Controlled
Copy

CCP-TP-029

Revision 16

CCP
Single Sample Manifold Headspace Gas Sampling and Analysis Methods and Equipment Calibration

EFFECTIVE DATE: 11/16/2006

J.R. Stroble

PRINTED NAME

APPROVED FOR USE

RECORD OF REVISION

Revision Number	Date Approved	Description of Revision
7	01/30/2002	Added trans-1,2-Dichloroethylene to Table 1 and 5.
8	09/20/2002	Revised Sections 2 and 4 and Table 4 in response to CBFO adequacy review. Revised Section 2 in response to Industrial Hygiene review. Revised Sections 2, 4, Tables 2, 4, 6, 8 and 9 per SME request.
9	09/26/2002	Revised based on comments at the NTS Certification Audit; revised Steps 2.3.16, 4.2.3 through 4.2.5, and 4.7.2.
10	10/18/2002	Revised Steps 4.2.6[C.1], 4.7.2[B], 4.12.1[C], 4.12.2.[E], and 4.12.3[D] as a result of new PID configuration. Steps 2.3.17 and 4.1.2 were also revised.
11	02/12/2003	Revised Step. Changed table reference in Step 2.4.3 and removed table reference in Step 2.4.3[A].
12	09/25/2003	Revised Tables 1 and 5 to include Hanford specific information and updated for consistency with other HSG procedures.
13	06/22/2004	Inserted a Nov. 2003 Audit Recommendation to revise Step 4.9.1[A.5] and add a new NOTE prior to the step. Updated Section 2.1 References and Section 3.0 Responsibilities.
14	10/21/2004	To incorporate nonconforming reports for flammable TICs. Incorporated changes as a result of NTS Audit.
15	04/25/2005	Revised based on TRAMPAC Rev. 20.
16	11/16/2006	Revised to implement the Waste Isolation Pilot Plant Hazardous Waste Facility Permit requirements resulting from the Section 311/Remote-Handled (RH) Permit Modification Request (PMR).

Controlled
Copy

TABLE OF CONTENTS

1.0 PURPOSE 5
1.1 Scope 5

2.0 REQUIREMENTS 7
2.1 References 7
2.2 Training Requirements 8
2.3 Equipment List 8
2.5 Precautions and Limitations 12
2.6 Prerequisite Actions 13
2.7 Definitions 13

3.0 RESPONSIBILITIES 14
3.1 HSG Lead Operator (LO) 14
3.2 HSG Operator 14
3.3 Facility Records Custodian 14

4.0 PROCEDURE 15
4.1 Liquid Standards 15
4.2 Gas Standards 17
4.3 Process Gases 20
4.4 Initial Calibration (ICAL) 21
4.5 Minimum Detection Limit (MDL) and Method Performance Samples 25
4.6 Quality Control (QC) Samples 27
4.7 Calculations 31
4.8 Drum Sample Analysis 33
4.9 Tentatively Identified Compounds (TIC) 35
4.10 Photoionization Detector (PID) 37
4.11 Calibration/Verification Procedure 37
4.12 Combustible Gas Analysis 38
4.13 Maintenance 39

5.0 RECORDS 43

LIST OF TABLES

Table 1 - Target Analyte List and QAOs 44
Table 2 - 4-Bromofluorobenzene Key Ions and Abundance Criteria 45
Table 3 - Recommended GS/MS System Operating Conditions for Varian Model 3800 GC and Varian Saturn 2000 MS 46
Table 4 - Calibration Criteria for Volatile Organic Compounds 47
Table 5 - Characteristic Ion for Volatile Organic Compounds 48
Table 6 - Summary of Laboratory Quality Control Samples and Frequencies for Gas Volatile Organic Compounds Analysis 49
Table 7 - Hydrogen and Methane Analysis Quality Assurance Objectives 50
Table 8 - Summary of GC Calibration Requirements for Hydrogen and Methane Analysis 51
Table 9 - Summary of Laboratory Quality Control Samples and Frequencies for Hydrogen and Methane Analysis 52
Table 10 - Internal Standard Criteria 53

1.0 PURPOSE

This procedure is used to collect and analyze headspace gas (HSG) from waste containers using a single sample on-line HSG sampling and analysis manifold.

1.1 Scope

This procedure implements applicable requirements of CCP-PO-001, *CCP Transuranic Waste Characterization Quality Assurance Project Plan* (QAPjP). The analytical instrument employed uses multiple detectors to simultaneously analyze for hydrogen, methane, and Waste Isolation Pilot Plant (WIPP) Volatile Organic Compounds (VOCs). The Single Sample Manifold HSG Sampling and Analysis System has the capability of venting drums, installing filters, collecting a representative HSG sample, and analyzing the sample for hydrogen, methane, and VOCs. Combined results are reported in a single sampling and analysis batch data report (BDR).

The analytical methods presented in this procedure are equivalent in performance to those specified by the U.S. Department of Energy (DOE)-Carlsbad Field Office (CBFO) for transuranic (TRU) waste container HSG characterization: a) “Modified Method TO-14 for the Gas Chromatography/Mass Spectrometry Determination of Volatile Organic Compounds in Waste Container Headspace"; b) American Society for Testing of Materials (ASTM) Method 1946-82, “Standard Method for Analysis of Reformed Gas by Gas Chromatograph", and c) EPA-SW-846, Method 8260B, “Volatile Organic Compounds by Gas Chromatography/Mass Spectroscopy (GC/MS)". Analytical method performance has been demonstrated through documented system and instrument tests, as well as successful participation in the HSG Performance Demonstration Program (PDP) analysis of blind samples.

This procedure is used for the analysis of VOCs listed in Table 1, Target Analyte List and QAOs in the range from less than Program Required Quantitation Limits (PRQLs) to levels of approximately 500 to 1200 parts per million by volume (ppmv), that have been collected from waste container headspace using the automated drum venting system (DVS). This procedure uses a fixed volume 100 μL sample loop and a split/splitless injector to meet minimum VOC concentrations specified in CCP-PO-001, while extending the upper limit of linear calibration. This procedure is based upon the introduction of VOCs onto a capillary column using a fixed volume injection loop. A MS is used to identify all of the VOCs listed in Table 1 (NOTE: m and p-xylene are undifferentiable using this method and are reported as m,p-xylene), and is used for quantitation up to a concentration level of approximately 1200 ppmv (limited by the upper linear limit of the calibration curve) by direct injection and analysis.

This procedure is also used for the analysis of hydrogen and methane in the range from less than the PRQL specified in Table 7, Hydrogen and Methane Analysis Quality Assurance Objectives, to volume percent concentrations.

The laboratory shall be required to analyze blind audit samples. These audit samples are part of the PDP. Details of this program are in DOE/CAO-95-1076, *Performance Demonstration Program Plan for Analysis of Simulated Headspace Gases* .

2.0 REQUIREMENTS

2.1 References

Baseline Documents

- *Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA® Passivated Canisters Sampling and Gas Chromatographic Analysis,* Compendium Method TO-14, EPA, 1988
- 04-4001, Rev. A, *ModuRAE Operation and Maintenance Manual*
- CCP-HSP-001, *CCP Headspace Gas Health and Safety Plan*

Referenced Documents

- *Varian 3800 Gas Chromatograph Operators Manual*
- *Varian Saturn 2000 Operators Manual, and Varian Custom Solutions Analysis System,* S/N1471, February 6, 1998
- NIST *Mass Spectral Library of Organic Compounds*
- ASTM Method 1946-82, *Standard Method for Analysis of Reformed Gas by Gas Chromatograph*
- *Volatile Compounds by Gas Chromatography/Mass Spectroscopy (GC/MS),* EPA-SW-846, Method 8260
- DOE/WIPP 01-3194, *CH-TRU Waste Content Codes,* Appendix B
- EPA-SW-846, Method 8260B, *Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry* (GC/MS)
- CCP-PO-001*, CCP Transuranic Waste Characterization Quality Assurance Project Plan*
- CCP-PO-002, *CCP Transuranic Waste Certification Plan*
- CCP-QP-002*, CCP Training and Qualification Plan*
- CCP-QP-005, *CCP TRU Nonconforming Item Reporting and Control*
- CCP-QP-008*, CCP Records Management*

- CCP-QP-011, *CCP Notebooks and Logbooks*
- CCP-TP-007, *CCP Single Sample Manifold Headspace Gas Sampling and Analysis Operating Procedure*
- CCP-TP-009, *CCP Single Sample Manifold Data Handling Procedure*
- CCP-TP-032, *CCP Single Sample Manifold Data Validation Procedure*
- DOE/CAO-95-1076, *Performance Demonstration Program Plan for Analysis of Simulated Headspace Gases*

2.2 Training Requirements

2.2.1 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.

2.3 Equipment List

NOTE

The parameters presented in Table 3, Recommended GS/MS system Operating Conditions for Varian Model 3800 GC and Varian Saturn 2000 MS, are recommended operating conditions by the vendor, Varian, Inc.

2.3.1 Gas Chromatograph (GC)

[A] The Varian model 3800 GC is self-compensating for temperature and pressure.

[B] The column oven shall be capable of temperatures greater than 200 ºC.

2.3.2 Column

NOTE

The length and diameter of the column used must be documented in the HSG Operational Log. The length and diameter of the column used must be the same as used in the most recent HSG PDP blind sample analysis cycle.

[A] A 60 meter X 0.32 millimeter (mm) I.D. Varian VA-624 1.8 μm stationary film thickness or Restek Rtx-624 1.8 μm stationary film thickness.

[B] TCD column – 2 m X 1/8 inch 5A Molecular Sieve.

2.3.3 Mass Spectrometer (MS) Detector

[A] A Varian Saturn 2000 capable of scanning from 29-300 amu every 3 seconds or less, using 70 volts (nominal) electron energy in the electron impact mode and producing a mass spectrum that meets all the criteria listed in Table 2, 4-Bromofluorbenzene Key Ions and Abundance Criteria, when 50 nanograms (ng) (or an appropriate amount) of 4-bromofluorobenzene (BFB) is injected through the gas chromatograph inlet.

2.3.4 GC/MS Interface

[A] A GC-to-MS interface that gives acceptable calibration data at the PRQL specified in Table 1, for all analytes and achieves all acceptable instrument performance criteria.

2.3.5 Flame Ionization Detector (FID)

[A] Piped in parallel with MS after the capillary column for methane. The detector is sufficiently sensitive to meet the QAOs given in Table 7.

2.3.6 Thermal Conductivity Detector (TCD)

[A] Piped in parallel to the capillary column, the detector is a TCD type for hydrogen. The detector is sufficiently sensitive to meet the QAOs given in Table 7.

2.3.7 Detector Temperature Control

[A] The detector temperature shall be maintained at a constant temperature, ± 0.3 °C (as specified by the manufacturer), during the course of the sample run and the corresponding reference run. The MS detector and/or transfer line temperature shall be greater than or equal to the maximum column temperature.

2.3.8 Pressure Vacuum Gauge

[A] Pressure sensors that are pneumatically connected to the manifold and can measure absolute pressure from 0.05 mm Hg (with a resolution of 0.01 mm Hg) to 1000 mm Hg. The pressure sensors shall have an operation range of 15 °C to 40 °C.

2.3.9 Vacuum Pump

[A] A dry vacuum pump capable of reducing the manifold pressure to 0.05 mm Hg.

CAUTION

If an oil pump is used, precautions such as a molecular sieve or cryogenic trap shall be used to prevent diffusion of oil vapors back into the manifold.

2.3.10 Sample Inlet System

[A] A constant Volume 100 μL Gas Sampling Loop is used. The sample is collected using the automated sampling manifold connected to the sample inlet. The inlet system is operated at ambient pressure by having the sample loop vented to atmosphere. The system also allows for connection of sample canister to the manifold.

2.3.11 Data System

[A] A data system that allows the continuous acquisition and storage of all mass spectra obtained during the chromatographic program shall be interfaced to the MS. The data system shall have software that allows searching of a GC/MS data file for ions of a specified mass and plotting ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software shall also be available that allows integrating the ion abundances in any EICP between specified times or scan-number limits. Data reduction software shall be available that enables the qualitative and quantitative determination of target and non-target analytes using user-built mass spectral libraries and response factors based on EICP peak areas. The data system shall be capable of searching a compatible National Institute of Standards and Technology (NIST) Mass Spectral Library.

2.3.12 Syringes

[A] Gas-tight syringes with removable needles shall range in volume from 5 mL to 50 mL for gas-phase standards.

[B] Syringes with fixed needles shall range from 1 μL to 500 μL for liquid standards.

2.3.13 Vials

[A] 1 mL or 2 mL amber vials with Teflon or Teflon laminated silicone rubber septum inserts and seals on a screw cap. The vials must be cleaned in accordance with U.S. Environment Protection Agency (EPA) wash procedures or procured and certified as clean by the manufacturer. These vials shall be used for the storage of liquid standards once removed from ampules.

2.3.14 Stainless Steel Two Stage Pressure Regulators

[A] Stainless steel regulators shall be used to connect and regulate compressed gases and gas standards to the GC/MS. Use of brass regulators is prohibited.

NOTE

All applicable Material Safety Data Sheets (MSDSs) will be reviewed, and primary and secondary containers will be labeled as necessary.

2.3.15 Reagents

[A] GC-grade methanol shall be used to dilute BFB stock standards.

NOTE

In addition to compounds referenced in Table 1, site/waste stream-specific compounds shall be included in the gas calibration standards if the compound is added to the target analyte list.

2.3.16 Gases

[A] Stock calibration gas standards shall contain all target analytes listed in Table 1 and Table 7.

[B] Continued Calibration Verification (CCV) stock gas standards shall contain all target analytes listed in Table 1 and Table 7.

[C] All gas standards shall be replaced according to supplier's specified expiration date.

[D] Certified gas mixtures of known hydrogen and methane composition are required for making a standard calibration curve.

[E] Gas calibration standards shall be purchased from approved vendor, shall be certified by the manufacturer, or should be traceable to a nationally recognized standard.

2.3.17 Liquids

[A] Stock solutions shall be purchased as certified solutions, including the manufacturer's analytical report. The standards shall be accompanied by a certificate of analysis from the manufacturer that documents traceability. All opened standards shall be replaced if any indication of degradation exists, or every six months, which ever comes first. Unopened liquid standards (in manufacturer's ampules) shall be replaced prior to the manufacturer's expiration date. Opened standard stock solutions shall be stored in amber, Teflon-sealed screw-cap vials, in a refrigerator maintained at temperature of -10 °C or less and protected from direct light.

2.4 Software

2.4.1 Varian MS Workstation

2.5 Precautions and Limitations

2.5.1 **IF** this procedure can **NOT** be implemented as written, **THEN** work will be STOPPED and the HSG Lead Operator (LO) will be notified. Work will **NOT** be resumed until this procedure is corrected.

2.5.2 All VOCs are identified using the MS. If the VOC concentration is within the linear range of the MS, a quantitative result will automatically be calculated. Sample dilution is **NOT** performed.

2.5.3 Samples are to be analyzed in on-line analytical batches. An on-line analytical batch is defined as a suite of samples, processed as a unit using the same analytical method and analytical instrument, within a specific, 12-hour time period beginning at the time of injection of the BFB tune analysis. CCP-TP-009, *CCP Single Sample Manifold Data Handling Procedure* addresses data handling and batch reporting.

2.5.4 Contamination may occur in the analytical system if the sampling manifold is **NOT** properly cleaned at the time of assembly or prior to first use. If sampling manifold contamination is suspected, an automated clean and purge cycle is performed, using humidified, ultra-high-purity (UHP) nitrogen. Following the clean/purge cycle, an equipment blank (humidified nitrogen) is analyzed with a photoionization detector (PID) to confirm manifold cleanliness.

2.5.5 Cross-contamination can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Cross-contamination is controlled by a clean/purge/verify/evacuation process:

[A] Purge with UHP nitrogen;

[B] Flush with UHP humidified nitrogen;

[C] Verify system cleanliness using a PID;

[D] Pump-down the sample manifold to 100 mtorr, and

[E] Maintain the temperature of the sample manifold to greater than 25 °C.

2.5.6 Teflon plastic coating, Teflon thread sealants, or flow controllers which have rubber components in the analytical system shall **NOT** be used. All components are to be constructed of relatively inert materials, such as stainless steel or Teflon.

2.5.7 This procedure may involve the use of hazardous materials, operations, and equipment. It is the responsibility of users of this procedure to consult appropriate site personnel and the HSG LO, concerning health and safety issues to establish appropriate health and safety practices. Consideration should be given to safety concerns regarding chemical and radiation exposure.

2.5.8 Samples, reagents and calibration standards may be flammable. Keep away from heat, sparks, and open flame. Provide adequate ventilation.

2.6 Prerequisite Actions

2.6.1 None.

2.7 Definitions

2.7.1 None.

3.0 RESPONSIBILITIES

3.1 HSG Lead Operator (LO)

3.1.1 Performs as the field supervisor for the implementation of this procedure.

3.1.2 Oversees all operations for HSG sampling and calibration.

3.2 HSG Operator

3.2.1 Performs the activities for HSG sampling, calibration and GC/MS maintenance.

3.3 Facility Records Custodian

3.3.1 Receives, processes, and transmits all records generated by this procedure in accordance with CCP-QP-008, *CCP Records Management*.

4.0 PROCEDURE

4.1 Liquid Standards

4.1.1 Basic Information

[A] BFB standards must be prepared prior to operation of the DVS. BFB standards shall be obtained with certifications of analysis documenting traceability from the manufacturer or have a known, valid relationship to a nationally recognized standard (such as NIST).

[B] Calibration standards will **NOT** be used past their expiration dates.

[C] Calibration standards expiration dates identified, as mmyy shall expire the last day of that month.

[D] GC-grade methanol shall be used to dilute the BFB calibration standards. The dilution shall be performed by injecting the standard solution beneath the surface of the solvent to prevent losses due to volatilization of the standard. All equipment and materials shall be cleaned prior to use.

[E] The BFB stock standards are purchased as certified standards in Class A glassware (e.g., flame sealed Class A glass ampules) and stored at -10 °C or less when **NOT** in use.

[F] Liquid standards vials, once opened, shall be labeled and dated with an expiration date **NOT** to exceed six months or the expiration date provided by the vendor, whichever is the shorter time. The manufacturer's expiration dates on unopened liquid standard vials or ampules shall be considered the valid expiration dates. Expired standards shall be segregated and shall **NOT** be used.

[G] Liquid standards dilution is performed by a HSG Operator, with the following information recorded in the HSG Operational Logbook:

[G.1] HSG Operator name

[G.2] Date prepared

[G.3] Standard lot number

[G.4] Amount of solvent used

[G.5] Amount of standard used

[G.6] Standard initial concentration

[G.7] Diluted standard final concentration

[H] All standard vials shall be marked with:

[H.1] Standard name

[H.2] Date of expiration

[H.3] HSG Operator initials

[H.4] Sample lot number

4.1.2 BFB Liquid Standard Preparation

[A] The BFB standard is a certified liquid standard (NIST-traceable) purchased from an approved vendor.

[B] Prepare a BFB standard by diluting stock liquid with methanol.

[C] The BFB standard is prepared to provide 20-50 ng of BFB onto the column using a 1 μL injection.

[D] Prepare a 50 μg/mL BFB solution by diluting 10 μL of stock 5000 mg/mL into 990 μL of methanol.

[E] Record BFB standard preparation in the HSG Operational Logbook.

4.2 Gas Standards

NOTE

Internal Standard, Online Control Standard (OCS), VOC, CCV and hydrogen/methane standards are to be purchased as certified gas standards. The standard shall be purchased from an approved vendor. Gas standards are contained in cylinders determined by the supplier to be non-reactive with the gaseous compounds and intended to preserve the stability of the standard indefinitely. Gas standards shall be labeled as unusable if the cylinder has exceeded the manufacturer's expiration date, or the cylinder has been shown to become unstable due to low vapor pressure or temperature issues.

4.2.1 Internal Standard

[A] Internal standards shall be procured as certified compressed gas standards. The recommended compounds are bromochloromethane, chlorobenzene-d5, and 1,4-difluorobenzene. Other compounds identified in SW-846, Method 8260 may be used and documented if necessary to eliminate co-elution or interference with target compounds.

4.2.2 OCS Standard

[A] The OCS standard shall be procured as certified gas standard.

[B] The OCS shall contain at least six VOC analytes from Table 1, including hydrogen~~,~~ and methane.

[C] The Table 1 VOC concentrations of the OCS sample are between 10 ppmv and 100 ppmv. The hydrogen and methane concentrations of the OCS sample will be 0.2 volume %.

[D] The OCS standard shall **NOT** be derived from the same source as the initial calibration (ICAL) standard.

4.2.3 VOC Calibration Standards

[A] VOC calibration standards shall be procured as certified compressed gas standards.

[B] The stock gas standard is diluted using a gas-tight syringe from the cylinder for each initial calibration concentration level is noted by the chemist in the HSG Operational Logbook as follows:

[B.1] Purge the gas tight syringe a minimum of three times.

[B.2] Draw the determined amount of calibration gases into a 50 mL syringe to create the desired dilution (i.e., 9 mL of stock calibration gas and 41 mL of atmospheric gas).

[B.3] Manually inject 50 mL of the gas mixture, using the 50 mL gas-tight syringe into the gas injection port.

[B.4] Analyze the standard in accordance with CCP-TP-007, *CCP Single Sample Manifold Headspace Gas Sampling and Analysis Procedure*.

[B.5] Repeat steps 4.2.3[B.1] through 4.2.3[B][B.4] for further dilutions, as necessary, to obtain, at a minimum, a five-point calibration curve.

[B.6] Record all dilution values for each concentration level in the HSG Operational Logbook.

4.2.4 Hydrogen and Methane Calibration Standards

[A] Hydrogen and methane calibration standards shall be procured as certified compressed gas standards (independent cylinder or included with the VOCs).

[B] The stock gas standard is diluted using a gas tight syringe from the cylinder for each initial calibration concentration level is noted by the HSG Operator in the HSG Operational Logbook as follows:

[B.1] Purge the gas tight syringe a minimum of three times.

[B.2] Draw the determined amount of calibration gases into a 50 mL syringe to create the desired dilution (i.e., 9 mL of stock calibration gas and 41 mL of atmospheric gas).

[B.3] Manually inject 50 mL of the gas mixture, using the 50 mL gas tight syringe into the gas injection port.

[B.4] Analyze the standard in accordance with CCP-TP-007.

[B.5] Repeat steps 4.2.4[B][B.1] through 4.2.4[B][B.4] for further dilutions as necessary to obtain, at a minimum, a three-point calibration curve.

[B.6] Record all dilution values for each concentration level in the HSG Operational Logbook.

4.2.5 American Society for Testing of Materials (ASTM) Type I or Type II Water

[A] ASTM Type I or Type II water shall be procured with a maximum 1.0 umho/cm conductance at 25 °C.

[B] The system shall be purged with UHP Nitrogen and humidified with ASTM Type I or Type II water.

[C] The humidifier is isolated during system evacuations to prevent manifold flooding.

4.2.6 PID Calibration Standard

[A] The PID calibration shall contain 100 ppmv isobutylene or other certified VOC gas standard as specified by the manufacturer's instructions.

[A.1] **IF** an alternate calibration standard is used, **THEN** note in the HSG Operational Logbook.

[B] UHP Nitrogen shall be used for zeroing the PID.

[C] The PID verification gas shall contain 10 ppmv isobutylene or other certified VOC gas standard that meets manufacturer's specifications.

[C.1] **IF** an alternative verification standard is used, **THEN** note in the HSG Operational Logbook.

[D] The PID calibration and verification standards shall be procured from an approved vendor.

4.2.7 CCV Standard

[A] The CCV standard shall be procured as a certified gas standard.

[B] The CCV shall contain all of the VOC analytes from Table 1, hydrogen, and methane.

[C] The Table 1 VOC concentrations of the CCV sample are between 15 ppmv and 300 ppmv. The hydrogen and methane concentrations of the CCV sample will be 0.15 volume %.

[D] The CCV standard shall **NOT** be derived from the same source as the ICAL standard.

4.3 Process Gases

NOTE
Process gases referred to in this section support the GC/MS in its operation. Process gases shall be procured with a certificate of analysis.

4.3.1 Hydrogen

[A] Hydrogen is used to support combustion in the FID.

[B] Hydrogen shall be UP.

4.3.2 Air

[A] Air is used to support combustion in the FID.

[B] Air shall be Zero grade.

4.3.3 Helium

[A] Helium is used as the GC/MS column carrier gas.

[B] Helium shall be UP.

4.3.4 Nitrogen

[A] Nitrogen is used as the carrier gas in TCD to eliminate interference.

[B] Nitrogen is used in the drilling sequence to provide an inert atmosphere.

[C] Nitrogen is used as the equipment blank.

[D] Nitrogen is used in the humidified nitrogen purge cycle.

[E] All nitrogen shall be UHP and shall contain less than 1.0 ppm VOCs.

4.4 Initial Calibration (ICAL)

NOTE

See Table 4, Calibration Criteria for Volatile Organic Compounds, for additional calibration requirements.

4.4.1 Setup

[A] Create an analytical method file for instrument control that contains the instrument configuration and operating conditions (input is necessary before the Varian MS Workstation accepts the analytical method as valid and complete). This method file is automatically referenced on each data file produced, which uses the method.

NOTE

Complete calibration may involve several 12-hour periods. BFB analysis is required **AND** must be acceptable for each 12-hour period of calibration injections.

[B] The ICAL of the GC/MS combines the MS, FID and TCD into one method in the Varian MS Workstation. The method and analytical files used to establish the ICAL are archived when the ICAL is no longer valid.

[C] The ICAL will be submitted to Project Level Validation. The HSG personnel will retain a copy of the ICAL.

[D] The ICAL will be referenced in all BDRs that it applies to.

[E] Save the ICAL method name to include the instrument ID and date.

[F] Analyze the standards in accordance with CCP-TP-007.

4.4.2 MS ICAL

[A] An ICAL of the MS is needed if:

[A.1] The instrument has never been calibrated.

[A.2] The CCV continues to fail.

[A.3] The OCS continues to fail.

[A.4] A major change has been made to the analytical system such as replacing the MS trap components or GC column.

[B] The ICAL shall include all target compounds in Table 1.

[C] The correlation coefficient (R^2) for each VOC target compound shall be greater than 0.990.

[D] The Relative Standard Deviation (%RSD) for each VOC target compound shall be less than 35 percent.

[E] **IF** a linear equation is used,
THEN five concentrations shall be used to generate it.

[F] **IF** a quadratic equation is used,
THEN six concentrations shall be used to generate it.

[G] One concentration level in the calibration curve shall be below the PRQL listed in Table 1.

[H] Target compounds shall be quantitated from the primary ion listed in Table 5, Characteristic Ion for Volatile Organic Compounds.

[H.1] **IF** a secondary quantitation ion(s) is used,
THEN the reference spectrum shall also contain the same secondary quantitation ion(s) and that the ICAL reference was quantitated from that secondary ion.

[I] The VOC concentration units shall be in ppmv.

[J] A copy of the calibration gas standard certifications shall be included in the ICAL sent to Project Level Validation.

[K] A calibration curve shall be printed for each target analyte.

[L] Sample spectrum and reference spectrum shall match for proper identification.

[M] Isomers or compounds that share common ions shall be properly identified.

[N] The upper curve limit on the MDL spreadsheet shall be updated with every calibration using the highest concentration for each compound.

[O] The initial calibration average response factors shall be updated with every calibration. The response factors will be entered in the current revision of the BDR Template.xls on the percent difference (%D) worksheet for each compound.

4.4.3 Internal Standard

[A] Internal standards shall be used to quantify TICs only.

[B] Internal standards shall have a concentration of 100 ppmv.

[C] Internal standards in the CCV, shall meet the acceptance criteria listed in Table 10, Internal Standard Criteria.

[D] Internal standards will have a two-point calibration, with zero being the second point.

[E] A calibration curve shall be printed for each internal standard.

4.4.4 FID and TCD ICAL

NOTE

See Table 8, Summary of GC Calibration Requirements for Hydrogen and Methane Analysis, for additional calibration requirements.

[A] An ICAL of the FID and TCD is needed if:

[A.1] The instrument has never been calibrated.

[A.2] The CCV of hydrogen and methane continues to fail.

[A.3] The OCS continues to fail for hydrogen and methane.

[A.4] A major change has been made to the analytical system such as replacing detector components or GC column.

[B] The ICAL shall include hydrogen and methane.

[C] The R^2 for hydrogen and methane is greater than 0.990.

[D] The Relative Standard Deviation (%RSD) shall be less than 35 percent.

[E] Three concentration levels for methane (on the FID) and three concentration levels for hydrogen (on the TCD) shall be used to generate the calibration curves for hydrogen and methane.

[F] One concentration level shall be below the PRQL in Table 7.

[G] The hydrogen and methane units shall be in volume %.

[H] A copy of the calibration gas standard certification shall be included in the ICAL sent to Project Level Validation.

[I] A calibration curve shall be printed for hydrogen and methane.

[J] Evaluate the data for proper peak integration of hydrogen and methane, based on professional judgment.

4.4.5 The retention time (RT) window for each analyte is determined by using the average of the analyzed ICAL standards. The RT window is set at ± 0.4 minutes or less for all target compounds. Based on the professional judgment of the HSG operator, manual compound integration may be required to account for normal instrument variation or to eliminate interferences of closely eluding compounds. However, manual integration may be required due to interference of the matrix. The analyst will determine if the interference requires changing the RT or the RT window. Manual changes will be reported in the case narrative.

[A] The VOCs, hydrogen and methane RT windows shall be set so that there is no overlap that will cause false positive results, except for structural isomers. Structural isomers will be quantitated as a mix.

[B] The RTs for the MSD shall be determined by identifying the peaks in the calibration standard chromatogram.

[C] The apex of the peak shall be used to determine RT.

[D] The sample spectrum shall match the reference spectrum generated from the ICAL.

[E] The correct RT shall be entered into the method compound table within the Varian software.

4.5 Minimum Detection Limit (MDL) and Method Performance Samples

4.5.1 All GC/MS units using this procedure shall demonstrate acceptable MDL compliance prior to the analysis of actual samples. Demonstration of MDL shall be achieved by analyzing Method Performance Samples (see Tables 6 and 9). These samples are to be commercially purchased and shall contain VOCs, hydrogen and methane at concentrations appropriate to demonstrate the QAOs specified in Tables 1 and 7. The analysis of seven samples shall meet the criteria specified for precision, accuracy, and MDL in Tables 1 and 7. Demonstration of MDL and Method Performance Samples shall be at a minimum of every six months by performing analysis on seven samples.

4.5.2 The MDL shall be determined for all target VOCs, hydrogen and methane.

4.5.3 Method Performance Samples are prepared with stock gas calibration standards and shall contain all of the analytes listed in Table 1 and Table 7 at concentrations appropriate to meet the QAOs specified in Table 1 and Table 7.

[A] Purge the gas tight syringe a minimum of three times.

[B] Draw the determined amount of calibration gases into a 50 mL syringe.

[C] Manually inject 50 mL of the gas standard into the gas injection port.

[D] Analyze the standard in accordance with the sampling procedure CCP-TP-007.

[E] Repeat Steps 4.5.3[A] through 4.5.3[D] to obtain seven Method Performance Samples that meet the QAOs listed in Table 1 and Table 7.

[F] Record the operation in the HSG Operational Logbook.

4.5.4 Generate the raw data analysis reports using the Varian MS Workstation when the samples are finished.

4.5.5 Calculate the MDL, and %RSD and %R values using the BDR Template.xls (tab labeled MDL) spreadsheet.

4.5.6 Verify the acceptance criteria for the MDLs listed in Table 1 and Table 7 has been met.

NOTE

Samples may **NOT** be analyzed until the measured MDLs are less than the Table 1 and Table 7 MDLs and PRQLs.

4.5.7 **IF** the acceptance criteria have **NOT** been met, **THEN** begin corrective actions.

4.5.8 Print a copy of the MDL, and Method Performance Samples spreadsheet. The spreadsheet is included in every BDR submitted for Project Level Validation. These are to be included in the first data report after the ICAL.

4.5.9 The DVS system shall demonstrate acceptable performance prior to the analysis of actual samples.

4.6 Quality Control (QC) Samples

NOTE

The system Quality Assurance (QA)/QC Samples are analyzed as follows:

BFB and continuing calibration verification samples are injected directly into the GC/MS.

OCS, Field blank, or equipment blank, and duplicate samples are collected “on-line" through the entire system and analyzed.

4.6.1 4-Bromofluorobenzene Tune (BFB)

[A] The BFB shall be analyzed at the beginning of each 12-hour analysis period prior to a CCV.

[B] The BFB shall demonstrate that the GC/MS system meets the BFB Tune criteria specified in Table 2.

[C] The BFB is analyzed in accordance with CCP-TP-007.

4.6.2 Continuing Calibration Verification (CCV)

[A] CCV standards shall be analyzed following the BFB using CCP-TP-007, prior to the analysis of any samples, to verify the calibration curves and RT windows. The concentration of the continuing calibration standard shall be between the highest and lowest concentration in the initial calibration.

[B] The DVS shall analyze CCV Samples at the frequency specified in Tables 6 and 9. A sample consists of a certified standard gas mixture and shall be from sources independent of those used for instrument calibration. These samples shall contain compounds at concentrations in the calibration range of the instrument. The CCV sample analysis is designed to ensure that the laboratory’s calibrations are correct for each analytical batch of samples processed. CCV sample results shall be considered acceptable if the following is met:

[B.1] %D for VOCs is less than or equal to 30 percent.

[B.2] %R for hydrogen and methane is 70 to 130 percent of the certified known value.

[B.3] %R for Internal Standard is 50 to 200 percent and RT is ± 0.5 minutes of the initial calibration.

[C] **IF** the %R, %D, or RT DO **NOT** meet criterion, **THEN** the CCV standard shall be reanalyzed.

[D] **IF** the source of the problem can **NOT** be determined, **THEN** a new calibration for VOCs, hydrogen and methane shall be generated before quantitative analysis sampling begins.

4.6.3 On-Line Control Sample (OCS)

[A] The OCS shall be analyzed at the beginning of each 12-hour analysis period following the CCV.

[B] The OCS shall include a minimum of six target analytes from Table 1, including hydrogen and methane.

[C] The OCS shall include a minimum of six target VOC analytes from 10 to 100 ppmv and hydrogen and methane at approximately 0.2 volume %.

[D] The standards used for the OCS shall be independent of the standards used for ICAL.

[E] The %R for all compounds shall be 70 to 130 percent of the certified known value.

[F] **IF** the %R criterion is **NOT** met, **THEN** the OCS standard shall be reanalyzed.

[G] **IF** the source of the problem can **NOT** be determined, **THEN** a new calibration for VOCs, hydrogen, and methane shall be generated before quantitative sample analysis begins.

4.6.4 Blank Analysis

[A] The GC/MS shall analyze blanks at the frequency specified in Tables 6 and 9. The field blank shall consist of ambient air collected near the drum sampling equipment and routed through the entire sample collection system. Field blank, or if needed, an equipment blank, shall be acceptable if the concentrations of VOCs, hydrogen and methane less than or equal to 3x the MDL specified in Tables 1 and 7.

[A.1] **IF** the field blank results do **NOT** meet the acceptance criteria,
THEN an equipment blank shall be run to ensure sample lines and equipment is free of contamination. No analyses can be performed until blanks are below this level.

[B] **IF** the FBLANK fails,
THEN an equipment blank must be run to verify that the contamination is external to the HSG sampling equipment. The equipment blanks shall consist of UHP Nitrogen. The same procedures used to analyze on-line samples shall be used to prepare and analyze the field and equipment blanks.

[C] The FBLANK or the alternate equipment blank shall be analyzed at the beginning of each 12-hour analysis period following the OCS.

[D] **IF** a target analyte(s) is found in the blank above three times the Method Detection Limit (MDL),
THEN flag the target analyte(s) with a “Z" in all associated drum sample(s), initiate a Nonconformance Report (NCR) in accordance with CCP-QP-005, *CCP TRU Nonconforming Item Reporting and Control*, **AND** discuss the impact in the case narrative.

[E] **IF** a target analyte(s) is found in the blank greater than MDL,
THEN flag the target analyte(s) with a “B" in all associated drum sample(s).

4.6.5 Duplicate Analysis

NOTE

A duplicate OCS shall be run when the drum sample and the drum duplicate do **NOT** contain any analytes greater than PRQL or analytes are above the linear range.

[A] The DVS shall analyze on-line duplicate samples in a frequency specified in Table 6, Summary of Laboratory Quality Control Samples and Frequencies for Gas Volatile Organic Compounds Analysis and Table 9, Summary of Laboratory Quality Control Samples and Frequencies for Hydrogen and Methane Analysis. Duplicate results shall be considered acceptable if the relative percent difference (RPD) is less than or equal to 25 percent for analytes greater than PRQL in both samples.

[B] Analyzing a drum duplicate or OCS duplicate shall demonstrate precision of the HSG sampling system.

[C] The drum duplicate or alternate OCS duplicate shall be analyzed once per 12-hour analysis period.

[D] **IF** any compound(s) have a RPD greater than 25 percent, **THEN** flag the compound(s) with a “Z" and initiate an NCR in accordance with CCP-QP-005., **AND** discuss the impact in the case narrative.

[E] Samples will be analyzed in accordance with CCP-TP-007.

4.6.6 Performance Demonstration Program (PDP)

[A] PDP Samples will be analyzed in accordance with CCP-TP- 007, along with the analysis and reporting instructions that accompany the PDP samples.

4.7 Calculations

NOTE

The calculations contained in the final report are performed by the BDR Template and are **NOT** hand calculated.

4.7.1 CCV and OCS QAO Calculation

[A] The validity of the MS ICAL curve is checked by calculating the %D for each compound.

[B] HSG sampling and analysis system functionality verification is performed by %R using the OCS.

(Accuracy is the degree of agreement between a measured result and a known value.)

$$\%R = \left[\frac{Measured}{Known}\right] \times 100$$

Where:

Measured = concentration amount from the analysis
Known = concentration amount from the diluted stock standard

[C] HSG sampling and analysis equipment calibration is verified by the %D of the CCV, which is a function of precision.

$$\%D = \frac{|C_1 - C_2|}{C_1} \times 100$$

Where C_1 = initial measurement
C_2 = second or additional measurement

4.7.2 Duplicate QAO Calculation

[A] Precision is a measure of the agreement among multiple measurements.

[B] Precision shall be performed as follows:

[B.1] For duplicate measurements, the precision, expressed as the RPD, is calculated as:

$$RPD = \frac{C_1 - C_2}{\frac{(C_1 + C_2)}{2}} * 100$$

Where:

C_1 and C_2 = two values obtained by analyzing the duplicate samples
C_1 = the larger of the two observed values

4.7.3 MDL and Method Performance Calculations

NOTE
All GC/MS units using this procedure shall demonstrate acceptable MDL compliance prior to the analysis of actual samples. These calculations are contained within the Excel® BDR-TEMPLATE workbook spreadsheet “MDL."

[A] For three or more replicate measurements the precision, expressed as the %RSD, is calculated as follows:

$$\% RSD = \left[\frac{s}{m}\right] \times 100$$

Where:
s = standard deviation of measurements
m = mean of replicate analyses

[B] Determine the MDL as follows:

$MDL = S \times t_{(n-1,\ 1-a=0.99)}$

Where:

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

4.7.4 Determination of TIC (estimated concentration)

$$\frac{C_{IS}}{A_{IS}} \times A_{TIC} = C_{TIC}$$

Where:
C_{IS} = Concentration of the Internal Standard
C_{TIC} = Concentration of the TIC
A_{IS} = Area counts of the Internal Standard
A_{TIC} = Area counts of the TIC

4.7.5 RRT Calculation

$$RRT_{Sample} = \frac{(\text{Retention Time of Analyte})_{Sample}}{(\text{Retention Time of Internal Standard})_{Sample}}$$

$$RRT_{Standard} = \frac{(\text{Retention Time of Analyte})_{Standard}}{(\text{Retention Time of Internal Standard})_{Standard}}$$

$$RRT = RRT_{Sample} - RRT_{Standard}$$

4.8 Drum Sample Analysis

NOTE
The Varian software performs both qualitative and quantitative calculations.

4.8.1 Qualitative Analysis

[A] Analytes listed in Table 1 are identified by comparison of the sample mass spectrum with the reference mass within the Retention Time Window (RTW). Reference mass spectra are obtained through analysis of calibration standards and verified with a NIST/EPA mass spectral library search. The following criteria shall be satisfied to verify identification:

[A.1] All ions present in the reference mass spectrum at a relative intensity greater than 10 percent of the most abundant ion, shall be present in the sample spectrum.

[A.2] A NIST/EPA mass spectral library search for all peaks in the chromatogram shall be provided.

[A.3] The relative intensities of these ions shall agree within ± 30 percent between the sample spectra and reference spectrum.

[A.4] Structural isomers (very similar mass spectra) should be identified separately if the height of the valley between the isomer peaks is less than 25 percent of the sum of the two peaks. Otherwise, structural isomers are identified as isomeric pairs.

NOTE

RT windows are conservatively set at a maximum of ± 0.40 minutes. This parameter coupled with RTs of the internal standards, being greater than 13 minutes, ensures that the maximum difference in RRT of 0.051, as compared to the initial calibration also ensures that a ± 0.06 RRT criteria is obtained.

[A.5] Verify that the RRT units are within ± 0.06 RRT units of the initial calibration by verifying the compound is within its retention time window.

[B] Analytes listed in Table 7 are identified by comparison of the calibration standard RT and the sample RT.

4.8.2 Quantitative Analysis

[A] Once a compound has been qualitatively identified, the quantitation of that compound shall be based on the integrated abundance from the EICP of the primary characteristic ion (Table 5) or other secondary ion(s) identified by the instrument's manufacturer (e.g., acetone uses masses 43 and 58) as appropriate for quantitation.

[B] Quantitation is based on calibration curves generated from the analysis of external calibration standards. Quantitation is performed automatically using the Varian MS Workstation and current calibration curves.

[C] If a compound's concentration exceeds the linear range of the calibration curve, the compound is qualified "E", indicating an exceedance of the calibration range.

[D] If applicable, re-quantitate the "E" flagged compound(s) with an approved method that extends the linear range.

[E] Quantitation for hydrogen and methane are performed automatically using the instrument's software and current calibration curves.

4.9 Tentatively Identified Compounds (TIC)

4.9.1 For samples containing compounds **NOT** listed in Table 1, that have total ion current peak area greater than 10 percent of the nearest (determined by RT) internal standard, a library search of a recent NIST mass spectral database shall be performed. The 10 percent area criterion is locked into the Varian software within the method that is used to quantify samples, and is established before sample analysis begins. Guidelines for making tentative identification of these unknown compounds are:

[A] The relative intensities of major ions in the reference spectrum (ions greater than 10 percent of the most abundant ion) should be present in the sample spectrum.

[B] The relative intensities of major ions should agree within ± 20 percent.

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

[D] 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 co-eluting peaks in accordance with EPA-SW-846, Method 8260B. Data system library reduction programs can sometimes create these discrepancies.

[E] Ions present in the sample spectrum but **NOT** in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds in accordance with Method 8260B.

[F] Only after visual comparison of the sample spectrum with the results of the library search, shall the GC/MS Operator assign a tentative identification.

[G] TICs are initially reviewed at the data generation level in accordance with CCP-TP-009 and then validated at the ITR level using CCP-TP-032, *CCP Single Sample Manifold Data Validation Procedure*.

NOTE

The NIST Library used must contain, at a minimum, all Volatile Organic Compounds contained in Title 40 CFR 261, Appendix VIII. It is recommended that the NIST Library used also contain all possible flammable VOCs **NOT** contained in Appendix VIII in order to properly quantitate and establish a reliable flammable VOC concentration for CCP-PO-002, *CCP Transuranic Waste Certification Plan* requirements.

[H] All flammable TICs (excluding the volatile organic compounds (VOCs) that have been evaluated for shipment in the TRUPACT-II and HalfPACT shipping packages as listed in the current revision of DOE/WIPP 01-3194, *CH-TRU Waste Content Codes,* Appendix B) that exceed a concentration of 500ppmV will be reported as a nonconformance, in accordance with CCP-QP-005.

[I] A NIST/EPA mass spectral library search shall be provided for all required peaks in the chromatograms for samples.

[J] When the above criteria are **NOT** met, but the identification is correct in the technical judgment of the data reviewer, report the TIC as is.

[K] **IF** more than one possible match exists,
THEN the TIC may be reported as “either compound X or compound Y."

[L] **IF** isomer specificity is in question,
THEN the TIC result may be changed to a non-specific result (e.g., 1,3, 5-trimethyl benzene to trimethyl benzene isomer).

[M] **IF** identification is uncertain but other samples have a TIC of similar RT and the same ions,
THEN identification information may be inferred.

[N] The concentration of the tentatively identified compounds shall be estimated using the internal standard analyte nearest the RT of the TIC (free of interferences). Quantitation is performed by dividing the area count of the TIC by the response factor of the internal standard. The resulting concentration shall be reported to identify which internal standard compound was used to determine the TIC concentration.

4.10 Photoionization Detector (PID)

4.10.1 The PID is connected to the sample manifold and used to verify system cleanliness, to the detection limits specified in Table 1. The PID is operated using a computer connection located near the system operating station and interfaces with the PLC to provide a signal output on the touch screen. PID shall be re-calibrated when the calibration verification fails.

4.10.2 The PID used is an Organic Vapor Analyzer (OVA), intended to detect possible contamination of the HSG system. The PID is calibrated using two points per the manufacturer's procedure. UHP Nitrogen is used to zero the PID and a certified gas calibration standard of 100 ppmv isobutylene. The PID calibration shall be documented on Attachment 4, Process Parameters of CCP-TP-007. Any PID cleanliness/contamination check with a value exceeding 10 ppmv shall require repeating the check.

4.11 Calibration/Verification Procedure

NOTE

The ModuRAE is calibrated using a two-point calibration process. UHP nitrogen "Zero Gas" which contains no detectable organic gases or vapors is used to set the zero point. Then a standard reference gas which contains a known concentration of a given gas is used to set the second point of reference. The recommended standard calibration gas is a 100 ppmv isobutylene gas, balance air. The calibration procedures are described below.

4.11.1 Setup Calibration Gas and Meters

[A] Disconnect the clear hose from the PID barb and connect the cal gas hose. Make sure that the adapter fits over the gas inlet barb tightly to avoid any leakage.

4.11.2 Zero Gas Calibration

[A] Wait for at least one minute to warm up the module.

[B] Set the "zero gas" bottle regulator to 10 pounds per square inch (psi).

[C] Turn ON the gas flow.

[D] Open the calibration window on the side of the ModuRAE.

[E] Adjust the "Offset" potentiometer using a small screwdriver until the voltage reading is "zero."

4.11.3 Standard Gas Calibration/Verification

[A] Connect the standard reference gas bottle to the gas inlet barb.

[B] Turn on the gas flow from the bottle.

[C] Wait for about 30 seconds so that the gas flow is steady.

[D] Adjust the “Gain" potentiometer using a small screwdriver until the voltage or current reading is stabilized at 1.0V (100 ppm).

[E] Turn off the calibration gas bottle.

[F] Remove volt meter or current meter.

[G] Enter results on Attachment 4 of CCP-TP-007.

4.12 Combustible Gas Analysis

NOTE
If required by site, a Lower Explosive Limit (LEL) option is available.

4.12.1 The combustible gas analyzer is automatically operated via the PLC process control software. An LEL measurement is made during the gas sample collection operation; this signal is sent to the PLC controller and displayed at the operator’s touch screen.

4.12.2 Detcon model series FP-FP-524C stand alone sensor assemblies are designed to detect, monitor, display, and alarm when combustible hydrocarbon gases are present in ambient air. Detection range is from 0-100 percent LEL. Method of detection is by diffusion absorption requiring no moving parts.

4.12.3 The assembly accommodates all calibration adjustments: zero, span (course and fine), low alarm, high alarm, and temperature control. This provides maintenance technicians with the means of making adjustments without maintaining communication with the PLC.

4.12.4 Verification and calibration shall be performed according to NFT’s operational documentation and noted in HSG Operational Logbook.

[A] Verification shall be performed weekly.

[B] Calibration shall be performed as needed.

4.13 Maintenance

NOTE

The HSG Operator is restricted to the following maintenance procedures. Maintenance beyond the scope of this procedure is restricted to qualified Nuclear Filter Technologies personnel. Site-specific work control procedures will be followed at all times. All work, maintenance and service shall be recorded in a HSG Operational Logbook according to CCP-QP-011, *CCP Notebooks and Logbooks.*

4.13.1 GC/MS Maintenance

[A] The Varian 3800 GC and Saturn 2000 are serviced and maintained by HSG Operators and Varian qualified service personnel. The HSG Operator can perform routine and minor service of the GC columns and MS trap. Maintenance procedure steps are found in the Saturn Maintenance Tutorial Software. The operator shall follow the instructions step by step. Surfaces of all HSG sampling equipment components that will come in contact with the sample HSG are thoroughly inspected and cleaned prior to assembly. Manifolds and sampling heads shall be purged with humidified zero air, nitrogen, or helium and leak-checked after assembly.

4.13.2 Sample Chamber Maintenance

NOTE

The drum seal shall be replaced when cuts or abrasions cause the seal test to fail.

[A] Remove and Replace Drum Seal

[A.1] Press the Emergency Stop Button.

[A.2] Access the empty drum cabinet.

[A.3] Loosen and remove gas transfer line.

[A.4] Loosen and remove six fastening bolts.

[A.5] Remove drum seal from sample chamber housing.

[A.6] Loosen and remove gas transfer tee.

[A.7] Remove curved tubing from drum seal.

Controlled
Copy

[A.8] Replace curved tubing on new drum seal.

[A.9] Replace and tighten tee.

[A.10] Place new drum seal on sample chamber housing.

[A.11] Replace and tighten the six fastening bolts.

[A.12] Connect and tighten the gas transfer line.

[A.13] Reset the Emergency Stop Button.

NOTE

Inside the sample chamber are two lip seals. The upper lip seal is accessed through the glove ports and the lower lip seal through the drum cabinet. The lip seal shall be replaced when cuts or abrasions cause the seal test to fail.

[B] Remove and Replace Lip Seals

[B.1] Upper Lip Seal

(a) Press the Emergency Stop Button.

(b) Working through the glove ports, remove the six fastening bolts in the seal retainer.

(c) Remove the seal retainer.

(d) Gently pry the seal from the housing.

(e) Tap a new seal into the housing.

(f) Replace the seal retainer.

(g) Replace the six fastening bolts.

(h) Reset the Emergency Stop Button.

[B.2] Lower Lip Seal

(a) Press the Emergency Stop Button.

(b) Access the empty drum cabinet.

(c) Gently pry the Lip Seal from the housing.

(d) Tap a new Lip Seal into the housing.

(e) Reset the Emergency Stop Button.

NOTE

Inside the sample chamber are Roulon sleeve bearings. They are accessed through drum cabinet. The Roulon sleeve bearing shall be replaced when cuts or abrasions cause the seal test to fail.

[C] Remove and Replace Roulon Sleeve Bearing

[C.1] Press the Emergency Stop Button.

[C.2] Access the empty drum cabinet.

[C.3] Gently pry the lip seal from the housing.

[C.4] Slide out the old Roulon sleeve bearings from the sample chamber housing.

[C.5] Slide in the new Roulon sleeve bearings into the sample chamber housing.

[C.6] Tap a new lip seal into the housing.

[C.7] Reset the Emergency Stop Button.

NOTE

Inside the glovebox is an in-line 0.5 micron filter. It is accessed through the glove ports. The in-line filter element shall be replaced monthly or earlier if deemed necessary. Document the change-out in the HSG Operational Logbook.

[D] Remove and Replace Sample Transfer Line

[D.1] Press the Emergency Stop Button.

[D.2] Remove glove fasteners.

Controlled
Copy

[D.3] Remove the gloves from the glove ports.

[D.4] Remove the insulation.

[D.5] Loosen and remove the filter housing.

[D.6] Replace the filter per the instructions in the element kit.

[D.7] Place new VCR gaskets in the housing connections.

[D.8] Tighten the housing connections.

[D.9] Replace the insulation.

[D.10] Place the gloves on the ports.

[D.11] Replace glove fasteners.

[D.12] Reset the Emergency Stop Button.

Controlled
Copy

5.0 RECORDS

5.1 No records are generated during the performance of this procedure. Data generated during the performance of this procedure is recorded and becomes a record in CCP-TP-007 and CCP-TP-009.

Table 1 - Target Analyte List and QAOs

Compound	CAS No.	Precision[a] (%RSD or RPD) (less than or equal to value below)	Accuracy [a] (%R)	MDL[b] (ng)	PRQL[b] (ppmv)	Complete-ness (%)
Benzene [e]	71-43-2	25	70-130	10	10	90
Bromoform	75-25-2	25	70-130	10	10	90
Carbon Disulfide[h]	75-15-0	25	70-130	10	10	90
Carbon Tetrachloride [d]	56-23-5	25	70-130	10	10	90
Chlorobenzene [e]	108-90-7	25	70-130	10	10	90
Chloroform	67-66-3	25	70-130	10	10	90
Chloromethane [h]	74-87-3	25	70-130	10	10	90
1,1-Dichloroethane [e]	75-34-3	25	70-130	10	10	90
1,2-Dichloroethane [d,e]	107-06-2	25	70-130	10	10	90
1,1-Dichloroethylene [e]	75-35-4	25	70-130	10	10	90
cis-1,2-Dichloroethylene [e]	156-59-2	25	70-130	10	10	90
trans-1,2-Dichloroethylene[e]	156-60-5	25	70-130	10	10	90
Ethyl Benzene [e]	100-41-4	25	70-130	10	10	90
Ethyl Ether [e]	60-29-7	25	70-130	10	10	90
Methylene Chloride [d]	75-09-2	25	70-130	10	10	90
1,1,2,2-Tetrachloroethane	79-34-5	25	70-130	10	10	90
Tetracholorethylene	127-18-4	25	70-130	10	10	90
Toluene [e]	108-88-3	25	70-130	10	10	90
1,1,1-Trichloroethane [d]	71-55-6	25	70-130	10	10	90
Trichloroethylene [d]	79-01-6	25	70-130	10	10	90
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	25	70-130	10	10	90
m-Xylene [c,e]	108-38-3	25	70-130	10	10	90
o-Xylene [d,e]	95-47-6	25	70-130	10	10	90
p-Xylene [c,e]	106-42-3	25	70-130	10	10	90
Acetone	67-64-1	25	70-130	150	100	90
Butanol	71-36-3	25	70-130	150	100	90
Methanol	67-56-1	25	70-130	150	100	90
Methyl Ethyl Ketone	78-93-3	25	70-130	150	100	90
Methyl Isobutyl Ketone	108-10-1	25	70-130	150	100	90

a Criteria apply to PRQL concentrations.
b Values based on delivering 10 mL to the analytical system.
c These xylene isomers cannot be resolved by the analytical methods employed in this program and shall be reported as “m,p-xylene" (undifferentiated).
d Critical Target Compounds (CTCs)
e Flammable VOC
f Required only for Plutonium Finishing Plant (PFP) waste stream at Hanford.

Notes:
%RSD = Percent relative standard deviation.
RPD = Relative percent difference.
%R = Percent recovery.
MDL = Method detection limit (total number of nanograms delivered to the analytical system per sample).
PRQL = Program required quantitation limit.

Table 2 - 4-Bromofluorobenzene Key Ions and Abundance Criteria

Page 1 of 1

MASS	ION ABUNDANCE CRITERIA
50	15 to 40 percent of mass 95
75	30 to 60 percent of mass 95
95	Base peak, 100 percent relative abundance
96	5 to 9 percent of mass 95
173	<2 percent of mass 174
174	>50 percent of mass 95
175	5 to 9 percent of mass 174
176	> 95 percent and <101 percent of mass 174
177	5 to 9 percent of mass 176

Table 3 - Recommended GS/MS System Operating Conditions for Varian Model 3800 GC and Varian Saturn 2000 MS Page 1 of 1

Electronic energy:	70 volts (nominal)
Mass range:	28 to 300 amu (“full VOC scan mode" equivalent)
Scan time:	One scan/second or enough to give 5 scans/peak
Column type:	60 m X 0.32 mm I.D., 1.8 um film thickness
Initial column temperature:	40°C
Initial column holding time:	5 minutes
Column temperature program:	5°C C/min to 170°C
Final column temperature:	170°C
Injector temperature:	120°C
Transfer line temperature:	200°C
Ion trap temperature	120°C
Flow Conditions:	
Helium carrier input pressure	80 psi
Nitrogen carrier input pressure	80 psi
Column temperature	40°C
Initial relays	-1-2-3
Front carrier	Set the pressure to 11.8 psi
Middle carrier	Set the pressure to 17 psil
FID H2	30 mL/min
FID make-up	Off
FID air	300 mL/min
TCD	2m x ⅛" molecular sieve 5A 45/60
Regulator Pressure Settings	Air - 60 psig Nitrogen - 80 psig
Transfer Lines	To FID - 325 cm x 0.32 mm deactivated fused silica
	To Mass Spec - 64 cm x 0.10 mm deactivated fused silica

NOTE:
The parameters presented in Recommended GS/MS System Operating Conditions for Varian Model 3800 GC and Varian Saturn 2000 MS, Table 3 may be modified to overcome interferences, optimize equipment efficiency or sensitivity. All parameters and changes shall be documented.

Table 4 - Calibration Criteria for Volatile Organic Compounds Page 1 of 1

Instrument/ Technique	Procedure	Frequency of Procedure	Acceptance Criteria
GC/MS	BFB Tune	Every 12 hours	Abundance criteria for all key ions are met (see Table 2)
	Minimum 5-pt Initial Calibration (5 standards minimum)	Initially, and as needed	$R^2 \geq 0.990$ %RSD < 35%
	Continuing Calibration	Every 12 hours	%D for all compounds $\leq$ 30 of initial calibration
	Blank Analysis (Field or Equipment)	Once per batch	Any detected analyte: $\leq$ 3* MDL
	Duplicate Analysis	Once per batch	RPD $\leq$ 25%
Photoionization Detector (PID)	Initial Calibration	Initially, and as needed per manufacturer's procedures, or PID verification value does not meet criteria	PID verification: 10 ± 1 ppm

Table 5 - Characteristic Ion for Volatile Organic Compounds Page 1 of 1

Volatile Organic Compound	Primary Ion*	Secondary Ion*
Acetone	43	58
Benzene	78	
Bromoform	173	171,175
Butanol	56	43
Carbon Disulfide	76	
Carbon Tetrachloride	117	
Chlorobenzene	112	
Chloroform	83	
Chloromethane	50	
1,1-Dichloroethane	63	
1,2-Dichloroethane	62	
1,1-Dichloroethylene	61	
cis-1,2-Dichloroethylene	61	
trans-1,2-Dicloroethylene	61	
Ethyl Benzene	91	
Ethyl Ether	59	45
Methanol[a]	31	
Methyl Ethyl Ketone	43	72
Methyl Isobutyl Ketone	43	85
Methylene Chloride	49	
1,1,2,2-Tetrachlorothane	83	
Tetrachloroethylene	166	
Toluene	91	
1,1,1-Trichloroethane	97	
Trichloroethylene	130	
1,1,2-Trichloro-1,2,2-trifluoroethane	101	
m-Xylene	91	
o-Xylene	91	
p-Xylene	91	

a Analysts are required to determine the most appropriate secondary ions for these compounds.
* Primary and secondary ion masses specified by Varian Instruments for Saturn 2000 MS unit.

Table 6 - Summary of Laboratory Quality Control Samples and Frequencies for Gas Volatile Organic Compounds Analysis Page 1 of 1

QC Sample	Minimum Frequency	Acceptance Criteria	Corrective Action[a]
Method performance samples	Seven (7) samples initially and four (4) semiannually	Meet Table 1 QAOs	Repeat until acceptable
On-line duplicates	One (1) per on-line batch	RPD ≤ 25%[b]	Nonconformance if RPD >25%
On-line Equipment/Field blanks	Daily prior to sample analysis	Analyte amounts ≤ 3 x MDLs	Nonconformance if analyte amounts > 3 *MDLs
OCS and CCV samples	One (1) per on-line batch	70-130 %R (OCS) ≤ 30%D (CCV)	Nonconformance if %R <70 or > 130 %D > 30%
Blind audit samples	Samples and frequency controlled by the Headspace Gas PDP Planc	Specified in the Headspace Gas PDP Plan	Specified in the Headspace Gas PDP Plan

a Corrective action only if final, reported QC sample results do not meet the acceptance criteria of the Waste Analysis Plan.
b Applies only to concentrations greater than the PRQLs listed in Table 1.
c *Performance Demonstration Program Plan for Analysis of Simulated Headspace Gases* (Gas PDP Plan).

MDL = Method Detection Limit
PDP = Performance Demonstration Program
QAO = Quality Assurance Objective
%R = Percent Recovery
RPD = Relative Percent Difference

Table 7 - Hydrogen and Methane Analysis Quality Assurance Objectives

Page 1 of 1

Analyte	CAS Number	Precision (%RSD or RPD)	Accuracy[a] (%R)	MDL (vol%)	PRQL (vol%)	Completeness (Percent)
Hydrogen	1333-74-0	25	70-130	0.05	0.1	90
Methane	74-82-8	25	70-130	0.05	0.1	90

[a] Criteria apply to PRQL concentrations

%RSD = Percent relative standard deviation
RPD = Relative percent difference
%R = Percent recovery
MDL = Method detection limit
PRQL = Program required quantitation limit

Table 8 - Summary of GC Calibration Requirements for Hydrogen and Methane Analysis

Page 1 of 1

Technique	Procedure	Frequency of Procedures	Acceptance Criteria
GC	Minimum 3-pt initial calibration (3 standards minimum) Continuing calibration On-line Control Standard	Initially and as needed Every 12 hours	%RSD of response factor for each analyte ≤ 35% or Linear regression plot yields straight line of Correlation Coefficient $R^2 \geq 0.995$ %R of 70-130 for each analyte

%D = Percent difference
%R = Percent recovery
%RSD = Percent relative standard deviation

Table 9 - Summary of Laboratory Quality Control Samples and Frequencies for Hydrogen and Methane Analysis Page 1 of 1

QC Sample	Minimum Frequency	Acceptance Criteria	Corrective Action[a]
Method performance Samples	Seven (7) samples initially and four (4) semiannually	Meet Table 7 QAOs	Repeat until acceptable
On-line duplicates	One (1) per on-line batch	RPD $\leq$ 25[b]	Nonconformance if RPD > 25
Equipment & Field blanks	One (1) per on-line batch	Analyte concentrations $\leq$ 3X MDL	Nonconformance if analyte concentrations > 3X MDL
CCV sample On-line Control Standard	One (1) per on-line batch	70-130 %R	Nonconformances if %R < 70 or > 130

[a] Corrective Action is required only if final, reported QC sample results do not meet the acceptance criteria

[b] Applies only to concentrations greater than the PRQL listed in Table 7.

QAO = Quality Assurance Objective
%R = Percent Recovery
RPD = Relative Percent Difference

Controlled
Copy

Table 10 - Internal Standard Criteria

Instrument	Compounds	Response[1]	Retention Time[1]
GC/MS	Bromochloromethane	50% - 200%[2]	±0.5 minutes[3]
GC/MS	Chlorobenzene, d5	50% - 200%[2]	±0.5 minutes[3]
GC/MS	1,4-difluorobenzene	50% - 200%[2]	±0.5 minutes[3]

[1] Based on initial calibration
[2] Based on Method 8260B, Section 7.4.7
[3] Based on Method 8260B, Section 7.4.6