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Revision 1

CCP Determination of Nonhalogenated Volatile Organics by Gas Chromatography

EFFECTIVE DATE: 08/22/2007

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APPROVED FOR USE

RECORD OF REVISION

Revision Number	Date Approved	Description of Revision
0	05/02/2007	Initial Issue.
1	08/22/2007	To correct the LCS/MS spiking solution preparation, and for various editorial changes.

1. ABSTRACT

This Central Characterization Project (CCP) procedure describes the dual column gas chromatographic separation and detection of nonhalogenated volatile organic compounds (NHVOCs) in extracts of solid samples. Results are obtained from a primary column with confirmation occurring simultaneously on a second column with a different stationary phase. Deuterated isopropanol is used as a surrogate to monitor method performance.

2. APPLICABILITY

This method is used for characterizing samples of homogeneous solids and soil/gravel for selected NHVOCs listed in Table 1, Total NHVOC Target Analyte List and Quality Assurance objectives, per the requirements of the Waste Isolation Pilot Plant (WIPP) Waste Analysis Plan (WAP). This method implements EPA SW-846 Method 8015B, "Non-Halogenated Organics Using GC/FID" and Method 8000B, "Determinative Chromatographic Separations," and is appropriate for NHVOC concentrations ranging from <10 mg\kg to weight percent levels. This procedure functions as an Idaho Cleanup Project (ICP) Use Type 2 document for performing operations within 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

Solid samples undergo aqueous extraction followed by analysis using dual-column gas chromatography (GC) with flame ionization detection (FID). Interferences arise from sludges containing slightly soluble halogenated hydrocarbons such as 1,1,1-trichloroethane, 1,1,2-trichloro-1,2,2-trifluoroethane, carbon tetrachloride, dichloromethane, and trichloroethylene. While these compounds will partially coextract, they can be chromatographically separated. Ethanol and 1,1,2-trichloro-1,2,2-trifluoroethane elute closely to acetone and the analyst must take care to correctly identify the acetone peak.

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 personal protective equipment (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 radiological work permit (RWP) per MCP-7, "Radiological Work Permit."

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

4.3 Physical Hazards

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

4.3.2 Dispose of syringe needles in appropriate containers.

4.4 Thermal Hazards

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

4.5 Waste Disposition

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

5. APPARATUS AND REAGENTS

5.1 Apparatus

5.1.1 Vials, Volatile Organic Analysis (VOA), 20-mL, with polytetrafluoroethylene (PTFE) lined screw caps.

5.1.2 Test tubes, glass, 16 mm O.D. × 125 mm (17-mL), or equivalent, with PTFE lined screw caps.

5.1.3 Test tubes, glass, 9-mL or equivalent, with PTFE lined screw caps.

5.1.4 Centrifuge, capable of 1000 rpm with appropriate tube holders.

5.1.5 Vortex mixer.

5.1.6 Vials, glass, 2-mL autosampler, screw top with PTFE lined caps, or equivalent.

5.1.7 "Y" connector, Supelco fused silica or J&W Scientific press-fit Y-shaped glass 3-way union splitter, or equivalent.

5.1.8 Gas Chromatograph (GC) with the following:

5.1.8.1 Oven temperature control: capable of programming from ambient to >100°C with multiple temperature ramps in one program.

5.1.8.2 Detectors: dual flame ionization detectors (FIDs) with sufficient sensitivity to meet the quality assurance objectives listed in Table 1.

5.1.8.3 Carrier gas flow: the system must have the capability to manually or automatically regulate the flow of carrier gas (ultra-high-purity helium) through the injection port and analytical capillary columns and provide make-up gas for the detector.

5.1.8.4 Split/splitless injection port, set up using the splitless operation mode.

5.1.8.5 Analytical columns: fused silica columns with the following coatings:

5.1.8.5.1 1st (quantitation) column:

Phase: 6% cyanopropylphenyl/94% dimethyl polysiloxane (e.g. J&W DB-624), or equivalent

Length: 30 meters

Film thickness: 3 µm

Internal diameter: 0.53 mm.

5.1.8.5.2 2nd (confirmation) column:

Phase: 100% dimethyl polysiloxane (e.g. J&W DB-1), or equivalent

Length: 30 meters

Film thickness: 3 µm

Internal diameter: 0.53 mm.

5.1.8.6 Guard Columns/Retention Gaps: Deactivated fused silica, 0.53 mm I.D., 0.5 - 1 m in length.

5.1.8.7 SGE OCA-4 on-column adapter, or equivalent.

5.1.8.8 Data System: capable of accurately determining peak areas, receiving and displaying signal output from the GC/FID system for the entire chromatographic run, reprocessing data, external standard calculations and data archival.

5.1.8.9 Autosampler. HP Model 7673 GC/SF Inject Autosampler, Agilent (formerly HP) Model 7683 Series Injector, or equivalent.

5.1.8.10 Autosampler syringes. HP/Agilent 10 or 5 µL, or equivalent

5.1.9 Syringes, assorted sizes

5.1.10 Transfer container for planchets

5.1.11 Analytical balance, capable to weighing to 0.01 gram

5.1.12 Syringe filter, 0.22 micron nylon, and 0.45 micron nylon.

5.1.13 Disposable Pasteur pipets, glass, 2-mL, with suction bulbs or equivalent

5.1.14 Planchets, stainless steel, various sizes

5.1.15 Heat lamp

5.1.16 Helium gas, ultra high purity (UHP) (carrier and detector make-up gas)

5.1.17 Hydrogen, UHP, or better (FID gas)

5.1.18 Compressed air (FID gas)

5.1.19 Bottle, 1-L or other appropriate size, cleaned for volatile organic compound (VOC) organic use

5.1.20 Spatula, stainless steel or Teflon

5.2 Reagents

Use Reagent grade chemicals and organic-pure American Society for Testing and Materials (ASTM) Type II (or better) conductivity water when preparing reagents and standards, unless otherwise specified.

5.2.1 Stock Standards

Purchase manufacturer/vendor-certified stock standard solutions. Use all purchased standards within the manufacturer's specified shelf life, or within six months of the supplier's vial being opened, whichever occurs first. Store all stock standards at 4 ± 2°C.

5.2.1.1 Calibration Stock Standard. Purchase a stock standard containing equal parts of each Table 1 target analyte.

5.2.1.2 Laboratory Control Standard (LCS)/Matrix Spiking (MS) Stock Standard. Purchase a stock standard containing equal parts of each Table 1 target analyte from a second source (second source is defined as an alternate supplier).

5.2.1.3 Isopropanol-d_8 Surrogate Stock Material, ≥98% pure

5.2.2 Working Standards

Store all working standards at 4 ± 2°C.

5.2.2.1 LCS/MS Spiking Solution. Prepare from the LCS/MS Stock Standard to contain 2000 µg/mL of each target analyte in water. Use the LCS/MS spiking solution for up to 6 months from preparation.

5.2.2.2 Isopropanol-d_8 Surrogate Spiking Solution. Prepare from the Isopropanol-d_8 Surrogate Stock Material to contain 2000 µg/mL in water. Use the Surrogate Spiking Solution up to six months from preparation.

5.2.2.3 Calibration Standards. Prepare a minimum of five calibration standards containing all Table 1 target analytes and the surrogate from the Calibration Stock Standard and the Surrogate Stock Material. Typical concentrations are

0.5, 2.5, 15, 75, and 200 µg/mL in water. (One of the standards must be below the solution-equivalent of the Program Required Quantitation Limit (PRQL) in Table 1; for a 3-g sample, approximately 20 mg/L). Use the calibration standards within 7 days of preparation.

5.2.2.4 Daily Continuing Calibration Verification (CCV) Standard. Prepare a midpoint standard containing all Table 1 target analytes and the surrogate by diluting the Calibration Stock Standard and the Surrogate Stock Material in water. The 75 µg/mL calibration standard may be used as the CCV Standard. Use the CCV Standard within 7 days of preparation.

5.2.3 Sand, organic-free. Purchase sea sand, Fisher catalog # S25 or equivalent. Bake the sand for a minimum of 4 hours at 400 °C, cool in a desiccator, and store in a tightly closed glass container.

5.2.4 Method Performance Demonstration Standards

5.2.4.1 Method Detection Limits (MDLs) Standards

Prepare a minimum of seven (7) standards.

5.2.4.1.1 Prepare standards by spiking organic-free sand with solutions containing each Table 1 target analyte and the isopropanol-d_8 surrogate.

5.2.4.1.1.1 Weigh 3-g aliquots of organic-free sand into 20-mL VOA vials.

5.2.4.1.1.2 Prepare for analysis per Steps 7.1.4 through 7.1.15.

5.2.4.2 Precision and Accuracy (P&A) Standards

Prepare a minimum of seven (7) standards for initial P&A demonstrations or a minimum of four (4) standards for continuing P&A demonstrations.

5.2.4.2.1 Prepare standards by spiking organic-free sand with solutions containing each Table 1 target analyte and the isopropanol-d_8 surrogate.

5.2.4.2.1.1 Weigh 3-g aliquots of organic-free sand into 20-mL VOA vials.

5.2.4.2.1.2 Prepare for analysis per Steps 7.1.4 through 7.1.15.

NOTE: *This yields solid standards with analyte concentrations of approximately 100 mg/kg, the program-required quantitation limit (PRQL).*

6. SAMPLE HANDLING

6.1 Store all samples and extracts produced from these samples at 4 °C before analysis.

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

6.2 Extract and analyze all samples within 14 days from the date of collection.

6.3 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. Analytical batch can contain up to 20 samples, excluding laboratory quality control (QC), 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. Instrument operation may occur concurrently or independently from sample or standard and preparation activities. Sequence of instrument and data station setup, QC sample prep, data evaluation, and interpretation tasks may vary.*

7.1 Extraction of Samples

NOTE 1: *All water used during preparation and analysis steps is organic-free ASTM Type II (or better) conductivity water, unless otherwise specified.*

NOTE 2: *Steps 7.1.1 through 7.1.3 do not need to be performed in sequence.*

7.1.1 Prepare a laboratory blank (LB) by weighing 3 g of organic–free sand into a 20 mL glass VOA vial with PTFE septa, and recording the weight to 0.01 g in the Sample Preparation Logbook.

7.1.2 Prepare a LCS by weighing 3 g of organic-free sand in a 20-mL glass VOA vial with PTFE septa, and recording the weight to 0.01 g in the Sample Preparation Logbook.

7.1.3 Record the weight of the samples (found on the chain of custody form or other documentation accompanying samples) in the Sample Preparation Logbook.

7.1.4 Inject water (the solvent) and spiking solutions into each sample vial as follows:

7.1.4.1 Weigh the sample vial on the analytical balance and record the tare weight to 0.1 g in the Sample Preparation Logbook.

7.1.4.2 Inject at least 10 mL water into the sample vial with a syringe through the septum.

7.1.4.3 Inject Isopropanol-d_8 Surrogate Spiking Solution into all sample vials (including the LB, MS, matrix spike duplicate (MSD), LCS, MDL or P&A) through the septum.

7.1.4.3.1 IF preparing samples or P&A standards, THEN inject 150 µL.

7.1.4.3.2 IF preparing MDL standards, THEN inject sufficient surrogate spiking solution to result in a final concentration approximately 2–10 times the anticipated MDL.

7.1.4.4 Inject LCS/MS Spiking Solution into the sample vials identified as LCS, MS, MSD, MDL or P&A through the septum.

7.1.4.4.1 IF preparing batch QC samples or P&A standards, THEN inject 150 µL.

7.1.4.4.2 IF preparing MDL standards, THEN inject sufficient spiking solution to result in final concentrations approximately 2–10 times the anticipated MDLs.

NOTE: *Minimum required frequency for the LCS, MS, and MSD is one per analytical batch.*

7.1.4.5 Remove the cap.

7.1.4.6 Add water gently into the sample vial so that no headspace will remain when the cap is replaced.

7.1.4.7 Replace the cap.

7.1.4.8 Weigh the sample vial and record (to one decimal place) the gross weight in the Sample Preparation Logbook.

NOTE: *The following step may be performed at any time in the process.*

7.1.4.9 Determine the total extract volume (mL) by converting net weight to volume (density of water is 1.00 g/mL).

7.1.5 Vortex each sample vial for 2 minutes.

7.1.6 Allow the sample to settle.

7.1.7 Remove the cap from the sample vial.

7.1.8 Pour the extract into a 17-mL test tube.

7.1.8.1 Pour the extract with as little agitation as possible to avoid loss of analyte.

7.1.8.2 Fill the test tube to the top and cap the test tube.

7.1.9 Place the 17-mL test tube in a centrifuge and spin at approximately 1000 rpm for at least 10 minutes.

7.1.10 Gently pour the sample into a syringe with a 0.45-micron prefilter and a 0.22-micron nylon filter attached.

7.1.11 Install the plunger and filter the sample into a new 9-mL glass test tube.

7.1.11.1 IF filters plug,
THEN change filters.

7.1.12 Perform radiological screening of all extracts except the LB, LCS, MDL, P&A, Performance Demonstration Program (PDP) samples, and trip blanks.

7.1.12.1 Pipet 100 µL of sample extract onto a stainless steel planchet.

7.1.12.2 Dry the planchet using a heat lamp.

7.1.12.3 IF a heavy residue remains after drying,
THEN check with supervision before proceeding.

7.1.12.4 Place the planchet in a plastic transfer container.

7.1.12.5 Notify the Radiation Control Technician (RCT) that the sample is ready for gross alpha/beta counting.

7.1.12.6 IF the count of the extract is >6 counts per minute (cpm) alpha or >30 cpm beta/gamma,
THEN dilute the extract with water and re-screen until the extract meets the above conditions.

7.1.12.7 Record any dilutions of the extract in the Sample Preparation Logbook.

7.1.13 Remove aliquots of the aqueous extract from the 9-mL test tube, using a glass Pasteur pipet, and fill at least 2 Teflon-capped autosampler vials (2-mL) so that no headspace exits.

NOTE: *Only one vial is required for analysis. Additional vials are prepared as a backup, if needed.*

7.1.14 Discard the remaining volume of extract per ACLP-0.40.

7.1.15 Refrigerate the extract vials at 4 ± 2 °C until analysis is performed.

7.2 Typical GC/FID Operating Parameters

NOTE: *Operating parameters may be optimized as necessary as long as actual operating parameters used for sample analysis match those used for the associated initial calibration (ICAL).*

7.2.1 Set up the GC/FID as follows:

Initial column temperature:	35°C
Initial column holding time:	4 minutes
Column temperature program:	10°C/minute
Final column temperature:	115°C
Final analytical run time:	12 minutes

NOTE: *After the final analytical run time, the temperature is ramped up and the run time extended until the matrix peaks are cleared from the columns (conditions will depend on sample matrix).*

Injector temperature:	120°C
Detector temperature:	250°C
Carrier gas:	Helium at 5.0 mL/minute per column, constant flow
Detector make-up gas:	Helium; adjust flow to maximize detector sensitivity (≤30 mL/min)
FID gas flows:	Set hydrogen and air flow rates to the FID per the manufacturer's instructions to maintain as flame stability throughout the run, (usually 30 mL/min H_2 and 430 mL/min air).
Injector port:	Insert guard column 3-5 mm into the bottom of the on-column adapter and insert adapter into the injector port.

7.3 GC/FID Calibration

7.3.1 Retention Time (RT) Windows Determination

NOTE: *Step 7.3.1 is to be performed initially, then as needed based on instrumentation maintenance or QC results.*

7.3.1.1 Determine RT Windows for all target analytes and the surrogate on both analytical columns.

7.3.1.1.1 Inject 0.5 µL of a calibration standard containing all target analytes and the surrogate a minimum of three times over a period of approximately 72 hours.

NOTE: *Injections over a period of less than 72 hours may result in RT windows that are too tight.*

7.3.1.1.2 Calculate the mean absolute RT and standard deviation for each target analyte and the surrogate on each column from the three injections (see Equation 9.3 for calculation of the standard deviation).

7.3.1.1.3 Determine the RT window for each target analyte and the surrogate on each column as ±3 times the standard deviation of the mean absolute retention time.

7.3.1.1.3.1 IF the standard deviation is 0.000, THEN use the 0.01 minutes as the default standard deviation.

7.3.1.2 IF changes in instrument operating conditions or maintenance could affect the retention times, THEN redetermine the RT windows.

7.3.1.3 Set the RT windows in the data station no wider than the determined RT windows.

7.3.2 Initial Calibration (ICAL)

NOTE: *Step 7.3.2 is to be performed initially, then as needed based on instrumentation maintenance or QC results.*

7.3.2.1 Set up the data station to accept data for the specified standards and enter the standard concentrations into the data station calibration table in units of µg/mL.

7.3.2.2 Start the GC and data station to acquire calibration data.

7.3.2.2.1 Inject 0.5 µL of five (minimum) calibration standards.

NOTE: *The WIPP WAP requires at least one calibration standard at concentrations below the PRQL. Any calibration standard less than 20 µg/mL fulfills this requirement for a 3-g sample.*

7.3.2.3 Evaluate calibration data using the data system software.

NOTE: *The calibration table provides an external standard calibration plot (linear regression) of peak area versus concentration.*

7.3.2.4 Compare the ICAL standard RTs for each target analyte/surrogate on both columns to the RT windows determined in Step 7.3.1.

7.3.2.4.1 IF all ICAL RTs are within the RT windows, THEN GO TO Step 7.3.2.5.

7.3.2.4.2 IF any ICAL RT is outside the RT windows, and instrumental error is identified, THEN correct instrumental error and repeat the ICAL.

7.3.2.4.3 IF any ICAL RT is outside the RT windows and no instrumental error is identified, THEN redetermine the RT windows per Step 7.3.1 and repeat the ICAL.

7.3.2.5 Construct a linear regression using instrument response (peak area) as the dependent variable (y) and standard concentration (µg/mL) as the independent variable (x).

7.3.2.5.1 Do not force the regression through the origin.

7.3.2.5.2 Do not include the origin as a data point in the regression.

7.3.2.6 Evaluate the calibration plot correlation coefficient (r^2) calculated by the data station for each target analyte/surrogate on each column.

NOTE: *The ICAL is acceptable if all RTs are within the RT windows AND $r \geq 0.990$ for all target analytes and surrogates on both columns. Sample analysis cannot proceed until these criteria are met.*

7.3.2.7 IF r <0.990, for any target analyte or surrogate on either column
THEN evaluate the calibration plot for that analyte/column.

7.3.2.7.1 IF a single calibration standard appears to be the source of the nonlinearity,
THEN reprepare and reanalyze that standard, update the calibration table, and repeat Steps 7.3.2.4, 7.3.2.5, and 7.3.2.6.

7.3.2.7.2 IF no single standard can be identified as the source of the nonlinearity,
THEN reprepare all calibration standards and repeat the ICAL.

7.4 Sample Analysis: 12-hour Analytical Shift

7.4.1 Verify the ICAL at the beginning of each 12-hour analytical shift by injecting 0.5 µL of the CCV standard (75 µg/mL).

NOTE: *For samples analyzed during the same 12-hour shift as an ICAL, the 75 µg/mL ICAL standard is the CCV.*

7.4.1.1 Set up the data station to accept data for the calibration solution.

7.4.1.2 Start the GC and data station to acquire analysis data.

7.4.1.3 Evaluate the calibration data using the data system quantitation routines.

7.4.1.4 Compare the retention time for each target analyte/surrogate on both columns to the RT determined in Step 7.3.1.

7.4.1.4.1 IF all RTs are within the RT windows,
THEN GO TO Step 7.4.1.5.

7.4.1.4.2 IF any of the RTs do NOT fall within the RT windows and instrumental error is identified,
THEN correct the instrumental error and reanalyze the CCV.

7.4.1.4.3 IF any of the RTs do NOT fall within the RT windows and no instrumental error is identified,
THEN determine new RT windows per Step 7.3.1 and perform a new ICAL per Step 7.3.2.

7.4.1.5 Calculate the percent difference (%D) between the known and the found values of the CCV for all target analytes/surrogates on both columns, using Equation 9.4.

7.4.1.5.1 IF %D ≤15 for all target analytes/surrogates on both columns,
THEN continue with sample analysis (Step 7.4.2).

7.4.1.5.2 IF %D >15 for any target analyte/surrogate
THEN evaluate the instrument for potential problems (e.g., septum needs replacement), perform minor maintenance as necessary,
AND reanalyze the CCV standard.

7.4.1.5.3 IF the reanalyzed CCV passes the ≤15 %D criteria,
THEN continue with sample analysis (Step 7.4.2).

7.4.1.5.4 IF the reanalyzed CCV still fails the ≤15 % criteria,
THEN reprepare and reanalyze the CCV standard (Step 7.4.1) to eliminate standard preparation as the source of error.

7.4.1.5.5 IF the reprepared CCV now passes the ≤15 %D criteria,
THEN continue with sample analysis (Step 7.4.5).

7.4.1.5.6 IF the reprepared CCV still fails the ≤15 %D criteria,
THEN perform a new ICAL per Step 7.3.2.

7.4.2 Use the absolute RT of each analyte in the CCV as the midpoint of the RT window for that analyte during the 12-hour analytical shift.

7.4.2.1 IF samples are being run in the same 12-hour analytical shift as the ICAL,
THEN use the RT of the mid-point (75 µg/mL) standard to set the center of the RT windows.

7.4.3 Inject 0.5 µL of the LB.

7.4.3.1 Set up the data station to accept data for the lab blank solution.

7.4.3.2 Start the GC and data station to acquire analysis data.

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

7.4.3.4 Evaluate surrogate recoveries.

7.4.3.4.1 IF surrogate recoveries on both columns are within control limits specified in Step 8.3.4,
THEN evaluate blank concentrations per Step 7.4.3.5.

7.4.3.4.2 IF surrogate recovery on either column is NOT within control limits specified in Step 8.3.4,
THEN reanalyze the LB.

7.4.3.4.2.1 IF surrogate recoveries on both columns for the reanalysis are within control limits specified in Step 8.3.4,
THEN evaluate blank concentrations per Step 7.4.3.5.

7.4.3.4.2.2 IF surrogate recovery on either column is NOT within control limits specified in Step 8.3.4
AND the holding time has NOT expired,
THEN reextract all samples associated with the LB.

7.4.3.4.2.3 IF surrogate recovery on either column is NOT within control limits specified in Step 8.3.4 AND the holding time has expired,
THEN continue with sample analysis and qualify reported data from associated samples per Step 8.3.4.5.

NOTE: *Reextraction and reanalysis of samples after holding times have expired may be performed for informational purposes. Such reextractions, if performed, are discussed in the report narrative.*

7.4.3.5 IF the concentrations of all target analytes are ≤3× MDL in Table 1,
THEN continue with sample analysis (Step 7.4.4).

7.4.3.6 IF the concentration of any target analyte in the LB is >3 × MDL in Table 1,
THEN analyze a method blank (MB), consisting of organic-pure water, to determine if the source of the contamination is in the instrument or occurred during extraction.

7.4.3.6.1 IF the MB indicates that the instrument is the source of contamination (i.e., analyte concentrations comparable to the LB),
THEN decontaminate the instrument and reanalyze the LB.

7.4.3.6.1.1 IF the reanalyzed LB passes the ≤3×MDL criteria,
THEN continue with sample analysis (Step 7.4.4).

7.4.3.6.1.2 IF the reanalyzed LB still fails the ≤3×MDL criteria,
THEN halt analysis until the source of the problem is identified and corrected.

7.4.3.6.2 IF the results of the MB indicate that the extraction/preparation is the source of the contamination,
THEN repeat the extraction/preparation of all samples in the analytical batch.

7.4.3.6.2.1 IF insufficient sample volume remains to repeat the extraction OR the sample holding times have expired,
THEN proceed with analysis and flag all sample results for the affected target analyte.

7.4.4 Inject 0.5 µL of prepared sample (including LCS, MS, MSD, MDL or P&A).

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

7.4.4.2 Start the GC and data station to acquire analysis data.

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

7.4.4.4 IF a sample saturates the detector or exceeds the calibration range of any target analyte by a factor of 10,
THEN analyze a blank to check for system contamination.

7.4.4.4.1 IF the blank meets acceptance criteria (≤3× MDL in Table 1 for all target analytes),
THEN continue with sample analysis.

7.4.4.4.2 IF the blank is NOT free of contamination (i.e., >3× MDL for all target analytes),
THEN decontaminate the system and demonstrate a passing MB before continuing with sample analysis.

7.4.4.5 IF any sample results exceed the calibration range,
THEN dilute the sample with organic-pure water and reanalyze it.

7.4.4.6 Evaluate surrogate recoveries.

7.4.4.6.1 IF surrogate recoveries on both columns are within control limits specified in Step 8.3.4, THEN evaluate sample data for reporting per Section 7.5.

7.4.4.6.2 IF surrogate recovery on either column is NOT within control limits specified in Step 8.3.4, THEN reanalyze the sample.

7.4.4.6.2.1 IF surrogate recoveries on both columns are within control limits specified in Step 8.3.4, THEN evaluate data for reporting per Section 7.5.

7.4.4.6.2.2 IF surrogate recovery on either column is NOT within control limits specified in Step 8.3.4 AND the holding time has NOT expired, THEN reextract the sample.

7.4.4.6.2.3 IF surrogate recovery on either column is NOT within control limits specified in Step 8.3.4 AND the holding time has expired, THEN evaluate the sample data for reporting per Section 7.5 and qualify reported data per Step 8.3.4.5.

NOTE: *Reextraction and reanalysis of samples after holding times have expired may be performed for informational purposes. Such reextractions, if performed, are discussed in the report narrative.*

7.4.5 Inject 0.5 µL of the CCV Standard at the end of the analytical shift AND within 12 hours of the beginning CCV injection.

7.4.5.1 Set up the data station to accept data for the calibration solution.

7.4.5.2 Start the GC and data station to acquire analysis data.

7.4.5.3 Evaluate the calibration data using the data system quantitation routines.

7.4.5.4 Compare the retention time for each target analyte/surrogate on both columns to the 12-hour RT windows (centered on the beginning CCV RTs) determined in Step 7.4.2.

7.4.5.4.1 IF all RTs are within the RT windows, THEN GO TO Step 7.4.5.5.

7.4.5.4.2 IF any of the RTs do NOT fall within the RT windows
AND instrumental error is identified,
THEN correct the error and reanalyze all samples from the analytical shift.

7.4.5.4.3 IF any of the RTs do NOT fall within the RT windows
AND instrumental error is NOT identified,
THEN contact laboratory supervision for direction.

7.4.5.5 Calculate the percent difference (%D) between the known and the found values of the CCV for all target analytes/surrogates on both columns, using Equation 9.4.

7.4.5.5.1 IF %D ≤15 for all target analytes/surrogates on both columns,
THEN evaluate the data for reporting per Section 7.5.

7.4.5.5.2 IF %D >15 for any target analyte/surrogate,
THEN reprepare and reanalyze the CCV standard (Step 7.4.5) to eliminate standard preparation as the source of error.

7.4.5.5.3 IF the reprepared CCV passes the ≤15 %D criteria,
THEN evaluate the data for reporting per Section 7.5.

7.4.5.5.4 IF the reprepared CCV fails the ≤15 %D criteria,
THEN correct the problem and reanalyze all samples from the analytical shift.

7.5 Qualitative and Quantitative Data Evaluation Using Dual-Column Confirmation

7.5.1 Qualitative Identification

7.5.1.1 Evaluate the 1st and 2nd column chromatograms of each sample for the presence of peaks within the daily RT windows for target analytes/surrogate.

7.5.1.2 IF a peak is present within the daily RT window for an analyte on both columns
AND the concentration on both columns is ≥MDL,
THEN report the analyte as present in the sample.

7.5.2 Quantitative Evaluation

7.5.2.1 Calculate the relative percent difference (RPD) of the concentrations determined from column 1 and column 2 using Equation 9.6.

7.5.2.2 IF the RPD between column 1 and column 2 is ≤40 %,
THEN report the data as follows:

7.5.2.2.1 IF the column 1 RT window is free from interfering peaks,
THEN report the column 1 value.

7.5.2.2.2 IF the column 1 RT window contains interfering peaks and the column 2 RT window is free from interfering peaks,
THEN report the column 2 value.

7.5.2.2.3 IF both column 1 and column 2 RT windows contain interfering peaks,
THEN report the value from the column having the least interference.

7.5.2.3 IF the RPD between column 1 and column 2 results is >40 %,
THEN check the chromatogram for evidence of an obvious overlapping peak or electronic spike.

7.5.2.3.1 IF there is evidence of peak overlap,
THEN report the lower of the two values.

7.5.2.3.2 IF there is an electronic noise spike affecting the peak on one column,
THEN report the value from the other column.

7.5.2.3.3 IF there is no evidence of anomaly,
THEN report the higher of the two values.

7.5.2.4 Calculate sample concentrations in units of mg/kg (see Equation 9.9).

7.5.2.5 Report sample results to two significant figures.

7.5.2.6 Flag sample results with data qualifiers per CCP-TP-188, *CCP Analytical Data Recording, Review and Reporting*, and corrective actions defined in Section 8.

8. QUALITY CONTROL REQUIREMENTS

Quality assurance objectives for this method are listed in Table 1. QC requirements necessary to meet those objectives are specified in this section.

8.1 Method Performance Demonstration

Before analyzing any sample, demonstrate initial acceptable method performance. Demonstrate acceptable continuing method performance semiannually.

8.1.1 Method Detection Limits

8.1.1.1 Determine MDLs for each GC/FID used.

8.1.1.2 Determine MDLs from preparation and analysis of a minimum of seven, (7) replicate standards (see Item 5.2.4.1) containing all target analytes and the surrogate in concentrations approximately 2 to 10 times the anticipated MDLs.

8.1.1.3 Calculate the mean value and standard deviation of the seven replicates for each target analyte/surrogate for both columns (see Equation 9.3).

8.1.1.4 Calculate the MDL for each compound on both columns, using Equation 9.8.

8.1.1.5 Compare the calculated MDLs to the program-required MDLs in Table 1.

NOTE: *Calculated MDLs less than or equal to the program-required MDLs in Table 1 are acceptable for use.*

8.1.1.6 If calculated MDLs do NOT meet the acceptance criteria, identify and correct the problem and redetermine the MDLs.

8.1.1.7 Redetermine MDLs semiannually, using a minimum of 7 replicate standards.

8.1.1.8 Redetermine MDLs when changes in instrument operating conditions or maintenance could affect MDL accuracy.

8.1.2 Method Precision and Accuracy (P&A) Determination

8.1.2.1 Determine P&A from preparation and analysis of a minimum of seven, (7) replicate standards (see Item 5.2.4.2) containing all target analytes and the surrogate in quantifiable concentrations ≤PRQL.

8.1.2.2 Calculate the mean value, mean percent recovery (%R) and percent relative standard deviation (%RSD) (see Equations 9.5.1 and 9.7) of the seven replicates for each target analyte/surrogate for both columns.

8.1.2.3 Compare the mean %R and %RSD to the required accuracy and precision quality assurance objectives in Table 1.

8.1.2.4 If the mean %R is within the Table 1 accuracy criteria. and the %RSD is within the Table 1 precision criteria for all target analytes on both columns, P&A is successfully demonstrated.

8.1.2.5 If the mean %R or the %RSD do NOT meet the Table 1 criteria, identify and correct the problem and repeat the P&A determination.

8.1.2.6 Re-demonstrate P&A semiannually, using a minimum of four (4) replicate standards.

8.2 Instrument Quality Control

8.2.1 Initial Calibration (ICAL)

8.2.1.1 Perform an external standard calibration (linear regression) for all analytes on both columns using a minimum of five (5) standards per Step 7.3.2 before analyzing any samples.

8.2.1.2 Set the concentration of at least one calibration standard at or below the Table 1 PRQL (see Step 7.3.2.2).

8.2.1.3 Ensure that the ICAL regression coefficients (r) for all compounds on both columns are ≥0.990 before proceeding with sample analysis.

8.2.2 Continuing Calibration Verification (CCV)

8.2.2.1 Verify the ICAL at the beginning and at the end of each 12-hour analytical shift by the analysis of a mid-range CCV containing all target analytes and the surrogate. See Steps 7.4.1 and 7.4.5.

8.2.2.2 Ensure that the RTs (both columns) of the beginning CCV are within the RT windows determined per Step 7.3.1.

8.2.2.3 Ensure that the RTs (both columns) of the ending CCV are within the daily RT window (centered on the RTs of the beginning CCV).

8.2.2.4 Ensure that the %D between the known and measured values of the standard is ≤15 for all target analytes and the surrogate on both columns.

8.2.2.5 If a CCV does NOT meet acceptance criteria, follow corrective actions in Step 7.4.1 (beginning CCV) or Step 7.4.5 (ending CCV).

8.2.3 Blank Verification

8.2.3.1 Verify the cleanliness of the analytical system at the beginning of each 12-hour shift, after the CCV but before sample analysis, by analysis of a blank sample. (The extracted LB may be used for this purpose, see Step 8.3.2).

8.2.3.2 Ensure that all analyte concentrations on both columns are ≤3 times the MDL in Table 1 before proceeding with sample analysis. See Steps 7.4.3.5 and 7.4.3.6.

8.2.3.3 If any target analytes are detected in the blank (≥MDL on both columns), ensure that all associated sample results are flagged with a "B" qualifier for the affected analyte.

8.3 Analytical Batch Quality Control

The following QC samples are required for each analytical batch.

8.3.1 Laboratory Control Sample (LCS)

8.3.1.1 Prepare/extract and analyze at least one unique LCS per analytical batch.

8.3.1.2 Use a standard from a different source than that used for the calibration standards, containing all target analytes.

8.3.1.3 Calculate %R for all target analytes and surrogate on both columns (see Equation 9.5.1).

8.3.1.4 If LCS %R results (both columns) do <u>NOT</u> meet the accuracy criteria in Table 1, reanalyze the LCS once to eliminate the sample injection as the source of the problem.

8.3.1.5 If the reanalysis of the LCS still fails to meet acceptance criteria (target analyte or surrogate recoveries), reextract and reanalyze all samples associated with the LCS.

8.3.1.6 If there is insufficient sample volume to reextract and reanalyze samples associated with a failed LCS or the 14-day holding time has expired, ensure that all associated samples results are flagged with a "Z" qualifier for the affected analyte, AND ensure a nonconformance report (NCR) is initiated per CCP-QP-005, *CCP TRU Nonconforming Item Reporting and Control* .

8.3.1.7 Evaluate surrogate recovery (both columns) per instructions in Step 8.3.4.

8.3.2 Laboratory Blank (LB)

8.3.2.1 Prepare/extract and analyze a minimum of one unique LB per analytical batch.

8.3.2.1.1 If samples are extracted in multiple groups within an analytical batch, extract an LB with each group.

8.3.2.2 If target analytes are detected in the LB (≥MDL on both columns), ensure that all associated sample results are flagged with a "B" qualifier for the affected analyte.

8.3.2.3 If LB target analyte concentrations exceed three times the MDLs in Table 1 and the blank contamination is <u>NOT</u> traced to the instrument system (see blank verification, Step 8.2.3), reprepare/reextract and reanalyze all samples associated with the noncompliant blank.

8.3.2.4 If there is insufficient sample volume to reprepare/reextract samples associated with a failed LB or the 14-day holding time has expired, ensure that all associated sample results are flagged with "BZ" qualifiers for the affected analyte, and ensure an NCR is initiated per CCP-QP-005.

8.3.2.5 Evaluate LB surrogate recovery on both columns per instructions in Step 8.3.4, and perform corrective actions as specified in Step 7.4.3.4.2.

8.3.2.5.1 If samples were reextracted and reanalyzed within holding times due to LB surrogate failure
and the LB surrogate recovery on both columns meets acceptance criteria for the reextraction, report sample results from the reextractions only, and discuss the reextraction/reanalysis in the report narrative.

8.3.2.5.2 If samples were reextracted and reanalyzed within holding times due to LB surrogate failure
and the LB surrogate recovery on either column did NOT meet acceptance criteria for the reextraction,
ensure an NCR is initiated per CCP-QP-005, report sample results as directed by the NCR disposition, and flag surrogate results and associated sample results with a “Z” qualifier.

8.3.2.5.3 If samples cannot be reextracted and reanalyzed due to an LB surrogate failure within holding times,
ensure an NCR is initiated per CCP-QP-005, report sample results as directed by the NCR disposition, flag surrogate results and associated sample results with a “Z” qualifier, and discuss any reextractions/reanalyses performed outside holding times in the report narrative.

8.3.3 Matrix Spike (MS) and Matrix Spike Duplicate (MSD)

8.3.3.1 Prepare/extract duplicate matrix spikes on an individual field sample at least once (MS and MSD) per analytical batch.

8.3.3.2 Calculate the %Rs for MS and the MSD, using Equation 9.5.2.

8.3.3.3 Calculate the relative percent differences (RPDs) between the MS and MSD results, using Equation 9.6.

8.3.3.4 If the MS or MSD %Rs does NOT meet the accuracy criteria in Table 1,
ensure that all associated sample results are flagged with a "Z" qualifier for affected analytes.

8.3.3.5 If the RPDs between the MS and MSD results do NOT meet the precision criteria in Table 1,
ensure that all associated sample results are flagged with a "Z" qualifier for affected analytes.

8.3.3.6 If MS/MSD %R or RPD failure can be traced to a cause other than the sample matrix,
ensure an NCR is initiated per CCP-QP-005.

8.3.4 Surrogate Compound

8.3.4.1 Ensure that each sample and analytical batch QC is spiked with surrogate isopropanol-d_8 before extraction.

8.3.4.2 Calculate the surrogate %R for each sample and QC sample on both columns, using Equation 9.5.1.

8.3.4.3 If <30 samples of similar matrix have been analyzed,
use default control limits of 60% to 150% to evaluate the surrogate recoveries.

8.3.4.4 If ≥30 samples of similar matrix have been analyzed,
calculate the control limits as the mean recovery ±3 standard deviations.

8.3.4.5 If surrogate recoveries do NOT meet the control limits,
perform corrective actions as specified in Step 7.4.4.6.2.

8.3.4.5.1 If a sample was reextracted and reanalyzed within holding times due to surrogate failure and surrogate recoveries for the reextraction meet the control limits,
report the results from the reextraction only and discuss the reextraction/reanalysis in the report narrative.

8.3.4.5.2 If a sample was reextracted and reanalyzed within holding times due to surrogate failure and surrogate recoveries on either column did NOT meet acceptance criteria for the reextraction,
report both the original and reextracted results, flag surrogate data with "Z" qualifiers and discuss the surrogate failures in the report narrative.

8.3.4.5.3 If samples cannot be reextracted and reanalyzed due to surrogate failure within holding times,
flag surrogate data with "Z" qualifiers and discuss the surrogate failure in the report narrative.

8.3.4.5.3.1 If reextractions and reanalyses performed outside holding times indicate that the surrogate failure was NOT due to sample matrix, ensure an NCR is initiated per CCP-QP-005.

9. CALCULATIONS

9.1 Correlation Coefficient (r)

NOTE: *The correlation coefficient is calculated by GC/FID data station as r^2. The correlation coefficient r is determined by taking the square root of the data station r^2 value. The equation below is provided for verification only.*

$$r = \frac{\sum_i \left(\left(C_i - \overline{C} \right) \left(A_i - \overline{A} \right) \right)}{\sqrt{\left(\sum_i \left(C_i - \overline{C} \right)^2 \right) \left(\sum_i \left(A_i - \overline{A} \right)^2 \right)}}$$

where

C_i = concentration of analyte being injected

$\overline{C}$ = concentration calculated from the regression line

A_i = total area response for the analyte

$\overline{A}$ = area response from the regression line.

9.2 Linear Regression Calibration

NOTE: *This calculation is performed by the GC/FID data station. The equation is provided for verification only.*

$$A_i = bC_i + a$$

where

A_i = total area response for the target analyte

C_i = analyte concentration (µg/mL) of the ith calibration standard

a = y-intercept of the linear regression

b = slope of the linear regression.

9.3 Standard deviation (SD)

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}$$

where

x_i = RT or C for each of the calibration levels

$\bar{x}$ = Mean RT for each compound from the initial calibration or mean C for precision calculations

n = number of data points.

9.4 Percent Difference (%D)

$$\%D = \frac{|(C_t) - (C_m)|}{C_t} \times 100$$

where

C_t = CCV true concentration (µg/mL)

C_m = CCV measured (found) concentration (µg/mL).

9.5 Percent Recovery (%R)

9.5.1 LCS, Surrogates, and P&A Standards

$$\%R = \frac{C_m}{C_t} \times 100$$

where

C_m = measured (found) concentration (mg/kg)

C_t = true concentration (mg/kg).

9.5.2 MS and MSDs

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

where

SSR = measured concentration of the spiked sample (mg/kg)

SR = measured concentration of the unspiked sample (mg/kg)

SA = concentration of spike added (mg/kg).

9.6 Relative Percent Difference (RPD)

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where

C_1 and C_2 = the results of duplicate measurements (e.g., MS and MSD %R), OR 1st and 2nd column values (mg/kg).

9.7 Percent Relative Standard Deviation (%RSD)

where

$$\%RSD = \frac{s}{\bar{y}} \times 100$$

s = standard deviation (Equation 9.3) (mg/kg)

$\bar{y}$ = mean of replicate analyses (mg/kg).

9.8 Method Detection Limits (MDLs)

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

where

s = standard deviation

$t_{(n-1,\ 1-\alpha = 0.99)}$ = t-distribution value appropriate to a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

9.9 Sample Concentration (mg/kg)

$$Concentration\ (mg/kg) = \frac{C_x \times V_t \times D}{W_x} \times \frac{10^3\ g}{kg} \times \frac{10^{-3}\ mg}{\mu g}$$

where

C_x = calculated concentration (µg/mL) from the GC/FID data station

V_t = volume of total extract (mL)

W_x = initial sample weight (g)

D = dilution factor.

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
- Retention Time (RT) Window Determination Files

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 NHVOC Sample Preparation Logbooks
- Copy of applicable pages of GC/FID Run Logbooks
- Instrument Printouts/Raw Data

11. REFERENCES

11.1 ACLP-0.21, “Work Control Procedure for Analysis of Nonroutine Samples”

11.2 ACLP-0.24, “Laboratory Spill Cleanup”

11.3 ACLP-0.40, “Analytical Laboratories Waste Management”

11.4 Associated Instrument Manuals

11.5 EPA SW-846, “Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods,” Third Edition, Method 8015B, “Non-Halogenated Organics Using GC/FID,” U. S. Environmental Protection Agency, 1986.

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

11.7 MCP-7, "Radiological Work Permit"

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-3635, "Chemical Hygiene Plan"

11.13 Hazardous Waste Facility Permit Issued to Waste Isolation Pilot Plant, EPA No. NM48901398088, by the New Mexico Environment Department (WIPP WAP).

Table 1. Total NHVOC Target Analyte List and Quality Assurances Objectives.

Compound	CAS #	Precision[a] (%RSD or RPD)	Accuracy[a] (%R)	MDL[b] (mg/kg)	PRQL (mg/kg)	Completeness (%)
Methanol	67-56-1	≤50	60–150	10	100	90
Acetone	67-64-1	≤50	60–150	10	100	90
Ethyl ether	60-29-7	≤50	60–150	10	100	90
Methyl ethyl ketone	78-93-3	≤50	60–150	10	100	90
Isobutanol	78-83-1	≤50	60–150	10	100	90
Butanol	71-36-3	≤50	60–150	10	100	90
Pyridine	110-86-1	≤50	60–150	10	100	90

%RSD = Percent relative standard deviation
RPD = Relative percent difference
%R = Percent recovery
MDL = Method detection limit (maximum permissible value)
PRQL = Program required quantitation limit
a = Criteria apply to PRQL concentrations.
b = Estimate, to be determined.