analytes (Table 1) per instruction in the following steps.

NOTE: *Six calibration standards are required if second order regressions are used for quantitation.*

7.4.1.2 Prepare a least one calibration standard at concentrations near but greater than the method detection limit (MDL) for each analyte.

7.4.1.3 Prepare at least one calibration standard at concentrations below the program requirement quantitation limits (PRQLs) (see Table 5) for each analyte.

7.4.1.4 Prepare other calibration standards at concentrations defining the range of the method.

7.4.2 Initial Calibration for Extracted Solid Matrix Samples

7.4.2.1 Fill a 40-mL vial with organic-free reagent water minimizing headspace.

7.4.2.2 Add secondary dilution standards into the organic-free reagent water in the VOA vial using an appropriate micro syringe. Recommended calibration concentrations and standard volumes are:

Calibration Conc. (µg/L)	Vol. of standard (µL)
10	8
20	16
50	40
100	80
150	120
200	160

7.4.2.3 Cap the vial and load it into the autosampler.

7.4.2.4 Set up the purge and trap procedure to run the appropriate vials.

7.4.2.5 Analyze the calibration standards per Step 7.4.3.

7.4.2.6 Remove the 40-mL vials from the autosampler after analysis and dispose of vial contents and vials per ACLP-0.40.

7.4.3 Acquire and Evaluate ICAL Data

7.4.3.1 Perform GC/MS analysis to acquire data for each ICAL standard.

NOTE: *SW-846 Methods 8000B and 8260B require a minimum of five calibration points for valid average relative response factor or a linear regression modeled calibration curve, and require a minimum of six calibration points for a valid quadratic regression modeled calibration curve.*

7.4.3.1.1 Set up the data station to accept data for the specified solution using primary characteristic ions for quantitation of all analytes.

NOTE: *Secondary characteristic ions may be used for quantitation if, and only if, there are interferences with the primary ion.*

7.4.3.1.2 Start the GC/MS and data station to acquire analysis data.

7.4.3.1.3 Evaluate the analysis data using the data system quantitation routines.

NOTE: *All ICAL calculations are performed by the instrument data system.*

7.4.3.2 Calculate individual and average response factors (RRF) and the percent relative standard deviation (%RSD) for each compound relative to the nearest internal standard.

NOTE: *Once an internal standard has been selected for an analyte, this assignment CANNOT be changed for any subsequent analytical activity using the current ICAL.*

7.4.3.3 Verify that the average RRFs for the five system performance check compounds (SPCCs) meet the following criteria:

Chloromethane	≥0.10
1,1-Dichloroethane	≥0.10
Bromoform	≥0.10
Chlorobenzene	≥0.30
1,1,2,2-Tetrachloroethane	≥0.30.

NOTE: *SPCCs are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system.*

7.4.3.4 <u>IF</u> SPCC compounds do not meet the minimum values, <u>THEN</u> perform the following checks and correct any problems identified.

7.4.3.4.1 Check for cold spots in the transfer lines.

7.4.3.4.2 IF chloromethane RRF is low,
THEN check for purge flow that is too high.

NOTE: *Chloromethane is the most likely compound to be lost if the purge flow is too fast.*

7.4.3.4.3 IF bromoform RRF is low,
THEN check for purge flow that is too low.

NOTE 1: *Bromoform is the most likely compound to be lost if the purge flow is too slow.*

NOTE 2: *Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve bromoform response.*

7.4.3.4.4 IF tetrachloroethane or 1,1-dichloroethane RRFs are low,
THEN use a new sorbent trap.

NOTE: *Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.*

7.4.3.4.5 IF purge flows, ion ratios or sorbent traps were changed,
THEN reanalyze the ICAL standards.

7.4.3.5 Verify that the %RSDs of the six calibration check compounds (CCCs) are ≤30%. The CCCs are:

1,1-Dichloroethene	Toluene
Chloroform	Ethylbenzene
1,2-Dichloropropane	Vinyl chloride.

7.4.3.5.1 IF any CCC %RSD is >30%,
THEN eliminate a system leak and/or column reactive sites and then repeat the calibration.

7.4.3.6 Verify that the average RRFs of all non-SPCC compounds are ≥0.010.

7.4.3.7 Check that the retention times of each compound in all calibration standards agree within ±30 seconds.

NOTE: *The ±30 second criteria are more conservative than the SW-846 Method 8260B guidance of ±0.06 relative retention time (RRT) units.*

7.4.3.8 IF the analyte %RSD ≤15%,
THEN use the average RRF for quantitation.

7.4.3.9 IF the analyte %RSD >15%,
THEN construct a linear regression of area ratio ($A_s \times C_{is}/A_{is}$) versus concentration.

7.4.3.9.1 Calculate the correlation coefficient (r).

7.4.3.9.2 IF r ≥ 0.990,
THEN use the linear regression for quantitation. .

7.4.3.10 IF the analyte %RSD > 15 %
AND the linear regression correlation coefficient (r) does not meet the acceptance criteria,
THEN construct a quadratic regression (second-order) of area ratio ($A_s \times C_{is}/A_{is}$) vs. concentration, using a minimum of six calibration points.

7.4.3.10.1 Calculate the coefficient of determination (COD).

7.4.3.10.2 IF COD ≥ 0.990,
THEN use the quadratic regression for quantitation .

7.4.3.11 IF the analyte %RSD > 15%
AND neither the linear regression correlation coefficient (r) or quadratic regression COD meet the acceptance criteria,
THEN consult with laboratory supervision for direction.

7.5 Continuing Calibration Verification

NOTE: *The 50 µg/L standard used for calibration verification is (or is near) the midpoint of initial calibration curves for nearly every compound in every matrix. When dealing with different calibration ranges for some compounds, it is impossible to produce a single continuing calibration standard solution that is at the midpoint for every compound in every matrix.*

7.5.1 Perform a continuing calibration check (CCAL) for the appropriate sample matrix before analyzing samples within the 12-hour shift initiated by the passing BFB tune injection.

NOTE: *For samples analyzed within the same 12-hour shift as an ICAL of the appropriate sample matrix, the 50 µg/L (mid-range) ICAL standard may be used as the CCAL for that shift.*

7.5.1.1 Prepare a 50 µg/L standard as described in Steps 7.4.2.1 through 7.4.2.4 and 7.4.2.6.

7.5.2 Perform GC/MS analysis to acquire CCAL data.

7.5.2.1 Set up the data station to accept data for the specified solution.

7.5.2.2 Start the GC/MS and data station to acquire analysis data.

7.5.2.3 Evaluate the analysis data using the data system quantitation routines.

7.5.3 Evaluate the validity of initial calibration curve.

NOTE: *With the exception of %D for modeled compounds on the ion-trap system, RRF and %D calculations are performed by the instrument data systems.*

7.5.3.1 Calculate the RRF and the percent difference (%D) for each compound (see Equations 9.1 and 9.9).

7.5.3.1.1 Evaluate the CCAL against the acceptance criteria in Table 4.

7.5.3.1.2 <u>IF</u> any of the acceptance criteria are not met for any compound,
<u>THEN</u> reattempt the CCAL.

7.5.3.1.3 IF any of the acceptance criteria are still not met for any compound,
THEN perform a new ICAL.

7.6 Analyze a Method Blank

7.6.1 Analyzing an Extracted Laboratory Blank (LB) as the Method Blank (MB)

NOTE: *A non-extracted MB (Step 7.6.2) may be used provided that an acceptable extracted LB for the analytical batch is analyzed.*

7.6.1.1 Fill a 40-mL vial with organic-free reagent water.

7.6.1.2 Remove 0.80 mL with an appropriate syringe.

7.6.1.3 Add 0.80 mL of the LB extract to the 40-mL vial using an appropriate syringe.

7.6.1.4 Cap the vial.

7.6.1.5 Load the autosampler with the specified sample vials.

7.6.1.6 Set up the purge and trap procedure to run the appropriate vials.

7.6.1.7 Analyze the blank per step 7.6.3.

7.6.1.8 Remove the 40-mL vials from the autosampler after purging and dispose of vial contents and vials per ACLP-0.40.

7.6.2 Analyzing a Non-Extracted MB

7.6.2.1 Fill a 40-mL vial with organic-free reagent water.

7.6.2.2 IF autosampler does NOT automatically add surrogate standard,
THEN add 40 µL surrogate secondary dilution standard.

7.6.2.3 Cap the vial.

7.6.2.4 Load the autosampler with the specified sample vials.

7.6.2.5 Set up the purge and trap procedure to run the appropriate vials.

7.6.2.6 Analyze the blank per step 7.6.3.

7.6.2.7 Remove the 40-mL VOA vials from the autosampler after purging, and dispose of vial contents and vials per ACLP-0.40.

7.6.3 Acquire and Evaluate Blank Data

7.6.3.1 Perform GC/MS analysis to acquire blank data.

7.6.3.1.1 Set up the data station to accept data for the specified solution.

7.6.3.1.2 Start the GC/MS and data station to acquire analysis data.

7.6.3.1.3 Evaluate the analysis data using the data system quantitation routines.

7.6.3.2 Evaluate the method blank against the acceptance criteria in Table 4.

7.6.3.2.1 IF the MB meets acceptance criteria,
THEN proceed with the analysis sequence.

7.6.3.2.2 IF any of the MB acceptance criteria are NOT met,
THEN reattempt the method blank.

7.6.3.2.3 IF an extracted LB was used for the MB AND acceptance criteria are NOT met,
THEN analyze an independent MB (instrument blank) to identify the source of the contamination.

7.6.3.2.3.1 IF the independent MB meets acceptance criteria,
THEN reextract all samples associated with the noncompliant LB as allowed by holding time requirements.

7.6.3.2.4 IF any of the MB acceptance criteria are still NOT met,
THEN consult with supervision to determine the cause of the problem and appropriate corrective actions.

7.7 Analyze a Laboratory Control Sample (LCS)

7.7.1 Perform Steps 7.6.1.1 through 7.6.1.6 substituting the LCS extract for the LB extract in Step 7.6.1.3.

7.7.2 Acquire and Evaluate LCS Data

7.7.2.1 Perform GC/MS analysis to acquire LCS data.

7.7.2.1.1 Set up the data station to accept data for the specified solution.

7.7.2.1.2 Start the GC/MS and data station to acquire analysis data.

7.7.2.1.3 Evaluate the analysis data using the data system quantitation routines.

7.7.2.2 Evaluate the LCS against the acceptance criteria in Table 4.

7.7.2.2.1 IF any of the acceptance criteria are NOT met, THEN reattempt the LCS.

7.7.2.2.2 IF any of the acceptance criteria are still NOT met,
THEN consult with supervision to determine the cause of the problem and appropriate corrective actions.

7.8 Analyze Samples

NOTE: *Highly contaminated samples or extracts will not be analyzed neat or at dilutions that would result in damage or gross contamination of the analytical system.*

7.8.1 Check the extracts for yellow coloration indicating very high VOC contamination.

7.8.2 Dilute (e.g., use less extract) any colored sample for the first analytical run when necessary to avoid system contamination.

7.8.3 Perform Steps 7.6.1.1 through 7.6.1.6, substituting the sample extract for the LB extract in Step 7.6.1.3.

7.8.4 Acquire and Evaluate Sample Data

7.8.4.1 Perform GC/MS analysis to acquire sample data.

7.8.4.1.1 Set up the data station to accept data for the specified solution.

7.8.4.1.2 Start the GC/MS and data station to acquire analysis data.

7.8.4.1.3 Evaluate the analysis data using the data system quantitation routines.

7.8.4.2 Evaluate the sample against the acceptance criteria in Table 4.

7.8.4.2.1 IF any of the acceptance criteria are NOT met (excluding MS/MSD % recovery and RPD), THEN reanalyze the sample.

7.8.4.2.2 IF any of the acceptance criteria are still NOT met,
THEN consult with supervision.

7.8.4.3 IF any sample result exceeds the calibration range, THEN dilute the sample such that the over-range analyte is brought into the upper half of the calibration range and reanalyze it.

7.8.4.4 IF any sample saturates the detector or exceeds the calibration range of any target analyte by a factor of 2, THEN evaluate the following sample for possible data impact due to cross-contamination, considering the following factors:

A. Was the over-range analyte(s) detected in the following sample within the calibration range?

B. Was the over-range analyte(s) <MDL in the following sample?

C. If detected in the following sample, did the over-range analyte(s) exceed the calibration range?

7.8.4.4.1 IF the data for the following sample is adversely impacted by possible cross-contamination,
THEN reanalyze that sample after the system is demonstrated to be free of contamination by analysis of a passing blank.

7.8.4.5 IF the initial analysis of a sample was performed on a dilution due to suspected high concentration levels AND results of the initial analysis indicate that the sample can be safely analyzed at a lesser dilution, THEN reanalyze the sample at a lesser dilution that will not impair the analytical system.

7.9 Data Interpretation

7.9.1 Qualitative Analysis of Calibrated Compounds

7.9.1.1 Base qualitative identification of calibrated compounds on retention time and comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum.

7.9.1.2 Use a calibration standard associated with the same ICAL to generate the reference mass spectra.

NOTE: *The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum.*

7.9.1.3 Identify a compound as present when the following criteria are met:

A. The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

B. The relative retention time (RRT) of the sample component is within ±0.06 RRT units of the RRT of the standard component.

C. The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum (e.g., for an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%).

7.9.1.4 Identify structural isomers that produce very similar mass spectra as individual isomers if they have sufficiently different GC retention times.

NOTE: *Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights.*

7.9.1.4.1 IF insufficient GC resolution is achieved, THEN identify structural isomers as isomeric pairs.

NOTE 1: *Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra are important.*

NOTE 2: *Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.*

7.9.2 Tentatively Identified Compounds (TICs)

NOTE: *Data system library reduction programs can sometimes create discrepancies. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.*

7.9.2.1 Perform a mass spectral library search to tentatively identify sample components not associated with the calibration standards.

7.9.2.1.1 Analyze samples using a spectral reference library that contains, at a minimum, all available spectra for compounds that appear in the 20.4.1.200 NMAC (incorporating 40 CFR Part 261) Appendix VIII list.

7.9.2.2 Perform a mass spectral library search on all nontarget analyte sample components present with a minimum of 10% of the area of the nearest internal standard.

7.9.2.3 Assign tentative identification to nontarget compounds per the following SW-846 guidance:

A. Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

B. The relative intensities of the major ions should agree within ±20% (e.g., for an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance should be between 30% and 70%).

C. Molecular ions present in the reference spectrum should be present in the sample spectrum.

D. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or the presence of coeluting compounds.

E. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks.

7.9.3 Quantitative Analysis

7.9.3.1 Quantitate identified target compounds using the integrated abundance from the extracted ion current profile (EICP) of the primary characteristic ion (Table 3), using the internal standard technique.

7.9.3.1.1 Examine the full chromatogram.

7.9.3.1.2 Evaluate the peak integration, and accept or edit it as necessary.

7.9.3.1.3 IF manual integration is performed, THEN ensure that the manual integration is documented.

7.9.3.2 Report estimated TIC concentrations using the equation from Section 9.11 appropriate for the sample matrix, based on the following assumptions:

A. Use the nearest internal standard

B. Assume RRF = 1

C. Use the total ion area counts for both the TIC and the internal standard.

8. QUALITY CONTROL REQUIREMENTS

8.1 General QC Requirements

8.1.1 Refer to Table 4 for general QC requirements.

8.2 Method Performance

Determine MDLs and demonstrate method P&A prior to sample analysis. Determine MDLs on each instrument used for analysis. Redetermine MDLs and P&A if analytical conditions change significantly, or semianually, whichever is more frequent.

8.2.1 Prepare at least seven QC reference samples containing all target analytes at approximately 2–10 times the anticipated MDL.

8.2.2 Extract and analyze per Section 7.

8.2.3 Calculate the average concentration measured (Equation 9.2) and the standard deviation (Equation 9.3) for each analyte.

8.2.4 Calculate the average %R (Equation 9.10) for accuracy and the %RSD (Equation 9.4) for precision of each analyte.

8.2.5 Calculate MDLs for each analyte using Equation 9.13.

8.2.6 Compare the determined MDLs, average %R, and %RSD to the quality assurance objectives (QAOs) in Table 5.

8.2.7 IF any of the QAOs are NOT met,
THEN repeat method performance steps until MDLs, average %R, and %RSD are within the acceptance criteria.

9. CALCULATIONS

NOTE: *Some or all of these calculations may be performed by the instrument data system.*

9.1 Relative Response Factor (RRF)

$$RRF = \frac{A_x C_{is}}{A_{is} C_x}$$

where

A_x	=	area of the quantitation ion for the compound being measured
A_{is}	=	area of the quantitation ion for the specific internal standard
C_{is}	=	concentration of the internal standard closest in retention time to C_x
C_x	=	concentration of the compound being measured.

9.2 Arithmetic Mean

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

where

$\bar{x}$	=	arithmetic mean
x_i	=	i^{th} data point
n	=	total number of data points.

9.3 Standard Deviation (s)

$$s = \sqrt{\frac{\sum_{i=1}^{n}(RRF_i - \overline{RRF})^2}{n-1}}$$

where

RRF_i	=	RRF for each of the calibration levels
$\overline{RRF}$	=	mean RRF for each compound from the initial calibration
n	=	number of RF values (e.g., 5).

9.4 Percent Relative Standard Deviation (%RSD)

$$\%RSD = \frac{SD}{\overline{RRF}} \times 100\%$$

where

%RSD	=	percent relative standard deviation
$\overline{RRF}$	=	mean of the ICAL RRFs for a compound
SD	=	standard deviation of the ICAL RRFs for a compound.

9.5 Correlation Coefficient (r)

$$r = \frac{\left[n\sum_{i=1}^{n} x_i y_i\right] - \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i}{\sqrt{n\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2}\sqrt{n\sum_{i=1}^{n} y_i^2 - \left(\sum_{i=1}^{n} y_i\right)^2}}$$

where

x	=	C_s (concentration of target analyte)
y	=	instrument response $(A_s \times C_{is})/A_{is}$ (area counts of quantitation ion of target analyte times concentration of internal standard, all divided by area counts of quantitation ion of internal standard).

9.6 Least Squares Linear Regression

$$y = mx + b$$

where

y	=	instrument response (as above)
m	=	slope of the line
x	=	concentration of the calibration standard (as above)
b	=	the intercept.

9.7 Coefficient of Determination (COD)

$$COD = \frac{\sum_{i=1}^{n}\left(y_{obs} - \bar{y}\right)^2 - \left(\frac{n-1}{n-p}\right)\sum_{i=1}^{n}\left(y_{obs} - Y_i\right)^2}{\sum_{i=1}^{n}\left(y_{obs} - \bar{y}\right)^2}$$

where

y_{obs}	=	observed area for each concentration from each initial calibration standard
$\bar{y}$	=	mean observed response from the initial calibration
Y_i	=	calculated (or predicted) area at each concentration from the initial calibration
n	=	total number of calibration points
p	=	number of adjustable parameters in the polynomial equation (i.e., 3 for a second-order or quadratic regression).

9.8 Quadratic Regression

$$y = ax^2 + bx + c$$

where

y	=	instrument response (as in Equation 9.5)
x	=	concentration of the calibration standard (as in Equation 9.5)
a	=	regression factor relating instrument response and concentration
b	=	regression factor relating instrument response and concentration
c	=	the intercept.

9.9 Percent Difference (%D)

$$\%D = \frac{|(C_i - C_c)|}{C_i} \times 100$$

where

C_i	=	known standard concentration, or $\overline{RRF}$ from ICAL
C_c	=	measured concentration using selected quantitation method (i.e., average, linear, or quadratic), or RRF from CCAL.

9.10 Percent Recovery (%R)

$$\%R = \frac{SSR - SR}{SA} \times 100$$

where

%R	=	percent recovery
SSR	=	spiked sample result concentration
SR	=	sample result concentration (ZERO for LCS, MDL, P&A, & surrogates)
SA	=	spike added concentration.

9.11 Sample Concentration

9.11.1 Surrogates in Unextracted Method Blanks

$$Concentration\,(\mu g/L) = \frac{(A_x \times C_s \times V_o)}{(A_{is} \times \overline{RRF} \times V_s)}$$

where

A_x	=	area of quantitation ion for compound being measured
C_s	=	concentration of internal standard purged (µg/L)
A_{is}	=	area of quantitation ion for the internal standard
$\overline{RRF}$	=	RRF for compound being measured
V_o	=	total volume of water purged (mL)
V_s	=	volume of sample used (mL).

9.11.2 Extracted Solids

$$Concentration\left(\mu g/kg\right) = \frac{\left(A_x \times C_s \times V_o \times V_t\right)}{\left(A_{is} \times \overline{RRF} \times V_s \times W_s\right)}$$

where

A_x	=	area of quantitation ion for compound being measured
C_s	=	concentration of internal standard purged (µg/L)
A_{is}	=	area of quantitation ion for the internal standard
$\overline{RRF}$	=	RRF for compound being measured
V_o	=	total volume of water purged (mL)
V_t	=	volume of total extract (mL)
V_s	=	volume of extract added for purging (mL)
W_s	=	weight of sample extracted (g).

Divide the final µg/kg concentration by 1000 to convert to reporting units of mg/kg.

9.12 Relative Percent Difference (RPD)

$$RPD = \frac{|MS\%R - MSD\%R|}{(0.5)(MS\%R + MSD\%R)} \times 100$$

where

MS%R	=	matrix spike %R
MSD%R	=	matrix spike duplicate %R.

9.13 Method Detection Limit (MDL)

$$MDL = t_{(n-1,\alpha=0.99)} \times s$$

where

s = standard deviation

$t_{(n-1,\alpha=.99)}$ = one side t – statistic.

n = number of samples	t-statistic
3	6.96
4	4.54
5	3.75
6	3.36
7	3.14
8	3.00
9	2.90
10	2.82

10. RECORDS

Records generated during the performance of this procedure are maintained as QA records in accordance with CCP-QP-008, *CCP Records Management*. The records are the following:

QA/Nonpermanent

- Method Detection Limit (MDL) Determination File
- Precision and Accuracy (P&A) Demonstration File
- Initial Calibration (ICAL) File

The following records generated during the performance of this procedure will be compiled into the Supporting Data Package in accordance with CCP-TP-188, *CCP Analytical Data Recording, Review and Reporting.*

QA/Nonpermanent

- Copy of applicable pages of Run Logbooks
- Instrument Printouts/Raw Data
- Copy of applicable pages of Sample Preparation Logbook

11. REFERENCES

11.1 EPA SW-846, "Test Methods for Evaluating Solid Waste: Physical/Chemical Methods," Third Edition, Method 5035A, "Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples," U.S. Environmental Protection Agency, 1986

11.2 EPA SW-846, "Test Methods for Evaluating Solid Waste: Physical/Chemical Methods," Third Edition, Method 8000B, "Determinative Chromatographic Separations," U.S. Environmental Protection Agency, 1986

11.3 EPA SW-846, "Test Methods for Evaluating Solid Waste: Physical/Chemical Methods," Third Edition, Method 8260B, "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)," U.S. Environmental Protection Agency, 1986

11.4 Hazardous Waste Facility Permit Issued to Waste Isolation Pilot Plant by the New Mexico Environment Department, EPA # NM4890139088 (WIPP WAP)

11.5 ACLP-0.21, "Work Control Procedure for the Analysis of Nonroutine Samples"

11.6 ACLP-0.24, "Laboratory Spill Clean-up"

11.7 ACLP-0.40, "Analytical Laboratories Waste Management"

11.8 CCP-QP-002, *CCP Training and Qualification Plan*

11.9 CCP-QP-005, *CCP TRU Nonconforming Item Reporting and Control*

11.10 CCP-QP-008, *CCP Records Management*

11.11 CCP-TP-188, *CCP Analytical Data Recording, Review and Reporting*

11.12 MCP-7, "Radiological Work Permit"

11.13 MCP-2703, "Carcinogens"

11.14 MCP-3635, "Chemical Hygiene Plan"

11.15 TPR-7590, "Filling Dewars with Liquid Nitrogen."

Appendix A

Tables

Table 1. VOC Target Analytes, Surrogates and Internal Standards.

Analyte	CAS#[a]	WAP Target Analyte
Benzene (MS)	71-43-2	X
Bromochloromethane (IS)	74-97-5	
4-Bromofluorobenzene (Surr)	460-00-4	
Bromoform (SPCC)	75-25-2	X
Carbon disulfide	75-15-0	X
Carbon tetrachloride	56-23-5	X
Chlorobenzene (SPCC, MS)	108-90-7	X
Chlorobenzene-d_5 (IS)	3114-55-4	
Chloroform (CCC)	67-66-3	X
Chloromethane (SPCC)	74-87-3	
1,1-Dichloroethane (SPCC)	75-34-3	
1,2-Dichloroethane	107-06-2	X
1,2-Dichloroethane-d_4 (Surr)	1760-07-0	
1,1-Dichloroethene (CCC, MS)	75-35-4	X
trans-1,2-Dichloroethene	156-60-5	X
1,2-Dichloropropane (CCC)	78-87-5	
1,4-Difluorobenzene-d_4 (IS)	540-36-3	
Ethylbenzene (CCC)	100-41-4	X
Methylene chloride	75-09-2	X
1,1,2,2-Tetrachloroethane (SPCC)	79-34-5	X
Tetrachloroethene	127-18-4	X
Toluene (CCC, MS)	108-88-3	X
Toluene-d_8 (Surr)	2037-26-5	
1,1,1-Trichloroethane	71-55-6	X
1,1,2-Trichloroethane	79-00-5	X
Trichloroethene (MS)	79-01-6	X
Trichlorofluoromethane	75-69-4	X
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	X
Vinyl chloride (CCC)	75-01-4	X

Analyte	CAS#[a]	WAP Target Analyte
o-Xylene	95-47-6	X
m-Xylene[b]	108-38-3	X
p-Xylene[b]	106-42-3	X

a. Chemical Abstract Service Registry Number.
b. Cannot be resolved by this method; reported as m/p-xylene combination.
(MS) Matrix spike compound
(CCC) Calibration check compound
(SPCC) System performance check compound
(Surr) Surrogate
(IS) Internal standard

Table 2. BFB Mass Intensity Specifications (4-Bromofluorobenzene).

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

Table 3. Characteristic Masses (m/z) For Purgeable Organic Compounds.

Compound	Primary Ion(s)	Secondary Ions
Benzene	78	
Bromoform	173	175, 254
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chlorobenzene	112	77, 114
Chloroform	83	85
Chloromethane	50	49, 51, 52
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
Ethylbenzene	91	106
Methylene chloride	84	86, 49
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	97, 130, 132
Trichlorofluoromethane	101	103
1,1,2-Trichlorotrifluoroethane	151	153,101
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
Internal Standards/Surrogates		
1,4-Difluorobenzene	114	
Chlorobenzene-d_5	117	
Bromochloromethane	128	49, 130
4-Bromofluorobenzene	95	174, 176
1,2-Dichloroethane-d_4	102	67
Toluene-d_8	98	

Table 4. Summary of Laboratory QC Acceptance Criteria for VOC Analysis .

BFB Tune criteria to be met. See Table 2
Initial Calibration criteria to be met. See Step 7.4.3
Continuing Calibration criteria to be met.
Internal Standard
Area 50–200 % of last 50 standard
Retention time ±30 seconds of last 50 standard
SPCC relative response criteria
≥ 0.10 for chloromethane, 1,1-dichloroethane, and bromoform
≥ 0.30 for chlorobenzene, and 1,1,2,2-tetrachloroethane
≥ 0.01 for all other compounds
CCC % D criteria
≤ 20 % for 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride
Method Blank criteria to be met.
Internal Standard
Area 50–200 % of last 50 standard
Retention time ±30 seconds of last 50 standard
Surrogate recovery criteria
1,2-dichloroethane-d_4 80–120*
toluene-d_8 88–110*
bromofluorobenzene 86–115*
*These limits may be used as defaults until in-house limits are calculated per matrix as the mean ±3 standard deviations of a 30-sample minimum data set.

Target detection
≤3× program-required MDL (≤3 mg/kg, see Table 5).
Laboratory Blank criteria to be met.
Internal Standard
Area 50–200 % of last 50 standard
Retention time ±30 seconds of last 50 standard
Surrogate recovery criteria
1,2-dichloroethane-d_4 80–120*
toluene-d_8 88–110*
bromofluorobenzene 86–115*
*These limits may be used as defaults until in-house limits are calculated per matrix as the mean ±3 standard deviations of a 30-sample minimum data set.

Target detection
≤ 3 × program-required MDL (≤ 3 mg/kg, see Table 5).

LCS criteria to be met.

Internal Standard

Area	50–200 % of last 50 standard
Retention time	±30 seconds of last 50 standard

Surrogate recovery criteria

1,2-dichloroethane-d_4	80–120*
toluene-d_8	88–110*
bromofluorobenzene	86–115*

*These limits may be used as defaults until in-house limits are calculated per matrix as the mean ±3 standard deviations of a 30-sample minimum data set.

Target recovery

1,1-dichloroethene	≥MDL–234†
benzene	37–151†
trichloroethene	71–157†
toluene	47–150†
chlorobenzene	37–160†

† If a solid laboratory control sample material which has established statistical control limits is used, then the established control limits for that material should be used.

Sample criteria to be met.

Within 12 hours of last acceptable tune

Internal Standard

Area	50–200 % of last 50 standard
Retention time	±30 seconds of last 50 standard

Surrogate recovery criteria

1,2-dichloroethane-d_4	80–120*
toluene-d_8	88–110*
bromofluorobenzene	86–115*

*These limits may be used as defaults until in-house limits are calculated per matrix as the mean ±3 standard deviations of a 30-sample minimum data set.

Matrix Spike and Matrix Spike Duplicate criteria to be met.

Within 12 hours of last acceptable tune

Internal Standard	
Area	50–200% of last 50 standard
Retention time	±30 seconds of last 50 standard
Surrogate recovery criteria	
1,2-dichloroethane-d_4	80–120*
toluene-d_8	88–110*
bromofluorobenzene	86–115*

*These limits may be used as defaults until in-house limits are calculated per matrix as the mean ±3 standard deviations of a 30-sample minimum data set.

Spike analytes	
Recovery criteria	
1,1-dichloroethene	D–234[a]
benzene	37–151[a]
trichloroethene	71–157[a]
toluene	47–150[a]
chlorobenzene	37–160[a]
RPD criteria	
1,1-dichloroethene	≤250[a]
benzene	≤45[a]
trichloroethene	≤36[a]
toluene	≤29[a]
chlorobenzene	≤38[a]

a. Criteria apply to PRQL concentrations (See Table 5). Corrective actions for failed QC samples are specified in Section 7

When final reported QC samples do not meet the acceptance criteria, data are qualified per CCP-TP-188. Nonconformances do not apply to matrix related exceedances. Nonconformance reports per CCP-QP-005, *CCP TRU Nonconforming Item Reporting and Control* are required if QC failure(s) are not matrix related.

Table 5. VOC Target Analyte List and Quality Assurance Objectives.

Compound	CAS Number	Precision[a] (%RSD or RPD)	Accuracy[a] (%R)	MDL (mg/kg)	PRQL (mg/kg)	Complete-ness (%)
Acetone	67-64-1	≤50	60–150	10	100	90
Benzene	71-43-2	≤45	37–151	1	10	90
Bromoform	75-25-2	≤47	45–169	1	10	90
2-Butanone	78-93-3	≤50	60–150	10	100	90
Carbon disulfide	75-15-0	≤50	60–150	1	10	90
Carbon tetrachloride	56-23-5	≤30	70–140	1	10	90
Chlorobenzene	108-90-7	≤38	37–160	1	10	90
Chloroform	67-66-3	≤44	51–138	1	10	90
1,2-Dichloroethane	107-06-2	≤42	49–155	1	10	90
1,1-Dichloroethylene	75-35-4	≤250	D–234[b]	1	10	90
trans-1,2-Dichloroethylene	156-60-5	≤50	60–150	1	10	90
Ethyl benzene	100-41-4	≤43	37–162	1	10	90
Methylene chloride	75-09-2	≤50	D–221[b]	1	10	90
1,1,2,2-Tetrachloroethane	79-34-5	≤55	46–157	1	10	90
Tetrachloroethylene	127-18-4	≤29	64–148	1	10	90
Toluene	108-88-3	≤29	47–150	1	10	90
1,1,1-Trichloroethane	71-55-6	≤33	52–162	1	10	90
1,1,2-Trichloroethane	79-00-5	≤38	52–150	1	10	90
Trichloroethylene	79-01-6	≤36	71–157	1	10	90
Trichlorofluoromethane	75-69-4	≤110	17–181	1	10	90
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	≤50	60–150	1	10	90
Vinyl chloride	75-01-4	≤200	D–251[b]	1	4	90
m-Xylene[c]	108-38-3	≤50	60–150	1	10	90
o-Xylene	95-47-6	≤50	60–150	1	10	90
p-Xylene[c]	106-42-3	≤50	60–150	1	10	90

a. Applies to laboratory control samples and laboratory matrix spikes. If a solid laboratory control sample material which has established statistical control limits is used, then the established control limits for that material should be used for accuracy requirements.
b. Detected; result must be greater than zero.
c. These xylene isomers cannot be resolved by GC/MS and are reported as the m/p-xylene total.