Varian, Inc.
2700 Mitchell Drive
Walnut Creek, CA 94598-1675/usa

VARIAN

Environmental Applications Manual

Methods 524.2, 525.2, 8260B, 8270D

QUALITY SYSTEM
ISO 9001
CERTIFIED

Printed in U.S.A. 03-914895-00:3

Contents

1. EPA Method 524.2

EPA Method 524.2,"Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry" is one of the most commonly used methods for VOC analysis in surface water, ground water, and drinking water.

This chapter of the Varian Environmental MS Application Manual will assist chemists in rapidly setting up the 210-MS/220-MS systems for the analysis of water samples by EPA Method 524.2. The accompanying CD for this manual contains a subdirectory, called EPA524_2, which contains a PDF version of this section of the manual along with other important files that will be described in detail below.

Following this introduction is the Scope and Summary of EPA Method 524.2. The full method is available (in PDF format) in Appendix II of the included CD in for complete review. This and other methods can be obtained from the National Environmental Methods Index at http://www.nemi.gov/.

The Analytical Section provides guidance on how to achieve the requirements of Method 524.2. A complete description of the apparatus, materials (analytical standards), and conditions is given. Also included are GC column recommendations and proven methods for GC, AutoSampler, MS acquisition, and MS data handling. Acquisition parameters were selected to fulfill the tune requirements. The data handling parameters were chosen to assure positive identification and accurate quantitation, and to satisfy QA/QC requirements.

Finally, the Results Section contains a selection of data generated with the 210-MS/220-MS GC/MS system using the conditions recommended in this manual. Examples included are results for Tune Verification, Initial Calibration, and Method Detection Limit calculations (statistical process).

The Varian EnviroPro™ Software can be used to generate a variety of useful quality control summary reports in standard Contract Laboratory Program (CLP) format. Appendix I contains a series of PDF files as example reports for a typical volatile or semi-volatile method (EPA Method 524.2 and EPA 8270 are shown). The reports are easily adaptable to other EPA methods that require extensive quality control reporting.

1.1 List of Abbreviations

BFB	Bromofluorobenzene
CCC	Continuing Calibration Check
DOC	Demonstration of Capability
ICC	Initial Calibration Check
IS	Internal Standard
LCS	Lab Control Sample
LFB	Lab Forrtified Blank
LMB	Lab Method Blank
LTB	Lab Trip Blank
LRB	Lab Reagent Blank
MDL	Method Detection Limit
MS	Matrix Spike
MS/MSD	Matrix Spike/Matrix Spike Duplicate
PAT	Purge and Trap
QCS	Quality Control Sample
RRF	Relative Response Factors
RS	Recovery Standard
SPCC	System Performance Check Compounds
SS	Surrogate Standard

1.2 Scope and Application

EPA Method 524.2: Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry.

This is a general purpose method for the identification and simultaneous measurement of purgeable volatile organic compounds in surface water, groundwater, and drinking water in any stage of treatment . The method is applicable to a wide range of organic compounds, including the four trihalomethane disinfection by-products, that have sufficiently high volatility and low water solubility to be removed from water samples with purge and trap procedures. The following compounds can be determined by this method.

Table 1-1 Target Analytes

Analyte	Chemical Abstract Service Registry Number
Acetone*	67-64-1
Acrylonitrile*	107-13-1
Allyl chloride*	107-05-1
Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
2-Butanone*	78-93-3
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon disulfide*	75-15-0
Carbon tetrachloride	56-23-5
Chloroacetonitrile*	107-14-2
Chlorobenzene	108-90-7
1-Chlorobutane*	109-69-3
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7

Analyte	**Chemical Abstract Service Registry Number**
trans-1,4-Dichloro-2-butene*	110-57-6
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-59-4
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7
1,1-Dichloropropene	563-58-6
1,1-Dichloropropanone*	513-88-2
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Diethyl ether*	60-29-7
Ethylbenzene	100-41-4
Ethyl methacrylate*	97-63-2
Hexachlorobutadiene	87-68-3
Hexachloroethane*	67-72-1
2-Hexanone*	591-78-6
Isopropylbenzene	98-82-8
4-Isopropyltoluene	99-87-6
Methacrylonitrile*	126-98-7
Methylacrylate*	96-33-3
Methylene chloride	75-09-2
Methyl iodide*	74-88-4
Methylmethacrylate*	80-62-6
4-Methyl-2-pentanone*	108-10-1
Methyl-t-butyl ether*	1634-04-4
Naphthalene	91-20-3
Nitrobenzene*	98-95-3
2-Nitropropane*	79-46-9
Pentachloroethane*	76-01-7
Propionitrile*	107-12-0
n-Propylbenzene	103-65-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Tetrahydrofuran*	109-99-9
Toluene	108-88-3
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1

Analyte	Chemical Abstract Service Registry Number
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl chloride	75-01-4
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

** New Compound in Revision 4.0.*

Method detection limits (MDLs) are compound, instrument and especially matrix dependent and vary from approximately 0.02-1.6 µg/L. The applicable concentration range of this method is primarily column and matrix dependent, and is approximately 0.02-200 µg/L when a wide-bore thick-film capillary column is used. Narrow-bore thin-film columns may have a capacity which limits the range to about 0.02-20 µg/L. Volatile water soluble, polar compounds which have relatively low purging efficiencies can be determined using this method. Such compounds may be more susceptible to matrix effects, and the quality of the data may be adversely influenced.

Analytes that are not separated chromatographically but which have different mass spectra and noninterfering quantitation ions, can be identified and measured in the same calibration mixture or water sample as long as their concentrations are somewhat similar. Analytes that have very similar mass spectra cannot be individually identified and measured in the same calibration mixture or water sample unless they have different retention times. Coeluting compounds with very similar mass spectra, typically many structural isomers, must be reported as an isomeric group or pair. Two of the three isomeric xylenes and two of the three dichlorobenzenes are examples of structural isomers that may not be resolved on the capillary column, and if not, must be reported as isomeric pairs. The more water soluble compounds (>2% solubility) and compounds with boiling points above 200 °C are purged from the water matrix with lower efficiencies. These analytes may be more susceptible to matrix effects.

1.3 Summary of Method

Volatile organic compounds and surrogates with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through the aqueous sample. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb the trapped sample components into a capillary gas chromatography (GC) column interfaced to a mass spectrometer (MS). The column is temperature programmed to facilitate the separation of the method analytes which are then detected with the MS. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

Table 1-2 Quality Control Matrix Table

QC Type	Concentration Level	Frequency	Acceptance Criteria
Tune	Introduce 5-10 ppb of BFB into the PAT GC/MS System (Less than 25 ng)	Every 12 hours	Mass 50 15-40% of base peak Mass 75 30-80% of m/z 95 Mass 95 Base Peak Mass 96 < 5-9% of m/z 95 Mass 173 <2% of m/z 174 Mass 174 >50% of m/z 95 Mass 175 5-9% of m/z 174 Mass 176 >95% but <101% of m/z 174 Mass 177 5-9% of m/z 176
Performance Test Solution	None Required	None Required	None Required.
ICC	Consisting of at least 5 standard concentrations per analyte. The lowest calibration standard must be at or below the MRL (Minimum Reporting Level).	When first using this method on an instrument, after major instrument maintenance, or when indicated by a change in instrument response.	Linear or second order fit is OK. IF RRFs are used, they must be less than 20%.
LTB	Reagent Water prepared, shipped and analyzed as a sample.	Collected with every sample batch.	No analytes of interest present at or above the MRL.
LRB	Reagent Water prepared and analyzed as a sample.	One per analytical run .	No analytes of interest present at or above the MDL.
CCC	Same as the LFB, since calibration standards are procedural (purged)	One analyzed per group of 20 samples or one per work shift (Every 12 hours)	Limits are 70-130% recovery
IS	Fluorobenzene recommended in method; optional internal standards are OK to use	Run in every sample. The IS is evaluated for recovery.	In CCCs or samples, the absolute areas of the quant ions of the IS must be ± 50% of the average areas of the initial calibration, and ± 30% of the quant ion areas of the most recent CCC.
SS	1,2-Dichlorobenzene-d4 and Bromofluorobenzene are recommended. Others can be used.	Run in every sample.	Recovery must be within 70-130% of the target concentration.
LFB	All of the analytes of interest at 2 to 10 µg/L	One analyzed per group of 20 samples or one per work shift	Limits are 70-130% recovery

QC Type	Concentration Level	Frequency	Acceptance Criteria
QCS	All of the analytes of interest at 5 to 10 µg/L.	Quarterly.	Same as the LFB or CCC.
MS	Not required in the method.	Not required.	Not Required.
Duplicate sample	Lab Duplicate	At a frequency of one analyzed per batch.	RPD within 30%. MSD analyte recovery same as the MS.
DOC	4 LFBs in reagent water between 2-5 µg/L	Initially, annually and with each new technician.	Mean percent recovery for each analyte must be 80-120%, and the RSD must be less than <20%.
MDL	7 LFBs. Concentrations typical are 0.2, 0.5, and 2.0 ppb	Annually.	Calculated values for mean accuracy and RSD. No precision and accuracy limits apply.

1.4 Analytical Section

In this section parameters for the equipment, accessories, and supplies are specified to assure optimum performance of the analysis. While both older and newer products may improve overall results, these accessories were carefully selected for best performance. Deviation from the suggested equipment, supply or condition may result in lost performance.

1.4.1 Equipment and supplies

Sample containers

40 mL screw top vials with Teflon® faced silicon septum. Use pre-cleaned for EPA trace-level analysis.

Varian Part Number [VPN]: DY63006800 (72 vials/septa)

Purge and Trap (PAT) Concentrator

Tekmar Stratum™ Purge and Trap Concentrator

- The unit must be equipped with either a 25 mL or 5 mL fritted sparge vessel

99764211	Sparger, 25 mL fritted, 1/2" (glassware only)
CP914441	Sparger, 5 mL fritted, 1/2" (glassware only)

NOTE: *A larger sample volume will allow split injection of the desorbed sample. Larger split ratios are an advantage, as less water and methanol are transferred to the analytical column. If using a 25 mL sparger, a volume of no less than 15 mL must be used, because the method requires less than 15mL of volume above the purged sample (Section 6.2.1 of EPA 524.2)*

Tekmar Stratum Strat-Traps as described below

T145864403	Strat-Trap, Vocarb 3000
T149908403	Strat-Trap, #9 (Proprietary packing material)

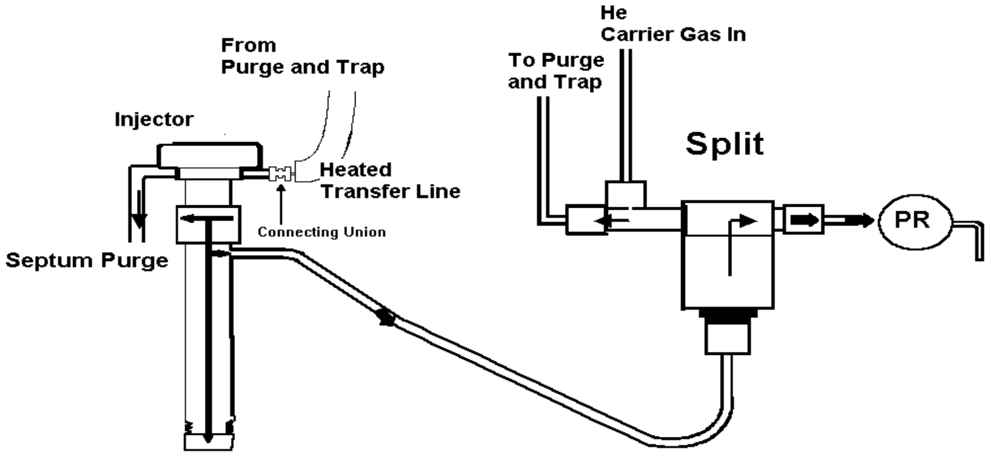
Unit will be shipped from Tekmar with the #9 trap (factory tested), and the Vocarb 3000 trap will be included as a separate item. Both traps have been found to work for the EPA Method 524.2 method target analytes.

NOTE: *The trap was selected to reduce the amount of retained water during the purging process. The 40 mL/min He purge flow will carry some water vapor to the trap along with the VOCs. On the new Strat-Traps much of this water vapor will pass through and only a small amount of it will be retained. If more hygroscopic material (such as silica gel) is contained in the trap, the retained water amount will be greater and will interfere with some of the analytes.*

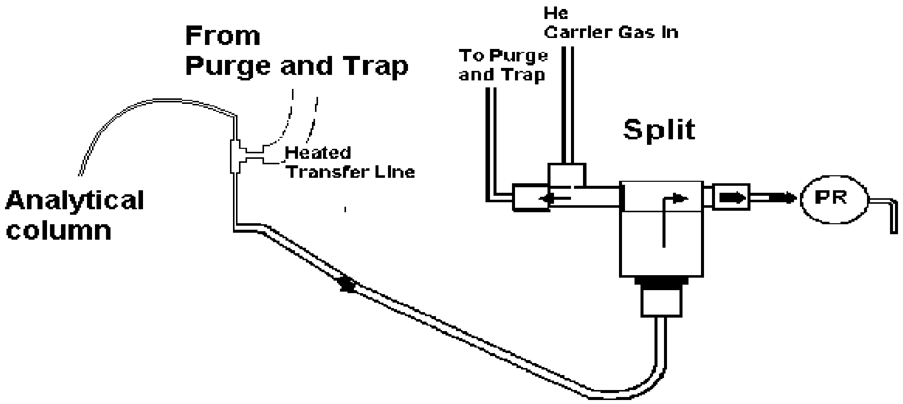
GC Pneumatics/ Inlets

The GC must be equipped with a type 25 Electronic Flow Controller (EFC) attached to a 1177 injector [VPN 45-11005-01], a 1079 injector [VPN 45-12005-11], or using direct coupling of the transfer line to the GC column via the EFC splitter. In all cases a split injection of the desorbed analytes into the analytical column will take place at an optimized split ratio. Larger split ratios are desirable, so as to minimize the amount of water transferred to the analytical column. Split ratios as high as 1:200 have been used on narrow-bore columns. If the 1177 or 1079 injectors are used, the single goose-neck, split insert should be placed in the injector (VPN: 03-926119-27 for 1177 and VPN: 03-918464-00 for 1079). Syringe injections via the injector will be possible with this configuration. If direct connection is established between the PAT transfer line and the analytical column via a "T" to the EFC, syringe injection will not be possible, but the chromatographic performance will be improved.

For best results set the septum purge flow very low (0.1 mL/min) so analytes are not lost during desorb step. Also, note the column head pressure at the starting temperature conditions, because each column (listed below) will be different. *IMPORTANT: Take note of this pressure and calibrate the EFC by entering the observed pressure and a septum purge flow of 0.1 mL/min.*



Split connection of the Purge and Trap system to a capillary column via an injector.



Split Connection without injector using Type 25 EFC only.

Analytical Columns

The following analytical columns are suggested for use with the 210-MS/220-MS system:

Varian Part Number [VPN]: CP9100 FactorFour™ VF-624-MS, 20 m x 0.15 mm ID, DF= 0.84

Varian Part Number [VPN]: CP9105 FactorFour VF-624-MS, 60 m x 0.0.32 mm ID, DF= 1.8

Varian Part Number [VPN]: CP9102 FactorFour VF-624-MS, 30 m x 0.25 mm ID, DF= 1.4

These are FactorFour low-bleed columns designed specifically for volatile organic chemicals analysis.
The 20M column will have the advantages of high resolution, fast run times, and low bleed.

NOTE: *It is important to use one of the suggested columns, since these will provide the best resolution of the analytes from methanol and water. Methanol is always present in the calibration standards and a significant portion will be purged out, transferred to the trap and desorbed with the other analytes. Similarly water is also always trapped on hydrophobic sorbent traps, and some of it will be introduced into the analytical column.*

Volatiles Consumables Kit

The kit contains routine supplies for daily operation and maintenance. Kit includes:

Volatile Organic Chemicals Parts and Supplies for EPA Methods 524.2 & 8260B **03-930824-91**		
Syringe	03-925902-05	10 µL conical tipped needle
Injector Parts		
1177 Split/Splitless Injector	03-926119-27	Insert 4 mm ID open single gooseneck liner, non-Siltek
	CR298713	BTO septa pkg of 50
	8850103100	The o-ring that seals the 1177 injector insert pkg of 25
1079 PTV Injector	03-926119-45	Insert for 1079 pkg of 5 – 3.4 mm ID open single gooseneck
	CR298777	BTO septa for the 1079 injector pkg of 50
	03-925342-01	Graphite ferrule that seals the 1079 injector insert pkg of 10

Volatile Organic Chemicals Parts and Supplies for EPA Methods 524.2 & 8260B **03-930824-91**		
Ferrules	2869458001	For 30 m or 20 m columns pkg of 10 40/60 graphite/Vespel®
	CR213105	For 60 m columns pkg of 10 40/60 graphite/Vespel
Purge and Trap		
Stratum PAT Trap	T145864403	Strat-Trap, Vocarb 3000
Stratum PAT Trap	14-3928-403	Strat-Trap, #9 (Proprietary packing material)
VOA Vials	DY63006800	Std 40 mL VOA vials with Teflon-faced septa, EPA cleaned

GC/MS Interface

With the configuration suggested above (EFC type 25 pneumatics in split mode) the column will be connected to the detector in the normal fashion, about 1-2 mm of the column protruding from the end of the 210-MS/220-MS transfer line.

NOTE: *Always reduce the column and the MS transfer line temperature if the column flow is interrupted for maintenance.*

1.4.2 Data Analysis and Calculations

Fully calibrated methods with data handling parameters (integration, identification, and quantification) for commonly monitored VOCs in 524.2 are on the Varian Environmental MS Applications Manual CD, included with a hard copy of this manual. For Method 524.2 there is 1 method file (.mth file) and 1 raw data file (.SMS file) representing a calibration mixture of 60 compounds, (mixes ULDWM589N plus ULDWM544). The table below describes which files are associated with the 524.2 method:

Calibration Mixture	Method File (.mth)	Data File (.SMS)
60 Common VOCs	524_2-210_220MS.mth	524_2_200.SMS

Make a copy of this Varian Workstation method and example data file. The operator will likely need to make changes in retention times or some other parameters for further optimization.

Tuning the Mass Spectrometer

To assure that the BFB tune criteria specified in the method is met, use the suggested acquisition parameters. (See analytical parameters)

The amount of BFB entering the detector must be 10 ng or less. Typically, a 5 to 10 ppb aqueous concentration is used, depending on the volume purged.

BFB must pass the specifications noted in the QC matrix table above before analysis can begin. The analytical parameters in Table 1-12 give a good starting point for passing the tune. Fine adjustments to key parameters may be necessary for passing the tune requirement. Once set, the tune should be stable for an extended period and will only need to be monitored at the required frequency (12 hr intervals). See Section 1.8 Troubleshooting for parameters to adjust in the case of a failing tune.

NOTE: *Section 10.2.2 of Method 524.2 suggests that an average spectrum be taken across a GC peak in order to check the tune. This is only a suggestion; one is allowed to use a single scan to pass tune criteria* *in this method. Use the Varian EnviroPro “find tune” feature for tuning under EPA 524.2 to find a passing scan or scans in a BFB peak.*

Analytes Monitored and Calibration Levels

While Method EPA 524.2 lists 84 analytes, which may be monitored by the procedures specified in the Method, the actual number of analytes measured will depend on the laboratory requirements. Very often only a subset of these analytes are monitored.

A list of 85 analytes with retention time and suggested quan ion specifications can be found in Table 1-14.

Method 524.2 (Section 1.6.3 of the reference method) does not specify the exact calibration levels or ranges to be performed other than at least 5 calibration levels covering a calibration range of a factor of 100.

The attached method includes nine calibration levels covering a calibration range from 0.2-100 ppb. Edit the levels and range as desired.

Integration Parameters

The integration parameters were selected to assure reliable integration even at the lowest calibration level. These parameters may need to be adjusted and the analyst should review them for each analyte using the lowest level calibration data file. The most commonly adjusted parameters are:

- Identification Window
- Peak Width
- Area Reject Value
- Slope Sensitivity (occasionally)
- Smoothing

Review the MS Workstation Software Reference Manual "Guidelines for Optimizing Method Integration Parameters" section to clarify integration topics and processes. Manual integration may be required for some compounds at low concentrations. Reasons for manual integration must be documented in the finished data package.

The MS Workstation Software loads a desktop shortcut to the Software Reference manual. “Guidelines for Optimizing Integration Parameters” can be found in the “MS Data Review / Quantitation” section of the reference manual.

Quantitation Parameters

Once the initial calibration is completed, the analyst must review the curve fitting parameters for each component to assure proper quantitation of samples to be processed.

Curve Fitting, Handling the Origin, Regression Weight Factors

- Average RRF:

  Average RRF calculation is performed by the data system when “linear with forced zero and 1/x2, or 1/nx2 regression weighting" is selected for curve fitting.
- Linear
- Quadratic

The EPA Method 524.2 allows linear or quadratic curve fitting as stated in section 10.2.7 of the reference method. These two curve fit options are most commonly used by analytical laboratories.

Handling of the Origin

- Ignore
- Include
- Force

Review the Cal Curve for each analyte and specify the handling of the origin based on the collected data. Typically, the origin point is ignored in the calculations.

Selection of the Regression Weighting Factor

- None
- 1/n
- 1/x
- 1/nx
- 1/x2
- 1/nx2

The most often used factors are 1/x2, and 1/nx2 for trace level analysis.

Improper selection of these parameters will undermine the accuracy of the reported results of the unknown samples or quality control samples. All samples and quality control in a given run must be calculated using identical curve fitting and weighting parameters.

1.5 Reagents and Standards

1.5.1 Stock Standards

Calibration STDs are available in convenient packaging and concentrations. A few suggestions may make the preparation of calibration solutions easier:

- For maximum flexibility and performance use the 2000 µg/mL (or higher) standard concentrations. This level will allow easy dilutions into mixed substocks.
- Select standards that will have the "gases" (freons, vinyl chloride, bromo- and chloromethane, chloroethane) in a separate ampule. Mixes are also available that have the six gases plus other compounds. **IMPORTANT: Once opened, the stability of the gas mixture cannot be**

guaranteed, and a new vial most likely will be needed at the next calibration. Gases such as chloromethane and chloroethane decrease in concentration rapidly, even when stored tightly capped in a freezer. The reliable "lifetime" of the other standards, if properly stored, is longer and they may be used again.

- Limit the number of standard vials; purchase standards that have the highest number of analytes in every mixture.

Recommended Standards from Varian

Internal/Surrogate Standard

[VPN]: ULSTM320N 2000 µg/mL in Methanol, 4 x 1 mL

Fluororobenzene (IS)

4-Bromofluorobenzene (SUR)

1,2-Dichlorobenzene-d4 (SUR)

GCMS Tune Standard (BFB)

[VPN]: ULSTS110N 2000 µg/mL in Methanol, 4 x 1 mL

4-Bromofluorobenzene

Target Analytes

[VPN]: ULDWM589N 2000 µg/mL, in Methanol, 4 x 1 mL
54 Analytes

Benzene
Bromobenzene
Bromochloromethane
Bromodichloromethane
Bromoform
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Carbon tetrachloride
Chlorobenzene
Chloroform
2-Chlorotoluene
4-Chlorotoluene
Dibromochloromethane
1,2-Dibromo-3-chloropropane
1,2-Dibromoethane
Dibromomethane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
cis-1,2-Dichloroethene
trans-1,2-Dichloroethene
1,2-Dichloropropane
1,3-Dichloropropane
2,2-Dichloropropane
1,1-Dichloropropene
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
Ethylbenzene
Hexachlorobutadiene
Isopropylbenzene
4-Isopropyltoluene
Methylene chloride
Naphthalene
n-Propylbenzene
Styrene
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
1,2,3-Trichlorobenzene
1,2,4-Trichlorobenzene
1,1,1-Trichloroethane
1,1,2-Trichloroethan
Trichloroethene
1,2,3-Trichloropropane
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
o-Xylene
m-Xylene
p-Xylene

[VPN]: ULDWM592 Rev 4.0 Additions, 2000 µg/mL, in Methanol, 4 x 1 mL

24 Analytes

Acetone
Acrylonitrile
Allyl chloride
2-Butanone (MEK)
Methylmethacrylate
1,1-Dichloro-2-propanone
Diethyl ether
Ethyl methacrylate
Hexachloroethane
2-Hexanone
Methacrylonitrile
Methyl iodide
Methylacrylate
Carbon disulfide
Chloroacetonitrile
1-Chlorobutane
trans-1,4-Dichloro-2-butene
Methyl-t-butyl ether (MTBE
4-Methyl-2-pentanone
Nitrobenzene
2-Nitropropane
Pentachloroethane
Propionitrile
Tetrahydrofuran

[VPN]: ULDWM544 "Gases", 2000 µg/mL in Methanol, 4 x 1 mL

Bromomethane
Chloroethane
Chloromethane
Dichlorodifluoromethane
Trichlorofluoromethane
Vinyl chloride

1.5.2 Fortification Solutions for Internal and Surrogates Standards (IS/SS)

Manual sample loading: 25 mL samples

Add 25 µL of the internal standard / surrogate standard, (VPN: ULSTM320N) and 775 µL of methanol to a small sample vial (such as an AutoSampler vial or a graduated 1.0 mL vial). Spike all samples (25 mL) with 2 µL of this mix. The concentration of the internal and surrogate standards will be 5 ppb. Load the sample into a 25-50 mL gas tight syringe, and directly inject into the 3-port valve at the top of the purge vessel. Do not allow air to enter the syringe. This method of sample introduction is not usually performed in production laboratories, as it is labor intensive and prone to operator technique errors.

Manual and Automated (Archon) Injection of IS/SS

The Archon AS automatically fortifies the samples with µl of Internal STD/surrogate STD while it is being transported from the 40 mL VOA vial into the purge vessel via a Valco SS valve. This provides a convenient way to add a small amount of standard very accurately to the sample, resulting in superior precision and accuracy.

Preparation of the IS/SUR standard mixture for the Archon sampler: The IS/SUR solution is prepared in p**urge and trap grade methanol** and placed in the Archon IS sample vial. The concentration added depends upon the purge volume and final concentration desired. For a nominal 5 ppb final aqueous concentration for purge volumes of 5, 10, and 20 mL, see Table 1-3 below.

*Table 1-3 Concentration of IS/SUR solution added to Archon for a given purge volume**

Concentration of IS/SUR in Methanol (µg/mL)*	Purge Volume (mL)	Final Aqueous Concentration (ppb)
25	5	5
50	10	5
100	20	5

*Assumes 1.0 µL of the IS/SUR solution is added by the Archon

**Preparation of 5-10 mL will nearly fill the Archon IS sample vial. Example: Dilute 125 µL, 250 µL, or 500 µL of the 2000 ppm stock solution of the IS and SUR to final volume of 10.0 mL methanol.

1.5.3 Preparation of Aqueous Calibration Standards

The method requires a minimum of five calibration levels over the calibration range. Since different laboratories will perform different calibration ranges, standard preparation for 0.2 ppb to 100 ppb concentrations is given below.

Calibration standards will be prepared differently if the Archon AutoSampler is used with 40 mL sample vials or if no AutoSampler is used and 5-20 mL of aqueous calibration standards are deposited manually into the purge vessel. Calibration standard preparation using the Archon autosampler will be discussed here.

It is extremely important to limit the amount of methanol added to the aqueous calibration standards. Too much methanol will cause excessive background and un-wanted ion-molecule reactions in the ion trap, resulting in poor accuracy and precision. Two sample preparation approaches are given below. Preparation #1 uses a series of 100 mL volumetric flasks, to which no more than 10 µL is added to prepare any aqueous calibration level. Preparation #2 uses an aqueous stock solution, which is volumetrically diluted down into a series of 100mL volumetric flasks, resulting in solutions that contain no more that 10 µL MeOH per 100 mL. Methanol is also subsequently “back-added” to standards such that all standards will have exactly the same amount (i.e. 10 µL methanol/100 mL sample).

Note that in either preparation approach, it is best to prepare these calibration standards fresh daily, especially since the gases are measured by most analytical laboratories. Also, stock solutions containing the gases are only good for about one week after they are opened.

Aqueous Sample Preparation Procedure #1

Purchased Stock Standards- These mixes are at 2000 µg/mL

VOC Mix/Stock Std	Varian Part No. [VPN]
VOC Mix 1 (60 analytes)*	ULDWM589
VOC Mix 2 (24 analytes)	ULDWM592

*Once this standard is opened, the volatile gases are not very stable. The chemist should have additional ampules of this mix available.

Step 1 is to create a 1:1 mix of the stock solutions above, then perform serial dilutions of this mixture to create two more substock standards in purge and trap grade methanol. Step 2 is to add these substocks directly to 9x100 mL volumetric flasks using a 10 µL Hamilton Syringe, then back-adding methanol as described in Table 1-4.

Step 1: Place three 1.5 mL amber autosampler vials in a tray holder. Using a 1.0 mL gas tight syringe add exactly 900 µL methanol to two of the vials, and leave one vial empty. To the empty vial, add 500 µL VOC Mix 1 and 500 µL VOC mix 2. Mix by inverting gently five times. Label this vial 1000 µg/ml mixed substock solution. Next, add 100 µL of the 1000 µg/ml mixed substock to one of the vials containing 900 µL methanol. Mix gently by inverting five times. Label this 100 µg/ml mixed substock solution. Finally, take 100 µL of the 100 µg/ml mixed substock and add it to the last vial containing 900 µL methanol. Mix, and label as the 10 µg/ml mixed substock. Make sure all are capped tightly. Gases in all substocks are good for only one week when stored in a freezer.

NOTE: *Take care to wash the syringes three times with pure methanol each time after a syringe was used to transfer a stock or substock standard to prevent carryover. Use a 100 µL or a 250 µL syringe for the 100 µL serial dilutions.*

Step 2: Use the following table to prepare the calibration standards in 9 x 100 mL clean and DI-rinsed volumetric flasks. Before spiking, fill each volumetric flask to the mark with Milli-Q reagent grade water. Add the substock solutions by inserting the syringe needle beneath the surface of the water, quickly inject the required amount, and withdraw the needle. Always rinse the syringe with pure methanol after contact with any substock solution; Also, “prime” the syringe with the substock to be added prior to injection into the volumetric flasks.

NOTE: *As with any sample preparation procedure, proper technique is critical to achieve excellent precision and accuracy. It is a good idea to dedicate a set of syringes in the lab for VOC work to avoid contamination with common lab solvents such as dichloromethane. Use common sense and store VOC samples and solvents away from each other.* ***Keep special PAT methanol away from all other lab solvents****.*

Table 1-4 Amount of each substock added to 100 mL with a 10 µL Hamilton Syringe

Final Aqueous	**10µg/mL**	**100µg/mL**	**1000µg/mL**	**µL Back-added**
Concentration (µg/L)	Mixed Substock(µL)	Mixed Substock(µL)	Mixed Substock(µL)	Pure PAT Methanol
0.2	2.0			8.0
0.5	5.0			5.0
1.0	10.0			0.0
2.0		2.0		8.0
5.0		5.0		5.0
10.0		10.0		0.0
20.0			2.0	8.0
50.0			5.0	5.0
100.0			10.0	0.0

After spiking each volumetric flask, cap immediately and invert gently 3-5 times to mix. When the set is complete, pour off gently into 40 mL VOA vials, ensuring that there is no headspace. Each flask is enough for two vials if desired.

NOTE: *It is recommended to load these standards on the Archon and run them on the same day they are prepared to avoid eventual loss of the gases through the septum. Be sure the Archon reservoir is full of fresh DI water, drain lines are clear, and the He switch inside the Archon (for reservoir pressure) is in the “ON” position. Ensure there is enough IS/SURR solution in the Archon IS vial.*

Aqueous Sample Preparation Procedure #2

This approach is based on preparing a relatively concentrated mixed aqueous stock solution and diluting down into 100 mL flasks using conventional volumetric glassware pipettes and gas-tight syringes (for the lower concentrations).

Prepare a 200 ppb aqueous mixed substock by adding 100 µL each of VOC Mix 1 and VOC Mix 2 to a 1 L volumetric flask filled to the mark with Milli-Q water. Gently mix the solution 3-5 times. Prepare dilutions into 100 mL volumetric flasks using the table below. For the lower concentrations, be sure to add some Milli-Q water to the 100 mL flask so as to minimize the headspace above the sample prior to dilution to the mark.

Table 1-5 Dilutions for Sample Preparation #2

Final Conc. (µg/L)	Volume (mL) of 200 ppb substock to 100 mL	Dilution technique
0.2	0.1	100-250 µL gas-tight
0.5	0.25	1.0 mL gas-tight
1.0	0.5	1.0 mL gas-tight
2.0	1.0	1.0 mL gas-tight
5.0	2.5	5.0 mL gas-tight
10.0	5.0	5.0 mL gas-tight
20.0	10.0	10.0 mL gas-tight
50.0	25.0	25 mL Vol pipette
100	50.0	50 mL Vol pipette

As mentioned above, be sure to analyze these the same day they are prepared.

Aqueous Sample Preparation for Manual Injections

For manual loading of the purge vessel, use either sample preparation approach to prepare the aqueous calibration standards in 100 mL volumetric flasks. Next, add the IS/SURR solution to each calibration standard. If 20 mL of sample is to be loaded with an IS/SURR concentration of 5 ppb, simply prepare an IS/SURR substock in methanol at 500 µg/mL and add 1 µL to each 100 mL flask, mix, and load into the purge vessel.

Automated Aqueous Dilutions Using the Archon

The Archon can be used to dilute an aqueous standard with reagent water that comes from the reservoir bottle on the Archon. The available dilution factors are: 2x, 5x, 10x, 20x, 50x, and 100x.

The dilution factor in the Archon shows the ratio of the total volume of water sample and blank water blended together to the final volume of 24.3 mL. For example, if the dilution factor is 50, 1 volume of sample is being diluted with 49 volumes of blank water from the reservoir. Important points to consider if using this feature:

1. Use a 25 mL sparge vessel. The dilution algorithm uses a final volume of about 24 mL, and it is best to dispense the entire volume into the sparge vessel. If smaller volumes are chosen, poor mixing may result inside the Archon syringe, especially at high dilution ratios.
2. It is best to use multiple vials of aqueous substocks to dilute from, (i.e. 10 ppb and 100 ppb) to cover the calibration range.
3. Not recommend to perform dilutions out of the same prepared aqueous substock standard, as the volatile gases may be lost.
4. Example dilution chart for 10 ppb and 100 ppb aqueous standards:

Final Concentration, ppb	Dilution Factor (DF) for 10 ppb aqueous substock	Dilution Factor (DF) for 100 ppb aqueous substock
0.5	20X	--
1.0	10X	--
2.0	5X	--
5.0	2X	--

Final Concentration, ppb	Dilution Factor (DF) for 10 ppb aqueous substock	Dilution Factor (DF) for 100 ppb aqueous substock
10.0	--	10X
20.0	--	5X
50.0	--	2X
100.0	--	No Dilution

NOTE: *It is always best to use a minimum amount of methanol in the starting aqueous standards. A 1 L sample of the 10 and 100 ppb solutions mentioned above could be prepared from a 1000 ppm mixed stock by adding 10 µL and 1 µL, respectively.*

1.6 Set-up of Instrumental Conditions

Fully calibrated methods with data handling parameters (integration, identification, and quantification) for key 524.2 analytes are on the Varian Environmental MS Applications Manual CD, included with this manual. Refer to the EPA524_2 subdirectory and copy the method on your analytical system to start. See Section 1.4.2.

1.6.1 Purge and Trap with Archon Autosampler Conditions

EPA Method 524.2 specifies purge-and trap conditions, many of which are simply “recommended”. However, it is important to note that the purge time (11 min) and the desorb time (about four minutes) cannot be changed by the chemist if running samples for EPA compliance monitoring. Also, a dry purge time is not allowed. A dry purge is typically used to dry the trap before desorb to reduce the amount of water and MeOH entering the column. A short desorb time would have the same effect.

For EPA 524.2, a 20 mL sample volume was used to generate the data presented in this manual. The 20 mL sample offers the advantage of getting more sample onto the sorbent trap and as a result, a higher split ratio (up to 200:1 with narrow-bore 20 m column) can be used to minimize water and MeOH from entering the column and allows faster sample transfer from the ½” trap to the capillary column. A 5 mL purge vessel with 5 mL sample will also work if the split ratio is decreased to between 50:1 and 100:1.

The following purge-and –trap conditions apply to any column mentioned in section 3.1 above. Split ratios will need to be optimized for each column type, balancing overall sensitivity with water/methanol interference.

25 mL sparge vessel (20 mL purge volume)

Tekmar Strat-Trap #9

40 mL/min He purge flow

GC Insert: 1177 4mm ID single goose-neck deactivated insert, installed goose-neck down

See Table 1-6 for general purge and trap settings for EPA Method 524.2.

Table 1-6 Recommended Tek-Link Purge and Trap Settimgs

Purge and Trap Conditions- Tek-Link			
Variable	Value	Variable	Value
Valve Oven Temp.	150° C	Sample Preheat Time	1.00 min.
Transfer Line Temp.	150° C	Preheat Temp.	40° C
Sample Mount Temp.	40° C	Purge Time	*11.0 min.*
Purge Ready Temp.	35° C	Purge Temp.	0° C
Condenser Ready Temp.	40° C	Purge Flow	40 mL/min
Condenser Purge Temp.	20° C	Dry Purge Time	*0.0 min.*
Standby Flow	5 mL/min.	Dry Purge Temp.	20° C
Pre-purge Time	0.00 min.	Dry Purge flow	100 mL/min.
Pre-purge Flow	40 mL/min.	Desorb Preheat Temp.	245° C
Sample Heater	OFF	Desorb Drain	ON
GC Start	Start of Desorb	Desorb Time	*4.00 min.*
Bake Time	7.00 min.	Desorb Temp	250° C
Bake Temp.	260° C	Desorb Flow	100 mL/min.
Bake Flow	300 mL/min.	Condenser Bake Temp.	200° C

The operator has the ability to change the GC/MS method in workstation to optimize the split ratio. Also, the Archon autosampler parameters can be changed during an automated run by calling methods at the end of a given method operation. Typical Archon parameters of importance to reduce carryover are listed in Table 1-7.

Table 1-7 Recommended Archon Autosampler Parameters

Archon Parameter	**Setting**
Sample volume	5, 10, or 20 mL
# of Syringe Washes/Flushes	3
Wash volume	Set to 5 mL over sampling volume
Desorb time	Set to 4.0 min
Cycle time	Set to total run time of GC+PAT cycle

NOTE: *Carryover should be less than 0.5% (Tekmar Spec) when a blank is run after a 50 ppb CAL standard. Increasing the bake time and flow, along with increased Archon vessel/syringe rinses will reduce carryover. It is also good practice to place a blank (or run blank injection from Archon reservoir) after the 50 ppb std in a CAL run and 2 blanks after a 100 ppb standard to minimize chance of carryover into samples at very trace levels. If the system becomes contaminated due to a foam-over event, carryover will be a significant problem as active sites will be inside the concentrator. See Section1.8 - Troubleshooting for more details.*

1.6.2 GC/MS Conditions 60 m x 0.32 mm x 1.8 µm Column

Table 1-8 GC Conditions for 60 m Column

Column Oven Temperature Program				
Temp(°C)	Rate(°C/min)	Hold (min)	Total (min)	
35	NA	6.00	6.00	
220	10	6.50	31.00	
Injector Conditions (1177)		**Injector Split States**		
Temp	160 °C	Time(min)	Split State	Split Ratio
Col Flow	1.0 mL/min	Initial	ON	20
Pressure Pulse	None	3.00	ON	50
Constant Flow	ON	4.10	ON	20
Septum Purge Flow	0.1 mL/min			

Table 1-9 MS Conditions for the 60 m Column

MS Conditions				
Segment	Start (min)	End (min)	Low Mass (m/z)	High Mass (m/z)
Fil/Delay	0.00	4.00	NA	NA
Gases	4.00	7.90	47	150
Other VOCs	7.90	31.00	35	260
Target	12-15000	µscans averaged	3	
Max Ion Time	25000 µsec	Mult Offset	25-50 V	
Background Mass	34 m/z	Emission Current	10-20 µAmps	
Rf Dump	300 m/z	Scan Time	0.55-0.65 sec/scan	

1.6.3 GC/MS Conditions for the 20 m x 0.15 mm x 0.84 µm

Table 1-10 GC Conditions for 20 m Column

Column Oven Temperature Program				
Temp(°C)	Rate (°C/min)	Hold (min)	Total (min)	
35	NA	2.00	2.00	
200	10	0.00	18.50	
240	50	0.00	19.30	
Injector Conditions (1177)		**Injector Split States**		
Temp	160° C	Time (min)	Split State	Split Ratio
Column Flow (constant)	0.8 mL/min	Initial	ON	20
Pressure Pulse	None	0.01	ON	100
Constant Flow	ON	5.00	ON	20
Septum Purge Flow	0.1 mL/min			

Table 1-11 MS Conditions for 20 m Column

MS Conditions				
Segment	Start (min)	End (min)	Low Mass (m/z)	High Mass (m/z)
Fil/Delay	0.00	1.00	NA	NA
Gases	1.00	2.40	47	150
Other VOCs	2.40	17.00	35	260
Target	12-15000		µscans averaged	2
Max Ion Time	25000 µsec		Mult Offset	50-100 V
Bakground Mass	34 m/z		Emission Current	10-25 µAmps
Rf Dump	300 m/z		Scan Time	0.50 sec/scan

Table 1-12 BFB Suggested MS Segment Breaks

Suggested Segment Breaks and Ion Time Factors for BFB Tuning			
Low mass(m/z)	**High mass(m/z)**	**Ionization Stoage Level**	**Ionization Factor**
10	70	34	120%
71	78	34	70%
79	150	34	100%
151	650	34	100%

NOTE: *The ionization factors may need to be adjusted from these starting values for BFB tuning. Once the optimum values are found, the tune should be very stable and pass routinely.*

Peak Table of Suggested Quantitation Ions

Table 1-13

Peak#	**Peak Name**	**RT (min)**	**Quan Ions**
20	Fluorobenzene	14.405	96
1	Dichlorodifluoromethane	3.553	85
2	Chloromethane	4.018	47+49+51
3	Vinyl chloride	4.303	62
4	Bromomethane	5.218	94+96
5	Chloroethane	5.510	47+49+51
6	Trichlorofluoromethane	6.200	101
7	1,1-Dichloroethene	7.666	61
8	Methylenechloride	9.023	49
9	Ethene, 1,2-dichloro-, (E)-	9.641	61
10	1,1-Dichloroethane	10.690	63
11	Propane, 2,2-dichloro-	11.965	77
12	Ethene, 1,2-dichloro-, (Z)-	12.021	61

Peak#	**Peak Name**	**RT (min)**	**Quan Ions**
13	Bromochloromethane	12.537	49
14	Chloroform	12.698	83
15	1,1,1-Trichloroethane	13.049	97
16	Carbon Tetrachloride	13.370	117
17	1-Propene, 1,1-dichloro-	13.401	75
18	Benzene	13.810	78
19	1,2-Dichloroethane	13.929	62
21	Trichloroethylene	15.165	130
22	1,2-Dichloropropane	15.649	63
23	Dibromomethane	15.910	93
24	Bromodichloromethane	16.198	83
25	1-Propene, 1,3-dichloro-, (Z)-	17.095	75
26	Toluene	17.725	91
27	1-Propene, 1,3-dichloro-, (E)-	18.205	75
28	1,1,2-Trichloroethane	18.599	97
29	Tetrachloroethylene	18.850	166
30	1,3-Dichloropropane	18.954	76
31	Dibromochloromethane	19.403	129
32	1,2-Dibromoethane	19.674	107
33	Chlorobenzene	20.647	112
34	Ethylbenzene	20.780	91
35	1,1,1,2-Tetrachloroethane	20.799	131
36	m,p-Xylene	21.018	91
37	o-Xylene	21.859	91
38	Styrene	21.890	104
39	Bromoform	22.358	171+173+175
40	Isopropylbenzene	22.577	105
41	Bromofluorobenzene	23.008	95
42	1,1,2,2-Tetrachloroethane	23.267	83
43	Bromobenzene	23.355	77
44	1,2,3-Trichloropropane	23.397	75
45	n-Propylbenzene	23.435	91
46	2-Chlorotoluene	23.722	126
47	1,3,5-Trimethylbenzene	23.792	105
48	4-Chlorotoluene	23.946	91
49	tert-Butylbenzene	24.474	119
50	1,2,4-Trimethylbenzene	24.603	105
51	sec-Butylbenzene	24.940	105
52	4-Isopropyltoluene	25.216	119
53	1,3-Dichlorobenzene	25.316	146
54	1,4-Dichlorobenzene	25.508	146
55	n-Butylbenzene	26.090	91
56	1,2-Dichlorobenzene-d4	26.279	150

Peak#	Peak Name	RT (min)	Quan Ions
57	1,2 -Dichlorobenzene	26.320	146
58	1,2-Dibromo-3-chloropropane	27.960	75
59	1,2,4-Trichlorobenzene	29.730	182
60	1,3-Butadiene,1,1,2,3,4,4-hexachloro-	29.986	225
61	Naphthalene	30.312	128
62	1,2,3-Trichlorobenzene	30.903	182

Table 1-14 Extended peak table

Peak#	Retention Time	Compound Name	Quan Ion(s)
1	12.642	Fluorobenzene (IS)	96
2	4.009	Dichlorodifluoromethane	85
3	4.544	Chloromethane	47+49+51
4	6.216	Vinyl chloride	62
5	3.444	Bromomethane	94+96
6	4.526	Chloroethane	47+49+51
7	6.773	Trichlorofluoromethane	101
8	8.613	Diethyl ether	59
9	9.201	1,1-Dichloroethene	61
10	9.540	Acetone	43
11	9.776	Carbondisulfide	76
12	10.261	Allyl Chloride	41
13	10.624	Methylene chloride	49
14	9.243	Ethene, 1,2-dichloro-, (E	61
15	11.277	Methyl tert-butyl ether	73
16	11.340	Acrylonitrile	52
17	12.295	1,1-Dichloroethane	63
18	13.535	Propane, 2,2-dichloro-	77
19	13.557	Ethene, 1,2-dichloro-,(Z	61
20	13.596	2-Butanone	43
21	13.758	Methyl acrylate	55
22	13.789	Propionitrile	54
23	14.050	Bromochloromethane	49
24	14.058	Methacrylonitrile	67
25	14.133	Tetrahydrofuran	71
26	14.179	Chloroform	83
27	14.554	1,1,1-Trichloroethane	97
28	14.746	Butyl chloride	56
29	14.850	Carbon Tetrachloride	117
30	14.871	1-Propene, 1,1-dichloro-	75
31	15.272	Benzene	78
32	15.364	1,2-Dichloroethane	62
33	16.496	Trichloroethylene	130

Peak#	Retention Time	Compound Name	Quan Ion(s)
34	16.973	1,2-Dichloropropane	63
35	17.070	Methyl methacrylate	69
36	17.195	Dibromomethane	93
37	17.440	Bromodichloromethane	83
38	17.921	2-Nitropropane	43
39	18.279	1-Propene, 1,3-dichloro-,	75
40	17.951	Chloroacetonitrile	75
41	18.508	MIK (4-methyl-2-pentanone	43
42	18.631	1,1-Dichloropropanone	43
43	18.885	Toluene	91
44	18.258	1-Propene, 1,3-dichloro-,	75
45	19.335	Ethyl methacrylate	69
46	18.505	2-Hexanone	85
47	19.652	1,1,2-Trichloroethane	97
48	19.897	Tetrachloroethylene	166
49	19.992	1,3-Dichloropropane	76
50	20.393	Dibromochloromethane	129
51	20.672	1,2-Dibromoethane	107
52	21.559	Chlorobenzene	112
53	21.689	1,1,1,2-Tetrachloroethane	131
54	21.687	Ethylbenzene	91
55	22.679	m,p-Xylene	91
56	22.679	o-Xylene	91
57	22.703	Styrene	104
58	23.112	Bromoform	171+173+175
59	23.340	Isopropylbenzene	105
60	23.614	Bromofluorobenzene	95
61	24.921	1,1,2,2-Tetrachloroethan	83
62	24.043	trans-1,4-Dichloro-2-bute	88
63	24.053	Bromobenzene	77
64	22.255	1,2,3-Trichloropropane	75
65	24.128	n-Propylbenzene	91
66	24.386	2-Chlorotoluene	126
67	24.457	1,3,5-Trimethylbenzene	105
68	24.593	4-Chlorotoluene	91
69	25.095	tert-Butylbenzene	119
70	25.207	Pentachloroethane	167
71	24.457	1,2,4-Trimethylbenzene	105
72	25.520	sec-Butylbenzene	105
73	25.773	4-Isopropyltoluene	119
74	25.840	1,3-Dichlorobenzene	146
75	26.017	1,4-Dichlorobenzene	146
76	26.575	n-Butylbenzene	91

Peak#	Retention Time	Compound Name	Quan Ion(s)
77	26.764	1,2 -Dichlorobenzene	146
78	25.272	1,2-Dichlorobenzene-d4	150
79	27.248	Hexachloroethane	201
80	28.266	1,2-Dibromo-3-chloropropa	75
81	28.702	Nitrobenzene	77
82	30.997	1,2,4-Trichlorobenzene	182
83	30.164	1,3-Butadiene, 1,1,2,3,4,	225
84	30.475	Naphthalene	128
85	30.997	1,2,3 -Trichlorobenzene	182

1.7 Results Section

1.7.1 Sample Chromatograms

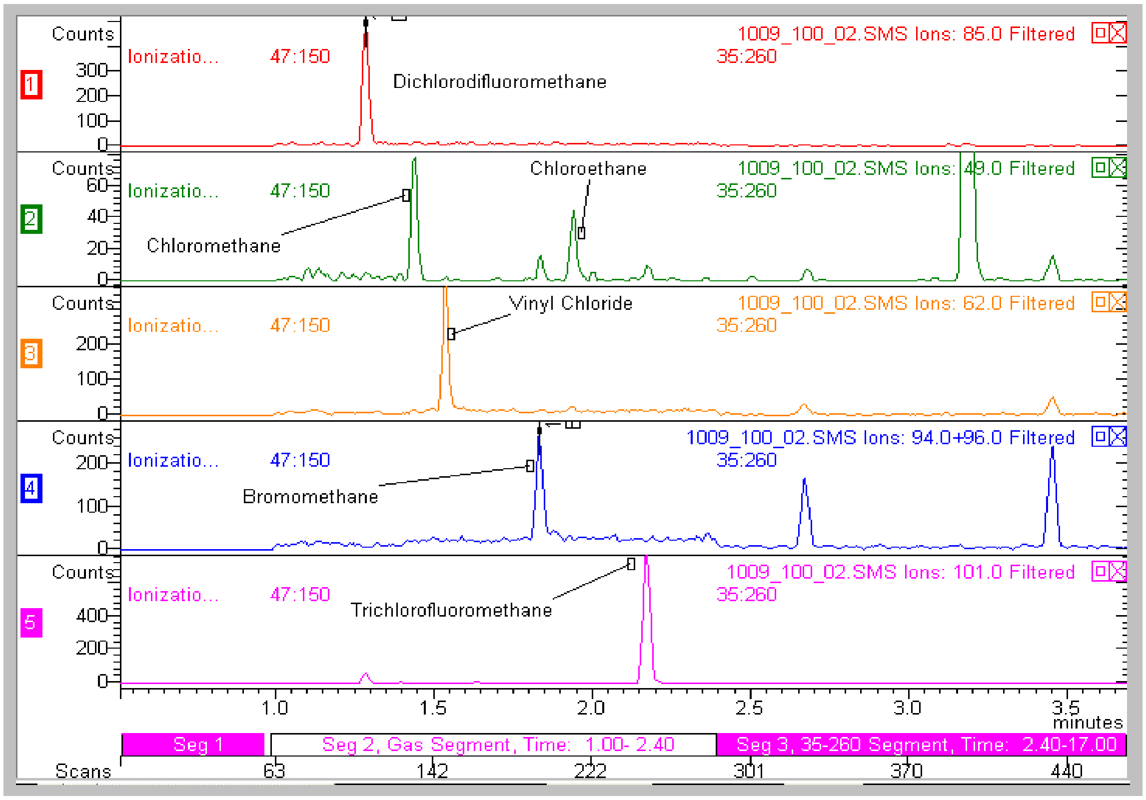


Figure 1.1: 6 Volatile gases at 0.2 ppb

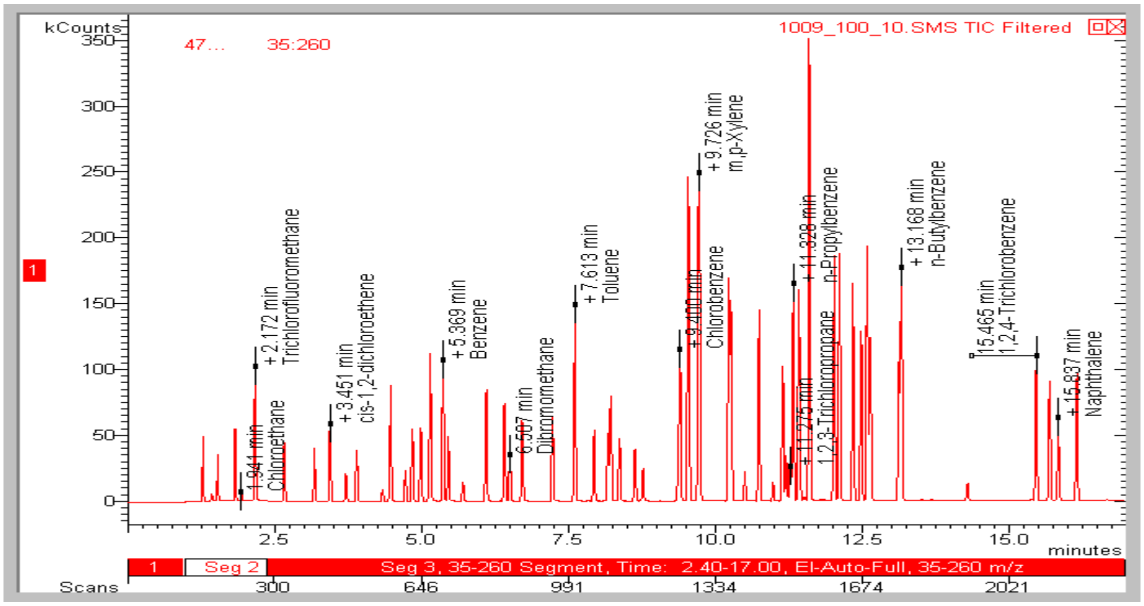
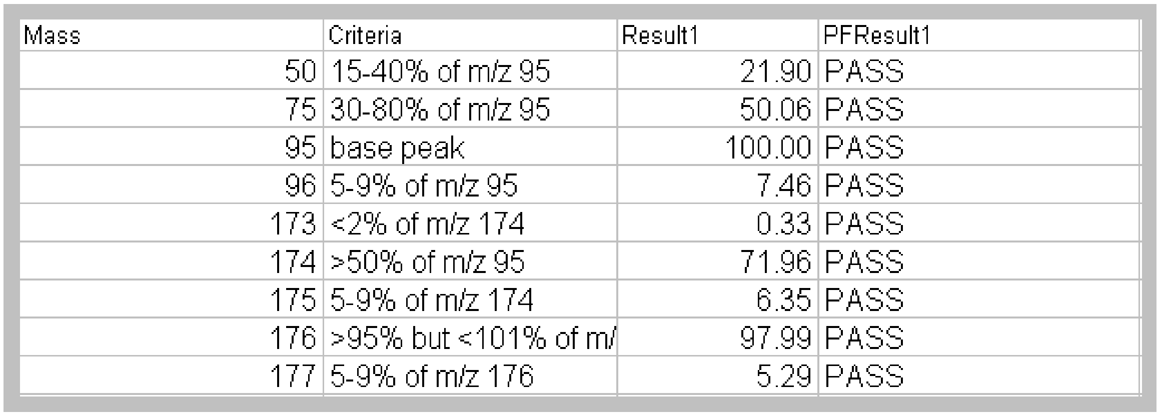


Figure 1.2: TIC, 10 ppb 60 Compound VOC mixture

1.7.2 Tune Verification



Mass	Criteria	Result1	PFResult1
50	15-40% of m/z 95	21.90	PASS
75	30-80% of m/z 95	50.06	PASS
95	base peak	100.00	PASS
96	5-9% of m/z 95	7.46	PASS
173	<2% of m/z 174	0.33	PASS
174	>50% of m/z 95	71.96	PASS
175	5-9% of m/z 174	6.35	PASS
176	>95% but <101% of m/	97.99	PASS
177	5-9% of m/z 176	5.29	PASS

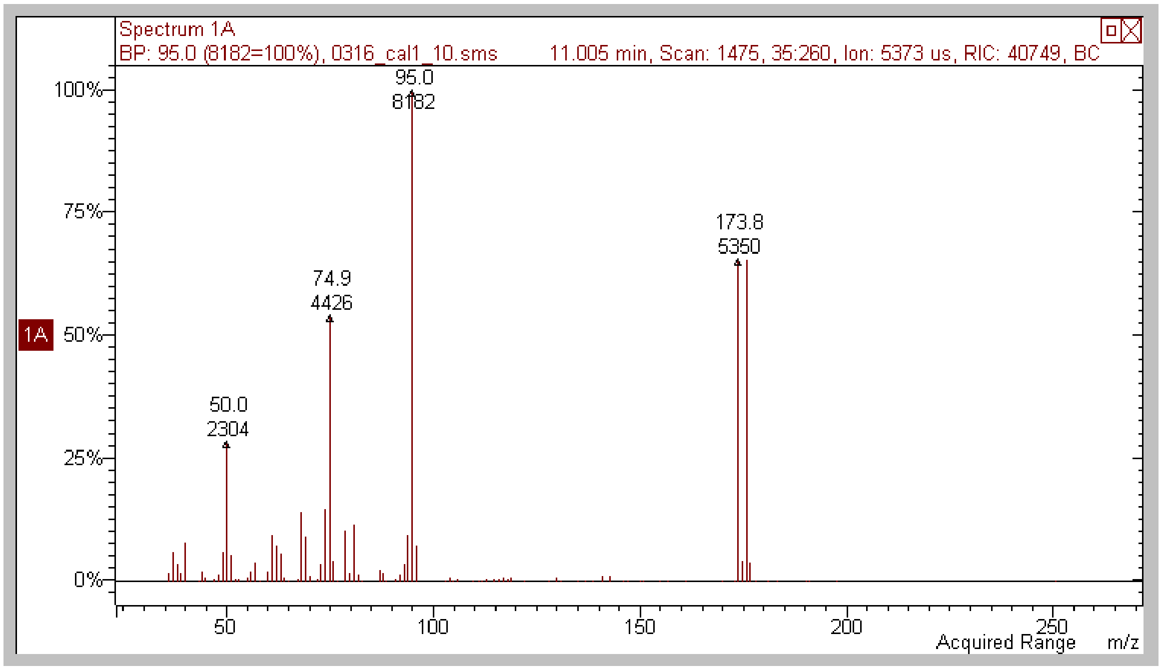


Figure 1.3: BFB spectrum taken on the 210-MS with the 20 m column

1.7.3 Calibration Statistics (Data from the 20 m Column)

Calibration Levels - RRF1 – RRF9, 0.2 ppb – 100 ppb (9 Calibration Levels) - Linear Fit			
Compound Name	**Corr. Coeff.**	**Avg. RRF**	**% RSD**
Dichlorodifluoromethane	0.995469	0.727322	13.17
Chloromethane	0.993578	0.140692	12.28
Vinyl chloride	0.995698	0.547291	8.38
Bromomethane	0.992864	0.651604	8.22
Chloroethane	0.998156	0.084896	12.98
Trichlorofluoromethane	0.999173	1.50503	8.81
1,1-Dichloroethene	0.995818	0.62498	6.74
Methylene chloride	0.999163	0.371251	14.76
cis-1,2-dichloroethene	0.998443	0.598479	3.65
1,1-Dichloroethane	0.997839	0.50797	26.23
2,2-Dichloropropane	0.998635	0.352564	11.62
trans-1,2-dichloroethene	0.99758	1.10444	5.10
Bromochloromethane	0.998089	0.395501	4.42
Chloroform	0.995434	0.687732	7.93
1,1,1-Trichloroethane	0.997497	0.958543	3.99
Carbon Tetrachloride	0.999067	0.472718	5.67
1,1-Dichloropropene	0.995743	0.302854	5.91

Calibration Levels - RRF1 – RRF9, 0.2 ppb – 100 ppb **(9 Calibration Levels) - Linear Fit**			
Compound Name	**Corr. Coeff.**	**Avg. RRF**	**% RSD**
Benzene	0.995862	0.821174	5.12
1,2-Dichloroethane	0.99738	0.563799	9.26
Trichloroethene	0.996622	0.305715	5.59
1,2-Dichloropropane	0.996588	0.283706	7.12
Dibromomethane	0.996179	0.330193	5.29
Bromodichloromethane	0.998317	0.498847	4.64
trans-1,3-dichloropropene	0.996362	0.361777	5.97
Toluene	0.999875	1.92586	5.95
cis-1,3-dichloropropene	0.996126	0.298105	4.83
1,1,2-trichloroethane	0.999958	0.244746	5.20
Tetrachloroethene	0.999775	0.292841	9.50
1,3-dichloropropane	0.999482	0.231185	4.96
Dibromochloromethane	0.998979	0.340222	5.19
1,2-Dibromoethane	0.999676	0.271486	4.42
Chlorobenzene	0.999883	1.08037	4.11
1,1,1,2-Tetrachloroethane	0.998338	0.426437	7.05
Ethylbenzene	0.998677	2.16225	4.34
m,p-Xylene	0.998936	3.84708	4.74
o-Xylene	0.999335	1.92662	3.39
Styrene	0.999707	1.07492	6.48
Bromoform	0.999852	0.174913	5.97
Isopropylbenzene	0.999474	1.67008	4.44
SS-4-Bromofluorobenzene	0.979401	0.430146	4.86
Bromobenzene	0.999333	0.505113	5.15
1,1,2,2-Tetrachloroethane	0.99985	0.26107	3.85
1,2,3-Trichloropropane	0.998342	0.175446	5.42
n-Propylbenzene	0.998903	2.3596	6.54
2-Chlorotoluene	0.999103	0.498523	4.60
4-Chlorotoluene	0.989411	0.460012	9.63
1,3,5-Trimethylbenzene	0.999514	1.92825	3.12
tert-Butylbenzene	0.998786	1.57268	5.68
1,2,4-Trimethylbenzene	0.997759	1.91095	4.22
sec-Butylbenzene	0.998736	2.04304	5.66
1,3-Dichlorobenzene	0.99941	1.72628	4.64
p-Isopropyltoluene	0.999784	3.53276	4.50
1,4-Dichlorobenzene	0.999469	1.70876	6.28
1,2-Dichlorobenzene	0.99915	1.52156	4.75
n-Butylbenzene	0.99991	3.8423	5.93

Calibration Levels - RRF1 – RRF9, 0.2 ppb – 100 ppb
(9 Calibration Levels) - Linear Fit

Compound Name	Corr. Coeff.	Avg. RRF	% RSD
1,2-Dibromo-3-chloropropane	0.999765	0.399192	13.44
1,2,4-Trichlorobenzene	0.999671	1.08424	4.28
Hexachlorobutadiene	0.998951	0.837769	7.89
Naphthalene	0.998989	1.55811	7.78
1,2,3-Trichlorobenzene	0.999633	0.906094	4.59
Overall	**0.998**	**0.974**	**6.77**

Auto Calibration with Archon, 0.5 to 50 ppb, 25 mL Volume

RRF1 – RRF7 (7 Calibration Levels) - Linear Fit

Calibration Level			
Compound Name	**Corr. Coeff.**	**Avg. RRF**	**% RSD**
Dichlorodifluoromethane	0.9999	0.2660	3.3
Chloromethane	0.9980	0.0827	11.1
Vinyl chloride	0.9998	0.3811	7.0
Bromomethane	0.9994	0.5088	6.5
Chloroethane	0.9995	0.0678	7.8
Trichlorofluoromethane	0.9996	1.1963	6.6
1,1-Dichloroethene	0.9995	0.6124	7.0
Methylene chloride	0.9991	0.2821	14.4
cis-1,2-dichloroethene	1.0000	0.5804	5.4
1,1-Dichloroethane	0.9964	0.4147	24.4
2,2-Dichloropropane	0.9997	0.3504	3.5
trans-1,2-dichloroethene	0.9996	1.0439	3.4
Bromochloromethane	0.9996	0.2895	2.5
Chloroform	0.9993	0.6353	4.7
1,1,1-Trichloroethane	0.9999	1.0122	5.1
Carbon Tetrachloride	0.9995	0.4781	8.1
1,1-Dichloropropene	0.9997	0.3145	7.4
Benzene	0.9998	0.8166	4.2
1,2-Dichloroethane	1.0000	0.4077	5.4
Trichloroethene	0.9997	0.2907	4.3
1,2-Dichloropropane	0.9992	0.2408	3.6
Dibromomethane	0.9999	0.2385	4.0
Bromodichloromethane	0.9999	0.4126	4.6
trans-1,3-dichloropropene	0.9996	0.3029	4.9
Toluene	0.9975	2.1121	6.1
cis-1,3-dichloropropene	0.9998	0.2326	2.7
1,1,2-trichloroethane	0.9993	0.1963	3.5

Auto Calibration with Archon, 0.5 to 50 ppb, 25 mL Volume **RRF1 – RRF7 (7 Calibration Levels) - Linear Fit**			
Calibration Level			
Compound Name	**Corr. Coeff.**	**Avg. RRF**	**% RSD**
Tetrachloroethene	0.9997	0.3016	4.8
1,3-dichloropropane	0.9999	0.1809	5.2
Dibromochloromethane	0.9999	0.2843	7.0
1,2-Dibromoethane	0.9991	0.2095	5.3
Chlorobenzene	0.9998	1.0061	3.4
1,1,1,2-Tetrachloroethane	0.9999	0.3739	5.6
Ethylbenzene	0.9995	2.3952	4.3
m,p-Xylene	0.9991	4.2701	4.0
o-Xylene	0.9973	2.0633	4.9
Styrene	0.9992	0.9923	4.1
Bromoform	0.9999	0.1304	2.5
Isopropylbenzene	0.9992	1.8914	4.3
SS-4-Bromofluorobenzene	0.9772	0.4174	5.8
Bromobenzene	0.9984	0.4384	6.9
1,1,2,2-Tetrachloroethane	0.9993	0.2045	7.0
1,2,3-Trichloropropane	0.9995	0.1363	10.1
n-Propylbenzene	0.9955	2.6851	7.3
2-Chlorotoluene	0.9985	0.5071	5.1
4-Chlorotoluene	0.9875	0.4497	8.1
1,3,5-Trimethylbenzene	0.9973	2.1918	4.2
tert-Butylbenzene	0.9994	1.7937	4.1
1,2,4-Trimethylbenzene	0.9990	2.0585	3.7
sec-Butylbenzene	0.9972	2.3972	7.5
1,3-Dichlorobenzene	0.9998	1.6057	5.8
p-Isopropyltoluene	0.9991	4.0249	7.9
1,4-Dichlorobenzene	0.9990	1.5338	4.8
1,2-Dichlorobenzene	0.9987	1.2707	7.4
n-Butylbenzene	0.9991	4.4661	8.4
1,2-Dibromo-3-chloropropane	0.9982	0.2719	7.5
1,2,4-Trichlorobenzene	0.9986	0.9579	6.6
Hexachlorobutadiene	0.9992	0.8944	12.4
Naphthalene	0.9984	1.1553	7.5
1,2,3-Trichlorobenzene	0.9995	0.7582	6.8
Overall	**0.9986**	**0.9681**	**6.2009**

1.7.4 Method Detection Limit Results

EPA 524.2 VOC MDL, Reps Target 0.20 ppb, Stratum and 20 m x 0.25 x 0.15 column with #9 Strat-Trap (Total of 7 replicates)					
REP 1 – REP7	**Avg**	**StdDEV**	**%RSD**	**%Recovery**	**MDL**
Peak Name					
Dichlorodifluoromethane	0.153	0.028267	18.5	76.5	0.088785
Chloromethane	0.199	0.032648	16.4	99.6	0.102548
Vinyl chloride	0.166	0.016206	9.7	83.2	0.050902
Bromomethane	0.231	0.019056	8.3	115.4	0.059856
Chloroethane	0.221	0.037494	17.0	110.4	0.117769
Trichlorofluoromethane	0.164	0.013765	8.4	81.9	0.043236
1,1-Dichloroethene	0.206	0.011427	5.6	102.9	0.035892
Methylene chloride	0.224	0.01548	6.9	111.8	0.048622
cis-1,2-dichloroethene	0.186	0.009502	5.1	93.2	0.029845
1,1-Dichloroethane	0.239	0.017024	7.1	119.4	0.053472
trans-1,2-dichloroethene	0.187	0.013301	7.1	93.4	0.041777
2,2-Dichloropropane	0.120	0.017596	14.6	60.2	0.055269
Bromochloromethane	0.191	0.007111	3.7	95.6	0.022337
Chloroform	0.182	0.008494	4.7	90.9	0.026679
1,1,1-Trichloroethane	0.202	0.011402	5.6	101.0	0.035813
Carbon Tetrachloride	0.199	0.017478	8.8	99.6	0.054898
1,1-Dichloropropene	0.187	0.016119	8.6	93.6	0.050629
Benzene	0.204	0.009822	4.8	102.1	0.030852
1,2-Dichloroethane	0.215	0.009727	4.5	107.3	0.030553
Trichloroethene	0.233	0.012659	5.4	116.6	0.03976
1,2-Dichloropropane	0.192	0.009037	4.7	96.0	0.028385
Dibromomethane	0.202	0.008446	4.2	101.0	0.026529
Bromodichloromethane	0.193	0.016537	8.6	96.4	0.051943
trans-1,3-dichloropropene	0.197	0.012672	6.4	98.6	0.039802
Toluene	0.191	0.008597	4.5	95.6	0.027003
cis-1,3-dichloropropene	0.201	0.010808	5.4	100.6	0.033947
1,1,2-trichloroethane	0.194	0.028751	14.8	97.2	0.090307
Tetrachloroethene	0.141	0.008699	6.2	70.5	0.027322
1,3-dichloropropane	0.194	0.016252	8.4	96.9	0.051049
Dibromochloromethane	0.217	0.013837	6.4	108.4	0.043464
1,2-Dibromoethane	0.220	0.012954	5.9	110.1	0.040689
Chlorobenzene	0.188	0.008499	4.5	93.9	0.026696
1,1,1,2-Tetrachloroethane	0.173	0.011146	6.4	86.6	0.03501
Ethylbenzene	0.192	0.006161	3.2	95.8	0.01935
m,p-Xylene	0.192	0.00729	3.8	95.9	0.022898
o-Xylene	0.206	0.00916	4.5	102.9	0.028771

EPA 524.2 VOC MDL, Reps Target 0.20 ppb, Stratum and 20 m x 0.25 x 0.15 column with #9 Strat-Trap (Total of 7 replicates)					
REP 1 – REP7	**Avg**	**StdDEV**	**%RSD**	**%Recovery**	**MDL**
Peak Name					
Styrene	0.220	0.007895	3.6	110.0	0.024799
Bromoform	0.203	0.015475	7.6	101.4	0.048607
Isopropylbenzene	0.185	0.008638	4.7	92.7	0.027133
SS-4-Bromofluorobenzene	5.056	0.106818	2.1	101.1	0.335516
Bromobenzene	0.188	0.010753	5.7	93.8	0.033774
1,1,2,2-Tetrachloroethane	0.183	0.023853	13.1	91.3	0.074921
1,2,3-Trichloropropane	0.217	0.030089	13.9	108.5	0.094509
n-Propylbenzene	0.189	0.00509	2.7	94.6	0.015987
2-Chlorotoluene	0.212	0.010628	5.0	105.8	0.033382
1,3,5-Trimethylbenzene	0.198	0.010981	5.5	99.1	0.03449
4-Chlorotoluene	0.207	0.014765	7.1	103.5	0.046376
tert-Butylbenzene	0.187	0.01039	5.6	93.3	0.032635
1,2,4-Trimethylbenzene	0.202	0.008939	4.4	100.9	0.028077
sec-Butylbenzene	0.189	0.011202	5.9	94.4	0.035184
1,3-Dichlorobenzene	0.204	0.016324	8.0	101.9	0.051274
p-Isopropyltoluene	0.192	0.010189	5.3	95.9	0.032003
1,4-Dichlorobenzene	0.178	0.01021	5.7	89.1	0.032069
1,2-Dichlorobenzene	0.185	0.013874	7.5	92.6	0.043577
n-Butylbenzene	0.174	0.013018	7.5	87.1	0.04089
1,2-Dibromo-3-chloropropane	0.148	0.031234	21.1	73.9	0.098106
1,2,4-Trichlorobenzene	0.194	0.011402	5.9	97.0	0.035813
Hexachlorobutadiene	0.176	0.01817	10.3	88.1	0.057071
Naphthalene	0.202	0.016327	8.1	100.9	0.051283
1,2,3-Trichlorobenzene	0.187	0.011429	6.1	93.3	0.035898
Overall			**7.4**	**96.9**	**0.0493**

1.8 Troubleshooting

The following table outlines common potential problems and proposed solutions. Multiple problems on the same PAT system are often difficult to resolve and may require a service representative. Always try the least invasive (or easiest) procedure first when troubleshooting. Ask “what has changed?” and review maintenance logs to help trace back when a problem may have started.

Observed Problem	Potential Cause(s)	Solutions
Bad overall peak shape	PAT contamination, bad sorbent trap, bad column, leaking at sorbent trap fittings	Change sorbent trap, change column, run leak-check, clean entire PAT sample pathway
Sudden loss of sensitivity	Foam-over into 6-port valve, leaks (PAT or GC/MS system), broken column.	Leak check PAT, check column, clean PAT pathway and change trap (foam-over)
Low response for 6 gases	Old gas standard, split ratio too high, bad sorbent trap, leaks in PAT, wrong insert in injector, too much water and methanol	Prepare new stds from un-opened stock, leak check PAT, decrease split ratio, change sorbent trap, check sample prep to ensure minimum methanol used
BFB tune fails	210-MS/220-MS settings not optimized, too much water, contaminated PAT, MS saturated, multiplier voltage too low	Adjust ionization time factors, increase multiplier +100V, clean contaminated PAT and replace sorbent trap, decrease amount injected if MS saturated, check moisture filters on He gas lines
High mass noise	Dirty ion trap	Clean ion trap
Gradual loss of sensitivity	MS multiplier “settling in”	Increase multiplier if peak areas drop low out of range from initial calibration.
Ghost peaks	Bad sorbent trap, dirty PAT system, dirty MeOH, bad column, dirty reagent water, peaks (targets) in contaminated sample preservation solutions	Replace sorbent trap, clean PAT sample pathway, use only PAT grade MeOH, replace column, change DI/carbon cartridge, change preservatives
Carryover	Dirty purge vessel, dirty PAT pathway, no water in Archon reservoir, rinse volumes too low, heavily contaminated sample, foam-over, short and/or low-temp bake cycle	Clean PAT purge vessel and sample pathway, change sorbent trap, Check reservoirs and rinse volumes, check He switch for Archon is ON, increase bake time and/or temp.
Loss of brominated compounds	Actives sites in PAT system or analytical column	Clean PAT pathway, change trap, change column, clean ion trap
Poor reproducibility of Internal/Surrogate standards	Archon IS/SURR vial empty or not properly primed, Archon He switch off, failed valve in Archon that delivers the IS/SS, leaks in PAT, bad sorbent trap	Check Archon IS/SS vial, replace sorbet trap, ensure He switch is ON, check for leaks in PAT
Sporadic target analytes gone or very poor response	Check for carbon flecks in bottom of VOA vials	Be sure to filter DI water if carbon flecks are visible

Observed Problem	Potential Cause(s)	Solutions
Corrosion in PAT	HCl from sample preservation reagent	Run blanks at end of run to help clean PAT sample pathway

1.8.1 Operating Tips

1. Do not use opened gas standards for more than five days - one week. Store in freezer.
2. Do not over tighten fittings on sparge vessel
3. If method allows, try dry purge (1 min at 300 mL/min.) and short desorb time (1-2 min), however--watch out for chloromethane loss
4. Optimize for highest split flow possible, balance against required sensitivity
5. Run one blank after the 50 and 100 ppb std to eliminate potential carryover in calibration runs
6. Run 2-3 blanks before the routine run to clean out PAT system
7. Minimize methanol in prepared aqueous standards to 10 µL or less
8. Prepare QC samples as needed fresh daily
9. Install foam eliminator if many samples are expected to contain surfactants
10. Watch out for MEK, MIBK, acetone, and other oxegenates that are often found in contaminated MeOH and also can leach from some DI water systems

2. EPA Method 525.2

EPA Method 525.2, "Determination of Organic Compounds in Drinking Water by Liquid - Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry," is one of the most commonly used methods for semivolatile compound analysis in drinking water. The method lists over 100 compounds that may be analyzed by the suggested procedures, but usually only a subset of the listed target compounds are monitored in any measurement.

This chapter of the Varian Environmental MS Application Manual will assist chemists in rapidly setting up the 210-MS/220-MS and 240-MS GC/MS systems for the analysis of water samples by EPA Method 525.2. The accompanying CD for this manual contains a subdirectory, called EPA525_2, which contains a PDF version of this section of the manual along with other important files that will be described in detail below.

Following this introduction is the Scope and Summary of EPA Method 525.2. The full method is available (in PDF format) on the attached CD in Appendix II for complete review. This and other methods can be obtained from the National Environmental Methods Index at http://www.nemi.gov/.

The Analytical Section provides guidance how to achieve the requirements of Method 525.2. A complete description of the apparatus, materials (analytical standards), and conditions is given. Also included are GC column recommendations and proven methods for GC, AutoSampler, MS acquisition, and MS data handling. Acquisition parameters were selected to fulfill the tune requirements. The data handling parameters were chosen to assure positive identification and accurate quantitation, and to satisfy QA/QC requirements.

Finally, the Results Section contains a selection data generated with both the 210-MS/220-MS and 240-MS GC/MS systems using the conditions recommended in this manual. Examples included are results of Tune Verification, Initial Calibration, and Method Detection Limit calculations (statistical process) for each instrument configuration.

The Varian EnviroPro™ Software can be used to generate a variety of useful quality control summary reports in standard Contract Laboratory Program (CLP) format. Appendix I contains a series of PDF files as example reports for a typical volatile or semi-volatile method (EPA Method 524.2 and EPA 8270 are shown). The reports are easily adaptable to other EPA methods that require extensive quality control reporting.

2.1 List of Abbreviations

BFB	Bromofluorobenzene
CCC	Continuing Calibration Check
DOC	Demonstration of Capability
ICC	Initial Calibration Check
IS	Internal Standard
LCS	Lab Control Sample
LFB	Lab Forrtified Blank
LMB	Lab Method Blank
LTB	Lab Trip Blank
LRB	Lab Reagent Blank
MDL	Method Detection Limit
MS	Matrix Spike
MS/MSD	Matrix Spike/Matrix Spike Duplicate
PAT	Purge and Trap
QCS	Quality Control Sample
RRF	Relative Response Factors
RS	Recovery Standard
SPCC	System Performance Check Compounds
SS	Surrogate Standard

2.2 Scope and Application

EPA Method 525.2: Determination of Organic Compounds in Drinking Water by Liquid-solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry.

This is a general purpose method that provides procedures for determination of organic compounds in finished drinking water, source water, or drinking water in any treatment stage. The method is applicable to a wide range of organic compounds that are efficiently partitioned from the water sample onto a C18 organic phase chemically bonded to a solid matrix in a disk or cartridge and sufficiently volatile and thermally stable for gas chromatography. Single-laboratory accuracy and precision data have been determined with two instrument systems using both disks and cartridges for the following compounds:

Table 2-1 Target Analytes

Analyte	MW[1]	Chemical Abstracts Service Registry Number
Acenaphthylene	152	208-96-8
Alachlor	269	15972-60-8
Aldrin	362	309-00-2
Ametryn	227	834-12-8

Analyte	MW[1]	Chemical Abstracts Service Registry Number
Anthracene	178	120-12-7
Atraton	211	1610-17-9
Atrazine	215	1912-24-9
Benz[a]anthracene	228	56-55-3
Benzo[b]fluoranthene	252	205-82-3
Benzo[k]fluoranthene	252	207-08-9
Benzo[a]pyrene	252	50-32-8
Benzo[g,h,i]perylene	276	191-24-2
Bromacil	260	314-40-9
Butachlor	311	23184-66-9
Butylate	217	2008-41-5
Butylbenzylphthalate	312	85-68-7
Carboxin[2]	235	5234-68-4
Chlordane components:		
Alpha-chlordane	406	03-71-9
Gamma-chlordane	406	5103-74-2
Trans nonachlor	440	39765-80-5
Chlorneb	206	2675-77-6
Chlorobenzilate	324	510-15-6
Chlorpropham	213	101-21-3
Chlorothalonil	264	1897-45-6
Chlorpyrifos	349	2921-88-2
2-Chlorobiphenyl	188	2051-60-7
Chrysene	228	218-01-9
Cyanazine	240	21725-46-2
Cycloate	215	1134-23-2
Dacthal(DCPA)	330	1861-32-1
DDD, 4,4'-	318	72-54-8
DDE, 4,4'-	316	72-55-9
DDT, 4,4'-	352	50-29-3
Diazinon[2]	304	333-41-5
Dibenz[a,h]anthracene	278	53-70-3
Di-n-butylphthalate	278	84-74-2
2,3-Dichlorobiphenyl	222	16605-91-7
Dichlorvos	220	62-73-7
Dieldrin	378	60-57-1
Diethylphthalate	222	84-66-2
Di(2-ethylhexyl)adipate	370	103-23-1
Di(2-ethylhexyl)phthalate	390	117-81-7
Dimethylphthalate	194	131-11-3
2,4-Dinitrotoluene	182	121-14-2
2,6-Dinitrotoluene	182	606-20-2
Diphenamid	239	957-51-7

Analyte	MW[1]	Chemical Abstracts Service Registry Number
Disulfoton[2]	274	298-04-4
Disulfoton sulfoxide[2]	290	2497-07-6
Disulfoton sulfone	306	2497-06-5
Endosulfan I	404	959-98-8
Endosulfan II	404	33213-65-9
Endosulfan sulfate	420	1031-07-8
Endrin	378	72-20-8
Endrin aldehyde	378	7421-93-4
EPTC	189	759-94-4
Ethoprop	242	13194-48-4
Etridiazole	246	2593-15-9
Fenamiphos[2]	303	22224-92-6
Fenarimol	330	60168-88-9
Fluorene	166	86-73-7
Fluridone	328	59756-60-4
Heptachlor	370	76-44-8
Heptachlor epoxide	386	1024-57-3
2,2',3,3',4,4',6-Heptachlorobiphenyl	392	52663-71-5
Hexachlorobenzene	282	118-74-1
2,2',4,4',5,6'-Hexachlorobiphenyl	358	60145-22-4
Hexachlorocyclohexane, alpha	288	319-84-6
Hexachlorocyclohexane, beta	288	319-85-7
Hexachlorocyclohexane, delta	288	319-86-8
Hexachlorocyclopentadiene	270	77-47-4
Hexazinone	252	51235-04-2
Indeno[1,2,3,c,d]pyrene	276	193-39-5
Isophorone	138	78-59-1
Lindane	288	58-89-9
Merphos[2]	298	150-50-5
Methoxychlor	344	72-43-5
Methyl paraoxon	247	950-35-6
Metolachlor	283	51218-45-2
Metribuzin	214	21087-64-9
Mevinphos	224	7786-34-7
MGK	264	275 113-48-4
Molinate	187	2212-67-1
Napropamide	271	15299-99-7
Norflurazon	303	27314-13-2
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	426	40186-71-8

Analyte	MW[1]	Chemical Abstracts Service Registry Number
Pebulate	203	1114-71-2
2,2’,3’,4,6-Pentachlorobiphenyl	324	60233-25-2
Pentachlorophenol	264	87-86-5
Phenanthrene	178	85-01-8
Permethrin, cis-	390	54774-45-7
Permethrin, trans	390	51877-74-8
Prometon	225	1610-18-0
Prometryn	241	7287-19-6
Pronamide	255	23950-58-5
Propachlor	211	1918-16-7
Propazine	229	139-40-2
Pyrene	202	129-00-0
Simazine	201	122-34-9
Simetryn	213	1014-70-6
Stirofos	364	22248-79-9
Tebuthiuron	228	34014-18-1
Terbacil	216	5902-51-2
Terbufos[2]	288	13071-79-9
Terbutryn	241	886-50-0
2,2',4,4'-Tetrachlorobiphenyl	290	2437-79-8
Toxaphene		001-35-2
Triademefon	293	43121-43-3
2,4,5-Trichlorobiphenyl	256	15862-07-4
Tricyclazole	189	41814-78-2
Trifluralin	335	1582-09-8
Vernolate	203	1929-77-7
Aroclor 1016		12674-11-2
Aroclor 1221[3]		11104-28-2
Aroclor 1232[3]		11141-16-5
Aroclor 1242[3]		53469-21-9
Aroclor 1248[3]		12672-29-6
Aroclor 1254		11097-69-1
Aroclor 1260		11096-82-5

[1] Monoisotopic molecular weight calculated from the atomic masses of the isotopes with the smallest masses.

[2] Only qualitative identification of this analyte is possible because of its instability in aqueous matrices. Merphos, carboxin, disulfoton, and disulfoton sulfoxide showed instability within one hour of fortification. Diazinon, fenamiphos, and terbufos showed significant losses within seven days under the sample storage conditions specified in this method.

[3] This method was validated using Aroclors 1016, 1254, and 1260 which were selected to represent these Aroclors. The extraction conditions and determinative techniques should produce accuracy and precision data comparable to those for the Aroclors tested.

Attempting to determine all of the above analytes in all samples is not practical and not necessary in most cases. If all the analytes must be determined, multiple calibration mixtures will be required.

Method detection limit (MDL) is defined as the statistically calculated minimum amount that can be measured with 99% confidence that the reported value is greater than zero. The MDL is compound dependent and is particularly dependent on extraction efficiency and sample matrix. These MDLs are not necessarily required by regulation, but were demonstrated in the validation of the method. The calibration concentration range demonstrated in this method is 0.01 or 0.05-10 µg/L for most analytes.

2.3 Summary of Method

Organic compound analytes, internal standards, and surrogates are extracted from a water sample by passing 1 L of sample water through a cartridge or disk containing a solid matrix with a chemically bonded C_{18} organic phase (liquid-solid extraction, LSE). The organic compounds are eluted from the LSE cartridge or disk with small quantities of ethyl acetate followed by methylene chloride, and this extract is concentrated further by evaporation of some of the solvent. The sample components are separated, identified, and measured by injecting an aliquot of the concentrated extract into a high-resolution fused silica capillary column of a gas chromatography/mass spectrometry (GC/MS) system. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a database. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

Table 2-2 Quality Control Matrix Table

SOC Analyses by EPA 525.2			
QC Type	**Concentration Level**	**Frequency**	**Acceptance Criteria**
Tune	Introduce 5 ng of Decafluorotriphenylphosphine (DFTPP)into the GC.	Analyzed at the beginning of the run, and every 12 hours. A single spectrum or average across the peak may be used to check the tune. Use the tune feature in the EnviroPro Software for evaluating the instrument tune.	Mass 51 10-80% of the base peak Mass 68 < 2% of mass 69 Mass 69 present Mass 70 < 2% of mass 69 Mass 127 10-80% of the base peak Mass 197 <2% of mass 198 Mass 198 Base peak or >50% of mass 442 Mass 199 5-9% of Mass 198 Mass 275 10-60% of the base peak Mass 365 >1% of the base peak Mass 441 Present and < mass 443 Mass 442 Base peak or >50% of mass 198 Mass 443 15-24% of mass 442
System Resolution (SPCC)	Anthracene, benzo(a)anthracene, chrysene, & phenanthrene, all at 2.0 µg/mL.	Analyzed at the beginning of the run, and every 12 hours. **(Required when analytes in the SPCC are requested for sample analysis.)**	System resolution: anthracene and phenanthrene valley height < 3.5%; chrysene and benzo(a)anthrancene valley height < 25%. Avg peak height of the 2 peaks.
Analyte Degradation (SPCC)	Endrin and DDT at 2.0 µg/mL.	Analyzed at the beginning of the run, and every 12 hours. Required when analytes in the SPCC are requested for sample analysis.	The abundance of endrin, aldehyde, and/or endrin ketone and DDE and/or DDD should be <20% of endrin and DDT, respectively.
IICC	A calibration curve consisting of at least 5 standard	When first using this method on an instrument, after major instrument	Linear fit. May use second order for non-method compounds.

SOC Analyses by EPA 525.2

QC Type	Concentration Level	Frequency	Acceptance Criteria
	concentrations per analyte. The lowest calibration standard must be at or below the MRL.	maintenance, or when indicated by a change in instrument response.	Min. RRF = 0.990
LTB	Reagent Water prepared, shipped and analyzed as a sample.	Whenever provided by the client.	No analytes of interest present at or above the MRL.
LMB	Reagent Water prepared and analyzed as a sample.	One extracted per extraction day (12 hour workshift). Analyze once.	No analytes of interest present at or above the MRL.
CCC	Calibration standard(s) at varied concentrations within the calibration range.	Analyzed at the beginning of the run and every 12 hours throughout the run.	Analytes +/-30% of true value. 10% of the analytes can fail high, no analyte can fail in 3 consecutive CCCs.
IIS	Phenanthrene-d10 and Chrysene-d12 at a concentration of 5.0 µg/L.	Run in every sample.	In CCCs, the absolute areas of the quant ions must be +/- 50% of the average areas of the initial calibration, and +/-30% of the quant ion areas of the most recent CCC.
Field Samples	———————	———————	In extracted samples and QC,the areas must be +/-30% of the areas in the previous CCC.
RS	Pyrene - d10 at 5.0 µg/L.	Run in every sample.	See Internal Standard.
SS	2,4,5,6-Tetrachloro-m-xylene, 4,4'-Dichlorobiphenyl and Triphenylphosphate at 5.0 µg/L. Method allows other surrogates.	Run in every sample.	Surrogate recovery must be within +/- 30% of the target. In CCCs, the absolute areas of the quant ions must be +/- 50% of the average areas of the initial calibration, and +/-30% of the quant ion areas of the most recent CCC.
LFB	All of the analytes of interest at a mid range concentration.	One analyzed per group of 20 samples or less extracted together.	** Use either +/-30% or a lab established limit.
QCS	All of the analytes of interest at a mid range concentration.	Quarterly.	Same as the LFB.
MS	All of the analytes of interest at a mid range concentration.	At a frequency of 5% of all samples analyzed.	Analyte recovery same as the LFB.
MSD or LD	Either a Matrix Spike Duplicate, or a lab duplicate.	At a frequency of 5% of all samples analyzed.	RPD within 20%. MSD analyte recovery same as the LFB.
IDC or DOC	4 LFBs at a mid level concentration.	Initially and with each new technician.	Mean percent recovery same as LFB. RSD <30%.
MDL	7 LFBs at a low concentration.	Annually.	Calculated value must be < target and >1/10 target for method compounds. Calculated value must be < target for non-method compounds.

2.4 Analytical Section

In this section parameters for the equipment, accessories, and supplies are specified to assure optimum performance of the analysis. While both other and new products may improve overall results, the accessories were carefully selected for optimum performance. Deviation from the suggested equipment, supplies or conditions may result in lost performance.

2.4.1 Equipment and Supplies

Analytical columns

30 m x 0.25 mmID x 0.25 µm film FactorFour VF-5ms [VPN CP8944]

25 m x 0.20 mmID x 0.33 µm film FactorFour VF-5ms [VPN CP8936]

VPN 03-930824-00 Semi-Volatile Consumables Kit. Kit includes:

Semi-Volatile Organic Chemicals Parts and Supplies for EPA Methods 525.2 & 8270D		
03-930824-00		
Syringe	03-925902-05	10 µL conical tipped needle
Injector Parts		
1177 Split/Splitless Injector		
	RT210462145	Insert 4 mm ID open single gooseneck liner, Siltek, -fritted
	CR298713	BTO septa pkg of 50
	8850103100	The o-ring that seals the 1177 injector insert pkg of 25
1079 PTV Injector		
	RT217092145	Insert for 1079, Siltek
	CR298777	BTO septa for the 1079 injector pkg of 50
	03-925342-01	Graphite ferrule that seals the 1079 injector insert pkg of 10
Ferrules		
	2869458001	For 30 m columns pkg of 10 40/60 graphite/Vespel
Vials		
	03-926120-16	Ultra vials and septa 2 ml amber glass wide opening screw

GC/MS Systems

210-MS/220-MS GCMS or 240-MS GC/MS equipped with an 1177 injector and Electronic Flow Controller (EFC) type 21 [Injector: VPN 45-11101-01]. The sample is introduced in splitless mode. The injector should be equipped with a 4 mm, Siltek Fritted insert [VPN: RT210462145], installed goose-neck down.

Septum Purge Flow calibration should be carried out at pressure pulse column pressure (typically 30-45 psi) and set to 2 mL/min.

Model 8400 AutoSampler.

Important: Use the conical needle type on the syringe. This will prevent coring of the septum during injections. Syringe [VPN: 0392590205]

For best result, use the BTO septa [VPN: CR298713] for the 1177 injector. For the AutoSampler, use the Ultra clean vials and septa. [VPN: 392611979].

GC/MS Interface

Capillary direct into the mass spectrometer via the 210-MS/220-MS/240-MS transferline.

NOTE: *Always reduce the column, MS transfer line, and ion trap electrode temperatures if the column flow is interrupted for maintenance. The temperature of the column should be below 50 °C and the transfer line and ion trap less than 100 °C. Failure to do this will damage the instrument!*

To assure that the DFTPP tune criteria specified in the method is met, use the suggested acquisition parameters (See Sections 2.6.2 – 2.6.4). The amount of DFTPP entering the detector should be 5 ng or less.

NOTE: *Ensure that mass calibration (when necessary) is performed at the operating column flow rate, NOT under pressure pulse conditions.*

GC/MS Data System

The Varian MS Workstation Software fulfills the requirements of the method.

2.4.2 Data Analysis and Calculations

Fully calibrated methods with data handling parameters (integration, identification, and quantification) for the common regulated group of 525.2 analytes are on the Varian Environmental MS Applications Manual CD, included with a hard copy of this manual. For Method 525.2 there are three method files (.mth files) and three raw data files (.SMS files) representing the three different instrument configurations. All of these are in a subdirectory on the CD called EPA525_2. The table below describes which files are associated with which instrument configuration:

Instrument Configuration	Method File (.mth)	Data File (.SMS)
210-MS or 220-MS	525 _2_210_220MS.mth	525_2_210_220MSdata.SMS
240-MS Internal Ionization Source	525_2_240MS_INT.mth	525_2_240_INTdata.SMS
240-MS External Ionization Source	525_2_240MS_EXT.mth	525_2_240EXTdata .SMS

Choose the appropriate method and example data file and make a copy of them. The operator will likely need to make changes in retention times or some other parameters for further optimization.

Tuning the Mass Spectrometer

The amount of DFTPP entering the detector must be 5 ng or less. DFTPP must pass the specifications given in the QC Matrix table before analysis can begin. The analytical parameters in Sections 2.6.2 – 2.6.4 give a good starting point for passing the tune. Fine adjustments to key parameters may be necessary for passing the tune requirement. Once set, the tune should be stable for an extended period and will only need to be monitored at the required frequency (12 hr intervals). See Section 2.8, Troubleshooting for parameters to adjust in the case of a failing tune.

NOTE: Use the Varian EnviroPro “find tune” feature for tuning under EPA 525.2 to find a passing scan or scans in a DFTPP peak.

Analytes Monitored and Calibration Levels

While Method 525.2 lists (Section 2.2 of the reference method) a large number of analytes that may be monitored by the procedures specified in the Method, the actual number of analytes measured will depend on the laboratory requirements. Usually, only a subset of the analytes listed in the method is monitored in a single analysis.

Adjust the retention times of the analytes based on the calibration run performed on a given instrument. Also, modify the compound lists as needed for the analysis.

Calibration Levels and Ranges

Method 525.2 suggests six calibration levels covering the 0.1–10 μg/mL range.

The attached methods includes 8-9 calibration points covering a range of 0.01- 10μg/mL (ppm).

NOTE: *Analyte ranges will vary depending upon the data quality objectives and compound response in the GC/MS. Ethyl acetate or Dichloromethane may be used to prepare the calibration standards.*

Integration Parameters

The integration parameters in the 525.2 method files provided were selected to assure reliable integration even at the lowest calibration level. These parameters may need to be adjusted and the analyst should review the integration parameters for each analyte using the lowest level calibration data file. The most commonly adjusted parameters are:

- Identification Window
- Peak Width
- Area Reject Value
- Slope Sensitivity (occasionally)
- Smoothing

Review the MS Workstation Software Reference Manual section entitled "Guidelines for Optimizing Method Integration Parameters" to clarify integration topics and processes. “Guidelines for Optimizing Integration Parameters” can be found in the “Quantitation Method” section of the Software Reference Manual.

Quantitation Parameters

Once the initial calibration is complete the analyst must review the curve fitting parameters for each analyte to assure proper quantitation of the samples to be processed.

Curve Fitting, Handling the origin, Regression weight factors

Curve Fitting

In addition to average RRF calculations, the method allows linear curve fitting as stated in Section 10.2.7 of the reference method.

- For Average RRF:

In the Varian Workstation Software, specify *Linear* for *Curve Fit Type, Force* for *Origin Point*, and $1/x^2$ or $1/nx^2$ for *Regression Weighting*. These parameters will deliver calculations based on average RRFs.

Criteria to use the Average RRF calculations:

%RSD for each analyte must be below 30%.

- For Linear Regression (most commonly used)

The correlation coefficient "r^2" indicates the quality of a fit. $r^2 = 1$ would mean a perfect fit.

NOTE: *Although the 525.2 Method does not specify a required minimum value for the correlation coefficient, $r^2 = 0.990$ or higher is considered to be acceptable by other EPA methods.*

Handling of the Origin

- Ignore (normally used for linear regression fits)
- Include
- Force (if average RRFs method is used for calculations)

Selection of the Regression Weighting Factor

- None
- 1/n
- 1/x
- 1/nx
- $1/x^2$
- $1/nx^2$

The most often used factors are $1/x^2$ and $1/nx^2$ for trace level analysis.

Review the Calibration Curve for each analyte and specify the handling of the origin and the regression weighting factor based on the collected data. Changing these parameters will change the value of r^2. Improper selection of these parameters will undermine the accuracy of the reported results for unknown samples or quality control samples.

2.5 Reagents and Standards

2.5.1 Stock Standards

Calibration standards are available in convenient packaging and concentrations. A few suggestions may make the preparation of calibration solutions easier:

- For maximum flexibility and performance use 100 µg/mL standard concentrations. This level will allow easy dilutions.
- Limit the number of standard vials; purchase standards that have the highest number of analytes in every mixture.
- Prepare standards in DRY ethyl acetate or DCM. Ethyl acetate can easily pick up moisture, resulting in target analyte degradation. Keep solvent bottles tightly capped and stored in vented cabinets.

The target analyte list is usually a sub-set of the analytes listed in the method. The data objectives will determine which analytes will be included in the target list. Standards for the commonly monitored target analytes are listed below along with internal standard, surrogate standards and GC/MS performance check compound mixtures.

Recommended Standards from Varian:

GCMS Performance Check Solution

[VPN] ULGCM160A, 3 performance check compounds,

1000 µg/mL in acetone, 4 x 1 mL

Decafluorotripehnylphosphine (DFTPP)

Endrin

4,4'-DDT

Internal and Surrogate Standards

[VPN] ULISM510, 3 internal standard and 4 surrogate compounds

500 µg/mL in acetone, 4 x 1 mL

Acenaphthene-d_{10}

Phenenthrene-d_{10}

Chrysene-d_{12}

1,3-Dimethyl-2-nitrobenzene Perylene-d_{12}

Triphenylphosphate

Pyrene-d_1

Target Analytes	
Convenient, All-In-One Solutions	
Semivolatile Mix **[VPN] ULSVM525**, 33 analytes 100 µg/mL in acetone, 4 x 1 mL	
Acenaphthylene	2,4-Dinitrotoluene
Anthracene	2,6-Dinitrotoluene
Benz[a]anthracene	Fluorene
Benzo[b]fluoranthene	Hexachlorobenzene
Benzo[k]fluoranthene	2,2',4,4',5,6'-Hexachlorobiphenyl
Benzo[ghi]perylene	2,2',3,3',4,4',6-Heptachlorobiphenyl
Benzo[a]pyrene Butyl benzyl phthalate	Hexachlorocyclopentadiene Indeno [1,2,3-cd]pyrene
2-Chlorobiphenyl	Isophorone
Chrysene	2,2',3,3',4,5',6,6'-Octachlorobiphenyl
Dibenz[a,h]anthracene	2,2',3'4,6-Pentachlorobiphenyl
2,3-Dichlorobiphenyl	Pentachlorophenol (400 µg/mL)
Bis(2-ethylhexyl) adipate	Phenanthrene
Bis(2-ethylhexyl) phthalate	Pyrene
Diethyl phthalate	2,2',4,4'-Tetrachlorobiphenyl
Dimethyl phthalate	2,4,5-Trichlorobiphenyl
Di-n-butyl phthalate	

Target Analytes	
Convenient, All-In-One Solutions	
Organochlorine Pesticide Mix **[VPN] ULPPM525E**, 29 analytes 100 µg/mL in acetone, 4 x 1 mL	
Alachlor	Endosulfan I
Aldrin	Endosulfan II
Atrazine	Endosulfan sulfate
α-BHC	Endrin
β-BHC	Endrin aldehyde
γ-BHC (lindane)	Etridiazole
δ-BHC	α-Chlordane
Chlorobenzilate	γ-Chlordane
Chlorothalonil	Heptachlor
Chloroneb	Heptachlor epoxide (B)
Decthal (DCPA)	Methoxychlor
4,4’-DDD	Permethrin
4,4’-DDT	(mixed isomers, 200 µg/mL)
4,4’-DDE	Simazine
Dieldrin	trans-Noncachlor

Target Analytes	
Convenient, All-In-One Solutions	
Nitrogen/Phosphorous Pesticide Mix **[VPN] ULNPM525C**, 40 analytes 100 µg/mL in acetone, 4 x 1 mL	
Alachlor	Mevinphos
Ametryn	MGK-264, mixed isomers
Atraton	Molinate
Atrazine	Napropamide
Bromacil	Norflurazon
Butachlor	Pebulate
Butylate	Prometon
Chlorpropham	Prometryn
Chloropyrifos	Pronamide
Cycloate	Propachlor
Cyanazine	Propazine
Dichlorvos	Simetryn
Diphenamid	Stirofos
EPTC	Tebuthiuron
Ethoprop	Terbacil
Fenarimol	Terbutryn

Target Analytes	
Convenient, All-In-One Solutions	
Nitrogen/Phosphorous Pesticide Mix **[VPN] ULNPM525C**, 40 analytes 100 µg/mL in acetone, 4 x 1 mL	
Fluridone	Triadimefon
Hexazinone	Tricyclazole
Methyl paraoxon	Trifluralin
Metolachlor	Vernolate

Target Analytes	
Convenient, All-In-One Solutions	
Nitrogen/Phosphorous Pesticide Mix **ULNPM525B**, 6 analytes, 100 µg/mL in acetone, 4 x 1 mL	
Carboxin	Fenamiphos
Diazinon	Merphos
Disulfoton	Terbufos

Target Analytes	
Convenient, All-In-One Solutions	
525.2 Regulated Compound Mix **Accu-Std M-525-REG-5X** 500 µg/mL in acetone 1 mL	
2,4-Dinitrotoluene	g-Chlordane
2,6-Dinitrotoluene	Heptachlor
Alachlor	Heptachlor epoxide (Isomer B)
Aldrin	Hexachlorobenzene
alpha-Chlordane	Hexachlorocyclopentadiene
Atrazine	Lindane
Benzo(a)pyrene	Methoxychlor
bis(2-Ethylhexyl)adipate	Metolachlor
bis(2-Ethylhexyl)phthalate	Metribuzin
Butachlor	Propachlor
Cyanazine	Simazine
Dieldrin	trans-Nonachlor
Endrin	

2.5.2 Working Calibration Standards

Initial Calibration

Set the acquisition parameters as suggested in the Analytical section and inject 2-5 ng DFTPP. The conditions specified will assure that the DFTPP tune and the Endrin and 4,4'-DDT degradation criteria are met.

Calibration solutions of 10, 5, 2, 1, 0.5, 0.2, 0.1, 0.05, 0.02 and 0.01 µg/mL are suggested for most of the analytes. Pentachlorophenol is typically included at a concentration four times that of the other analytes.

The % RSD for each analyte should be less than 30% in order to use the mean response factors for calculations.

As an alternative to calculating the mean response factors, a linear regression (provided by the Varian Workstation Software) can be used. **NOTE: Quadratic curve fitting may not be used in the EPA 525.2 method.**

2.6 Set-up of Instrumental Conditions

Fully calibrated methods with data handling parameters (integration, identification, and quantification) for the common regulated group of 525.2 analytes are on the Varian Environmental MS Applications Manual CD, included with this manual. Refer to the EPA525_2 subdirectory and copy method on you analytical system to start. See Section 2.4.2.

NOTE: *Conditions presented here are for the regulated 525.2 compounds. They will need to be adjusted if running other compounds in the method.*

2.6.1 CP-8400 AutoSampler Conditions

Syringe Size: 10 µL <u>NOTE: Use conical needle</u>

Injection Mode: Std Split/Splitless

Solvent Depth (%): 90

Sample Depth (%): 95

Default Clean Vial: I (Solvent: Ethylacetate or Dichloromethane)

Default Clean Volume (µL): 7.0

Default Clean Strokes: 1

Default Clean Speed (µL/sec): 5.0

Clean Mode Pre-Inj. Solvent Flushes: 1

Clean Mode Post-Inj Solvent Flushes: 3

Clean Mode Pre-Inj Sample Flushes: 1

Clean Mode Clean Solvent Source: I

2.6.2 Varian 210-MS/220-MS GC/MS Conditions

Column: Varian FactorFour (VF-5ms), 30 m x 0.25 mm ID x 0.25 µm film thickness [VPN: CP8944].

Column Oven Temperature Program				
Temp (°C)	Rate (°C)/min)	Hold (min)	Total (min)	
70	NA	1.5	1.5	
200	10	0.0	14.5	
270	5	0.0	28.5	
300	10	0.0	41.5	
Injector Conditions		**Injector Split States**		
Temp	250 °C	Time (min)	Split State	Split Ratio
Col Flow	1.2 mL/min	Initial	ON	20
Pressure Pulse	45 psi for 0.8 min	0.01	OFF	OFF
Constant Flow	ON	0.90	ON	20

MS Conditions				
Segment	Start (min)	End (min)	Low Mass (m/z)	High Mass (m/z)
Fil/Delay	0.00	5.00	NA	NA
Analysis	5.00	34.00	50	450
Target	12000	µscans averaged	3	
Max Ion Time	25000 µsec	Mult Offset	50-100 V	
Bakground Mass	44 m/z	Emission Current	10-12 uamps	
Mass Defect	0	Manifold Temp	80 °C	
Trap Temp	220 °C	Transfer line Temp	280 °C	
Rf Dump	650 m/z	Scan Time	0.75 sec/scan	

Suggested Segment Breaks and Ion Time Factors for DFTPP Tuning			
Low mass (m/z)	**High mass (m/z)**	**Ionization Stoage Level**	**Ionization Factor**
10	99	35	70%
100	270	40	170%
271	399	40	85%
400	650	40	40%

NOTE: *Do not perform air/water tests or mass calibrations under pressure pulse conditions. The MS internal parameters are set for normal analytical conditions (approx 1.0 ml/min) to deliver reliable results for these operations. During the pressure pulse the column flow is much higher and will result inaccurate readings.*

2.6.3 Varian 240-MS Internal Ionization Mode Conditions

Column: Varian FactorFour (VF-5ms), 30 m x 0.25 mm ID x 0.25 µm film thickness [VPN: CP8944].

Column Oven Temperature Program				
Temp (°C)	Rate (°C)/min)	Hold (min)	Total (min)	
45	NA	1.5	1.50	
240	20	2.0	13.75	
300	40	4.0	18.75	
Injector Conditions		**Injector Split States**		
Temp	250 °C	Time (min)	Split State	Split Ratio
Col Flow	1.0 mL/min	Initial	ON	50
Pressure Pulse	30 psi for 0.9 min	0.01	OFF	OFF
Constant Flow	ON	0.80	ON	50

240-MS Internal Source Conditions				
Segment	Start(min)	End(min)	Low Mass(m/z)	High Mass(m/z)
Fil/Delay	0.00	6.75	NA	NA
Analysis	6.75	18.75	45	450
Target TIC	6000	µscans averaged	2	
Max Ion Time	25000 µ sec	Mult Offset	50-100 V	
Bakground Mass	44 m/z	Emission Current	20 µamps	
Mass Defect	0	Manifold Temp	50 °C	
Trap Temp	220 °C	Transfer line Temp	280 °C	
Rf Dump	650 m/z	Scan Time	0.39 sec/scan	

Suggested Segment Breaks and Ion Time Factors for DFTPP Tuning			
Low mass (m/z)	High mass (m/z)	Ionization Stoage Level	Ionization Factor
10	130	25	225%
131	399	35	80%
400	1000	35	40%

2.6.4 240-MS External Ionization Mode Conditions

Column: Varian FactorFour (VF-5ms), 25 m x 0.25 mm ID x 0.33 µm film thickness [VPN: CP8936].

Column Oven Temperature Program				
Temp (°C)	Rate (°C)/min)	Hold (min)	Tota l(min)	
40	NA	1.00	1.00	
125	65	0.00	2.31	
320	15	1.00	16.30	
Injector Conditions		**Injector Split States**		
Temp	240 °C	Time (min)	Split State	Split Ratio
Col Flow	1.4 mL/min	Initial	ON	20
Pressure Pulse	45 psi for 0.80 min	0.01	OFF	OFF
Constant Flow	ON	0.70	ON	20

240-MS External Source Conditions				
Segment	Start (min)	End (min)	Low Mass (m/z)	High Mass (m/z)
Fil/Delay	0.00	4.00	NA	NA
Analysis	4.01	16.30	44	450
Target TIC	10000	µscans averaged	2	
Max Ion Time	25000 µsec	Mult Offset	50-100 V	
Bakground Mass	44 m/z	Emission Current	25 µamps	
Mass Defect	0	Manifold Temp	50 °C	
Trap Temp	180 °C	Transfer line Temp	280 °C	
Source Temp	250 °C	Scan Time	0.39 sec/scan	

Suggested Segment Breaks and Ion Time Factors for DFTPP Tuning			
Low mass (m/z)	High mass (m/z)	Ionization Stoage Level	Ionization Factor
10	130	25	225%
131	399	35	85%
400	1000	35	35%

Table 2-3 Peak Table of Suggested Quantitation Ions

Peak #	RT (min.)	Peak Name	Quan Ion
8	11.731	Acenaphthene-d10 (IS I)	162
22	15.316	Phenanthrene-d10 (IS II)	188
56	24.661	Chrysene-d12 (IS III)	240
1	6.699	Isophoron	82
2	7.616	Benzene, 1,2-dimethyl-3-nitro-	134

Peak #	RT (min.)	Peak Name	Quan Ion
3	9.663	Hexachlorocyclopentadiene	237
4	11.202	Dimethyl phthalate	163
5	11.214	Etridiazole	211
6	11.335	2,6-Dinitrotoluene	165
7	11.388	Acenaphthylene	152
9	11.924	Chloroneb	191
10	11.92	2-Chlorobiphenyl	188
11	12.281	2,4-Dinitrotoluene	165
12	12.892	Diethyl Phthalate	149
13	13.038	Fluorene	165
14	14.271	alpha-Lindane	183
15	14.292	2,3-Dichlorobiphenyl	222
16	14.349	Hexachlorobenzene	284
17	14.673	Simazine	201
18	14.757	Atrazine	200
19	14.854	beta-Lindane	183
20	14.864	Pentachlorophenol	266
21	15.017	gamma-Lindane	183
23	15.512	Phenanthrene	178
24	15.411	Chlorothalonil	266
25	15.512	Anthracene	178
26	15.678	delta-Lindane	183
27	15.982	2,4,5-Trichlorobiphenyl	258
28	16.499	Alachlor	188
29	16.731	Heptachlor	100
30	17.223	di-n-Butyl Phthalate	149
31	17.401	2,2',4,4'-Tetrachlorobiphenyl	292
32	17.665	DCPA	301
33	17.67	Aldrin-R	263
34	18.744	Heptachlor epoxide	353
35	18.818	2,2',3',4,6-Pentachlorobiphenyl	326
36	19.421	gamma-Chlordane	373
37	19.743	Pyrene-d10	212
38	19.806	Pyrene	202
39	19.798	alpha-Chlordane	373
40	19.871	trans-Nonachlor	409
41	20.429	4,4'-DDE	246
42	20.625	2,2',4,4',5,6'-Hexachlorobiphenyl	360
43	20.624	Dieldrin	79
44	21.272	Endrin	243
45	21.433	Chlorobenzilate	251
46	21.618	Endosulfan	195
47	21.747	4,4'-DDD	235

Peak #	RT (min.)	Peak Name	Quan Ion
48	22.078	Endrin Aldehyde	245
49	22.755	Butyl Benzyl Phthalate	149
50	22.821	Endosulfan sulfate	272
51	22.928	4,4'-DDT	235
52	23.277	bis(2-Ethylhexyl) Adipate	111
53	23.511	Triphenyl Phosphate	325
54	24.521	2,2',3,3',4,4',6-Heptachlorobiphenyl	394
55	24.578	Benz[a]anthracene	228
57	24.69	2,2',3,3',4,5',6,6'-Octachlorobiphenyl	430
58	24.622	Chrysene	228
59	24.762	Methoxychlor	227
60	25.373	bis(2-Ethylhexyl) Phthalate	149
61	27.781	cis-Permethrin	183
62	28.021	trans-Permethrin	183
63	28.982	Benzo[b]fluoranthene	252
64	29.097	Benzo[k]fluoranthene	252
65	30.065	Benzo[a]pyrene	252
66	30.267	Perylene-d12	264
67	33.318	Indeno[1,2,3-cd]fluoranthene	276
68	33.442	Dibenz[a,h]anthracene	278
69	34.19	Benzo[ghi]perylene	276

Nitrogen Phosphorous pesticides

Cmpd. Number	RT (min)	Peak Name	Quan Ions
8	11.726	Acenaphthene-d10 IS I	162
22	15.308	Phenanthrene-d10 IS II	188
46	24.638	Chrysene-d12 IS III	240
1	7.608	Benzene, 1,3-dimethyl-2- nitro-	134
2	8.387	Dichlorvos	109
3	9.954	EPTC	128
4	10.852	Mevinphos	127
5	10.887	Butylate	146
6	11.125	Vernolate	128
7	11.311	Pebulate	128
9	12.132	Tebuthiuron	156
10	12.387	Molinate	126
11	13.141	Propachlor	120
12	13.437	Ethoprophos	158
13	13.482	Cycloate	154
14	13.701	Chlorpropham	127
15	13.724	Trifluralin	264

Cmpd. Number	RT (min)	Peak Name	Quan Ions
16	14.504	Atraton	195
17	14.621	Prometon	210
18	14.829	Propazine	214
19	15.028	Terbufos	231
20	15.129	Pronamide	173
21	15.147	Diazinon	179
23	15.437	Disulfoton	88+89
24	15.471	Methylparaoxon	109
25	15.544	Terbacil	161
26	16.611	Simetryn	213
27	16.696	Ametryn	212
28	16.752	Prometryn	184
29	17.09	Terbutryn	226
30	17.312	Bromacil	207
31	17.478	Metolachlor	162
32	17.519	Chlorpyrifos	197
33	17.684	Cyanazine	225
34	17.815	Triadimefon	208
35	18.166	Diphenamide	167
36	18.522	MGK-264	164
37	19.499	Stirofos	109
38	19.561	Butachlor	160
39	19.734	Pyrene-d10	212
40	19.914	Fenamiphos	154
41	19.992	Napropamide	72
42	20.407	Tricyclazole	189
43	20.742	Carboxin	143
44	22.655	Norflurazon	145
45	23.505	Triphenyl phosphate	325
47	26.661	Fenarimol	139

2.7 Analytical Results

2.7.1 Sample Chromatograms

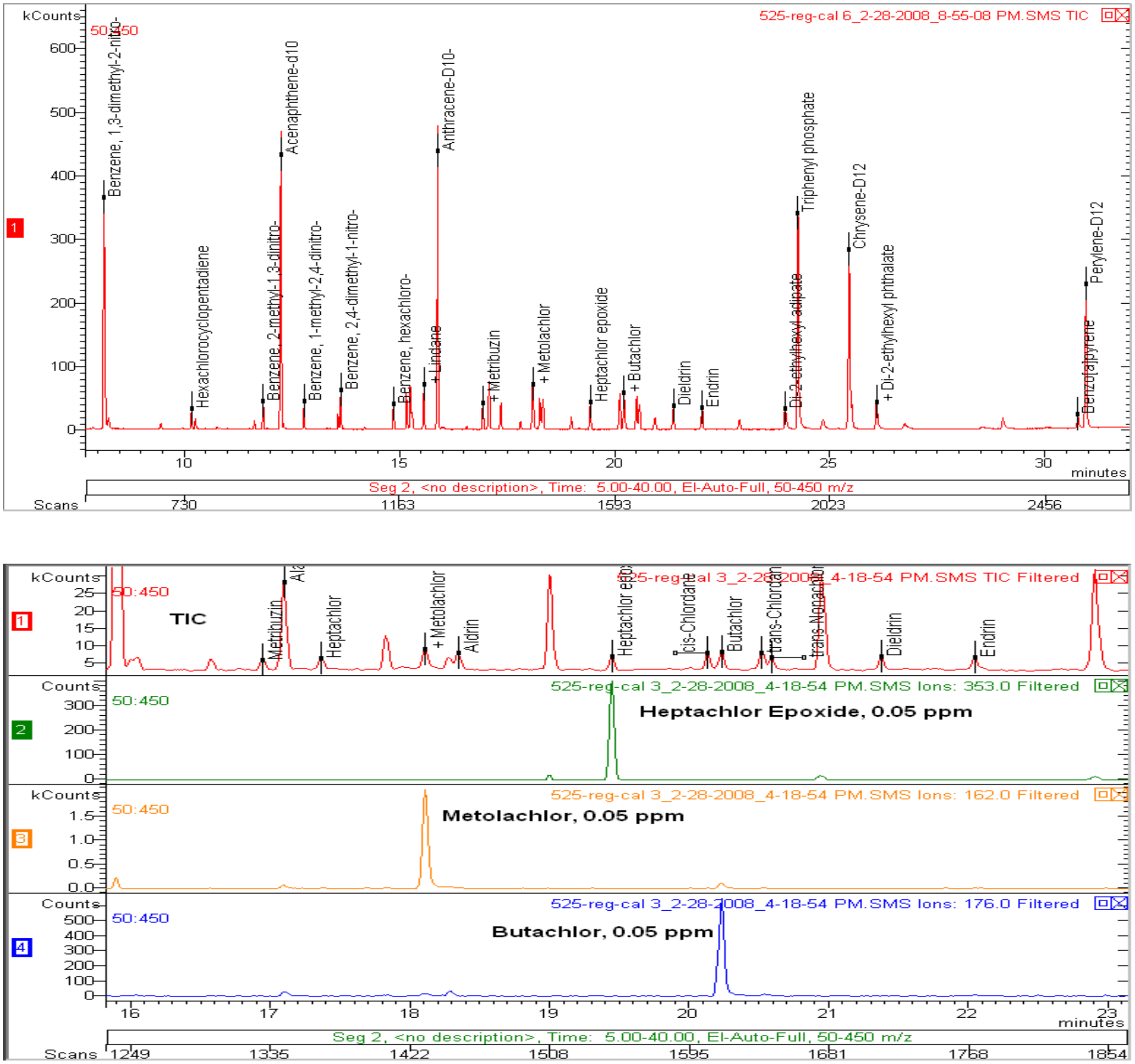


Figure 2.1: ***210-MS/220-MS:*** *Top: TIC of 1 ppm Regulated 525.2 Mixture, Bottom: Select compounds, extracted ion chromatograms at 0.05 ppm on the 210-MS/220-MS.*

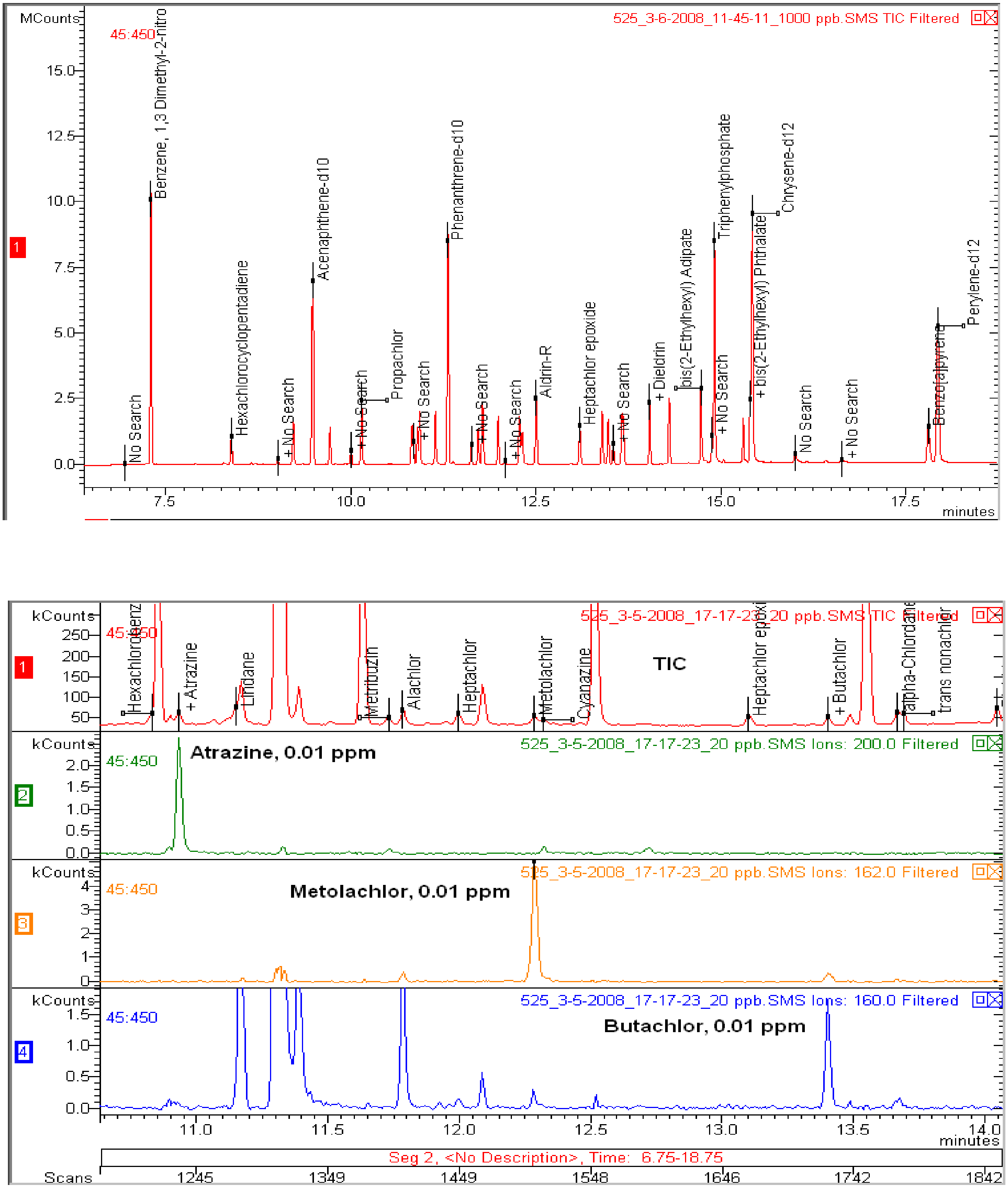


*Figure 2.2: **240-MS Internal Ionization Mode**: Top: 1 ppm Regulated 525.2 compounds, TIC at 1 ppm. Bottom: Selected extracted ion chromatograms, 0.01 ppm on the 240-MS.*

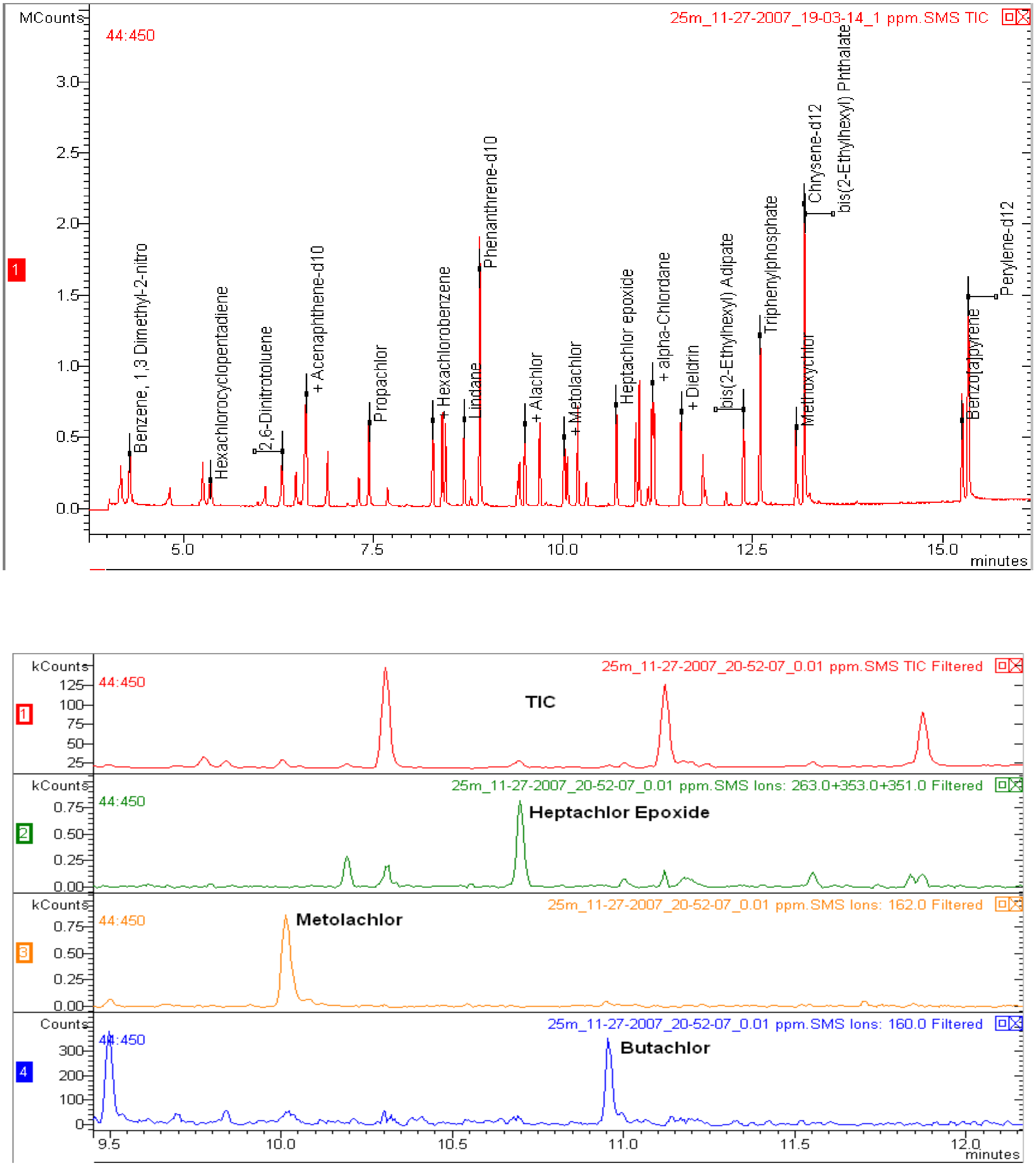
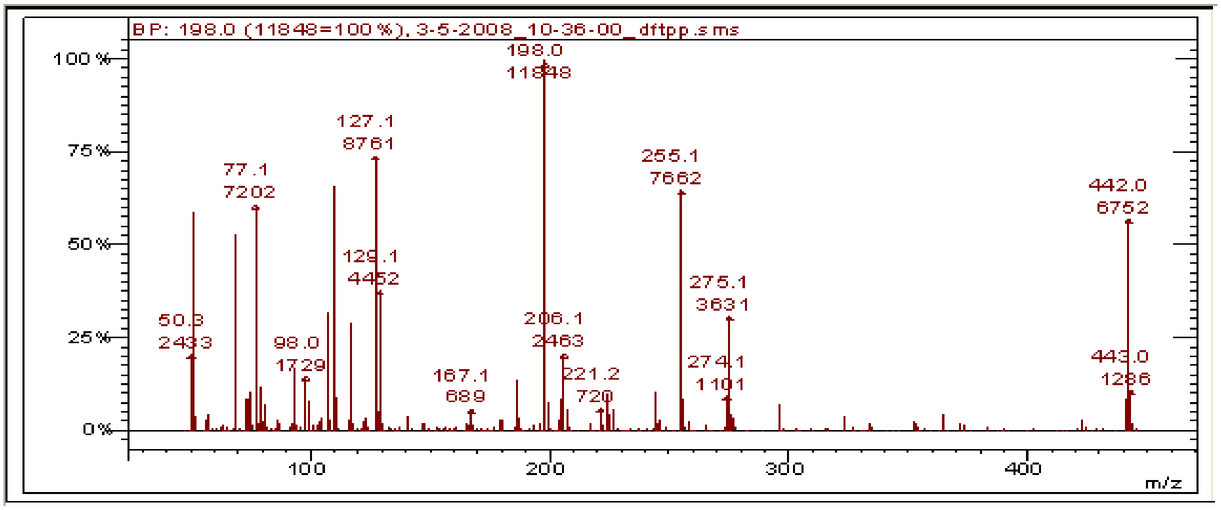


*Figure 2.3: **240-MS External Ionization Mode:** Top: 1 ppm Regulated 525.2 compounds, TIC at 1 ppm. Bottom: Selected extracted ion chromatograms, 0.01 ppm on the.*

2.7.2 Tune Verification Example

DFTPP 525.2 Report



Lab File ID 3-5-2008_10-36-00_dftpp.sms

Injection Date: 3/5/2008

Injection Time: 10:36

Mass	Criteria	Result1	PFResult1
51	10-80% of base peak	58.79	PASS
68	<2% of m/z 69	1.25	PASS
69	Present	52.84	PASS
70	<2% of m/z 69	1.49	PASS
127	10-80% of base peak	73.94	PASS
197	<2% of m/z 198	0.17	PASS
198	Base peak or >50% of m/z 442	100.00	PASS
199	5-9% of m/z 198	7.50	PASS
275	10-60% of base peak	30.65	PASS
365	>1% of base peak	4.58	PASS
441	Present and <m/z 443	78.93	PASS
442	Base peak or >50% of m/z 198	56.99	PASS
443	15-24% of m/z 442	19.05	PASS

2.7.3 Calibration Statistics

Table 2-4 Initial Calibration for Regulated 525.2 Compounds Mixture on the 210-MS/220-MS

Initial Calibration for Regulated 525.2 Compounds Mixture on the 210-MS/220-MS			
Calibration Levels (0.01 ppm – 10.0 ppm) – Linear Fit			
Compound Name	**Corr. Coeff.**	**Avg. RRF**	**% RSD**
Benzene, 1,3-dimethyl-2-nitro-	0.9881	1.0201	3.4890
Hexachlorocyclopentadiene	0.9998	1.2436	4.8676
Benzene, 2-methyl-1,3-dinitro-	0.9998	0.7883	6.7096
Benzene, 1-methyl-2,4-dinitro-	0.9993	1.2091	9.9535
Benzene, 2,4-dimethyl-1-nitro-	0.9990	1.4628	9.5505
Benzene, hexachloro-	0.9986	0.3759	8.3151
Simazine	0.9978	0.6449	11.6245
Atrazine	0.9979	0.5427	9.9239
Lindane	1.0000	1.9307	9.6114
Metribuzin	0.9987	0.7193	8.4270
Alachlor	0.9965	0.3859	19.1562
Heptachlor	0.9980	0.3579	4.2347
Metolachlor	0.9988	2.4083	8.6408
Cyanazine	0.9990	0.2521	12.5097
Aldrin	0.9988	0.1122	7.5587
Heptachlor epoxide	0.9996	0.4524	5.0660
cis-Chlordane	0.9996	0.3899	7.7381
Butachlor	0.9976	0.7599	9.5862
trans-Chlordane	0.9992	0.7111	6.8367
trans-Nonachlor	0.9995	0.2170	6.7598
Dieldrin	0.9993	0.2932	15.8493
Endrin	0.9991	0.1160	9.6562
Di-2-ethylhexyl adipate	0.9990	1.2727	15.0248
Triphenyl phosphate	0.9882	0.5688	3.4768
Methoxychlor	0.9920	0.4086	12.920
Di-2-ethylhexyl phthalate	0.9982	1.9250	12.9337
Benzo[a]pyrene	0.9978	0.9633	10.7022
Average	**0.9979**		**9.3001**

Table 2-5 Initial Calibration on 240-MS, Internal Ionization Mode, 525.2 Regulated Compound Mix

Initial Calibration on 240-MS, Internal Ionization Mode, 525.2 Regulated Compound Mix			
Calibration Levels (0.01 ppm – 10.0 ppm) – Linear Fit			
Compound Name	**Corr. Coeff.**	**Avg. RRF**	**% RSD**
Benzene, 1,3 Dimethyl-2-nitro	0.9782	0.3923	4.7492
Hexachlorocyclopentadiene	0.9988	0.6177	12.0813
2,6-Dinitrotoluene	0.9999	0.6936	14.2312
2,4-Dinitrotoluene	0.9997	0.6470	21.4272
Propachlor	0.9953	1.9997	7.3017
Hexachlorobenzene	1.0000	0.5727	5.1319
Simazine	0.9925	0.3874	12.3551
Atrazine	0.9966	0.5920	11.1595
Lindane	1.0000	1.6216	3.9657
Metribuzin	0.9987	0.4576	11.5143
Alachlor	0.9997	0.8571	10.6110
Heptachlor	0.9984	0.7000	11.4124
Metolachlor	0.9996	1.2269	11.2076
Cyanazine	0.9959	0.5171	23.0854
Aldrin-R	0.9941	0.9143	14.8703
Heptachlor epoxide	0.9980	0.3877	11.8808
Butachlor	0.9990	1.0310	14.8678
gamma-Chlordane	0.9982	0.5747	15.8128
alpha-Chlordane	0.9997	0.8286	9.8031
trans nonachlor	0.9997	0.2646	9.0028
Dieldrin	0.9995	1.2801	10.4355
Endrin	0.9997	0.1642	12.3861
bis(2-Ethylhexyl) Adipate	0.9962	2.9083	16.0049
Triphenylphosphate	0.9855	0.7644	3.8619
Methoxychlor	0.9922	1.3588	29.6119
bis(2-Ethylhexyl) Phthalate	0.9931	1.4812	18.1266
Benzo[a]pyrene	0.9967	1.8559	13.1931
Overall Average	**0.9965**		**12.5960**

Table 2-6 Initial Calibration on 240-MS External Ionization Mode for Regulated 525.2 Mixture

Initial Calibration on 240-MS External Ionization Mode for Regulated 525.2 Mixture			
Calibration Levels (0.01 ppm – 10.0 ppm) – Linear Fit			
Compound Name	**Corr.**	**Avg. RRF**	**% RSD**
Hexachlorocyclopentadiene	0.9999	0.6966	26.0546
2,6-Dinitrotoluene	1.0000	0.7334	16.7599
2,4-Dinitrotoluene	0.9994	0.6915	20.9491
Propachlor	1.0000	1.8705	15.6481
Hexachlorobenzene	0.9989	0.8784	7.1324
Simazine	0.9999	0.1507	19.9118
Atrazine	0.9999	0.2511	9.8334
Lindane	0.9969	0.2066	6.7837
Metribuzin	0.9998	0.1650	17.1945
Alachlor	0.9993	0.2027	11.6441
Heptachlor	0.9991	0.1996	11.1772
Metolachlor	0.9996	0.5817	9.3337
Cyanazine	0.9998	0.2201	21.6825
Aldrin-R	0.9986	0.2757	3.6479
Heptachlor epoxide	0.9991	0.3945	4.8124
Butachlor	0.9992	0.4901	14.9744
gamma-Chlordane	0.9978	0.7455	4.5304
alpha-Chlordane	0.9977	1.0858	4.8794
trans nonachlor	0.9963	0.4211	12.5459
Dieldrin	0.9998	0.5273	8.0292
Endrin	0.9997	0.1553	11.4486
bis(2-Ethylhexyl) Adipate	0.9997	1.2028	22.0080
Methoxychlor	0.9985	0.6673	28.7144
bis(2-Ethylhexyl) Phthalate	1.0000	0.8182	20.6647
Benzo[a]pyrene	1.0000	0.8865	9.1639
Average	**0.9992**		**13.5810**

2.7.4 Method Detection Limit (MDL) Results

Table 2-7 Method Detection Limits (MDLs) on the 210-MS/220-MS (7 replicates at 0.05 ppm)

Method Detection Limits (MDLs) on the 210-MS/220-MS (7 replicates at 0.05 ppm)					
EPA Method 525.2 Regulated/Unregulated List- 220-MS					
MDL Replicates at 0.050 ppm, REP1 – REP7					
Peak Name	**Avg**	**StdDEV**	**%RSD**	**%Recovery**	**MDL**
Hexachlorocyclopentadiene	0.0467	0.002928	6.3	93.4	0.009196
Benzene, 2-methyl-1,3-dinitro-	0.0473	0.001113	2.4	94.6	0.003495
Benzene, 1-methyl-2,4-dinitro-	0.0439	0.001773	4.0	87.7	0.005568
Benzene, 2,4-dimethyl-1-nitro-	0.0456	0.003259	7.2	91.1	0.010236
Benzene, hexachloro-	0.0524	0.00276	5.3	104.9	0.00867
Simazine	0.0476	0.003952	8.3	95.1	0.012414
Atrazine	0.0391	0.003288	8.4	78.3	0.010327
Lindane	0.0471	0.00234	5.0	94.3	0.00735
Metribuzin	0.0340	0.003958	11.6	68.0	0.012432
Alachlor	0.0246	0.00237	9.6	49.1	0.007446
Heptachlor	0.0404	0.003309	8.2	80.9	0.010395
Metolachlor	0.0349	0.004298	12.3	69.7	0.013501
Cyanazine	0.0266	0.004237	15.9	53.1	0.013308
Aldrin	0.0519	0.001864	3.6	103.7	0.005856
Heptachlor epoxide	0.0499	0.001864	3.7	99.7	0.005856
cis-Chlordane	0.0504	0.001718	3.4	100.9	0.005397
Butachlor	0.0377	0.003147	8.3	75.4	0.009885
trans-Chlordane	0.0506	0.00282	5.6	101.1	0.008858
trans-Nonachlor	0.0523	0.003638	7.0	104.6	0.011428
Dieldrin	0.0516	0.004614	8.9	103.1	0.014491
Endrin	0.0496	0.001988	4.0	99.1	0.006244
Di-2-ethylhexyl adipate	0.0183	0.00499	27.3	36.6	0.015675
Methoxychlor	0.0169	0.002545	15.1	33.7	0.007993
Di-2-ethylhexyl phthalate	0.0260	0.006164	23.7	52.0	0.019362
Benzo[a]pyrene	0.0304	0.00535	17.6	60.9	0.016803
Overall			**9.3**	**81.2**	**0.0101**

Table 2-8 Method Detection Limits (MDLs) on the 240-MS in Internal Ionization Mode (7 replicates at 0.01 ppm)

Method Detection Limits (MDLs) on the 240-MS in Internal Ionization Mode (7 replicates at 0.01 ppm)					
EPA Method 525.2 Regulated List on the 240-MS Internal Mode					
MDL Replicates at 0.010 ppm, REP1 – REP7					
Peak Name	**Avg**	**StdDEV**	**%RSD**	**%Recovery**	**MDL**
Hexachlorocyclopentadiene	0.0107	0.000488	4.6	107.1	0.001533
2,6-Dinitrotoluene	0.0101	0.001345	13.3	101.4	0.004225
2,4-Dinitrotoluene	0.0114	0.001134	9.9	114.3	0.003562
Propachlor	0.0101	0.000378	3.7	101.4	0.001187
Hexachlorobenzene	0.0113	0.001113	9.9	112.9	0.003495
Simazine	0.0086	0.001512	17.6	85.7	0.004749
Atrazine	0.0104	0.001134	10.9	104.3	0.003562
Lindane	0.0104	0.000535	5.1	104.3	0.001679
Metribuzin	0.0106	0.000787	7.4	105.7	0.002471
Alachlor	0.0113	0.000756	6.7	112.9	0.002374
Heptachlor	0.0106	0.000976	9.2	105.7	0.003065
Metolachlor	0.0104	0.000535	5.1	104.3	0.001679
Cyanazine	0.0099	0.001676	17.0	98.6	0.005265
Aldrin-R	0.0086	0.001134	13.2	85.7	0.003562
Heptachlor epoxide	0.0111	0.00069	6.2	111.4	0.002167
Butachlor	0.0106	0.000535	5.1	105.7	0.001679
gamma-Chlordane	0.0117	0.000756	6.5	117.1	0.002374
alpha-Chlordane	0.0099	0.00069	7.0	98.6	0.002167
trans nonachlor	0.0096	0.001134	11.8	95.7	0.003562
Dieldrin	0.0090	0.000577	6.4	90.0	0.001813
Endrin	0.0097	0.003039	31.3	97.1	0.009547
bis(2-Ethylhexyl) Adipate	0.0077	0.000488	6.3	77.1	0.001533
Methoxychlor*	0.0539	0.00069	1.3	107.7	0.002167
bis(2-Ethylhexyl) Phthalate*	0.0336	0.004237	12.6	67.1	0.013308
Benzo[a]pyrene	0.0124	0.001813	14.6	124.3	0.005694
Overall			**9.7**	**101.5**	**0.0035**

* Methoxychlor and bis(2-ethylhexyl) phthalate are at 0.05 ppm

Table 2-9 Method Detection limits (MDLs) on the 240-MS in the External Ionization Mode (7 replicates at 0.05 ppm)

Method Detection limits (MDLs) on the 240-MS in the External Ionization Mode (7 replicates at 0.05 ppm)					
EPA Method 525.2 Regulated List					
MDL Replicates at 0.05 ppm, REP1 – REP7					
Peak Name	**Avg**	**StdDEV**	**%RSD**	**%Recovery**	**MDL**
Hexachlorocyclopentadiene	0.0431	0.002545	5.9	86.3	0.007993
2,6-Dinitrotoluene	0.0444	0.001718	3.9	88.9	0.005397
2,4-Dinitrotoluene	0.0406	0.001272	3.1	81.1	0.003997
Propachlor	0.0423	0.002059	4.9	84.6	0.006466
Hexachlorobenzene	0.0501	0.00261	5.2	100.3	0.008196
Simazine	0.0433	0.00243	5.6	86.6	0.007633
Atrazine	0.0447	0.001976	4.4	89.4	0.006207
Lindane	0.0480	0.002309	4.8	96.0	0.007254
Metribuzin	0.0420	0.002236	5.3	84.0	0.007023
Alachlor	0.0461	0.003024	6.6	92.3	0.009497
Heptachlor	0.0439	0.002035	4.6	87.7	0.006393
Metolachlor	0.0444	0.000976	2.2	88.9	0.003065
Cyanazine	0.0416	0.001618	3.9	83.1	0.005083
Aldrin-R	0.0480	0.002236	4.7	96.0	0.007023
Heptachlor epoxide	0.0483	0.00138	2.9	96.6	0.004335
Butachlor	0.0416	0.00207	5.0	83.1	0.006502
gamma-Chlordane	0.0479	0.001574	3.3	95.7	0.004943
alpha-Chlordane	0.0480	0.001155	2.4	96.0	0.003627
trans nonachlor	0.0481	0.002193	4.6	96.3	0.006888
Dieldrin	0.0447	0.001254	2.8	89.4	0.003937
Endrin	0.0473	0.00236	5.0	94.6	0.007414
bis(2-Ethylhexyl) Adipate	0.0393	0.000756	1.9	78.6	0.002374
Methoxychlor	0.0614	0.001397	2.3	122.9	0.004389
bis(2-Ethylhexyl) Phthalate	0.0510	0.008083	15.8	102.0	0.025388
Benzo[a]pyrene	0.0430	0.001	2.3	86.0	0.003141
Overall			**4.5**	**91.5**	**0.0066**

2.8 Troubleshooting

The following table outlines common potential problems and proposed solutions. Multiple problems on the same analytical system are often difficult to resolve and may require a service representative. Always try the least invasive (or easiest) procedure first when troubleshooting. Ask “what has changed?” , maintain and review maintenance logs to help trace back when a problem may have started.

Observed Problem	Potential Cause(s)	Solutions
Bad overall peak shape	Leaks, bad liner, dirty electrodes, bad column	Change liner and check for leaks at transferline and column nuts. Change septum. Change column.
Sudden loss of sensitivity	Broken column, bad filament, “killer” sample, leaking septum, leaks	Check column and transferline nuts for leaks, change septum, repair or replace column, change filaments.
Fails Endrin SPCC breakdown	Dirty liner, dirty column, leaking injector body	Replace liner, cut front 0.5 m of column, check for leaks, clean injector body (with methanol), replace column
DFTPP tune fails	210-MS/220-MS or 240-MS parameters not set correctly; overloading ion trap; low multiplier voltage	Adjust ionization time factors, increase multiplier +100V, decrease amount injected if MS saturated, check moisture filters on He gas lines, adjust other MS parameters such as scan rate, # of microsans across peak, count threshold
High mass noise	Dirty ion trap	Clean ion trap
Gradual loss of sensitivity	MS multiplier “settling in”	Increase multiplier if peak areas drop low out of range from initial calibration.
Ghost peaks	Dirty autosampler rinse solvents/vial, septa particles in liner, column phase degradation, leaks, dirty septa on autosampler vial	Replace septa and liner, use clean autosampler rinse vial and autosampler vials, avoid multiple injections from same vial, use foil on autosampler rinse vials, check leaks, replace column
Carryover	Dirty sample, poor rinse cycle, dirty autosampler syringe, particles in liner	Replace/clean liner, replace autosampler syringe, increase number of rinse cycles and/or use other rinse solvents
Peak tailing, calibration curves with high RSDs	Active sites on liner, column, or reactive surface on trap electrodes	Replace liner or column; increase trap or source temperature; clean or replace trap electrodes
Poor reproducibility of peak	Dirty inlet, bad column, low	Replace liner/inlet or column;

Observed Problem	Potential Cause(s)	Solutions
areas for Internal/Surrogate standards	multiplier voltage, plugged autosampler syringe, poorly optimized injection method	replace autosampler syringe, turn up multiplier as it ages, optimize splitless injection.

2.8.1 Operating Tips

The following tips may help with routine operation:

1. Avoid using standards that have been opened and subject to evaporative loss.
2. Use fresh, dry solvents daily in the autosampler rinse positions, and routinely check for plugged syringe.
3. Use foil instead of septa on the autosampler solvent rinse vials.
4. Replace septum on autosampler vials daily to avoid sample evaporation. Return promptly to freezer.
5. Install fritted insert goose-neck down.
6. Avoid contact with plastic pipette tips for stock and calibration standards- phthalate and adipates are target analytes and easily contaminate standards and reagents. Use glass Hamilton syringes for preparing calibration standards.
7. Cool transferline, trap, and injector to below 80 °C before doing any maintenance on the GC/MS system. Air on hot columns or electrode surfaces will cause rapid degradation and loss of system performance.

3. EPA Method 8260B

EPA Method 8260B,"Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)" is a commonly used method for VOC analysis in a variety of waste matrices to include water and soil. The method allows sample introduction by a variety of devices: Purge and Trap (EPA method 5030B and 5035); Automatic static headspace (EPA method 5021); Azeotropic distillation (EPA method 5031); Vacuum Distillation (EPA method 5032); Desorption of trapped air contaminants (EPA method 5041, VOST); Air sampling from Tedlar bags (EPA method 0040); and Direct Injection method (EPA method 3585).

This chapter of the Varian Environmental MS Application Manual will assist chemists in rapidly setting up the 210-MS/220-MS system for the analysis of water samples by EPA Method 8260B. The accompanying CD for this manual contains a subdirectory, called EPA8260, which contains a PDF version of this section of the manual along with other important files that will be described in detail below.

Following this introduction is the Scope and Summary of EPA Method 8260B. The full method is available (in PDF format) on the attached CD in Appendix II for complete review. This and other methods can be obtained from the National Environmental Methods Index at http://www.nemi.gov/.

The Analytical Section provides guidance how to achieve the requirements of Method 8260B. A complete description of the apparatus, materials (analytical standards), and conditions is given. Also included are GC column recommendations and proven methods for GC, AutoSampler, MS acquisition, and MS data handling. Acquisition parameters were selected to fulfill the tune requirements. The data handling parameters were chosen to assure positive identification and accurate quantitation, and to satisfy QA/QC requirements.

Finally, the Results Section contains a selection of data generated with the 210-MS/220-MS GC/MS system using the conditions recommended in this manual. Examples included are results of Tune Verification, Initial Calibration, and Method Detection Limit calculations (statistical process).

The Varian EnviroPro™ Software can be used to generate a variety of useful quality control summary reports in standard Contract Laboratory Program (CLP) format. Appendix I contains a series of PDF files as example reports for a typical volatile or semi-volatile method (EPA Method 524.2 and EPA 8270 are shown). The reports are easily adaptable to other EPA methods that require extensive quality control reporting.

3.1 List of Abbreviations

BFB	Bromofluorobenzene
0CCC	Continuing Calibration Check
DOC	Demonstration of Capability
ICC	Initial Calibration Check
IS	Internal Standard
LCS	Lab Control Sample
LFB	Lab Forrtified Blank
LMB	Lab Method Blank
LTB	Lab Trip Blank
MDL	Method Detection Limit
MS	Matrix Spike
MS/MSD	Matrix Spike/Matrix Spike Duplicate
PAT	Purge and Trap
QCS	Quality Control Sample
RRF	Relative Response Factors
RS	Recovery Standard
SPCC	System Performance Check Compounds
SS	Surrogate Standard

3.2 Scope and Application

EPA Method 8260B: Volatile Organic Compounds by Gas Chromatography Mass Spectrometry (GC/MS).

Method 8260B is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

Table 3-1 Compounds in Method 8260B

		Appropriate Preparation Technique*					
Compound	**CAS No. ****	**5030/ 5035**	**5031**	**5032**	**5021**	**5041**	**Direct Inject**
Acetone	67-64-1	pp	c	c	nd	c	c
Acetonitrile	75-05-8	pp	c	nd	nd	nd	c
Acrolein (Propenal)	107-02-8	pp	c	c	nd	nd	c
Acrylonitrile	107-13-1	pp	c	c	nd	c	c
Allyl alcohol	107-18-6	ht	c	nd	nd	nd	c
Allyl chloride	107-05-1	c	nd	nd	nd	Nd00	c

		Appropriate Preparation Technique*					
Compound	**CAS No. ****	**5030/ 5035**	**5031**	**5032**	**5021**	**5041**	**Direct Inject**
Benzene	71-43-2	c	nd	c	c	c	c
Benzyl chloride	100-44-7	c	nd	nd	nd	nd	c
Bis (2-chloroethyl) sulfide	505-60-2	pp	nd	nd	nd	nd	c
Bromoacetone	598-31-2	pp	nd	nd	nd	nd	c
Bromochloromethane	74-97-5	c	nd	c	c	c	c
Bromodichloromethane	75-27-4	c	nd	c	c	C00	c
4-Bromofluorobenzene (surr)	460-00- 4	c	n d	c	c	c	c
Bromoform	75-25-2	c	nd	c	c	c	c
Bromomethane	74-83-9	c	nd	c	c	c	c
n-Butanol	71-36-3	ht	c	nd	nd	nd	c
2-Butanone (MEK)	78-93-3	pp	c	c	nd	nd	c
t-Butyl alcohol	75-65-0	pp	c	nd	nd	nd	c
Carbon disulfide	75-15-0	pp	nd	c	nd	c	c
Carbon tetrachloride	56-23-5	c	nd	c	c	c	c
Chloral hydrate	302-17-0	pp	nd	nd	nd	nd	c
Chlorobenzene	108-90-7	c	nd	c	c	c	c
Chlorobenzene-d5 (IS)		c	nd	c	c	c	c
Chlorodibromomethane	124-48-1	c	nd	c	nd	c	c
Chloroethane	75-00-3	c	nd	c	c	c	c
2-Chloroethanol	107-07-3	pp	nd	nd	nd	nd	c
2-Chloroethyl vinyl ether	110-75-8	c	nd	c	nd	nd	c
Chloroform	67-66-3	c	nd	c	c	c	c
Chloromethane	74-87-3	c	nd	c	c	c	c
Chloroprene	126-99-8	c	nd	nd	nd	nd	c
3-Chloropropionitrile	542-76-7	I	nd	nd	nd	nd	pc
Crotonaldehyde	4170-30-3	pp	c	nd	nd	nd	c
1,2-Dibromo-3-chloropropane	96-12-8	pp	nd	nd	c	nd	c
1,2-Dibromoethane	-93-4	c	nd	nd	c	nd	c
Dibromomethane	74-95-3	c	nd	c	c	c	c
1,2-Dichlorobenzene	95-50-1	c	nd	nd	c	nd	c
1,3-Dichlorobenzene	541-73-1	c	nd	nd	c	nd	c
1,4-Dichlorobenzene	106-46-7	c	nd	nd	c	nd	c
1,4-Dichlorobenzene-d4 (IS)		c	nd	nd	c	nd	c
cis-1,4-Dichloro-2-butene	1476-11-5	c	nd	c	nd	nd	c
trans-1,4-Dichloro-2-butene	110-57-6	pp	nd	c	nd	nd	c
Dichlorodifluoromethane	75-71-8	c	nd	c	c	nd	c
1,1-Dichloroethane	75-34-3	c	nd	c	c	c	c
1,2-Dichloroethane	07-06-2	c	nd	c	c	c	c

		Appropriate Preparation Technique*					
Compound	**CAS No. ****	**5030/ 5035**	**5031**	**5032**	**5021**	**5041**	**Direct Inject**
1,2-Dichloroethane-d4 (surr)		c	nd	c	c	c	c
1,1-Dichloroethene	75-35-4	c	nd	c	c	c	c
trans-1,2-Dichloroethene	156-60-5	c	nd	c	c	c	c
1,2-Dichloropropane	78-87-5	c	nd	c	c	c	c
1,3-Dichloro-2-propanol	96-23-1	pp	nd	nd	nd	nd	c
cis-1,3-Dichloropropene	10061-01-5	c	nd	c	nd	c	c
trans-1,3-Dichloropropene	10061-02-6	c	nd	c	nd	c	c
1,2,3,4-Diepoxybutane	1464-53-5	c	nd	nd	nd	nd	c
Diethyl ether	60-29-7	c	nd	nd	nd	nd	c
1,4-Difluorobenzene (IS)	540-36-3	nd	nd	nd	nd	c	nd
1,4-Dioxane	123-91-1	pp	c	c	nd	nd	c
Epichlorohydrin	106-89-8	I	nd	nd	nd	nd	c
Ethanol	64-17-5	I	c	c	nd	nd	c
Ethyl acetate	141-78-6	I	c	nd	nd	nd	c
Ethylbenzene	100-41-4	c	nd	c	c	c	c
Ethylene oxide	75-21-8	pp	c	nd	nd	nd	c
Ethyl methacrylate	97-63-2	c	nd	c	nd	nd	c
Fluorobenzene (IS)	462-06-6	c	nd	nd	nd	nd	nd
Hexachlorobutadiene	87-68-3	c	nd	nd	c	nd	c
Hexachloroethane	67-72-1	I	nd	nd	nd	nd	c
2-Hexanone	591-78-6	pp	nd	c	nd	nd	c
2-Hydroxypropionitrile	78-97-7	I	nd	nd	nd	nd	pc
Iodomethane	74-88-4	c	nd	c	nd	c	c
Isobutyl alcohol	78-83-1	pp	c	nd	nd	nd	c
Isopropylbenzene	98-82-8	c	nd	nd	c	nd	c
Malononitrile	109-77-3	pp	nd	nd	nd	nd	c
Methacrylonitrile	126-98-7	pp	I	nd	nd	nd	c
Methanol	67-56-1	I	c	nd	nd	nd	c
Methylene chloride	75-09-2	c	nd	c	c	c	c
Methyl methacrylate	80-62-6	c	nd	nd	nd	nd	c
4-Methyl-2-pentanone (MIBK)	108-10-1	p	c	c	nd	nd	c
Naphthalene	91-20-3	c	nd	nd	c	nd	c
Nitrobenzene	98-95-3	c	nd	nd	nd	nd	c
2-Nitropropane	79-46-9	c	nd	nd	nd	nd	c
N-Nitroso-di-n-butylamine	924-16-3	pp	c	nd	nd	nd	c
Paraldehyde	123-63-7	pp	c	nd	nd	nd	c
Pentachloroethane	76-01-7	I	nd	nd	nd	nd	c
2-Pentanone	107-87-9	pp	c	nd	nd	nd	c
2-Picoline	109-06-8	pp	c	nd	nd	nd	c

Compound	CAS No. **	Appropriate Preparation Technique* 5030/ 5035	5031	5032	5021	5041	Direct Inject
1-Propanol	71-23-8	pp	c	nd	nd	nd	c
2-Propanol	67-63-0	pp	c	nd	nd	nd	c
Propargyl alcohol	107-19-7	pp	I	nd	nd	nd	c
Beta-Propiolactone	57-57-8	pp	nd	nd	nd	nd	c
Propionitrile (ethyl cyanide)	107-12-0	ht	c	nd	nd	nd	pc
n-Propylamine	107-10-8	c	nd	nd	nd	nd	c
Pyridine	110-86-1	I	c	nd	nd	nd	c
Styrene	100-42-5	c	nd	c	c	c	c
1,1,1,2-Tetrachloroethane	630-20-6	c	nd	nd	c	c	c
1,1,2,2-Tetrachlroethane	79-34-5	c	nd	c	c	c	c
Tetrachloroethene	127-18-4	c	nd	c	c	c	c
Toluene	108-88-3	c	nd	c	c	c	c
Toluene-d8 (surr)	2037-26-5	c	nd	c	c	c	c
o-Toluidine	95-53-4	pp	c	nd	nd	nd	c
1,2,4-Trichlorobenzene	120-82-1	c	nd	nd	c	nd	c
1,1,1-Trichloroethane	71-55-6	c	nd	c	c	c	c
1,1,2-Trichloroethane	79-00-5	c	nd	c	c	c	c
Trichloroethene	79-01-6	c	nd	c	c	c	c
Trichlorofluoromethane	75-69-4	c	nd	c	c	c	c
1,2,3-Trichloropropane	96-18-4	c	nd	c	c	c	c
Vinyl acetate	108-05-4	c	nd	c	nd	nd	c
Vinyl chloride	75-01-4	c	nd	c	c	c	c
o-Xylene	95-47-6	c	nd	c	c	c	c
m-Xylene	108-38-3	c	nd	c	c	c	c
p-Xylene	106-42-3	c	nd	c	c	c	c

* See Sec. 1.2 for other appropriate sample preparation techniques

** Chemical Abstract Service Registry Number

c = Adequate response by this technique
ht = Method analyte only when purged at 80 C
nd = Not determined
I = Inappropriate technique for this analyte
Pc = Poor chromatographic behavior
pp = Poor purging efficiency resulting in high Estimated Quantitation Limits
surr = Surrogate
IS = Internal Standard

There are various techniques by which these compounds may be introduced into the GC/MS system. The more common techniques are listed in the table above. Purge and trap, by Methods 5030 (aqueous samples) and 5035 (solid and waste oil samples), is the most commonly used technique for volatile organic analytes. However, other techniques are also appropriate and necessary for some analytes. These include direct injection following dilution with hexadecane (Method 3585) for waste oil samples; automated static headspace by Method 5021 for solid samples; direct injection of an aqueous sample (concentration permitting) or injection of a sample concentrated by azeotropic distillation (Method 5031); and closed system vacuum distillation (Method 5032) for aqueous, solid, oil and tissue samples. For air samples, Method 5041 provides methodology for desorbing volatile organics from trapping media (Methods 0010, 0030, and 0031). In addition, direct analysis utilizing a sample loop is used for sub-sampling from Tedlar® bags (Method 0040). Method 5000 provides more general information on the selection of the appropriate introduction method.

Method 8260 can be used to quantitate most volatile organic compounds that have boiling points below 200 °C. Volatile, water soluble compounds can be included in this analytical technique by the use of azeotropic distillation or closed-system vacuum distillation. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Table 3-1 for analytes that have been evaluated on a Purge and Trap GC/MS system. Also, the method detection limits for 5 mL sample volumes are presented. The following compounds are also amenable to analysis by Method 8260:

Bromobenzene
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Chloroacetonitrile
1-Chlorobutane
1-Chlorohexane
2-Chlorotoluene
4-Chlorotoluene
Dibromofluoromethane
cis-1,2-Dichloroethene
1,3-Dichloropropane
2,2-Dichloropropane
1,1-Dichloropropene
p-Isopropyltoluene
Methyl acrylate
Methyl-t-butyl ether
Pentafluorobenzene
n-Propylbenzene
1,2,3-Trichlorobenzene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene

The estimated quantitation limit (EQL) of Method 8260 for an individual compound is somewhat instrument dependent and also dependent on the choice of sample preparation/introduction method. Using standard quadrupole instrumentation and the purge and trap technique, limits should be approximately 5 µg/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 µg/L for ground water. Somewhat lower limits may be achieved using an ion trap mass spectrometer or other instrumentation of improved design. No matter which instrument is used, EQLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

3.3 Summary of Method

The volatile compounds are introduced into the gas chromatograph by the purge and trap method or by other methods. The analytes are introduced directly to a wide-bore capillary column or cryofocussed on a capillary pre-column before being flash evaporated to a narrow-bore capillary for analysis. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).

Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. (Wide-bore capillary columns normally require a jet separator, whereas narrow-bore capillary columns may be directly interfaced to the ion source). Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

Table 3-2 Quality Control Matrix Table

QC Type	Concentration Level	Frequency	Acceptance Criteria
Tune	Introduce 5-50 ng of BFB into the PAT GC/MS System	Every 12 hours	Mass 50 15-40% of base peak Mass 75 30-80% of m/z 95 Mass 95 Base Peak Mass 96 < 5-9% of m/z 95 Mass 173 <2% of m/z 174 Mass 174 >50% of m/z 95 Mass 175 5-9% of m/z 174 Mass 176 >95% but <101% of m/z 174 Mass 177 5-9% of m/z 176
SPCC	Mid-level in calibration curve range	Every 12 hours	Minimum mean RF for calibration: Chloromethane 0.1 1,1-Dichloroehtane 0.1 Bromoform 0.1 Chlorobenzene 0.3 1122-Tetrachloroethane 0.3 For routine runs: Minimum RFs above must be met
ICC	Consisting of at least 5 standard concentrations per analyte.	When first using this method on an instrument, after major instrument maintenance, or when indicated by a change in instrument response.	RSD for each analyte should be less than 15% if average RF used to calculate data; Otherwise, use linear or quadratic fit using the data system.
LTB	Reagent Water prepared, shipped and analyzed as a sample.	Collected with every sample batch.	No analytes of interest present at or above the minimum reporting limit (MRL) OR project-specific limit.
LMB	Reagent Water prepared and analyzed as a sample.	One per analytical run or group of 20 samples.	No analytes of interest present at or above the MDL, or less than level defined in the labs quality assurance plan, or less than 5% of the regulatory limit for that analyte.
CCC	Mid-level in calibration curve range	One analyzed per group of 20 samples or one per work shift (Every 12 hours)	RSD must be less than 30% for the CCC compounds in initial calibration: 1,1-Dichloroethene

QC Type	Concentration Level	Frequency	Acceptance Criteria
			Chloroform 1,2-Dichloropropane Toluene Ethylbenzene Vinyl chloride +/-20% Recovery for routine runs
IS	Fluorobenzene, Chlorobenzene-d5, 1,2-Dichlorobenzene-d4 are all recommended. Others can be used.	Run in every sample. The IS is evaluated for recovery.	Area response of IS in CCCs must be within –50% to +100% from that in the mid-point std level of the most recent calibration.
SS	1,2-Dichlorethane-d4, Toluene-d8, and Bromofluorobenzene are recommended. Others can be used.	Run in every sample.	Recovery should be 70-130%, however a laboratory must generate specific statistical limits according to section 8.6 of Method 8000B.
LCS	A clean matrix similar to the sample, spiked mid-range of calibration curve.	One analyzed per group of 20 samples or one per work shift	Limits are 70-130% recovery or based on statistical limits derived by the laboratory.
QCS	All of the analytes of interest at mid-level calibration range	Quarterly.	Same as CCC. Used as an external check of the calibration solutions.
MS/MSD	Mid-range in calibration	One MS/MSD per set of 20 samples.	70-130 % recovery limits, or lab determined statistical limits according to Method 8000B.
Duplicate sample	Lab Duplicate	At a frequency of one per 20 samples	RPD within 20% for the results. Lab may run an MS and a lab duplicate instead of an MS/MSD, one set per 20 samples.
DOC	4 reagent water spikes at mid-level concentration	Initially, annually and with each new technician.	Mean percent recovery for each analyte must be 70-130%, and the RSD must be less than <20%. See performance data per analyte in 8260B method.
MDL	7 reagent water spikes. Typical are 0.5 to 10 ppb	Annually.	Calculate values for mean accuracy and RSD. No precision and accuracy limits apply.

3.4 Analytical Section

In this section parameters for the equipment, accessories, and supplies are specified to assure optimum performance of the analysis. While both other and newer products may improve overall results, these accessories were carefully selected for best performance. Deviation from the suggested equipment, supply or condition may result in lost performance.

3.4.1 Equipment and Supplies

Sample Containers

40 mL screw top vials with Teflon faced silicon septum. Best if vials are pre-cleaned for EPA trace-level analysis

Varian Part Number [VPN]: DY63006800 (72 vials/septa)

Purge and Trap (PAT) Concentrator

Tekmar Stratum™ Purge and Trap concentrator

- The unit must be equipped with either a 25 mL or 5 mL fritted sparge vessel. (5 mL vessel recommended for 8260B).

14-2334-24	Sparger, 25 mL fritted, 1/2" (glassware only)
CP914441	Sparger, 5 mL fritted, 1/2" (glassware only)

  NOTE: *If a 25 mL vessel is used, a volume of no less than 15 mL must be sampled, because the method requires less than 15 mL of volume above the purged sample.*

- Tekmar Stratum Strat-Traps as described below

14-5864-403	Strat-Trap, Vocarb 3000
T149908403	Strat-Trap, #9 (Proprietary packing material)

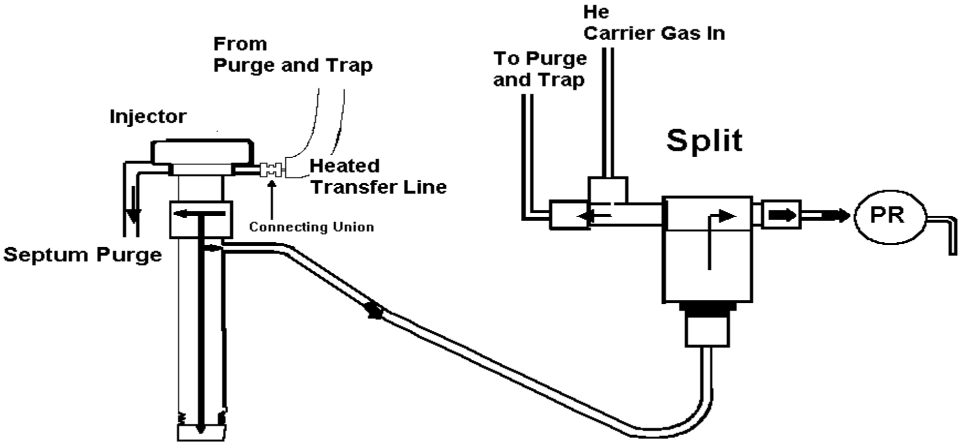
  Unit will be shipped from Tekmar with the #9 trap (factory tested), and the Vocarb 3000 trap will be included as a separate item. Both traps have been found to work for Method 8260B.

  NOTE: *The trap was selected to reduce the amount of retained water during the purging process. The 35-40 mL/min He purge flow will carry some water vapor to the trap along with the VOCs. On the new Strat-Traps much of this water vapor will pass through and only a small amount of it will be retained. If more hygroscopic material (such as silica gel) is contained in the trap, the retained water amount will be greater and will interfere with some of the analytes.*

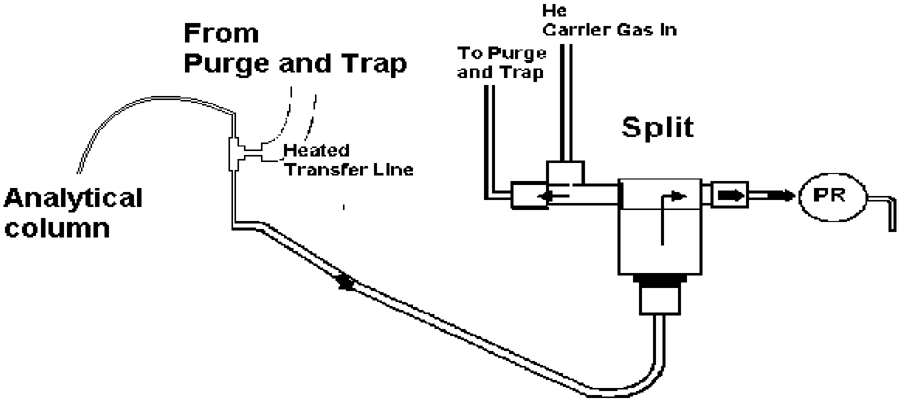
GC Pneumatics/ Inlets

The GC must be equipped with a type 25 Electronic Flow Controller (EFC) attached to a 1177 injector [VPN 45-11005-01], a 1079 injector [VPN 45-12005-11] or using direct coupling of the transfer line to the GC column via the EFC's splitter. In all cases a split injection of the desorbed analytes into the analytical column will take place at an optimized split ratio. Larger split ratios are desirable, so as to minimize the amount of water transferred to the analytical column. Split ratios as high as 1:200 have been used on narrow-bore columns. If the 1177 or 1079 injectors are used, the single goose-neck, split insert should be placed in the injector. (VPN: 03-926119-27 for 1177 and VPN: 03-918464-00 for 1079). Syringe injections via the injector will be possible with this configuration. If direct connection is established between the PAT transfer line and the analytical column via a "T" to the EFC, syringe injection will not be possible, but the chromatographic performance may be improved.

For best results set the septum purge flow very low (0.1 mL/min) so analytes are not lost during the desorb step. Also, note the column head pressure at the starting temperature conditions, because each column (listed below) will be different. *IMPORTANT: Take note of this pressure and calibrate the EFC by entering the observed pressure and a septum purge flow of 0.1 mL/min.*



Split connection of the Purge and Trap system to a capillary column via an injector.



Split Connection without injector using Type 25 EFC only.

Analytical Columns

The following analytical columns are suggested for use with the Stratum:

Varian Part Number [VPN]: CP9100 FactorFour VF-624-MS, 20 m x 0.15 mm ID, DF= 0.84

Varian Part Number [VPN]: CP9105 FactorFour VF-624-MS, 60 m x 0.32 mm ID, DF= 1.8

Varian Part Number [VPN]: CP9102 FactorFour VF-624-MS, 30 m x 0.25 mm ID, DF= 1.4

These are FactorFour low-bleed columns designed specifically for volatile organic chemical analysis. The 20 m column will have the advantages of high resolution, fast run times, low bleed, and use of higher split ratios.

NOTE: *It is important to use one the suggested columns, since these will provide the best resolution of the analytes from methanol and water. Methanol is always present in the calibration standards and a* *significant portion will be purged out, transferred to the trap and desorbed with the other analytes. Similarly water is also always trapped on hydrophobic sorbent traps, and some of it will be introduced to the analytical column.*

Volatiles Consumables Kit

The kit contains routine supplies for daily operation and maintenance. Kit includes:

Volatile Organic Chemicals Parts and Supplies for EPA Methods 524.2 & 8260B **03-930824-01**		
Syringe	03-925902-05	10 µL conical tipped needle
Injector Parts		
1177 Split/Splitless Injector	03-926119-27	Insert 4 mm ID open single gooseneck liner, non-Siltek
	CR298713	BTO septa pkg of 50
	8850103100	The o-ring that seals the 1177 injector insert pkg of 25
1079 PTV Injector	03-926119-45	Insert for 1079 pkg of 5 – 3.4 mm ID open single gooseneck
	CR298777	BTO septa for the 1079 injector pkg of 50
	03-925342-01	Graphite ferrule that seals the 1079 injector insert pkg of 10
Ferrules		
	2869458001	For 30 m or 20 m columns pkg of 10 40/60 graphite/Vespel
	CR213105	For 60 m columns pkg of 10 40/60 graphite/Vespel
P&T		
Stratum PAT Trap	T145864403	Strat-Trap, Vocarb 3000
Stratum PAT Trap	14-3928-403	Strat-Trap, #9 (Proprietary packing material)
VOA Vials	DY63006800	Std 40 mL VOA vials with Teflon-faced septa, EPA cleaned

GC/MS Interface

With the configuration suggested above (EFC type 25 pneumatics in split mode) the column will be connected to the detector in the normal fashion, about 1-2 mm of the column protruding from the end of the 210-MS/220-MS transfer line.

NOTE: *Always reduce the column and the MS transfer line temperature if the column flow is interrupted for maintenance.*

3.4.2 Data Analysis and Calculations

Fully calibrated methods with data handling parameters (integration, identification, and quantification) for commonly monitored VOCs in 8260B are on the Varian Environmental MS Applications Manual CD, included with this manual. For Method 8260B there are two method files (.mth files) and two raw data files (.SMS files) representing two different calibration mixtures. One mix contains the common VOCs with the early eluting gases (60 compounds, mixes **ULDWM589N** plus **ULDWM544**)**,** the other contains 24 components, primarily oxygenates (**ULDWM592**)**.** All of these are in a subdirectory on the CD called EPA8260. The table below describes which files are associated with which calibration mixtures:

Calibration Mixture	Method File (.mth)	Data File (.SMS)
60 Common VOCs	8260_60mix_200.mth	8260_60mixData.SMS
24 Oxygenates	8260_24mix_200.mth	8260_24mixData.SMS

Choose the appropriate method and example data file and make a copy of them. The operator will likely need to make changes in retention times or some other parameters for further optimization.

Tuning the Mass Spectrometer

To assure that the BFB tune criteria specified in the method is met, use the suggested acquisition parameters. (Section 3.6.3)

The amount of BFB is typically 5 to 50 ng as suggested in the method. It is recommended to use no more than 20 ng. BFB is usually introduced through the purge and trap process.

BFB must pass the specifications given in QC Matrix Table above before analysis can begin. The analytical parameters in Section 3.6.3 give a good starting point for passing the tune. Fine adjustments to key parameters may be necessary for passing the tune requirement. Once set, the tune should be stable for an extended period and will only need to be monitored at the required frequency (12 hr intervals). See Section 3.7 under troubleshooting for parameters to adjust in the case of a failing tune.

> ***NOTE:*** *The method suggests that an average spectrum be taken across a GC peak in order to check the tune, i.e. average the apex scan and the scan before and after the apex. The method also allows the instrument manufacturer to determine how an acceptable tune is to be obtained from the data. For Varian ion traps, it is recommended to use the Varian EnviroPro software "find tune" function to find an acceptable spectrum in the BFB peak.*

Analytes Monitored and Calibration Levels

While Method 8260B lists a large number of analytes, which may be monitored by the procedures specified in the Method, the actual number of analytes measured will depend on the laboratory requirements. Very often only a subset of these analytes are monitored.

Method 8260B does not specify the exact calibration levels or ranges to be performed other than at least five calibration levels covering the calibration range. The attached method includes eight calibration levels covering a calibration range from 0.5-100 ppb. Edit the levels and range as desired.

Integration Parameters

The integration parameters in the 8260B.mth method were selected to assure reliable integration even at the lowest calibration level. These parameters may need to be adjusted and the analyst should review them for each analyte using the lowest level calibration data file. The most commonly adjusted parameters are:

- Identification Window
- Peak Width
- Area Reject Value
- Slope Sensitivity or Tangent Value (occasionally)
- Smoothing

Review the MS Workstation Software Reference Manual "Guidelines for Optimizing Method Integration Parameters" section to clarify integration topics and processes. Manual integration may be required for some compounds at low concentrations. Reasons for manual integration must be documented in finished data packages prepared by laboratories doing compliance work.

The MS Workstation software loads a desktop shortcut to the Software Reference Manual. “Guidelines for Optimizing Integration Parameters” can be found in the “MS Data Review / Quantitation” section of the Reference Manual.

Quantitation Parameters

Once the initial calibration is completed, the analyst must review the curve fitting parameters for each component to assure proper quantitation of samples to be processed.

Curve Fitting, Handling the origin, regression weight factors

- Average RRF:

  Average RRF calculation is performed by the 210-MS data system when “linear with forced zero and 1/x2, or 1/nx2 regression weighting" is selected for curve fitting.
- Linear
- Quadratic

Method 8260B allows linear or quadratic curve fitting as stated in 8000B. This would be the case for analytes having RSD values for the calibration curve greater than 15%. If a curve is used, please note that the following one option is allowed in 8260B concerning treatment of the origin:

Handling of the Origin

- **Ignore- Must use for all data using linear or quadratic curve fitting**
- Include- Not Allowed in 8260B
- Force- Not Allowed in 8260B

Review the Cal Curve for each analyte and specify the handling of the origin as “Ignore”.

Selection of the Regression Weighting Factor

- None
- 1/n
- 1/x
- 1/nx
- 1/x2
- 1/nx2

The most often used factors are 1/x2, and 1/nx2 for trace level analysis.

Improper selection of these parameters will undermine the accuracy of the reported results of the unknown samples or quality control samples. All samples and quality control in a given run must be calculated using identical curve fitting and weighting.

3.5 Reagents and Standards

3.5.1 Stock Standards

Calibration STDs are available in convenient packaging and concentrations. A few suggestions may make the preparation of calibration solutions easier:

- For maximum flexibility and performance use the 2000 µg/mL (or higher) standard concentrations. This level will allow easy dilutions into mixed substocks.
- Select standards which will have the "gases" (freons, vinyl chloride, bromo- and chloromethane, chloroethane) in a separate ampule. Mixes are also available that have the 6 gases plus other compounds. **IMPORTANT: Once opened, the stability of the gas mixture cannot be guaranteed, and a new vial most likely will be needed at the next calibration.** Gases such as chloromethane and chloroethane decrease in concentration rapidly, even when stored tightly capped in a freezer. The reliable "lifetime" of the other standards, if properly stored, is longer and they may be used again.
- Limit the number of standard vials; purchase standards that have the highest number of analytes in every mixture.

Recommended Standards from Varian

Internal/Surrogate Standard

[VPN]: ULSTM320N 2000 µg/mL in Methanol, 4 x 1 mL

Fluorobenzene (IS)

4-Bromofluorobenzene (SUR)

1,2-Dichlorobenzene-d4 (SUR)

GCMS Tune Standard (BFB)

[VPN]: ULSTS110N 2000 µg/mL in Methanol, 4 x 1 mL

4-Bromofluorobenzene

Analytes

[VPN]: ULDWM589N 2000 µg/mL, in Methanol, 4 x 1 mL

54 Analytes

Benzene
Bromobenzene
Bromochloromethane
Bromodichloromethane
Bromoform
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Carbon tetrachloride
Chlorobenzene
Chloroform
2-Chlorotoluene
4-Chlorotoluene
Dibromochloromethane
1,2-Dibromo-3-chloropropane
1,2-Dibromoethane
Dibromomethane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
cis-1,2-Dichloroethene
trans-1,2-Dichloroethene
1,2-Dichloropropane
1,3-Dichloropropane
2,2-Dichloropropane
1,1-Dichloropropene
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
Ethylbenzene
Hexachlorobutadiene
Isopropylbenzene
4-Isopropyltoluene
Methylene chloride
Naphthalene
n-Propylbenzene
Styrene
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
1,2,3-Trichlorobenzene
1,2,4-Trichlorobenzene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
1,2,3-Trichloropropane
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
o-Xylene
m-Xylene
p-Xylene

Analytes

[VPN]: ULDWM592, 2000 µg/mL, in Methanol, 4 x 1 mL
24 Analytes

Acetone
Acrylonitrile
Allyl chloride
2-Butanone (MEK)
Methylmethacrylate
1,1-Dichloro-2-propanone
Diethyl ether
Ethyl methacrylate
Hexachloroethane
2-Hexanone
Methacrylonitrile
Methyl iodide
Methylacrylate
Carbon disulfide
Chloroacetonitrile
1-Chlorobutane
trans-1,4-Dichloro-2-butene
Methyl-t-butyl ether (MTBE)
4-Methyl-2-pentanone
Nitrobenzene
2-Nitropropane
Pentachloroethane
Propionitrile
Tetrahydrofuran

Analytes

[VPN]: ULDWM544 "Gases", 2000 µg/mL in Methanol, 4 x 1 mL

Bromomethane
Chloroethane
Chloromethane
Dichlorodifluoromethane
Trichlorofluoromethane
Vinyl chloride

3.5.2 Fortification Solutions for Internal and Surrogate Standards (IS/SS)

Manual and Automated (Archon) injection of IS/SS

Add 25 µL of the internal standard / surrogate standard, (VPN: ULSTM320N) and 775 µL of methanol to a small sample vial (such as a 1.5 mL AutoSampler vial). Spike all samples (25 mL) with 2 µL of this mix. The concentration of the internal and surrogate standards will be 5 ppb. Load the sample into a 25-50 mL gas tight syringe, and directly inject into the 3-port valve at the top of the purge vessel. Do not allow air to enter the syringe. This method of sample introduction is not usually performed in production laboratories, as it is labor intensive and prone to operator technique errors.

Sample introduction via the Archon Auto Sampler: 5, 10, or 20 mL sample aliquot

The Archon AS automatically fortifies the samples with 1 µl of Internal STD/surrogate STD while it is being transported from the 40 mL VOA vial into the purge vessel via a Valco SS valve. This provides a convenient way to add a small amount of standard very accurately to the sample, resulting in superior precision and accuracy.

Preparation of the IS/SUR standard mixture for the Archon sampler:

The IS/SUR solution is prepared in p**urge and trap grade methanol** and placed in the Archon IS sample vial. The concentration added depends upon the desired purge volume and final concentration. For a nominal 5 ppb final aqueous concentration for purge volumes of 5, 10, and 20 mL, see Table 3-3 below.

*Table 3-3 Concentration of IS/SUR solution added to Archon for a given purge volume**

Concentration of IS/SUR in Methanol (µg/mL)	Purge Volume (mL)	Final Aqueous Concentration (ppb)	Volume of 2000 µg/mL IS/SUR to 5.0 mL methanol
25	5	5	62.5 µL
50	10	5	125 µL
100	20	5	250 µL

*Assumes 1.0 µL of the IS/SUR solution is added by the Archon

3.5.3 Preparation of Aqueous Calibration Standards

The method requires a minimum of five calibration levels over the calibration range. Since different laboratories will perform different calibration ranges, standard preparation for 0.2 ppb to 100 ppb concentration is given below.

Calibration standards will be prepared differently if the Archon AutoSampler is used with 40 mL sample vials or if no AutoSampler is used and 5-20 mL of aqueous calibration standards are deposited manually into the purge vessel. Calibration standard preparation using the Archon autosampler will be discussed here.

It is extremely important to limit the amount of methanol added to the aqueous calibration standards. Too much methanol will cause excessive background and unwanted ion-molecule reactions in the ion trap, resulting in poor accuracy and precision. Two sample preparation approaches are given below. Preparation #1 uses a series of 100 mL volumetric flasks, to which no more than 10 µL is added to prepare any aqueous calibration level. Preparation #2 uses an aqueous stock solution, which is volumetrically diluted down into a series of 100 mL volumetric flasks, resulting in solutions that contain no more that 10 µL MeOH per 100 mL. Methanol is also “back-added” to standards such that all standards will have exactly the same amount (i.e. 10 µL methanol/100 mL sample).

Note that in either preparation approach, it is best to prepare these calibration standards fresh daily, especially since the gases are measured by most analytical laboratories. Also, stock solutions containing the gases are only good for about one week after they are opened.

Aqueous Sample Preparation Procedure #1

Purchased Stock Standards- These mixes are at 2000 µg/mL.

VOC Mix/Stock Std	Varian Part No. [VPN]
VOC Mix 1 (60 analytes)*	ULDWM589
VOC Mix 2 (24 analytes)	ULDWM592

*Once this standard is opened, the volatile gases are not very stable. The chemist should have additional ampules of this mix available.

Step 1 is to create a 1:1 mix of the stock solutions above, then perform serial dilutions of this mixture to create two more substock standards in purge and trap grade methanol. Step 2 is to add these substocks directly to 9x100 mL volumetric flasks using a 10 µL Hamilton Syringe, then back-adding methanol as described in Table 3-4.

Step 1: Place three 1.5 mL amber autosampler vials in a tray holder. Using a 1.0 mL gas tight syringe add exactly 900 µL methanol to two of the vials, and leave one vial empty. To the empty vial, add 500 µL VOC Mix 1 and 500 µL VOC mix 2. Mix by inverting gently 5 times. Label this vial 1000 µg/ml mixed substock solution. Next, add 100 µL of the 1000 µg/ml mixed substock to one of the vials containing 900 µL methanol. Mix gently by inverting 5 times. Label this 100 µg/ml mixed substock solution. Finally, take 100 µL of the 100 µg/ml mixed substock and add it to the last vial containing 900 µL methanol. Mix, and label as the 10 µg/ml mixed substock. Make sure all are capped tightly. Gases in all substocks are good for only one week when stored in a freezer.

NOTE: *Take care to wash the syringes three times with pure methanol each time after a syringe was used to transfer a stock or substock standard to prevent carryover. Use a 100 µL or a 250 µL syringe for the 100 µL serial dilutions.*

Step 2: Use the following table to prepare the calibration standards in 9 x 100 mL clean and DI-rinsed volumetric flasks. Before spiking, fill each volumetric flask to the mark with Milli-Q reagent grade water. Add the substock solutions by inserting the syringe needle beneath the surface of the water, quickly inject the required amount, and withdraw the needle. Always rinse the syringe with pure methanol after contact with any substock solution; Also, “prime” the syringe with the substock to be added prior to injection into the volumetric flasks.

NOTE: As with any sample preparation procedure, proper technique is critical to achieve excellent precision and accuracy. It is a good idea to dedicate a set of syringes in the lab for VOC work to avoid contamination with common lab solvents such as dichloromethane. Use common sense and store VOC samples and solvents away from each other. ***Keep special PAT methanol away from all other lab solvents****.*

Table 3-4 Amount of each substock added to 100 mL with a 10 µL Hamilton Syringe

Final Aqueous	**10 µg/mL**	**100 µg/mL**	**1000 µg/mL**	**µL Back-added**
Concentration (µg/L)	**Mixed Substock(µL)**	**Mixed Substock(µL)**	**Mixed Substock(µL)**	**Pure PAT Methanol**
0.2	2.0			8.0
0.5	5.0			5.0
1.0	10.0			0.0
2.0		2.0		8.0
5.0		5.0		5.0
10.0		10.0		0.0
20.0			2.0	8.0
50.0			5.0	5.0
100.0			10.0	0.0

After spiking each volumetric flask, cap immediately and invert gently 3-5 times to mix. When the set is complete, poor off gently into 40 mL VOA vials, ensuring that there is no headspace. Each flask is enough for two vials if desired.

NOTE: *It is recommended to load these standards on the Archon and run them on the same day they are prepared to avoid eventual loss of the gases through the septum. Be sure the Archon reservoir is full of fresh DI water, drain lines are clear, and the He switch inside the Archon (for reservoir pressure) is in the "ON" position. Ensure there is enough IS/SURR solution in the Archon IS vial.*

Aqueous Sample Preparation Procedure #2

This approach is based on preparing a relatively concentrated mixed aqueous stock solution and diluting down into 100 mL flasks using conventional volumetric glassware pipettes and gas-tight syringes (for the lower concentrations).

Prepare a 200 ppb aqueous mixed substock by adding 100 µL each of VOC Mix 1 and VOC Mix 2 to a 1 L volumetric flask filled to the mark with Milli-Q water. Gently mix the solution 3-5 times. Prepare dilutions into 100 mL volumetric flasks using the table below. For the lower concentrations, be sure to add some Milli-Q water to the 100 mL flask so as to minimize the headspace above the sample prior to dilution to the mark.

Table 3-5 Dilutions for Sample Preparation #2

Final Conc. (µg/L)	**Volume (mL) of 200 ppb substock to 100 mL**	**Dilution technique**
0.2	0.1	100-250 µL gas-tight
0.5	0.25	1.0 mL gas-tight
1.0	0.5	1.0 mL gas-tight
2.0	1.0	1.0 mL gas-tight
5.0	2.5	5.0 mL gas-tight
10.0	5.0	5.0 mL gas-tight
20.0	10.0	10.0 mL gas-tight
50.0	25.0	25 mL Vol pipette
100	50.0	50 mL Vol pipette

As mentioned above, be sure to analyze these the same day they are prepared.

Aqueous Sample Preparation for Manual Injections

For manual loading of the purge vessel, use either sample preparation approach to prepare the aqueous calibration standards in 100 mL volumetric flasks. Next, add the IS/SURR solution to each calibration standard. If 20 mL of sample is to be loaded with an IS/SURR concentration of 5 ppb, simply prepare an IS/SURR substock in methanol at 500 µg/mL and add 1 µL to each 100 mL flask, mix, and load into the purge vessel.

Automated Aqueous Dilutions using the Archon

The Archon can be used to dilute aqueous standards with reagent water that comes from the reservoir bottle on the Archon. The available dilution factors are: 2x, 5x, 10x, 20x, 50x, and 100x.

The dilution factor in the Archon shows the ratio of the total volume of water sample and blank water blended together to the final volume of 24.3 mL. For example, if the dilution factor is 50, 1 volume of sample is being diluted with 49 volumes of blank water from the reservoir. Important points to consider if using this feature:

1. Use a 25 mL sparge vessel. The dilution algorithm uses a final volume of about 24 mL, and it is best to dispense the entire volume into the sparge vessel. If smaller volumes are chosen, poor mixing may result inside the Archon syringe, especially at high dilution ratios.
2. It is best to use multiple vials of aqueous substocks to dilute from, (i.e. 10 ppb and 100 ppb) to cover the calibration range.
3. Not recommend to perform dilutions out of the same prepared aqueous substock standard, as the volatile gases may be lost.
4. Example dilution chart for 10 ppb and 100 ppb aqueous standards:

Final Concentration, ppb	**Dilution Factor (DF) for 10 ppb aqueous substock**	**Dilution Factor (DF) for 100 ppb aqueous substock**
0.5	20X	--
1.0	10X	--
2.0	5X	--
5.0	2X	--
10.0	--	10X
20.0	--	5X
50.0	--	2X
100.0	--	No Dilution

NOTE: *It is always best to use a minimum amount of methanol in the starting aqueous standards. A 1 L sample of the 10 and 100 ppb solutions mentioned above could be prepared from a 1000 ppm mixed stock by adding 10 µL and 1 µL, respectively.*

Soil sample analysis using the Archon

The Archon is capable of needle sparging directly in a standard 40 mL VOA vial. Soil sampling is not covered in the scope of this manual. Please consult the Archon Purge and Trap AutoSampler System Operation Manual for details on how to set up soil analysis.

3.6 Set-up of Instrumental Conditions

Fully calibrated methods with data handling parameters (integration, identification, and quantification) for key 8260B analytes are on the Varian Environmental MS Applications Manual CD, included with a hard copy of this manual. Refer to the EPA8260 subdirectory and copy the method on your analytical system to start. See Section 3.4.2.

3.6.1 Purge and Trap and Archon Autosampler Conditions

EPA Method 8260B specifies purge and trap conditions, many of which are simply “recommended”. **The method offers the user the flexibility to change the desorb time, flow rate, and dry purge times**. A dry purge is typically used to dry the trap before desorb to reduce the amount of water and MeOH entering the column. A short desorb time has the same effect. These parameters need to be carefully optimized; the conditions in this manual are a good starting point.

For 8260B, a 5 mL sample volume (5 mL sparger) was used to generate the data presented in this manual.

The following purge and trap conditions apply to any column mentioned in Section 3.4.1. Split ratios will need to be optimized for each column type, balancing overall sensitivity with water/methanol interference.

5 mL sparge vessel (5 mL purge volume)

Tekmar Strat-Trap #9

35-40 mL/min He purge flow

GC Insert: 1177 4mm ID single goose-neck, installed goose-neck down

See Table 3-6 for general purge and trap settings for Method 8260B

Table 3-6 Recommended Tek-Link Purge and Trap Settings

Purge and Trap Conditions- Tek-Link			
Variable	***Value***	***Variable***	***Value***
Valve Oven Temp.	150 °C	Sample Preheat Time	1.00 min.
Transfer Line Temp.	150 °C	Preheat Temp.	40 °C
Sample Mount Temp.	40 ° C	Purge Time	11.00 min.
Purge Ready Temp.	35 °C	Purge Temp.	0 °C
Condenser Ready Temp.	40 °C	Purge Flow	40 mL/min
Condenser Purge Temp.	20 °C	Dry Purge Time	0.00 min.
Standby Flow	5 mL/min.	Dry Purge Temp.	20 °C
Pre-purge Time	0.00 min.	Dry Purge flow	100 mL/min.
Pre-purge Flow	40 mL/min.	Desorb Preheat Temp.	245 °C
Sample Heater	OFF	Desorb Drain	ON
GC Start	Start of Desorb	Desorb Time	2.00 min.
Bake Time	7.00 min.	Desorb Temp	250 °C
Bake Temp.	270 °C	Desorb Flow	100 mL/min.
Bake Flow	300 mL/min.	Condenser Bake Temp.	200 °C

The operator has the ability to change the GC/MS method in the workstation to optimize the split ratio. Also, the Archon autosampler parameters can be changed during an automated run by calling methods at the end of a given method operation. Typical Archon parameters of importance to reduce carryover are listed in Table 3-7.

Table 3-7 Recommended Archon Autosampler Parameters

Archon Parameter	**Setting**
Sample volume	5, 10, or 20 mL
# of Syringe Washes/Flushes	2-3
Wash volume	Set to 2 mL over sampling volume
Desorb time	Set to 2.0 min
Cycle time	Set to total run time of GC+PAT cycle

NOTE: *Carryover should be less than 0.5% (Tekmar Spec) when a blank is run after a 50 ppb CAL standard. Increasing the bake time and flow, along with increased Archon vessel/syringe rinses will reduce carryover. It is also good practice to place a blank (or run blank injection from Archon reservoir) after the 50 ppb std in a CAL run and two blanks after a 100 ppb standard to minimize chance of carryover into samples at very trace levels. If the system becomes contaminated due to a foam-over event, carryover will be a significant problem as active sites will be inside the concentrator. See Section 3.8 Troubleshooting for more details.*

3.6.2 GC/MS Conditions for the 60 m x 0.32 mm x 1.8 µm Column

Table 3-8 GC Conditions for 60 m Column

Column Oven Temperature Program				
Temp(°C)	***Rate (°C/min)***	***Hold (min)***	***Total (min)***	
35	NA	6.00	6.00	
220	10	6.50	31.00	
Injector Conditions (1177)		Injector Split States		
Temp	160 °C	Time (min)	Split State	Split Ratio
Col Flow	1.0 mL/min	Initial	ON	20
Pressure Pulse	None	3.00	ON	50
Constant Flow Septum Purge Flow	ON 0.1 mL/min	4.10	ON	20

Table 3-9 MS Conditions for the 60 m Column

MS Conditions				
Segment	***Start (min)***	***End (min)***	***Low Mass (m/z)***	***High Mass (m/z)***
Fil/Delay	0.00	4.00	NA	NA
Gases	4.00	7.90	47	150
Other VOCs	7.90	31.00	35	260

MS Conditions				
Segment	***Start (min)***	***End (min)***	***Low Mass (m/z)***	***High Mass (m/z)***
Target TIC	12-15000	µscans averaged	3	
Max Ion Time	25000 µsec	Mult Offset	25-50 V	
Background Mass	34 m/z	Emission Current	10-20 µamps	
Rf Dump	300 m/z	Scan Time	0.55-0.65 sec/scan	

3.6.3 GC/MS Conditions for the 20 m x 0.15 mm x 0.84 µm Column

Table 3-10 GC Conditions for 20 m Column

Column Oven Temperature Program				
Temp (°C)	***Rate (°C/min)***	***Hold (min)***	***Total (min)***	
35	NA	2.00	2.00	
200	10	0.00	18.50	
240	50	0.00	19.30	
Injector Conditions (1177)		Injector Split States		
Temp	160 °C	Time (min)	Split State	Split Ratio
Col Flow	0.8 mL/min	Initial	ON	20
Pressure Pulse	None	0.01	ON	100
Constant Flow	ON	5 min	ON	20
Septum Purge Flow	0.1 mL/min			

Table 3-11 MS Conditions for 20 m Column

MS Conditions				
Segment	***Start (min)***	***End (min)***	***Low Mass (m/z)***	***High Mass (m/z)***
Fil/Delay	0.00	1.00	NA	NA
Gases	1.00	2.40	47	150
Other VOCs	2.40	17.00	35	260
Target TIC	12-15000	µscans averaged	2	
Max Ion Time	25000 µsec	Mult Offset	50-100 V	
Bakground Mass	34 m/z	Emission Current	10-25 µamps	
Rf Dump	300 m/z	Scan Time	0.50 sec/scan	

BFB Suggested MS Segment Breaks

Suggested Segment Breaks and Ion Time Factors for BFB Tuning			
Low mass (m/z)	High mass (m/z)	Ionization Storage Level	Ionization Factor
10	70	34	120%
71	78	34	70%

Suggested Segment Breaks and Ion Time Factors for BFB Tuning			
Low mass (m/z)	High mass (m/z)	Ionization Storage Level	Ionization Factor
79	150	34	100%
151	650	34	100%

***NOTE:** The ionization factors may need to be adjusted from these starting values for BFB tuning. Once the optimum values are found, the tune should be very stable and pass routinely.*

Peak Table of Suggested Quantitation Ions #1

Peak #	Peak Name	RT (min)	Quan Ions
20	Fluorobenzene	14.405	96
1	Dichlorodifluoromethane	3.553	85
2	Chloromethane	4.018	47+49+51
3	Vinyl chloride	4.303	62
4	Bromomethane	5.218	94+96
5	Chloroethane	5.510	47+49+51
6	Trichlorofluoromethane	6.200	101
7	1,1-Dichloroethene	7.666	61
8	Methylenechloride	9.023	49
9	Ethene, 1,2-dichloro-, (E)-	9.641	61
10	1,1-Dichloroethane	10.690	63
11	Propane, 2,2-dichloro-	11.965	77
12	Ethene, 1,2-dichloro-, (Z-	12.021	61
13	Bromochloromethane	12.537	49
14	Chloroform	12.698	83
15	1,1,1-Trichloroethane	13.049	97
16	Carbon Tetrachloride	13.370	117
17	1-Propene, 1,1-dichloro-	13.401	75
18	Benzene	13.810	78
19	1,2-Dichloroethane	13.929	62
21	Trichloroethylene	15.165	130
22	1,2-Dichloropropane	15.649	63
23	Dibromomethane	15.910	93
24	Bromodichloromethane	16.198	83
25	1-Propene, 1,3-dichloro-, (Z)-	17.095	75
26	Toluene	17.725	91
27	1-Propene, 1,3-dichloro-, (E)-	18.205	75
28	1,1,2-Trichloroethane	18.599	97
29	Tetrachloroethylene	18.850	166
30	1,3-Dichloropropane	18.954	76
31	Dibromochloromethane	19.403	129
32	1,2-Dibromoethane	19.674	107
33	Chlorobenzene	20.647	112

Peak #	Peak Name	RT (min)	Quan Ions
34	Ethylbenzene	20.780	91
35	1,1,1,2-Tetrachloroethane	20.799	131
36	m,p-Xylene	21.018	91
37	o-Xylene	21.859	91
38	Styrene	21.890	104
39	Bromoform	22.358	171+173+175
40	Isopropylbenzene	22.577	105
41	Bromofluorobenzene	23.008	95
42	1,1,2,2-Tetrachloroethane	23.267	83
43	Bromobenzene	23.355	77
44	1,2,3-Trichloropropane	23.397	75
45	n-Propylbenzene	23.435	91
46	2-Chlorotoluene	23.722	126
47	1,3,5-Trimethylbenzene	23.792	105
48	4-Chlorotoluene	23.946	91
49	tert-Butylbenzene	24.474	119
50	1,2,4-Trimethylbenzene	24.603	105
51	sec-Butylbenzene	24.940	105
52	4-Isopropyltoluene	25.216	119
53	1,3-Dichlorobenzene	25.316	146
54	1,4-Dichlorobenzene	25.508	146
55	n-Butylbenzene	26.090	91
56	1,2-Dichlorobenzene-d4	26.279	150
57	1,2 -Dichlorobenzene	26.320	146
58	1,2-Dibromo-3-chloropropane	27.960	75
59	1,2,4-Trichlorobenzene	29.730	182
60	1,3-Butadiene,1,1,2,3,4,4-hexachloro-	29.986	225
61	Naphthalene	30.312	128
62	1,2,3-Trichlorobenzene	30.903	182

Peak Table of Suggested Quantitation Ions #2

Peak #	Retention Time	Compound Name	Quan Ion(s)
1	12.642	Fluorobenzene (IS)	96
2	4.009	Dichlorodifluoromethane	85
3	4.544	Chloromethane	47+49+51
4	6.216	Vinyl chloride	62
5	3.444	Bromomethane	94+96
6	4.526	Chloroethane	47+49+51
7	6.773	Trichlorofluoromethane	101
8	8.613	Diethyl ether	59
9	9.201	1,1-Dichloroethene	61

Peak #	Retention Time	Compound Name	Quan Ion(s)
10	9.540	Acetone	43
11	9.776	Carbondisulfide	76
12	10.261	Allyl Chloride	41
13	10.624	Methylene chloride	49
14	9.243	Ethene, 1,2-dichloro-, (E	61
15	11.277	Methyl tert-butyl ether	73
16	11.340	Acrylonitrile	52
17	12.295	1,1-Dichloroethane	63
18	13.535	Propane, 2,2-dichloro-	77
19	13.557	Ethene, 1,2-dichloro-,(Z	61
20	13.596	2-Butanone	43
21	13.758	Methyl acrylate	55
22	13.789	Propionitrile	54
23	14.050	Bromochloromethane	49
24	14.058	Methacrylonitrile	67
25	14.133	Tetrahydrofuran	71
26	14.179	Chloroform	83
27	14.554	1,1,1-Trichloroethane	97
28	14.746	Butyl chloride	56
29	14.850	Carbon Tetrachloride	117
30	14.871	1-Propene, 1,1-dichloro-	75
31	15.272	Benzene	78
32	15.364	1,2-Dichloroethane	62
33	16.496	Trichloroethylene	130
34	16.973	1,2-Dichloropropane	63
35	17.070	Methyl methacrylate	69
36	17.195	Dibromomethane	93
37	17.440	Bromodichloromethane	83
38	17.921	2-Nitropropane	43
39	18.279	1-Propene, 1,3-dichloro-,	75
40	17.951	Chloroacetonitrile	75
41	18.508	MIK (4-methyl-2-pentanone	43
42	18.631	1,1-Dichloropropanone	43
43	18.885	Toluene	91
44	18.258	1-Propene, 1,3-dichloro-,	75
45	19.335	Ethyl methacrylate	69
46	18.505	2-Hexanone	85
47	19.652	1,1,2-Trichloroethane	97
48	19.897	Tetrachloroethylene	166
49	19.992	1,3-Dichloropropane	76
50	20.393	Dibromochloromethane	129
51	20.672	1,2-Dibromoethane	107
52	21.559	Chlorobenzene	112

Peak #	Retention Time	Compound Name	Quan Ion(s)
53	21.689	1,1,1,2-Tetrachloroethane	131
54	21.687	Ethylbenzene	91
55	22.679	m,p-Xylene	91
56	22.679	o-Xylene	91
57	22.703	Styrene	104
58	23.112	Bromoform	171+173+175
59	23.340	Isopropylbenzene	105
60	23.614	Bromofluorobenzene	95
61	24.921	1,1,2,2-Tetrachloroethan	83
62	24.043	trans-1,4-Dichloro-2-bute	88
63	24.053	Bromobenzene	77
64	22.255	1,2,3-Trichloropropane	75
65	24.128	n-Propylbenzene	91
66	24.386	2-Chlorotoluene	126
67	24.457	1,3,5-Trimethylbenzene	105
68	24.593	4-Chlorotoluene	91
69	25.095	tert-Butylbenzene	119
70	25.207	Pentachloroethane	167
71	24.457	1,2,4-Trimethylbenzene	105
72	25.520	sec-Butylbenzene	105
73	25.773	4-Isopropyltoluene	119
74	25.840	1,3-Dichlorobenzene	146
75	26.017	1,4-Dichlorobenzene	146
76	26.575	n-Butylbenzene	91
77	26.764	1,2 -Dichlorobenzene	146
78	25.272	1,2-Dichlorobenzene-d4	150
79	27.248	Hexachloroethane	201
80	28.266	1,2-Dibromo-3-chloropropa	75
81	28.702	Nitrobenzene	77
82	30.997	1,2,4-Trichlorobenzene	182
83	30.164	1,3-Butadiene, 1,1,2,3,4,	225
84	30.475	Naphthalene	128
85	30.997	1,2,3 -Trichlorobenzene	182

3.7 Analytical Results

3.7.1 Sample Chromatograms

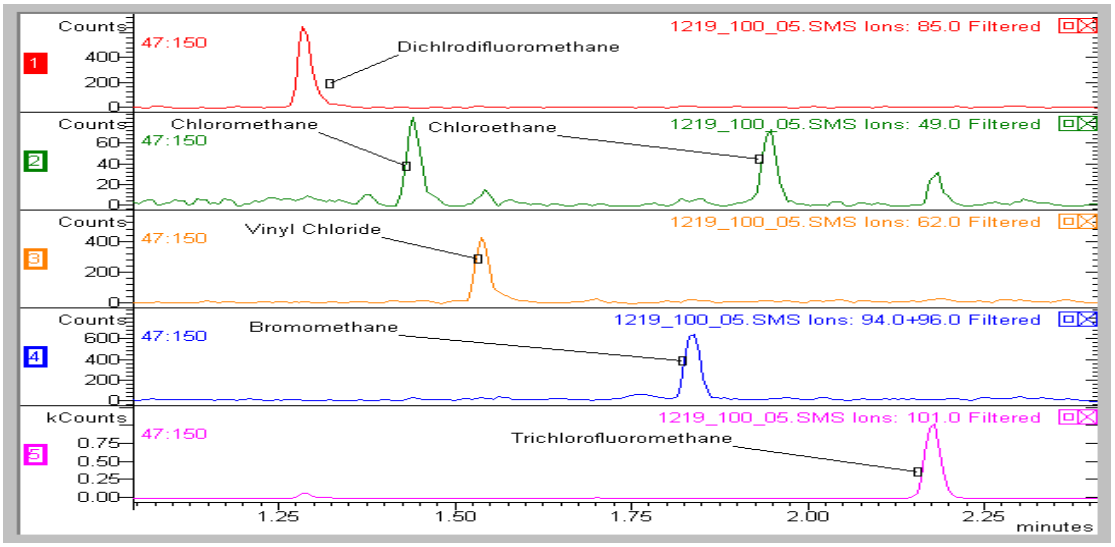


Figure 3.1: 6 Volatile gases at 0.5 ppb, 5 mL purge volume

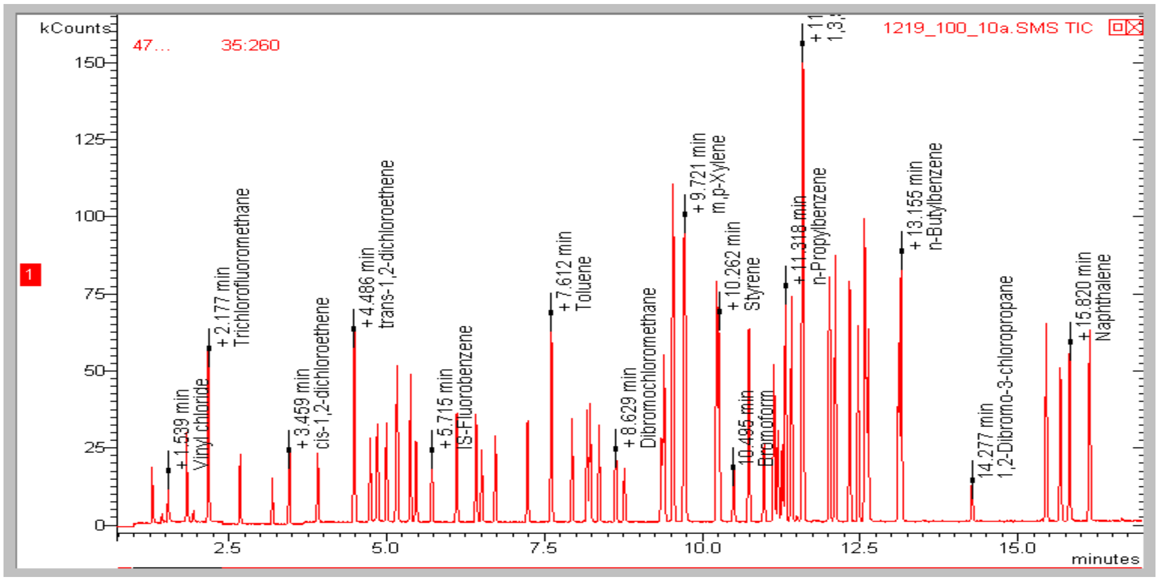
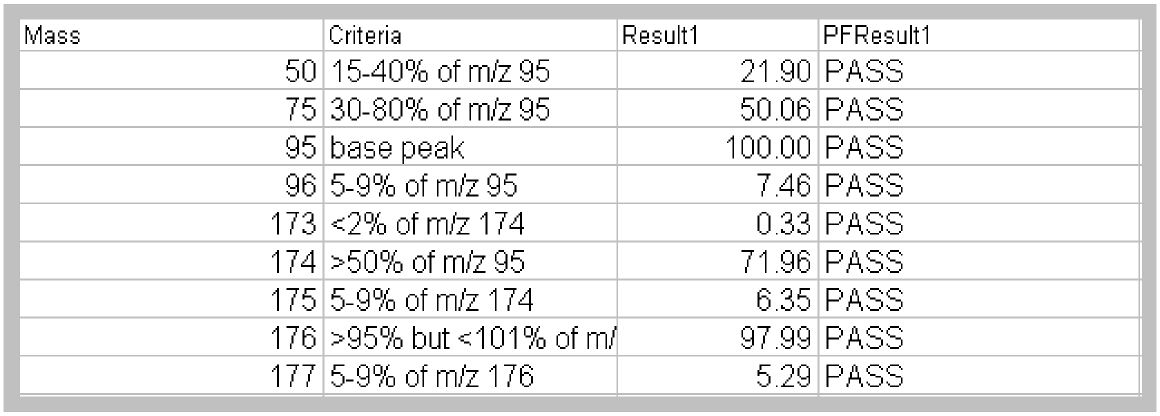


Figure 3.2: TIC, 10 ppb 60 compound VOC mixture

3.7.2 Tune Verification and SPCC



Mass	Criteria	Result1	PFResult1
50	15-40% of m/z 95	21.90	PASS
75	30-80% of m/z 95	50.06	PASS
95	base peak	100.00	PASS
96	5-9% of m/z 95	7.46	PASS
173	<2% of m/z 174	0.33	PASS
174	>50% of m/z 95	71.96	PASS
175	5-9% of m/z 174	6.35	PASS
176	>95% but <101% of m/	97.99	PASS
177	5-9% of m/z 176	5.29	PASS

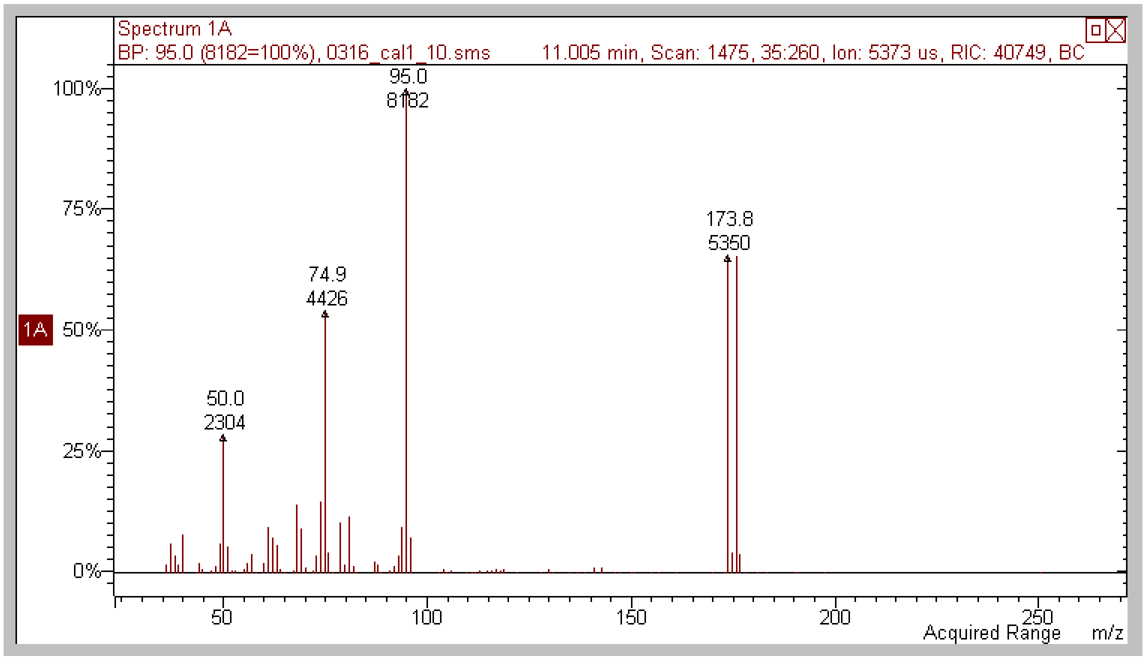


Figure 3.3: BFB spectrum taken on 20M column

System Performance Check Compounds and CCCs (SPCCs and CCCs) from initial calibration data (Calibration from 0.5 to 100 ppb on 20 m column) – Linear Curve Fit

Compound Name	Corr (r^2)	Avg. RRF	Min. RRF	% RSD	CCC	SPCC
Chloromethane	0.9968	0.1084	0.1000	10.5	PASS	PASS
1,1-Dichloroethene	0.9979	0.5712	0.1000	8.3	PASS	PASS
1,1-Dichloroethane	0.9998	0.6648	0.1000	7.2	PASS	PASS
Chlorobenzene	0.9998	1.0513	0.3000	2.7	PASS	PASS
Bromoform	0.9996	0.2992	0.1000	7.5	PASS	PASS
1,1,2,2-Tetrachloroethane	0.9995	0.5465	0.3000	7.4	PASS	PASS

3.7.3 Calibration Statistics

Table 3-12 Initial Calibration Data for Method 8260B, 5 mL sample purge volume on 20 m column

Calibration Levels 0.5 to 100 ppb – Linear Fit			
Compound Name	**Corr. Coeff.**	**Avg. RRF**	**% RSD**
Dichlorodifluoromethane	0.9744	0.4316	20.3
Chloromethane	0.9968	0.1084	10.5
Vinyl chloride	0.9952	0.4445	7.6
Bromomethane	0.9960	0.5091	20.3
Chloroethane	0.9993	0.0714	11.0
Trichlorofluoromethane	0.9947	1.2685	14.7
1,1-Dichloroethene	0.9979	0.5712	8.3
Methylene chloride	0.9993	0.3419	15.7
cis-1,2-dichloroethene	0.9985	0.5595	5.7
1,1-Dichloroethane	0.9998	0.6648	7.2
2,2-Dichloropropane	0.9970	0.3346	10.2
trans-1,2-dichloroethene	0.9986	1.1260	3.2
Bromochloromethane	0.9991	0.4850	5.8
Chloroform	0.9978	0.6944	3.1
1,1,1-Trichloroethane	0.9984	0.9373	4.8
Carbon Tetrachloride	0.9992	0.4487	8.5
1,1-Dichloropropene	0.9996	0.2945	7.2
Benzene	0.9999	0.8554	4.6
1,2-Dichloroethane	0.9999	0.7592	4.7
Trichloroethene	0.9965	0.2875	5.6
1,2-Dichloropropane	0.9996	0.2997	3.0
Dibromomethane	0.9996	0.5022	5.2
Bromodichloromethane	1.0000	0.5818	2.2
trans-1,3-dichloropropene	0.9989	0.4377	4.5
Toluene	1.0000	1.9478	3.2
cis-1,3-dichloropropene	0.9990	0.4292	6.0
1,1,2-trichloroethane	0.9995	0.3630	5.8
Tetrachloroethene	0.9969	0.2700	10.4
1,3-dichloropropane	0.9993	0.3393	3.5
Dibromochloromethane	0.9992	0.4828	5.0
1,2-Dibromoethane	0.9996	0.4541	7.0
Chlorobenzene	0.9998	1.0513	2.7
1,1,1,2-Tetrachloroethane	0.9991	0.4463	5.1
Ethylbenzene	0.9989	2.1940	4.3

Calibration Levels 0.5 to 100 ppb – Linear Fit			
Compound Name	**Corr. Coeff.**	**Avg. RRF**	**% RSD**
m,p-Xylene	0.9992	3.9780	4.0
o-Xylene	0.9997	2.0515	4.0
Styrene	0.9999	1.0912	4.5
Bromoform	0.9996	0.2992	7.5
Isopropylbenzene	0.9987	1.6869	4.9
SS-4-Bromofluorobenzene	0.9864	0.4778	4.2
Bromobenzene	0.9997	0.5490	4.5
1,1,2,2-Tetrachloroethane	0.9995	0.5465	7.4
1,2,3-Trichloropropane	0.9995	0.3797	7.6
n-Propylbenzene	0.9992	2.4619	5.2
2-Chlorotoluene	0.9999	0.4979	4.1
4-Chlorotoluene	0.9968	0.4944	7.0
1,3,5-Trimethylbenzene	0.9990	2.1230	5.7
tert-Butylbenzene	0.9980	1.6347	6.4
1,2,4-Trimethylbenzene	0.9989	2.1178	5.3
sec-Butylbenzene	0.9979	2.1571	7.2
1,3-Dichlorobenzene	0.9971	1.5566	4.4
p-Isopropyltoluene	0.9978	3.1031	5.7
1,4-Dichlorobenzene	0.9949	1.5954	4.8
1,2-Dichlorobenzene	0.9985	1.5462	3.8
n-Butylbenzene	0.9991	3.5147	6.9
1,2-Dibromo-3-chloropropane	0.9986	0.7523	6.5
1,2,4-Trichlorobenzene	0.9994	1.2546	2.8
Hexachlorobutadiene	0.9952	0.7012	13.4
Naphthalene	0.9999	2.9125	8.7
1,2,3-Trichlorobenzene	0.9998	1.2461	3.2
Overall	**0.9980**	**1.0287**	**6.6**

Table 3-13 Auto Calibration with Archon Autosampler (25 mL purge volume, 1:200 split ratio, 20 m column)

Auto Calibration with Archon, 0.5 to 50 ppb, 25 mL Volume - Linear Fit			
Calibration Level			
Compound Name	**Corr. Coeff.**	**Avg. RRF**	**% RSD**
Dichlorodifluoromethane	0.9999	0.2660	3.3
Chloromethane	0.9980	0.0827	11.1
Vinyl chloride	0.9998	0.3811	7.0
Bromomethane	0.9994	0.5088	6.5
Chloroethane	0.9995	0.0678	7.8
Trichlorofluoromethane	0.9996	1.1963	6.6
1,1-Dichloroethene	0.9995	0.6124	7.0
Methylene chloride	0.9991	0.2821	14.4
cis-1,2-dichloroethene	1.0000	0.5804	5.4
1,1-Dichloroethane	0.9964	0.4147	24.4
2,2-Dichloropropane	0.9997	0.3504	3.5
trans-1,2-dichloroethene	0.9996	1.0439	3.4
Bromochloromethane	0.9996	0.2895	2.5
Chloroform	0.9993	0.6353	4.7
1,1,1-Trichloroethane	0.9999	1.0122	5.1
Carbon Tetrachloride	0.9995	0.4781	8.1
1,1-Dichloropropene	0.9997	0.3145	7.4
Benzene	0.9998	0.8166	4.2
1,2-Dichloroethane	1.0000	0.4077	5.4
Trichloroethene	0.9997	0.2907	4.3
1,2-Dichloropropane	0.9992	0.2408	3.6
Dibromomethane	0.9999	0.2385	4.0
Bromodichloromethane	0.9999	0.4126	4.6
trans-1,3-dichloropropene	0.9996	0.3029	4.9
Toluene	0.9975	2.1121	6.1
cis-1,3-dichloropropene	0.9998	0.2326	2.7
1,1,2-trichloroethane	0.9993	0.1963	3.5
Tetrachloroethene	0.9997	0.3016	4.8
1,3-dichloropropane	0.9999	0.1809	5.2
Dibromochloromethane	0.9999	0.2843	7.0
1,2-Dibromoethane	0.9991	0.2095	5.3
Chlorobenzene	0.9998	1.0061	3.4
1,1,1,2-Tetrachloroethane	0.9999	0.3739	5.6
Ethylbenzene	0.9995	2.3952	4.3
m,p-Xylene	0.9991	4.2701	4.0
o-Xylene	0.9973	2.0633	4.9

Auto Calibration with Archon, 0.5 to 50 ppb, 25 mL Volume - Linear Fit			
Calibration Level			
Compound Name	**Corr. Coeff.**	**Avg. RRF**	**% RSD**
Styrene	0.9992	0.9923	4.1
Bromoform	0.9999	0.1304	2.5
Isopropylbenzene	0.9992	1.8914	4.3
SS-4-Bromofluorobenzene	0.9772	0.4174	5.8
Bromobenzene	0.9984	0.4384	6.9
1,1,2,2-Tetrachloroethane	0.9993	0.2045	7.0
1,2,3-Trichloropropane	0.9995	0.1363	10.1
n-Propylbenzene	0.9955	2.6851	7.3
2-Chlorotoluene	0.9985	0.5071	5.1
4-Chlorotoluene	0.9875	0.4497	8.1
1,3,5-Trimethylbenzene	0.9973	2.1918	4.2
tert-Butylbenzene	0.9994	1.7937	4.1
1,2,4-Trimethylbenzene	0.9990	2.0585	3.7
sec-Butylbenzene	0.9972	2.3972	7.5
1,3-Dichlorobenzene	0.9998	1.6057	5.8
p-Isopropyltoluene	0.9991	4.0249	7.9
1,4-Dichlorobenzene	0.9990	1.5338	4.8
1,2-Dichlorobenzene	0.9987	1.2707	7.4
n-Butylbenzene	0.9991	4.4661	8.4
1,2-Dibromo-3-chloropropane	0.9982	0.2719	7.5
1,2,4-Trichlorobenzene	0.9986	0.9579	6.6
Hexachlorobutadiene	0.9992	0.8944	12.4
Naphthalene	0.9984	1.1553	7.5
1,2,3-Trichlorobenzene	0.9995	0.7582	6.8
Overall	**0.9986**	**0.9681**	**6.2009**

Table 3-14 Calibration Data for 8260B, Oxygenated Compounds, 5 mL purge volume, 20 m column

Calibration Levels (0.5 ppb – 100 ppb) – Linear Fit			
Compound Name	**Corr. Coeff.**	**Avg. RRF**	**% RSD**
Diethyl ether	0.9967	0.1397	6.5884
Acetone	0.9956	0.1102	25.8715
Methyl iodide	0.9972	0.4569	16.5953
Carbon disulfide	0.9953	0.5421	10.5457
Allyl chloride	0.9976	0.4881	5.4920
Acrylonitrile	0.9967	0.1935	12.4538
MTBE	0.9988	0.5252	4.4227

Calibration Levels (0.5 ppb – 100 ppb) – Linear Fit			
Compound Name	**Corr. Coeff.**	**Avg. RRF**	**% RSD**
2-Butanone	0.9972	0.1366	14.4424
Propionitrile	0.9900	0.0369	21.4192
Methyl acrylate	0.9978	0.0479	13.3002
Methacrylonitrile	0.9900	0.2923	12.4773
THF	0.9945	0.0333	14.0668
Butyl chloride	0.9982	0.3769	7.9951
Methyl methacrylate	0.9968	0.7544	9.2608
2-Nitropropane	0.9944	0.1432	21.7936
Chloroacetonitrile	0.9915	0.0102	15.6128
MIK	0.9970	0.5448	11.7831
1,1-Dichloropropanone	0.9912	0.1155	13.7568
Ethyl methacrylate	0.9984	0.4549	10.4575
2-Hexanone	0.9977	0.3888	18.3009
trans-1,4-Dichloro-2-butene	0.9928	0.4247	11.9583
Hexachloroethane	0.9977	0.5990	7.1490
Nitrobenzene	0.9957	0.0405	16.0072
Overall	**0.996**		**13.1**

3.7.4 Method Detection Limit Results

Table 3-15 Method Detection Limits, 5 mL purge volume

EPA Method 8260B VOC MDL, Reps Target 0.50 ppb, Stratum and 20 m x 0.25 x 0.15 column with #9 Strat-Trap, 7 replicates					
Peak Name	**Avg**	**StdDEV**	**%RSD**	**%Recovery**	**MDL**
Dichlorodifluoromethane	0.377	0.071277	18.9	75.4	0.223882
Chloromethane	0.505	0.033649	6.7	100.9	0.105691
Vinyl chloride	0.491	0.063158	12.9	98.3	0.19838
Bromomethane	0.507	0.054671	10.8	101.5	0.171723
Chloroethane	0.459	0.026842	5.8	91.8	0.08431
Trichlorofluoromethane	0.498	0.067586	13.6	99.5	0.212288
1,1-Dichloroethene	0.491	0.021877	4.5	98.1	0.068717
Methylene chloride	0.784	0.042575	5.4	156.7	0.133728
cis-1,2-dichloroethene	0.514	0.032988	6.4	102.9	0.103617
1,1-Dichloroethane	0.556	0.018698	3.4	111.3	0.058731
trans-1,2-dichloroethene	0.448	0.02469	5.5	89.5	0.07755
2,2-Dichloropropane	0.269	0.01753	6.5	53.9	0.05506
Bromochloromethane	0.508	0.020918	4.1	101.5	0.065704
Chloroform	0.500	0.018928	3.8	100.1	0.059454

EPA Method 8260B VOC MDL, Reps Target 0.50 ppb, Stratum and 20 m x 0.25 x 0.15 column with #9 Strat-Trap, 7 replicates

Peak Name	Avg	StdDEV	%RSD	%Recovery	MDL
1,1,1-Trichloroethane	0.439	0.026229	6.0	87.9	0.082385
Carbon Tetrachloride	0.476	0.009299	2.0	95.2	0.029209
1,1-Dichloropropene	0.428	0.04395	10.3	85.7	0.138046
Benzene	0.491	0.011131	2.3	98.1	0.034963
1,2-Dichloroethane	0.519	0.029646	5.7	103.9	0.093119
Trichloroethene	0.574	0.040468	7.1	114.8	0.12711
1,2-Dichloropropane	0.490	0.032205	6.6	98.0	0.101155
Dibromomethane	0.504	0.036143	7.2	100.9	0.113524
Bromodichloromethane	0.493	0.027715	5.6	98.6	0.087054
trans-1,3-dichloropropene	0.523	0.031368	6.0	104.7	0.098527
Toluene	0.449	0.031788	7.1	89.8	0.099846
cis-1,3-dichloropropene	0.515	0.037673	7.3	102.9	0.11833
1,1,2-trichloroethane	0.504	0.02053	4.1	100.8	0.064484
Tetrachloroethene	0.282	0.029334	10.4	56.4	0.092138
1,3-dichloropropane	0.473	0.042867	9.1	94.5	0.134647
Dibromochloromethane	0.478	0.023536	4.9	95.7	0.073927
1,2-Dibromoethane	0.386	0.036262	9.4	77.3	0.1139
Chlorobenzene	0.494	0.03088	6.3	98.7	0.096994
1,1,1,2-Tetrachloroethane	0.442	0.041107	9.3	88.4	0.129118
Ethylbenzene	0.432	0.025417	5.9	86.4	0.079833
m,p-Xylene	0.439	0.02965	6.8	87.8	0.093132
o-Xylene	0.487	0.037907	7.8	97.5	0.119066
Styrene	0.538	0.024636	4.6	107.5	0.077383
Bromoform	0.523	0.044538	8.5	104.6	0.139895
Isopropylbenzene	0.410	0.028743	7.0	82.0	0.090281
SS-4-Bromofluorobenzene	4.914	0.185922	3.8	98.3	0.58398
Bromobenzene	0.461	0.038982	8.5	92.1	0.122443
1,1,2,2-Tetrachloroethane	0.352	0.053114	15.1	70.4	0.166832
1,2,3-Trichloropropane	0.454	0.034686	7.6	90.8	0.10895
n-Propylbenzene	0.436	0.026686	6.1	87.2	0.083821
2-Chlorotoluene	0.491	0.031662	6.4	98.2	0.09945
1,3,5-Trimethylbenzene	0.410	0.023338	5.7	82.0	0.073305
4-Chlorotoluene	0.338	0.025349	7.5	67.5	0.079621
tert-Butylbenzene	0.365	0.028088	7.7	73.1	0.088225
1,2,4-Trimethylbenzene	0.432	0.025072	5.8	86.5	0.078752
sec-Butylbenzene	0.378	0.043328	11.5	75.6	0.136094
1,3-Dichlorobenzene	0.570	0.015389	2.7	114.0	0.048336
p-Isopropyltoluene	0.458	0.024357	5.3	91.7	0.076507
1,4-Dichlorobenzene	0.596	0.017367	2.9	119.1	0.05455
1,2-Dichlorobenzene	0.558	0.021399	3.8	111.5	0.067213

EPA Method 8260B VOC MDL, Reps Target 0.50 ppb, Stratum and 20 m x 0.25 x 0.15 column with #9 Strat-Trap, 7 replicates					
Peak Name	**Avg**	**StdDEV**	**%RSD**	**%Recovery**	**MDL**
n-Butylbenzene	0.414	0.026236	6.3	82.8	0.082408
1,2-Dibromo-3-chloropropane	0.503	0.058281	11.6	100.7	0.183059
1,2,4-Trichlorobenzene	0.518	0.039185	7.6	103.6	0.123081
Hexachlorobutadiene	0.305	0.04999	16.4	61.1	0.157017
Naphthalene	0.561	0.036451	6.5	112.2	0.114492
1,2,3-Trichlorobenzene	0.485	0.023646	4.9	97.0	0.074273
Overall			**7.1**	**94.2**	**0.1108**

Table 3-16 MDLs for Oxygenates, 5 mL purge volume

EPA Method 8260B VOC MDL, Reps Target 0.50 ppb, Stratum and 20 m x 0.25 x 0.15 column with #9 Strat-Trap REP1 – REP7, 7 replicates					
Oxygenated Compounds					
Peak Name	**Avg**	**StdDEV**	**%RSD**	**%Recovery**	**MDL**
Diethyl ether	0.421	0.027288	6.5	84.1	0.085711
Acetone	0.466	0.050369	10.8	93.2	0.158208
Methyl iodide	0.523	0.019121	3.7	104.5	0.06006
Carbon disulfide	0.590	0.066707	11.3	118.0	0.209526
Allyl chloride	0.479	0.042547	8.9	95.7	0.13364
Acrylonitrile	0.475	0.083665	17.6	94.9	0.262793
MTBE	0.460	0.033538	7.3	92.0	0.105343
2-Butanone	0.568	0.087509	15.4	113.5	0.274867
Propionitrile	0.375	0.128412	34.3	74.9	0.403341
Methyl acrylate	0.448	0.104589	23.3	89.7	0.328515
Methacrylonitrile	0.484	0.035297	7.3	96.9	0.110869
THF	0.597	0.134479	22.5	119.3	0.422399
Butyl chloride	0.516	0.023493	4.6	103.1	0.07379
Methyl methacrylate	0.552	0.069651	12.6	110.5	0.218774
2-Nitropropane	0.365	0.097716	26.8	73.0	0.306925
MIK	0.461	0.05431	11.8	92.3	0.170589
1,1-Dichloropropanone	0.530	0.059444	11.2	105.9	0.186714
Ethyl methacrylate	0.493	0.048814	9.9	98.6	0.153325
2-Hexanone	0.436	0.058125	13.3	87.2	0.18257
SS-Bromofluorobenzene	4.977	0.250656	5.0	99.5	0.787309
trans-1,4-Dichloro-2-butene	0.464	0.040387	8.7	92.8	0.126857
Hexachloroethane	0.517	0.030762	5.9	103.5	0.096623
Nitrobenzene	0.498	0.101086	20.3	99.6	0.317513
Overall			**13.0**	**97.5**	**0.2251**

3.8 Troubleshooting

The following table outlines common potential problems and proposed solutions. Multiple problems on the same PAT system are often difficult to resolve and may require a service representative. Always try the least invasive (or easiest) procedure first when troubleshooting. Ask “what has changed?” and review maintenance logs to help trace back when a problem may have started.

Observed Problem	**Potential Cause(s)**	**Solutions**
Bad overall peak shape	PAT contamination, bad sorbent trap, bad column, leaking at sorbent trap fittings	Change sorbent trap, change column, run leak-check, clean entire PAT sample pathway
Sudden loss of sensitivity	Foam-over into 6-port valve, leaks (PAT or GC/MS system), broken column.	Leak check PAT, check column, clean PAT pathway and change trap (foam-over)
Low response for 6 gases	Old gas standard, split ratio too high, bad sorbent trap, leaks in PAT, wrong insert in injector, too much water and methanol, dry purge too long	Prepare new stds from un-opened stock, leak check PAT, decrease split ratio, change sorbent trap, check sample prep to ensure minimum methanol used, shorten dry purge time and/or flow rate
BFB tune fails	210-MS/220-MS settings not optimized, too much water, contaminated PAT, MS saturated, multiplier voltage too low	Adjust ionization time factors, increase multiplier +100V, clean contaminated PAT and replace sorbent trap, decrease amount injected if MS saturated, check moisture filters on He gas lines
High mass noise	Dirty ion trap	Clean ion trap
Gradual loss of sensitivity	MS multiplier “settling in”	Increase multiplier if peak areas drop low out of range from initial calibration.
Ghost peaks	Bad sorbent trap, dirty PAT system, dirty MeOH, bad column, dirty reagent water, peaks (targets) in contaminated sample preservation solutions	Replace sorbent trap, clean PAT sample pathway, use only PAT grade MeOH, replace column, change DI/carbon cartridge, preservatives
Carryover	Dirty purge vessel, dirty PAT pathway, no water in Archon reservoir, rinse volumes too low, heavily contaminated sample, foam-over, short and/or low-temp bake cycle	Clean PAT purge vessel and sample pathway, change sorbent trap, Check reservoirs and rinse volumes, check He switch for Archon is ON, increase bake time and/or temp.
Loss of brominated compounds	Actives sites in PAT system or analytical column	Clean PAT pathway, change trap, change column, clean ion trap

Observed Problem	Potential Cause(s)	Solutions
Poor reproducibility of Internal/Surrogate standards	Archon IS/SURR vial empty or not properly primed, Archon He switch off, failed valve in Archon that delivers the IS/SS, leaks in PAT, bad sorbent trap	Check Archon IS/SS vial, replace sorbet trap, ensure He switch is ON, check for leaks in PAT
Sporadic target analytes gone or very poor response	Check for carbon flecks in bottom of VOA vials	Be sure to filter DI water if carbon flecks are visible
Corrosion in PAT	HCl from sample preservation reagent	Run blanks at end of run to help clean PAT sample pathway

3.8.1 Operating Tips

1. Do not use opened gas standards for more than five days -one week.
2. Do not over tighten fittings on sparge vessel
3. If method allows, try dry purge (1 min at 300 mL/min.) and short desorb time (1-2 min), however watch out for chloromethane loss
4. Optimize for highest split flow possible, balance against required sensitivity
5. Run one blank after the 50 and 100 ppb std to eliminate potential carryover in calibration runs
6. Run 2-3 blanks before the routine run to clean out PAT system
7. Minimize methanol in prepared aqueous standards to 10 µL or less
8. Prepare QC samples as needed fresh daily
9. Install foam eliminator if many samples are expected to contain surfactants
10. Watch out for MEK, MIBK, acetone, and other oxegenates that are often found in contaminated MeOH and also can leach from some DI water systems

4. EPA Method 8270D

EPA Method 8270D, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)" is a commonly used method for semivolatile compound analysis in a variety of waste matrices including solid waste, air, water and soil. The method lists over 200 compounds which may be analyzed by the suggested procedures, but only a subset of the listed target compounds are monitored in a given measurement. The method also refers to a variety of sample preparation and clean up methods.

This chapter of the Varian Environmental MS Application Manual will assist chemists in rapidly setting up the 210-MS/220-MS ion trap and the 300/320-MS quadrupole GC/MS systems for the analysis of samples by EPA Method 8270D. The accompanying CD for this manual contains a subdirectory, called EPA8270, which contains a PDF version of this section of the manual along with other important files that will be described in detail below.

Following this introduction is the Scope and Summary of EPA Method 8270D. The full method is available (in PDF format) on the attached CD in Appendix II for complete review. This and other methods can be obtained from the National Environmental Methods Index at http://www.nemi.gov/.

The Analytical Section provides guidance how to achieve the requirements of Method 8270D. A complete description of the apparatus, materials (analytical standards), and conditions is given. Also included are GC column recommendations and proven methods for GC, AutoSampler, MS acquisition, and MS data handling. Acquisition parameters were selected to fulfill the tune requirements. The data handling parameters were chosen to assure positive identification and accurate quantitation, and to satisfy QA/QC requirements.

Finally, the Results Section contains a selection data generated with both the 210-MS/220-MS and 300/320-MS GC/MS systems using the conditions recommended in this manual. Examples included are results of Tune Verification, Initial Calibration, and Continuing Calibration (CCC) compounds and System Performance Check Compounds (SPCCs) for each instrument configuration.

The Varian EnviroPro™ Software can be used to generate a variety of useful quality control summary reports in standard Contract Laboratory Program (CLP) format. Appendix I contains a series of PDF files as example reports for a typical volatile or semi-volatile method (EPA Method 524.2 and EPA 8270 on the CD). The reports are easily adaptable to other EPA methods that require extensive quality control reporting.

4.1 List of Abbreviations

BFB	Bromofluorobenzene
CCC	Continuing Calibration Check
DOC	Demonstration of Capability
ICC	Initial Calibration Check
IS	Internal Standard
LCS	Lab Control Sample
LFB	Lab Forrtified Blank
LMB	Lab Method Blank
LTB	Lab Trip Blank
MDL	Method Detection Limit
MS	Matrix Spike
MS/MSD	Matrix Spike/Matrix Spike Duplicate
PAT	Purge and Trap
QCS	Quality Control Sample
RRF	Relative Response Factors
RS	Recovery Standard
SPCC	System Performance Check Compounds
SS	Surrogate Standard

4.2 Scope and Application

EPA Method 8270: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS).

Method 8270 is used to determine the concentration of semivolatile organic compounds in extracts prepared from many types of solid waste matrices, soils, air sampling media, and water samples. Direct injection of a sample may be used in limited applications. The following compounds can be determined by this method:

CD-ROM 8270D Revision 4 2006

		Appropriate Preparation Techniques *				
Compounds	**CAS No****	**3510**	**3520**	**3540/ 3541**	**3550**	**3580**
Acenaphthene	83-32-9	X	X	X	X	X
Acenaphthene-d10		X	X	X	X	X
Acenaphthylene	208-96-8	X	X	X	X	X
Acetophenone	98-86-2	X	ND	ND	ND	X
2-Acetylaminofluorene	53-96-3	X	ND	ND	ND	X

		Appropriate Preparation Techniques *				
Compounds	**CAS No****	**3510**	**3520**	**3540/ 3541**	**3550**	**3580**
1-Acetyl-2-thiourea	591-08-2	LR	ND	ND	ND	LR
Aldrin	309-00-2	X	X	X	X	X
2-	117-79-3	X	ND	ND	ND	X
Aminoazobenzene	60-09-3	X	ND	ND	ND	X
4-Aminobiphenyl	92-67-1	X	ND	ND	ND	X
3-Amino-9-	132-32-1	X	X	ND	ND	ND
Anilazine	101-05-3	X	ND	ND	ND	X
Aniline	62-53-3	X	X	ND	X	X
o-Anisidine	90-04-0	X	ND	ND	ND	X
Anthracene	120-12-7	X	X	X	X	X
Aramite	140-57-8	HS(43)	ND	ND	ND	X
Aroclor 1016	12674-11-2	X	X	X	X	X
Aroclor 1221	11104-28-2	X	X	X	X	X
Aroclor 1232	11141-16-5	X	X	X	X	X
Aroclor 1242	53469-21-9	X	X	X	X	X
Aroclor 1248	12672-29-6	X	X	X	X	X
Aroclor 1254	11097-69-1	X	X	X	X	X
Aroclor 1260	11096-82-5	X	X	X	X	X
Azinphos-methyl	86-50-0	HS(62)	ND	ND	ND	X
Barban	101-27-9	LR	ND	ND	ND	LR
Benzidine	92-87-5	CP	CP	CP	CP	CP
Benzoic acid	65-85-0	X	X	ND	X	
Benz(a)anthracene	56-55-3	X	X	X	X	X
Benzo(b)fluoranthene	205-99-2	X	X	X	X	X
Benzo(k)fluoranthene	207-08-9	X	X	X	X	X
Benzo(g,h,i)perylene	191-24-2	X	X	X	X	X
Benzo(a)pyrene	50-32-8	X	X	X	X	X
p-Benzoquinone	106-51-4	OE	ND	ND	ND	ND
Benzyl alcohol	100-51-6	X	X	ND	X	X
α-BHC	319-84-6	X	X	X	X	X
β-BHC	319-85-7	X	X	X	X	X
δ-BHC	319-86-8	X	X	X	X	X
γ-BHC (Lindane)	58-89-9	X	X	X	X	X
Bis(2-	111-91-1	X	X	X	X	X
Bis(2-chloroethyl)	111-44-4	X	X	X	X	X
Bis(2-chloroisopropyl)	108-60-1	X	X	X	X	X
Bis(2-ethylhexyl)	117-81-7	X	X	X	X	X
4-Bromophenyl phenyl	101-55-3	X	X	X	X	X
Bromoxynil	1689-84-5	X	ND	ND	ND	X
Butyl benzyl phthalate	85-68-7	X	X	X	X	X

		Appropriate Preparation Techniques *				
Compounds	**CAS No****	**3510**	**3520**	**3540/ 3541**	**3550**	**3580**
Captafol	2425-06-1	HS(55)	ND	ND	ND	X
Captan	133-06-2	HS(40)	ND	ND	ND	X
Carbaryl	63-25-2	X	ND	ND	ND	X
Carbofuran	1563-66-2	X	ND	ND	ND	X
Carbophenothion	786-19-6	X	ND	ND	ND	X
Chlordane (NOS)	57-74-9	X	X	X	X	X
Chlorfenvinphos	470-90-6	X	ND	ND	ND	X
4-Chloroaniline	106-47-8	X	ND	ND	ND	X
Chlorobenzilate	510-15-6	X	ND	ND	ND	X
5-Chloro-2-	95-79-4	X	ND	ND	ND	X
4-Chloro-3-	59-50-7	X	X	X	X	X
3-	6959-48-4	X	ND	ND	ND	X
1-Chloronaphthalene	90-13-1	X	X	X	X	X
2-Chloronaphthalene	91-58-7	X	X	X	X	X
2-Chlorophenol	95-57-8	X	X	X	X	X
4-Chloro-1,2-	95-83-0	X	X	ND	ND	ND
4-Chloro-1,3-	5131-60-2	X	X	ND	ND	ND
4-Chlorophenyl phenyl	7005-72-3	X	X	X	X	X
Chrysene	218-01-9	X	X	X	X	X
Chrysene-d12 (IS)		X	X	X	X	X
Coumaphos	56-72-4	X	ND	ND	ND	X
p-Cresidine	120-71-8	X	ND	ND	ND	X
Crotoxyphos	7700-17-6	X	ND	ND	ND	X
2-Cyclohexyl-4,6-	131-89-5	X	ND	ND	ND	LR
4,4'-DDD	72-54-8	X	X	X	X	X
4,4'-DDE	72-55-9	X	X	X	X	X
4,4'-DDT	50-29-3	X	X	X	X	X
Demeton-O	298-03-3	HS(68)	ND	ND	ND	X
Demeton-S	126-75-0	X	ND	ND	ND	X
Diallate (cis or trans)	2303-16-4	X	ND	ND	ND	X
2,4-Diaminotoluene	95-80-7	DC,0E(	ND	ND	ND	X
Dibenz(a,j)acridine	224-42-0	X	ND	ND	ND	X
Dibenz(a,h)anthracen	53-70-3	X	X	X	X	X
Dibenzofuran	132-64-9	X	X	ND	X	X
Dibenzo(a,e)pyrene	192-65-4	X	X	ND	ND	ND
Di-n-butyl phthalate	84-74-2	X	X	X	X	X
Dichlone	117-80-6	OE	ND	ND	ND	X
1,2-Dichlorobenzene	95-50-1	X	X	X	X	X
1,3-Dichlorobenzene	541-73-1	X	X	X	X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X	X

		Appropriate Preparation Techniques *				
Compounds	**CAS No****	**3510**	**3520**	**3540/ 3541**	**3550**	**3580**
1,4-Dichlorobenzene-		X	X	X	X	X
3,3'-Dichlorobenzidine	91-94-1	X	X	X	X	X
2,4-Dichlorophenol	120-83-2	X	X	X	X	X
2,6-Dichlorophenol	87-65-0	X	ND	ND	ND	X
Dichlorovos	62-73-7	X	ND	ND	ND	X
Dicrotophos	141-66-2	X	ND	ND	ND	X
Dieldrin	60-57-1	X	X	X	X	X
Diethyl phthalate	84-66-2	X	X	X	X	X
Diethylstilbestrol	56-53-1	AW,0S(	ND	ND	ND	X
Diethyl sulfate	64-67-5	LR	ND	ND	ND	LR
Dihydrosaffrole	56312-13-1	ND	ND	ND	ND	ND
Dimethoate	60-51-5	HE,HS(	ND	ND	ND	X
3,3'-	119-90-4	X	ND	ND	ND	LR
Dimethylaminoazoben	60-11-7	X	ND	ND	ND	X
7,12-	57-97-6	CP(45)	ND	ND	ND	CP
3,3'-	119-93-7	X	ND	ND	ND	X
α, α -	122-09-8	ND	ND	ND	ND	X
2,4-Dimethylphenol	105-67-9	X	X	X	X	X
Dimethyl phthalate	131-11-3	X	X	X	X	X
1,2-Dinitrobenzene	528-29-0	X	ND	ND	ND	X
1,3-Dinitrobenzene	99-65-0	X	ND	ND	ND	X
1,4-Dinitrobenzene	100-25-4	HE(14)	ND	ND	ND	X
4,6-Dinitro-2-	534-52-1	X	X	X	X	X
2,4-Dinitrophenol	51-28-5	X	X	X	X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X	X	X	X	X
Dinocap	39300-45-3	CP,HS(	ND	ND	ND	CP
Dinoseb	88-85-7	X	ND	ND	ND	ND
Dioxathion	78-34-2	ND	ND	ND	ND	ND
Diphenylamine	12-39-4	X	X	X	X	X
5,5-Diphenylhydantoin	57-41-0	X	ND	ND	ND	X
1,2-Diphenylhydrazine	122-66-7	X	X	X	X	X
Di-n-octyl phthalate	117-84-0	X	X	X	X	X
Disulfoton	298-04-4	X	ND	ND	ND	X
Endosulfan I	959-98-8	X	X	X	X	X
Endosulfan II	33213-65-9	X	X	X	X	X
Endosulfan sulfate	1031-07-8	X	X	X	X	X
Endrin	72-20-8	X	X	X	X	X
Endrin aldehyde	7421-93-4	X	X	X	X	X
Endrin ketone	53494-70-5	X	X	X	X	X

		Appropriate Preparation Techniques *				
Compounds	**CAS No****	**3510**	**3520**	**3540/ 3541**	**3550**	**3580**
EPN	2104-64-5	X	ND	ND	ND	X
Ethion	563-12-2	X	ND	ND	ND	X
Ethyl carbamate	51-79-6	DC(28)	ND	ND	ND	X
Ethyl	62-50-0	X	ND	ND	ND	X
Famphur	52-85-7	X	ND	ND	ND	X
Fensulfothion	115-90-2	X	ND	ND	ND	X
Fenthion	55-38-9	X	ND	ND	ND	X
Fluchloralin	33245-39-5	X	ND	ND	ND	X
Fluoranthene	206-44-0	X	X	X	X	X
Fluorene	86-73-7	X	X	X	X	X
2-Fluorobiphenyl	321-60-8	X	X	X	X	X
2-Fluorophenol (surr)	367-12-4	X	X	X	X	X
Heptachlor	6-44-8	X	X	X	X	X
Heptachlor epoxide	1024-57-3	X	X	X	X	X
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclopenta	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Hexachlorophene	70-30-4	AW,CP	ND	ND	ND	CP
Hexachloropropene	1888-71-7	X	ND	ND	ND	X
Hexamethylphosphora	680-31-9	X	ND	ND	ND	X
Hydroquinone	123-31-9	ND	ND	ND	ND	X
Indeno(1,2,3-	193-39-5	X	X	X	X	X
Isodrin	465-73-6	X	ND	ND	ND	X
Isophorone	78-59-1	X	X	X	X	X
Isosafrole	120-58-1	DC(46)	ND	ND	ND	X
Kepone	143-50-0	X	ND	ND	ND	X
Leptophos	1609-90-5	X	ND	ND	ND	X
Malathion	121-75-5	HS(5)	ND	ND	ND	X
Maleic anhydride	108-31-6	HE	ND	ND	ND	X
Mestranol	72-33-3	X	ND	ND	ND	X
Methapyrilene	91-80-5	X	ND	ND	ND	X
Methoxychlor	72-43-5	X	ND	ND	ND	X
3-Methylcholanthrene	56-49-5	X	ND	ND	ND	X
4,4'-Methylenebis						
(2-chloroaniline)	101-14-4	OE,OS(	ND	ND	ND	LR
(N,N-dimethylaniline)	101-61-1	X	X	ND	ND	ND
Methyl	66-27-3	X	ND	ND	ND	X
2-Methylnaphthalene	91-57-6	X	X	ND	X	X
Methyl parathion	298-00-0	X	ND	ND	ND	X

		Appropriate Preparation Techniques *				
Compounds	**CAS No****	**3510**	**3520**	**3540/ 3541**	**3550**	**3580**
2-Methylphenol	95-48-7	X	ND	ND	ND	X
3-Methylphenol	108-39-4	X	ND	ND	ND	X
4-Methylphenol	106-44-5	X	ND	ND	ND	X
Mevinphos	7786-34-7	X	ND	ND	ND	X
Mexacarbate	315-18-4	HE,HS(	ND	ND	ND	X
Mirex	2385-85-5	X	ND	ND	ND	X
Monocrotophos	6923-22-4	HE	ND	ND	ND	X
Naled	300-76-5	X	ND	ND	ND	X
Naphthalene	91-20-3	X	X	X	X	X
Naphthalene-d8 (IS)		X	X	X	X	X
1,4-Naphthoquinone	130-15-4	X	ND	ND	ND	X
1-Naphthylamine	134-32-7	OS(44)	ND	ND	ND	X
2-Naphthylamine	91-59-8	X	ND	ND	ND	X
Nicotine	54-11-5	DE(67)	ND	ND	ND	X
5-Nitroacenaphthene	602-87-9	X	ND	ND	ND	X
2-Nitroaniline	88-74-4	X	X	ND	X	X
3-Nitroaniline	99-09-2	X	X	ND	X	X
4-Nitroaniline	100-01-6	X	X	ND	X	X
5-Nitro-o-anisidine	99-59-2	X	ND	ND	ND	X
Nitrobenzene	98-95-3	X	X	X	X	X
Nitrobenzene-d5 (surr)		X	X	X	X	X
4-Nitrobiphenyl	92-93-3	X	ND	ND	ND	X
Nitrofen	1836-75-5	X	ND	ND	ND	X
2-Nitrophenol	88-75-5	X	X	X	X	X
4-Nitrophenol	100-02-7	X	X	X	X	X
5-Nitro-o-toluidine	99-55-8	X	X	ND	ND	X
Nitroquinoline-1-oxide	56-57-5	X	ND	ND	ND	X
N-Nitrosodi-n-	924-16-3	X	ND	ND	ND	X
N-Nitrosodiethylamine	55-18-5	X	ND	ND	ND	X
N-	62-75-9	X	X	X	X	X
N-	10595-95-6	X	ND	ND	ND	X
N-	86-30-6	X	X	X	X	X
N-Nitrosodi-n-	621-64-7	X	X	X	X	X
N-Nitrosomorpholine	59-89-2	ND	ND	ND	ND	X
N-Nitrosopiperidine	100-75-4	X	ND	ND	ND	X
N-Nitrosopyrrolidine	930-55-2	X	ND	ND	ND	X
Octamethyl	152-16-9	LR	ND	ND	ND	LR
4,4'-Oxydianiline	101-80-4	X	ND	ND	ND	X
Parathion	56-38-2	X	X	ND	ND	X
Pentachlorobenzene	608-93-5	X	ND	ND	ND	X

		Appropriate Preparation Techniques *				
Compounds	**CAS No****	**3510**	**3520**	**3540/ 3541**	**3550**	**3580**
Pentachloronitrobenze	82-68-8	X	ND	ND	ND	X
Pentachlorophenol	87-86-5	X	X	X	X	X
Perylene-d12 (IS)		X	X	X	X	X
Phenacetin	62-44-2	X	ND	ND	ND	X
Phenanthrene	85-01-8	X	X	X	X	X
Phenanthrene-d10		X	X	X	X	X
Phenobarbital	50-06-6	X	ND	ND	ND	X
Phenol	108-95-2	DC(28)	X	X	X	X
Phenol-d6 (surr)		DC(28)	X	X	X	X
1,4-Phenylenediamine	106-50-3	X	ND	ND	ND	X
Phorate	298-02-2	X	ND	ND	ND	X
Phosalone	2310-17-0	HS(65)	ND	ND	ND	X
Phosmet	732-11-6	HS(15)	ND	ND	ND	X
Phosphamidon	13171-21-6	HE(63)	ND	ND	ND	X
Phthalic anhydride	85-44-9	CP,HE(	ND	ND	ND	CP
2-Picoline (2-	109-06-8	X	X	ND	ND	ND
Piperonyl sulfoxide	120-62-7	X	ND	ND	ND	X
Pronamide	23950-58-5	X	ND	ND	ND	X
Propylthiouracil	51-52-5	LR	ND	ND	ND	LR
Pyrene	129-00-0	X	X	X	X	X
Pyridine	110-86-1	ND	ND	ND	ND	ND
Resorcinol	108-46-3	DC,OE(	ND	ND	ND	X
Safrole	94-59-7	X	ND	ND	ND	X
Strychnine	57-24-9	AW,0S(	ND	ND	ND	X
Sulfallate	95-06-7	X	ND	ND	ND	X
Terbufos	13071-79-9	X	ND	ND	ND	X
Terphenyl-d14 (surr)	1718-51-0	X	X	ND	X	X
1,2,4,5-	95-94-3	X	ND	ND	ND	X
2,3,4,6-	58-90-2	X	ND	ND	ND	X
Tetrachlorvinphos	961-11-5	X	ND	ND	ND	X
Tetraethyl	3689-24-5	X	X	ND	ND	ND
Tetraethyl	107-49-3	X	ND	ND	ND	X
Thionazine	297-97-2	X	ND	ND	ND	X
Thiophenol	108-98-5	X	ND	ND	ND	X
Toluene diisocyanate	584-84-9	HE(6)	ND	ND	ND	X
o-Toluidine	95-53-4	X	ND	ND	ND	X
Toxaphene	8001-35-2	X	X	X	X	X
2,4,6-Tribromophenol	118-79-6	X	X	X	X	X
1,2,4-	120-82-1	X	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	ND	X	X

		Appropriate Preparation Techniques *				
Compounds	**CAS No****	**3510**	**3520**	**3540/ 3541**	**3550**	**3580**
2,4,6-Trichlorophenol	88-06-2	X	X	X	X	X
Trifluralin	1582-09-8	X	ND	ND	ND	X
2,4,5-Trimethylaniline	137-17-7	X	ND	ND	ND	X
Trimethyl phosphate	512-56-1	HE(60)	ND	ND	ND	X
1,3,5-Trinitrobenzene	99-35-4	X	ND	ND	ND	X
Tris (2,3-	126-72-7	X	ND	ND	ND	LR
Tri-p-tolyl phosphate	78-32-0	X	ND	ND	ND	X
O,O,O-Triethyl	126-68-1	X	ND	ND	ND	X

* See Sec. 1.2 of the reference method for other acceptable preparation methods.

** Chemical Abstract Service Registry Number

Key to Analyte List

IS = This compound may be used as an internal standard.
Surr = This compound may be used as a surrogate.
AW = Adsorption to walls of glassware during extraction and storage.
CP = Nonreproducible chromatographic performance.
DC = Unfavorable distribution coefficient (number in parenthesis is percent recovery).
HE = Hydrolysis during extraction accelerated by acidic or basic conditions (number in parenthesis is percent recovery).
HS = Hydrolysis during storage (number in parenthesis is percent stability).
LR = Low response.
ND = Not determined.
OE = Oxidation during extraction accelerated by basic conditions (number in parenthesis is percent recovery).
OS = Oxidation during storage (number in parenthesis is percent stability).
X = Greater than 70 percent recovery by this technique.

In addition to the sample preparation methods listed in the above analyte list, Method 3542 describes sample preparation for semivolatile organic compounds in air sampled by Method 0010, Method 3545 describes an automated solvent extraction device for semivolatiles in solids, and Method 3561 describes a supercritical fluid extraction of solids for PAHs .

Method 8270 can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols.

In most cases, Method 8270 is not appropriate for the quantitation of mulitcomponent analytes, e.g., Aroclors, Toxaphene, Chlordane, etc., because of limited sensitivity for those analytes. When these analytes have been identified by another technique, Method 8270 may be appropriate for confirmation of the presence of these analytes when concentration in the extract permits. Refer to Methods 8081 and 8082 for guidance on calibration and quantitation of multicomponent analytes such as the Aroclors, Toxaphene, and Chlordane.

The following compounds may require special treatment when being determined by this method:

1. Benzidine may be subject to oxidative losses during solvent concentration and its chromatographic behavior is poor.
2. Under the alkaline conditions of the extraction step from aqueous matrices, "-BHC, (-BHC, Endosulfan I and II, and Endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected.
3. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
4. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.
5. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.
6. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.
7. Pyridine may perform poorly at the GC injection port temperatures listed in the method. Lowering the injection port temperature may reduce the amount of degradation. The analyst needs to use caution if modifying the injection port temperature as the performance of other analytes may be adversely affected.
8. Toluene diisocyanate rapidly hydrolyses in water (half-life of less then 30 min.). Therefore, recoveries of this compound from aqueous matrices should not be expected. In addition, in solid matrices, toluene diisocyanate often reacts with alcohols and amines to produce urethane and ureas and consequently cannot usually coexist in a solution containing these materials.
9. In addition, analytes in the list provided above are flagged when there are limitations caused by sample preparation and/or chromatographic problems.
10. The estimated quantitation limit (EQL) of Method 8270 for determining an individual compound is approximately 660 µg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for ground water samples (see Table 4-1). EQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

4.3 Summary of Method

The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation (refer to Method 3500) and, if necessary, sample cleanup procedures (refer to Method 3600).

The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

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

The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

Table 4-1 Quality Control Summary Table

QC Type	Concentration Level	Frequency	Acceptance Criteria
Tune	Introduce 5 ng of DFTPP into the GC/MS System	Every 12 hours	Mass 51 30-60% of the base peak Mass 68 < 2% of mass 69 Mass 69 present Mass 70 < 2% of mass 69 Mass 127 40-60% of the base peak Mass 197 <1% of mass 198 Mass 198 Base peak Mass 199 5-9% of Mass 198 Mass 275 10-30% of the base peak Mass 365 >1% of the base peak Mass 441 Present and < mass 443 Mass 442 >40% of mass 198 Mass 443 17-23% of mass 442
SPCC	Mid-level in calibration curve range	Every 12 hours	Minimum mean RF for calibration: N-Nitroso-di-N-propylamine 0.05 Hexachlorocyclopentadiene 0.05 2, 4-Dinitrophenol 0.05 4-Nitrophenol 0.05 For routine runs: Minimum RFs above must be met
Initial Calibration	Consisting of at least 5 standard concentrations per analyte.	When first using this method on an instrument, after major instrument maintenance, or when indicated by a change in instrument response.	% RSD for each analyte should be less than 15% if average RF used to calculate data; Otherwise, use linear or quadratic fit using the data system.
LMB	Reagent Water prepared and analyzed as a sample.	One per analytical run or group of 20 samples.	No analytes of interest present at or above the MDL, or less than level defined in the labs quality assurance plan, or less than 5% of the regulatory limit for that analyte.

QC Type	Concentration Level	Frequency	Acceptance Criteria
CCC	Mid-level in calibration curve range	One analyzed per group of 20 samples or one per work shift (Every 12 hours)	% RSD must be less than 30% for the CCC compounds in initial calibration: Phenol 1,4-Dichlorobenzene 2-Nitrophenol 2,4-Dichlorophenol Hexachlorobutadiene 4-chloro-3-methyl phenol 2,4,6-Trichlorophenol Acenapthene Pentachlorophenol Fluoroanthene Di-n-octyl phthalate Benzo(a) pyrene +/-20% Recovery for routine runs
IS	1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenatpthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12 are all recommended. Others can be used.	Run in every sample. The IS is evaluated for recovery.	Area response of IS in CCCs must be within –50% to +100% from that in the mid-point std level of the most recent calibration.
SS	2-Fluorobiphenyl, Phenol-d5, Nitrobenzene-d5, 2,4,6-Tribromophenol, p-Terphenyl-d14, 2-Fluorophenol are recommended. Others can be used.	Run in every sample.	Recovery should be 70-130%, however a laboratory must generate specific statistical limits according to section 8.6 of Method 8000B.
LCS	A clean matrix similar to the sample, spiked mid-range of calibration curve.	One analyzed per group of 20 samples or one per work shift	Limits are 70-130% recovery or based on statistical limits derived by the laboratory.
QCS	All of the analytes of interest at mid-level calibration range	Quarterly.	Same as CCC. Used as an external check of the calibration solutions.
MS/MSD	Mid-range in calibration	One MS/MSD per set of 20 samples.	70-130 % recovery limits, or lab determined statistical limits according to Method 8000B.
Duplicate sample	Lab Duplicate	At a frequency of one per 20 samples	% RPD within 20% for the results. Lab may run an MS and a lab duplicate instead of an MS/MSD, one set per 20 samples.
DOC	4 reagent water spikes at mid-level concentration	Initially, annually and with each new technician.	Mean percent recovery for each analyte must be 70-130%, and the RSD must be less than <20%. See performance data per analyte in 8270D method.
MDL	7 reagent water spikes. Typical are 0.5 to 10 ppb	Annually.	Calculate values for mean accuracy and % RSD. No precision and accuracy limits apply.

4.4 Sample Preparation 3000 Series Methods List

Matrix	***Methods***
Air	3542
Water	3510, 3520, 3535
Soil/sediment	3540, 3541, 3545, 3550, 3560, 3561
Waste	3540, 3541, 3545, 3550, 3560, 3561, 3580

4.4.1 Extract Cleanup Methods List

Analytes of Interest	***Methods***
Aniline & aniline derivatives	3620
Phenols	3630, 3640, 8041
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3610, 3620, 3630, 3660, 3665
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorus pesticides	3620
Petroleum Waste	3611, 3650
All base, neutral, and acid priority pollutants	3640

4.5 Analytical Section

In this section parameters for the equipment, accessories, and supplies are specified to assure optimum performance of the analysis. While new products may improve overall results, the accessories specified here were carefully selected to deliver the best analytical data. Deviation from the suggested equipment, supplies or conditions may result in lost performance.

4.5.1 Equipment and Supplies

Analytical Column

FactorFour VF-5ms Fused Silica Column: 30 m × 0.25 mm ID × 0.25 μm film thickness column [VPN CP8944].

VPN 03-930824-00 Semi-Volatile Consumables Kit. Kit includes:

Semi-Volatile Organic Chemicals Parts and Supplies for EPA Methods 525.2 & 8270D **03-930824-90**		
Syringe	03-925902-05	10 µL conical tipped needle
Injector Parts		
1177 Split/Splitless Injector	RT210462145	Insert 4 mm ID open single gooseneck liner, Siltek, -fritted
	CR298713	BTO septa pkg of 50
	8850103100	The o-ring that seals the 1177 injector insert pkg of 25
1079 PTV Injector	RT217092145	Insert for 1079, Siltek
	CR298777	BTO septa for the 1079 injector pkg of 50
	03-925342-01	Graphite ferrule that seals the 1079 injector insert pkg of 10
Ferrules	2869458001	For 30 m columns pkg of 10 40/60 graphite/Vespel
Vials	03-926120-16	Ultra vials and septa 2 mL amber glass wide opening screw

GC/MS Systems

A 210-MS/220-MS ion trap GCMS or a 300/320-MS quadrupole GC/MS equipped with an 1177 injector and Electronic Flow Controller (EFC) type 21 [Injector: VPN 45-11101-01]. The sample introduction takes place in split mode. The injector must be equipped with a 4 mm, Siltek Frited insert [VPN RT210462145]. For best results, use the BTO septa [VPN: CR298713] for the injector.

Model 8400 AutoSampler. Use the Ultra vials and septa [VPN 392612016].

GC/MS Interface

Capillary direct into the mass spectrometer.

NOTE: *Always reduce the column and the MS transfer line temperatures if the column flow is interrupted for maintenance.*

4.5.2 Data Analysis and Calculations

Fully calibrated methods with data handling parameters (integration, identification, and quantification) for 64 commonly analyzed compounds by 8270D are on the Varian Environmental MS Applications Manual CD, included with a hard copy of this manual. For Method 8270D there are two method files (.mth files) and two raw data files (.SMS files) representing the two different instrument configurations. All of these are in a subdirectory on the CD called EPA8270. The table below describes which files are associated with which instrument configuration:

Instrument Configuration	**Method File (.mth)**	**Data File (.SMS)**
210-MS or 220-MS	8270-210_220MS.mth	8270_200trap.SMS
300 or 320-MS	8270-300_320MS.mth	8270_300quad.xms

Choose the appropriate method and example data file and make a copy of them. The operator will likely need to make changes in retention times or some other parameters for further optimization.

Tuning the MS

To assure that the DFTPP tune criteria specified in the method is met, use the suggested acquisition parameters in Section 4.6.2. The amount of DFTPP entering the detector should be about 5 ng.

NOTE: *Ensure that mass calibration (when necessary) is performed at the column analytical flow, NOT under pressure pulse conditions.*

Analytes Monitored, Calibration Levels, Injection Sequence

While Method 8270D lists in Section 4.1 a large number of analytes that may be monitored by the procedures specified in the method, the actual number of analytes measured will depend on the laboratory requirements. Only a subset of the analytes listed in Section 4.2 can be monitored in a single analysis (8270C, Section 5.6.1 in the reference method).

Adjust the retention times and integration parameters of the analytes based on the calibration runs performed on the given instrument.

Calibration Levels and Ranges

EPA Method 8270D does not specify the calibration levels or ranges to be used other than at least 5 calibration levels covering the typical sample concentration range should be performed.

The attached methods include nine calibration levels covering a calibration range from 1-160 ppm for most compounds. Some compounds may have less depending upon their response in the analytical system.

Injection Sequence

EPA method 8270D does not specify the injection sequence of calibration standards. For certain reactive compounds, such as 2,4-nitrophenol, 2-methyl-4,6-dinitrophenol and pentachlorophenol, reverse injection from high concentration to low concentration may reduce degradation and adsorption of these compounds on active sites during analysis. However, the results generated in this manual were injected from low to high concentration.

Integration Parameters

The integration parameters in the methods were selected to assure reliable integration even at the lowest calibration level. These parameters may need to be adjusted and the analyst should review the integration parameters for each analyte using the lowest level calibration data file. The most commonly adjusted parameters are:

- Peak Window
- Peak Width
- Peak Area Reject
- Slope Sensitivity (occasionally)
- Peak Smoothing
- Manual integration
- Spectra match criteria

Review the MS Workstation Software Reference Manual section entitled "Guidelines for Optimizing Method Integration Parameters" to clarify integration topics and processes. “Guidelines for Optimizing Integration Parameters” can be found in the “Quantitation Method” section of the Software Reference Manual.

Quantitation Parameters

Once the initial calibration is complete the analyst must review the curve fitting parameters for each component to assure proper quantitation of samples to be processed.

Curve Fitting, Handling the Origin, Regression Weight Factors

Besides the average RRF calculations, linear, quadratic or cubic curve fitting are also allowed as stated in sections 7.5.2 and 7.5.3 of EPA Method 8000B.

- Average RRF:

  For the Varian Workstation, specify "linear curve fitting with forced zero and $1/x^2$, or $1/nx^2$ regression weighting”. These parameters will deliver calculations based on average RRF.

  Conditions to use the Average RRF calculations:

  %RSD for each analyte <u>should</u> be below 15%, **or** the average %RSD of all analytes <u>must</u> be below 15% (section 7.5.1.2 of Method 8000B), and the %RSD of the CCC compounds <u>must</u> be below 30%.
- Linear (minimum 5 levels)

  (Correlation coefficient should be 0.99 or greater for each analyte)
- Quadratic (minimum 6 levels)

  (Correlation coefficient should be 0.99 or greater for each analyte)
- Cubic (minimum 7 levels)

  (Correlation coefficient should be 0.99 or greater for each analyte)

Handling of the Origin

- Ignore (if linear, quadratic or cubic curve fitting is selected)
- Force (if average RRFs method is used for calculations)

Selection of the Regression Weighting Factor

None
1/n
1/x
1/nx
$1/x^2$
$1/nx^2$

The most often used factors are $1/x^2$ and $1/nx^2$ for trace level analysis.

Review the Calibration Curve for each analyte and specify the curve fitting parameters based on the collected data.

Improper selection of these parameters will undermine the accuracy of the reported results for unknown samples or quality control samples.

4.6 Reagents and Standards

4.6.1 Stock Standards

Calibration standards are available in convenient packaging and concentrations. A few suggestions may make the preparation of calibration solutions easier:

- For maximum flexibility and performance use the 1000 – 4000 μg/mL standard concentrations. This level will allows for easy dilutions.
- Limit the number of standard vials; purchase standards that have the highest number of analytes in every mixture.

The data objectives will determine which analytes will be included in the target list and what concentration range will be used for calibration. Standards for the commonly monitored target analytes are listed below along with internal standard, surrogate standard, calibration check compounds (CCCs), system performance check compounds (SPCCs) mixtures, and matrix spike solutions.

Internal Standards

[VPN] ULUS108N 4000 μg/mL in methylene chloride, 1 mL

Acenaphthene-d_{10}
Chrysene-d_{12}
1,4-Dichlorobenzene-d_4
Naphthalene-d_8
Perylene-d_{12}
Phenathrene-d_{10}

GCMS Tune Standards

[VPN] ULGCM150 1000 μg/mL in methylene chloride, 4 x 1 mL

Decafluorotriphenylphosphine (DFTPP)
Benzidine
Pentachlorophenol
4,4’- DDT

Calibration and Analyte Standards

Convenient, All-In-One Solutions

[VPN] ULSVM8270 Semivolatiles Mix #1, 64 analytes

1000 μg/mL in methylene chloride/benzene 3:1, 4 x 1 mL

Acenaphthene
Acenaphthylene
Anthracene
Azobenzene
Benz[a]anthracene
Benzo[b]fluoranthene
Benzo [k]fluoranthene
Benzo[ghi]perylene
Benzo[a]pyrene
bis-(2-chloroethoxy)methane
bis-(2-chloroethyl) ether
Dibenz [a,h] anthracene
Dibenzofuran
Di-*n*-butyl phthalate
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
2,4-Dichlorophenol
Diethyl phthalate
2,4-Dimethylphenol
Dimethyl phthalate
2,4-Dinitrophenol
2-Methyl-4,6-dinitrophenol
2-Methylnaphthalene
2-Methylphenol
4-Methylphenol
Naphthalene
2-Nitroaniline
3-Nitroaniline
4-Nitroaniline
Nitrobenzene
2-Nitrophenol
4-Nitrophenol

Calibration and Analyte Standards

Convenient, All-In-One Solutions

[VPN] ULSVM8270 Semivolatiles Mix #1, 64 analytes

1000 μg/mL in methylene chloride/benzene 3:1, 4 x 1 mL

bis-(2-ethylhexyl) phthalate
bis-(2-chloroisopropyl) ether
4-Bromophenyl phenyl ether
Butylbenzyl phthalate
Carbazole
4-Chloroaniline
4-Chloro-3-mehtylphenol
2-Chloronaphthalene
2-Chlorophenol
4-Chlorophenyl phenyl ether
Chrysene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Di-*n*-octyl phthalate
Fluoranthene
Fluorene
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Ideno[1,2,3-cd]pyrene
Isophorone
N-nitrosodimethylamine
N-nitrosodi-*n*-propylamin
Pentachlorophenol
Phenanthrene
Phenol
Pyrene
1,2,4-Trichlorobenzene
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol

Calibration and Analyte Standards

Convenient, All-In-One Solutions

[VPN] ULSVM8271 Semivolatiles Mix #2, 35 analytes

1000 μg/mL in methylene chloride, 4 x 1 mL

Acetophenone
2-Acetylaminofluorene
4-Aminobiphenyl
Aniline
Benzyl alcohol
2,6-Dichlorophenol
p-(Dimethylamino)azobenzene
7,12-Dimethylbenz[a]anthracene
m-Dinitrobenzene
Dinoseb (DNBP)
Diphenylamine
Ethyl methanesulfonate
Hexachloropropene
Isosafrole
3-Methylcholanthrene
Methyl methanesulfonate
3-Methylphenol *(m-cresol)*
1-Naphthylamine
2-Naphthylamine
N-nitrosodi-n-butylamine
N-nitrosodiethylamine
N-nitrosomethylethylamine
N-nitrosomorpholine
N-nitrosopiperdine
N-nitrosopyrrolidine
5-Nitro-*o*-toluidine
Pentachlorobenzene
Pentachloroethane
Pentachloronitrobenzene
Phenacetin
Safrole
1,2,4,5-Tetrachlorobenzene
2,3,4,6-Tetrachlorophenol
o-Toluidine
1,3,5-Trinitrobenzene

Smaller Subgroups of the 8270 Target Analyte List

[VPN] ULSVM8271 Semivolatiles Mix #2, 35 analytes

1000 μg/mL in methylene chloride, 4 x 1 mL

Acenaphthene
Acenaphthylene
Anthracene
Benz[a]anthracene
Benzo[b]fluorathene
Benzo[g,h,i]pyrene
Benzo[a]pyrene
Chrysene
Dibenz[a,h]pyrene
Fluoranthene
Indeno[1,2,3-cd]pyrene
Naphthalene
Phenathrene
Pyrene

[VPN] ULSVM8271 Semivolatiles Mix #2, 35 analytes

1000 µg/mL in methylene chloride, 4 x 1 mL

Benzo[k]fluoranthene
Fluorene

[VPN] ULUS116N PAH Mix #2, 2 analytes

2000 µg/mL in methylene chloride/benzene 1:1, 1 x 1 mL

7,12-Dimethylbenz[a]anthracene
3-Methylcholanthrene

[VPN] ULUS111 Chlorinated Hydrocarbon Mix, 13 analytes

2000 µg/mL in methylene chloride, 1 x 1 mL

2-Chloronaphthalene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocylopentadiene
Hexachloroethane
Hexachloropropene
Pentachlorobenzene
Pentachloroethane
1,2,4,5-Tetrachlorobenzene
1,2,4-Trichlorobenzene

[VPN] ULUS104N Toxic Subtances Mix #2, 8 analytes

2000 µg/mL in methylene chloride, 1 x 1 mL

Aniline
Benzyl alcohol
4-Chloroaniline
Dibenzofuran
2-Methylnaphthalene
2-Nitroaniline
3-Nitroaniline
4-Nitroaniline

[VPN] ULUS114 Base/Neutral Mix #3, 13 analytes

2000 µg/mL in methylene chloride, 1 x 1 mL

2-Acetylaminofluorene
4-Aminobiphenyl
3,3’-Dichlorobenzidine
p-(Dimethylamino)azobenzene
3,3’-Dimethylbenzidine
α,α-Dimethylphenethylamine
Diphenylamine
1-Naphthylamine
2-Naphthylamine
5-Nitro-*o*-toluidine
Phenacetin
p-Phenylenediamine
o-Toluidine

[VPN] ULUS115 Base/Neutral Mix #4, 13 analytes

2000 µg/mL in methylene chloride, 1 x 1 mL

Acetophenone
m-Dinitrobenzene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Ethyl methanesulfonate
Isophorone
Isosafrole
Methyl methanesulfonate
1,4-Naphthoquinone
Nitrobenzene
Pentachloronitrobenzene
Safrole
1,3,5-Trinitrobenzene

[VPN] ULUS107N Phenols Mix, 11 analytes

2000 μg/mL in methylene chloride, 1 x 1 mL

4-Chloro-3-methylphenol
2-Chlorophenol
2,4-Dichlorophenol
2,4-Dimethylphenol
2,4-Dinitrophenol
2-Methyl-4,6-dinitrophenol
2-Methyl-4,6-dinitrophenol
2-Nitrophenol
4-Nitrophenol
Pentachlorophenol
Phenol
2,4,6-Trichlorophenol

[VPN] ULUS117N Phenols Mix #2, 8 analytes

2000 μg/mL in methylene chloride, 1 x 1 mL

o-Ccresol
m-Cresol
p-Cresol
2,6-Dichlorophenol
Dinoseb (DNBP)
Hexachlorophene
2,3,4,6-Tetrachlorophenol
2,4,5-Trichlorophenol

[VPN] ULUS110 Ethers and Phthalates Mix, 11 analytes

2000 μg/mL in methylene chloride, 1 x 1 mL

bis-(2-Chloroethoxy)methane
bis-(2-Chloroethyl)ether
bis-(2-Ethylhexyl)phthalate
bis-(2-Chloroisopropyl)ether
4-Bromophenyl phenyl ether
Butyl benzyl phthalate
4-Chlorophenyl phenyl ether
Diethyl phthalate
Dimethyl phthalate
Di-*n*-butyl phthalate
Di-*n*-octyl phthalate

[VPN] ULUS113N Nitrosamines Mix, 9 analytes

2000 μg/mL in methylene chloride, 1 x 1 mL

N-nitrosodi-*n*-butylamine
N-nitrosodiethylamine
N-nitrosodimethylamine
N-nitrosodiphenylamine
N-nitrosodi-*n*-propylamine
N-nitrosomethylethylamine
N-nitrosomorpholine
N-nitrosopiperidine
N-nitrosopyrrolidine

[VPN] ULUS112B, Chlorinated Pesticides Mix, 17 analytes

2000 μg/mL in acetone, 1 x 1 mL

Aldrin
α-BHC
β-BHC
δ-BHC
γ-BHC
4,4'-DDD
4,4'-DDE
4,4'-DDT
Dieldrin
Endosulfan I
Endosulfan II
Endosulfan sulfat
Endrin
Endrin aldehyde
Heptachlor
Heptachlor epoxide (B)
Methoxylchlor

[VPN] ULUS119 Organophosphorous Pesticides Mix, 9 analytes

2000 μg/mL in methylene chloride, 1 x 1 mL

Dimethoate
Disulfoton
Famphur
Thionazin
O,O,O-Triethyl phosphorothioate
Methyl parathion
Parathion
Phorate
Sulfotepp

[VPN] ULUS118 Pesticide Mix, 6 analytes

2000 µg/mL in methylene chloride, 1 x 1 mL

Aramite
Chlorobenzilate
Diallate
Isodrin
Kepone
Pronamide

[VPN] ULUS120AN Pyridines Mix, 4 analytes

2000 µg/mL in acetone, 1 x 1 mL

Methapyrilene
4-Nitroquinoline-1-oxide
2-Picoline
Pyridine

Surrogate Standards

[VPN] ULISM280N Base Neutral Surrogate Mix, 3 analytes

1000 µg/mL in methylene chloride, 4 x 1 mL

Nitrobenzene-d_5
2-Fluorobiphenyl
p-Terphenyl-d_{14}

[VPN] ULISM290N Acid Surrogate Mix, 3 analytes

2000 µg/mL in methanol, 4 x 1 mL

2-Fluorophenol
Phenol-d_5
2,4,6-Tribromophenol

Matrix Spiking and Laboratory Control Standards (LCS)

[VPN] ULCLP300N Base/Neutral Matrix Spiking Solution

1000 µg/mL in methylene chloride, 4 x 1 mL

Acenaphthene
1,4-Dichlorobenzene
2,4-Dinitrotoluene
N-nitrosodi-*n*-propylamine
Pyrene
1,2,4-Ttrichlorobenzene

[VPN] ULCLP400N Acid Matrix Spiking Solution

2000 µg/mL in methanol, 4 x 1 mL

4-Chloro-3-methylphenol
2-Chlorophenol
4-Nitrophenol
Pentachlorophenol
Phenol

System Performance Check Compounds Mixture

[VPN] ULCLP320 SPCC Mix, 4 analytes

1000 µg/mL in methylene chloride, 4 x 1 mL

2,4-Dinitrohpenol
4-Nitrophenol

[VPN] ULCLP320 SPCC Mix, 4 analytes

1000 µg/mL in methylene chloride, 4 x 1 mL

Hexachlorocyclopentadiene
N-nitrosodi-*n*-propylamine

Calibration Check Compound Mixtures

[VPN] ULCLP310 Base Calibration Check Mix

1000 µg/mL in methylene chloride, 4 x 1 mL

Acenaphthene
Benzo[a]pyrene
1,4-Dichlorobenzene
Di-*n*-octyl phthalate
Fluoranthene
Hexachlorobutadiene
N-nitrosodiphenylamine

[VPN] ULCLP410 Acid Calibration Check Mix

2000 µg/mL in methanol, 4 x 1 mL

4-Chloro-3-methylphenol
2,4-Dichlorophenol
2-Nitrophenol
Phenol
Pentachlorophenol
2,4,6-Trichlorophenol

4.7 Set-up of Instrumental Conditions

Fully calibrated methods with data handling parameters (integration, identification, and quantification) for common 8270D analytes are on the Varian Environmental MS Applications Manual CD, included with this manual. Refer to the EPA8270 subdirectory and copy method on your analytical system to start. See Section 4.5.2.

4.7.1 CP-8400 AutoSampler Conditions

Syringe Size (µL): 10
Injection Mode: Std Split/Splitless
Solvent Depth (%): 90
Sample Depth (%): 95

Default Clean Vial: I
Default Clean Volume (µL): 5.0
Default Clean Strokes: 1
Default Clean Speed (µL/sec): 5.0

Clean Mode Pre-Inj. Solvent Flushes: 2

Clean Mode Pre-Inj. Sample Flushes: 1

Clean Mode Post-Inj. Solvent Flushes: 1

Clean Mode Clean Solvent Source: I

For the 8400 AutoSampler use the Ultra vials and septa. [VPN 392612016]. The recommended syringe for 8400 Autosampler is Hamilton 701N 10 µL (26s/2"/2) [VPN 03-925902-05] (**conical style needle point**)

4.7.2 Varian 210-MS/220-MS GC/MS Conditions

NOTE: *For Septum Purge Flow Calibration: Use 3-5 mL/min, calibrated at the pressure pulse condition*

Column Oven Temperature Program				
Temp (°C)	**Rate (°C /min)**	**Hold (min)**	**Total (min)**	
40	NA	2.0	2.0	
220	10.0	2.0	22.0	
300	15.0	1.0	28.3	
320	25.0	3.87	33.0	

Injector Conditions		Injector Split States		
Temp	270 °C	Time(min)	Split State	Split Ratio
Col Flow	1.2 mL/min	Initial	ON	20
Pressure Pulse	40 psi for 0.4 min	20.0	ON	20
Constant Flow	ON			

MS Conditions				
Segment	Start (min)	End (min)	Low Mass (m/z)	High Mass (m/z)
Fil/Delay	0.00	3.00	NA	NA
Analysis	3.00	33.00	45	450

Target TIC	6000	µscans averaged	3
Max Ion Time	25000 µsec	Multiplier Offset	0 V
Background Mass	44 m/z	Emission Current	10-12 µamps
Mass Defect	0	Manifold Temp	60 °C
Trap Temp	210-230 °C	Transfer line Temp	280 °C
Rf Dump	650 m/z	Scan Time	0.70 sec/scan

Suggested Segment Breaks and Ion Time Factors for DFTPP Tuning			
Low mass (m/z)	High mass (m/z)	Ionization Storage Level	Ionization Factor
10	75	37	120
76	130	37	240
131	270	37	90
271	332	37	45
333	399	37	70
400	650	37	22

NOTE: *8270D allows use of SIM or SIS detection techniques (Section 4.6.3 of 8270D). Use SIS to eliminate excessive background and/or to increase sensitivity if necessary.*

4.7.3 Varian 300/320-MS GC/MS Conditions

Column Oven Temperature Program				
Temp (°C)	Rate (°C /min)	Hold (min)	Total (min)	
45	NA	2.0	2.0	
220	15.0	5.0	18.67	
300	10.0	2.0	28.67	
310	15.0	1.0	30.33	
Injector Conditions		**Injector Split States**		
Temp	280 °C	Time(min)	Split State	Split Ratio
Column Flow	1.5 mL/min	Initial	ON	50
Pressure Pulse	40 psi for 0.5 min			
Constant Flow	ON			

MS Conditions				
Segment	Start (min)	End (min)	Low Mass (m/z)	High Mass (m/z)
Fil/Delay	0.00	3.00	NA	NA
Analysis	3.00	33.00	45	450
Scan Time	0.250 sec	Source Temperature	220 C	
SIM Width	0.70 amu	EDR	ON	
Quad 1	Calibrated	Emission Current	50 uamps	
Quad 2	Calibrated	Manifold Temp	40 C	
Trap Temp	210-230 C	Transfer line Temp	280 C	

NOTE: *8270D allows use of SIM detection techniques (Section 4.6.3 of 8270D). Use SIM to eliminate excessive background and/or to increase sensitivity if necessary.*

Use a standard EI ion volume in the source.

Peak Table of Suggested Quantitation Ions

Peak #	RT	Compound Name	Surrogate (SS)	IS	Quan Ion
1	3.224	N-nitrosodimethylamine		IS I	74
2	7.454	Phenol		IS I	94
3	7.637	Bis(2-chloroethyl) ether		IS I	93
4	7.685	Phenol, 2-chloro-		IS I	128
5	8	Benzene, 1,3-dichloro-		IS I	146
6	8.128	1,4-Dichlorobenzene-d4	IS I		115
7	8.163	Benzene, 1,4-dichloro-		IS I	146
8	8.471	Benzene, 1,2-dichloro-		IS I	146
9	8.715	o-Cresol		IS I	107
10	8.761	bis(2-chloroisopropyl) e		IS I	45
11	9.036	N-nitrosodi-n-propylamin		IS I	70
12	9.054	p-cresol		IS I	107
13	9.177	Ethane, hexachloro-		IS II	201
14	9.375	Benzene, nitro-		IS II	77
15	9.904	Isophorone		IS II	82
16	10.08	Phenol, 2-nitro-		IS II	139
17	10.232	Phenol, 2,4-dimethyl-		IS II	107
18	10.455	Bis(2-chloroethoxy) meth		IS II	93
19	10.611	Phenol, 2,4-dichloro-		IS II	162
20	10.792	Benzene, 1,2,4-trichloro		IS II	182
21	10.902	Naphthalene-d8	IS II		136
22	10.949	Naphthalene		IS II	128
23	11.144	p-Chloroaniline		IS II	127
24	11.262	Hexachlorocyclopentadien		IS III	225
25	12.319	4-chloro-3-methylphenol		IS II	107
26	12.563	Naphthalene, 1-methyl-		IS II	141
27	12.937	1,3-Cyclopentadiene, 1,2		IS III	237
28	13.267	Phenol, 2,4,6-trichloro-		IS III	196
29	13.33	Phenol, 2,4,5-trichloro-		IS III	196
30	13.699	Naphthalene, 1-chloro-		IS III	162
31	14.017	2-Nitroaniline		IS III	108
32	14.492	Dimethyl phthalate		IS III	163
33	14.625	2,6-dinitro-toluene		IS III	165
34	14.665	Acenaphthylene		IS III	152
35	15.009	Acenaphthene-d10	IS III		164
36	15.083	Acenaphthene		IS III	153
37	15.25	Phenol, 2,4-dinitro-		IS III	184
38	15.464	4-Nitrophenol		IS III	109
39	15.5	Dibenzofuran		IS III	168

Peak #	**RT**	**Compound Name**	**Surrogate (SS)**	**IS**	**Quan Ion**
40	15.564	Benzene, 1-methyl-2,4-di		IS III	165
41	16.181	Diethyl Phthalate		IS III	149
42	16.312	Fluorene		IS III	165
43	16.374	4-Chlorophenyl phenyl et		IS III	204
44	16.444	4-Nitroaniline		IS III	108
45	15.003	3-Nitroaniline		IS III	138
46	16.508	Phenol, 2-methyl-4,6-dinitro		IS IV	198
47	16.742	Azobenzene		IS IV	77
48	17.528	Benzene, 4-bromo-1-pheno		IS IV	248
49	17.595	Hexachlorobenzene		IS IV	284
50	18.087	Phenol, pentachloro-		IS IV	266
51	18.525	Phenanthrene-d10	IS IV		188
52	18.579	Phenanthrene		IS IV	178
53	18.698	Anthracene		IS IV	178
54	19.151	Carbazole		IS IV	167
55	20.101	Di-n-butyl phthalate		IS IV	149
56	21.699	fluoranthene		IS IV	202
57	22.444	Pyrene		IS IV	202
58	24.495	Benzyl butyl phthalate		IS V	149
59	25.55	Chrysene		IS V	228
60	25.571	Chrysene-d12	IS V		240
61	25.625	Benz[a]anthracene			228
62	25.817	bis-(2-ethylhexyl) phthalate		IS V	149
63	27.023	Di-n-octyl phthalate		IS VI	149
64	27.559	Benzo[b]fluoranthene		IS VI	252
65	27.608	Benzo[k]fluoranthene		IS VI	252
66	28.156	Benzo[a]pyrene	IS VI		252
67	28.276	Perylene-d12		IS VI	264
68	29.979	Indeno[1,2,3-cd]pyrene		IS VI	276
69	30.02	Dibenz[a,h]anthracene		IS VI	278
70	30.432	Benzo[ghi]perylene		IS VI	276

4.8 Analytical Results

4.8.1 Sample Chromatograms

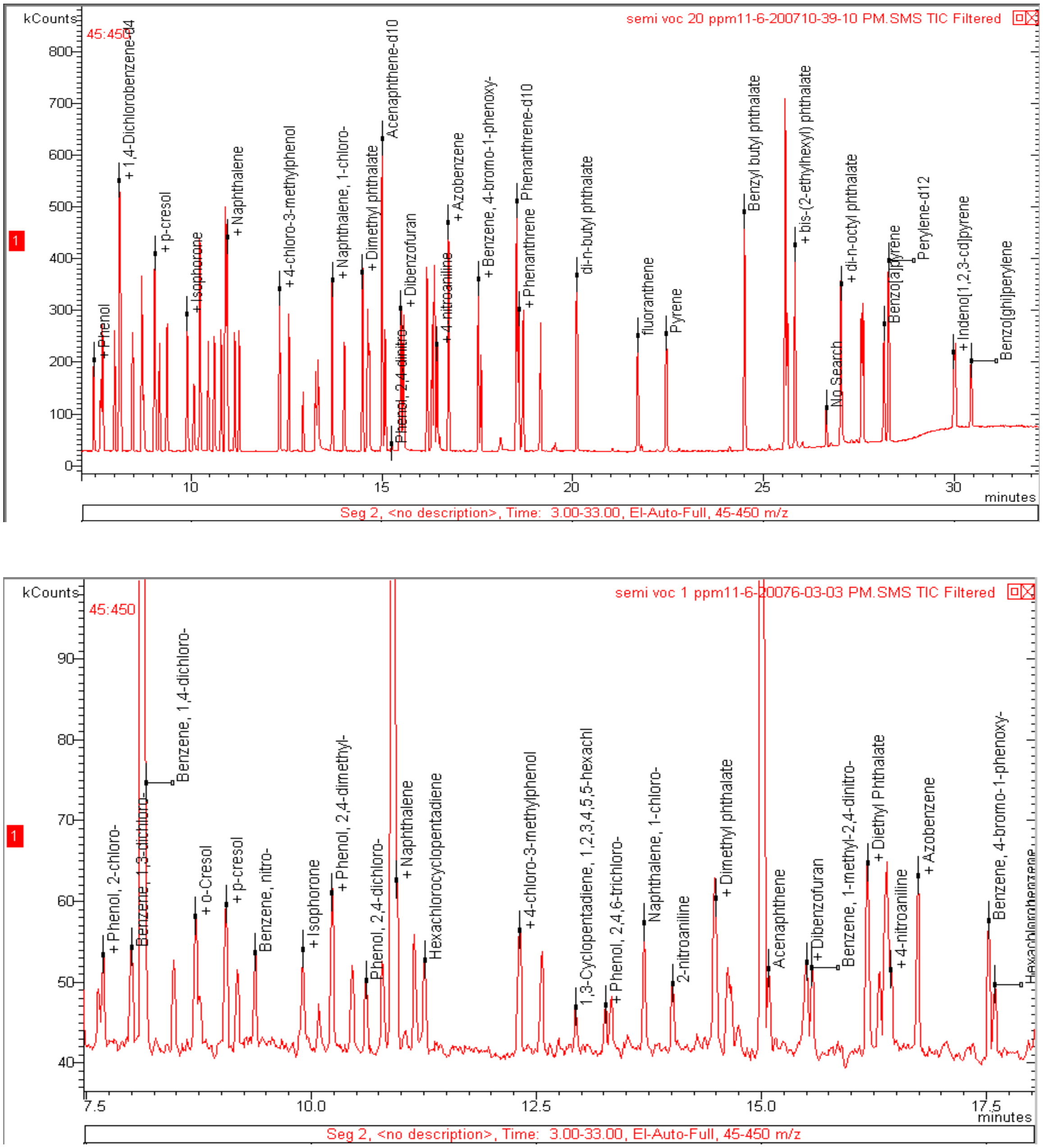


*Figure 4.1: **210-MS/220-MS**: Top: TIC of 20 ppm calibration standard for 8270D. Bottom: TIC of 1 ppm calibration standard, 7.5 to 18 min. Internal and surrogate standards are at a concentration of 40 ppm in both standards.*

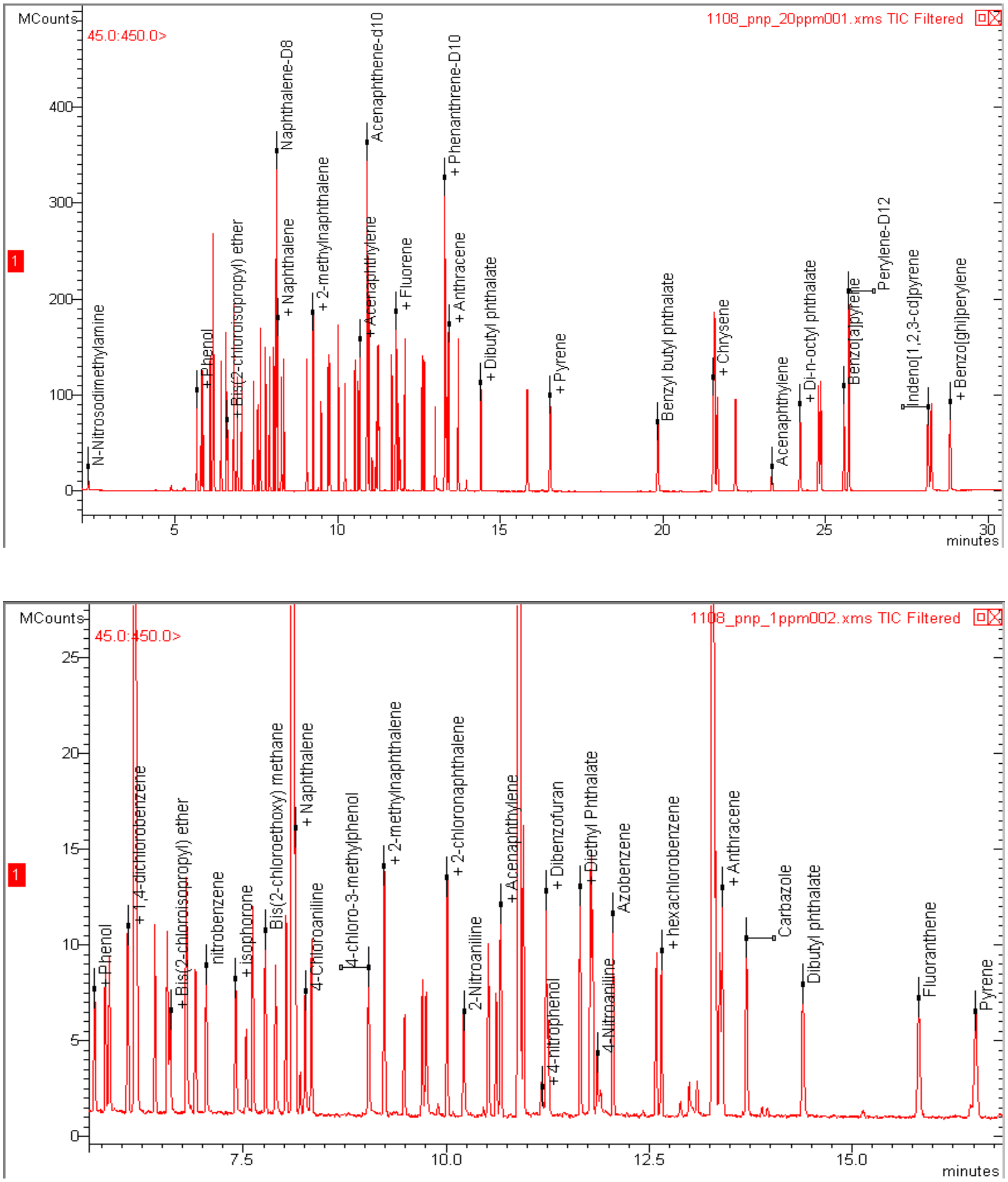


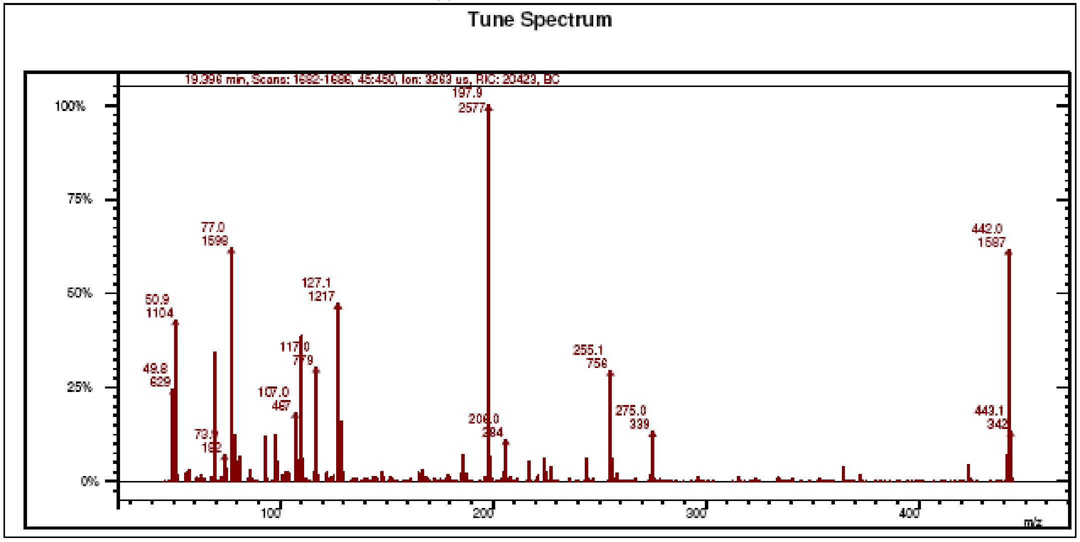
*Figure 4.2: **300/320-MS**: Top: TIC of 20 ppm calibration standard for 8270D. Bottom: TIC of 1 ppm calibration standard, 6.0 to 18 min. Internal and surrogate standards are at a concentration of 40 ppm in both standards.*

4.8.2 Tune Verification Samples

DFTPP 8270D Tune Report and Tune Statistics on the 210-MS/220-MS

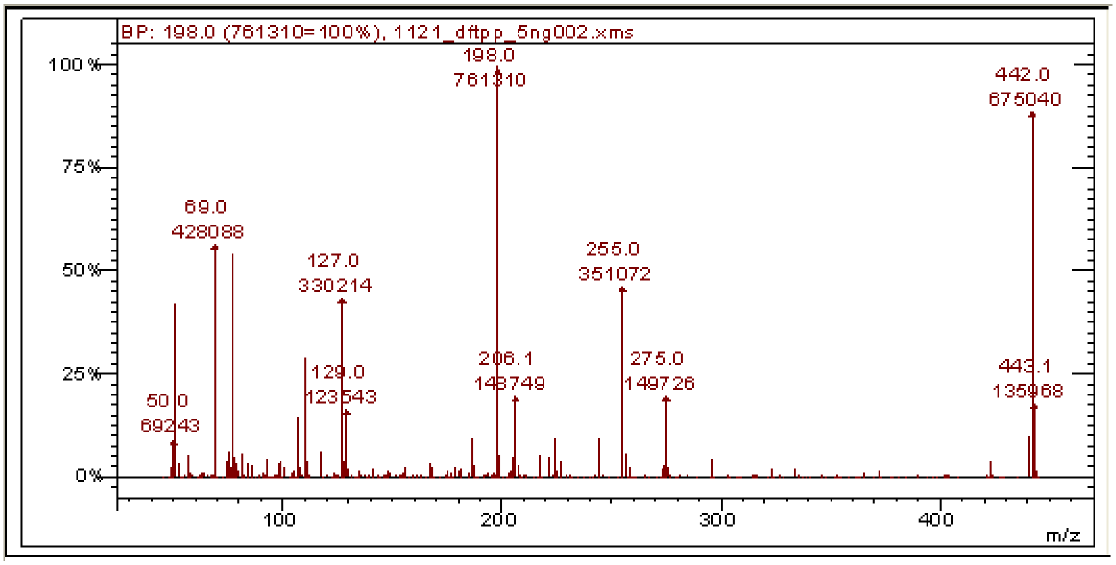
Acquisition Date: 11/7/2007 11:18:24 AM

Data File Name: c:\semi voc 8270-110607\dftpp_11-7-2007.sms



m/z	*Acceptance Criterion*	*Value*	*P/F*
51	30-60% of m/z 198	42.84	Pass
69	present	34.38	Pass
70	less than 2% of m/z 69	0	Pass
127	40 to 60% of m/z 198	47.23	Pass
197	<1% of m/z 198	0.93	Pass
198	base peak	100.00	Pass
199	5-9% of m/z 198	6.67	Pass
275	10-30% of m/z of 198	13.15	Pass
365	>1% of m/z 198	4	Pass
441	present and <m/z 443	51.75	Pass
442	>40% of m/z 198	61.58	Pass
443	17-23% of m/z 442	21.55	Pass

DFTPP 8270D Report and Tune Statistics on the 300/320-MS



Lab File ID 1121_dftpp_5ng002.xms

Injection Date: 11/21/2007

Injection Time: 11:57

m/z	*Acceptance Criterion*	*Value*	*P/F*
51	30-60% of m/z 198	42.13	PASS
68	<2% of m/z 69	1.37	PASS
69	Present	56.23	PASS
70	<2% of m/z 69	0.35	PASS
127	40-60% of m/z 198	43.37	PASS
197	<1% of m/z 198	0.62	PASS
198	Base peak	100.00	PASS
199	5-9% of m/z 198	5.19	PASS
275	10-30% of m/z 198	19.67	PASS
365	>1% of m/z 198	1.37	PASS
441	Present and <m/z 443	55.29	PASS
442	>40% of m/z 198	88.67	PASS
443	17-23% of m/z 442	20.14	PASS

4.8.3 Calibration Statistics

Semivolatile Organics Calibration Data on 210-MS/220-MS

RRF1 – RRF9 (Calibration Range: 1 ppm – 160 ppm) – Linear Fit

Compound Name	Corr (R^2)	Avg. RRF	% RSD	CCC	SPCC
N-nitrosodimethylamine	0.997	0.372	9.01		
Phenol	0.999	1.773	5.59	PASS	
Bis(2-chloroethyl) ether	0.999	1.009	6.39		
Phenol, 2-chloro-	0.999	1.754	4.99		
Benzene, 1,3-dichloro-	0.997	0.723	7.41		
1,4-Dichlorobenzene-d4					
Benzene, 1,4-dichloro-	0.998	0.727	7.66	PASS	
Benzene, 1,2-dichloro-	0.996	0.700	6.58		
o-Cresol	0.999	1.400	3.50		
bis(2-chloroisopropyl) ether	0.998	1.029	5.09		
N-nitrosodi-n-propylamine	0.998	0.632	5.35		PASS
p-cresol	0.999	1.953	4.60		
Ethane, hexachloro-	0.994	0.332	7.51		
Benzene, nitro-	0.997	1.226	4.89		
Isophorone	0.998	2.092	4.77		
Phenol, 2-nitro-	0.999	0.262	15.92	PASS	
Phenol, 2,4-dimethyl-	0.998	1.518	4.29		
Bis(2-chloroethoxy) methane	0.998	1.260	4.52		
Phenol, 2,4-dichloro-	0.997	0.392	5.19	PASS	
Benzene, 1,2,4-trichloro-	0.995	0.408	5.33		
Naphthalene-d8					
Naphthalene	0.999	3.010	3.10		
p-Chloroaniline	0.996	1.235	12.23		
Hexachlorocyclopentadiene	0.998	0.830	6.52		PASS
4-chloro-3-methylphenol	0.998	3.155	5.53	PASS	
Naphthalene, 1-methyl-	0.997	0.798	5.48		
1,3-Cyclopentadiene, 1,2,3,4,5,5-hexa	0.994	0.456	8.09		
Phenol, 2,4,6-trichloro-	0.994	0.533	15.81	PASS	

RRF1 – RRF9 (Calibration Range: 1 ppm – 160 ppm) – Linear Fit					
Compound Name	**Corr (R^2)**	**Avg. RRF**	**% RSD**	**CCC**	**SPCC**
Phenol, 2,4,5-trichloro-	0.998	0.675	18.74		
Naphthalene, 1-chloro-	0.998	1.909	5.98		
2-nitroaniline	0.997	0.951	8.36		
Dimethyl phthalate	0.999	3.599	4.51		
2,6-dinitro-toluene	0.999	0.731	8.64		
acenaphthylene	1.000	1.876	3.72		
Acenaphthene-d10					
Acenaphthene	1.000	1.400	7.07	PASS	
Phenol, 2,4-dinitro-	0.997	0.059	34.99		PASS
4-nitrophenol	0.999	0.910	22.45		PASS
Dibenzofuran	0.999	2.564	4.68		
Benzene, 1-methyl-2,4-dinitro-	0.999	1.061	15.43		
Diethyl Phthalate	0.998	3.409	23.02		
Fluorene	0.999	1.563	5.79		
4-Chlorophenyl phenyl ether	0.998	1.800	6.99		
4-nitroaniline	0.995	1.968	6.44		
3-Nitroaniline	0.999	2.113	19.56		
Phenol, 2-methyl-4,6-dinitro-	0.999	0.179	51.62		
Azobenzene	0.997	3.575	4.41		
Benzene, 4-bromo-1-phenoxy-	0.998	0.701	5.31		
Hexachlorobenzene	0.994	0.214	10.04		
Phenol, pentachloro-	0.996	0.289	25.68	PASS	
Phenanthrene-d10					
Phenanthrene	0.999	1.206	4.12		
Anthracene	0.999	1.204	3.54		
Carbazole	0.999	1.171	3.90		
di-n-butyl phthalate	0.996	2.865	6.85		
fluoranthene	0.999	1.270	3.42	PASS	
Pyrene	0.999	1.207	3.06		
Benzyl butyl phthalate	0.997	1.329	8.33		

RRF1 – RRF9 (Calibration Range: 1 ppm – 160 ppm) – Linear Fit

Compound Name	Corr (R^2)	Avg. RRF	% RSD	CCC	SPCC
Chrysene	0.993	1.345	9.64		
Chrysene-d12					
Benz[a]anthracene	0.996	1.168	7.05		
bis-(2-ethylhexyl) phthalate	0.993	1.963	8.20	PASS	
di-n-octyl phthalate	0.997	3.229	12.86		
Benzo[b]fluoranthene	0.996	1.420	12.32		
Benzo[k]fluoranthene	0.998	1.449	12.03	PASS	
Benzo[a]pyrene	0.998	1.377	13.18		
Perylene-d12					
Indeno[1,2,3-cd]pyrene	0.995	0.756	13.83		
Dibenz[a,h]anthracene	0.994	0.695	15.96		
Benzo[ghi]perylene	0.996	0.600	12.95		
Average	**0.997**		**10.03**		

Semivolatile Organics Calibration Data on 300/320-MS

RRF1 – RRF8 (Calibration Range: 1 ppm – 150 ppm) – Linear Fit

Compound Name	Corr (R^2)	Avg. RRF	% RSD	CCC	SPCC
N-Nitrosodimethylamine	0.9962	1.1007	9.3		
Phenol	0.9974	1.9779	11.3	PASS	
Bis(2-chloroethyl) ether	0.9966	1.7787	14.5		
2-chlorophenol	0.9986	1.5162	13.2		
1,4-dichlorobenzene	0.9983	1.6380	15.8	PASS	
1,3-dichlorobenzene	0.9989	1.5627	13.6		
1,2-dichlorobenzene	0.9992	1.5668	15.6		
o-cresol	0.9994	0.4117	8.1		
Bis(2-chloroisopropyl) ether	0.9885	1.6861	24.9		
N-nitroso-N-propyl-1-Propanamine	0.9967	0.3683	11.0		PASS
p-cresol	0.9996	0.4505	9.7		
hexachloroethane	0.9981	0.1994	12.4		
nitrobenzene	0.9962	0.4662	13.5		
isophorone	0.9982	0.6980	11.5		

RRF1 – RRF8 (Calibration Range: 1 ppm – 150 ppm) – Linear Fit					
Compound Name	**Corr (R^2)**	**Avg. RRF**	**% RSD**	**CCC**	**SPCC**
2-nitrophenol	0.9985	0.2151	7.5	PASS	
2,4-dimethylphenol	0.9990	0.3960	11.2		
Bis(2-chloroethoxy) methane	0.9938	0.4184	17.4		
2,4-dichlorophenol	0.9995	0.3275	5.2	PASS	
1,2,4-trichlorobenzene	0.9996	0.3477	11.3		
Naphthalene	0.9987	1.0959	16.5		
4-Chloroaniline	0.9992	0.4060	8.5		
hexachlorobutadiene	0.9989	0.1863	7.5		
4-chloro-3-methylphenol	0.9992	0.7548	7.5	PASS	
2-methylnaphthalene	0.9995	1.5767	12.8		
Hexachlorocyclopentadiene	0.9997	0.3539	4.9		PASS
2,4,5-trichlorophenol	0.9997	0.4629	5.1		
2,4,6-trichlorophenol	0.9975	0.4664	7.4	PASS	
2-chloronaphthalene	0.9999	1.4704	11.7		
2-Nitroaniline	0.9990	0.5517	5.2		
Dimethyl phthalate	0.9995	1.4806	10.6		
2,4-dinitrotoluene	0.9981	0.3452	5.5		
Acenaphthylene	0.9997	2.0013	13.1		
3-Nitroaniline	0.9988	0.4189	8.8		
Acenaphthene	0.9997	1.3722	13.6	PASS	
2,4-dinitrophenol	0.9992	0.1614	29.6		PASS
4-nitrophenol	0.9946	0.3476	11.9		PASS
Dibenzofuran	0.9999	1.2228	16.1		
2,6-dinitrotoluene	0.9979	0.2692	6.8		
Diethyl Phthalate	0.9995	1.0387	26.5		
Fluorene	0.9996	1.0034	14.8		
4-chlorophenyl phenyl ether	0.9996	0.4727	16.8		
4-Nitroaniline	0.9948	0.2723	10.1		
2-methyl-4,6-dinitrophenol	0.9969	0.1342	20.7		
Azobenzene	0.9999	0.2747	11.8		
4-bromophenyl phenyl	0.9987	0.3172	8.9		

RRF1 – RRF8 (Calibration Range: 1 ppm – 150 ppm) – Linear Fit

Compound Name	**Corr (R^2)**	**Avg. RRF**	**% RSD**	**CCC**	**SPCC**
ether					
hexachlorobenzene	0.9994	0.3802	11.5		
pentachlorophenol	0.9995	0.1975	20.2	PASS	
Phenanthrene	0.9997	1.3062	15.7		
Anthracene	0.9991	1.3069	14.9		
Carbazole	0.9988	1.2143	11.0		
Dibutyl phthalate	0.9996	1.3991	9.8		
Fluoranthene	0.9998	1.2303	7.6	PASS	
Pyrene	0.9998	1.2803	7.3		
Benzyl butyl phthalate	0.9988	0.6354	5.5		
Chrysene	0.9999	1.2161	7.8		
Benz[a]anthracene	0.9998	1.1528	9.7		
Bis(2-ethylhexyl) phthalate	0.9998	0.8394	5.7	PASS	
Acenaphthylene	0.9957	0.8387	7.5		
Di-n-octyl phthalate	1.0000	1.4158	5.0		
Benzo[b]fluoranthene	0.9999	1.2830	5.9		
Benzo[k]fluoranthene	0.9999	1.3199	8.2	PASS	
Benzo[a]pyrene	0.9999	1.1696	8.7		
Indeno[1,2,3-cd]pyrene	0.9993	1.0688	8.0		
Dibenz[a,h]anthracene	0.9994	1.1633	7.3		
Benzo[ghi]perylene	0.9991	1.2097	9.5	PASS	
Average	**0.9986**		**11.3**		

4.9 Troubleshooting

The following table outlines common potential problems and proposed solutions. Multiple problems on the same analytical system are often difficult to resolve and may require a service representative. Always try the least invasive (or easiest) procedure first when troubleshooting. Ask “what has changed?”, maintain and review maintenance logs to help trace back when a problem may have started.

Observed Problem	Potential Cause(s)	Solutions
Bad overall peak shape	Leaks, bad liner, dirty electrodes or ion volume, bad column	Change liner and check for leaks at transferline and column nuts. Change septum, clean electrodes or ion volumes.
Sudden loss of sensitivity	Broken column, bad filament, “killer” sample, leaking septum, leaks	Check column and transferline nuts for leaks, change septum, repair or replace column, change filaments.
SPCC compounds fail	Dirty liner, dirty column, leaking injector body, dirty source/ion volume	Replace liner, cut front 0.5M of column, check for leaks, clean injector body (with methanol), clean ion volume, source, or electrodes; replace column
DFTPP tune fails	Tuning parameters not set correctly; overloading in an ion trap; low multiplier voltage	Adjust ionization time factors, use tune to target ratios in quads, increase multiplier +100V, decrease amount injected if MS saturated, check moisture filters on He gas lines, adjust other MS parameters such as scan rate, # of microscans across peak, count threshold
High mass noise	Dirty ion trap, dirty source	Clean ion trap, clean ion source
Gradual loss of sensitivity	MS multiplier “settling in,” build up of active sites	Increase multiplier if peak areas drop low out of range from initial calibration, recalibrate quad system, replace ion volume
Ghost peaks	Dirty autosampler rinse solvents/vial, septa particles in liner, column phase degradation, leaks, dirty septa on autosampler vial	Replace septa and liner, use clean autosampler rinse vial and autosampler vials, avoid multiple injections from same vial, use foil on autosampler rinse vials, check leaks, replace column
Carryover	Dirty sample, poor rinse cycle,	Replace/clean liner, replace

Observed Problem	Potential Cause(s)	Solutions
	dirty autosampler syringe, particles in liner	autosampler syringe, increase number of rinse cycles and/or use other rinse solvents
Peak tailing, calibration curves with high RSDs	Active sites on liner, column, or reactive surface on trap electrodes	Replace liner or column; increase trap or source temperature; clean or replace trap electrodes
Poor reproducibility of peak areas for Internal/Surrogate standards	Dirty inlet, bad column, low multiplier voltage, plμgged autosampler syringe, poorly optimized injection method	Replace liner/inlet or column; replace autosampler syringe, turn up multiplier as it ages, optimize splitless injection.

4.9.1 Operating Tips

The following tips may help with routine operation:

1. Avoid using standards that have been opened and subject to evaporative loss.
2. Use fresh solvents daily in the autosampler rinse positions, and routinely check for plugged syringe.
3. Use foil instead of septa on the autosampler solvent rinse vials.
4. Replace septa on autosampler vials daily to avoid sample evaporation. Return promptly to freezer.
5. Install fritted insert goose-neck down.
6. Avoid contact with plastic pipette tips for stock and calibration standards- phthalate and adipates are target analytes and easily contaminate standards and reagents
7. Cool transferline, trap, and injector to below 80 °C before doing any maintenance on the GC/MS system. Air on hot columns or electrode surfaces will cause rapid degradation and loss of system performance.