

July 23, 1998

Mr. Jim Peeler  
Emission Monitoring Inc.  
8901 Glenwood Avenue  
Raleigh, North Carolina 27612-7503

Dear Mr. Peeler:

In your March 3, 1998 letter you made five requests to the Environmental Protection Agency (EPA). They were:

1. EPA acceptance of your method as an alternative to Method 18 to determine compliance for several subparts in part 60, 61, and 63.
2. EPA acceptance of your method as an alternative to Method 25 to determine compliance for several subparts in part 60, 61, and 63.
3. EPA acceptance of your method as an alternative to Method 25 in several subparts in part 264 and 265.
4. EPA acceptance of your method as an alternative to Method 106 to determine compliance for subpart F in part 61.
5. EPA proposal of your method in Appendix M, part 51.

We have reviewed your request and have made the following conclusions:

**Method 18 and 106 Alternative Requests in parts 60, 61, 63, 264, and 265**

The laboratory and field data submitted through October 17, 1997 supports the concept of use of the performance based method as an alternative to Method 18 and Method 106 to meet federal testing requirements of the subparts noted in Table 1 when all the pollutants of concern form a subgroup of those target compounds identified in the applicability section of the subject method. For your convenience, the method's target compounds are re-listed in Table 2 of this letter. Of course, since your method is performance based, the quality assurance (QA) and quality control (QC) inherent in the method must be attained at each test site and documented in the test report as a condition of this approval. A copy of this method, "Determination of Gaseous

Organic Compounds By Direct Interface Gas Chromatography-Mass Spectrometry” dated October 27, 1997, has been posted on the Emission Measurement Center Web site as file CTM-28.

Because the cited subparts cover a wide range of different affected facilities with a range of pollutants of concern, it is not practical to definitively list those affected facilities where the pollutants of concern include only those pollutants on the method’s target list. This obligation of proof is one the affected facility must assume to the satisfaction of the key decision maker (for a compliance test this would be the appropriate regulatory authority) during the design of the test program. Engineering knowledge of the process, previous test programs at similar affected facilities, or confirmation by preliminary sampling are some ways to approach this obligation.

However, when the list of pollutants of concern as potential emissions includes compounds that are not on the method’s target list (Table 2), then the additional system continuing calibration check after each run, as detailed in section 1.4.5 of the method, must be followed, met, documented and submitted with the data report as a condition of this approval. In other words, in this situation, treat the compound not in Table 2 as though it were water soluble while following this method. Alternatively, you or any petitioner may seek to gain EPA approval to extend the method’s target list of compounds through submission of a combination of appropriate laboratory and field verifications for additional compounds as part of a new alternative request.

<b>Table 1: Summary of subparts affected by this approval</b>				
Part	Subpart	Standard	Reference Section	Clarification of approval
60	DDD	Polymer Manufacturing	60.564(b), (c),(d)	Total Organic Compounds (TOC) Method 18
60	III	SOCMI Air Oxidation	60.614	TOC-Method 18
60	NNN	SOCMI Distillation	60.664	TOC-Method 18
60	RRR	SOCMI Reactors	60.704	TOC- Method 18
60	SSS	% reduction; capture/destruction efficiency	60.715	TOC-Method 18
60	VVV	% reduction; capture/destruction efficiency	60.745	TOC-Method 18

<b>Table 1: Summary of subparts affected by this approval</b>				
Part	Subpart	Standard	Reference Section	Clarification of approval
61	F	Vinyl chloride and Ethylene Dichloride	61.67	Method 18
61	J	Equipment leaks (fugitive emission sources) of benzene- net heating value	refers to subpart V	net heating value- Method 18
61	L	Benzene from Coke By-Product Recovery	61.139(g)	Method 18
61	V	Equipment leaks (fugitive emission sources)-net heating value	61.245(e)(3)	net heating value- Method 18
61	FF	Benzene	61.355(f)& (I)	Method 18
63	G	SOCMI process vents	63.115(c), 63.116, & 63.128	Method 18
63	H	Equipment leak -exemption from in- HAP service	63.180(d)(1)	Method 18-
63	U	Group I Polymer & Resins batch front-end process, % reduction	63.488(b)(5)& 63.490	Method 18
63	U	Group I Polymer & Resins back end process	63.496	Method 18
63	U	Group I Polymer & Resins back end process producing styrene butadiene rubber by emulsion process	63.500	Method 18-carbon disulfide
63	W	Epoxy resins & Non-nylon polyamides,	63.525	Method 18
63	CC	Petroleum Refineries-misc process vents	63.645	Method 18
63	DD	Off-site Waste & recovery operations	63.694	Method 18

<b>Table 1: Summary of subparts affected by this approval</b>				
Part	Subpart	Standard	Reference Section	Clarification of approval
63	EE	Magnetic tape manufacturing operations	63.705	Method 18
63	GG	Aerospace manufacturing & rework facilities	63.750	Method 18
63	JJ	Wood furniture manufacturing operations	63.805	Method 18
63	JJJ	Group IV Polymers & resins- PET & polystyrene continuous process affected sources	63.1318	Method 18
63	JJJ	Group IV Polymers & resins- batch process vents	63.1323	Method 18

<b>Table 2: Method Target Compounds</b>	
Compound/CAS#	Compound/CAS#
Benzene 71432	m&p Xylene 108383&106423
Bromodichloromethane 75274	Bromomethane 74839
Carbon Disulfide 75150	Carbon Tetrachloride 56235
Chloroform 67663	Chlorobenzene 108907
Styrene 100425	cis-1,3 Dichloropropene 10061015
Toluene 108883	1,2Dichloroethane 107062?
cis-1,2 Dichloroethene 156592	1,1 Dichloroethene 75354
Dibromochloromethane 124481	trans-1,2Dichloroethene 156605
1,1 Dichloroethane 75343	trans-1,3 Dichloropropene 542756
1,2 Dichloropropane 78875	Trichloroethene 79016
Methylene Chloride 75092	o-xylene 95476
1,1,2,2 Tetrachloroethane 79345	1,1,2 Trichloroethane 79005

<b>Table 2: Method Target Compounds</b>	
1,1,1 Trichloroethane 71556	Ethyl benzene 100414
Methyl Ethyl Ketone 78933	Ethyl chloride 75003

In considering this request we had to decide whether or not the statistically significant bias correction factors derived following Method 301, should be carried forward for future applications of the method. We have concluded that since the method is performance based with specified QA and QC limits that it is not appropriate except at Solvay Calciners 1, 2, or 3. Hence, future applications should not employ correction factors unless Method 301 is followed to derive source specific correction factors. The QA and QC requirements act as surrogate confirmation that the data quality objectives (DQO) of  $\pm 20\%$  accuracy and  $\pm 10\%$  precision for each measurement value are met.

Your request for approval for use in Subpart AA of parts 264 and 265 is being deferred. We refer you to Sections 260.20 and 260.21 which discuss the procedure you must follow and the criteria considered by EPA. Note that one of the criteria for an equivalent method under this rule is proof of equal or superior precision. If you want to pursue this process, we will work with you to identify the appropriate Administrator's delegated official.

### **Method 25 and 25A Alternative Request**

We have denied your request for use of this method as an alternative to Method 25 and Method 25A. Both Method 25 and 25A, when specified in a regulation, inherently define the compounds of interest in terms of what the method collects, detects, and reports as a surrogate compound. The pollutant definition and the method principles are mixed together. Method 18 and the candidate method, on the other hand, identify and quantify each pollutant. You did not include acceptable procedures to adequately account for this fact.

Some of the cited regulations do allow for several methods. In those regulations where Method 18 is also cited as acceptable, your omission is a moot point however, since the agency has already established an acceptable procedure for that regulation to account for the difference in methods. For instance, in some regulations the numerical emission limit is different depending on the test method used. This was done as part of the formal rulemaking process and hence although the numerical limit is different, the stringency of the standard is considered to be equivalent. In these cases you could comply, as an alternative, to the Method 18 related part of the regulation.

### **Request for EPA Proposal in Appendix M, Part 51**

We are considering your request. As a part of our decision making we will ask several of our state Agency contacts for their opinion of the need. Even if the decision is to propose, we anticipate the administrative process to take about 18 months to proposal.



If you have any questions about this determination, please call William Lamason at (919) 541-5374 or Terry Harrison at (919) 541-5233.

Sincerely,

/s/

William F.Hunt, Jr.  
Director  
Emissions, Monitoring, and  
Analysis Division

cc: Bruce Jordan, MD 13  
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Elaine Stanley, ORC  
Robert Van Heuvelen, ORE  
Linda Murphy, Region I  
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Winston Smith, Region IV  
David Kee, Region V  
Robert Hanneschlager, Region VI  
Art Spratlin, Region VII  
Richard Long, Region VIII  
David Howekamp, Region IX  
Anita Frankel, Region X

## DETERMINATION OF GASEOUS ORGANIC COMPOUNDS BY DIRECT INTERFACE GAS CHROMATOGRAPHY-MASS SPECTROMETRY

### INTRODUCTION

This document describes the key elements of a sampling and analytical method for measurement of specific volatile organic hazardous air pollutants (VOHAPs) using a direct interface gas chromatograph/mass spectrometer (GCMS) for on-site analysis of emissions from stationary sources. The method provides concentration measurement results for the extracted gas samples. The performance-based approach validates each GCMS analysis by placing boundaries on the instrument response to internal standards and their specific mass spectral relative abundances.

### 1.0 SCOPE and APPLICATION

1.1 Analytes. This method employs a direct interface GCMS measurement system designed for the identification and quantification of the specific 36 volatile organic compounds listed below. The method has potential to be extended to many other compounds provided the performance criteria detailed in this method are met.

Benzene-71432	Dibromochloromethane-124481	Carbon Tetrachloride-56235
Bromodichloromethane-75274	1,1-Dichloroethane-107062	Chlorobenzene-108907
Carbon Disulfide-75150	1,2-Dichloropropane-78875	c-1,2-Dichloropropene-10061015
Chloroform-67663	Ethyl benzene-100414	1,2,-Dichloroethane-156592
Methyl iso-Butyl Ketone-108101	Ethyl chloride-75003	1,1-Dichloroethene-75354
Styrene-100425	Methylene Chloride-75092	t-1,2-Dichloroethene-156605
Tetrachloroethylene-127184	1,1,2,2-Tetrachloroethane-79349	Methyl Ethyl Ketone-78933
Toluene-108883	1,1,1-Trichloroethane-71556	2-Hexanone-591786
Bromoform-75252	1,1,2-Trichloroethane-79005	t-1,2-Dichloropropene-542756
Vinyl Acetate-108054	p-Xylene-106423	Trichloroethene-79016
Vinyl Chloride-75014	Bromomethane-74839	m-Xylene-108383
Chloromethane-74873		o-Xylene-95476
cis-1,2-Dichloroethene-156592		

### 1.2 Applicability.

1.2.1 The method is applicable for the determination of the above listed compounds in emissions from stationary sources. Individual volatile hazardous air pollutants (VOHAPs) are detected and quantified by direct interface of a gas chromatograph/mass spectrometer (GCMS) measurement system to the source effluent. This method applies specifically to full scan operation (between 45 and 300 amu) of the mass spectrometer.

1.2.2 The method is applicable to direct measurement of unconditioned sample streams having moisture content less than the saturation value at applicable instrument operating limits. Sample streams having higher



moisture content require conditioning before introduction into the analytical instrumentation that prevents moisture condensation within the instrument. Additional QA requirements are provided in the method for the analysis of polar, water-soluble compounds

### 1.3 Method Range and Sensitivity.

1.3.1 The instrument range shall be sufficient to measure from 150 ppbv to 100 ppmv. Measurement of concentrations outside of this range may be conducted provided that the specific performance requirements of the method are met and either a) the concentrations used to prepare the three-point and conduct the continuing calibration concentration are adjusted appropriately or b) the three-point calibration is extended to include additional concentrations. The sensitivity of the GCMS measurement system for the individual target analytes depends upon: a) the specific instrumental response for each target analyte, and the number of mass spectral quantification ions available, b) the amount of instrument noise, and c) the percent moisture content of the sample gas.

### 1.4 Data Quality Objectives

1.4.1 The overall data quality objectives are to achieve an accuracy of  $\pm 20\%$  and precision of  $\pm 10\%$  for each measurement value. Specific method performance criteria are detailed in Section 10 and listed in Tables 1, 2, 3, and 4. Achieving the method performance criteria enable meeting the data quality objectives.

1.4.2 The mass spectrometer tune should be established according to the manufacturers written instructions.

1.4.2.1 If NIST Library search able mass spectra are needed to identify compounds not included in the three-point calibration or to facilitate comparison with other mass spectral analyses, the mass spectrometer tune must be able to produce mass spectra for bromofluorobenzene (BFB) that meet the relative abundance criteria listed in Table 2. NIST Library search able spectra are not required for the quantification of target analytes.

1.4.2.2 Table 3 presents a specific example of applicable MS tune limits for the mixture of two recommended internal standards (1,3,5 (TRIS) trifluoromethylbenzene and bromopentafluorobenzene (BPFB)). These criteria have been demonstrated to produce an acceptable instrumental response for BFB. Table 4 presents a specific example of applicable ion abundance criteria for the two co-injected, GC separated, internal standards. Proper and consistent GCMS response is ensured in each run by meeting the Table 3 and Table 4 QA criteria.

1.4.3 An initial three-point calibration must be conducted to establish the instrument response for each target analyte over the measurement range. At a minimum, duplicate GCMS analyses at each of three calibration levels are required. The percent relative standard deviation (RSD) must be within 20% for these analyses. The signal to noise ratio also must be sufficient to establish the target analytes responses at the lowest concentration level in full scan operation. A signal to noise ratio of 10:1, and an average relative response factor  $>0.25$  (Section 10. Equation 2) should be sufficient. The same MS tune conditions, GC operating conditions, and data quantification procedures that are used to establish the three-point calibration curve must be used also to acquire and quantify samples and to perform continuing calibrations.

1.4.4 A system continuing calibration check must be conducted each day before performing effluent measurements, before resuming sampling after each instrument shut down for maintenance or corrective action, and before analyzing additional samples after twelve hours of continuous operation. The six surrogate check compounds listed in Table 5 may be used to determine the validity of the three-point calibration curve for the 36 analytes listed in 1.1. Acceptable results are indicated if analysis of the continuing system calibration using the three-point calibration curve produces results within  $\pm 20\%$  of the expected value (i.e., manufacturer's certified value for compressed gas standards). Acceptable continuing calibration results for each analyte or each surrogate allow use of the previously developed three-point calibration for analysis of effluent samples for those analytes or for those analytes that correspond to each surrogate (see Table 6).

1.4.5 A system continuing calibration check must be performed after each test run when analyzing for polar, water-soluble compounds when moisture removal is used. (The polar-water soluble compounds include methyl ethyl ketone, 2-hexanone, vinyl acetate, and methyl isobutyl ketone.) This continuing calibration check must be performed immediately after sampling the effluent (i.e., while the potential for residual moisture in the sample conditioning components is greatest). Unacceptable results for this continuing calibration check invalidate the run for polar, water-soluble compounds. Such results may indicate loss of water-soluble compounds in the sample conditioning components. Corrective action shall be taken before the next sample run. Specific sampling

system designs that have been demonstrated to achieve adequate sample recoveries for water soluble compounds at higher moisture levels than encountered during the test are exempt from the requirement to conduct the post-test continuing calibration check. (Such demonstrations can be accomplished by performing analyte spiking at elevated moisture levels. The tester shall maintain documentation of such sampling system demonstrations.) For sampling systems that qualify for this exemption, the effluent shall be sampled for a period of at least 15 minutes prior to conducting the system continuing calibration check in 1.4.4.

## 2.0 METHOD SUMMARY

2.1 Analytical Principle. Gas chromatography (GC) is a means of separating gaseous mixtures of molecules by their affinity for the column's stationary and mobile phases. Sample gas is introduced into the GCMS via a pneumatic valve assembly or equivalent. In this application, an internal standard mixture must be quantitatively co-added to every sample.

2.1.1 As molecules elute from the GC column, they must be separated from the mobile phase carrier gas and enter the mass spectrometer. Because the GC operates at near ambient pressure and the MS operates at greatly reduced pressure (approximately  $1 \times 10^{-5}$  Torr), an interface is required. Upon entering the mass spectrometer, separated molecules are subjected to ionizing energy that causes an electron(s) to be ejected from the molecule. The result is a positively charged molecule (for electron ionization) that fragments while achieving a stable electronic configuration.

2.1.2 The mass spectrometer scans a defined mass range (from 45-300 amu in this application) enabling detection of the individually charged fragments, which are virtually unique for every molecule. Positive identification of target analytes is achieved by; 1) comparing eluting analyte GC peak retention times in the total ion chromatogram to those contained in the three-point calibration, and 2) by examining the mass spectral pattern of the eluted peaks.

2.1.3 The compounds listed in 1.1 and the internal standards can be separated and detected in a 10 to 15 minute isothermal GC run.

2.2 Sampling. The sample interface system must have a response time that provides a fully equilibrated sample to the GCMS analyzer within the GC sample analysis cycle time. The sample interface system should include provisions to facilitate direct calibrations of the GCMS instrument and system calibrations where calibration gases are introduced at the extractive probe outlet, upstream of the primary particulate filter. The sample interface system also must extract continuously effluent sample during the period between the consecutive GCMS sample acquisitions.

2.2.1 Sample Extraction. Sample is extracted from the stack or duct and passes through the entire sample interface system at a constant rate. The sample interface consists of a heated primary particulate filter, a heated pump, heated Teflon sample line, and sample conditioning unit. All sample extraction components must be maintained at temperatures sufficient to prevent moisture condensation within the measurement system components. (Other sampling techniques involving bags, canisters, adsorbents, etc. are not addressed by this method.)

2.2.2 Sample Conditioning. The conditioning unit is operated to protect the GCMS instrument from particulate and other condensable mater and remove excess sample moisture, if necessary. The following information is provided as an example of an acceptable arrangement. All components within the conditioning unit (except for the condenser, if applicable) must be maintained at, or above, the temperature of the GC introduction valve assembly. The secondary particulate filters should be maintained at a temperature approximating that of the GC introduction valve assembly. Sample gases that are free of condensable acids and that contain less than the saturated moisture at the highest dew point (i.e., lowest temperature, and highest pressure) within the instrument can be analyzed without moisture removal by allowing the entire sample stream to bypass the condenser. Sample streams containing higher moisture levels may be dried by directing the entire sample stream through the condenser to reduce the moisture content to an acceptable level. Alternatively, a portion of the sample stream may be directed through the condenser and a portion of the sample stream may bypass the condenser to reduce the loss of certain analytes. The flow of sample that bypasses the condenser and the condenser operating temperature must be carefully chosen based on knowledge of the unconditioned gas stream moisture content. The flow rate of sample

gas through the condenser and the total sample flow rate must be monitored using calibrated precision rotometers and recorded.

2.2.3. Sample Transfer Line. A connection line that is heated to the temperature of the GC introduction valve conveys sample gas exiting the conditioning unit to the GCMS analyzer. An internal sample pump within the GCMS analyzer is required to draw sample gas through the connection line at a rate substantially less than the total sampling rate. The excess sample gas exiting the conditioning unit must be vented at atmospheric pressure so that the inlet on the connection line is not pressurized.

2.3 Operator Requirements. The operator should have rudimentary knowledge of the GCMS instrumental operating conditions that are sufficient to determine if the operation is consistent with the data quality objectives of the method.

### 3.0 DEFINITIONS

Refer to Appendix A of this document for a list of definitions.

### 4.0 INTERFERENCES

4.1 Analytical Interferences. Analytical interferences are defined as those interferences which result in chromatographic peak and quantion overlap to such an extent that quantification of specific target compounds is prohibited. The nature of the GCMS technique virtually eliminates analytical interferences.

4.2 Sampling System Interferences. Sampling system interferences prevent the transport of target analytes to the instrumentation or have the potential to damage the measurement system components. Water, reactive particulate matter, adsorptive sites within the sampling system components, and acid gases are examples of such potential sampling system interferences. Specific provisions and performance criteria are included in this method to detect the presence of sampling system interferences.

### 5.0 SAFETY

5.1 Target Analytes. Many of the compounds listed in Section 1 are toxic and carcinogenic. Therefore, exposure to these chemicals should be limited. Compound mixtures are contained in compressed gas cylinders, and the appropriate safety precautions should be taken to avoid accidents in their transport and use.

5.2 Sampling Location. This method may involve sampling at locations having a high positive or negative pressure, or have a high temperature, elevated height, or high concentration of hazardous or toxic pollutants.

5.3 Mobile or Remote Laboratory. A leak check of the sampling system and an inspection of sample exhaust equipment should be performed before sampling the calibration standards or effluent to protect personnel in the laboratory.

### 6.0 EQUIPMENT AND SUPPLIES

The equipment and supplies are based on the generalized sampling system schematic shown in Figure 1.

#### 6.1 Instrumentation

6.1.1 Gas Chromatograph/Mass Spectrometer. A GCMS system capable of separating the analyte mixture and detecting compounds having a 45-300 atomic mass unit (amu) range. This system must also include a means

of co-injecting a gaseous internal standard mixture with sample gas at a precise and known ratio. A personal computer with compatible GCMS software is needed for data quantification.

6.1.2 Data Acquisition System. A data acquisition system and appropriate software that enables the analyst to acquire and quantify the target analytes and which allows for adequate storage of data.

## 6.2 Sampling System

6.2.1 Sampling Probe. Glass, stainless steel or other appropriate material of sufficient length and physical integrity to sustain heating, prevent adsorption of analytes and to reach the gas sampling point.

6.2.2 Pump. A leak-free, heated head pump (KNF Neuberger or equivalent) capable of maintaining an adequate sample flow rate (at least 1.5 lpm).

6.2.3 Calibration Assembly. Apparatus allowing the introduction of calibration gases into the sampling system at the probe outlet, upstream of the primary particulate filter. The apparatus shall be designed to ensure that calibration gases are introduced at the same pressure as effluent samples or shall include provisions for monitoring the sample pressure at the calibration introduction point both during calibrations and during effluent sampling. The calibration assembly shall ensure that the calibration gases are at the same temperature as the sample gases at the introduction point.

6.2.4 Sampling Line. Heated to a temperature sufficient to prevent sample condensation, and fabricated of stainless steel, Teflon<sup>™</sup>, or other material that minimizes adsorption of analytes and transports effluent to the GCMS. The length of heated transport line should be minimized.

6.2.5 Sample Condenser System. Peltier Cooler (or equivalent) capable of reducing the moisture of the sample gas to a level acceptable for sample injection.

6.2.6 Sample Flow Rotometers. Calibrated rotometers capable of withstanding sample gas conditions.

6.2.7 Sample Transfer Line. Sample line used to convey sample from the sample interface system to the inlet of the GCMS instrumentation. Heated to a temperature sufficient to prevent sample condensation and fabricated of stainless steel, Teflon<sup>™</sup>, PEEK<sup>™</sup>, or other material to minimize adsorption of analytes. The length of heated transport line should be minimized.

6.2.8 Particulate Filters. A filter (Balston<sup>™</sup> or equivalent) rated at 0.3 micron for particulate removal is required, and should be placed immediately after the heated probe, and at any place in the sampling system where the physical conditions of the flue gas are changed (i.e. moisture removal).

## 6.3 Auxiliary Equipment

6.3.1 Calibration Gas Manifold. Gas manifold capable of delivering nitrogen or calibration gases through sampling system, or directly to the instrumentation. The calibration gas manifold should include provisions to provide for accurate dilution of the calibration gases as necessary.

6.3.2 Mass Flow Meters or Controllers. To measure accurately calibration gas flow rate. The meters/controllers should have a stated calibrated range and accuracy (e.g.,  $\pm 2\%$  of scale from 0-500 cc/min or 0-5 L/min).

6.3.3 Digital Bubble Meter (or equivalent). NIST traceable with an accuracy of  $\pm 2\%$  of reading and with an adequate range to calibrate mass flow meters or controllers and rotometers at the specific flow rates  $\pm 10\%$  required to perform the method.

6.3.4 Teflon Tubing. Diameter and length suitable to connect cylinder regulators.

6.3.5 Stainless Steel Tubing. 316, appropriate length and diameter for heated connections.

6.3.6 Gas Regulators. Appropriate for individual gas cylinders and constructed of materials that minimize adsorption of analytes.

## 7.0 REAGENTS AND STANDARDS

7.1 Calibration Gases. Compressed calibration gas standards having a manufacturer's certification of analysis (i.e., a certified analytical accuracy) must be used for the initial calibration and for the continuing calibrations. (Commercially available compressed gaseous standards typically carry manufacturer's certificates of analysis of  $\pm 5$  to  $\pm 10\%$  accuracy.)

7.2 Internal Standards. Gaseous internal standard mixtures for co-injection with sample gas having a manufacturer's certification must be used.

7.3 High Purity (HP) Nitrogen or Zero Air. For purging sample lines, sampling system components and for performance of blank runs.

## 8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Initial Calibration. An initial three-point calibration for each target compound at nominal concentrations of 300 ppb, 1 ppm and 10 ppm must be prepared to quantify the GCMS data. There are two options available for generating the necessary gas concentrations. (Because of the incompatibility of some target compounds, several cylinders at each concentration are needed to construct a calibration for all of the 36 target analytes listed in 1.1.)

8.1.1 Option 1. Obtain calibration gas standards for the target compounds at the three specified concentration levels.

8.1.2 Option 2. Obtain 10 ppm calibration standards for the target analytes. Perform successive dilutions of the 10 ppm standard with nitrogen using mass flow meters that are calibrated against a NIST traceable digital bubble meter at the specific flow rates ( $\pm 10\%$ ) necessary for dilutions. Dilute the 10 ppm standard to 1 ppm and 300 ppb. If Option 2 is used, analyze the surrogate continuing calibration check standard (see Table 5), or other independent manufacturer's certified gas standard, as a QA audit using the three-point calibration. The audit gas must be a separate gaseous standard. Audit results using the calibrated GCMS must be within  $\pm 20\%$  of the manufacturer's certified value for each compound (or for each surrogate compound) to use the three-point calibration for analysis of those analytes (or those analytes for which the surrogates represent).

8.1.3 Perform duplicate GCMS analysis at each concentration level. Calculate relative response factors (RRF's) and average relative response factors (ARRF's) for each target compound at each concentration level (Section 10 Eq 1 and 2). The %RSDs from the three sets of duplicate analyses must be within 20%.

Tables 1-6 contain method QA/QC performance criteria for conducting initial three-point calibrations, and for continuing calibration checks.

### 8.2 Pretest Preparations and Evaluations.

8.2.1 Flow Rate and Moisture Determination. Perform EPA Methods 1 through 3 if effluent flow rates are required. Perform Method 4, or use wet-bulb dry-bulb measurements, saturation calculations or other applicable means that will afford a moisture determination within  $\pm 2\%$ . (If the moisture content of the flue gas is greater than the applicable instrument operating limit, the sample gas must be conditioned before introduction into the GCMS.)

8.2.2 Sample Interface Preparation. Assemble the sampling system (Figure 1 is a generalized schematic of one possible sampling system configuration). Allow the sample interface system components to reach operating temperatures. Operate the sample interface system at a constant sampling rate during the entire test.

8.2.3 MS Tune. Perform the mass spectrometer instrumental tune according to the manufacturer's written instructions. See criteria for the recommended TRIS/BPFB blend listed in Table 3.

8.2.4 Calibration. Perform the surrogate system continuing calibration check (or other continuing calibration check). The continuing calibration check standards must be introduced into the sampling system at the extractive probe outlet, upstream of the particulate matter filter. The standards must flow through the sampling system for a period sufficient to ensure equilibration within the sampling system components but not longer than the GC run time. The calibration check responses must agree to within  $\pm 20\%$  of the manufacturer's certified value for the compressed gas standards. Tables 1, 3, and 4 contain calibration QA/QC criteria. Tables 5 and 6 provide surrogate compound calibration check information.

8.2.5 System Zero Analysis. After performing the surrogate system continuing calibration, perform a system zero by directing nitrogen or zero air through the entire sampling system including the particulate filter. Analyze nitrogen samples until the measurement system background levels are less than 50 ppb for the target analytes of interest.

### 8.3 Sampling

8.3.1 Sample Analysis. Extract effluent sample gas through the sampling system for a period equal to or greater than GC run time before acquisition of the first sample. Perform sample analysis according to manufacturers written procedures. Continuously extract the effluent between consecutive GCMS sample acquisitions to ensure constant sample equilibration within the sample interface system. Each sample analysis shall represent the emissions concentration over a period of approximately 15 minutes. The QA/QC criteria listed in Table 1 must be met for each run.

8.3.2 Run Duration. Each test run shall be composed of a minimum of three samples, unless otherwise specified in the applicable regulation. For sample run durations longer than 45 minutes, continue to acquire and analyze additional samples for each 15 minute period.

8.4 Data Storage and Reporting. Identify all samples with a unique file name. Store backup copies of data files. Report the results for the individual GCMS analyses, and the mean of all samples for each target analyte for each run. Include copies of the three-point calibration including %RSD, RRFs and ARRFs, surrogate continuing system calibration(s) results and other method QA/QC activities in the test report.

## 9.0 QUALITY CONTROL

9.1 Follow the manufacturer's written instructions for the set-up, tune, operation, and calibration of the GCMS instrument and any sample interface equipment. All hardware or software settings of temperatures, pressures, and other operational parameters used for sample acquisition and data quantification shall be the same as those used when constructing the three-point calibration.

9.2 Records of the manufacturer's certificates of analysis for calibration standards and internal standards must be stored and included in all test reports.

## 10 CALIBRATION AND STANDARDIZATION

10.1 Tune. Perform mass spectrometer tune according to the manufacturer's written instructions.

10.2 Initial Three-Point Calibration. Calibrate the GCMS with mixtures of the target analytes. The mixtures should be prepared at nominal concentrations of 300 ppb, and 1 and 10 ppm in a balance of ultra high purity nitrogen (the dilution technique described in Section 8.1.2 may be employed).

The internal standards must be co-injected with each external calibration standard. The flow mixture should approximate a ratio of 1:10 (one part internal standard to 9 parts sample gas).

Analyze the three levels of standards in duplicate. Calculate the mean of the six relative response factors (RRFs) for each target analyte and report as the average relative response factors (ARRFs). Table 1 contains the QA/QC criteria for valid initial and surrogate continuing system calibration checks. See the following equations for a complete explanation.

Equation 1: RRF = Relative Response Factor

$$\mathbf{RRF} = (A_x/A_{is}) \times (C_{is}/C_x)$$

$A_x$  = Peak area of selected target VOHAP quantion.

$A_{is}$  = Peak area of corresponding selected internal standard quantion.

$C_{is}$  = Concentration of corresponding selected internal standard.

$C_x$  = Concentration of target VOHAP.

Equation 2: ARRF = Average Relative Response Factor

$$\mathbf{ARRF} = (\mathbf{RRF}_i) / n$$

$RRF_i$  = Individual RRFs calculated from calibration run.

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n = 6

Equation 3: %RSD = Percent Relative Standard Deviation

$$\%RSD = (s \times 100)/ARRF$$

s = Standard Deviation

The %RSD of the RRFs must be <20% for all target analytes to establish a valid calibration curve.

10.3 Surrogate Continuing (system) Calibration Check (CCC). A system continuing calibration check must be performed each day before performing effluent measurements, before resuming sampling after each instrument shut down for maintenance or corrective action, and before analyzing additional samples after twelve hours of continuous operation. The surrogate continuing calibration mixture is a manufacturer certified gas standard that is not from the same gas cylinder used to develop the initial three-point calibration. Alternatively, the continuing calibration check may be performed for all of the target analytes using the mid-range concentration level used to develop the three-point calibration. (Section 8.1.2 requires the use of an independent standard to audit the three-point calibration when developed by dilution techniques.) Direct the continuing system calibration standard through the entire measurement system including the particulate filters, and calculate the %D.

Equation 4: %D = Difference of Results from Expected Value

$$\%D = (\text{Expected Value} - \text{Instrument Analysis Results})/\text{Expected Value} \times 100$$

Expected Value = Certified Value of Cylinder

Instrument Analysis Results = Instrument output

The results from Equation 4 must be within  $\pm 20\%$  of the manufacturers certified value for a successful continuing calibration for all target analytes, or for all surrogates that represent those target analytes. Additionally, the response factors of the internal standards must be within -50% to +100% of their average response factors obtained during the initial three-point calibration. If these criteria are not met, corrective action must be taken. If the corrective action does not result in a successful CCC, a new three-point calibration must be performed. Table 1 lists the acceptance criteria for calibrations and quantification.

## 11 ANALYTICAL PROCEDURE

11.1 Sampling and Instrumental Analysis. Refer to Figure 2 for method operation flowchart.

## 12 DATA ANALYSIS AND CALCULATIONS

12.1 Quantitation of Results. Use the following equation to quantify the concentration of VOHAPs in gas samples.

5) ppmv Target VOHAP = parts per million by volume of target VOHAP in sample

$$\text{ppmv Target VOHAP} = (A_x / \text{ARRF})(C_{is} / A_{is})$$

$A_x$  = Peak area of target VOHAP quantion.

$A_{is}$  = Peak area of corresponding selected internal standard quantion.

$C_{is}$  = Concentration of corresponding selected internal standard.

ARRF = Average Relative Response Factor of target VOHAP calculated from three-point calibration.

The internal standards used to quantify the results and the individual quantification ions used must be identified in the test report.

12.2 Alternative Quantification Calculations. Alternative quantification algorithms may be used in the development of calibration files and sample analysis quantification. For example, regression analyses may be performed to determine the “best fit line” for the three-point calibration responses for each analyte rather than relying on the average relative response factor. In some cases, calculation procedures allowing a non-zero y-axis intercept may improve the accuracy of measurement results. Such procedures may show improvement of the RSDs for the three-point calibration. For each analyte, a consistent numerical procedure must be applied in developing the three-point calibration and in performing all sample analysis for the test series.

## 13 METHOD PERFORMANCE

13.1 Instrument Performance. Gaseous internal standards must be co-injected with every sample. The internal standards are used to verify continuously the tune status and GC performance. Tables 1, 3 and 4 specify criteria to ensure meeting the overall method data quality objectives.

## 14 POLLUTION PREVENTION

Take appropriate measures to prevent excess venting of calibration standards to the atmosphere.

## 15 REFERENCES

- 1). Method 624 - Purgeables, U.S. EPA 40 CFR part 136, App. A, (49 FR 43234), October 26, 1984.
- 2). “EPA Method Study 29 EPA Method 624 - Purgeables,” EPA 600/4-84-054, National Technical Information Service, PB84-209915, Springfield, Virginia 22161, June 1984.
- 3). Method 1624 - Volatile Organic Compounds by Isotope Dilution GCMS, U.S. EPA Office of Water Regulations and Standards, Industrial Technology Division, Office of Water, June 1989.
- 4). Peeler, J.W., Kinner, L.L., and DeLuca, S., “General Field Test Method Approval Process and Specific Application for a Direct Interface GCMS Source Test Method,” Air and Waste Management Association, Nashville, TN, 96-RP132.01, June 23-28, 1996.



- 5). Kinner, L.L., and Peeler, J.W., "Evaluation of HAPSITE and a Direct Interface GCMS Test Method for Measurement of Volatile Organic Compounds in Stationary Source Emissions" Prepared for Leybold Inficon Inc., July 1997.

## 16 TABLES, FIGURES AND FLOWCHARTS

- 16.1 Table 1. Table 1 outlines the method QA/QC criteria.
- 16.2 Table 2. Table 2 outlines the mass spectral relative abundance criteria for BFB.
- 16.3 Table 3. Table 3 outlines recommended tune criteria for a blended mixture of BPFB/TRIS
- 16.4 Table 4. Table 4 outlines recommended mass spectral relative abundance criteria for the GC separated BPFB and TRIS.
- 16.5 Table 5. Table 5 contains the surrogate continuing system calibration compounds.
- 16.6 Figure 1. Figure 1 illustrates a generalized sampling system diagram.
- 16.7 Figure 2. Figure 2 is a flowchart representing the GCMS operational method.

TABLE 1. Calibration and Sampling QA/QC Criteria

Operational Mode	IS Recommended Requirements	GC Retention Time Requirements	Extracted Ion Chromatographic Criteria	Accuracy and Sensitivity
<b>Mass Spectrometer Tune</b>	See Table 3			
<b>Three-Point Calibration</b>	See Table 4	RTs for individual VOHAPS must be within ±6% of each other from run to run.	<p>% RSDs calculated from the individual RRFs at each calibration point must be ±20% for each target analyte.</p> <p>The RFs of the internal standards must be within -50 %- 100% of the mean for the initial three-point calibration.</p>	<p>ARRFs must be ≥0.25 to ensure proper instrumental response.</p> <p>A signal to noise of 10:1 is recommended for the low concentration level.</p>
<b>Surrogate Continuing Calibration Check (CCC)</b>	See Table 4	RTs for individual VOHAPS must be within ±6% of the initial three-point calibration.	The RFs of the internal standards must be within -50 %- 100% of their ARFs from the initial three-point calibration.	Surrogate Continuing System Calibration results must be within ±20% of the manufacturers certified value from analysis by the three-point calibration for valid continuing calibration.

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<b>Sampling</b>	See Table 4	RTs for detected VOHAPS must be within $\pm 6\%$ of those in the initial three-point calibration.	The RFs of the internal standards must be within -50 %- 100% of their ARFs from the initial three-point calibration.	Spectral ions of greater than 10% abundance in the identified compounds mass spectrum must also be contained in the reference calibration spectrum for that particular target analyte.
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Table 2. Relative Ion Abundance Criteria for Bromofluorobenzene

Mass Fragment	ION ABUNDANCE CRITERIA
50	15-40%
75	30-60%
95	Base Peak
96	5-9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5-9% of mass 174
176	>95% but <101% of mass 174
177	5-9% of mass 174

Table 3. Instrument Performance for Blended TRIS/BPFB Internal Standard Mixture in Tune

Mass Fragment	Percent Relative Low Abundance	Percent Relative High Abundance
50	5	8
55	5	8
69	33	36
93	39	45
117	100	100
167	50	65
248	30	99
263	20	50
282	10	30

Table 4. Instrument Performance for Separated Internal Standard Mixture

Internal Standard	Mass	Ion Abundance Criteria
<b>Tris</b>	50	5-20% of mass 69
	69	Base Peak
	75	40-60% of mass 69
	213	50-90% of mass 69
	263	75-95% of mass 69
	282	30-70% of mass 69
<b>BPFB</b>	93	20-50% of mass 117
	117	Base Peak
	167	45-75% of mass 117
	245	< 2% of mass 246
	246	> 25% of mass 117
	247	5-9% of mass 246
	248	> 25% of mass 117
	249	5-9% of mass 248

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Table 5 Surrogate System Continuing Calibration Compounds

COMPOUND	CLASS REPRESENTING	MOLECULAR WEIGHT	QUANT-ION	RETENTION TIME
Methylene Chloride	Chlorinated	84	84	2:41 mins
Methyl Ethyl Ketone (MEK)	Polar	72	72	2:57 mins
Carbon Tetrachloride	Chlorinated	152	117	3:35 mins
Toluene	Aromatic	92	91	5:08 mins
Chlorobenzene	Chlorinated Aromatic	112	112	7:22 mins
O-Xylene	Aromatic	91	91	9:44 min

Table 6 Surrogates and Corresponding Analytes

Compound	Retention Time*	Suggested Quantion	Surrogate	Suggested Surrogate Quantion
Chloromethane	1:09	50	Methylene Chloride	49/84
vinyl chloride	1:11	62	Methylene Chloride	49/84
Bromomethane	1:13	94	Methylene Chloride	49/84
Chloroethane	1:15	64	Methylene Chloride	49/84
Methylene Chloride	1:25	49	Methylene Chloride	49/84
1,1-dichloroethene	1:25	61	Methylene Chloride	49/84
carbon disulfide	1:31	76	Toluene	91/92
t-1,2-dichloroethene	1:34	96	Methylene Chloride	49/84
1,1-dichloroethane	1:36	63	Methylene Chloride	49/84
vinyl acetate	1:36	86	MEK	72
Methyl Ethyl Ketone	1:40	72	MEK	72
c-1,2-dichloroethene	1:44	61	Methylene Chloride	49/84
chloroform	1:48	83	Methylene Chloride	49/84
1,2-dichloroethane	1:58	62	Methylene Chloride	49/84
1,1,1-trichloroethane	2:01	97	Methylene Chloride	49/84
benzene	2:10	78	Toluene	91/92
carbon tetrachloride	2:12	117	Carbon	117
1,2-dichloropropane	2:25	63	Carbon	117
bromodichloromethane	2:29	129	Carbon	117
trichloroethene	2:30	95	Carbon	117
c-1,2-dichloropropene	2:54	75	Carbon	117
MIBK	2:56	85	MEK	72
t-1,2-dichloropropene	3:12	75	Carbon	117
1,1,2-trichloroethane	3:17	83	Carbon	117
Toluene	3:31	91	Toluene	91/92
2-hexanone	3:48	58	MEK	72
dibromochloromethane	3:49	129	Carbon	117
Tetrachloroethylene	4:33	94	Carbon	117
chlorobenzene	5:27	77	Chlorobenzene	112
ethylbenzene	6:07	91	Toluene	91/92
bromoform	6:28	173	Carbon	152
p-xylene	6:30	91	o-xylene	91
m-xylene	6:30	91	o-xylene	91
styrene	7:17	104	o-xylene	91
1,1,2,2-tetrachloroethane	7:30	83	Carbon	117/152
o-xylene	7:31	91	o-xylene	91

\* Retention Time based on a 60 C isothermal separation on a SPB - 1 GC Column, 30 meters long, 0.32 mm ID,

1 micron film thickness

## APPENDIX A - DEFINITIONS

AMU = Atomic Mass Unit, molecular weight of positively charged fragmented ions detected by mass spectrometer electron multiplier.

ARRF = Average Relative Response Factor (see Section 10.2, equation 2)

Blank Analysis = Injection of zero air or nitrogen into the GCMS to determine background levels of the target analytes.

BFB = Bromofluorobenzene, A standard mass spectrometer tuning compound.

BPFB = Bromopentafluorobenzene, one of the recommended internal standards.

CCC = Continuing calibration check. Performed before each testing day, before resuming sampling after instrument shutdown or malfunction, and before continuation of sampling after 12 hours of continuous instrument operation.

GC = Gas Chromatograph

GCMS = Analytical technique using a mass spectrometer as a GC detector.

Internal Standard (IS) = Compounds used as markers in the analysis of GCMS data. The purpose of the internal standards is to correct for hardware related error such as, different injection volumes, operational temperature fluctuations, and electron multiplier drift.

MS = Mass Spectrometer

ppbv = Parts per billion by volume

ppmv = Parts per million by volume

Quantion - Quantification ion, A specific ion in the analytes mass spectrum that is used for quantification.

RRF = Relative Response Factor (see Section 10.2, equation 1)

RT = Retention time, the time corresponding to the elution of a peak (scan number) from the chromatographic column measured from the injection point.

System Calibration = A means of injecting the calibration standard(s) through the entire sampling system. In a system calibration, the sample pump draws calibration gas only through the sampling system. See Figure 1.

System Zero = A means of injecting dry nitrogen or zero gas through the entire sampling system to determine the system background levels of the target analytes.

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Three-point calibration = The initial instrument calibration using 300 ppb, 1 and 10 ppm VOHAP mixture standards.

TRIS = 1,3,5-trifluoromethylbenzene, One of the recommended internal standards