VOLATILE ORGANIC COMPOUNDS BY VACUUM DISTILLATION IN COMBINATION WITH GAS CHROMATOGRAPHY/MASS SPECTROMETRY (VD/GC/MS)

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed standard operating procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentrations of volatile organic compounds, and some low-boiling semivolatile organic compounds, in a variety of liquid, solid, and oily waste matrices, as well as animal tissues. This method differs from the use of method 5032/8260 in the use of internal standards to measure matrix effects and compensate analyte responses for matrix effects. This method is applicable to nearly all types of matrices, including water, soil, sediment, sludge, oil, and animal tissue. This method should be considered for samples where matrix effects are anticipated to severely impact analytical results. The following compounds have been determined by this method:

Compound	CAS Registry No.[a]	Response Quality
Acetone	67-64-1	c
Acetonitrile	75-05-8	c
Acetophenone	98-86-2	c
Acrolein	107-02-8	c
Acrylonitrile	107-13-1	c
Allyl Chloride	107-05-1	c
t-Amyl ethyl ether (TAEE) (4,4-Dimethyl-3-oxahexane)	919-94-8	c
t-Amyl methyl ether (TAME)	994-05-8	c
Aniline	62-53-3	Q
Benzene	71-43-2	c
Bromochloromethane	75-97-5	c
Bromodichloromethane	75-27-4	c
Bromoform	75-25-2	c

Compound	CAS Registry No.[a]	Response Quality
Bromomethane	74-83-9	c
2-Butanone	78-93-3	c
t-Butyl alcohol (TBA)	75-65-0	c
n-Butylbenzene	104-51-8	c
sec-Butylbenzene	135-98-8	c
tert-Butylbenzene	98-06-6	c
Carbon disulfide	75-15-0	c
Carbon tetrachloride	56-23-5	c
Chlorobenzene	108-90-7	c
Chlorodibromomethane	124-48-1	c
Chloroethane	75-00-3	c
Chloroform	67-66-3	c
Chloromethane	74-87-3	c
2-Chlorotoluene	95-49-8	c
4-Chlorotoluene	106-43-4	c
Cyclohexane	110-82-7	c
1,2-Dibromo-3-chloropropane	96-12-8	c
Dibromomethane	74-95-3	c
1,2-Dichlorobenzene	95-50-1	c
1,3-Dichlorobenzene	541-73-1	c
1,4-Dichlorobenzene	106-46-7	c
cis-1,4-Dichloro-2-butene	764-41-0	c
trans-1,4-Dichloro-2-butene	110-57-6	c
Dichlorodifluoromethane	75-71-8	c
1,1-Dichloroethane	75-34-3	c
1,2-Dichloroethane	107-06-2	c
1,1-Dichloroethene	75-35-4	c
trans-1,2-Dichloroethene	156-60-5	c
cis-1,2-Dichloroethene	156-59-2	c
1,2-Dichloropropane	78-87-5	c
1,3-Dichloropropane	142-28-9	c
2,2-Dichloropropane	594-20-7	c
1,1-Dichloropropene	563-58-6	c
cis-1,3-Dichloropropene	10061-01-5	c
trans-1,3-Dichloropropene	10061-02-6	c
Diethyl ether	60-29-7	c
Diisopropyl ether (DIPE)	108-20-3	c

Compound	CAS Registry No.[a]	Response Quality
1,4-Dioxane	123-91-1	c
Ethanol	64-17-5	c
Ethyl acetate	141-78-6	c
Ethylbenzene	100-41-4	c
Ethyl *t*-butyl ether (ETBE)	637-92-3	c
Ethyl methacrylate	97-63-2	c
Hexachlorobutadiene	87-68-3	c
2-Hexanone	591-78-6	c
Iodomethane	74-88-4	c
Isobutyl alcohol	78-83-1	c
Isopropylbenzene	98-82-8	c
p-Isopropyltoluene	99-87-6	c
Methacrylonitrile	126-98-7	c
Methyl acetate	79-20-9	c
Methyl cyclohexane	108-87-2	c
Methyl *t*-butyl ether (MTBE)	1634-04-4	c
Methylene chloride	75-09-2	c
Methyl methacrylate	80-62-6	c
1-Methylnaphthalene	90-12-0	c
2-Methylnaphthalene	91-57-6	c
4-Methyl-2-pentanone	108-10-1	c
Naphthalene	91-20-3	c
Nitrobenzene	98-95-3	c
N-Nitrosodibutylamine	924-16-3	Q
N-Nitrosodiethylamine	55-18-5	Q,pc
N-Nitrosodimethylamine	62-75-9	Q,pc
N-Nitrosodi-*n*-propylamine	621-64-7	Q
N-Nitrosomethylethylamine	10595-95-6	Q,pc
Pentachloroethane	76-01-7	c
2-Picoline	109-06-8	Q,pc
Propionitrile	107-12-0	c
n-Propylbenzene	103-65-1	c
Pyridine	110-86-1	c
Styrene	100-42-5	c
1,1,2,2-Tetrachloroethane	79-34-5	c
Tetrachloroethene	127-18-4	c
Tetrahydrofuran	109-99-9	c

Compound	CAS Registry No.[a]	Response Quality
Toluene	108-88-3	c
o-Toluidine	95-53-4	Q
1,2,3-Trichlorobenzene	87-61-6	c
1,2,4-Trichlorobenzene	120-82-1	c
1,1,1-Trichloroethane	71-55-6	c
1,1,2-Trichloroethane	79-00-5	c
Trichloroethene	79-01-6	c
Trichlorofluoromethane	75-69-4	c
1,2,3-Trichloropropane	96-18-4	c
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	c
1,2,4-Trimethylbenzene	95-63-6	c
1,3,5-Trimethylbenzene	108-67-8	c
Vinyl chloride	75-01-4	c
o-Xylene	95-47-6	c
m-Xylene	108-38-3	c
p-Xylene	106-42-3	c
Diethylether-d_{10}	2679-89-2	RV IS, RT
Acetone-C_{13}	666-52-4	RV IS
Methylenechloride-d_2	1665-00-5	surrogate
Nitromethane-C_{13}		surrogate
Hexafluorobenzene	392-56-3	FP, RV IS, RT
Tetrahydrofuran-d_8	1693-74-9	RV IS
Ethylacetate-C_{13}	84508-45-2	surrogate
Pentafluorobenzene	363-72-4	BP IS
Benzene-d_6	1076-43-3	surrogate
1,2-Dichloroethane-d_6	17060-07-0	FP, RV IS
Fluorobenzene	462-06-6	FP, RV IS, RT
1,4-Difluorobenzene	540-36-3	RV IS
1,2-Dichloropropane-d_6		surrogate
1,4-Dioxane-d_8	17647-74-4	RV IS, RT
Toluene-d_8	2037-26-5	BP IS
Pyridine-d_5	7291-22-7	RV IS, surrogate

Compound	CAS Registry No.[a]	Response Quality
1,1,2-Trichloropropane-d_3		surrogate
1,2-Dibromoethane-d_4	22581-63-1	RV IS
Chlorobenzene-d_5	3114-55-4	RV IS
o-Xylene-d_{10}	56004-61-6	RV IS
4-Bromofluorobenzene	460-00-4	surrogate
Bromobenzene-d_5	4165-57-5	BP IS
1,2-Dichlorobenzene-d_4	2199-69-1	BP IS, RT
Decafluorobiphenyl	434-90-2	surrogate
Nitrobenzene-d_5	4165-60-0	surrogate
Acetophenone-d_5	28077-31-4	surrogate, RT
1,2,4-Trichlorobenzene-d_3		BP IS, RT
Naphthalene-d_8	1146-65-2	BP IS, surrogate
1-Methylnaphthalene-d_{10}	38072-94-5	surrogate BP IS

[a] Chemical Abstract Service Registry Number

c	=	Adequate response by this technique
pc	=	Poor chromatographic behavior
Q	=	Compound very sensitive to experimental conditions and response may be insufficient under conditions optimal for most analytes
FP	=	First Pass internal standard
RV-IS	=	Relative volatility internal standard
BP-IS	=	Boiling point internal standard
surrogate	=	Compound added to samples for measurement
RT	=	Retention time reference standard

1.2 This method can be used to quantitate most volatile organic compounds that have a boiling point below 245°C and a water-to-air partition coefficient below 15,000, which includes compounds that are miscible with water. Note that this range includes compounds not normally considered to be volatile analytes (e.g., nitrosamines, aniline, and pyridine). When compounds that are indicated with a "Q" or "pc" are the primary focus for determination, experimental conditions (e.g., GC column selection and vacuum distiller conditions) should be re-evaluated.

1.3 This method is based on a vacuum distillation and cryogenic trapping procedure (Method 5032) followed by gas chromatography/mass spectrometry (GC/MS). The method incorporates internal standard-based matrix correction, where the analysis of multiple internal standards is used to predict matrix effects. The normalization of matrix effects has the impact of making method 8261 analyses matrix independent and allows multiple matrices to be analyzed

within a sample batch. As a result, the calculations involved are specific to this method, and may not be used with data generated by another method. This method includes all of the necessary steps from sample preparation through instrumental analysis.

1.4 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 5000, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 Use of this method is restricted to use by, or under the supervision of, personnel appropriately experienced who are familiar with the techniques of vacuum distillation and trained 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.

2.0 SUMMARY OF METHOD

2.1 Method 8261 uses vacuum to vaporize analytes, separating them from the sample matrix. The volatilized material passes through a condenser column where a majority of vaporized water is condensed. A trap, cooled to cryogenic temperature, then condenses the analytes that have been volatilized from the sample and have passed through the condenser column. The volatile compounds are introduced into the gas chromatograph by a vacuum distiller. The responses of analytes separated by the gas chromatograph (GC) are measured by a mass spectrometer, interfaced to the gas chromatograph, using the ions identified in Table 3.

2.2 An aliquot of a liquid, solid, or tissue sample is transferred to a sample flask (reagent water is added to the aliquot of soil, tissue, or oil.), spiked with the internal standard mixture identified in Sec. 7.6, which is then attached to the vacuum distillation apparatus (see Figure 1). The sample volumes recommended in the method may be varied, depending on analytical requirements, while using the same calibration curve. The internal standard corrections will compensate for variations in sample size as explained in Sec. 12.

2.2 The pressure in the sample chamber is reduced using a vacuum pump and remains at approximately 10 torr (the vapor pressure of water) as water is removed from the sample. The vapor is passed over a condenser coil chilled to approximately 5°C, which results in the condensation of water vapor. The uncondensed distillate is cryogenically trapped in a section of stainless steel tubing (no absorbant) and chilled cryogenically with liquid nitrogen.

2.3 After distillation, the condensate contained in the cryotrap is thermally desorbed and transferred to the gas chromatograph using helium as a carrier gas. 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, or the effluent from the

trap is sent to an injection port operating in the split mode for injection to a narrow-bore capillary column. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).

2.4 Analytes eluted from the gas chromatographic 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.)

2.5 It must be emphasized that the vacuum distillation conditions are optimized to generally remove analytes from the sample matrix and to isolate water from the distillate. The conditions may be varied to optimize the method for any given analyte or group of analytes. The length of time required for distillation may vary due to matrix effects or the analyte group of interest. Operating parameters may be varied to achieve optimum analyte recovery.

2.6 Quantitation is accomplished in three specific steps.

2.6.1 The first step is the measurement of the response of each analyte at the mass spectrometer. The amount (mass) of analyte introduced into the mass spectrometer is determined by comparing the response (area) of the quantitation ion for the analyte from a sample analysis to the quantitation ion response generated during the initial calibration.

NOTE: The response as noted in this method differs from the response factor as described in Method 8260, where a value is calculated based on a retention time that is relative to the nearest internal standard. For a more through explanation of the Method 8261 theory and chemistry principles please refer to the document found at the following link: http://www.epa.gov/nerlesd1/chemistry/vacuum/training/pdf/theory-rev5.pdf

2.6.2 The second step is the determination of internal standard recovery. The recommended internal standards are listed in Table 6. The internal standard recovery is equal to the total internal standard compound response for a sample divided by its average response during initial calibration. The internal standard recoveries are used to determine recovery as a function of chemical properties. Using the resultant function, recovery is is then calculated for the analytes using their respective chemical properties (see Sec. 12).

2.6.3 Finally, using the recovery , sample size, and quantity of analyte detected at the mass spectrometer, the concentration of analyte is calculated.

2.6.4 The software that generates the matrix corrections is freely available from the EPA at http://www.epa.gov/nerlesd1/chemistry/vacuum/default.htm.

2.7 This method includes specific calibration and quality control steps that supersede the general requirements provided in Methods 8000 and 8260.

3.0 DEFINITIONS

Terms specific to this procedure are provided in this section. Also refer to Chapter One and the manufacturer's instructions for other definitions that may be relevant to this procedure.

RV	Relative volatility in method 8261 is a chemical property that describes the ability of a compound to be distilled from water. The value is closely related to their water to air partition coefficient (K) and is determined experimentally. Either relative volatility or K-values can be used to describe this effect and Table 3 lists relative volatility values for the compounds in Table 1 that are equivalent to K (Ref. 7).
RV - IS	An internal standard used to measure effects relating to relative volatility. The relative volatility or gas-liquid partitioning internal standards are added to the sample to measure the recovery of analytes relative to how the compound partitions between gas and liquid (partition coefficient K). Compounds that are going to be used as relative volatility internal standards that have boiling points above 40°C must first be evaluated for potential losses due to condensation and a correction made to their recoveries when condensation is evident. Relative volatility internal standards are also known as distillation performance surrogates.
BP	Boiling point of a compound.
BP - IS	An internal standard used to measure effects relating to boiling point. The boiling point or condensation internal standards are added to the sample to measure the recovery of analytes relative to how the compounds condense on apparatus and sample surfaces during a vacuum distillation. The boiling point internal standards are identified in Table 3.
Cryotrap	Component of vacuum distiller where distillates are cryogenically frozen prior to transfer to GC.
R,r	Recovery of compound that is measured using internal standards. The uncertainty associated in the measurement of R is r.
R_T, r_T	Recovery of a compound reflecting boiling point (R_β) and relative volatility (R_α) recoveries measured by internal standards. The uncertainty associated in the measurement of R_T is r_T.
R_α, r_α	Recovery of a compound that relates to its relative volatility as measured by its RV-IS. The uncertainty associated in the measurement of R_α is r_α.
R_β, r_β	Recovery of a compound that relates to its boiling point as measured by its BP-IS. The uncertainty associated in the measurement of R_β is r_β.
RF	Response factor is the response of the quantitation ion of a compound detected by a mass spectrometer. Response factor, as noted in Method 8261, is in units of area counts divided by mass (*e.g.*, cts/ngs).
RT	Internal standard used to measure consistency of chromatographic retention times.
Reference Run	Analysis used as a reference point for internal standard comparisons in order to measure matrix effects on calibration standards. After a calibration curve is generated the calibration is the reference for subsequent analyses.

IS — Internal standards are used to correct the response of analytes as their associated internal standards may vary from their calibrated response. In method 8261 internal standard are compounds added to a sample prior to analysis and they are used to normalize the response of analytes for their chemical properties, relative volatility, and boiling point. While method 8260 internal standards are used to normalize the responses of analytes as a function of retention time, the Method 8261 internal standards normalize as functions of relative volatility and boiling point. For a more through explanation of the Method 8261 chemistry principles please refer to the document found at the following link: http://www.epa.gov/nerlesd1/chemistry/vacuum/training/pdf/theory-rev5.pdf

FP — First pass internal standard. First pass internal standards are used to identify effects that are due to relative volatility on boiling point internal standards. First pass internal standards are only used to clarify boiling point internal standards recoveries.

Surrogate — Compound added to a sample before analysis and used as a metric for method performance.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis (e.g., an elevated baseline in the chromatograms). All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Four for general guidance on the cleaning of glassware.

4.2 Major contaminant sources are volatile materials in the laboratory. The laboratory where the analysis is to be performed should be free of solvents other than water and methanol. Many common solvents, most notably acetone and methylene chloride, are frequently found in laboratory air at low levels. The sample chamber should be loaded in an environment that is clean enough to eliminate the potential for contamination from ambient sources. In addition, the use of non-PTFE thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. Subtracting blank values from sample results is not permitted. If reporting values for situations where the laboratory feels is a false positive result for a sample, the laboratory should fully explain this in text accompanying the uncorrected data and / or include a data qualifier that is accompanied with an explanation.

4.3 Contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile or semivolatile organic compounds. The recommended vacuum distillation procedure (11.2.2) provides sufficient decontamination to limit memory of previous volatile compounds to less than one percent in a following run. The memory of a semivolatile compound can be as high as five percent. To minimize the contamination further, a clean sample vessel and O-ring should be put in at the port that contained the high-concentration sample and reagent blanks analyzed until the system is shown free of contamination. As a precaution, sample syringes or other sample aliquoting devices should be rinsed with two portions of organic-free reagent water between samples. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross-contamination.

Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established. Note: in instances of gross contamination by higher boiling compounds (e.g., components of fuels) an overnight decontamination routine may be required (see vendor specifications for decontamination procedures).

4.4 After analysis, the sample vessel should be washed with a soap solution and rinsed with organic-free reagent water. When samples contain high levels of organic matter (e.g., biota), sonication and rinsing the sample vessel with methanol may be required. Overnight heating to over 100 °C is recommended.

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

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

4.7 Use of sensitive mass spectrometers to achieve lower quantitation levels will increase the potential to detect laboratory contaminants as interferences.

5.0 SAFETY

This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Vacuum distillation apparatus (See Figure 1) -- The basic apparatus consists of a sample chamber connected to a condenser that is attached to a heated six-port valve (V4) which is attached to a cryogenically cooled trap (cryotrap). The condenser is flushed with nitrogen gas after each distillation. Vacuum is supplied by a vacuum pump through the six-port

valve during distillations and through a larger orifice valve connected directly to the condenser for evacuating the condenser (after nitrogen flushing) and system lines between sample distillations.

6.1.1 The sampling valve (V4) is connected to the following: condenser (by way of vacuum pump valve - V3), vacuum pump, cryotrap, gas chromatograph/mass spectrometer. The six-port sampling valve (V4) should be heated to at least 160 °C to prevent condensation and potential carryover.

6.1.2 The condenser is operated at two different temperatures. The lower temperature is between -5°C and 10°C, and the upper temperature is 95°C. The lower temperature is used to condense water and should be at a consistent temperature throughout the interior surface. The condenser is heated to the upper temperature to remove water and potential contaminants. The initial apparatus described in Reference 9 used circulating fluids (see Figure 1) but other means of controlling temperatures may be used.

6.1.3 The apparatus internal transfer lines are heated to 95 °C, a temperature sufficient to prevent condensation of analytes onto condenser walls, valves, and connections. The transfer line from the sampling valve to the gas chromatograph should be heated to a temperature between 150°C and the upper temperature utilized by the GC program.

6.1.4 Vacuum is supplied by a pump with displacement $\geq$1 ft^3min^{-1} and capable of reaching 10^{-4} torr. This vacuum should be sufficient to volatilize >0.3 g of water from a 5 mL water sample in 7.5 min. The vacuum of the system should be monitored for integrity. Improperly seated seals or errors in operation will cause elevated pressure readings.

6.1.5 The cryotrap condenser distillate contained in the 1/8-in stainless steel tubing can be blocked when the condenser temperature is not sufficient to trap water or a sample contains a large amount of volatile compounds. These problems may be detected by a rapid drop in pressure readings recorded in the vacuum distillation log file.

6.1.6 The vacuum distiller software controls all conditions of the vacuum distillation apparatus during distillation and decontamination routines. The software also records all vacuum distiller readings (time, temperatures, pressure) in a log file that allows interpretation of the vacuum distillation process. The log file is considered integral to each distillation and should be consulted when errors are suspected.

6.1.7 Any apparatus used must demonstrate appropriate performance for the intended application (see Tables 10 through 15).

6.2 Gas chromatograph/mass spectrometer system

6.2.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection with appropriate interface for sample introduction device. The system includes all required accessories, such as syringes, analytical columns, and gases.

6.2.1.1 The GC should be equipped with variable constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation.

6.2.1.2 For some column configurations, the column oven must be cooled to less than 30°C, therefore, a subambient oven controller may be necessary.

6.2.1.3 The capillary column is either directly coupled to the source or interfaced through a jet separator, depending on the size of the capillary and the requirements of the GC/MS system.

6.2.1.4 Capillary pre-column interface - This device is the interface between the sample introduction device and the capillary gas chromatograph, and is necessary when using cryogenic cooling. The interface condenses the desorbed sample components and focuses them into a narrow band on an uncoated fused-silica capillary pre-column. When the interface is flash heated, the sample is transferred to the analytical capillary column.

6.2.1.5 During the cryofocussing step, the temperature of the fused-silica in the interface is maintained at -150°C under a stream of liquid nitrogen. After the desorption period, the interface must be capable of rapid heating to 250°C in 15 seconds or less to complete the transfer of analytes.

6.2.2 Gas chromatographic columns - The following columns have been found to provide good separation of volatile compounds, however they are not listed in preferential order based on performance and the ability to achieve project-specific data quality objectives.

6.2.2.1 Column 1 - 30 - 75 m x 0.53 mm ID capillary column coated with DB-624 (J&W Scientific), Rt_x-502.2 (RESTEK), or VOCOL (Supelco), 3-µm film thickness, or equivalent.

6.2.2.2 Column 2 - 30 m x 0.25 - 0.32 mm ID capillary column coated with 95% dimethyl - 5% diphenyl polysiloxane (DB-5, Rt_x-5, SPB-5, or equivalent), 1-µm film thickness.

6.2.2.3 Column 3 - 60 m x 0.32 mm ID capillary column coated with DB-624 (J&W Scientific), 1.8-µm film thickness, or equivalent.

6.2.2.4 Column 4 - 20m x 0.18mm ID, 1.0um column film thickness.

6.3 Mass spectrometer

6.3.1 Capable of scanning from m/z 35 to 270 every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 4-bromofluorobenzene (BFB) which meet the criteria as outlined in Sec. 11.3.1.

6.3.2 An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. Because ion-molecule reactions with water and methanol in an ion trap mass spectrometer may produce interferences that coelute with chloromethane and chloroethane, the base peak for both of these analytes will be at m/z 49. This ion should be used as the quantitation ion in this case. The mass spectrometer must be capable of producing a mass spectrum for BFB which meet the criteria as outlined in Sec. 11.3.1.

6.4 GC/MS interface - Two alternatives may be used to interface the GC to the mass spectrometer.

6.4.1 Direct coupling, by inserting the column into the mass spectrometer, is generally used for 0.25 - 0.32 mm ID columns.

6.4.2 A jet separator, including an all-glass transfer line and glass enrichment device or split interface, is used with a 0.53 mm column.

6.4.3 Any enrichment device or transfer line may be used, if all of the performance specifications described in Sec. 9.0 (including acceptable calibration at 50 ng or less) can be achieved. GC/MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass may be deactivated by silanizing with dichlorodimethylsilane.

6.5 Data system - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

6.6 Containers for liquid nitrogen -- Dewars or other containers suitable for holding the liquid nitrogen used to cool the cryogenic trap and sample loop.

6.7 Microsyringes -- 10-µL, 25-µL, 100-µL, 250-µL, 500-µL, and 1000-µL. Each of these syringes should be equipped with a 20-gauge (0.006 in ID) needle.

6.8 Syringe -- 5-mL and 10-mL glass gas-tight, with shutoff valve.

6.9 Balance-Analytical, capable of accurately weighing to 0.0001 g. and a top-loading balance capable of weighing to 0.01 g.

6.10 Disposable pipets - Pasteur.

6.11 Sample flask -- 100-mL borosilicate bulb joined to a 15-mm ID borosilicate O-ring connector, or equivalent. The flask must be capable of being evacuated to a pressure of 10 millitorr without implosion. The flask is sealed for sample storage with an O-ring capable of maintaining the vacuum in the chamber, a 15-mm ID O-ring connector cap, and a pinch clamp.

6.12 Volumetric flasks, Class A - 10-mL and 100-mL, with ground-glass stoppers.

6.13 Spatula - Stainless steel.

7.0 REAGENTS AND SUPPLIES

7.1 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination

7.2 Organic-free reagent water -- All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

7.3 Methanol -- CH_3OH, purge-and-trap grade, or equivalent. Store away from other solvents.

7.4 Stock standard solutions -- The solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

7.4.1 Place about 9.8 mL of methanol in a 10-mL tared, ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.4.2 Add the assayed pure standard material, as described below.

7.4.2.1 Liquids -- Using a 100-µL syringe, immediately add two or more drops of assayed pure standard material to the flask, then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

7.4.2.2 Gases -- To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the pure standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a septum. Attach polytetrafluoroethylene (PTFE) tubing to the side-arm relief valve and direct a gentle stream of gas onto the methanol meniscus.

7.4.3 Reweigh, dilute to volume, stopper, and mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (µg/µL) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.4.4 Transfer the stock standard solution into a bottle with a PTFE-lined screw-cap. Store, with minimal headspace and protected from light, at $\leq$6°C or as recommended by the standard manufacturer. Standards should be returned to the refrigerator or freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

7.4.5 Frequency of Standard Preparation

7.4.5.1 Standards for the permanent gases should be monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for gases usually need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Dichlorodifluoromethane and dichloromethane will usually be the first compounds to evaporate from the standard and should, therefore, be monitored very closely when standards are held beyond one week.

7.4.5.2 Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases usually need to be replaced after one month for working standards and three months for opened stocks or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently.

7.5 Secondary dilution standards

Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards in methanol containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Store in a vial with no headspace. Secondary standards for most compounds should be replaced after 2-4 weeks unless the acceptability of the standard can be documented. Secondary standards for gases should be replaced after one week unless the acceptability of the standard can be documented. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations. The analyst should also handle and store standards as stated in Sec. 7.4.4 and return them to the refrigerator or freezer as soon as standard mixing or diluting is completed to prevent the evaporation of volatile target compounds.

7.6 Surrogate standards - The recommended surrogates are presented in Table 6. These surrogates represent groupings of analytes (volatile, non-purgeable, and semivolatile compounds). Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described above, and a surrogate standard spiking solution should be prepared from the stock at an appropriate concentration in methanol. Each sample undergoing GC/MS analysis must be spiked with the surrogate spiking solution prior to analysis. If a more sensitive mass spectrometer is employed to achieve lower quantitation levels, then more dilute surrogate solutions may be required.

7.6.1 The range of compounds that are considered as volatile compounds by this method have boiling points less than 159 °C and relative volatility values $\leq$ 100. The surrogates that represent this group are methylene chloride-d_2, benzene-d_6, 1,2-dichloropropane-d_6, 1,1,2 trichloroethane-d_3 and 4-bromofluorobenzene.

7.6.2 The range of compounds that are considered as non-purgeable by this method are those that have relative volatility values greater than 100. The surrogates that represent this group are nitromethane-C^{13}, ethyl acetate-C^{13} and pyridine-d_5. Ethyl acetate-C^{13} has been found to quickly degrade in the presence of biologically active samples. Pyridine-d_5 is susceptible to chromatographic degradation in the presence of excessive water being transferred to the gas chromatograph from the vacuum distiller's cryotrap.

7.6.3 The range of compounds that are considered as semi-volatile compounds by this method have boiling points greater than 159 °C. The surrogates for this group include decafluorobiphenyl, nitrobenzene-d_5, acetophenone-d_5, and naphthalene-d_8.

7.7 Internal standard standards

This method incorporates internal standards that are added to each sample prior to analysis and are used to monitor and correct for matrix effects such as water-to-air partitioning (as relative volatility) and vapor pressure (as boiling point) and are listed in Table6. The specific internal standard used are described in the following paragraphs. Additional information is provided in the glossary. A stock solution containing all of the internal standard should be prepared in methanol at the concentrations listed in Table 6 using the same guidance given for stock standard solution preparation noted in Sec. 7.4. Each sample should be spiked with 5 µL of the internal standard spiking solution prior to analysis. The boiling points and relative volatility values for analytes and internal standard are presented in Table 4.

7.7.1 Relative volatility internal standard - These standards, listed in Table 4, are added to the sample to measure the recovery of analytes relative to how the compound partitions between gas and liquid (partition coefficient K). Compounds that are going to be used as relative volatility internal standards that have boiling points above 40 °C must first be evaluated for potential losses due to condensation and a correction made to their recoveries when condensation is evident. Relative volatility internal standards are also known as distillation performance internal standards.

7.7.2 Boiling point internal standards - These internal standards are listed in Table 8. These internal standards are added to the sample to measure the recovery of analytes relative to how the compounds condense on apparatus and sample surfaces during a vacuum distillation.

7.8 4-Bromofluorobenzene (BFB) standard -- A solution containing 25 ng/µL of BFB in methanol should be prepared. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then a more dilute BFB standard solution may be required.

7.9 Calibration standards -There are two types of calibration standards used for this method: initial calibration standards and calibration verification standards. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

7.9.1 Initial calibration standards should be prepared at a minimum of five different concentrations from the secondary dilution of stock standards (see Secs. 7.4 and 7.5) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC/MS system. Initial calibration standards should be mixed from fresh stock standards and dilution standards when generating an initial calibration curve.

7.9.2 Calibration verification standards should be prepared at a concentration near the mid-point of the initial calibration range from the secondary dilution of stock standards (see Secs. 7.4 and 7.5) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. See Sec. 11.4 for guidance on calibration verification.

7.9.3 It is the intent of EPA that all target analytes for a particular analysis be included in the initial calibration and calibration verification standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

7.9.4 The calibration standards must also contain the internal standards chosen for the analysis.

7.10 Liquid nitrogen -- For use in cooling the cryogenic trap (see Figure 1) and the condenser described in Reference 9, if employed.

7.11 Matrix spiking and laboratory control sample (LCS) standards - Matrix spiking is not a requirement of this method due to the direct measurement of matrix effects. See Method 5000 for instructions on preparing the LCS standard. The laboratory control standards should be from the same source as the initial calibration standards to restrict the influence of accuracy on the determination of recovery throughout preparation and analysis. The LCS standards should be prepared from volatile organic compounds which are representative of the compounds being investigated.

7.11.1 Some permits may require the spiking of specific compounds of interest. The standard should be prepared in methanol, with each compound present at an appropriate concentration.

7.11.2 If a more sensitive mass spectrometer is employed to achieve lower quantitation levels, more dilute laboratory control standard (LCS) solutions may be required.

7.12 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standards be stored with minimal headspace and protected from light, at $\leq 6^{\circ}C$ or as recommended by the standard manufacturer using screw-cap or crimp-top amber containers equipped with PTFE liners. Standards should be returned to the refrigerator or freezer as soon as the analyst has completed mixing or diluting the standards to prevent the loss of volatile target compounds.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 See the introductory material to Chapter Four, "Organic Analytes."

8.2 Aqueous samples should be stored with minimal or no headspace to minimize the loss of highly volatile analytes.

8.3 Samples to be analyzed for volatile compounds should be stored separately from standards and from other samples expected to contain significantly different concentrations of volatile compounds, or from samples collected for the analysis of other parameters such as semivolatiles.

NOTE: Storage blanks should be used to monitor potential cross-contamination of samples due to improper storage conditions. The specific of this type of monitoring activity should be outlined in a laboratory standard operating procedure pertaining to volatiles sample storage.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. In addition, discussions regarding the instrument QC requirements listed below can be found in the referenced sections of this method:

- The GC/MS must be tuned to meet the recommended BFB criteria prior to the initial calibration and for each 12-hr period during which analyses are performed. See Secs. 11.4.1 for further details.

- There must be an initial calibration of the GC/MS system as described in Sec. 11.3. In addition, the initial calibration curve should be verified immediately after performing the standard analyses using a second source standard (prepared using standards different from the calibration standards) spiked into organic-free reagent water. The suggested acceptance limits for this initial calibration verification analysis are 70 - 130%. Alternative acceptance limits may be appropriate based on the desired project-specific data quality objectives. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification. However, analyses may continue for those analytes that fail the criteria with an understanding these results could be used for screening purposes and would be considered estimated values.

- The GC/MS system must meet the calibration verification acceptance criteria in Sec. 11.4, each 12 hours.

- The RRT of the sample component must fall within the RRT window of the standard component provided in Sec. 11.4.4.

9.3 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000 for information on how to accomplish this demonstration of proficiency.

9.4 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences and/or contaminants from the analytical system,

glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

9.5 Sample quality control for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

9.5.1 Measuring the effect of the matrix is performed by the matrix internal standards by sample. The documentation of these effects is presented on QC reports generated by sample. An example is presented in Figure 3.

9.5.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. When the results of the matrix internal standards indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. Also note the LCS for water sample matrices is typically prepared in organic-free reagent water similar to the continuing calibration verification standard. In these situations, a single analysis can be used for both the LCS and continuing calibration verification.

9.5.3 See Method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house method performance criteria for evaluating method performance should be developed using the guidance found in Method 8000.

9.5.4 Method blanks - Before processing any samples, the analyst must demonstrate that all equipment and reagent interferences are under control. Each day a set of samples is extracted or, equipment or reagents are changed, a method blank must be analyzed. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source and eliminate it, if possible, before processing samples.

9.6 Surrogate recoveries

The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000 for information on developing and updating surrogate limits. Matrix effects and distillation performance may be monitored separately through the use of surrogates. The effectiveness of using the relative volatility and boiling point internal standards to correct matrix effects is monitored using the surrogates identified in Sec. 7.6.3. Advisory surrogate recovery windows by matrix are presented in Table 7.

9.7 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is

leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed), recalibration of the system must take place.

9.8 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10.0 CALIBRATION AND STANDARDIZATION

See Sec 11.4 for information on calibration and standardization.

11.0 PROCEDURE

11.1 Sample preparation

This method utilizes vacuum distillation prior to GC/MS analysis. Various sample volumes or weights may be employed, provided that the sensitivity of the method is adequate for project needs. Given the inherent recovery correction, changes in sample amount do not necessitate recalibration of the instrument using standards of the same volume.

11.1.1 Aqueous samples

Quickly transfer a 5-mL aliquot of the sample to the distillation flask, taking care not to introduce air bubbles or agitate the sample during the transfer. Add 5 µL of the internal standard spiking solution to the sample in the flask, and attach the flask to the vacuum distillation apparatus. 25-mL aliquots may be used to achieve lower quantitation levels without necessitating recalibration using 25-mL standard solutions.

11.1.2 Solid and soil samples

In order to minimize potential target analyte losses, an approximately 5-g aliquot of sample should be extruded with minimal exposure to the air directly from a suitable sample collection device into the tared sample chamber and immediately capped in order to attain the sample weight. Once the sample chamber is weighed, quickly remove the cap and add 5 µL of the internal standard spiking solution to the sample in the flask, and attach the flask to the vacuum distillation apparatus. Refer to Method 5035 for more information on sample collection and handling options, i.e., an empty vial approach or an approved coring device for volatile organic compounds that would applicable to this determinative technique.

NOTE: The tared sample chamber or flask weight must also include the cap device. The sample weight can then be obtained by subtracting the tared flask plus cap weight from the flask and cap plus sample weight.

11.1.2.1 Determination of percent dry weight -- When sample results are to be calculated on a dry weight basis, e.g., for fish tissue, a second aliquot of sample (5 - 10 g) must be collected.

WARNING: The drying oven should be contained in a hood or be vented. Significant laboratory contamination may result from drying a heavily contaminated sample.

Dry this aliquot overnight at 105° C. Allow it to cool in a desiccator before weighing. Calculate the % dry weight as described in Sec. 11.11.6.

11.1.2.2 If necessary, at least one additional aliquot of sample must be collected for high concentration analysis.

11.1.3 Tissue samples

Tissue samples which are fleshy may have to be minced into small pieces to get them through the neck of the sample chamber. This is best accomplished by freezing the sample in liquid nitrogen before any additional processing takes place. Biota containing leaves and other softer samples may be minced using clean scissors. Weigh out a 5-g aliquot and then rapidly transfer it to the sample chamber. Add 5 µL of the internal standard spiking solution to the sample in the flask, and attach the flask to the vacuum distillation apparatus.

11.1.4 Oil samples

Weigh out 0.2 to 1.0 g of oil, and then rapidly transfer it to the sample chamber. Add 5 µL of the internal standard spiking solution to the sample in the flask, and attach the flask to the vacuum distillation apparatus.

11.2 Establish the vacuum distillation operating conditions, using the following information as guidance.

11.2.1 All vacuum distiller lines should be heated sufficiently to minimize analyte carryover. The condenser column temperature should be set to a temperature that allows 0.3-0.5g of water from a 5 ml water sample to be distilled in 7.5 min or less. The temperature of the cryotrap and transfer time are predetermined by the analyst as that necessary to provide well resolved chromatographic peaks and sensitivity of analytes. One routine for optimizing condenser and cryotrap temperature and transfer time is available from the EPA (http://www.epa.gov/nerlesd1/chemistry/vacuum/training/default.htm, “Tuning the Vacuum Distiller, Optimizing Analyte Response and Chromatography”)

11.2.2 Recommended vacuum distillation operating conditions

Condenser[1]:	-5 °C to + 5 °C
Condenser bakeout:	95 °C
Cryotrap:	- 150 °C
Cryotrap desorb[1:]	100 °C to 150 °C
Cryotrap bakeout:	200 °C
Multiport valve:	150 °C to 200 °C
Transfer to GC line:	150 °C to 200 °C
System and autosampler lines: 95 °C	
Vacuum distillation time:	7.5 min.

Transfer time [1:]	3 min. to 6 min.
nitrogen flush condenser of water:	7 min.
System flush cycles:	16
Nitrogen inlet time:	0.05 to 0.1 min.
Evacuation time:	1.2 min.
Log sampling[2:]	per 15 sec.

[1] Set parameter or optimize as per vendor instructions.
[2] An electronic log file of all system readings should be saved as per vendor instructions.

11.2.3 Setting the transfer time and the desorb temperature is related to the chromatographic conditions used. Using shorter transfer times and lower desorb temperatures tend to minimize water transfer to the column and provide improved resolution of polar analytes. Higher desorb temperatures and longer transfer times tend to maximize analyte response.

11.3 Recommended chromatographic conditions are provided as examples based on an assortment of analyses used to generate performance data for this method. The actual conditions will ultimately be dependent on the compounds of interest, instrument, and column manufacturer's guidelines. The maximum temperatures of operation should always be verified with the specific manufacturer. Conditions can be changed significantly if compounds of interest are within a narrow range of boiling points and/or relative volatility.

11.3.1 Column 1 with jet separator. The following are example conditions which may vary depending on the instrument and column manufacturer's recommendations:

Carrier gas (He) flow rate:	4 mL/min
Column:	VOCOL (3μL film), 60m x 0.53 mm
Initial temperature:	-25°C, hold for 4 minutes
Temperature Ramp #1: 50 °C/min to 40 °C	
Temperature Ramp #2: 5 °C/min to 120 °C	
Temperature Ramp #3: 20 °C/min to 220 °C	
Final column temperature:	220 °C, hold for 6 min
Jet separator temperature:	210°C

11.3.2 Column 2 with split interface. The following are example conditions which may vary depending on the instrument and column manufacturer's recommendations:

Carrier gas (He) flow rate:	2 mL/min
Column:	Rtx-VMS (1.4μL film), 60m x 0.25 mm
Initial temperature:	-25°C, hold for 2 minutes
Temperature Ramp #1: 50 °C/min to 40 °C	
Temperature Ramp #2: 5 °C/min to 120 °C	
Temperature Ramp #3: 20 °C/min to 220 °C	
Final column temperature:	220 °C, hold for 7 min
Split ratio:	5:1

11.3.3 Column 3 with split interface. The following are example conditions which may vary depending on the instrument and column manufacturer's recommendations:

Carrier gas (He) flow rate:	1.5 mL/min
Column:	VOCOL (1.5μL film), 60m x 0.25 mm
Initial temperature:	-20°C, hold for 2.5 minutes
Temperature Ramp #1: 40 °C/min to 60 °C	

Temperature Ramp #2: 5 °C/min to 120 °C
Temperature Ramp #3: 20 °C/min to 220 °C
Final column temperature: 220 °C, hold for 9 min
Split ratio: 10:1

11.4 Initial calibration

11.4.1 Summary - The initial calibration is a multi-step function that ultimately determines the concentration to response (area or height) relationship. It is based upon the relationships of predicted recoveries (R) to boiling points (BP) and relative volatility (RV). The combined BP and RV relationships are used to modify the concentration to response relationships. Concentrations to response relationships are described by using the average response factor ($\overline{RF}$). The sequence of the initial calibration follows:

11.4.1.1 The mass spectrometer is hardware-tuned and verified with BFB.

11.4.1.2 Multiple concentration levels of initial calibration standards are analyzed.

11.4.1.3 A reference sample (usually a blank) is analyzed to establish the reference upon which the internal standard (IS) responses for the initial calibration are made. The ratios of the responses (areas or heights) from the calibration to the reference are called the IS measured recoveries.

11.4.1.4 The first pass (FP) relationships use compounds of near boiling points to approximate the relative volatility effects over the narrow range bracketed by the FP internal standards.

11.4.1.5 The relationships of the BP internal standards to their FP corrected measured recoveries are used to make corrections of the measured recoveries of the relative volatility (RV) internal standards.

11.4.1.6 The relationships of RV internal standards to their BP corrected measured recoveries are used to establish corrections based upon RV.

11.4.1.7 A total matrix correction (RT) is determined as the product of the BP (R_α) and RV (R_β) corrections.

11.4.1.8 The response factor (RF) is determined by incorporating R_T. The average $\overline{RF}$ is used to calculate the all subsequent sample results.

11.4.1.9 When using least squares regression (LSR) to develop the calibration model, it is recommended that x = concentration and y = response/R_T.

11.4.2 GC/MS operating conditions and tuning

11.4.2.1 Establish the GC/MS operating conditions, using the following as guidance:

Mass range: From m/z 35 - 270
Sampling rate: To result in at least five full mass spectra across the peak but not to exceed 1 second per mass spectrum

Source temperature:	According to manufacturer's specifications
Ion trap only:	Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

11.4.2.2 The GC/MS system must be hardware-tuned such that injecting 50 ng or less of BFB meets the manufacturer's specified acceptance criteria or as listed in Table 2. The tuning criteria as outlined in Table 2 were developed using quadrupole mass spectrometer instrumentation and it is recognized that other tuning criteria may be more effective depending on the type of instrumentation, e.g., Time-of-Flight, Ion Trap, etc. In these cases it would be appropriate to follow the manufacturer's tuning instructions or some other consistent tuning criteria. However no matter which tuning criteria is selected, the system calibration must not begin until the tuning acceptance criteria are met with the sample analyses performed under the same conditions as the calibration standards.

11.4.2.2.1 In the absence of specific recommendations on how to acquire the mass spectrum of BFB from the instrument manufacturer, the following approach should be used: Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired within 20 scans of the elution of BFB. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the BFB peak or any other discrete peak that does not coelute with BFB.

11.4.2.2.2 Use the BFB mass intensity criteria in the manufacturer's instructions as primary tuning acceptance criteria or those in Table 2 as default tuning acceptance criteria if the primary tuning criteria are not available. Alternatively, other documented tuning criteria may be used (e.g., CLP, Method 524.2, or manufacturer's instructions), provided that method performance is not adversely affected. The analyst is always free to choose criteria that are tighter than those included in this method or to use other documented criteria provided they are used consistently throughout the initial calibration, calibration verification, and sample analyses.

NOTE: All subsequent standards, samples, MS/MSDs, LCSs, and blanks associated with a BFB analysis must use identical mass spectrometer instrument conditions.

11.4.3 Set up the sample introduction system as described (see Sec. 11.1). A different calibration curve is necessary for each method because of the differences in conditions and equipment. A set of at least five different concentration levels of calibration standards is necessary (see Sec. 7.12 and Method 8000). Calibration must be performed using the same sample introduction technique as that used for samples.

11.4.3.1 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of organic-free reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask underneath the surface of the reagent water. Remove the needle as quickly as possible after injection and dilute

to the volume mark with additional reagent water. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be prepared daily. Transfer 5.0 mL (or 25 mL if lower detection limits are required) of each standard to a gas tight syringe along with 10 µL of internal standard. Then transfer the contents to the appropriate device or syringe. Some of the introduction methods may have specific guidance on the volume of calibration standard and the way the standards are transferred to the device.

11.4.3.2 The stability of the gas chromatograph (GC) is demonstrated by comparing the retention times of the components of interest to their respective retention time (RT) reference standards. Choose a RT reference standard that has similar polarity properties as the component of interest and a relative retention time (RRT) in the range of 0.80 to 1.20. Examples of RT reference standards are 1,2,4-trichlorobenzene, 1,2-dichlorobenzene, 1,4-dioxane-d_8, acetophenone-d_5, diethyl ether-d_{10}, fluorobenzene, and hexachlorobenzene.

11.4.3.3 Use the base peak ion from the standard, surrogate, or component of interest as the primary ion for quantitation (see Table 3). If interferences are noted, use the next most intense ion as the quantitation ion.

11.4.3.4 A reagent blank is analyzed to obtain reference responses for the BP and RV internal standards. Other reference responses may be used such as the average responses of the initial calibration, any single calibration level, laboratory fortified blank, etc. but a reagent blank is recommended.

11.4.4 Response factor calculations

11.4.4.1 Tabulate the responses of the quantitation ions of the BP and RV internal standards (see Table 3 and Table 6). Calculate the internal standard measured recoveries using the ratio of calibration internal standard response to reference (usually a reagent blank) internal standard response. The internal standard measured recovery follows:

$$\text{measured recovery} = \frac{A_{Cal}}{A_{Ref}}$$

where:

A_{Cal} = Peak area (or height) of the internal standard of the calibration.
A_{Ref} = Peak area (or height) of the internal standard of the reference.

11.4.4.2 Tabulate the area response of the characteristic ions (see Table 3) against the concentration for each target analyte, each internal standard, and each surrogate standard. Calculate response factors (RF) for each compound relative to its predicted recovery by the internal standards. See sec. 12 for detailed explanation.

The RF is calculated as follows:

$$RF = \frac{A_s}{R_T \times C_s}$$

where:

A_s = Peak area (or height) of the analyte.
C_s = Concentration of the analyte or surrogate.
R_T = Predicted recovery of analyte.

11.4.4.3 Calculate the mean response factor and the relative standard deviation(RSD) of the response factors for each target analyte using the following equations. The RSD should be less than or equal to 20% for each volatile target analyte, less than or equal to 25% of each semivolatile or non-purgeable analyte (Sec 7.6). It is also recommended that a minimum response factor for the most common target analytes as noted in Table 9, be demonstrated for each individual calibration level as a means to ensure that these compounds are behaving as expected. In addition, meeting the minimum response factor criteria for the lowest calibration standard is critical in establishing and demonstrating the desired sensitivity. Due to the large number of compounds that may be analyzed by this method, some compounds will fail to meet these criteria. For these occasions, it is acknowledged that the failing compounds may not be critical to the specific project and therefore they may be used as qualified data or estimated values for screening purposes. The analyst should also strive to place more emphasis on meeting the calibration criteria for those compounds that are critical project compounds, rather than meeting the criteria for those less important compounds.

$$\text{mean RF} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RF})^2}{n-1}}$$

$$RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

RF_i = RF for each of the calibration standards
$\overline{RF}$ = mean RF for each compound from the initial calibration
n = Number of calibration standards, e.g., 5

11.4.4.4 If more than 10% of the targeted volatile compounds included with the initial calibration exceed the 20% RSD limit, the chromatographic system is considered too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure beginning with Sec. 11.4.

11.4.4.5 If more than 20% of the targeted semivolatile compounds includedwith the initial calibration exceed the 25% RSD limit, the vacuum distiller/chromatographic system is considered too reactive for analysis to begin. Verify the vacuum distillation of each analysis is consistent:

- Water volatilized from sample 0.3 to 0.5 g
- Temperature readings of all components are as set

If no cause for the variation is found, verify the vacuum distiller transfer and desorb temperatures are appropriate for the GC/capillary column conditions, then repeat the calibration procedure beginning with Sec. 11.4.

11.4.4.6 If more than 20% of the targeted non-purgeable compounds included with the initial calibration exceed the 25% RSD limit, the vacuum distiller/chromatographic system is considered too reactive for analysis to begin. Verify the vacuum distillation of each analysis is consistent:

- Water volatilized from sample 0.3 to 0.5 g
- Temperature readings of all components are as set

Some of the polar compounds exhibit poor chromatography on columns intended for volatile compound separations. For these compounds, the presence of increasing amounts of water being transferred from the vacuum distiller can attenuate the response or degrade the chromatography to such an extent that integration is not straight-forward. Decreasing the amount of water introduced on-column (shorten transfer time, lower desorb temperature, or increase split-flow) should improve the chromatography. After corrective action is taken, repeat the calibration procedure beginning with Sec. 11.4.

11.4.5 Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. Late-eluting target analytes usually have much better agreement. The RRT is calculated as follows:

$$RRT = \frac{\text{Retention time of the analyte}}{\text{Retention time of the internal standard}}$$

11.4.6 Linearity of target analytes - If the RSD of any target analyte is 20% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Sec. 11.7).

11.4.6.1 If the RSD of any target analyte is greater than 20%, refer to Method 8000 for additional calibration options. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed. The average $\overline{RF}$ should not be used for compounds that have an RSD greater than 20% unless the concentration is reported as estimated.

11.4.6.2 When the RSD exceeds 20%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. Inspection of the calibration curve can also be done by obtaining the differences between the expected concentrations and the re-calculated concentrations of each calibration level (see Method 8000 for details). The inspection may indicate analytical

problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

11.4.6.3 Due to the large number of compounds that may be analyzed by this method, some compounds may fail to meet either the 20% RSD (25% for the semivolatile and non-purgeable analytes). If compounds fail to meet these criteria, the associated concentrations may still be determined but they must be reported as estimated. In order to report non-detects, it must be demonstrated that there is adequate sensitivity to detect the failed compounds at the applicable lower quantitation limit.

11.4.6.4 This method generates a rough approximation of the confidence intervals for reported concentrations; the RSD is used in this rough approximation (Sec 12.4).

11.4.6.5 The more polar analytes (i.e., aniline and pyridine) exhibit subtle variations in sensitivity by capillary column. The calibration ranges for these compounds, therefor are not the same for all column selections and there are instances where the lower concentration calibration points may not provide a measurable response. For these instances the lower calibration points are not to be used and the limits of quantitation increased to reflect the change.

11.5 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

11.5.1 Prior to the analysis of samples or calibration standards, inject or introduce 50 ng or less of the 4-bromofluorobenzene standard into the GC/MS system. The resultant mass spectra for the BFB must meet the criteria as outlined in Sec. 11.4.2 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

11.5.2 The initial calibration curve should be verified immediately after performing the standard analyses using a second source standard (prepared using standards different from the calibration standards) spiked into organic-free reagent water with a concentration preferably at the midpoint of the initial calibration range. The suggested acceptance limits for this initial calibration verification analysis are 70 - 130%. Alternative acceptance limits may be appropriate based on the desired project-specific data quality objectives. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification. However, analyses may continue for those analytes that fail the criteria with an understanding these results could be used for screening purposes and would be considered estimated values.

11.5.3 The initial calibration (Sec. 11.4) for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS. The results must be compared against the most recent initial calibration curve and should meet the verification acceptance criteria provided in Sec. 11.5.5.

NOTE: The BFB and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

11.5.4 A method blank should be analyzed prior to sample analyses in order to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. See Method 8000 for method blank performance criteria.

11.5.5 GC/MS Calibration verification standard criteria

11.5.5.1 Each of the most common target analytes in the calibration verification standard should meet the minimum response factors as noted in Table 9. This criterion is particularly important when the common target analytes are also critical project-required compounds. This is the same check that is applied during the initial calibration.

11.5.5.2 If the minimum response factors are not met, the system should be evaluated, and corrective action should be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

11.5.5.3 All volatile compounds of interest must be evaluated using a 20% variability criterion (25% for the semivolatile and non-purgeable as defined in Sec 7.6). Use percent difference when performing the average response factor model calibration.

11.5.5.4 If the percent difference or percent drift for a volatile compound is less than or equal to 20% (25% for the semivolatile and non-purgeable compounds), then the initial calibration for that compound is assumed to be valid. Due to the large numbers of compounds that may be analyzed by this method, some compounds will fail to meet the criteria. If the criterion is not met (i.e., greater than 20% difference or drift) for more than 20% of the compounds included in the initial calibration, then corrective action must be taken prior to the analysis of samples. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. For situations when the failed compound is present, the concentrations must be reported as estimated values.

11.5.5.5 Problems similar to those listed under initial calibration could affect the ability to pass the calibration verification standard analysis. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The calibration verification criteria must be met before sample analysis begins.

11.5.5.6 When calculating the calibration curves using the linear regression model, a minimum quantitation check on the viability of that curve should be performed using the response from the low concentration calibration standard. The calculated concentration of the low calibration point should be within ± 30% of the standard true concentration. Other recovery criteria may be applicable depending on the project's data quality objectives and for those

situations the minimum quantitation check criteria should be outlined in a laboratory standard operating procedure.

11.5.6 Internal standard retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

11.5.7 Internal standard response - If the EICP area for any of the volatile internal standards in the calibration verification standard changes by a factor of two (-50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

11.6 GC/MS analysis of samples

11.6.1 Summary -The analysis of samples is a multi-step function which uses the average response factors to determine sample concentrations. It is also based upon the relationships of predicted recoveries (R) to boiling points (BP) and relative volatility (RV). The combined BP and RV relationships are used to calculate sample concentration. Uncertainties described as standard deviations and errors of determination can be obtained from this method and used to develop approximate uncertainties surrounding the calculated sample concentration.

11.6.1.1 Samples are prepared as per Sec. 11.1 and analyzed by GC/MS.

11.6.1.2 The measured recoveries of the internal standards are calculated using the responses from the sample analysis, the average response factors, and the amount of internal standards added to the sample.

11.6.1.3 The first pass (FP) relationships use compounds of near boiling points to approximate the relative volatility effects over the narrow range bracketed by the FP internal standards.

11.6.1.4 The relationships of the BP internal standards to their FP corrected measured recoveries are used to make corrections of the measured recoveries of the relative volatility (RV) internal standards.

11.6.1.5 The relationships of RV internal standards to their BP corrected measured recoveries are used to establish corrections based upon RV.

11.6.1.6 A total matrix correction (R_T) is determined as the product of the BP (R_α) and RV (R_β) corrections.

11.6.1.7 The concentration is calculated from the response of the target, average response factor, and R_T. The error of determinations from the BP and RV corrections can be propagated along with the standard deviation of the average response factor to determine the approximate uncertainty of the calculated concentration.

11.6.2 It is highly recommended that the sample be screened to minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds. Some of the screening options available utilizing SW-846 methods are screening solid samples for volatile organics (Method 3815), automated headspace-GC/FID (Methods 5021/8015), automated headspace-GC/PID/ELCD (Methods 5021/8021), or waste dilution-GC/PID/ELCD (Methods 3585/8021) using the same type of capillary column. When used only for screening purposes, the quality control requirements in the methods above may be reduced as appropriate. Sample screening is particularly important when Method 8261 is used to achieve low detection levels.

11.6.3 BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

11.6.4 All samples and standard solutions must be allowed to warm to ambient temperature before analysis. Set up the vacuum distiller as in the calibration analyses.

11.6.5 The process of taking an aliquot destroys the validity of the remaining volume of an aqueous sample for future analysis when target analytes are at low concentration and taking the aliquot leaves significant headspace in the sample vial. Higher concentration samples, for example those which need to be diluted before analysis at a 5-mL purge volume, often show no detectable changes when a small aliquot is removed, the sample vial is immediately recapped, and the same vial reanalyzed at a later time. It is best practice not to analyze a sample vial repeatedly. Therefore, if only one VOA vial of a relatively clean aqueous matrix such as tap water is provided to the laboratory, to protect against possible loss of sample data, the analyst should prepare two aliquots for analysis at this time. A second aliquot in a syringe is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. For aqueous samples, one 20-mL syringe could be used to hold two 5-mL aliquots. If the second aliquot is to be taken from the syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

11.6.6 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and invert before compressing the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. If lower detection limits are required, use a 25-mL syringe, and adjust the final volume to 25.0 mL. The sample aliquot and the internal standard/surrogates are injected into the sample vessel. The sample vessel is attached to the vacuum distiller port taking care that the O-ring seal is free of debris and properly seated.

NOTE: For most applications pouring a sample aliquot directly into the syringe is preferred in order to minimize the loss of volatile constituents, however when smaller volumes are necessary to prepare dilutions, drawing the sample directly into the syringe is considered acceptable.

11.6.7 The following procedure may be used to dilute aqueous samples for analysis of volatiles. All steps must be performed without delays, until the diluted sample is in a gas-tight syringe.

11.6.7.1 Dilutions may be made in volumetric flasks (10- to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilution steps may be necessary for extremely large dilutions.

11.6.7.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask, and add slightly less than this quantity of organic-free reagent water to the flask.

11.6.7.3 Inject the appropriate volume of the original sample from the syringe into the flask underneath the reagent water surface. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat this procedure for additional dilutions.

11.6.7.4 Fill a 5-mL syringe with the diluted sample, as described in Sec. 11.6.6. Should smaller sample volumes be necessary to prepare dilutions, drawing the sample directly into the syringe is considered acceptable.

11.6.7.5 Systems with autosamplers allow the user to perform automated dilutions. Refer to instrument manufacturer's instructions for more information. In addition, if an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions.

11.6.8 Compositing aqueous samples prior to GC/MS analysis

11.6.8.1 The following compositing options may be considered depending on the sample composition and desired data quality objectives:

11.6.8.1.1 Flask compositing - for this procedure, a 300 to 500 mL round-bottom flask is immersed in an ice bath. The individual VOA grab samples, maintained at <6°C, are slowly poured into the round-bottom flask. The flask is swirled slowly to mix the individual grab samples. After mixing, multiple aliquots of the composited sample are poured into VOA vials and sealed for subsequent analysis. An aliquot can also be poured into a syringe for immediate analysis.

11.6.8.1.2 Purge device compositing - Equal volumes of individual grab samples are added to a purge device to a total volume of 5 or 25 mL. The sample is then analyzed.

11.6.8.1.3 Syringe compositing - In the syringe compositing procedure, equal volumes of individual grab samples are aspirated into a 25 mL syringe while maintaining zero headspace in the syringe. Either the total volume in the syringe or an aliquot is subsequently analyzed. The disadvantage of this technique is that the individual samples must be poured carefully in an attempt to achieve equal volumes of each. An alternate procedure uses multiple 5 mL syringes that are filled with the individual grab samples and then injected sequentially into the 25 mL syringe. If less than five samples are used for compositing, a proportionately smaller syringe may be used, unless a 25-mL sample is to be purged.

11.6.8.2 Introduce the composited sample into vacuum distiller. (see Sec. 11.1)

11.6.9 Add appropriate volumes of the surrogate spiking solution and the internal standard spiking solution to each sample either manually or by autosampler to achieve the desired concentrations. The surrogate and internal standards may be mixed and added as a single spiking solution.

If a more sensitive mass spectrometer is employed to achieve lower quantitation levels, more dilute surrogate and internal standard solutions may be required.

11.6.10 Add the laboratory control sample (LCS) to a clean matrix. See Sec. 9.5 and Method 5000 for more guidance on the selection and preparation of the LCS.

11.6.10.1 If a more sensitive mass spectrometer is employed to achieve lower quantitation levels, more dilute LCS solutions may be required.

11.6.11 The vacuum distiller should be operated as specified by the vendor or established by the analyst . See section 11.2.1 for guidance on vacuum distiller settings. Be sure that all connections are complete and sealed properly. Vacuum distiller log files should be saved and given file names that allow unique identification. Log files should be considered analytical documentation.

11.6.12 If the initial analysis of the sample or a dilution of the sample has a concentration of any analyte that exceeds the upper limit of the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion.

11.6.12.1 When ions from a compound in the sample saturate the detector, this analysis must be followed by the analysis of an organic-free reagent water blank. If the blank analysis is not free of interferences, then the system must be decontaminated (see vendor instructions for decontamination routines). Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences. Depending on the extent of the decontamination procedures, recalibration may be necessary.

11.6.12.2 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

11.6.13 The use of selected ion monitoring (SIM) is acceptable for applications requiring quantitation limits below the normal range of electron impact mass spectrometry. However, SIM may provide a lesser degree of confidence in the compound identification, since less mass spectral information is available. Using the primary ion for quantitation and the secondary ions for confirmation set up the collection groups based on their retention times. The selected ions are nominal ions and most compounds have small mass defect, usually less than 0.2 amu, in their spectra. These mass defects should be used in the acquisition table. The dwell time may be automatically calculated by the laboratory's GC/MS software or manually calculated using the following formula. The total scan time should be less than 1,000 msec and produce at least 5 to 10 scans per chromatographic peak. The start and stop times for the SIM groups are determined from the full scan analysis using the formula below:

$$\text{Dwell Time for the Group} = \frac{\text{Laboratory's Scan Time (msec)}}{\text{Total Ions in the Group}}$$

11.7 Analyte identification

11.7.1 The qualitative identification of each compound determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as being present when the following criteria are met.

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

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

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

11.7.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution should be verified on the mid-point concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported.

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

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

11.7.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the

analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications:

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

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

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

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

11.8 Quantitative analysis

11.8.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given analyte.

11.8.1.1 It is highly recommended to use the integration produced by the software if the integration is correct because the software should produce more consistent integrations. However, manual integrations are necessary when the software does not produce the proper integrations due to improper baseline selection, the correct peak is missed, a coelution is integrated, a peak is partially integrated, etc. The analyst is responsible for ensuring that the integration is correct whether performed by the software or done manually.

11.8.1.2 Manual integrations should not be substituted for proper maintenance of the instrument or setup of the method (e.g. retention time updates, integration parameter files, etc). The analyst should seek to minimize manual integration by properly maintaining the instrument, updating retention times, and configuring peak integration parameters.

11.8.2 If the RSD of a volatile compound's response factor is 20% or less (25% for semivolatile and non-purgeable compounds), then the concentration in the extract may

be determined using the average response factor ($\overline{RF}$) from initial calibration data (Sec. 11.3.5).

11.8.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 11.7.2) should be estimated. Tentatively identified non-target analytes should be determined as in method 8260 using the areas A_x (area of the unknown) and A_{is} (area of the most comparable internal standards). The areas should be determined from the total ion chromatograms, and the RF for the compound should be assumed to be 1. The resulting concentration should be reported indicating that the value is an estimate. The boiling point and the relative volatility of the tentatively identified non-target analyte is unknown thus it is recommended that the nearest internal standard have a relative volatility of less than 50. This internal standard should also be free of interferences.

11.8.4 Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution should be verified on the mid-point concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 The quantitation routine employed in this method differs significantly from that used in Method 8260 (using the Method 5032 sample preparation). Where Method 8260 uses one internal standard to correct injection/preparation variations for a given analyte, this method uses a series of internal standards to define the relationships of compound recoveries to their physical properties. Those relationships are used to extrapolate target analyte recoveries. Each target analyte and surrogate is calibrated using an external standard calibration procedure. The concentration of the analyte in the sample is determined using the predicted analyte recovery, sample size, and amount of analyte detected by the mass spectrometer. The relationships are solved using multiple internal standards and the errors associated with the solutions also calculated.

See Sec. 12.2 for the stepwise procedure to perform the internal standard corrections. The quantitation algorithms and sequence presented here are available from the EPA at: http://www.epa.gov/nerlesd1/chemistry/vacuum/default.htm

Other internal standard correction approaches may be employed when they have been demonstrated to improve the assessment of matrix effects. Large samples of biota (10 g or more) may require that the analyst address the partitioning of analytes between air and the organic phase. Such an approach is described in References 8 and 9.

12.2 Internal standard Corrections.

This method uses a battery of internal standard whose purpose is to measure and accordingly compensate (or normalize) the effects a sample matrix has on the recovery of compounds. It has been shown that a compound's boiling point and relative volatility are the primary properties that impact the recovery of a compound using this method. The responses of internal standards in an analysis are compared to calibration responses and their differences are measured as a function of boiling point and a function of relative volatility. Quantitation of target analytes and surrogates requires five distinct steps: determination of recovery described in sec 12.2.1, calculation of the relative volatility effects on the internal standards used to

measure boiling point effects (also referred to as first-pass corrections) described in Sec. 12.2.2, calculations of the boiling point effects described in Sec. 12.2.3, calculation of the relative volatility effects described in Sec. 12.2.4, and finally, recovery correction of the quantity of analyte measured by the mass spectrometer to reflect the matrix effects described Sec. 12.2.5. An explanation of these effects and the use of the following equations are given in greater detail in References 5 and 6. Software that performs all of the calculations presented is available from the EPA at: http://www.epa.gov/nerlesd1/chemistry/vacuum/default.htm

12.2.1 Determination of the measured recovery of internal standards.

The measured recovery for each internal standard is its MS response divided by its expected response. The expected response is the internal standard's average response factor ($\overline{RF}$) from the calibration curve multiplied by the amount of the internal standard that was added to the sample.

The measured recovery for each internal standard for the initial calibration standards are handled differently. The measured recovery is the ratio of the MS response divided by the MS response from a reference sample (see Sec. 11.4.4.1).

$$\text{measured recovery} = \frac{(A_s)}{(\overline{RF})(\text{amount added})}$$

where:

A_s = The peak area (or height) of the internal standard in the sample
$\overline{RF}$ = The average response factor of the internal standard from the initial calibration

12.2.2 Calculation of relative volatility effects on the boiling point internal standards

In order to separate the impact of boiling point and relative volatility on the internal standards, this first pass (FP) correction is limited to defining relative volatility effects over a limited range that includes the boiling point internal standards (Sec. 7.6.2). These first pass internal standards should also have similar low boiling points to minimize varying boiling point effects that would confound measurement of the effects of relative volatility. The GC/MS response of the boiling point internal standards are corrected for relative volatility effects using the first pass equations described below. Hexafluorobenzene (relative volatility =0.86 , boiling point = 81.5°C), fluorobenzene ((relative volatility=3.5 , boiling point = 85°C) and 1,2-dichloroethane-d_4 ((relative volatility=20 , boiling point = 84°C) are used to describe the first-pass recoveries. Two line equations determine relative volatility impact on the boiling point internal standards (solution of one line uses hexafluorobenzene and fluorobenzene and the other fluorobenzene and 1,2-dichloroethane-d_4) with the format:

$$R_{FP} = M_{FP} \times \ln(RV_{IS}) + B_{FP}$$

where:

R_{FP}	=	The recovery of the internal standard relating to its relative volatility
$\ln(RV_{IS})$	=	The natural logarithm of the relative volatility of the internal standard
M_{FP}, B_{FP}	=	Linear least squares regression constants for each analysis

The linear least squares regression constants for the two equations are solved using the measured recoveries (Sec. 12.2.1) of the three internal standards and their respective relative volatilities (RV). One equation addresses compounds with relative volatilities between 0.86 and 3.5 and the other between 3.5 and 20. The measured recoveries(Sec. 12.2.1)for all of the boiling point internal standards are now corrected for relative volatility effects by dividing their measured recovery by their respective R_{FP}.

$$R_{\beta\ IS} = \frac{\text{measured recovery}_{IS}}{M_{FP} \times \ln(RV_{IS}) + B_{FP}}$$

12.2.3 Calculation of boiling point effects on recovery

After the first pass normalization, the boiling point internal standards recoveries reflect just the boiling point effects. The relationship of recovery to boiling point is described by

$$R_{\beta} = M_{\beta} \times bp_{x} + B_{\beta}$$

where:

R_{β}	=	The recovery corresponding to the boiling point.
bp_{x}	=	A compound's boiling point.
M_{β} ,B_{β}	=	Linear least squares regression constants for each analysis.

Table 8 identifies the internal standards used for the boiling point corrections. The solution of the above equation is performed by groupings that cover a range of boiling point values. Each of the groups have multiple internal standards that allow several

solutions to the equation. The linear least squares regression constants for each of these equations are solved by using the first-pass normalized recovery ($R_{\beta\ IS}$) of the boiling point internal standards and their respective boiling points. These equations also provide a measurement of the uncertainty (r_β) in determining the recovery to boiling point functions. If the boiling point (BP) of a component of interest is outside of the BP range covered by the groupings then the recovery correction uses defaulted BP values. Use the lowest BP in the range as a default for BPs below the range. For BPs above the range, use the average BP of the two highest BPs in the range if there are three or more standards in that high BP group as the default for BPs otherwise use the highest BP as the default value. The measured recoveries (Sec. 12.2.1) for all of the relative volatility internal standards are now corrected for boiling point effects by dividing their measured recovery by their respective R_β.

$$R_{\alpha\ IS} = \frac{\text{measured recovery}_{IS}}{M_\beta \times bp_{IS} + B_\beta}$$

12.2.4 Calculation of the relative volatility effects on recovery

After the recoveries of the relative volatility internal standards are corrected for boiling point effects, recoveries reflect only matrix effects relating to relative volatility. The relationship of recovery to relative volatility is described by the following equation:

$$R_\alpha = M_\alpha \times \ln(RV_x) + B_\alpha$$

where:

R_α = Recovery corresponding to its relative volatility value.
$\ln(RV_x)$ = The natural logarithm of the relative volatility of compound, x.
M_α, B_α = Linear least squares regression constants for each analysis.

Table 5 identifies the internal standard used for the relative volatility corrections. The solution of the above equation is performed by groupings that cover a range of relative volatility values. Each of the groups have multiple internal standard that allow several solutions to the equation. The linear least squares regression constants for each of these equations are solved by using the boiling point corrected recovery (Ra IS) of the relative volatility internal standards and their respective relative volatilities. These equations also provide a measurement of the uncertainty (r_α) in determining the recovery to relative volatility functions. If the relative volatility (RV) of a component of interest is outside of the RV range covered by the groupings then the recovery correction uses defaulted RV values. Use the lowest RV in the range as a default for RVs below the range. For RVs above the range, use the average of the natural logs of RV, ln(RV), of the two highest RVs in the range if there are three or more standards in that high RV group as the default for RVs otherwise use the highest RF as the default value.

12.2.5 Correction of analyte response for matrix effects.

The measurement of matrix effects relating to boiling point and relative volatility for an analysis provide a means to accurately predict the recovery (with uncertainty) of

analytes within an analysis. The predicted recovery relating to relative volatility for an analyte is $R_\alpha \pm r_\alpha$ and the recovery relating to its boiling point is $R_\beta \pm r_\beta$. The predicted total relative recovery that includes relative volatility and boiling point effects is:

$$R_T = R_\alpha \times R_\beta$$

and

where:

$$\left(\frac{r_T}{R_T}\right)^2 = \left(\frac{r_\alpha}{R_\alpha}\right)^2 + \left(\frac{r_\beta}{R_\beta}\right)^2$$

R_α, r_α = Predicted recovery and uncertainty related to relative volatility using the appropriate grouping described in Table 4 to solve the equation identified in Sec. 12.2.3.

R_β, r_β = Predicted recovery and uncertainty related to boiling point using the appropriate grouping described in Table 5 to solve the equation identified in Sec. 12.2.2.

R_T, r_T = The predicted recovery and its uncertainty of an analyte for the analysis.

12.3 Calculation of sample concentration

The calculation of the concentration of an analyte in a sample is performed using the predicted recovery of the analyte as described in 12.2. The determination of the analyte concentration is as follows:

$$\text{concentration} = \frac{(A_s)(D)}{(\overline{RF})(R_T)(\text{sample size})}$$

where:

A_s = Area (or height) of the peak for the analyte in the sample.

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.

$\overline{RF}$ = Mean response factor from calibration (area per ng)

R_T, = The predicted recovery.

The algorithms used to calculate recoveries are presented in Figure 3. These reports were generated using the method 8261 software available at: http://www.epa.gov/nerlesd1/chemistry/vacuum/default.htm.

12.4 Optional reporting of the approximate uncertainty surrounding the calculated concentration.

Determining the uncertainty of a measurement is an important component of that measurement. Method 8261 attempts to determine as much of this uncertainty that is practical from this method. This expression of the uncertainty is considered a very rough approximation and every laboratory wishing to refine this approach is encouraged to do so.

From the equation that calculates concentration (Sec. 12.3) the following relationship of uncertainty is derived:

$$\left(\frac{\text{uncertainty}}{\text{concentration}}\right)^2 = \left(\frac{SD_{\overline{RF}}}{\overline{RF}}\right)^2 + \left(\frac{r_T}{R_T}\right)^2 + \left(\frac{\text{uncertanity}_{\text{sample size}}}{\text{sample size}}\right)^2 + \left(\frac{\text{uncertanity}_{A_x}}{A_s}\right)^2 + \left(\frac{\text{uncertainty}_D}{D}\right)^2$$

It will be assumed for the purposes of this method that the uncertainties attributable to sample size, instrument response, and dilutions are considered negligible. Thus the equation to determine the approximate uncertainty of the calculated concentrations will contain only the components of calibration using the average response, boiling point, and relative volatility. The approximating equation is reduced to the following form:

$$\left(\frac{\text{uncertainty}}{\text{concentration}}\right)^2 = \left(\frac{SD_{\overline{RF}}}{\overline{RF}}\right)^2 + \left(\frac{r_T}{R_T}\right)^2$$

where:

$SD_{\overline{RF}}$	=	Standard deviation of the average response factor.
$\overline{RF}$	=	The average response factor from the initial calibration.
R_T	=	The predicted recovery.
r_T	=	The uncertainty of the predicted recovery.

12.5 Calculation of surrogate recovery

The surrogates are used to monitor the overall performance of the analytical system. The recovery of each surrogate is calculated in a fashion similar to the analyte concentrations, correcting the mass spectrometer response for the recoveries of the other surrogates and the sample size, such that:

$$\text{recovery} = \frac{(A_s)}{(\overline{RF})(R_T)(\text{amount added})}$$

where:

A_s = Area (or height) of the peak for the analyte in the sample.
$\overline{RF}$ = Mean response factor from calibration (area per ng)
R_T = The predicted recovery.

Figure 4 illustrates the surrogate report that is obtained using software available from the following EPA website: http://www.epa.gov/nerlesd1/chemistry/vacuum/default.htm.

12.6 The response of the matrix internal standards may be greatly impacted by the sample. This method may be applied to unusual and difficult matrices and therefore the behavior of internal standards is not typically limited to a range of recoveries. Any limitation on internal standard recoveries should be based on the knowledge of sample matrix and expected behavior.

12.6.1 The recovery of matrix internal standards may exceed typical recoveries from calibration solutions.

12.6.1.1 The recovery of an internal standard with elevated relative volatility values will be greatly enhanced by the presence of salt in water. If method detection limits or reporting limits were not established for similar behaving analytes for the particular matrix, it is likely that general method detection limits or reporting limits will be valid although biased high.

12.6.1.2 The higher boiling point internal standards are susceptible to larger recovery variations. Elevated recoveries of these internal standards should be considered as noted in Sec. 12.6.1.1

12.6.1.3 If surrogates meet criteria and analyte responses are within calibration range (Sec. 12.7) an elevated recovery of internal standards does not necessarily impact accuracy. Typically the recovery of only the compounds with higher boiling points or relative volatility values will be those elevated. Should all internal standard responses be similarly elevated the possibility of inaccurate internal standard aliquot spike should be investigated.

12.6.2 The recovery of matrix internal standards may fall below typical recovery from calibration solutions.

12.6.2.1 Recovery of lipophilic compounds will be greatly depressed by samples containing elevated levels of organic matter such as biota or sediments. Method quantitation limits or reporting limits should reflect the matrix.

12.6.2.2 Recovery of many internal standards will be impacted by large sample sizes. Method quantitation limits or reporting limits should reflect the sample size.

12.6.2.3 If the recovery of well-behaved matrix internal standards (relative volatility <100 and boiling point < 150 °C) fall below 50% unexpectedly (low organic content sample and standard sample size) the analyst should verify results.

12.6.2.3.1 Inspect sample for obvious variations (particulate or organic matter).

12.6.2.3.2 Review vacuum distillation log file to ensure pressure readings are consistent with similar samples. These log files are generated by vacuum distiller software and record conditions during each distillation. If low pressure is not reached an improperly seated o-ring or vacuum failure is likely. If an unusually low vacuum is reached early in the distillation the presence of a large amount of gas (methane, CO_2) or solvent may be present in the sample.

12.6.2.3.3 If the sample analysis is proven faulty (e.g., based on finding as noted in Sec. 12.6.2.3.2) or can not be shown to be the result of sample matrix, a reanalysis should be performed.

12.6.3 When the matrix impacts an analyte's predicted recovery such that the reporting limit or method quantitation limit are not justified a revised limit should be calculated.

12.6.3.1 Reporting limits should be established based on the lower calibration point. If the predicted recovery of an analyte is low, the normal reporting limit may not be justified. For instance, if an analyte has a predicted recovery of 10% due to a matrix effect (water sample with organic residues), the typical reporting limit for a water sample would be 10 times too low. For analytes whose standard reporting limit is more than 50% lower than what is justified it should be corrected to reflect the low recoveries. All analyte reporting limits that are affected should be flagged.

12.6.3.2 If method quantitation limits are reported by sample these values should be flagged as noted in Sec. 12.6.3.1

12.6.3.3 Similarly if sample sizes are lower than the standard amount by more than 50%, the reporting limits should reflect the sample size.

12.6.3.4 Reporting limits may be increased with greater sample sizes if the analyte recoveries are not depressed more that 50% by the sample increase. The use of larger sample sizes should be validated based on the desired target

analyte sensitivity and the ability to calibrate and quantitate at the required concentration.

12.6.3.5 The recoveries of most compounds from low-organic content soil are equal to or higher than recoveries from water samples. Therefore the reporting limits for water samples can typically be applied to soils. For sediment and soil samples where organic content can be large the lower recovery of lipophilic compounds is expected and they should be treated as noted in Secs. 12.6.3.1 and 12.6.3.2.

12.6.3.6 Oil and biota samples can pose extreme matrix effects on the lipophilic compounds.

12.6.3.6.1 Target analyte sensitivity should be based on the ability to calibrate and quantitate at the required concentration in order to validate the established reporting limits and to generate expected recoveries. When the recoveries of analytes are found to fall more than 50% from expected recoveries corrections and flags as described in Secs. 12.6.3.1 and 12.6.2.2 apply.

12.6.3.6.2 Biota samples may be very limited in amount and sample amounts may need to be reduced with reporting limits increased as discussed for water and soil. Note: Biota samples are very susceptible to contamination during handling and special precautions to limit exposure to air should be used.

12.7 The mass spectrometer response of an analyte may not be within the calibration range. The fact that an analyte response is outside calibration is not readily apparent due to the modulation of response but the matrix internal standards. Therefore, the analytical results for analytes whose response exceeded the upper calibration response limit should be flagged. The analytical results for analytes whose response fall below the limit of quantitation should also be flagged.

12.8 Reporting matrix corrections

A graphical representation of the effect of the sample matrix on the recovery of the analytes may prove useful in evaluating method performance. Although not required, Figure 3 provides an example of one form of such documentation.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance goals for users of the methods. Instead, performance goals should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method.

13.2 The recovery of the target analytes spiked into three soils is summarized in Tables 10 and 11, along with the relative error of replicate recovery measurements and the precision of

the surrogate recoveries in these spiked samples. These data are provided for guidance purposes only.

13.3 Recovery data from an oil sample spiked with the target analytes are presented in Table 12. These data are provided for guidance purposes only.

13.4 Target analytes were spiked into water containing salt, soap, and glycerine, as a test of the effects of ionic strength, surfactants, etc., on the VD/GC/MS procedure. The recovery data from these analyses are provided in Tables 13 and 14. These data are provided for guidance purposes only.

13.5 The recovery of the target analytes spiked into various water volumes is summarized in Table 15, along with the relative error of replicate recovery measurements. These data are provided for guidance purposes only.

13.6 Example recovery data from fish tissue using a wide-bore capillary column are presented in Table 16. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

14.3 Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards that will require disposal.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. M. H. Hiatt, "Analysis of Fish and Sediment For Volatile Priority Pollutants," *Analytical Chemistry* 1981, 53 (9), 1541.

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3. United States Patent 5,411,707, May 2, 1995. "Vacuum Extractor with Cryogenic Concentration and Capillary Interface," assigned to the United States of America, as represented by the Administrator of the Environmental Protection Agency. Washington, DC.

4. Michael H. Hiatt, David R. Youngman and Joseph R. Donnelly, "Separation and Isolation of Volatile Organic Compounds Using Vacuum Distillation with GC/MS Determination," *Analytical Chemistry,* 1994, 66 (6), 905.

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7. "The Waste Management Manual for Laboratory Personnel," American Chemical Society, Department of Government Regulations and Science Policy, Washington, DC.

8. Michael H. Hiatt, "Analyses of Fish Tissue by Vacuum Distillation/Gas Chromatography/Mass Spectrometry," *Analytical Chemistry*, 1997, 69(6), 1127-1134.

9. Michael H. Hiatt, "Bioconcentration Factors for Volatile Organic Compounds in Vegetation," *Analytical Chemistry*, 1998, 70(5), 851-856.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method.

TABLE 1

EXAMPLE CHROMATOGRAPHIC RETENTION TIMES AND LOWER LIMITS OF DETECTION FOR VOLATILE ORGANIC COMPOUNDS ON CAPILLARY COLUMNS

Compound	Retention Time (minutes)			LOC[d]	
	Column 1[a]	Column 2[b]	Column 2'[c]	(ng, %)	
1,1,2-Trichloro-1,2,2-trifluoroethane		5.55		5	20
Dichlorodifluoromethane	6.50	6.00	3.13	5	
Methyl acetate		6.06		5	20
Carbon disulfide		6.18		5	20
MTBE		6.30		5	20
Chloromethane	7.40	6.54	3.40	5	13
Vinyl Chloride	7.76	6.91	3.93	5	4
Methyl cyclohexane		7.18		5	20
Acetylaldehyde	--	7.38		20	50
Bromomethane	8.70	7.90	4.80	5	22
Cyclohexane		7.91		5	20
Chloroethane	8.85	8.04	--	1.5	6
Trichlorofluoromethane	9.24	8.45	6.20	0.5	23
Ethanol	--	8.62		60	22
Diethyl ether	9.77	8.93		1	21
Acrolein	--	--			
Acetone	10.18	9.30		30[e]	20
1,1-Dichloroethene	10.19	9.40	7.83	0.5	2
t-Butylalcohol	--	9.64		60	7
Iodomethane	10.70	9.91		1	18
Allyl chloride	10.76	9.90		5	13
Acetonitrile	10.59	9.69		2	16
Methylene chloride	10.94	10.09	9.27	15[e]	20
Methyl t-butyl ether	--	10.22		2	5
Carbon disulfide	--	--			
Acrylonitrile	11.22	10.27		1	6
trans-1,2-Dichloroethene	11.34	10.40	9.90	0.5	23
di-Isopropyl ether	--	10.74		2	6
1,1-Dichloroethane	12.01	11.08	10.80	0.5	6
Ethyl t-butyl ether	--	11.32		2	3
Methacrylonitrile	13.13	12.06		1	23
Vinyl acetate	--	--			
2-Butanone	12.70	11.64		20	10
Propionitrile	12.87	11.80		1	20
2,2-Dichloropropane	12.85	11.87	11.87	0.5	5
cis-1,2-Dichloroethene	12.98	11.98	11.93	0.5	5
Chloroform	13.22	12.21	12.60	0.5	14
Bromochloromethane	13.53	12.53	12.37	1.5	3

TABLE 1 (cont.)

Compound	Retention Time (minutes)			LOC[d]	
	Column 1[a]	Column 2[b]	Column 2'[c]	(ng, %)	
1,1,1-Trichloroethane	13.85	12.84	12.83	0.5	5
1,1-Dichloropropene	14.10	13.06	13.10	0.5	8
t-Amylmethyl ether	--	13.11		2	12
Carbon tetrachloride	13.85	13.29	13.17	0.5	11
1,2-Dichloroethane	14.61	13.53	13.63	1.5	23
Benzene	14.62	13.59	13.50	1.5	9
Trichloroethene	15.70	14.61	14.80	0.5	15
1,2-Dichloropropane	16.06	14.95	15.20	1.5	8
Methyl methacrylate	16.12	14.85		3	11
Bromodichloromethane	16.55	15.45	15.80	0.5	25
1,4-Dioxane	16.64	15.43		5	23
Dibromomethane	16.69	15.63	5.43	1.5	1
2-Chloroethyl vinyl ether	--				
4-Methyl-2-pentanone	17.15	15.87		2	1
trans-1,3-Dichloropropene	17.61	16.44	16.70	2.5	5
Toluene	18.27	17.13	17.40	1.5	10
Pyridine	18.40	17.15		25	5
cis-1,3-Dichloropropene	18.69	17.42	17.90	2.5	10
Ethylmethacrylate	18.12	–		10	5
n-Nitrosodimethylamine	20.00	17.58		2500	25
2-Hexanone	20.30	17.61		10[e]	5
1,1,2-Trichloroethane	19.03	17.76	18.30	1.5	9
Tetrachloroethene	19.69	18.34	18.60	0.5	17
1,3-Dichloropropane	19.61	18.21	18.70	0.5	12
Dibromochloromethane	20.24	18.78	19.20	5	2
2-Picoline	20.70	18.95		2500	25
1,2-Dibromoethane	20.70	19.10	19.40	0.5	2
1-Chlorohexane	--	--	--		
Chlorobenzene	21.64	19.71	20.67	1.5	5
1,1,1,2-Tetrachloroethane	21.74	19.74	20.87	0.5	24
Ethylbenzene	21.74	19.71	21.00	0.5	9
n-Nitroso-methyl-ethylamine	21.89	19.70		2500	25
p-Xylene	21.89	19.83	21.30	1.5	1
m-Xylene	21.89	19.83	21.37	1.5	1
Styrene	22.83	20.55	22.40	0.5	11
o-Xylene	22.74	20.49	22.27	0.5	1
Isopropylbenzene (Cumene)	23.32	20.96	23.30	0.5	10
Bromoform	23.43	21.13	22.77	5	8
cis-1,4-Dichloro-2-butene	23.48	21.04		20	13
n-Nitrosodiethylamine	23.52	21.05		2500	25
1,1,2,2-Tetrachloroethane	23.64	21.23	24.07	1.5	8

TABLE 1 (cont.)

Compound	Retention Time (minutes) Column 1[a]	Column 2[b]	Column 2'[c]	LOC[d] (ng, %)	
1,2,3-Trichloropropane	23.86	21.42	24.13	1.5	1
n-Propylbenzene	23.92	21.47	24.33	0.5	14
trans-1,4-Dichloro-2-butene	23.98	21.47		20	14
1,3,5-Trimethylbenzene	24.15	21.67	24.83	0.5	4
Bromobenzene	24.03	15.86	24.00	0.5	21
2-Chlorotoluene	24.20	21.78	24.53	0.5	20
4-Chlorotoluene	24.26	21.83	24.77	0.5	7
Pentachloroethane	24.72	22.30		0.5	18
tert-Butylbenzene	24.61	22.13	26.60	0.5	9
1,2,4-Trimethylbenzene	24.66	22.18	31.50	0.5	5
sec-Butylbenzene	24.88	22.39	26.13	0.5	13
Aniline	25.08	22.63		100	20
p-Isopropyltoluene	25.03	22.55	26.50	1.5	3
1,3-Dichlorobenzene	25.17	22.80	26.37	5	19
1,4-Dichlorobenzene	25.29	22.92	26.60	0.5	16
Benzyl chloride	--				
n-Butylbenzene	25.49	23.09	27.32	0.5	21
1,2-Dichlorobenzene	25.71	23.46	27.43	0.5	7
n-Nitrosodi-n-propylamine	26.02	23.64		2500	25
Acetophenone	26.22	24.04		3	23
o-Toluidine	26.32	24.22		300	11
1,2-Dibromo-3-chloropropane	26.54	24.56	--	1.5	1
Hexachlorobutadiene	27.57	26.07	32.07	1.5	11
Nitrobenzene	26.65	24.70		10	23
1,2,4-Trichlorobenzene	27.45	25.93	31.50	0.5	9
Naphthalene	27.79	26.49	32.20	0.5	17
1,2,3-Trichlorobenzene	28.06	26.93	32.97	0.5	25
2-Methylnaphthalene	29.17	28.78		3	10
1-Methylnaphthalene	29.56	29.49		1	9
INTERNAL STANDARDS and SURROGATES					
Diethyl ether-d_{10}	9.71	8.83			
Acetone-d_6	10.18	9.30			
Methylene chloride-d_2	10.90	10.04			
Nitromethane-d_3	12.56	11.53			
Hexafluorobenzene	12.08	10.98			
Tetrahydrofuran-d_8	13.45	12.43			

TABLE 1 (cont.)

Compound	Retention Time (minutes)			Lower
	Column 1[a]	Column 2[b]	Column 2'[c]	(µg/L)
Ethyl acetate-$^{13}C_2$	12.90	11.77		
Pentafluorobenzene	13.21	12.05		
Benzene-d_6	14.53	13.51		
1,2-Dichloroethane-d_4	14.44	13.37		
Fluorobenzene	14.98	13.89	14.06	
1,4-Difluorobenzene	15.07	13.90		
1,2-Dichloropropane-d_6	15.86	14.74		
1,4-Dioxane-d_8	16.55	15.29		
Toluene-d_8	18.10	16.97		
Pyridine-d_5	18.32	17.05		
1,1,2-Trichloroethane-d_3	18.92	17.65		
1,2-Dibromomethane-d_4	20.52	18.97		
Chlorobenzene-d_5	21.55	19.65		
o-Xylene-d_{10}	22.55	20.34		
4-Bromofluorobenzene	23.75	21.34	23.63	
Bromobenzene-d_5	23.97	21.60		
1,2-Dichlorobenzene-d_4	25.68	23.41	27.25	
Decafluorobiphenyl	25.49	22.80		
Nitrobenzene-d_5	26.60	24.64		
Acetophenone-d_5	26.17	23.99		
1,2,4-Trichlorobenzene-d_3	27.43	25.88		
Naphthalene-d_8	27.74	26.41		
1-Methylnaphthalene-d_{10}	29.45	29.28		

[a] Column 1 - 60 meter x 0.53 mm ID 3μm film thickness VOCOL capillary. Hold at -25°C for 4 minutes, then program to 40°C at 50°C/min. Hold at 40°C for 0 minutes, then program to 120°C at 5°C/min. Hold at 120°C for 0 minutes, then program to 220°C at 22°C/min. Hold at 220°C for 6.15 minutes.

[b] Column 2 - 60 meter x 0.25 mm ID 1.5 μm film thickness VOCOL capillary using cryogenic oven. Hold at -20°C for 2.5 minutes, then program to 60°C at 40°C/min. Hold at 60°C for 0 minutes, then program to 120°C at 5°C/min. Hold at 120°C for 0 minutes, then program to 220°C at 20°C/min. Hold at 220°C for 9 minutes.

[c] Column 2' - 30 meter x 0.53 mm ID DB-624 wide-bore capillary, cooling GC oven to ambient temperatures. Hold at 10°C for 6 minutes, program to 70°C at 10 °C/min, program to 120°C at 5°C/min, then program to 180°C at 8°C/min.

[d] Lower limit of Calibration as total nanograms. Mass detected using standards in a 5-mL sample volume and column #2. Full scan acquisition mode was used. The % is the deviation found for the calibration range LOC to 5X LOC. The study that generated these

data used 25% as a threshold for determining the LOC and should be used for guidance only.

[e] Low end of calibration limited due to presence of compound in background.

TABLE 2

BFB (4-BROMOFLUOROBENZENE) MASS INTENSITY CRITERIA[a]

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

[a] The criteria in this table are intended to be used as default criteria if optimized manufacturer's operating conditions are not available. Alternate tuning criteria may be employed, (e.g., CLP or Method 524.2), provided that method performance is not adversely affected. See Sec. 11.3.1

TABLE 3

TABLE 3
(continued)

CHARACTERISTIC MASSES (m/z) FOR VOLATILE ORGANIC COMPOUNDS

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Acetone	58	43
Acetonitrile	40	41, 39
Acetophenone	105	77,120
Acetylaldehyde	44	43,42,41
Acrolein	56	55, 58
Acrylonitrile	53	52, 51
Allyl chloride	76	76, 41, 39, 78
tert-Amylmethyl ether	87	73,55
Aniline	66	93
Benzene	78	-
Bromobenzene	156	158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
2-Butanone	72	43, 72
n-Butylbenzene	134	91, 92
tert-Butylalcohol	59	43,57
sec-Butylbenzene	134	105
tert-Butylbenzene	134	91, 119
Carbon disulfide	76	78
Carbon tetrachloride	119	117
Chlorobenzene	112	77, 114
Chlorodibromomethane	129	208, 206
Chloroethane	64	66
2-Chloroethyl vinyl ether	63	65, 106
Chloroform	83	85
Chloromethane	50	52
2-Chlorotoluene	126	91
4-Chlorotoluene	126	91
1,2-Dibromo-3-chloropropane	157	75, 155
Dibromomethane	174	93, 95

TABLE 3
(continued)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
1,2-Dibromomethane	107	109
1,2-Dichlorobenzene	146	111, 148
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
cis-1,4-Dichloro-2-butene	75	75, 53, 77, 124, 89
trans-1,4-Dichloro-2-butene	75	53, 88
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
Diethyl ether	74	45, 59
Diisopropyl ether	87	45,59
1,4-Dioxane	88	88, 58, 43, 57
Ethanol	45	27,31, 46
Ethyl acetate	88	43, 45, 61
Ethylbenzene	106	91
Ethyl *tert*-butyl ether	87	59,57
Ethyl methacrylate	69	69, 41, 99, 86, 114
Hexachlorobutadiene	225	223, 227
2-Hexanone	58	100
Iodomethane	142	127, 141
Isobutyl alcohol	74	43, 41, 42
Isopropylbenzene	120	105
p-Isopropyltoluene	134	91, 119
Methacrylonitrile	41	39, 52, 66,67
Methyl-t-butyl ether	73	57
Methylene chloride	84	86, 49

TABLE 3
(continued)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Methyl methacrylate	69	69, 41, 100, 39
1-Methylnaphathalene	142	141
2-Methylnaphathalene	142	141
4-Methyl-2-pentanone	100	43, 58, 85
Naphthalene	128	127
Nitrobenzene	77	51, 123
N-Nitrosodibutylamine	84	158
N-Nitrosodiethylamine	102	57
N-Nitrosodimethylamine	74	42
N-Nitrosodi-*n*-propylamine	130	70
N-Nitrosomethylethylamine	88	56, 42
Pentachloroethane	167	167, 130, 132, 165, 169
2-Picoline	93	93, 66, 92, 78
Propionitrile	54	52, 55, 40
n-Propylbenzene	120	91
Pyridine	79	52
Styrene	104	78
1,1,1,2-Tetrachloroethane	131	133
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	166	129, 131, 164
Toluene	91	92
o-Toluidine	106	107
1,2,3-Trichlorobenzene	180	182, 145
1,2,4,-Trichlorobenzene	182	180, 145
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	97	83, 85
Trichloroethene	130	95, 97, 132
Trichlorofluoromethane	101	151, 153
1,2,3-Trichloropropane	110	75, 77
1,2,4-Trimethylbenzene	120	105
1,3,5-Trimethylbenzene	120	105
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91

TABLE 3
(continued)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Internal standard and Surrogates		
Acetone-^{13}C	59	44
Acetophenone-d_5	110	82
Benzene-d_6	84	83
Bromobenzene-d_5	161	82, 162
4-Bromofluorobenzene	174	95, 176
Chlorobenzene-d_5	82	117, 119
Decafluorobiphenyl	265	234
1,2-Dibromomethane-d_4	111	113
1,2-Dichlorobenzene-d_4	152	115, 150
1,2-Dichloroethane-d_4	65	102
1,2-Dichloropropane-d_6	67	69
Diethyl ether-d_{10}	84	66, 50
1,4-Difluorobenzene	114	63
1,4-Dioxane-d_8	96	64
Ethyl acetate-$^{13}C_2$	71	62
Fluorobenzene	96	77
Hexafluorobenzene	186	117
Methylene chloride-d_2	53	88, 90
Methylnaphthalene-d_{10}	152	150
Naphthalene-d_8	136	108
Nitrobenzene-d_5	82	128
Nitromethane-^{13}C	62	46
Pentafluorobenzene	168	99
Pyridine-d_5	84	56
Tetrahydrofuran-d_8	78	80
1,2,4-Trichlorobenzene-d_3	183	185
1,1,2-Trichloroethane-d_3	100	102,84
Toluene-d_8	98	100
o-Xylene-d_{10}	98	116

The ions listed above are those recommended, but not required, for use in this method. In general, the ions listed as the primary characteristic ion provide a better response or suffer from fewer interferences. However, either the primary ion or one of the secondary ions listed here may be used for quantitation of the analytes, provided that the same ions are used for both calibrations and sample analyses. In some instances, sample-specific interferences may occur that complicate the use of the characteristic ion that was used for the calibration. If such interferences occur, the use of a secondary ion for quantitation must be clearly documented and supported by multi-point calibration factors derived from the same ion.

TABLE 4

BOILING POINTS AND RELATIVE VOLATILITY VALUES FOR METHOD 8261 COMPOUNDS

Compound	b.p.[b] (°C)	K[d]	relative volatility values Avg.[e]	SD[f]
Dichlorodifluoromethane	-30		0.07	0.02
Chloromethane	-24		1.37	0.07
Vinyl chloride	-13		0.48	0.06
Bromomethane	4		1.82	0.12
Chloroethane	12		1.01	0.02
Trichlorofluoromethane	24		0.20	0.02
Diethyl ether	35		34.9	5.7
Acrolein	53	180	116.8	1
Acetone	56	580	600	32.0
1,1-Dichloroethene	37		0.63	0.07
Iodomethane	42		2.29	0.43
Allyl chloride	45		1.34	0.45
Carbon disulfide	46		0.31	
1,1,2-Trichloro-1,2,2-trifluoroethane	48		0.40	
Acetonitrile	82	1200	545	103.0
Methylene chloride	40	9.33	10.1	1.6
Acrylonitrile	78		161	32.0
trans-1,2-Dichloroethene	48		2.3	0.46
MTBE	55		33.7	
Methyl acetate	57		222	
1,1-Dichloroethane	57		4.12	0.08
Methacrylonitrile	90		102.9	2.4
2-Butanone	80	380	770	110
Cyclohexane	81		0.59	
Propionitrile	97		1420	320
2,2-Dichloropropane	69		1.37	0.18
cis-1,2-Dichloroethene	60		5.34	0.07
Chloroform	62	5.85	6.39	0.09
Bromochloromethane	68		15.4	0.4
1,1,1-Trichloroethane	74	1.41	1.31	0.04
1,1-Dichloropropene	104		0.88	0.03
Carbon tetrachloride	76		0.64	0.02
1,2-Dichloroethane	84	20.23	18.7	0.9
Benzene	80	4.36	3.55	0.27
Trichloroethene	87		2.34	0.09
1,2-Dichloropropane	96		10.9	0.2
Methyl methacrylate	101		71.4	4.1

TABLE 4
(continued)

Compound	b.p.[b] (°C)	K[d]	relative volatility values Avg.[e]	SD[f]
Methyl cyclohexane	101		0.62	
Bromodichloromethane	90		12.3	0.6
1,4-Dioxane	101	5750	6200	700
Dibromomethane	97		23.9	1.7
4-Methyl-2-pentanone	117		119.9	8.4
trans-1,3-Dichloropropene	112		14.1	0.7
Toluene	111	3.93	3.88	0.12
Pyridine	116		13100	600
cis-1,3-Dichloropropene	104		19.6	1.4
Ethyl methacrylate	117		48.4	2.8
N-Nitrosodimethylamine	154		129	37.3
2-Hexanone	128		131.1	2.1
1,1,2-Trichloroethane	114		26.2	2.4
Tetrachloroethene	121	1.55	1.43	0.03
Isobutyl alcohol	108		1750	156.0
1,3-Dichloropropane	120		24.9	1.9
Dibromochloromethane	120		19.2	1.4
2-Picoline	129		6800	5200
1,2-Dibromoethane	132		26.7	2.0
Chlorobenzene	132		6.07	0.24
1,1,1,2-Tetrachloroethane	130		11.6	0.6
Ethylbenzene	136	3.28	3.6	0.12
N-Nitrosomethylethylamine	165		1900	800
m+*p*-Xylenes	138		3.91	0.11
Styrene	145		6.87	0.36
o-Xylene	144	5.11	5.54	0.09
Isopropylbenzene	152	2.20	2.75	0.05
Bromoform	150		23.4	2.4
cis-1,4-Dichloro-2-butene	152		33.3	8.1
N-Nitrosodiethylamine	177		4900	2200
1,1,2,2-Tetrachloroethane	146		30.3	2.8
1,2,3-Trichloropropane	157		33.6	2.9
n-Propylbenzene	159	2.49	2.43	0.04
trans-1,4-Dichloro-2-butene	156		33.8	7.4
1,3,5-Trimethylbenzene	165	3.52	3.75	0.18
Bromobenzene	156		7.89	0.73
2-Chlorotoluene	159		4.04	0.17
4-Chlorotoluene	162		4.78	0.43
Pentachloroethane	162		13.2	3.3

TABLE 4
(continued)

Compound	b.p.[b] (°C)	K[d]	relative volatility values Avg.[e]	SD[f]
tert-Butylbenzene	169		2.72	0.05
1,2,4-Trimethylbenzene	169		4.5	0.4
sec-Butylbenzene	173		1.91	0.04
Aniline	184		13700	2300
p-Isopropyltoluene	183	2.25	2.5	0.07
1,3-Dichlorobenzene	173		5.72	0.73
1,4-Dichlorobenzene	174		6.14	0.84
n-Butylbenzene	183	1.65	1.88	0.08
1,2-Dichlorobenzene	180		7.86	1.19
N-Nitrosodi-*n*-propylamine	206		2400	2000
Acetophenone	203		161	
o-Toluidine	200		15200	2100
1,2-Dibromo-3-chloropropane	196		38.9	4.9
Hexachlorobutadiene	215		2.08	0.06
Nitrobenzene	211		87.5	
1,2,4-Trichlorobenzene	214		7.73	1.22
Naphthalene	218		16.7	2.2
1,2,3-Trichlorobenzene	218		11.3	1.6
N-Nitrosodibutylamine	240		21000	5000
2-Methylnaphthalene	245		67	17
1-Methylnaphthalene	245		67	17
Internal Standard and Surrogates				
Diethylether-d_{10}	35		32.5	
Acetone-d_6	57	600	600	
Methylene chloride-d_2	40		11.1	1.9
Nitromethane-^{13}C	101		510	
Hexafluorobenzene	82		0.86	0.06
Tetrahydrofuran-d_8	66		456	67.0
Ethyl acetate-$^{13}C_2$	77	150		150
Pentafluorobenzene	85		1.51	0.04
Benzene-d_6	79	4.4	3.92	0.27
1,2-Dichloroethane-d_4	84		20.0	20.0
Fluorobenzene	85		3.5	0.21
1,4-Difluorobenzene	88		3.83	0.07
1,2-Dichloropropane-d_6	95		11	0.1
1,4-Dioxane-d_8	101	5800	5800	

TABLE 4
(continued)

Compound	b.p.[b] (°C)	K[d]	relative volatility values Avg.[e]	SD[f]
Toluene-d_8	111		4.28	0.09
Pyridine-d_5	115	15000	15000	
1,1,2-Trichloroethane-d_3	112		26.6	0.7
1,2-Dibromoethane-d_4	131		26.0	1.7
Chlorobenzene-d_5	131		6.27	0.17
o-Xylene-d_{10}	143	5.1	6.14	0.2
4-Bromo-1-fluorobenzene	152		8.05	0.7
Bromobenzene-d_5	155		7.93	0.59
1,2-Dichlorobenzene-d_4	181		8.03	1.23
Decafluorobiphenyl	206		3.03	0.06
Acetophenone-d_5	202		161	20.0
Nitrobenzene-d_5	210		87.5	
1,2,4-Trichlorobenzene-d_3	213		7.88	1.19
Naphthalene-d_8	217		18	3.7
1-Methylnaphthalene-d_{10}	241			67

[b]Boiling point of analyte

[d]Partition coefficient of analyte between headspace and water at 20 °C. Used to experimentally interpolate relative volatility values.

[e]Average of 3 to 4 replicates

[f]One standard deviation

TABLE 5

RELATIVE VOLATILITY RANGES OF THE RELATIVE VOLATILITY INTERNAL STANDARDS

Relative Volatility Range	Internal standard Groups
Group 1	Hexafluorobenzene
0.07 to 3.83	Fluorobenzene
	1,4-Difluorobenzene
Group 2	1,4-Difluorobenzene
3.83 to 6.27	*o*-Xylene-d_{10}
	Chlorobenzene-d_5
Group 3	*o*-Xylene-d_{10}
6.27 to 29.2	Chlorobenzene-d_5
	1,2-Dibromoethane-d_4
	Diethylether-d_{10}
Group 4	1,2-Dibromoethane-d_4
29.2 to 477.5	Diethylether-d_{10}
	Tetrahydrofuran-d_8
	Acetone-C^{13}
Group 5	Tetrahydrofuran-d_8
477.5 to 5800	Acetone-C^{13}
	1,4-Dioxane-d_8
Group 6	Acetone-C^{13}
5800 to 15000	1,4-Dioxane-d_8
	Pyridine-d_5

TABLE 6

INTERNAL STANDARDS AND SURROGATES

Internal Standard	CAS Registry No.[a]	FUNCTION[a]	Amount Added[b] (ng)	Spike Solution (μg/mL)
Diethylether-d_{10}	2679-89-2	rel vol. IS	250	50
Acetone-C^{13}	666-52-4	rel vol. IS	3100	620
Methylenechloride-d_2	1665-00-5	surrogate-for volatile compounds	250	50
Nitromethane-C^{13}		surrogate for non-purging compounds	650	130
Hexafluorobenzene	392-56-3	first pass, rel vol. IS	250	50
Tetrahydrofuran-d_8	1693-74-9	rel vol. IS	250	50
Ethylacetate-C^{13}	84508-45-2	surrogate for non-purging compounds	2500	500
Pentafluorobenzene	363-72-4	boiling point IS	250	50
Benzene-d_6	1076-43-3	surrogate-for volatile compounds	250	50
1,2-Dichloroethane-d_6	17060-07-0	first pass, rel vol. IS	250	50
Fluorobenzene	462-06-6	first pass, rel vol. IS	250	50
1,4-Difluorobenzene	540-36-3	rel vol. IS	250	50
1,2-Dichloropropane-d_6		surrogate-for volatile compounds	250	50
1,4-Dioxane-d_8	17647-74-4	rel vol. IS	2400	480
Toluene-d_8	2037-26-5	boiling point IS	250	50
Pyridine-d_5	7291-22-7	rel vol. IS, surrogate for non-purging compounds	12500	2500

1,1,2-Trichloropropane-d_3		surrogate-for volatile compounds	250	50
1,2-Dibromoethane-d_4	22581-63-1	rel vol. IS	250	50
Chlorobenzene-d_5	3114-55-4	rel vol. IS	250	50
o-Xylene-d_{10}	56004-61-6	rel vol. IS	250	50
4-Bromofluorobenzene	460-00-4	surrogate-for volatile compounds	250	50
Bromobenzene-d_5	4165-57-5	boiling point IS	250	50
1,2-Dichlorobenzene-d_4	2199-69-1	boiling point IS	250	50
Decafluorobiphenyl	434-90-2	surrogate for semivolatile compounds	250	50
Nitrobenzene-d_5	4165-60-0	surrogate for semivolatile compounds	250	50
Acetophenone-d_5	28077-31-4	surrogate for semivolatile compounds	1050	210
1,2,4-Trichlorobenzene-d_3		boiling point IS	250	50
Naphthalene-d_8	1146-65-2	boiling point IS, surrogate for semivolatile compounds	500	100
1-Methylnaphthalene-d_{10}	38072-94-5	boiling point IS	1050	210

[a] The purpose for each compound in table: 1) relative volatility correction (rel. vol.), boiling point correction, or surrogates (volatile, non-purgeable, and semi-volatile compounds). Note that some compounds fill a dual purpose. Should additional suitable labeled compounds be found they can be added to this list.

[b] The total amount of compounds added (in 5 μL vulume) to each standard or sample, regardless of matrix or sample size. These amounts can be reduced for more sensitive instruments.

TABLE 7

ADVISORY RECOVERY RANGES FOR SURROGATES

SURROGATE COMPOUND	water limits		soil limits		oil limits	
	lower	upper	lower	upper	lower	upper
Volatile fraction						
Methylenechloride-d_2	75	125	75	125	75	125
Benzene-d_6	75	125	75	125	75	125
1,2-Dichloropropane-d_6	75	125	75	125	75	125
1,1,2-Trichloropropane-d_3	65	135[1]	50	150[1]	75	125
4-Bromofluorobenzene	75	125	75	125	75	125
non-Purgeable fraction						
Nitromethane-C^{13}	65	135	65	135	75	125
Ethylacetate-C^{13}	65	135	65	135	75	125
Pyridine-d_5	35	175[2]	35	175[2]	75	125
Semivolatile fraction						
Decafluorobiphenyl	50	175	35	175	50	150
Nitrobenzene-d_5	35	150	25	175	50	135
Acetophenone-d_5	35	150	25	175	50	135
Naphthalene-d_8	75	125	65	150	75	125

[1] Spectral interference common for this compound.
[2] Compound susceptable to chromatographic degradation. If compound outside windows all compounds in its relative volatility group (compounds with relative volatility > 5800) should be considered qualitative.

TABLE 8

BOILING POINT RANGES OF THE BOILING POINT INTERNAL STANDARDS

Boiling Point Range (°C)	Internal Standard Groups
Group 1	Pentafluorobenzene
85 to 155	Toluene-d_8
	Bromobenzene-d_5
Group 2	Bromobenzene-d_5
155 to 213	1,2-Dichlorobenzene-d_4
	1,2,4-Trichlorobenzene-d_3
Group 3	1,2,4-Trichlorobenzene-d_3
213 to 241	Naphthalene-d_8
	1-Methylnaphthalene-d_{10}

[a] The boiling point effects relating to an analyte with a boiling point of $\leq$ 85°C are assumed to be negligible.

TABLE 9

RECOMMENDED MINIMUM RESPONSE FACTOR CRITERIA FOR INITIAL AND CONTINUING CALIBRATION VERIFICATION

Volatile Compounds	Minimum Response Factor (RF)[1]
Dichlorodifluoromethane	200
Chloromethane	200
Vinyl chloride	200
Acetylaldehyde	50
Bromomethane	200
Chloroethane	200
Trichlorofluoromethane	200
Diethyl ether	400
Acetone	500
1,1-Dichloroethene	500
t-Butylalcohol	100
Iodomethane	200
Allyl chloride	200
Acetonitrile	200
Methylene chloride	1000
MTBE	1000
Methyl acetate	1000
Acrylonitrile	500
trans-1,2-Dichloroethene	500
di-Isopropyl ether	500
1,1-Dichloroethane	1000
Ethyl t-butyl ether	500
Methacrylonitrile	500
2-Butanone	100
Propionitrile	100
2,2-Dichloropropane	1000
cis-1,2-Dichloroethene	500
Chloroform	1000
Bromochloromethane	200
1,1,1-Trichloroethane	1000
1,1-Dichloropropene	200
t-Amylmethyl ether	100
Carbon disulfide	1000

TABLE 9
(continued)

Volatile Compounds	Minimum Response Factor (RF)[1]
Carbon tetrachloride	1000
1,2-Dichloroethane	1000
Benzene	1000
Cyclohexane	1000
Methyl cyclohexane	1000
Trichloroethene	500
1,2-Dichloropropane	500
Methyl methacrylate	500
Bromodichloromethane	500
1,4-Dioxane	50
Dibromomethane	500
4-Methyl-2-pentanone	50
trans-1,3-Dichloropropene	500
Toluene	1000
Pyridine	50
cis-1,3-Dichloropropene	500
ethylmethacrylate	50
N-Nitrosodimethylamine	5
2-Hexanone	100
1,1,2-Trichloroethane	500
Tetrachloroethene	500
1,3-Dichloropropane	500
Dibromochloromethane	500
2-Picoline	5
1,2-Dibromoethane	200
Chlorobenzene	1000
1,1,1,2-Tetrachloroethane	500
Ethylbenzene	1000
N-Nitrosomethylethylamine	5
m+*p*-Xylenes	1000
Styrene	1000
o-Xylene	1000
Isopropylbenzene	1000
Bromoform	200
cis-1,4-Dichloro-2-butene	20
N-Nitrosodiethylamine	5
1,1,2,2-Tetrachloroethane	500

TABLE 9
(continued)

Volatile Compounds	Minimum Response Factor (RF)[1]
1,2,3-Trichloropropane	200
1,1,2-Trichloro-1,2,2-trifluoroethane	1000
n-Propylbenzene	1000
trans-1,4-Dichloro-2-butene	20
1,3,5-Trimethylbenzene	1000
Bromobenzene	1000
2-Chlorotoluene	1000
4-Chlorotoluene	1000
Pentachloroethane	200
tert-Butylbenzene	500
1,2,4-Trimethylbenzene	1000
sec-Butylbenzene	1000
Aniline	10
p-Isopropyltoluene	1000
1,3-Dichlorobenzene	1000
1,4-Dichlorobenzene	1000
n-Butylbenzene	1000
1,2-Dichlorobenzene	1000
N-Nitrosodi-*n*-propylamine	5
Acetophenone	100
o-Toluidine	5
1,2-Dibromo-3-chloro propane	100
Hexachlorobutadiene	500
1,2,4-Trichlorobenzene	500
Naphthalene	1000
Nitrobenzene	100
1,2,3-Trichlorobenzene	200
2-Methylnaphthalene	100
1-Methylnaphthalene	100
Internal Standards and Surrogates	
Diethylether-d_{10}	400
Acetone-C^{13}	200
Methylenechloride-d_2	200
Nitromethane-C^{13}	100
Hexafluorobenzene	1000
Tetrahydrofuran-d_8	100

Volatile Compounds	Minimum Response Factor (RF)[1]
Ethylacetate-C^{13}	50
Pentafluorobenzene	1000
Benzene-d_6	1000
1,2-Dichloroethane-d_6	500
Fluorobenzene	1000
1,4-Difluorobenzene	1000
1,2-Dichloropropane-d_6	500
1,4-Dioxane-d_8	50
Toluene-d_8	1000
Pyridine-d_5	50
1,1,2-Trichloropropane-d_3	500
1,2-Dibromoethane-d_4	50
Chlorobenzene-d_5	1000
o-Xylene-d_{10}	1000
4-Bromofluorobenzene	500
Bromobenzene-d_5	500
1,2-Dichlorobenzene-d_4	500
Decafluorobiphenyl	100
Nitrobenzene-d_5	50
Acetophenone-d_5	50
1,2,4-Trichlorobenzene-d_3	500
Naphthalene-d_8	1000
1-Methylnaphthalene-d_{10}	100

[1] The response factor is determined in units of response (integrated area) per nanogram.

TABLE 10

EXAMPLE DATA FOR RECOVERY OF ANALYTES SPIKED INTO THREE SOILS

	Soil #1[a]			Soil #2[b]			Soil #3[c]		
Compound	% Rec[d]	Rel Error[e]	Sur Pre[f]	% Rec[d]	Rel Error[e]	Sur Pre[f]	% Rec[d]	Rel Error[e]	Sur Pre[f]
Dichlorodifluoromethane	128	28	0	122	30	92	22	4	4
Chloromethane	116	9	0	109	13	74	71	6	12
Vinyl chloride	114	14	0	118	18	87	94	7	15
Bromomethane	106	12	0	101	12	62	24	1	2
Chloroethane	109	11	0	110	11	75	15	0	2
Trichlorofluoromethane	111	11	0	125	14	98	12	0	2
Diethyl ether	20	8	1	18	8	6	10	1	1
Acetone	112	3	6	102	4	75	139	21	60
1,1-Dichloroethene	110	4	0	120	17	91	68	7	10
Iodomethane	106	6	0	96	15	56	94	3	6
Allyl chloride	116	8	0	111	12	77	88	4	10
Methylene chloride-d_6	105	6	2	96	6	60	101	3	2
Methylene chloride	104	5	2	94	4	57	94	4	2
Acrylonitrile	106	5	7	93	4	60	135	9	62
trans-1,2-Dichloroethene	99	8	0	93	9	53	85	5	6
1,1-Dichloroethane	109	5	1	103	2	66	179	0	0
Methacrylonitrile	106	3	6	69	7	35	152	2	11
2-Butanone	112	11	6	102	4	77	152	9	64
Propionitrile	122	4	6	109	2	83	167	6	64
2,2-Dichloropropane	105	1	0	115	7	83	89	1	10
cis-1,2-Dichloroethene	101	2	2	97	0	59	101	1	2
Chloroform	99	2	3	98	2	62	103	0	2
Isobutyl alcohol	103	9	6	105	6	75	NA	NA	NA
Bromochloromethane	98	0	2	93	2	59	105	1	2
1,1,1-Trichloroethane	99	1	0	112	6	78	85	1	10
1,1-Dichloropropene	102	2	2	120	7	87	83	1	12
Carbon tetrachloride	93	3	0	112	8	78	83	1	12
Benzene-d_6	102	1	1	99	1	60	102	1	1
1,2-Dichloroethane	99	1	2	94	0	108	108	1	3
Benzene	101	1	1	98	1	101	101	1	1
Trichloroethene	90	2	1	94	1	95	95	2	6
1,2-Dichloropropane-d_6	102	1	2	101	1	103	103	1	2
1,2-Dichloropropane	102	2	3	101	1	102	102	1	2

Table 10
(continued)

Compound	Soil #1[a] % Rec[d]	Soil #1[a] Rel Error[e]	Soil #1[a] Sur Pre[f]	Soil #2[b] % Rec[d]	Soil #2[b] Rel Error[e]	Soil #2[b] Sur Pre[f]	Soil #3[c] % Rec[d]	Soil #3[c] Rel Error[e]	Soil #3[c] Sur Pre[f]
Methyl methacrylate	152	2	9	149	11	145	145	4	13
Bromodichloromethane	94	2	2	95	1	103	103	1	2
1,4-Dioxane	110	1	5	103	1	123	123	2	29
Dibromomethane	93	2	5	93	1	105	105	1	9
4-Methyl-2-pentanone	125	2	8	112	6	147	147	4	13
trans-1,3-Dichloropropene	99	1	3	99	0	101	101	1	2
Toluene	99	0	3	99	1	96	96	1	1
Pyridine	95	5	8	119	1	71	71	3	43
cis-1,3-Dichloropropene	91	2	2	93	1	102	102	1	3
N-Nitrosodimethylamine	68	5	4	54	11	20	20	1	2
1,1,2-Trichloroethane-d_3	95	3	5	100	4	102	102	1	8
2-Hexanone	125	6	6	110	4	145	145	8	13
1,1,2-Trichloroethane	93	2	5	96	2	103	103	1	9
Tetrachloroethene	98	7	2	105	2	123	123	8	14
1,3-Dichloropropane	99	1	6	101	1	103	103	1	9
Dibromochloromethane	92	2	3	95	0	103	103	1	3
2-Picoline	71	5	3	66	20	62	62	8	15
1,2-Dibromoethane	104	1	5	108	1	108	109	0	9
Chlorobenzene	96	1	4	97	1	109	104	1	2
1,1,1,2-Tetrachloroethane	96	1	3	97	1	98	98	1	2
Ethylbenzene	102	0	2	99	1	52	96	1	1
N-Nitrosomethylethylamine	84	6	4	92	13	46	29	1	10
m+*p*-Xylenes	101	1	2	99	1	52	94	1	1
Styrene	97	1	3	96	1	49	96	0	3
o-Xylene	102	1	2	100	1	53	97	1	2
Isopropylbenzene	101	2	1	98	1	49	87	1	4
Bromoform	94	0	5	103	2	64	101	1	8
cis-1,4-Dichloro-2-butene	106	5	6	115	1	79	116	1	9
N-Nitrosodiethylamine	104	13	4	128	16	84	45	1	11
1,1,2,2-Tetrachloroethane	93	2	5	100	1	61	101	2	8
4-Bromo-1-fluorobenzene	94	2	3	93	1	45	99	0	2
1,2,3-Trichloropropane	111	6	6	120	1	86	115	1	9
n-Propylbenzene	100	3	1	95	0	45	85	1	5
trans-1,4-Dichloro-2-butene	103	4	5	114	3	76	119	1	10
1,3,5-Trimethylbenzene	103	1	1	93	2	42	91	1	2

Compound	Soil #1[a] % Rec[d]	Soil #1[a] Rel Error[e]	Soil #1[a] Sur Pre[f]	Soil #2[b] % Rec[d]	Soil #2[b] Rel Error[e]	Soil #2[b] Sur Pre[f]	Soil #3[c] % Rec[d]	Soil #3[c] Rel Error[e]	Soil #3[c] Sur Pre[f]
Bromobenzene	97	1	3	98	0	50	102	0	2
2-Chlorotoluene	98	1	1	90	2	41	94	1	1
4-Chlorotoluene	98	3	2	93	1	43	95	1	2
Pentachloroethane	88	2	2	86	3	39	72	4	2
tert-Butylbenzene	103	2	2	99	1	47	83	1	4
1,2,4-Trimethylbenzene	104	1	2	96	2	44	91	1	2
sec-Butylbenzene	99	4	2	93	3	43	83	1	8
Aniline	106	16	10	143	29	106	15	1	10
p-Isopropyltoluene	104	2	3	101	3	48	87	2	7
1,3-Dichlorobenzene	94	3	3	88	1	38	100	1	4
1,4-Dichlorobenzene	94	2	4	90	1	41	100	1	4
n-Butylbenzene	97	5	3	89	4	38	83	1	8
1,2-Dichlorobenzene	95	2	4	93	0	42	103	1	5
Benzyl alcohol	98	6	8	128	30	82	22	1	9
N-Nitrosodi-*n*-propylamine	120	16	9	185	27	168	108	3	38
Acetophenone-d_5	104	10	9	167	11	136	270	7	124
o-Toluidine	118	21	12	172	45	149	19	1	14
1,2-Dibromo-3-chloro propane	104	7	8	143	10	106	185	3	24
Hexachlorobutadiene	88	3	14	81	12	58	75	2	8
1,2,4-Trichlorobenzene	88	2	13	81	1	38	104	1	8
Naphthalene-d_8	88	5	17	109	5	69	141	2	12
Naphthalene	88	4	18	109	2	70	132	2	12
1,2,3-Trichlorobenzene	83	0	18	77	2	40	111	1	10
N-Nitrosodibutylamine	133	30	44	152	51	149	11	1	11
2-Methylnaphthalene	60	5	20	60	0	36	62	3	29

[a] Garden soil with 37% moisture and 21% organic matter. Three replicates were analyzed.

[b] Garden soil with 15% moisture and 16% organic matter. Three replicates were analyzed.

[c] Desert soil with 3% moisture and 1% organic matter. Seven replicates were analyzed.

[d] % Rec = Average of replicate accuracy results using internal standard corrections.

[e] Rel Error = Relative standard deviation of replicate analyses.

[f] Sur Pre = Average variation between the predicted analyte recoveries of the internal standard pairs for the replicate analyses. This precision value provides a measure of the inherent error in the overall measurement.

nalyte not sig NA nificantly present in vacuum distillate.

TABLE 11

EXAMPLE DATA FOR RECOVERY OF ANALYTES SPIKED INTO THREE SOILS AND ANALYZED BY VACUUM DISTILLATION GC/MS USING A NARROW-BORE COLUMN CAPILLARY COLUMN (NOTE: THIS IS A PLACE HOLDER FOR DATA TO BE ENTERED)

TABLE 11
(continued)

Compound	Soil #1[a]			Soil #2[b]			Soil #3[c]		
	% Rec[d]	Rel Error[e]	Sur Pre[f]	% Rec[d]	Rel Error[e]	Sur Pre[f]	% Rec[d]	Rel Error[e]	Sur Pre[f]
Dichlorodifluoromethane	128	28	0	122	30	92	22	4	4
Chloromethane	116	9	0	109	13	74	71	6	12
Vinyl chloride	114	14	0	118	18	87	94	7	15
Bromomethane	106	12	0	101	12	62	24	1	2
Chloroethane	109	11	0	110	11	75	15	0	2
Trichlorofluoromethane	111	11	0	125	14	98	12	0	2
Diethyl ether	20	8	1	18	8	6	10	1	1
Acetone	112	3	6	102	4	75	139	21	60
1,1-Dichloroethene	110	4	0	120	17	91	68	7	10
Iodomethane	106	6	0	96	15	56	94	3	6
Allyl chloride	116	8	0	111	12	77	88	4	10
Methylene chloride-d_6	105	6	2	96	6	60	101	3	2
Methylene chloride	104	5	2	94	4	57	94	4	2
Acrylonitrile	106	5	7	93	4	60	135	9	62
trans-1,2-Dichloroethene	99	8	0	93	9	53	85	5	6
1,1-Dichloroethane	109	5	1	103	2	66	179	0	0
Methacrylonitrile	106	3	6	69	7	35	152	2	11
2-Butanone	112	11	6	102	4	77	152	9	64
Propionitrile	122	4	6	109	2	83	167	6	64
2,2-Dichloropropane	105	1	0	115	7	83	89	1	10
cis-1,2-Dichloroethene	101	2	2	97	0	59	101	1	2
Chloroform	99	2	3	98	2	62	103	0	2
Isobutyl alcohol	103	9	6	105	6	75	NA	NA	NA
Bromochloromethane	98	0	2	93	2	59	105	1	2
1,1,1-Trichloroethane	99	1	0	112	6	78	85	1	10
1,1-Dichloropropene	102	2	2	120	7	87	83	1	12
Carbon tetrachloride	93	3	0	112	8	78	83	1	12
Benzene-d_6	102	1	1	99	1	60	102	1	1
1,2-Dichloroethane	99	1	2	94	0	108	108	1	3
Benzene	101	1	1	98	1	101	101	1	1
Trichloroethene	90	2	1	94	1	95	95	2	6
1,2-Dichloropropane-d_6	102	1	2	101	1	103	103	1	2
1,2-Dichloropropane	102	2	3	101	1	102	102	1	2
Methyl methacrylate	152	2	9	149	11	145	145	4	13
Bromodichloromethane	94	2	2	95	1	103	103	1	2
1,4-Dioxane	110	1	5	103	1	123	123	2	29
Dibromomethane	93	2	5	93	1	105	105	1	9
4-Methyl-2-pentanone	125	2	8	112	6	147	147	4	13
trans-1,3-Dichloropropene	99	1	3	99	0	101	101	1	2

TABLE 11
(continued)

Compound	Soil #1[a] % Rec[d]	Soil #1[a] Rel Error[e]	Soil #1[a] Sur Pre[f]	Soil #2[b] % Rec[d]	Soil #2[b] Rel Error[e]	Soil #2[b] Sur Pre[f]	Soil #3[c] % Rec[d]	Soil #3[c] Rel Error[e]	Soil #3[c] Sur Pre[f]
Toluene	99	0	3	99	1	96	96	1	1
Pyridine	95	5	8	119	1	71	71	3	43
cis-1,3-Dichloropropene	91	2	2	93	1	102	102	1	3
N-Nitrosodimethylamine	68	5	4	54	11	20	20	1	2
1,1,2-Trichloroethane-d_3	95	3	5	100	4	102	102	1	8
2-Hexanone	125	6	6	110	4	145	145	8	13
1,1,2-Trichloroethane	93	2	5	96	2	103	103	1	9
Tetrachloroethene	98	7	2	105	2	123	123	8	14
1,3-Dichloropropane	99	1	6	101	1	103	103	1	9
Dibromochloromethane	92	2	3	95	0	103	103	1	3
2-Picoline	71	5	3	66	20	62	62	8	15
1,2-Dibromoethane	104	1	5	108	1	108	109	0	9
Chlorobenzene	96	1	4	97	1	109	104	1	2
1,1,1,2-Tetrachloroethane	96	1	3	97	1	98	98	1	2
Ethylbenzene	102	0	2	99	1	52	96	1	1
N-Nitrosomethylethylamine	84	6	4	92	13	46	29	1	10
m+*p*-Xylenes	101	1	2	99	1	52	94	1	1
Styrene	97	1	3	96	1	49	96	0	3
o-Xylene	102	1	2	100	1	53	97	1	2
Isopropylbenzene	101	2	1	98	1	49	87	1	4
Bromoform	94	0	5	103	2	64	101	1	8
cis-1,4-Dichloro-2-butene	106	5	6	115	1	79	116	1	9
N-Nitrosodiethylamine	104	13	4	128	16	84	45	1	11
1,1,2,2-Tetrachloroethane	93	2	5	100	1	61	101	2	8
4-Bromo-1-fluorobenzene	94	2	3	93	1	45	99	0	2
1,2,3-Trichloropropane	111	6	6	120	1	86	115	1	9
n-Propylbenzene	100	3	1	95	0	45	85	1	5
trans-1,4-Dichloro-2-butene	103	4	5	114	3	76	119	1	10
1,3,5-Trimethylbenzene	103	1	1	93	2	42	91	1	2
Bromobenzene	97	1	3	98	0	50	102	0	2
2-Chlorotoluene	98	1	1	90	2	41	94	1	1
4-Chlorotoluene	98	3	2	93	1	43	95	1	2
Pentachloroethane	88	2	2	86	3	39	72	4	2
tert-Butylbenzene	103	2	2	99	1	47	83	1	4
1,2,4-Trimethylbenzene	104	1	2	96	2	44	91	1	2
sec-Butylbenzene	99	4	2	93	3	43	83	1	8
Aniline	106	16	10	143	29	106	15	1	10
p-Isopropyltoluene	104	2	3	101	3	48	87	2	7
1,3-Dichlorobenzene	94	3	3	88	1	38	100	1	4
1,4-Dichlorobenzene	94	2	4	90	1	41	100	1	4

TABLE 11
(continued)

Compound	Soil #1[a] % Rec[d]	Soil #1[a] Rel Error[e]	Soil #1[a] Sur Pre[f]	Soil #2[b] % Rec[d]	Soil #2[b] Rel Error[e]	Soil #2[b] Sur Pre[f]	Soil #3[c] % Rec[d]	Soil #3[c] Rel Error[e]	Soil #3[c] Sur Pre[f]
n-Butylbenzene	97	5	3	89	4	38	83	1	8
1,2-Dichlorobenzene	95	2	4	93	0	42	103	1	5
Benzyl alcohol	98	6	8	128	30	82	22	1	9
N-Nitrosodi-*n*-propylamine	120	16	9	185	27	168	108	3	38
Acetophenone-d_5	104	10	9	167	11	136	270	7	124
o-Toluidine	118	21	12	172	45	149	19	1	14
1,2-Dibromo-3-chloro propane	104	7	8	143	10	106	185	3	24
Hexachlorobutadiene	88	3	14	81	12	58	75	2	8
1,2,4-Trichlorobenzene	88	2	13	81	1	38	104	1	8
Naphthalene-d_8	88	5	17	109	5	69	141	2	12
Naphthalene	88	4	18	109	2	70	132	2	12
1,2,3-Trichlorobenzene	83	0	18	77	2	40	111	1	10
N-Nitrosodibutylamine	133	30	44	152	51	149	11	1	11
2-Methylnaphthalene	60	5	20	60	0	36	62	3	29

[a]Garden soil with 37% moisture and 21% organic matter. Three replicates were analyzed.
[b]Garden soil with 15% moisture and 16% organic matter. Three replicates were analyzed.
[c]Desert soil with 3% moisture and 1% organic matter. Seven replicates were analyzed.
[d]% Rec = Average of replicate accuracy results using internal standard corrections.
[e]Rel Error = Relative standard deviation of replicate analyses.
[f]Sur Pre = Average variation between the predicted analyte recoveries of the internal standard pairs for the replicate analyses. This precision value provides a measure of the inherent error in the overall measurement.
NA = Analyte not significantly present in vacuum distillate.

TABLE 12

EXAMPLE DATA FOR RECOVERY OF ANALYTES SPIKED INTO OIL
AND ANALYZED BY VACUUM DISTILLATION GC/MS USING A WIDE-BORE COLUMN
CAPILLARY COLUMN

Compound	% Rec[a]	Relative Error[b]	Internal Standard Precision[c]
Dichlorodifluoromethane	3	0	0
Chloromethane	141	18	2
Vinyl chloride	137	11	2
Bromomethane	120	29	0
Chloroethane	128	44	2
Trichlorofluoromethane	313	176	0
Diethyl ether	103	5	3
Acetone-d_6	70	8	12
Acrolein	526	166	28
Acetone	323	125	42
1,1-Dichloroethene	116	4	1
Iodomethane	105	6	1
Allyl chloride	119	16	1
Acetonitrile	24	4	4
Methylene chloride-d_6	104	7	2
Methylene chloride	106	10	2
Acrylonitrile	88	7	14
trans-1,2-Dichloroethene	116	4	0
1,1-Dichloroethane	103	2	1
Methacrylonitrile	94	4	4
2-Butanone	92	9	13
Propionitrile	85	4	13
Ethyl acetate-$^{13}C_2$	84	5	3
2,2-Dichloropropane	97	2	1
cis-1,2-Dichloroethene	105	2	1
Chloroform	97	2	2
Isobutyl alcohol	115	11	20
Bromochloromethane	98	3	2

TABLE 12
(continued)

Compound	% Rec[a]	Relative Error[b]	Internal Standard Precision[c]
1,1,1-Trichloroethane	97	3	1
1,1-Dichloropropene	120	4	3
Carbon tetrachloride	93	2	1
Benzene-d_6	100	2	1
1,2-Dichloroethane	101	3	3
Benzene	238	40	0
Trichloroethene	92	3	1
1,2-Dichloropropane-d_6	71	13	2
1,2-Dichloropropane	128	7	3
Methyl methacrylate	101	3	4
Bromodichloromethane	92	1	2
1,4-Dioxane	88	13	14
Dibromomethane	95	4	4
4-Methyl-2-pentanone	95	5	4
trans-1,3-Dichloropropene	103	2	4
Toluene	164	16	5
Pyridine	58	42	19
cis-1,3-Dichloropropene	94	1	4
Ethyl methacrylate	109	2	5
N-Nitrosodimethylamine	189	50	7
1,1,2-Trichloroethane-d_3	88	2	4
2-Hexanone	106	6	3
1,1,2-Trichloroethane	89	2	4
Tetrachloroethene	68	1	1
1,3-Dichloropropane	99	3	4
Dibromochloromethane	85	1	3
2-Picoline	33	24	8
1,2-Dibromoethane	106	2	3
Chlorobenzene	101	1	2
1,1,1,2-Tetrachloroethane	83	2	1

TABLE 12
(continued)

Compound	% Rec[a]	Relative Error[b]	Internal Standard Precision[c]
Ethylbenzene	114	3	1
N-Nitrosomethylethylamine	192	48	0
m+*p*-Xylenes	122	3	1
Styrene	102	1	2
o-Xylene	115	3	1
Isopropylbenzene	109	5	1
Bromoform	88	2	3
cis-1,4-Dichloro-2-butene	103	3	4
N-Nitrosodiethylamine	222	44	30
1,1,2,2-Tetrachloroethane	83	5	3
4-Bromo-1-fluorobenzene	93	2	2
1,2,3-Trichloropropane	103	4	4
n-Propylbenzene	122	4	1
trans-1,4-Dichloro-2-butene	95	3	4
1,3,5-Trimethylbenzene	93	9	2
Bromobenzene	98	2	2
2-Chlorotoluene	78	2	1
4-Chlorotoluene	93	2	2
Pentachloroethane	81	4	2
tert-Butylbenzene	120	55	3
1,2,4-Trimethylbenzene	127	8	3
sec-Butylbenzene	89	10	3
Aniline	NA	NA	NA[d]
p-Isopropyltoluene	NA	NA	NA
1,3-Dichlorobenzene	70	2	2
1,4-Dichlorobenzene	87	3	4
n-Butylbenzene	105	4	6
1,2-Dichlorobenzene	119	14	7
Benzyl alcohol	NA	NA	NA
n-Nitroso-di-*n*-propylamine	270	58	51

TABLE 12
(continued)

Compound	% Rec[a]	Relative Error[b]	Internal Standard Precision[c]
Acetophenone-d_5	175	31	34
o-Toluidine	108	69	36
1,2-Dibromo-3-chloropropane	84	14	6
Hexachlorobutadiene	119	6	20
1,2,4-Trichlorobenzene	94	5	14
Naphthalene-d_8	132	16	29
Naphthalene	123	15	32
1,2,3-Trichlorobenzene	80	3	21
n-Nitrosodibutylamine	2000	3600	3200
2-Methylnaphthalene	667	1644	4900

[a]Average of seven replicate analyses of 1 g of cod liver oil.

[b]Relative standard deviation of replicate analyses.

[c]Average variation between the predicted analyte recoveries of the internal standard pairs for the replicate analyses. This precision value provides a measure of the inherent error in the overall measurement.

[d]NA = Compound could not be accurately measured due to spectral interferences.

TABLE 13
EXAMPLE RECOVERY OF ANALYTES SPIKED INTO WATER SOLUTIONS AND ANALYZED BY VACUUM DISTILLATION GC/MS USING A WIDE-BORE CAPILLARY COLUMN

	Water[a]			Water/Glycerin[b]			Water/Salt[c]			Water/Soap[d]		
Compound	% Rec[e]	Rel Error[f]	IS Prec[g]	% Rec[e]	Rel Error[f]	IS Prec[g]	% Rec[e]	Rel Error[f]	IS Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]
Dichlorodifluoromethane	76	9	1	84	8	1	85	6	1	56	7	1
Chloromethane	81	6	1	86	8	1	83	10	1	77	3	1
Vinyl chloride	78	5	1	81	3	1	74	4	1	81	4	1
Bromomethane	101	5	1	103	2	0	116	47	1	102	4	1
Chloroethane	95	5	1	96	2	1	112	52	1	95	5	1
Trichlorofluoromethane	122	52	1	98	1	1	120	58	1	96	3	1
Diethyl ether	106	17	2	98	12	1	14	8	0	17	14	1
Acrolein	111	16	3	114	5	1	20	10	2	49	6	2
Acetone	114	17	5	286	41	16	88	5	20	71	10	3
1,1-Dichloroethene	102	10	1	98	6	1	20	12	0	93	9	1
Iodomethane	103	7	1	104	7	0	98	4	1	103	2	0
Allyl chloride	102	10	1	101	6	1	95	4	1	101	3	1
Acetonitrile	122	21	6	189	2	7	82	11	17	99	8	4
Methylene chloride-d_2	103	7	1	104	9	0	99	7	1	102	6	2
Methylene chloride	99	9	1	101	10	0	95	10	1	98	8	2
Acrylonitrile	97	1	7	95	3	7	112	21	27	93	3	4
trans-1,2-Dichloroethane	100	4	1	100	5	0	94	8	1	93	6	1
1,1-Dichloroethane	102	5	1	102	5	0	101	4	0	101	1	1
Methacrylonitrile	101	3	2	101	1	1	108	7	7.	104	2	4
2-Butanone	68	43	7	106	31	10	105	27	25	97	2	4
Propionitrile	100	6	6	109	9	14	111	31	22	103	3	4
2,2-Dichloropropane	100	1	1	99	1	1	100	1	1	102	1	1

TABLE 13
(continued)

Compound	Water[a]			Water/Glycerin[b]			Water/Salt[c]			Water/Soap[d]		
	% Rec[e]	Rel Error[f]	IS Prec[g]	% Rec[e]	Rel Error[f]	IS Prec[g]	% Rec[e]	Rel Error[f]	IS Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]
cis-1,2-Dichloroethene	100	1	1	100	1	0	97	2	0	103	0	1
Chloroform	100	1	1	100	2	1	100	2	0	103	1	2
Isobutyl alcohol	86	7	5	137	17	5	116	21	30	76	10	3
Bromochloromethane	102	1	1	102	1	0	100	0	1	102	1	1
1,1,1-Trichloroethane	100	1	1	99	1	1	98	3	1	99	1	1
1,1-Dichloropropene	95	3	1	96	3	1	94	3	1	99	3	1
Carbon tetrachloride	100	0	1	100	2	1	100	2	1	88	2	1
Benzene-d_6	99	1	1	99	1	1	99	1	0	100	1	1
1,2-Dichloroethane	101	1	1	101	1	1	99	1	1	100	1	2
Benzene	99	0	1	100	1	1	99	2	0	99	1	1
Trichloroethene	100	1	1	99	1	0	98	1	1	109	1	0
1,2-Dichloropropane-d_6	99	2	1	99	2	0	99	2	1	101	2	2
1,2-Dichloropropane	100	1	1	100	1	0	99	1	1	101	1	2
Methyl methacrylate	106	7	2	128	10	1	114	4	5	106	2	5
Bromodichloromethane	102	1	1	100	1	0	102	2	1	101	1	2
1,4-Dioxane	101	8	8	156	15	83	96	18	16	102	3	14
Dibromomethane	102	1	2	101	1	1	99	1	3	100	1	5
4-Methyl-2-pentanone	102	5	3	102	3	1	116	1	9	110	2	5
trans-1,3-Dichloropropene	99	1	1	100	0	1	99	2	1	103	1	1
Toluene	98	2	1	99	1	1	97	3	1	97	1	1
Pyridine	61	20	16	NA	NA	NA	104	24	37	128	7	36

TABLE 13
(continued)

Compound	Water[a]			Water/Glycerin[b]			Water/Salt[c]			Water/Soap[d]		
	% Rec[e]	Rel Error[f]	IS Prec[g]	% Rec[e]	Rel Error[f]	IS Prec[g]	% Rec[e]	Rel Error[f]	IS Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]
cis-1,3-Dichloropropene	99	1	1	99	1	1	97	2	1	100	1	2
Ethyl methacrylate	109	9	2	156	17	1	109	25	3	105	2	4
N-Nitrosodimethylamine	75	8	2	97	8	1	105	32	10	69	9	4
1,1,2-Trichloroethane-d_3	100	1	2	100	2	1	101	2	3	99	1	5
2-Hexanone	102	9	3	99	4	1	118	4	11	112	3	5
1,1,2-Trichloroethane	100	2	2	100	1	1	101	1	2	101	1	5
Tetrachloroethene	98	11	1	98	14	1	106	34	1	200	36	0
1,3-Dichloropropane	98	1	2	99	1	1	98	2	3	98	1	5
Dibromochloromethane	102	1	1	101	2	1	104	1	1	102	1	2
2-Picoline	NA	NA	NA	NA	NA	NA	169	69	26	217	28	33
1,2-Dibromoethane	100	1	2	100	1	1	101	1	2	104	1	5
Chlorobenzene	100	1	1	100	1	1	99	1	1	102	0	2
1,1,1,2-Tetrachloroethane	101	1	1	100	1	0	102	1	1	100	1	2
Ethylbenzene	97	2	1	99	2	1	98	1	0	97	2	1
N-Nitrosomethylethylamine	70	9	4	111	10	20	130	35	25	79	1	4
m+*p*-Xylenes	98	2	1	99	1	1	97	1	0	101	1	1
Styrene	98	0	1	99	1	1	97	3	1	102	0	3
o-Xylene	98	1	1	99	1	1	98	1	1	106	1	2
Isopropylbenzene	97	2	1	99	2	1	95	3	1	84	2	2
Bromoform	103	2	2	101	2	1	109	1	2	108	2	6
cis-1,4-Dichloro-2-butene	102	4	2	102	2	1	110	2	1	114	4	6

TABLE 13
(continued)

Compound	Water[a]			Water/Glycerin[b]			Water/Salt[c]			Water/Soap[d]		
	% Rec[e]	Rel Error[f]	IS Prec[g]	% Rec[e]	Rel Error[f]	IS Prec[g]	% Rec[e]	Rel Error[f]	IS Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]
N-Nitrosodiethylamine	78	9	6	133	11	60	128	31	18	78	2	9
1,1,2,2-Tetrachloroethane	101	2	2	100	3	1	111	2	2	82	3	4
4-Bromo-1-fluorobenzene	101	1	1	101	1	1	101	1	1	102	1	3
1,2,3-Trichloropropane	97	6	2	99	3	1	105	6	2	112	3	6
n-Propylbenzene	97	2	1	98	2	1	94	3	1	81	3	2
trans-1,4-Dichloro-2-butene	101	4	2	102	2	1	111	2	2	115	4	7
1,3,5-Trimethylbenzene	98	3	1	99	2	1	96	3	1	83	1	1
Bromobenzene	101	0	1	101	0	1	100	1	1	104	1	3
2-Chlorotoluene	96	4	1	99	3	1	95	3	1	88	2	2
4-Chlorotoluene	101	2	1	100	2	1	98	1	1	94	2	2
Pentachloroethane	103	10	1	100	9	1	94	18	1	29	8	1
tert-Butylbenzene	99	3	1	100	3	1	95	5	1	66	2	1
1,2,4-Trimethylbenzene	98	2	1	99	2	1	96	2	1	88	2	2
sec-Butylbenzene	98	3	1	99	2	1	93	3	2	74	2	2
Aniline	119	40	18	74	15	65	79	37	30	97	9	29
p-Isopropyltoluene	97	0	2	98	4	2	93	3	2	81	2	4
1,3-Dichlorobenzene	101	1	1	100	1	1	99	1	1	98	1	3
1,4-Dichlorobenzene	101	1	1	101	1	1	100	2	1	105	1	3
n-Butylbenzene	97	2	2	98	3	2	91	2	2	74	2	3
1,2-Dichlorobenzene	100	1	1	100	1	1	100	1	2	102	1	5
Benzyl alcohol	128	28	19	167	14	125	65	35	15	93	5	23

TABLE 13
(continued)

Compound	Water[a]			Water/Glycerin[b]			Water/Salt[c]			Water/Soap[d]		
	% Rec[e]	Rel Error[f]	IS Prec[g]	% Rec[e]	Rel Error[f]	IS Prec[g]	% Rec[e]	Rel Error[f]	IS Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]
N-Nitroso-di-*n*-propylamine	68	14	5	108	9	25	56	15	29	112	5	15
Acetophenone-d_5	71	20	7	81	7	7	99	66	23	156	7	17
o-Toluidine	127	42	21	66	20	61	97	49	41	115	15	37
1,2-Dibromo-3-chloropropane	101	9	3	99	5	3	111	25	4	156	7	15
Hexachlorobutadiene	101	2	2	102	4	3	92	3	3	74	2	4
1,2,4-Trichlorobenzene	101	1	2	100	1	3	102	1	3	104	1	5
Naphthalene-d_8	102	5	2	100	2	4	112	5	5	127	3	10
Naphthalene	101	4	2	101	2	4	110	2	5	125	3	9
1,2,3-Trichlorobenzene	100	2	2	100	1	4	100	3	5	93	3	8
N-Nitrosodibutylamine	208	109	43	400	32	384	90	69	67	98	21	43
2-Methylnaphthalene	84	6	8	91	10	12	98	27	24	55	3	11

[a]5-mL water samples
[b]1 g of glycerin added to 5 mL of water
[c]1 g of salt added to 5 mL of water
[d]0.2 g of concentrated soap added to 5 mL of water
[e]Average of four replicate analyses
[f]Relative standard deviation of replicate analyses
[g]Average variation between the predicted analyte recoveries of the surrogate pairs for the replicate analyses. This precision value provides a measure of the inherent error in the overall measurement.
[h]NA = compound not significantly present in vacuum distillate.

TABLE 14

EXAMPLE RECOVERY OF ANALYTES SPIKED INTO WATER SOLUTIONS AND ANALYZED BY VACUUM DISTILLATION GC/MS USING A NARROW-BORE CAPILLARY COLUMN

	Water[a]			Water/Glycerin[b]			Water/Salt[c]			Water/Soap[d]		
Compound	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]
Dichlorodifluoromethane	76	9	1	84	8	1	85	6	1	56	7	1
Chloromethane	81	6	1	86	8	1	83	10	1	77	3	1
Vinyl chloride	78	5	1	81	3	1	74	4	1	81	4	1
Bromomethane	101	5	1	103	2	0	116	47	1	102	4	1
Chloroethane	95	5	1	96	2	1	112	52	1	95	5	1
Trichlorofluoromethane	122	52	1	98	1	1	120	58	1	96	3	1
Diethyl ether	106	17	2	98	12	1	14	8	0	17	14	1
Acrolein	111	16	3	114	5	1	20	10	2	49	6	2
Acetone	114	17	5	286	41	16	88	5	20	71	10	3
1,1-Dichloroethene	102	10	1	98	6	1	20	12	0	93	9	1
Iodomethane	103	7	1	104	7	0	98	4	1	103	2	0
Allyl chloride	102	10	1	101	6	1	95	4	1	101	3	1
Acetonitrile	122	21	6	189	2	7	82	11	17	99	8	4
Methylene chloride-d_2	103	7	1	104	9	0	99	7	1	102	6	2
Methylene chloride	99	9	1	101	10	0	95	10	1	98	8	2
Acrylonitrile	97	1	7	95	3	7	112	21	27	93	3	4
trans-1,2-Dichloroethane	100	4	1	100	5	0	94	8	1	93	6	1
1,1-Dichloroethane	102	5	1	102	5	0	101	4	0	101	1	1
Methacrylonitrile	101	3	2	101	1	1	108	7	7.	104	2	4
2-Butanone	68	43	7	106	31	10	105	27	25	97	2	4
Propionitrile	100	6	6	109	9	14	111	31	22	103	3	4

TABLE 14
(continued)

Compound	Water[a]			Water/Glycerin[b]			Water/Salt[c]			Water/Soap[d]		
	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]
2,2-Dichloropropane	100	1	1	99	1	1	100	1	1	102	1	1
cis-1,2-Dichloroethene	100	1	1	100	1	0	97	2	0	103	0	1
Chloroform	100	1	1	100	2	1	100	2	0	103	1	2
Isobutyl alcohol	86	7	5	137	17	5	116	21	30	76	10	3
Bromochloromethane	102	1	1	102	1	0	100	0	1	102	1	1
1,1,1-Trichloroethane	100	1	1	99	1	1	98	3	1	99	1	1
1,1-Dichloropropene	95	3	1	96	3	1	94	3	1	99	3	1
Carbon tetrachloride	100	0	1	100	2	1	100	2	1	88	2	1
Benzene-d_6	99	1	1	99	1	1	99	1	0	100	1	1
1,2-Dichloroethane	101	1	1	101	1	1	99	1	1	100	1	2
Benzene	99	0	1	100	1	1	99	2	0	99	1	1
Trichloroethene	100	1	1	99	1	0	98	1	1	109	1	0
1,2-Dichloropropane-d_6	99	2	1	99	2	0	99	2	1	101	2	2
1,2-Dichloropropane	100	1	1	100	1	0	99	1	1	101	1	2
Methyl methacrylate	106	7	2	128	10	1	114	4	5	106	2	5
Bromodichloromethane	102	1	1	100	1	0	102	2	1	101	1	2
1,4-Dioxane	101	8	8	156	15	83	96	18	16	102	3	14
Dibromomethane	102	1	2	101	1	1	99	1	3	100	1	5
4-Methyl-2-pentanone	102	5	3	102	3	1	116	1	9	110	2	5
trans-1,3-Dichloropropene	99	1	1	100	0	1	99	2	1	103	1	1
Toluene	98	2	1	99	1	1	97	3	1	97	1	1
Pyridine	61	20	16	NA	NA	NA	104	24	37	128	7	36

TABLE 14
(continued)

Compound	Water[a]			Water/Glycerin[b]			Water/Salt[c]			Water/Soap[d]		
	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]
cis-1,3-Dichloropropene	99	1	1	99	1	1	97	2	1	100	1	2
Ethyl methacrylate	109	9	2	156	17	1	109	25	3	105	2	4
N-Nitrosodimethylamine	75	8	2	97	8	1	105	32	10	69	9	4
1,1,2-Trichloroethane-d_3	100	1	2	100	2	1	101	2	3	99	1	5
2-Hexanone	102	9	3	99	4	1	118	4	11	112	3	5
1,1,2-Trichloroethane	100	2	2	100	1	1	101	1	2	101	1	5
Tetrachloroethene	98	11	1	98	14	1	106	34	1	200	36	0
1,3-Dichloropropane	98	1	2	99	1	1	98	2	3	98	1	5
Dibromochloromethane	102	1	1	101	2	1	104	1	1	102	1	2
2-Picoline	NA	NA	NA	NA	NA	NA	169	69	26	217	28	33
1,2-Dibromoethane	100	1	2	100	1	1	101	1	2	104	1	5
Chlorobenzene	100	1	1	100	1	1	99	1	1	102	0	2
1,1,1,2-Tetrachloroethane	101	1	1	100	1	0	102	1	1	100	1	2
Ethylbenzene	97	2	1	99	2	1	98	1	0	97	2	1
N-Nitrosomethylethylamine	70	9	4	111	10	20	130	35	25	79	1	4
m+*p*-Xylenes	98	2	1	99	1	1	97	1	0	101	1	1
Styrene	98	0	1	99	1	1	97	3	1	102	0	3
o-Xylene	98	1	1	99	1	1	98	1	1	106	1	2
Isopropylbenzene	97	2	1	99	2	1	95	3	1	84	2	2
Bromoform	103	2	2	101	2	1	109	1	2	108	2	6
cis-1,4-Dichloro-2-butene	102	4	2	102	2	1	110	2	1	114	4	6
N-Nitrosodiethylamine	78	9	6	133	11	60	128	31	18	78	2	9

TABLE 14
(continued)

Compound	Water[a]			Water/Glycerin[b]			Water/Salt[c]			Water/Soap[d]		
	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]
1,1,2,2-Tetrachloroethane	101	2	2	100	3	1	111	2	2	82	3	4
4-Bromo-1-fluorobenzene	101	1	1	101	1	1	101	1	1	102	1	3
1,2,3-Trichloropropane	97	6	2	99	3	1	105	6	2	112	3	6
n-Propylbenzene	97	2	1	98	2	1	94	3	1	81	3	2
trans-1,4-Dichloro-2-butene	101	4	2	102	2	1	111	2	2	115	4	7
1,3,5-Trimethylbenzene	98	3	1	99	2	1	96	3	1	83	1	1
Bromobenzene	101	0	1	101	0	1	100	1	1	104	1	3
2-Chlorotoluene	96	4	1	99	3	1	95	3	1	88	2	2
4-Chlorotoluene	101	2	1	100	2	1	98	1	1	94	2	2
Pentachloroethane	103	10	1	100	9	1	94	18	1	29	8	1
tert-Butylbenzene	99	3	1	100	3	1	95	5	1	66	2	1
1,2,4-Trimethylbenzene	98	2	1	99	2	1	96	2	1	88	2	2
sec-Butylbenzene	98	3	1	99	2	1	93	3	2	74	2	2
Aniline	119	40	18	74	15	65	79	37	30	97	9	29
p-Isopropyltoluene	97	0	2	98	4	2	93	3	2	81	2	4
1,3-Dichlorobenzene	101	1	1	100	1	1	99	1	1	98	1	3
1,4-Dichlorobenzene	101	1	1	101	1	1	100	2	1	105	1	3
n-Butylbenzene	97	2	2	98	3	2	91	2	2	74	2	3
1,2-Dichlorobenzene	100	1	1	100	1	1	100	1	2	102	1	5
Benzyl alcohol	128	28	19	167	14	125	65	35	15	93	5	23
N-Nitroso-di-*n*-propylamine	68	14	5	108	9	25	56	15	29	112	5	15
Acetophenone-d_5	71	20	7	81	7	7	99	66	23	156	7	17

Compound	Water[a]			Water/Glycerin[b]			Water/Salt[c]			Water/Soap[d]		
	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]
o-Toluidine	127	42	21	66	20	61	97	49	41	115	15	37
1,2-Dibromo-3-chloropropane	101	9	3	99	5	3	111	25	4	156	7	15
Hexachlorobutadiene	101	2	2	102	4	3	92	3	3	74	2	4
1,2,4-Trichlorobenzene	101	1	2	100	1	3	102	1	3	104	1	5
Naphthalene-d_8	102	5	2	100	2	4	112	5	5	127	3	10
Naphthalene	101	4	2	101	2	4	110	2	5	125	3	9
1,2,3-Trichlorobenzene	100	2	2	100	1	4	100	3	5	93	3	8
N-Nitrosodibutylamine	208	109	43	400	32	384	90	69	67	98	21	43
2-Methylnaphthalene	84	6	8	91	10	12	98	27	24	55	3	11

[a]5-mL water samples
[b]1 g of glycerin added to 5 mL of water
[c]1 g of salt added to 5 mL of water
[d]0.2 g of concentrated soap added to 5 mL of water
[e]Average of four replicate analyses
[f]Relative standard deviation of replicate analyses
[g]Average variation between the predicted analyte recoveries of the surrogate pairs for the replicate analyses. This precision value provides a measure of the inherent error in the overall measurement.
[h]NA = compound not significantly present in vacuum distillate.

TABLE 15

EXAMPLE RECOVERY OF ANALYTES SPIKED INTO VARIOUS WATER VOLUMES AND ANALYZED BY VACUUM DISTILLATION GC/MS USING A NARROW-BORE CAPILLARY COLUMN

Compound	Water[a]		Water[b]		Water[c]		Water[d]	
	% Rec[e]	Rel Error[f]	% Rec[e]	Rel Error[f]	% Rec[e]	Rel Error[f]	% Rec[e]	Rel Error[f]
Methyl acetate	122	22	80	1	137	20	88	1
MTBE	103	8	110	1	112	3	107	2
1,1,2-Trichloro-1,2,2-trifluoroethane	100	8	110	1	103	8	114	6
Carbon disulfide	117	6	98	7	113	8	92	2
Cyclohexane	106	3	114	1	113	6	116	5
Methyl cyclohexane	99	14	111	1	92	10	114	5

[a]5-mL water samples spiked at 1 ppb
[b]5-mL water samples spiked at 50 ppb
[c]25-mL water samples spiked at 0.2 ppb
[d]25-mL water samples spiked at 10 ppb
[e]Average of three replicate analyses
[f]Relative standard deviation of replicate analyses

TABLE 16

EXAMPLE METHOD PERFORMANCE IN FISH TISSUE USING A WIDE-BORE CAPILLARY COLUMN

			Using Water Standards[a]			Using Tuna Standards[b]		
Compound	Surrogate Type	Spike (ppb)[c]	Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]	Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]
Dichlorodifluoromethane		1000	109	22	24	116	17	16
Chloromethane		1000	105	16	16	102	13	10
Vinyl chloride		1000	105	20	21	115	15	14
Bromomethane		1000	90	19	11	89	18	7
Chloroethane		1000	102	21	18	110	17	12
Trichlorofluoromethane		1000	97	24	21	125	18	16
Diethyl ether-d_{10}	Check	250	113	9	4	108	9	3
Ether		500	104	10	4	106	10	3
Acetone-d_6	Check	2500	41	27	0	149	20	1
Acetone		Cont	--	--	--	--	--	--
1,1-Dichloroethene		500	44	54	8	134	31	15
Iodomethane		500	10	101	1	57	129	3
Allyl chloride		500	55	75	9	96	79	9
Acetonitrile		Int	--	--	--	--	--	--
Methylene chloride-d_6	Check	250	94	18	3	109	19	2
Methylene chloride		500	74	24	2	91	22	2
Acrylonitrile		500	65	25	0	75	28	0
trans-1,2-Dichloroethene		500	77	29	7	84	32	5
Nitromethane-d_3	Check	250	121	42	3	133	41	2
1,1-Dichloroethane		500	89	74	1	53	40	0
Hexafluorobenzene	Alpha	250	--	--	--	--	--	--
Tetrahydrofuran-d_8	Alpha	250	--	--	--	--	--	--
Methacrylonitrile		500	103	17	5	100	17	5
2-Butanone		500	122	11	2	149	10	1
Propionitrile		500	113	8	5	120	8	3
Ethyl acetate-^{13}C	Check	2500	76	18	1	95	18	0

TABLE 16
(continued)

Compound	Surrogate Type	Spike (ppb)[c]	Using Water Standards[a] Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]	Using Tuna Standards[b] Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]
2,2-Dichloropropane		500	94	16	14	108	13	10
cis-1,2-Dichloroethene		500	102	6	3	100	7	2
Chloroform		500	101	6	4	100	7	3
Pentafluorobenzene	Alpha	250	--	--	--	--	--	--
Bromochloromethane		500	100	5	2	99	5	2
1,1,1-Trichloroethane		500	91	18	14	113	13	10
1,1-Dichloropropene		500	99	21	18	128	15	15
Carbon tetrachloride		500	80	22	15	122	17	14
Benzene-d_6	Alpha	500	--	--	--	--	--	--
1,2-Dichloroethane-d_4	Alpha	250	--	--	--	--	--	--
1,2-Dichloroethane		500	100	3	2	99	3	2
Benzene		500	102	3	1	101	3	1
Fluorobenzene	Alpha	250	--	--	--	--	--	--
1,4-Difluorobenzene	Alpha	250	--	--	--	--	--	--
Trichloroethene		500	71	10	6	86	8	5
1,2-Dichloropropane-d_6	Check	250	93	2	3	94	2	2
1,2-Dichloropropane		500	93	3	3	93	2	2
Methyl methacrylate		500	102	13	5	99	13	4
1,4-Dioxane-d_8	Alpha	2500	--	--	--	--	--	--
Bromodichloromethane		500	75	10	2	86	11	2
1,4-Dioxane		500	115	3	22	108	3	11
Dibromomethane		500	92	4	4	99	4	3
4-Methyl-2-pentanone		1000	128	20	8	108	21	6
trans-1,3-Dichloropropene		500	61	36	2	61	36	2
Toluene-d_8	Beta	250	--	--	--	--	--	--
Toluene		500	101	4	4	98	4	2
Pyridine-d_5	Check/Alpha	2500	51	25	25	72	16	21
Pyridine		500	62	21	27	81	13	20

TABLE 16
(continued)

Compound	Surrogate Type	Spike (ppb)[c]	Using Water Standards[a] Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]	Using Tuna Standards[b] Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]
cis-1,3-Dichloropropene		500	61	27	2	66	27	2
Ethyl methacrylate		500	100	12	5	95	12	4
N-Nitrosodimethylamine		3350	657	28	39	160	30	10
1,1,2-Trichloroethane-d_3	Check	250	80	6	4	93	6	3
2-Hexanone		500	141	23	9	114	23	7
1,1,2-Trichloroethane		500	82	5	4	93	5	3
Tetrachloroethene		500	73	16	11	106	12	10
1,3-Dichloropropane		500	99	2	5	97	2	3
Dibromochloromethane		500	61	11	3	90	19	3
1,2-Dibromoethane-d_4		250	--	--	--	--	--	--
2-Picoline		500	163	16	38	131	11	16
1,2-Dibromoethane		500	99	4	6	99	4	4
Chlorobenzene-d_5	Beta	250	--	--	--	--	--	--
Chlorobenzene		500	95	3	6	99	3	4
1,1,1,2-Tetrachloroethane		500	88	4	5	95	5	3
Ethylbenzene		500	111	7	4	110	7	2
N-Nitrosomethylethylamine		3350	516	31	31	182	27	7
m+*p*-Xylenes		500	107	6	4	107	6	2
Styrene		500	94	3	4	95.7	3	3
o-Xylene-d_{10}		250	--	--	--	--	--	--
o-Xylene		500	102	4	4	101	4	3
Isopropylbenzene		500	116	16	8	124	15	6
Bromoform		500	53	30	2	118	38	4
cis-1,4-Dichloro-2-butene		500	5	134	0	5	134	0
N-Nitrosodiethylamine		3350	356	31	62	168	28	18
1,1,2,2-Tetrachloroethane		500	37	62	2	144	72	5
4-Bromofluorobenzene	Check	250	92	4	4	97	3	4
1,2,3-Dichloropropane		500	103	10	5	98	11	4

TABLE 16
(continued)

Compound	Surrogate Type	Spike (ppb)[c]	Using Water Standards[a] Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]	Using Tuna Standards[b] Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]
Propylbenzene		500	113	17	10	125	16	8
trans-1,4-Dichloro-2-butene		500	0	0	0	0	0	0
1,3,5-Trimethylbenzene		500	115	9	4	113	10	3
Bromobenzene-d_5	Beta	250	--	--	--	--	--	--
Bromobenzene		500	96	4	5	97	3	4
2-Chlorotoluene		500	105	4	3	107	4	3
4-Chlorotoluene		500	101	4	3	104	5	3
Pentachloroethane		500	28	54	1	135	75	5
tert-Butylbenzene		500	118	19	10	126	19	8
1,2,4-Trimethylbenzene		500	112	9	5	107	10	4
sec-Butylbenzene		500	114	24	15	134	22	13
Aniline		500	80	36	37	57	38	15
p-Isopropyltoluene		500	124	21	16	127	20	12
1,3-Dichlorobenzene		500	94	5	7	98	4	5
1,4-Dichlorobenzene		500	93	6	7	96	5	6
n-Butylbenzene		500	109	22	17	128	20	15
1,2-Dichlorobenzene-d_4	Beta	250	--	--	--	--	--	--
1,2-Dichlorobenzene		500	91	10	10	96	9	7
Decafluorobiphenyl	Beta	250	--	--	--	--	--	--
N-Nitrosodi-*n*-propylamine		3350	288	51	47	179	50	21
Nitrobenzene-d_5	Check	250	374	105	283	176	58	40
Acetophenone-d_5	Check	1000	216	47	29	187	47	19
o-Toluidine		3350	67	39	34	58	41	18
1,2-Dibromo-3-chloropropane		500	97	39	12	107	40	10
Hexachlorobutadiene		500	108	27	20	122	28	18
1,2,4-Trichlorobenzene-d_3	Beta	250	--	--	--	--	--	--
1,2,4-Trichlorobenzene		500	94	12	14	94	9	11
Naphthalene-d_8	Check	500	85	14	18	93	12	14

TABLE 16
(continued)

Compound	Surrogate Type	Spike (ppb)[c]	Using Water Standards[a] Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]	Using Tuna Standards[b] Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]
Naphthalene		1000	95	11	22	95	9	16
1,2,3-Trichlorobenzene		500	88	8	23	96	9	18
N-Nitrosodibutylamine		3350	25	99	19	25	115	12
2-Methylnaphthalene		3350	194	21	74	96	23	26
1-Methylnaphthalene-d_{10}	Beta	1000	--	--	--	--	--	--

[a]Calibration standards were prepared using 5 mL of water as the matrix.
[b]Calibration standards were prepared using 1 g of tuna as the matrix.
[c]1-g samples were spiked, mixed ultrasonically, and allowed to equilibrate overnight (>1000 min) prior to analysis.
[d]Average percent recovery of seven replicate analyses of fish tissue taken from canned, water-packed tuna.
[e]Relative standard deviation
ND = Not determined
Int = Spectral interferences prevented accurate integrations.
Cont = The spike could not be distinguished from the background levels.

FIGURE 1

DIAGRAM OF VACUUM DISTILLATION APPARATUS

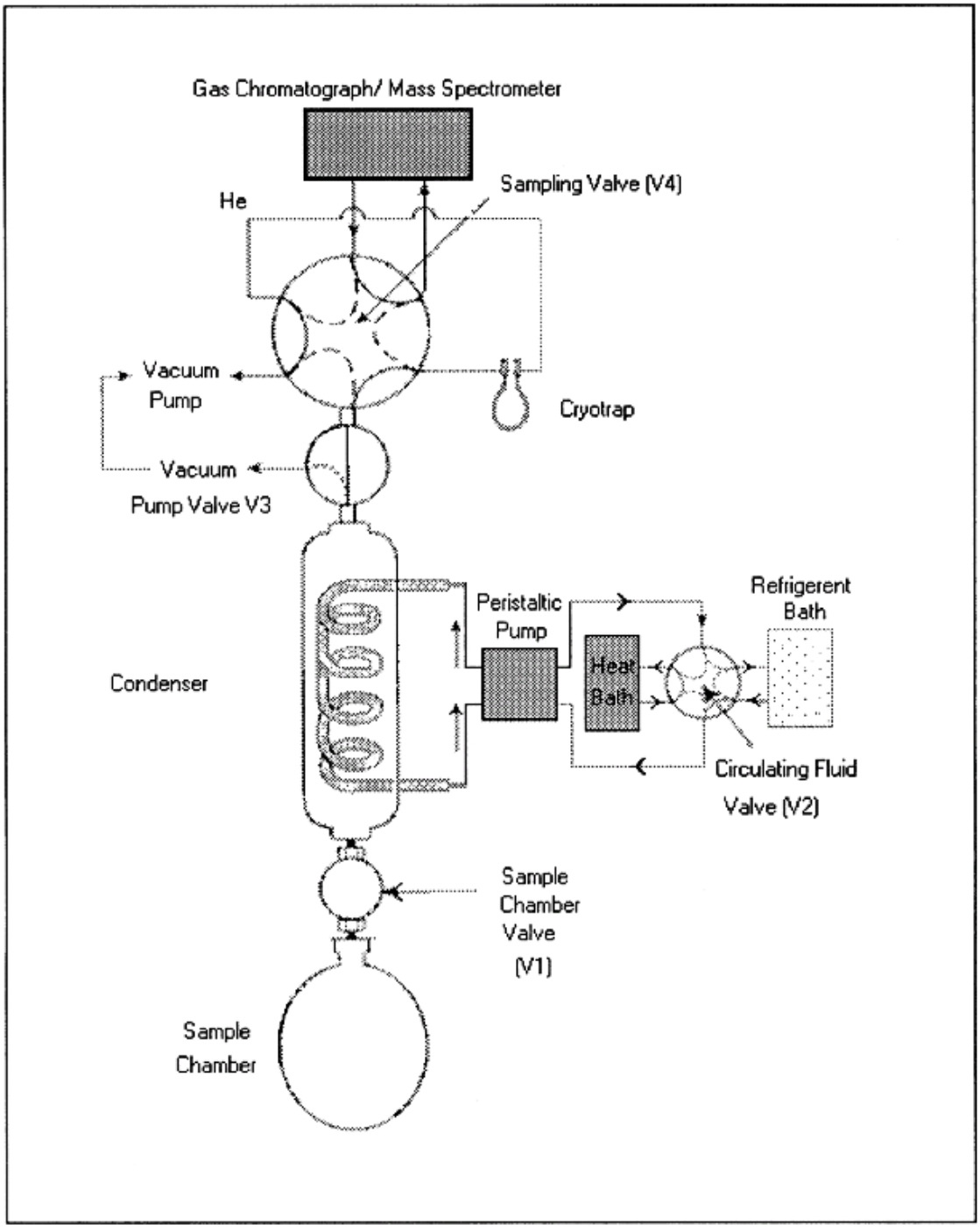


FIGURE 2

QUANTITATION REPORT EXAMPLE

Quantitation Curve Report - Linear: BP – Ln: RVW

Page: 1

File Identification: C:\SMCREPORTER\Cal_example\StandardA.txt
Process Date: 11/24/2004 8:57:19 AM
Sample Size: 5
Sample Type: water
Comment 1:
Comment 2:

Calibration File: C:\SMCREPORTER\CAL_EXAMPLE\EXAMPLE.CAL
Compound Library File: C:\SMCREPORTER\CAL_EXAMPLE\ALL.TXT
Surrogate Groups: C:\SMCREPORTER\CAL_EXAMPLE\SURR_6RELVOL.INI

Compound	ng/mL	Error	Pred.Recovery±Deviation
31: dichlorodifluoromethane	53.8	± 0.174	78.67 ± 0.25
32: chloromethane	46.6	± 0.148	80.21 ± 0.25
33: vinylchloride	36.6	± 0.118	78.67 ± 0.25
34: bromomethane	41.3	± 0.129	81.16 ± 0.25
35: chloroethane	46.3	± 0.148	79.20 ± 0.25
36: trichlorofluoromethane	49.6	± 0.160	78.67 ± 0.25
37: ether	91.9	± 8.71	75.14 ± 7.12
38: acetone	68.4	± 0.612	73.86 ± 0.66
39: 1,1-dichloroethene	49.2	± 0.159	78.67 ± 0.25
40: iodomethane	84.5	± 0.262	81.92 ± 0.25
41: allylchloride	51.0	± 0.162	80.14 ± 0.25
42: acetonitrile	168	± 1.50	73.84 ± 0.66
43: methylenechloride	40.6	± 3.44	79.15 ± 6.70
44: acrylonitrile	100	± 9.60	74.25 ± 7.12
45: trans-1,2-dichloroethene	47.3	± 0.147	81.93 ± 0.25
46: 1,1-dichloroethane	46.0	± 0.118	83.06 ± 0.21
47: methacrylonitrile	104	± 9.98	74.40 ± 7.11
48: 2-butanone	180	± 1.61	73.89 ± 0.66
49: propionitrile	130	± 1.20	73.53 ± 0.68
50: 2,2-dichloropropane	51.9	± 0.164	80.21 ± 0.25
51: cis-1,2-dichloroethene	47.4	± 0.124	81.62 ± 0.21
52: chloroform	49.2	± 4.06	81.15 ± 6.70
53: bromochloromethane	47.7	± 4.13	77.31 ± 6.70
54: 1,1,1-trichloroethane	47.1	± 0.149	80.06 ± 0.25
55: 1,1-dichloropropene	49.6	± 0.202	77.90 ± 0.32
56: carbontetrachloride	52.2	± 0.168	78.67 ± 0.25
57: 1,2-dichloroethane	39.8	± 3.49	76.46 ± 6.70
58: benzene	44.0	± 0.134	83.38 ± 0.25
59: trichloroethene	45.7	± 0.181	82.03 ± 0.33
60: 1,2-dichloropropane	45.3	± 3.85	78.39 ± 6.67
61: methylmethacrylate	96.0	± 9.15	74.07 ± 7.06
62: bromodichloromethane	52.3	± 4.48	78.17 ± 6.69
63: 1,4-dioxane	526	± 4.87	73.54 ± 0.68
64: dibromomethane	51.2	± 4.55	74.93 ± 6.66
65: 4-methyl-2-pentanone	215	± 20.57	73.00 ± 6.99
66: trans-1,3-dichloropropene	218	± 18.82	76.46 ± 6.60
67: toluene	43.2	± 0.155	82.12 ± 0.29
68: pyridine	817	± 126.7	88.62 ± 13.74
69: cis-1,3-dichloropropene	240	± 21.13	75.44 ± 6.63
70: ethylmethacrylate	87.8	± 8.35	73.51 ± 6.99
71: n-nitrosodimethylamine	2921	± 279.8	71.16 ± 6.82
72: 2-hexanone	85.6	± 8.20	72.41 ± 6.94
73: 1,1,2-trichloroethane	40.6	± 3.63	73.70 ± 6.59
74: tetrachloroethene	48.8	± 0.197	78.61 ± 0.32
75: 1,3-dichloropropane	47.1	± 4.19	73.62 ± 6.56
76: dibromochloromethane	56.5	± 4.96	74.73 ± 6.56
77: 2-picoline	721	± 117.1	83.88 ± 13.62
78: 1,2-dibromoethane	48.2	± 4.31	72.74 ± 6.51
79: chlorobenzene	45.5	± 0.167	78.57 ± 0.29
80: 1,1,1,2-tetrachloroethane	49.5	± 4.22	76.35 ± 6.51

Compound	ng/mL	Error	Pred.Recovery±Deviation
81: ethylbenzene	42.4	± 0.169	80.79 ± 0.32
82: n-nitroso-methyl-ethylamin	3475	± 770.0	68.47 ± 15.17
83: m,p-xylenes	45.1	± 0.163	80.61 ± 0.29
84: styrene	45.0	± 3.73	77.81 ± 6.45
85: o-xylene	47.1	± 0.173	78.43 ± 0.29
86: isopropylbenzene	43.7	± 0.176	79.06 ± 0.32
87: bromoform	60.5	± 5.28	73.65 ± 6.43
88: cis-1,4-dichloro-2-butene	188	± 17.82	72.00 ± 6.82
89: n-nitrosodiethylamine	3806	± 782.3	73.96 ± 15.20
90: 1,1,2,2-tetrachloroethane	35.2	± 3.12	72.56 ± 6.45
91: 1,2,3-trichloropropane	42.5	± 10.72	65.89 ± 16.61
92: propylbenzene	43.4	± 10.00	72.98 ± 16.82
93: trans-1,4-dichloro-2-buten	193	± 48.99	65.44 ± 16.59
94: 1,3,5-trimethylbenzene	40.3	± 8.92	77.29 ± 17.11
95: bromobenzene	46.2	± 11.54	69.86 ± 17.44
96: 2-chlorotoluene	43.5	± 10.02	73.92 ± 17.03
97: 4-chlorotoluene	44.7	± 10.10	74.58 ± 16.84
98: pentachloroethane	47.2	± 11.42	70.72 ± 17.09
99: tert-butylbenzene	42.2	± 9.10	78.29 ± 16.90
100: 1,2,4-trimethylbenzene	40.3	± 8.71	78.37 ± 16.91
101: sec-butylbenzene	42.0	± 8.83	79.14 ± 16.66
102: aniline	3074	± 769.7	94.15 ± 23.58
103: p-isopropyltoluene	39.4	± 7.82	84.97 ± 16.84
104: 1,3-dichlorobenzene	37.6	± 7.92	79.07 ± 16.64
105: 1,4-dichlorobenzene	36.4	± 7.62	79.17 ± 16.56
106: n-butylbenzene	38.3	± 7.59	83.99 ± 16.64
107: 1,2-dichlorobenzene	32.3	± 7.05	81.49 ± 17.79
108: n-nitrosodi-n-propylamine	2931	± 512.7	86.81 ± 15.19
109: acetophenone	80.4	± 16.22	85.70 ± 17.29
110: o-toluidine	4033	± 955.2	103.53 ± 24.52
111: 1,2-dibromo-3-chloropropan	46.2	± 9.57	83.47 ± 17.29
112: hexachlorobutadiene	42.3	± 0.158	106.39 ± 0.40
113: nitrobenzene	117	± 22.93	89.70 ± 17.51
114: 1,2,4-trichlorobenzene	43.2	± 3.59	104.37 ± 8.68
115: naphthalene	45.7	± 3.89	104.62 ± 8.90
116: 1,2,3-trichlorobenzene	46.6	± 3.97	104.47 ± 8.90
117: 2-methylnaphthalene	103	± 9.77	105.97 ± 10.10
118: 1-methylnaphthalene	102	± 9.70	105.97 ± 10.10

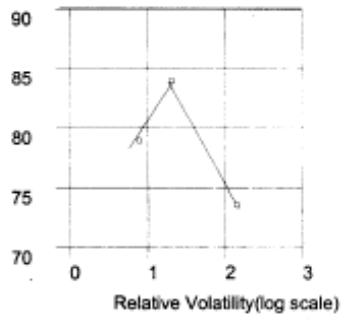
FIGURE 3

INTERNAL STANDARD REPORT EXAMPLE

Process Date: 11/24/2004 8:57:19 AM Surrogate Report - Page: 1
Compound Library File: C:\SMCREPORTER\CAL_EXAMPLE\ALL.TXT
Surrogate Groupings File: C:\SMCREPORTER\CAL_EXAMPLE\SURR_6RELVOL.INI
Data File: C:\SMCREPORTER\CAL_EXAMPLE\STANDARDA.TXT
Calibration File: C:\SMCREPORTER\CAL_EXAMPLE\EXAMPLE.CAL

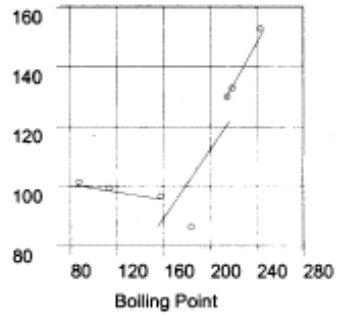
First Pass relative Volatility (Log) vs. Recovery
(Used to Estimate Rel vol effects on BP Surrogates)

Compound	BP	RVW	Meas.,Recovery(%)		Slope	Int.	Err%
hexafluorobenzene	81.5	0.86	78.66	, 78.66	3.566e-02	0.7919	0.00
Fluorobenzene	85	3.5	83.66	, 83.66			
Fluorobenzene	85	3.5	83.66	, 83.66	-5.938e-02	0.9110	0.00
1,2-dichloroethane-d4	84	20	73.31	, 73.31			



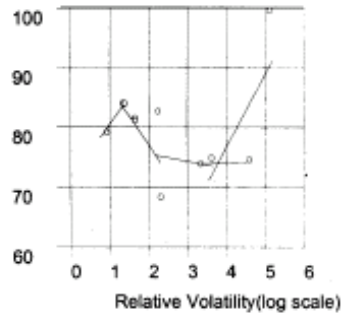
Recovery vs. Boiling Point - (First Pass Rel Vol Corrections) -- Boiling point range(85.00 - 229.00)

Compound	BP	RVW	Meas.,Recovery(%)		Slope	Int.	Err%
pentafluorobenzene	85	1.51	80.91	, 100.30	-6.534e-04	1.0573	0.25
toluene-d8	111	4.28	81.04	, 98.28			
bromobenzene-d5	155	7.93	75.40	, 95.68			
bromobenzene-d5	155	7.93	75.40	, 95.68	6.030e-03	-7.004e-02	20.48
1,2-dichlorobenzene-d4	181	8.03	67.28	, 85.45			
1,2,4-trichlorobenzene-d3	213	7.88	101.65	, 128.93			
1,2,4-trichlorobenzene-d3	213	7.88	101.65	, 128.93	8.125e-03	-4.431e-01	0.27
naphthalene-d8	217	18	97.45	, 131.80			
1-methylnaphthalene-d10	241	20*	111.09	, 151.53			



Recovery(bp corrected) vs. Relative Volatility (Ln) -- Relative Volatility range(0.86 - 14999.00)

Compound	BP	RVW	Meas.,Recovery(%)		Slope	Int.	Err%
hexafluorobenzene	81.5	0.86	78.66	, 78.66	3.322e-02	0.7917	0.25
Fluorobenzene	85	3.5	83.66	, 83.51			
1,4-difluorobenzene	88.5	3.83	83.41	, 83.46			
1,4-difluorobenzene	88.5	3.83	83.41	, 83.46	-5.528e-02	0.9088	0.21
o-xylene-d10	143	6.14	78.08	, 81.01			
chlorobenzene-d5	131	6.27	78.31	, 80.59			
o-xylene-d10	143	6.14	78.08	, 81.01	-4.368e-02	0.8925	6.70
chlorobenzene-d5	131	6.27	78.31	, 80.59			
1,2-dibromoethane-d4	131	26	79.84	, 82.17			
diethylether-d10	35	32.5	67.87	, 67.87			
1,2-dibromoethane-d4	131	26	79.84	, 82.17	-5.782e-03	0.7719	7.12
diethylether-d10	35	32.5	67.87	, 67.87			
tetrahydrofuran-d8	66	355	73.37	, 73.37			
acetone-C13	57	600	74.36	, 74.36			
tetrahydrofuran-d8	66	355	73.37	, 73.37	1.443e-03	0.7293	0.66
acetone-C13	57	600	74.36	, 74.36			
1,4-dioxane-d8	101	5800	73.44	, 74.09			
acetone-C13	57	600	74.36	, 74.36	6.230e-02	0.3123	14.00
1,4-dioxane-d8	101	5800	73.44	, 74.09			
pyridine-d5	115	15000	97.21	, 98.97			



* The relative volatility is outside the range of first pass surrogates. Value displayed is default.

FIGURE 4

CHECK SURROGATE REPORT EXAMPLE

Process Date:	11/24/2004 8:57:19 AM	Page: 2
Compound Library File:	C:\SMCREPORTER\CAL_EXAMPLE\ALL.TXT	
Surrogate Groupings File:	C:\SMCREPORTER\CAL_EXAMPLE\SURR_6RELVOL.INI	
Data File:	C:\SMCREPORTER\CAL_EXAMPLE\STANDARDA.TXT	
Calibration File:	C:\SMCREPORTER\CAL_EXAMPLE\EXAMPLE.CAL	

Check Surrogate Determinations

Volatile Compound Surrogates(boiling point<159)

Compound	Linear	Ln	Recovery	B.P.Predict	err	R.V.Predict	err	Total Predict	err	Recovery	err
methylenechloride-d2	40	11.10	75.9	100.0	0.0	78.7	6.7	78.7	6.7	96.4	8.2
benzene-d6	79	3.92	80.0	100.0	0.0	83.3	0.2	83.3	0.2	96.0	0.2
1,2-dichloropropane-d6	95	11.00	80.5	99.5	0.2	78.8	6.7	78.4	6.7	102.7	8.7
1,1,2-trichloroethane-d3	112	26.60	80.5	96.4	0.2	74.9	6.7	73.7	6.6	109.1	9.8
4-bromofluorobenzene	152	5.97	78.7	95.8	0.2	81.0	0.2	77.6	0.3	101.4	0.4
Group Averages										101.1	5.5

Non-Purgeable Volatile Compound Surrogates(rw> 100)

Compound	Linear	Ln	Recovery	B.P.Predict	err	R.V.Predict	err	Total Predict	err	Recovery	err
nitromethane-C13	101	510.00	80.2	99.1	0.2	73.8	0.7	73.2	0.7	109.6	1.0
ethylacetate-c13	77	150.00	75.0	100.0	0.0	74.3	7.1	74.3	7.1	100.9	9.7
pyridine-d5	115	15000.00	97.2	98.2	0.2	91.1	14.0	89.5	13.8	108.6	16.7
Group Averages										106.4	9.1

Semi-Volatile Compound Surrogates(boiling point>=159)

Compound	Linear	Ln	Recovery	B.P.Predict	err	R.V.Predict	err	Total Predict	err	Recovery	err
aniline-13C6	210	87.50	74.2	119.6	20.5	74.6	7.1	89.3	17.5	83.1	16.3
decafluorobiphenyl	206	3.03	97.2	117.2	20.5	82.9	0.3	97.1	17.0	100.1	17.5
nitrobenzene-d5	210	87.50	111.8	119.6	20.5	74.6	7.1	89.3	17.5	125.3	24.6
acetophenone-d5	202	161.00	70.9	114.8	20.5	74.3	7.1	85.2	17.3	83.1	16.8
naphthalene-d8	217	18.00	97.5	132.0	0.3	76.6	6.7	101.2	8.8	96.3	8.4
Group Averages										97.6	16.7