METHOD 8260D
VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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Disclaimer

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 methods used for the analysis of method-defined parameters, are intended to be guidance methods that contain general information on how to perform an analytical procedure or technique. A laboratory can use this guidance 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 referenced in this method are for guidance purposes only, and are not intended to be and must not be used as absolute quality control (QC) acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

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

Analytes and Appropriate Preparation Techniques

Compound	CAS No.[b]	5030	5035	5031	5032	5021	5041	Direct Inject
Acetone	67-64-1	*	*	✓	✓	-	✓	✓
Acetonitrile	75-05-8	*	*	✓	-	-	-	✓
Acrolein (Propenal)	107-02-8	*	*	✓	-	-	-	✓
Acrylonitrile	107-13-1	*	*	✓	*	-	✓	✓
Allyl alcohol	107-18-6	*	-	✓	-	-	-	✓
Allyl chloride	107-05-1	✓	*	-	-	-	-	✓
t-Amyl ethyl ether (TAEE, 4,4-Dimethyl-3-oxahexane)	919-94-8	*	*	-	-	✓*	-	✓
t-Amyl methyl ether (TAME)	994-05-8	*	*	-	-	✓*	-	✓
Benzene	71-43-2	✓	✓	-	✓	✓	✓	✓
Benzyl chloride	100-44-7	*	✓	-	-	-	-	✓
Bromoacetone	598-31-2	*	-	-	-	-	-	✓
Bromobenzene	108-86-1	✓	✓	-	✓	-	-	-
Bromochloromethane	74-97-5	✓	✓	-	✓	✓	✓	✓
Bromodichloromethane	75-27-4	✓	✓	-	✓	✓	✓	✓
Bromoform	75-25-2	*	*	-	✓	✓	✓	✓
Bromomethane	74-83-9	*	*	-	✓	✓	✓	✓
n-Butanol (1-Butanol, *n*-Butyl alcohol)	71-36-3	*	*	✓	-	✓	-	✓
2-Butanone (MEK)	78-93-3	*	*	✓	✓	-	-	✓
t-Butyl alcohol	75-65-0	*	*	✓	-	✓*	-	✓
n-Butylbenzene	104-51-8	✓	✓	-	✓	-	-	-
sec-Butylbenzene	135-98-8	✓	✓	-	✓	-	-	-
tert-Butylbenzene	98-06-6	✓	✓	-	✓	-	-	-
Carbon disulfide	75-15-0	*	*	-	✓	✓	✓	✓
Carbon tetrachloride	56-23-5	✓	✓	-	✓	✓	✓	✓
Chloral hydrate	302-17-0	*	-	-	-	-	-	✓
Chlorobenzene	108-90-7	✓	✓	-	✓	✓	✓	✓
1-Chlorobutane	109-69-3	✓	✓	-	✓	-	-	-
Chlorodibromomethane (Dibromochloromethane)	124-48-1	✓	✓	-	✓	-	✓	✓
Chloroethane	75-00-3	✓	✓	-	✓	✓	✓	✓
2-Chloroethanol	107-07-3	*	-	-	-	-	-	✓
2-Chloroethyl vinyl ether	110-75-8	*	*	-	-	-	-	✓
Chloroform	67-66-3	✓	✓	-	✓	✓	✓	✓

Compound	CAS No.[b]	5030	5035	5031	5032	5021	5041	Direct Inject
1-Chlorohexane	544-10-5	✓	✓	-	-	-	-	-
Chloromethane	74-87-3	*	*	-	✓	✓	✓	✓
Chloroprene (2-Chloro-1,3-butadiene)	126-99-8	✓	-	-	-	-	-	✓
2-Chlorotoluene	95-49-8	✓	✓	-	✓	-	-	-
4-Chlorotoluene	106-43-4	✓	✓	-	✓	-	-	-
Crotonaldehyde	4170-30-3	*	-	*	-	-	-	✓
Cyclohexane	110-82-7	✓	✓	-	✓	-	-	-
1,2-Dibromo-3-chloropropane (DBCP)	96-12-8	*	*	-	✓	✓	-	✓
1,2-Dibromoethane (EDB, Ethylene dibromide)	106-93-4	✓	✓	-	✓	✓	-	✓
Dibromomethane	74-95-3	✓	✓	-	✓	✓	✓	✓
1,2-Dichlorobenzene	95-50-1	✓	✓	-	✓	✓	-	✓
1,3-Dichlorobenzene	541-73-1	✓	✓	-	✓	✓	-	✓
1,4-Dichlorobenzene	106-46-7	✓	✓	-	✓	✓	-	✓
cis-1,4-Dichloro-2-butene	1476-11-5	*	✓	-	✓	-	-	✓
trans-1,4-Dichloro-2-butene	110-57-6	*	✓	-	✓	-	-	✓
Dichlorodifluoromethane	75-71-8	*	*	-	*	✓	-	✓
1,1-Dichloroethane	75-34-3	✓	✓	-	✓	✓	✓	✓
1,2-Dichloroethane	107-06-2	✓	✓	-	✓	✓	✓	✓
1,1-Dichloroethene (Vinylidene chloride)	75-35-4	✓	✓	-	✓	✓	✓	✓
cis-1,2-Dichloroethene	156-59-2	✓	✓	-	✓	✓	-	-
trans-1,2-Dichloroethene	156-60-5	✓	✓	-	✓	✓	✓	✓
1,3-Dichloropropane	142-28-9	✓	✓	-	✓	-	-	-
1,2-Dichloropropane	78-87-5	✓	✓	-	✓	✓	✓	✓
2,2-Dichloropropane	594-20-7	✓	✓	-	✓	-	-	-
1,3-Dichloro-2-propanol	96-23-1	*	-	-	-	-	-	✓
1,1-Dichloropropene	563-58-6	✓	✓	-	✓	-	-	-
cis-1,3-Dichloropropene	10061-01-5	✓	✓	-	✓	-	✓	✓
trans-1,3-Dichloropropene	10061-02-6	✓	✓	-	✓	-	✓	✓
1,2,3,4-Diepoxybutane	1464-53-5	✓	-	-	-	-	-	✓
Diethyl ether	60-29-7	*	*	-	*	-	-	✓
Diisopropyl ether (DIPE)	108-20-3	*	✓	-	-	✓*	-	✓
1,4-Dioxane	123-91-1	*	*	✓	*	-	-	✓
Epichlorohydrin	106-89-8	*	*	-	-	-	-	✓
Ethanol	64-17-5	*	*	✓	*	✓*	-	✓
Ethyl acetate	141-78-6	*	*	✓	✓	-	-	✓
Ethyl benzene	100-41-4	✓	✓	-	✓	✓	✓	✓
Ethyl methacrylate	97-63-2	✓	✓	-	✓	-	-	✓
Ethyl *t*-butyl ether (ETBE)	637-92-3	✓*	✓*	-	-	✓*	-	✓
Ethylene oxide	75-21-8	*	-	✓	-	-	-	✓
Hexachlorobutadiene	87-68-3	*	✓	-	-	✓	-	✓
Hexachloroethane	67-72-1	*	*	-	✓	-	-	✓

Compound	CAS No.[b]	5030	5035	5031	5032	5021	5041	Direct Inject
2-Hexanone	591-78-6	*	*	-	✓	-	-	✓
Iodomethane (Methyl iodide)	74-88-4	✓	✓	-	✓	-	✓	✓
Isobutyl alcohol	78-83-1	*	*	✓	-	✓	-	✓
Isopropylbenzene	98-82-8	✓	✓	-	✓	✓	-	✓
p-Isopropyltoluene	99-87-6	✓	✓	-	✓	-	-	-
Malononitrile	109-77-3	*	-	-	-	-	-	✓
Methacrylonitrile	126-98-7	*	✓	✓	-	-	-	✓
Methanol	67-56-1	*	-	✓	-	-	-	✓
Methyl acetate	79-20-9	✓	✓	-	✓	-	-	-
Methyl acrylate	96-33-3	*	*	-	✓	-	-	-
Methyl methacrylate	80-62-6	✓	*	-	-	-	-	✓
Methyl tert-butyl ether (MTBE)	1634-04-4	✓*	✓*	-	✓	✓*	-	✓
Methylcyclohexane	108-87-2	✓	✓	-	✓	-	-	-
Methylene chloride (DCM)	75-09-2	✓	✓	-	✓	✓	✓	✓
4-Methyl-2-pentanone (MIBK)	108-10-1	*	*	✓	✓	-	-	✓
Naphthalene	91-20-3	*	*	-	✓	✓	-	✓
Nitrobenzene (NB)	98-95-3	✓	✓	-	-	-	-	✓
2-Nitropropane	79-46-9	✓	✓	-	-	-	-	✓
N-Nitroso-di-*n*-butylamine (*N*-Nitrosodibutylamine)	924-16-3	*	-	✓	-	-	-	✓
Paraldehyde	123-63-7	*	-	✓	-	-	-	✓
Pentachloroethane	76-01-7	*	*	-	*	-	-	✓
Pentafluorobenzene	363-72-4	✓	✓	-	✓	-	-	-
2-Pentanone	107-87-9	*	✓	✓	-	-	-	✓
2-Picoline (2-Methylpyridine)	109-06-8	*	*	✓	-	-	-	✓
1-Propanol (*n*-Propyl alcohol)	71-23-8	*	*	✓	-	-	-	✓
2-Propanol (Isopropyl alcohol)	67-63-0	*	*	✓	-	✓	-	✓
Propargyl alcohol	107-19-7	*	-	-	-	-	-	✓
β-Propiolactone	57-57-8	*	-	-	-	-	-	✓
Propionitrile (Ethyl cyanide)	107-12-0	✓	✓	✓	-	-	-	-
n-Propylamine	107-10-8	✓*	-	-	-	-	-	✓
n-Propylbenzene	103-65-1	✓	✓	-	✓	-	-	-
Pyridine	110-86-1	*	*	✓	*	-	-	✓
Styrene	100-42-5	*	*	-	✓	✓*	✓	✓
1,1,1,2-Tetrachloroethane	630-20-6	✓	✓	-	✓	✓	✓	✓
1,1,2,2-Tetrachloroethane	79-34-5	✓*	✓*	-	✓	✓*	✓	✓
Tetrachloroethene	127-18-4	✓*	✓	-	✓	✓*	✓	✓
Toluene	108-88-3	✓	✓	-	✓	✓	✓	✓
o-Toluidine	95-53-4	*	-	✓	-	-	-	✓
1,2,3-Trichlorobenzene	87-61-6	*	*	-	✓	✓	-	✓
1,2,4-Trichlorobenzene	120-82-1	*	*	-	✓	✓	-	✓
1,1,1-Trichloroethane	71-55-6	✓	✓	-	✓	✓	✓	✓
1,1,2-Trichloroethane	79-00-5	✓	✓	-	✓	✓	✓	✓
Trichloroethene (Trichloroethylene)	79-01-6	✓*	✓	-	✓	✓*	✓	✓

Compound	CAS No.[b]	5030	5035	5031	5032	5021	5041	Direct Inject
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	✓	✓	-	✓	-	-	-
1,1,1-Trichlorotrifluoroethane	354-58-5	✓	✓	-	✓	-	-	-
Trichlorofluoromethane	75-69-4	*	*	-	✓	✓	✓	✓
1,2,3-Trichloropropane	96-18-4	✓	✓	-	✓	✓	✓	✓
1,2,3-Trimethylbenzene	526-73-8	-	-	-	-	✓	-	-
1,2,4-Trimethylbenzene	95-63-6	✓	✓	-	✓	✓	-	-
1,3,5-Trimethylbenzene	108-67-8	✓	✓	-	✓	✓	-	-
Vinyl acetate	108-05-4	*	*	-	-	-	-	✓
Vinyl chloride	75-01-4	*	*	-	✓	✓	✓	✓
m-Xylene	108-38-3	✓	✓	-	✓	✓	✓	✓
o-Xylene	95-47-6	✓	✓	-	✓	✓	✓	✓
p-Xylene	106-42-3	✓	✓	-	✓	✓	✓	✓

[a] See Sec. 1.2 for other appropriate sample preparation techniques.
[b] Chemical Abstract Service Registry Number

KEY TO ANALYTE LIST

✓ Historically, adequate recovery and precision can be obtained for this analyte by this technique. However, actual recoveries may vary depending on the sample matrix, preparation technique, and analytical instrumentation. Data from a large multi-laboratory study for 5030 and 5035 is available in Table 2. Compounds with this flag had a relative standard deviation (RSD) ≤15% in a multi-laboratory study.

- Not determined

* This analyte exhibits known difficulties with reproducibility, response, recovery, stability, and/or chromatography that may reduce the overall quality or confidence in the result when using this preparation method combined with analysis by Method 8260 (e.g., multi-laboratory study data with a RSD > 15%). This analyte may require special treatment (see Sec. 1.3) to improve performance to a level that would meet the needs of the project and, where necessary, may also require the use of appropriate data qualifiers if the relevant performance criteria cannot be met.

✓* This analyte meets the criteria for adequate performance using this technique (see definition for ✓); however, it is known to exhibit problems listed in Sec. 1.3 (see definition for *).

1.2 The compounds listed above may be introduced into the gas chromatograph/mass spectrometer (GC/MS) system by various techniques. The techniques listed in the table above have performance data available. Purge-and-trap, by Methods 5030 (aqueous samples) and 5035 (solid and waste oil samples), is the most commonly used technique for VOCs. However, other techniques are also appropriate and may yield better performance for some analytes.

These include: direct injection after dilution with hexadecane (Method 3585) for waste oil samples; automated static headspace by Method 5021 for solid and aqueous samples; direct injection of an aqueous sample (concentration permitting) or injection of a sample concentrated by azeotropic distillation (Method 5031); and vacuum distillation (Method 5032) for aqueous, solid, oil and tissue samples. For air samples, Method 5041 provides methodology for desorbing VOCs from trapping media (Methods 0010, 0030, and 0031). In addition, direct

analysis utilizing a sample loop is used for sub-sampling from polytetrafluoroethylene (PTFE) bags (Method 0040), also referred to as Tedlar® bags. Method 5000 provides more general information on the selection of the appropriate introduction method.

1.3 Special considerations for compounds noted with * in the table in Sec. 1.1.

1.3.1 Recovery of bases from water will be affected by pH. Compounds such as pyridine, o-toluidine, n-propylamine and 2-picoline will have poor to no recovery from low pH water. 2-Chloroethyl vinyl ether is subject to hydrolysis at low pH.

1.3.2 Dehydrohalogenation may result in degradation of aqueous solutions of pentachloroethane and to a lesser extent, other halogenated compounds (e.g., dichlorobutenes and 1,1,2,2-tetrachloroethane) to other target analytes (especially tetrachloroethene and trichloroethene) if the pH is >4 (see Reference 6 in Sec. 16 for further information on this topic). The use of hydrogen carrier gas may also cause the dehydrohalogenation of these analytes.

1.3.3 Alcohols, ketones, ethers and other water-soluble compounds will have low responses. Elevated sample temperatures may be necessary during purges as heated samples will exhibit better performance of these analytes. However, ethers such as diethyl ether and MTBE hydrolyze more readily when heated in acid-preserved water. Acid preservation is not recommended for analysis of these target analytes at elevated sample temperature. Higher concentrations for calibration standards may also be appropriate. Methanol is used as a solvent for standards in this analysis. Therefore, special conditions and alternate standards will be required for analyses where it is a target analyte.

1.3.4 Aldehydes (e.g., acrolein, paraldehyde, crotonaldehyde) are included in the target list but have poor stability under the analytical conditions used in this method. Other methods may be more appropriate for these compounds.

1.3.5 Heavier target compounds (e.g., naphthalene, 1,2-dibromo-3-chloropropane and hexachlorobutadiene) will have lower overall response and greater variability with conditions and concentrations.

1.3.6 Compounds that are gases at room temperature (e.g., chlorofluorocarbons, chloromethane and vinyl chloride) are prone to loss through vial seals and in handling. In addition, compounds co-eluting with water and methanol will have their responses suppressed.

1.3.7 Vinyl chloride and styrene are subject to loss due to chemical reactivity. Preservation by acidification does not prevent this.

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 QC procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the SW-846 manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, 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 the Environmental Protection Agency (EPA or the Agency) 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 (DQOs) for the intended application.

1.5 This method is restricted to use by, or under supervision of, personnel appropriately experienced and trained in the use of GC/MS 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 VOCs are introduced into the GC by one of the preparation methods mentioned in Sec. 1.2. The analytes may be introduced directly to a capillary column, cryofocused on a capillary pre-column before being flash evaporated to a capillary column for analysis, or desorbed from a trap and sent to an injection port operating in the split mode for injection to a capillary column. The column is temperature-programmed to separate the analytes, which are then detected with a MS interfaced to the GC.

2.2 Analytes eluted from the capillary column are introduced into the MS via a direct connection or flow splitter. Some wide-bore capillary columns may require splitting the flow prior to the MS interface, whereas narrow-bore capillary columns may be directly interfaced to the ion source or used with a restrictor column at the MS interface. Identification of target analytes is accomplished by comparing their mass spectra and retention times (RTs) with the mass spectra and RTs of known standards for the target compounds. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard (IS) using an appropriate calibration curve for the intended application.

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

3.0 DEFINITIONS

Refer to Chapter One and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 In order to avoid compromising data quality, contamination of the analytical system by volatile materials from the laboratory must be reduced to the lowest practical level. Refer to each preparation method for specific guidance on QC procedures and to Chapter Four for general guidance on the cleaning of glassware. Refer to Method 8000 for a discussion of interferences.

4.2 Volatile preparation and analysis should be physically separated from laboratory areas where target solvents are used. Air supply for the volatiles area should provide positive pressure relative to other laboratory areas. The water supply used for blanks should be isolated from target solvents and free of plastic supply piping.

4.3 Cross contamination may occur when a sample containing low concentrations of VOCs is analyzed immediately after a sample containing high concentrations of VOCs. After

analysis of a sample containing high concentrations of VOCs, analysis of one or more blanks may be used to demonstrate that carryover is not a significant portion of the target response in subsequent samples.

4.4 For samples that may contain large amounts of surfactants, suspended solids, high boiling compounds, high concentrations of target analytes or other non-target interferences, screening samples with another technique prior to purge-and-trap GC/MS analysis is prudent to prevent system contamination.

4.5 Control of contaminants is assessed by analysis of blanks. Transport (trip), calibration and reagent blanks provide information about the presence of contaminants at different points in the analytical process. Where measured analyte concentrations are suspected of being biased high or having false positive results due to contamination, affected data should be qualified, and the data user should otherwise be informed of any suspected data quality issues. Subtracting blank values from sample results is not permitted.

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 Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals listed in this method. A reference file of safety data sheets (SDSs) must be available to all personnel involved in these analyses. If hydrogen is used as a carrier gas, see Appendix B.

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.

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

6.1.1 Purge-and-trap device for aqueous samples as described in Method 5030

6.1.2 Purge-and-trap device for solid samples as described in Method 5035

6.1.3 Automated static headspace device for solid and aqueous samples as described in Method 5021

6.1.4 Azeotropic distillation apparatus for aqueous and solid samples as described in Method 5031

6.1.5 Vacuum distillation apparatus for aqueous, solid and tissue samples as described in Method 5032

6.1.6 Desorption device for air trapping media for air samples as described in Method 5041

6.1.7 Air sampling loop for sampling from Tedlar® bags for air samples as described in Method 0040

6.2 GC/MS system

6.2.1 GC – An analytical system complete with a temperature-programmable GC suitable for splitless injection with an appropriate interface or direct split interface for sample introduction. The system includes all required accessories, including syringes, analytical columns, and gases. If hydrogen is used as a carrier gas, see Appendix B.

6.2.1.1 The GC should be equipped with flow controllers such that the column flow rate remains 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 sub-ambient oven controller may be necessary.

6.2.1.3 A capillary column can be directly coupled to the ion source of the MS or interfaced through a separator, depending on the size of the capillary and the requirements of the GC/MS system.

6.2.1.4 GC columns – The following columns have been found to provide good separation of VOCs:

- 30 m x 0.25 mm internal diameter (ID), 1.4-µm film thickness, DB-624 or VOCOL;
- 20 m x 0.18 mm ID, 1-µm film thickness, DB-VRX;
- 60 m x 0.32 mm ID, 1.5-µm or 1.8-µm film thickness, Rtx-Volatiles.

The following columns were used to generate performance data cited in the references:

- 30 m x 0.25 - 0.32 mm ID, 1-µm film thickness, DB-5, Rtx-5, SPB-5; and
- 75 m x 0.53 mm ID, 3-µm film thickness, DB-624, Rtx-502.2, or VOCOL.

6.2.2 MS

6.2.2.1 Capable of acquiring mass spectra from mass/charge (*m/z)* 35 to 270 at a rate fast enough to acquire at least five (but preferably 10 or more) mass spectra across each chromatographic peak of interest, using 70 volts (nominal) electron energy in the electron impact ionization mode. The MS must be capable of meeting the criteria as outlined in Sec. 11.3.1.

6.2.2.2 An ion trap MS 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/National Institute on Standards and Technology (NIST) library or equivalent. Because ion-molecule reactions with water and methanol in an ion trap MS may produce interferences that co-elute with chloromethane and chloroethane, the base peak for both of these analytes will be at *m/z* 49, which should also be used as the quantitation ion in this case. The MS must be capable of producing a mass spectrum which meets the criteria as outlined in Sec. 11.3.1.

6.2.2.3 A tandem MS (MS/MS) may be used if it has the necessary pumps, collision cell, collision gases, and high-vacuum system capable of performing transitions in product ion scan mode or the selected reaction monitoring mode (SRM) for the target analytes of interest. Recommendations for specific precursor and product ions in SRM are available for some target analytes from the manufacturers of the equipment. The system must be capable of documenting the performance of both MSs against manufacturer specifications for mass resolution, mass assignment, and sensitivity using the internal calibrant (e.g., perfluorotributylamine). It is recommended to check the performance of the system at least weekly or at a frequency appropriate to meet the needs of the project. At a minimum, the performance of the system must be checked just prior to the initial calibration (ICAL).

6.2.2.4 The use of a selected ion monitoring (SIM) or chemical ionization (CI) mass spectrometry are acceptable techniques for applications requiring quantitation limits below the normal range of electron impact mass spectrometry or to reduce interferences from the sample matrix.

6.2.3 GC/MS interface – One of the following examples may be used to interface the GC to the MS.

6.2.3.1 Direct coupling, by inserting the column into the MS through a heated transfer line, is generally used for capillary columns < 0.53 mm ID.

6.2.3.2 A jet separator, including an all-glass transfer line and glass enrichment device or split interface, is used with columns ≥ 0.53 mm ID.

6.2.3.3 Other interfaces may be used provided the performance specifications described in Sec. 11.3.1 are achieved.

6.2.4 Data system – A computer system that allows the continuous acquisition and storage of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the MS. 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. A recent version of the EPA/NIST mass spectral library, or equivalent, should also be available.

6.3 Microsyringes – 10, 25, 100, 250, 500, and 1000 µL gas-tight

6.4 Syringe valve – Two-way, with Luer ends (three each), if applicable to the purging device

6.5 Syringes – 5, 10, or 25 mL, gas-tight with shutoff valve

6.6 Balance – Analytical, capable of weighing 0.0001 g, and top-loading, capable of weighing 0.1 g

6.7 Glass VOA vials – 20, 40, 60 mL, with PTFE-lined screw-top or crimp-top caps (compatible with the autosampler if appropriate for the preparation technique)

6.8 Vials – for GC autosampler

6.9 Disposable pipets – Pasteur

6.10 Volumetric flasks, Class A – 5, 10, 50, 100 mL, with ground-glass stoppers

6.11 Spatula – Stainless steel

7.0 REAGENTS AND STANDARDS

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 (ACS), where such specifications are available at: http://pubs.acs.org/reagents/comminfo/techquestions.html. 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. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

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, demonstrated to be free from interferences for the compounds of interest at their lower limit of quantitation (LLOQ). Store this solvent apart from other solvents to avoid contamination.

7.4 Hexadecane – Reagent grade, or equivalent, demonstrated to be free from interferences for the compounds of interest at the levels of interest through the analysis of a solvent blank. The results of such a blank analysis must demonstrate that no interfering volatiles are present.

7.5 1:1 Volume/volume (v/v) hydrochloric acid (HCl/water) – Carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water.

7.6 Stock standard solutions – The solutions may be purchased as certified solutions or prepared from pure standard materials. Commercially prepared stock standards may be used at any concentration if they are certified by an accredited supplier or third party. Prepare stock standard solutions in methanol (or other appropriate solvent), using assayed liquids or gases, as appropriate.

7.7 Working standards – Using stock standard solutions, prepare working standards in methanol (or other appropriate solvent), containing the compounds of interest, either singly or mixed together. Working 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. Working standards for most compounds should be replaced after four weeks unless the integrity of the standard is suspected of being compromised prior to that time. Working 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.

7.8 Surrogate standards – Recommended general-use surrogates are toluene-d_8, 4-bromofluorobenzene (BFB), and 1,2-dichloroethane-d_4. Other compounds with physicochemical properties better resembling the analyte classes of interest may be used as surrogates (e.g., deuterated monitoring compounds in the EPA Contract Laboratory Program's (CLP) current statement of work, which can be found in Reference 14 in Sec. 16), provided they can be unambiguously identified and meet any applicable acceptance criteria described in Sec.

11 for ICAL and continuing calibration verification (CCV). A stock surrogate solution in methanol should be prepared, 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.

7.9 Internal standards (IS) – The recommended ISs are fluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. Other compounds may be used as ISs as long as they have RTs similar to their target compounds, they can be unambiguously identified and meet any applicable acceptance criteria described in Sec. 11. See Sec. 11.4.3 of Method 8000 for additional information. Prepare the ISs solution in methanol (or other appropriate solvent).

7.10 BFB tune verification standard – A standard solution of BFB in methanol (or other appropriate solvent) may be prepared for direct injection. If BFB is used as a surrogate, the surrogate solution may be used for this purpose.

7.11 Calibration standards – There are two types of calibration standards used for this method: standards made from the primary source (for ICAL and CCV) and standards made from a second source for initial calibration verification (ICV). When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

7.11.1 ICAL standards must be prepared at a minimum of five different concentrations from the working dilution of stock standards or from premixed certified solutions. Prepare these solutions in organic-free reagent water or in a solvent appropriate for the specific sample preparation method used. Include a minimum of five different concentrations in the calibration for average response factor (RF) or linear (first-order) calibration models or six different concentrations for a quadratic (second-order) model, with the low standard at or below the LLOQ (see Sec. 9.9 and Method 8000). At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the DQOs 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. ICAL standards should be mixed from fresh stock standards and dilution standards when generating an ICAL curve.

7.11.2 CCV standards should be prepared at a concentration near the mid-point of the ICAL from the same source as the ICAL.

7.11.3 Second source standards for ICV must be prepared using source materials from a second manufacturer or from a manufacturer's batch prepared independently from the batch used for calibration. Target analytes in the ICV are recommended to be prepared at concentrations near the mid-point of the calibration range. The standard should contain all calibrated target analytes that will be reported for the project, if readily available. See Secs. 9.3.2 and 11.3.6 for guidance and acceptance limits.

7.11.4 It is the intent of EPA that all target analytes for a particular analysis be included in the ICAL and CCV 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 standards.

7.12 Matrix spike and LCS standards – See Method 5000 for instructions on preparing the matrix spike standard. Matrix spikes and LCSs should be prepared with target analytes from the same source as the ICAL standards to restrict the influence of accuracy on the

determination of recovery throughout preparation and analysis. Add VOCs to matrix spikes and LCS standards that are representative of the compounds being investigated. It is recommended to include all reported target analytes in all LCS and matrix spiked samples. For some applications, a limited set of representative analytes is acceptable.

7.13 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that standards be stored with minimal headspace, protected from light, at ≤6 °C, or as recommended by the standard manufacturer using screw-cap or crimp-top amber containers equipped with PTFE liners. Returning standards to the refrigerator or freezer immediately after standard and sample preparation is completed will help maintain the integrity of the solutions and minimize loss of volatile target compounds. ISs and surrogates spiking solutions added by the instrument do not need to be refrigerated provided they are sealed to prevent loss.

7.14 Carrier gas – Helium or hydrogen may be used as a carrier gas. If hydrogen is used, analytical conditions may need to be adjusted for optimum performance and calibration, and all QC tests must be performed with hydrogen carrier gas. See Appendix B for guidance.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Sample collection, preservation and storage requirements may vary by EPA program and may be specified in a regulation or project planning document that requires compliance monitoring for a given contaminant. Where such requirements are specified in a regulation, follow those requirements. In the absence of specific regulatory requirements, use the following information as guidance in determining the sample collection, preservation and storage requirements.

8.1 See Chapter Four, "Organic Analytes", for storage condition and holding times.

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

8.3 Solid and waste samples should be collected in air-tight containers compatible with closed-system sample preparation and analysis techniques, if possible. Samples must be handled carefully to minimize loss of VOCs during sample collection, shipping, storage, preparation and analysis. Refer to Chapter 4 and to American Society for Testing and Materials (ASTM) D4547 (Reference 18) for more information.

8.4 Samples to be analyzed for VOCs 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.

8.5 Blanks should be used to monitor potential cross-contamination of samples due to improper handling or storage conditions. The specifics of this type of monitoring activity should be outlined in a laboratory SOP or project planning documents pertaining to volatiles sampling.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and 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 who will implement the project and assess the results. Each laboratory should maintain a formal QA program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and QC data should be maintained for reference or inspection.

9.2 Refer to Method 8000 for general QC procedures for organic determinative methods. Refer to Method 5000 for QC procedures to ensure the proper operation of the various sample preparation techniques. Any more specific QC procedures provided in this method will supersede those noted in Methods 8000 and 5000.

9.3 QC procedures necessary to evaluate GC system operation are found in Method 8000 and include evaluation of RT windows, calibration verification and chromatographic analysis of samples. In addition, discussions regarding the instrument QC categories, minimum frequency and criteria listed below can be found in the referenced sections of this method, and a summary is provided in Table 7. Quantitative sample analyses should not proceed for those analytes that do not meet the QC acceptance criteria. However, analyses may continue for those analytes that do not meet the criteria with an understanding that these results could be used for screening purposes and would be considered estimated values.

9.3.1 The GC/MS tune must be verified to meet acceptance criteria prior to ICAL. Acceptance criteria are primarily intended to verify mass assignments and mass resolution under the same conditions used for analysis. See Sec. 11.3.1 for further details.

9.3.2 There must be an ICAL of the GC/MS system as described in Sec. 11.3. Prior to analyzing samples, the ICAL must be verified using a second source ICV standard, if readily available (Refer to Sec. 11.3.6).

9.3.3 Calibration of the system must be verified periodically by analysis of a CCV standard. See Sec. 11.4 for the frequency and acceptance criteria.

9.4 Initial demonstration of proficiency (IDP) - Prior to implementation of a method, each laboratory must perform an IDP consisting of at least four replicate reference samples spiked into a clean matrix taken through the entire sample preparation and analysis. If an autosampler is used to make sample dilutions, the accuracy of the dilutions should be evaluated prior to sample analysis. Whenever a significant change to instrumentation or procedure occurs, the laboratory must demonstrate that acceptable precision and bias can still be obtained. Also, whenever new staff members are trained, each analyst must perform an IDP for the method or portion of the method for which the analyst is responsible. This demonstration should document that the new analyst is capable of successfully following the SOP established by the laboratory and meeting any applicable acceptance criteria specified therein. Refer to Sec. 9.3 of Method 8000 for more information on how to perform an IDP.

9.5 Blanks

9.5.1 Before processing any samples, the analyst must demonstrate through the analysis of a method blank (MB) or instrument blank that equipment and reagents are free from contaminants and interferences. If a peak is found in the blank that would prevent the identification or bias the measurement of an analyte, the analyst should determine the source and eliminate it, if possible. As a continuing check, each time a batch of samples is analyzed, and when there is a change in reagents, a MB must be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. MBs, trip blanks, and other field blanks must be carried through all stages of sample preparation and analysis. At least one MB must be analyzed on every instrument after calibration standard(s) and prior to the analysis of any samples. Blank(s) analyzed after a high concentration calibration standard can also be used to estimate the extent of decontamination needed to reduce the signal to an acceptable level (Sec. 9.5.2) after analyzing a sample at a similar concentration.

9.5.2 Blanks are generally considered to be acceptable if target analyte concentrations are less than one half the LLOQ or are less than project-specific requirements. Blanks may contain analyte concentrations greater than acceptance limits if the associated samples in the batch are unaffected (i.e., targets are not present in samples or sample concentrations/responses are >10X the blank). Other criteria may be used depending on the needs of the project.

9.5.3 If an analyte of interest is found in a sample in the batch near a concentration confirmed in the blank (refer to Sec. 9.5.2), the presence and/or concentration of that analyte should be considered suspect and may require qualification. Contaminants in the blank should meet most or all of the qualitative identifiers in Sec. 11.6 to be considered. Samples may require re-analysis if the blanks do not meet laboratory-established or project-specific criteria. Re-analysis is not necessary if the analyte concentration falls well below the action or regulatory limit or if the analyte is deemed not important for the project.

9.5.4 When new reagents or chemicals are received, the laboratory should monitor the blanks associated with samples for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation if the source shows no prior problems. However, if reagents are changed during a preparation batch, separate blanks must be prepared for each set of reagents.

9.5.5 The laboratory should not subtract the results of the MB from those of any associated samples. Such "blank subtraction" may lead to negative sample results. If the MB results do not meet project-specific acceptance criteria and reanalysis is not practical, then the data user should be provided with the sample results, the MB results, and a discussion of the corrective actions undertaken by the laboratory.

9.6 Sample QC for preparation and analysis – The laboratory must also have procedures for documenting the effect of the sample matrix on method performance (i.e., precision, bias, and method sensitivity). At a minimum, this must include the analysis of a MB, an LCS, and should include either a laboratory sample duplicate/matrix spike or matrix spike/matrix spike duplicate (where practical and sample volume is available for doing so) in each preparation batch, as well as monitoring the recovery of surrogates. These QC samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on the field samples.

9.6.1 A MB must be included with each analytical batch. MBs consist of an aliquot of clean (control) matrix similar to the sample and of a similar weight or volume. Other types of blanks (e.g., trip blanks, storage blanks, etc.) should be included when appropriate but are distinct from MBs.

9.6.2 An LCS must 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. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. When the results of the matrix spike analysis 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. The LCS for water sample matrices is typically prepared in organic-free reagent water similar to the CCV standard. The LCS for solid matrices is typically prepared in clean sand and organic-free reagent water, similar to the CCV standard. When an LCS is prepared in the same manner as a CCV, the same standard can be used as both the LCS and CCV. The CCV acceptance criteria may be used for evaluation in this situation. Consult Method 8000 for information on developing acceptance criteria for the LCS.

9.6.3 Documenting the effect of the matrix on target analyte measurements should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision of whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on knowledge of the samples, the project goals and should be addressed in the project planning documents. If samples are expected to contain reportable levels of target analytes, then laboratories may use one matrix spike and a duplicate analysis of a non-spiked field sample. If samples are not expected to contain reportable levels of target analytes, laboratories may use a matrix spike and matrix spike duplicate pair. Consult Method 8000 for information on developing acceptance criteria for the matrix spike/matrix spike duplicate pair. When spiking solid samples in an aqueous mixture, it is not practical to expect analyte behavior equivalent to an exposure that occurred in field conditions. Therefore, it is understood that matrix spikes are used to estimate the severity of matrix effects that can be observed within method constraints.

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

9.7 Surrogate recoveries – Surrogates must be added to every blank, field sample, laboratory QC, and field QC. The laboratory should evaluate surrogate recovery data from individual samples relative to the surrogate recovery acceptance criteria developed by the laboratory. See Method 8000 for information on evaluating surrogate data and developing and updating surrogate recovery acceptance criteria. Suggested surrogate recovery limits for field samples are 70 to 130% until laboratory or project-specific criteria can be developed. Limits will depend on the surrogates chosen, levels used, and instrument conditions. Procedures for evaluating the recoveries of multiple surrogates and associated corrective actions should be defined in the laboratory's SOP or in an approved project plan.

9.8 IS responses must be monitored to ensure sensitivity is maintained and to limit the potential for measurement bias of associated target analyte concentrations. IS responses in field samples are compared to responses of the same ISs in the ICAL standards or CCV standards, with suggested acceptance criteria provided in Sec. 11.5.6. When IS responses fall outside the acceptance range, further investigation is warranted, and results may require qualification for detects and non-detects.

9.9. Lower limit of quantitation (LLOQ) – The LLOQ is the lowest concentration at which the laboratory has demonstrated target analytes can be reliably measured and reported with a certain degree of confidence, which must be greater than or equal to the lowest point in the calibration curve. The laboratory shall establish the LLOQ at concentrations where both quantitative and qualitative criteria can consistently be met (see Sec. 11.6). The laboratory shall verify the LLOQ at least annually and whenever significant changes are made to the preparation and/or analytical procedure, to demonstrate quantitation capability at lower analyte concentration levels. The verification is performed by the preparation and/or analysis of an LCS (or matrix spike) at 0.5 - 2 times the established LLOQ. Additional LLOQ verification may be useful on a project-specific basis if a matrix is expected to contain significant interferences at the LLOQ. This verification may be accomplished with either clean control material (e.g., reagent water, solvent blank, Ottawa sand, diatomaceous earth, etc.) or a representative sample matrix, free of target compounds. Optimally, the LLOQ should be less than the desired decision level or regulatory action level based on the stated DQOs.

9.9.1 LLOQ verification

9.9.1.1 The verification of LLOQs using spiked clean control material represents a best-case scenario because it does not evaluate the potential matrix effects of real-world samples. For the application of LLOQs on a project-specific basis, with established DQOs, a representative matrix-specific LLOQ verification may provide a more reliable estimate of the lower quantitation limit capabilities.

9.9.1.2 The LLOQ verification is prepared by spiking a clean control material with the analyte(s) of interest at 0.5 - 2 times the LLOQ concentration level(s). Alternatively, a representative sample matrix free of targets may be spiked with the analytes of interest at 0.5 - 2 times the LLOQ concentration levels. This LLOQ check is carried through the same preparation and analytical procedures as environmental samples and other QC samples. LLOQ verification samples must be independent from the ICAL used to calculate the target analyte concentrations (i.e. not a recalculated calibration point). It is recommended to verify the LLOQ on every instrument where data is reported. However, at a minimum, the laboratory should rotate the verification among similar analytical instruments such that all are included within three years.

9.9.1.3 Recovery of target analytes in the LLOQ verification should be within established in-house limits or within other such project-specific acceptance limits to demonstrate acceptable method performance at the LLOQ. Until the laboratory has sufficient data to determine acceptance limits, the LCS criteria ±20% (i.e., lower limit minus 20% and upper limit plus 20%) may be used for the LLOQ acceptance criteria. This practice acknowledges the potential for greater uncertainty at the low end of the calibration curve. Practical, historically based LLOQ acceptance criteria should be determined once sufficient data points have been acquired.

9.9.2 Reporting concentrations below LLOQ – Concentrations that are below the established LLOQ may still be reported. However, these analytes must be qualified as estimated. The procedure for reporting analytes below the LLOQ should be documented in the laboratory's SOP or in a project-specific plan. Analytes below the LLOQ that are reported should meet most or all of the qualitative identification criteria in Sec. 11.6.

9.10 It is recommended that the laboratory adopt additional QA 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 Secs. 11.3 and 11.4 for information on calibration and standardization.

11.0 PROCEDURE

11.1 Various alternative methods are provided for sample introduction. All ISs, surrogates, and matrix spike compounds (when applicable) must be added to the samples before introduction into the GC/MS system. Consult the sample introduction method for the procedures by which to add such standards.

11.1.1 Direct injection – This includes: injection of an aqueous sample containing a very high concentration of analytes; injection of aqueous concentrates from Method 5031 (azeotropic distillation); and injection of a waste oil diluted with hexadecane (Method 3585). Direct injection of aqueous samples (non-concentrated) has very limited applications. Direct injection of aqueous samples is only used for the determination of volatiles at the toxicity characteristic (TC) regulatory limits or at mg/L or higher concentrations. Direct injection may also be used in conjunction with the test for ignitability in aqueous samples (along with Methods 1010 and 1020), to determine if alcohol is present at greater than 24%.

11.1.2 Purge and trap – This includes purge and trap for aqueous samples (Method 5030) and purge and trap for solid samples (Method 5035). Method 5035 also provides techniques for extraction of high concentration solid and oily waste samples by methanol (and other water-miscible solvents) with subsequent purge and trap from an aqueous matrix using Method 5030.

11.1.2.1 Traditionally, the purge and trap of aqueous samples is performed at ambient temperature, while purging of soil/solid samples is performed at 40 °C, to improve purging efficiency. Purging at a fixed temperature slightly above ambient (e.g., 35 °C) may improve reproducibility where ambient temperature is variable.

11.1.2.2 Aqueous and soil/solid samples may also be purged at higher temperatures as long as all calibration standards, field samples, and associated QC samples are purged at the same temperature, and the laboratory demonstrates acceptable method performance for the project. Purging of aqueous and soil/solid samples at elevated temperatures (i.e., 40 to 80 ^{o}C) may improve the purging performance of more highly water soluble compounds which have poor purging efficiencies at ambient temperatures.

11.1.3 Vacuum distillation – This technique may be used for the introduction of VOCs from aqueous, solid, or tissue samples (Method 5032) into the GC/MS system (see Method 8261).

11.1.4 Automated static headspace – This technique may be used for the introduction of VOCs from aqueous and solid samples (Method 5021) into the GC/MS system.

11.1.5 Cartridge desorption – This technique may be used for the introduction of VOCs from sorbent cartridges (Method 5041) used in the sampling of air. The sorbent cartridges are from the volatile organics sampling train (VOST) or sampling method for volatile organic compounds (SMVOC) (Method 0031).

11.2 Recommended chromatographic conditions are provided as examples based on analyses performed in EPA laboratories and studies used to generate performance data for this method. The actual conditions will depend on the compounds of interest, instrument, and manufacturer's guidelines for the column selected. The maximum temperature of operation should always be verified with the specific column manufacturer.

11.2.1 General conditions:

Injector temperature:	200 - 275 °C
Transfer line temperature:	200 - 300 °C

11.2.2 Direct split interface – The following are example conditions:

Carrier gas (He) flow rate:	1.3 mL/min
Column:	60 m x 0.25 mm ID, 1.4 µm DB-624
Initial temperature:	35 °C, hold for 3 min
Temperature program:	6 °C /min to 100 °C, 12 °C /min to 180 °C, 20 °C /min to 200 °C, hold for 7 minutes
Inlet temperature:	225 °C
Transfer line temperature:	230 °C
Split ratio:	30:1

11.2.3 Split injection:

Carrier gas (He) flow rate:	0.9 mL/min
Column:	20.0 m, 0.18 mm ID, 1.0 µm DB-VRX
Initial temperature:	30 °C, hold for 3 min
Temperature program:	10 °C /min to 100 °C, 20 °C /min to 240 °C; 1 minute hold
Inlet temperature:	250 °C
Transfer line temperature:	250 °C
Split ratio:	50:1

11.2.4 Split injection:

Carrier gas (He) flow rate:	0.7 mL/min
Column:	20 m x 0.18 mm x 1.0 µm DB-624
Initial temperature:	40 °C, hold for 4 min
Temperature program:	15 °C /min to 190 °C, Hold for 1.5 min at 250 °C
Split ratio:	35:1

11.2.5 Direct injection:

Carrier gas (He) flow rate:	4 mL/min
Column:	70 m x 0.53 mm DB-624
Initial temperature:	40 °C, hold for 3 min
Temperature program:	8 °C /min to 260 °C

11.2.6 Hydrogen carrier gas:

Flow rate:	1 mL/min
Column:	40 m x 0.18 mm x 1-µm film thickness Rtx-VMS
Initial temperature:	30 °C, hold for 4 min
Temperature program:	7 °C /min to 180 °C
Injector temperature:	200 °C
Transfer line temperature:	200 °C
Split ratio:	70:1

11.3 ICAL – Establish the GC/MS operating conditions, using the following as guidance:

Mass range:	*m/z* of 35 – 270
Acquisition rate:	To result in at least five mass spectra across the peak (but preferably ten or more)
Source temperature:	According to manufacturer's specifications
Ion trap only:	Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

11.3.1 The GC/MS system must produce mass spectra with sufficient mass accuracy, mass resolution, and signal to be used for quantitative analysis of specific *m/z* ratios of ions characteristic of the target analytes, surrogates, and ISs. Standardization of MS performance also simplifies comparison of mass spectra generated on different instruments, such as by searching unknown spectra against a commercially available mass spectral library. A common reference compound used to demonstrate MS performance for electron impact mass spectrometry is BFB. Table 3 provides BFB ion ratio evaluation criteria. These criteria are only appropriate for electron impact mass spectra acquired across the range of masses indicated in the table.

Acceptable system performance may also be demonstrated by meeting manufacturer specifications for mass resolution, mass accuracy, and sensitivity using the internal calibrant (e.g., Perfluorotributylamine, also known as PFTBA). Other reference compounds may also be appropriate for demonstrating acceptable MS performance depending on the system or conditions used for analysis (e.g., octafluoronaphthalene for negative ion CI). Regardless of how MS performance is evaluated, system calibration must not begin until performance criteria are met**,** and calibration standards and samples must be analyzed under the same conditions. If CI, SIM or tandem MS is used, the manufacturer's MS tuning criteria or one of the alternative procedures listed above may be substituted for the BFB tune requirement.

11.3.1.1 In the absence of other recommendations on how to acquire the mass spectrum of BFB, the following approach may be used:

Introduce BFB with the same technique to be used for analysis of calibration standards and samples. Scale the mass of BFB introduced to prevent high abundance masses from saturating the detector (e.g., ≤50 ng). Once the data is acquired, either select the mass spectrum at the peak apex for evaluation, or use an averaged mass spectrum (e.g., three highest abundance spectra, across entire BFB peak). Background subtraction is allowed and should only be used to eliminate column bleed or instrument background ions. No part of the BFB peak or any other discrete peak should be subtracted. The mass spectrum used for background subtraction may be either a single mass spectrum or an average mass spectrum across a short time range acquired within 20 seconds of the elution of BFB.

11.3.1.2 Compare BFB mass intensities to the criteria in Table 3. Alternatively, other documented ion ratio criteria may be used provided that method performance is not adversely affected. If hydrogen is used as a carrier gas, the Table 3 criterion for 96/95 *m/z* ratio of BFB will be difficult to achieve. A relative abundance of 5 to 15% for 96/95 *m/z* is acceptable due to interactions with the carrier gas and water vapor. The analyst is 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 ICAL, calibration verification, and sample analyses.

NOTE: All subsequent standards, field samples, and QC samples associated with this analysis must use identical MS instrument conditions with the exception of SIM analysis. BFB may be analyzed in full scan mode while standards, samples, and QC are analyzed in SIM.

NOTE: BFB tune checks are not appropriate for CI or tandem MS analysis using SRM. However, the laboratory must demonstrate, prior to the ICAL, that the MS system achieves mass accuracy and mass resolution criteria specified by the instrument manufacturer for the PFTBA internal calibrant or other appropriate chemical.

11.3.2 Set up the sample introduction system, and then prepare and analyze calibration standards as outlined in the preparation method of choice (see Sec. 11.1). ICAL standards must include at least five different standard concentrations for all target analytes (see Sec. 7.11.1 and Method 8000). Surrogates may be calibrated either at multiple concentrations in the ICAL or at a single concentration (i.e., constant amount added to each calibration standard, as with IS). The base peak *m/z* of each target analyte and IS is appropriate for use as the primary *m/z* for quantitation (see Table 1), but another prominent *m/z* in the mass spectrum may also be used for quantitation provided it is used consistently. If interferences are noted at the primary *m/z*, use an alternate *m/z*. Calibration range, chromatographic performance, and extent of any carryover will depend on the introduction technique, GC column and conditions, and the tolerance of the sample introduction system and GC/MS to solvent, water, and other introduced sample matrix components.

NOTE: LLOQs should be established at concentrations where both quantitative and qualitative verifications can be consistently and reliably met (see Secs. 9.9 and 11.6). Target analyte peaks in the calibration standard at the LLOQ should be visually inspected to ensure that peak signal is distinguishable from background and to verify qualitative analyte identification.

11.3.3 Additional considerations for SIM and SRM analysis

SIM and SRM may be useful for applications requiring quantitation limits below the normal range of electron impact quadrupole mass spectrometry, and both are allowable options for this method. Using the primary *m/z* for quantitation and at least one secondary *m/z* for confirmation, set up the collection groups based on their chromatographic retention times. The selected *m/z* values should include any mass defect noted in the target analyte mass spectra acquired on the instrument, usually less than 0.2 amu. The dwell time for each ion may be automatically calculated by the instrument software or may be calculated based on the peak widths of the analytes of interest, the number of spectra needed to be acquired across each peak, and the number of concurrent ions that need to be acquired in each segment. When fewer

masses are monitored in each segment, the acquisition time for each mass can be increased, thereby increasing the sensitivity of the system. The total cycle time for the MS should be short enough that at least five, but preferably ten or more, spectra are acquired per chromatographic peak.

When compounds are analyzed in SIM or SRM mode, the following best practices are recommended:

- Monitor at least two ions for each target analyte, and use the mid-point of the calibration curve to establish proper ion ratios for each compound. The ratios of primary and secondary ions are the only qualitative tool available in SIM and SRM runs (other than retention time) which increases their importance in proper identification. When interferences are expected or observed in a given matrix, acquiring multiple secondary ions may aid in qualitative identification.

- Verify that all monitored ions are correctly integrated in order to achieve proper ion ratios. Update the primary/secondary ion ratios and reference mass spectra after each ICAL using a mid-range ICAL standard.

11.3.4 Tabulate the response of the characteristic ions (see Table 1 for suggested ions) against the concentration for each target analyte and each IS. Calculate RFs for each target analyte relative to one of the ISs as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak response of the analyte or surrogate
A_{is} = Peak response of the IS
C_s = Concentration of the analyte or surrogate
C_{is}= Concentration of the IS

11.3.4.1 Calculate the mean RF and the relative standard deviation (RSD) of the RFs for each target analyte using the following equations.

$$\text{mean RF} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n} \qquad RSD = \frac{SD}{\overline{RF}} \times 100 \qquad SD = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RF})^2}{n-1}}$$

where:

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

11.3.4.2 The RSD should be ≤20% for each target analyte (see Sec. 11.3.5). Table 4 contains minimum RFs that may be used as guidance in determining whether the system is behaving properly and as a check to see if calibration standards are prepared correctly. Because the minimum RFs in Table 4 were determined using specific ions and instrument conditions that may vary, it is neither expected nor required that all analytes meet these minimum RFs. The information in this table is provided as guidance only. The laboratory

should establish procedures in its determinative SOP (e.g., laboratory established minimum RFs, signal to noise (S/N) checks, etc.) to ensure that the instrument is working properly and that calibration standards were correctly prepared.

NOTE: For a target analyte whose RF <0.01 (response of peak is <1/100 the response of the IS), it is recommended to increase its concentration in relation to other analytes to make the response more comparable.

11.3.5 Linearity of target analytes – If the RSD of any target analyte is ≤20%, then the RF is assumed to be constant over the calibration range, and the average RF may be used for quantitation (Sec. 11.7.2).

11.3.5.1 If the RSD of any target analyte RF is >20%, refer to Sec. 11.5 of Method 8000 for additional calibration options (e.g., narrowing the calibration range, changing calibration model, etc.), and apply one or more of these options in order to meet the ICAL acceptance criteria. Alternatively, the affected target analytes may be reported with an appropriate data qualifier, or the instrument may be recalibrated.

NOTE: When the RSD for the RF calibration model is >20%, plotting and visual inspection of a calibration curve can be a useful diagnostic tool. 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.

NOTE: Forcing the calibration model through the origin (for analytes that are consistently detected in the laboratory reagent blanks) allows for a better estimate of the background level of blank contaminants. An accurate estimate of background contamination is necessary to set method reporting limits for method analytes when blank levels are problematic.

11.3.5.2 If more than 10% of the compounds included with the ICAL exceed the 20% RSD limit and do not meet the coefficient of determination criterion (r^2≥0.99 or relative standard error (RSE) ≤20%) for alternate curve fits, then the chromatographic system is considered too imprecise for analysis to begin. Perform corrective actions as necessary (e.g., by adjusting moisture control parameters, replacing the analytical trap, column, or moisture trap, or adjusting desorb time), then repeat the calibration procedure beginning with Sec. 11.3. 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 LLOQ. Refer to Method 8000 for further discussion of RSE. Example RSE calculations can be found in Reference 16.

11.3.5.3 Due to the large number of compounds that may be analyzed by this method, it is likely that some compounds will not meet the acceptance criteria described above. For these occasions, it is acknowledged that those compounds that do not meet the criteria may not be critical to the specific project and therefore data generated may be used as qualified data or estimated values for screening purposes. The analyst should strive to place more emphasis on meeting the calibration criteria for those compounds that are critical to the project. The target analytes that do not meet the ICAL criteria should still be

identified to the data user and the resulting data qualified appropriately, but it is not necessary to meet criteria for compounds that will not be reported.

NOTE: It is considered inappropriate, once the calibration models have been finalized, to select an alternate fit solely to pass the recommended QC criteria for samples and associated QC on a case-by-case basis.

11.3.5.4 Calibration, especially when using linear regression models, has the potential for a significant bias at the lower portion of the calibration curve. The lowest calibration point should be recalculated (not reanalyzed) using the final calibration curve in which this standard is used (i.e., re-fitting the response from the low concentration calibration standard back into the curve). See Method 8000 for additional details. The recalculated concentration of the low calibration point, especially where linear regression fits are used, should be within ±50% of the standard's true concentration, and the recalculated concentrations of any calibration standards above the LLOQ should be within ±30%. Alternate criteria may be applied depending on the needs of the project. However, those criteria should be clearly defined in a laboratory SOP or a project-specific QAPP. Analytes which do not meet the re-fitting criteria should be evaluated for corrective action. If a failure occurs in the low point and it is equivalent to the LLOQ, the analyte should be reported as estimated near that concentration or the LLOQ should be reestablished at a higher concentration (See Method 8000 Sec. 11.5.4 for calculations).

11.3.6 ICV – Prior to analyzing samples, verify the ICAL using a standard obtained from a second source to the calibration standard, if possible, such as a second manufacturer or a manufacturer's batch prepared independently from the batch used for calibration, if readily available. This standard should be prepared in the same clean control matrix as that used for ICAL standards. Suggested acceptance criteria for the analyte concentrations in this standard are 70 - 130% of the expected analyte concentration(s). Alternative criteria may be appropriate based on project-specific DQOs. Quantitative sample analyses should not proceed for those analytes that do not meet the ICAL verification criteria. However, analyses may continue for those analytes that do not meet the criteria with an understanding that these results could be used for screening purposes and would be considered estimated values.

11.4 CCV – A CCV standard must be analyzed at the beginning of each twelve-hour analytical period prior to any sample analysis.

NOTE: Tune checks (Sec. 11.3.1) are only required prior to ICAL.

11.4.1 The ICAL function (Sec. 11.3) for each compound of interest must be verified once every twelve hours prior to sample analysis, using the same introduction technique and conditions as used for analysis of ICAL standards and samples. This is accomplished by analyzing a CCV standard (containing all the compounds that will be reported) prepared from the same stock solutions or source materials used for ICAL standards and at a concentration near the midpoint of the ICAL range. The results must be compared against the most recent calibration curve and should meet the CCV acceptance criteria provided in Secs. 11.4.3-11.4.5.

NOTE: This QC check may be omitted if samples are analyzed within twelve hours of ICAL, and injection of the last ICAL standard may be used as the starting time reference for evaluation.

11.4.2 A blank must also be analyzed after the CCV standard and prior to any samples in order to demonstrate that the total system (introduction device, transfer lines and GC/MS system) is free from contaminants. Analytes of interest for the project that did not meet the criteria should be identified to the data user and results qualified appropriately. If the blank indicates contamination, then it may be appropriate to analyze additional blanks to reduce any system contamination due to carryover from standards or samples. See Sec. 9.5 for MB performance criteria. See Method 8000 for information regarding MB performance criteria.

11.4.3 CCV standard criteria

11.4.3.1 The calculated concentration or amount of each analyte of interest in the CCV standard should fall within ±20% of the expected value.

NOTE: For the RF calibration model, % difference between the calculated RF of an analyte in the calibration verification standard and the RF_{avg} of that analyte from the ICAL is the same value as % drift for calculated vs. expected concentration. Refer to Method 8000 for guidance on calculating % difference and % drift.

11.4.3.2 If the % difference or % drift for a compound is ≤ 20%, then the ICAL for that compound is assumed to be valid. Due to the large number of compounds that may be analyzed by this method, it is likely that some compounds will not meet this criterion. If the criterion is not met (i.e., greater than 20% difference or drift) for more than 20% of the compounds included in the ICAL (or more than 20% of those that will be reported), then corrective action must be taken prior to analysis of samples. In these cases, the affected target analytes may still be reported as non-detects in field samples 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 measured in field samples, the reported concentrations must be qualified appropriately.

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

11.4.4 IS RT – If the absolute RT for any IS changes by more than 30 seconds from that in the mid-point standard level of the most recent ICAL 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.

11.4.5 IS responses – In order to demonstrate continued stability of the measurement system after ICAL, IS responses in the CCVs must be evaluated by comparing them to the responses of the same ISs in the ICAL standard(s). If the response of an IS changes by more than a factor of 2 (50 - 200%) relative to the response of that IS in the mid-point ICAL standard or the average of responses in the suite of ICAL standards (as defined in the laboratory's SOP), then corrective actions should be taken. These corrective actions may include but are not limited to replacing and/or reanalyzing the CCV standard, or retuning the MS and re-calibrating the instrument. When IS responses do not meet these criteria, system sensitivity may have

been compromised, and sample reanalysis is recommended, especially if any action limits for the project are near the LLOQ.

11.5 GC/MS analysis of samples

11.5.1 It is highly recommended that samples be screened to minimize contamination of the GC/MS system or sample introduction device from unexpectedly high concentrations of organic compounds. Some of the screening options available utilizing SW-846 methods are:

-Screening solid samples for VOCs (Method 3815), automated headspace,
-GC/flame ionization detector (FID) (Methods 5021/8015), automated headspace,
-GC/photo ionization detector (PID)/electrolytic conductivity detector (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 QC requirements in the methods above may be reduced as appropriate. Sample screening is particularly important when Method 8260 is used to achieve low quantitation levels.

11.5.2 Add appropriate volumes of the surrogates spiking solution and the IS spiking solution to each field sample and all associated QC samples either manually or by an autosampler to achieve the desired concentrations. The surrogates and ISs may be mixed and added as a single spiking solution.

11.5.3 Add an aliquot of the target compounds spiking solution (Sec. 7.12) to any sample aliquot(s) chosen for matrix spiking. Follow the same procedure in preparing the LCS, adding the spike to the same clean control material used for calibration standards preparation (e.g., reagent water, Ottawa sand, etc.). See Sec. 7.12 and Method 8000 for more guidance on the selection and preparation of the matrix spike and the LCS.

11.5.4 Introduce field samples and associated QC samples to the GC/MS under the same conditions used for analysis of ICAL standards. When screening results indicate high levels of target analytes and/or interferences, or if analyte concentrations are measured above the calibration range, prepare and analyze an appropriate dilution of the sample(s), or choose a preparation method that is more amenable to making dilutions (e.g., methanol extraction of solids instead of direct aqueous partitioning). Dilutions should be targeted so the response of the major constituents (previously saturated peaks) falls near the middle of the calibration range.

11.5.5 When the concentration of a compound in the sample is high enough to result in significant carryover to subsequent samples (Sec. 9.5), this analysis should be followed by at least one MB or instrument blank to demonstrate lack of carryover to the proceeding field sample. If analysis of one or more blanks is not sufficient to return the system to acceptable operating conditions, more extensive decontamination procedures may be required, and subsequent recalibration may be necessary. Alternatively, when analysis of a blank is not possible prior to the next sample, such as when an unattended autosampler is employed, the analyst should review the results for at least the next sample after the high-concentration sample. If analytes in the high-concentration sample are not present in the subsequent field sample, then the lack of carryover has been demonstrated.

11.5.6 IS responses and RTs should be monitored in all field samples and associated QC samples in order to provide sample-specific QA of proper analyte introduction to the GC/MS system and to anticipate the need for system inspection and/or maintenance. If the response of the primary *m/z* for any of the ISs in the field samples or associated QC samples varies by more than a factor of two (−50% to +100%) from that of the same IS in the mid-point ICAL standard, average of ICAL standards, or most recently analyzed CCV standard (as defined in the laboratory's SOP), corrective action should be taken. Any affected field samples and associated QC samples should be re-analyzed, or the associated data should be qualified.

11.6 Analyte identification

11.6.1 Qualitative identification of each compound determined by this method is based on RT and on comparison of the sample mass spectrum, after background correction, with a reference mass spectrum. Compounds are identified as present when the following criteria are met.

11.6.1.1 The intensities of the characteristic ions of a compound maximize in the same mass spectra or in adjacent mass spectra.

11.6.1.2 The RT is within ±10 seconds of the RT for this analyte in the midpoint ICAL standard or CCV standard analyzed at the beginning of the 12-hour period (delta RT 0.17 minute), or within ±10 seconds relative to the shift of the associated IS (delta RT of the IS ±10 seconds). Chromatograms should be carefully inspected to minimize the occurrence of both false positive and false negative results. If the RT for the IS has shifted, the sample should be inspected for similar shifts for the associated target analytes. If RT drift is significant, relative retention time (RRT) may be useful as an alternative to delta retention times. See Section 11.4 of Method 8000 for additional information.

NOTE: Some analytes may have RT shifting that is much greater than the associated IS (greater than ±10 seconds relative to the IS shift) and is still the target analyte. In those cases, it may be more useful to compare the delta RT with compounds that have similar chemistries to help identify the target. Also, dilutions or spiked samples are recommended to help determine the effects of matrix on the elution of the target and assist in target identification.

11.6.1.3 The relative intensities of the characteristic ions should agree within 30% of the intensities of these ions in the reference spectrum. For 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%. The reference mass spectrum used for this comparison must be generated by the laboratory using the conditions of this method (typically from a calibration standard). Qualitative identification of sample mass spectra not acquired in limited ion acquisition modes (i.e., SIM or SRM) may also be supported by comparison to a reference library as described in Sec. 11.6.2.

11.6.1.4 Unresolved structural isomers with similar mass spectra are identified as isomeric pairs. Isomers are considered resolved if the peaks are at least 50% resolved (i.e., the height of the valley between two isomer peaks is ≤ 50% of the average of the two peak heights, or 1−[valley height]/[average peak height] is ≥ 50%). The resolution should be verified on the mid-point concentration of the ICAL as well as the laboratory-designated CCV level if

closely eluting isomers are to be reported.

11.6.1.5 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.

11.6.1.6 Examination of EICPs of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes co-elute (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 co-eluting compound.

11.6.2 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 library search results may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications:

(1) Major ions in the library reference spectrum (ions greater than 10% of the most abundant ion) are present in the sample spectrum at similar relative intensities.

(2) The molecular ion in the library reference spectrum is present in the sample spectrum. If the molecular ion is not present, carefully review library matches in order to avoid misidentification.

(3) Major ions present in the sample spectrum but not in the reference spectrum are reviewed to determine whether they may be contributed by co-eluting compounds.

(4) Ions present in the reference spectrum but not in the sample mass spectra are reviewed for unintended subtraction. Data system library reduction programs can sometimes create these discrepancies.

(5) Mass spectral library search algorithms typically assign a match factor to the peak identity based on comparison of an unknown mass spectrum to library spectra. For spectra meeting the above conditions, match factors greater than 0.8 (80%) may be considered confirming evidence. Where a known limitation in data collection is identified (e.g., the presence of an incompletely resolved spectral interference), a lower match factor may be considered confirmatory. For multiple library spectra with similar match factors (e.g., for hydrocarbons with low abundance molecular ions, or structural isomers), the tentative identification assigned to the unknown may be better represented as a more generic structure (e.g., unknown hydrocarbon, C4 benzene structural isomer). See Reference 15 for more information.

11.7 Quantitation

11.7.1 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 IS used should be the one nearest the RT of that of a given analyte.

11.7.1.1 Where the integration produced by the software is acceptable, it is recommended to use it, because the software should produce more consistent integrations. Manual integrations are necessary when the software does not properly integrate peaks, such as when the baseline selection is improper; the correct peak is missed; a co-elution is integrated; the peak is partially integrated; etc. The analyst is responsible for ensuring that the integration is correct whether performed by the software or done manually.

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

11.7.2 If the RSD is 20% or less, then the RF calibration model is acceptable for the ICAL (Sec. 11.3.4). See Method 8000 for the equations describing IS calibration and either linear or non-linear calibrations.

11.7.3 Where applicable, the concentrations of any non-target analytes identified in the sample (Sec. 11.6.2) may be estimated using the RF calibration model formula, with the following modifications: The responses A_x and A_{is} as defined in Sec.11.3.4 should be from the total ion chromatograms, and the RF for the non-target analyte should be assumed to be 1. The resulting concentration should be clearly identified as an estimate. Use the nearest IS free of interferences.

11.7.4 Structural isomers that produce very similar mass spectra may be quantitated as individual isomers if they are sufficiently resolved. See Sec. 11.6.1.4.

11.7.5 Quantitation of multicomponent parameters such as gasoline-range organics (GROs) and total petroleum hydrocarbons (TPH) using the Method 8260-recommended IS quantitation technique is beyond the scope of this method. Typically, analyses for these parameters are performed using a GC/FID or GC with a MS detector capability that is available with Method 8015. However, it is acceptable to use the total ion chromatogram that is generated from this method with external standard calibration to quantitate such parameters. External standard calibration is recommended for these applications in order to reduce the need to subtract area contributed by multiple non-target peaks (such as the ISs) in the TPH chromatogram. See Sec. 11.4.2 in Method 8000 and Sec.11.3 in Method 8015 for additional guidance.

12.0 DATA ANALYSIS AND CALCULATIONS

See Sec. 11.7 for information on data analysis and calculations.

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 criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 This method has been tested using purge and trap (Method 5030) in a single laboratory using spiked water. Using a wide-bore capillary column, water was spiked at concentrations between 0.5 and 10 µg/L. Single laboratory accuracy and precision data for the method analytes are available at: http://www.epa.gov/hw-sw846/validated-test-method-8260d-volatile-organic-compounds-gas-chromatographymass-spectrometry.

13.3 Direct injection (Method 3585) has been used for the analysis of waste motor oil samples using a wide-bore column. Single laboratory precision and accuracy data are available at: http://www.epa.gov/hw-sw846/validated-test-method-8260d-volatile-organic-compounds-gas-chromatographymass-spectrometry for toxicity characteristic leaching procedure (TCLP) volatiles in oil. The performance data were developed by analyzing seven replicates each of new and used oil. The oils were spiked at the TCLP regulatory concentrations for most analytes, with the exceptions of the alcohols, ketones, ethyl acetate and chlorobenzene which are spiked at 5 ppm (well below the regulatory concentrations). Prior to spiking, the new oil (i.e., a Society of Automotive Engineers (SAE) 30-weight motor oil) was heated at 80 °C overnight to remove volatiles. The used oil (i.e., a mixture of used oil drained from passenger automobiles) was not heated and was contaminated with 20 - 300 ppm of benzene, toluene, ethylbenzene and xylene (BTEX) compounds and isobutanol. These contaminants contributed to high recoveries of the BTEX compounds in the used oil. Therefore, the data from the deuterated analogs of these analytes represent more typical recovery values.

13.4 Single laboratory accuracy and precision data were obtained for the Method 5035 analytes in three soil matrices: sand, a soil collected 10 feet below the surface of a hazardous waste landfill, and a surface garden soil. Sample preparation was by Method 5035. Each sample was fortified with the analytes at a concentration of 20 µg/kg. These data are available at: http://www.epa.gov/hw-sw846/validated-test-method-8260d-volatile-organic-compounds-gas-chromatographymass-spectrometry. All data were calculated using fluorobenzene, added to the soil sample prior to methanol extraction, as the IS. Some of the results were greater than 100% recovery, likely due to variance in IS response.

13.4.1 In general, the recoveries of the analytes from the sand matrix are the highest, the hazardous waste landfill soil results are somewhat less, and the surface garden soil recoveries are the lowest. This is due to the greater adsorptive capacity of the garden soil. This illustrates the necessity of analyzing matrix spike samples to assess the degree of matrix effects.

13.4.2 The recoveries of some of the gases, or very volatile compounds, such as vinyl chloride, trichlorofluoromethane, and 1,1-dichloroethene, were somewhat greater than 100%, likely due to the difficulty encountered in fortifying the soil with these compounds, allowing an equilibration period, then extracting them with a high degree of precision. The garden soil results (available at: http://www.epa.gov/hw-sw846/validated-test-method-8260d-volatile-organic-compounds-gas-chromatographymass-spectrometry) also include high recoveries for some aromatic compounds, including toluene, xylenes, and trimethylbenzenes. This is likely due to high levels of contamination of the soil prior to sample collection.

13.5 Performance data for non-purgeable volatiles using azeotropic distillation (Method 5031) are included in Reference 9.

13.6 Performance data for volatiles prepared using vacuum distillation (Method 5032) in soil, water, oil, and fish tissue matrices are included in Reference 11.

13.7 Single laboratory accuracy and precision data were obtained for the Method 5021 analytes in a garden soil matrix. Replicate samples were fortified with the analytes at a concentration of 20 µg/kg. These data are available at: http://www.epa.gov/hw-sw846/validated-test-method-8260d-volatile-organic-compounds-gas-chromatographymass-spectrometry. The recommended ISs were selected because they generated the best accuracy and precision data for the analytes in both types of soil.

13.7.1 Example LLOQs using Method 5021 are available at: http://www.epa.gov/hw-sw846/validated-test-method-8260d-volatile-organic-compounds-gas-chromatographymass-spectrometry and were calculated from results of seven replicate analyses of the sand matrix. Sand was chosen because it demonstrated the least degree of matrix effect of the soils studied. These LLOQs were calculated utilizing the procedure described in Chapter One and are intended to be a general indication of the capabilities of the method.

13.8 The LLOQ for samples taken by Method 0040 and analyzed by Method 8260 is estimated to be in the range of 0.03 to 0.9 parts-per-million (ppm). Data can be found at: http://www.epa.gov/hw-sw846/validated-test-method-8260d-volatile-organic-compounds-gas-chromatographymass-spectrometry. Matrix effects may cause the individual compound quantitation limits to be higher.

13.9 The recommended ISs with corresponding analytes assigned for quantitation that are appropriate for Method 5041 are available at: http://www.epa.gov/hw-sw846/validated-test-method-8260d-volatile-organic-compounds-gas-chromatographymass-spectrometry.

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: http://www.acs.org/content/dam/acsorg/about/governance/committees/chemicalsafety/publications/less-is-better.pdf.

15.0 WASTE MANAGEMENT

The EPA 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 at: http://www.labsafetyinstitute.org/FreeDocs/WasteMgmt.pdf.

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17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

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

Table 1

CHARACTERISTIC MASSES (*m/z*) FOR PURGEABLE ORGANIC COMPOUNDS

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Acetone	58	43
Acetonitrile	41	40, 39
Acrolein (Propenal)	56	55, 58
Acrylonitrile	53	52, 51
Allyl alcohol	57	58, 39
Allyl chloride	76	41, 39, 78
Benzene	78	-
Benzyl chloride	91	126, 65, 128
Bromoacetone	136	43, 138, 93, 95
Bromobenzene	156	77, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
iso-Butanol	74	43
n-Butanol (1-Butanol, *n*-Butyl alcohol)	56	41
2-Butanone	72	43
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91, 134
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chloral hydrate	82	44, 84, 86, 111
Chloroacetonitrile	48	75
Chlorobenzene	112	77, 114
1-Chlorobutane	56	49
Chlorodibromomethane	129	208, 206
Chloroethane	64 (49*)	66 (51*)
2-Chloroethanol	49	44, 43, 51, 80
Bis(2-chloroethyl) sulfide	109	111, 158, 160
2-Chloroethyl vinyl ether	63	65, 106
Chloroform	83	85
Chloromethane	50 (49*)	52 (51*)
Chloroprene	53	88, 90, 51
3-Chloropropionitrile	54	49, 89, 91
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane (DBCP)	75	155, 157
Dibromochloromethane	129	127
1,2-Dibromoethane (EDB, Ethylene dibromide)	107	109, 188

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Dibromomethane	93	95, 174
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	53, 77, 124, 89
trans-1,4-Dichloro-2-butene	53	88, 75
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene (Vinylidene chloride)	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
1,3-Dichloro-2-propanol	79	43, 81, 49
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
1,2,3,4-Diepoxybutane	55	57, 56
Diethyl ether	74	45, 59
1,4-Dioxane	88	58, 43, 57
Epichlorohydrin	57	49, 62, 51
Ethanol	31	45, 27, 46
Ethyl acetate	88	43, 45, 61
Ethyl benzene	91	106
Ethyl methacrylate	69	41, 99, 86, 114
Ethylene oxide	44	43, 42
Hexachlorobutadiene	225	223, 227
Hexachloroethane	201	166, 199, 203
2-Hexanone	43	58, 57, 100
2-Hydroxypropionitrile	44	43, 42, 53
Iodomethane (Methyl iodide)	142	127, 141
Isobutyl alcohol (2-Methyl-1-propanol)	43	41, 42, 74
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134, 91
Malononitrile	66	39, 65, 38
Methacrylonitrile	41	67, 39, 52, 66
Methyl acrylate	55	85
Methyl-*t*-butyl ether	73	57
Methyl iodide (Iodomethane)	142	127, 141
Methyl methacrylate	69	41, 100, 39
4-Methyl-2-pentanone	100	43, 58, 85
Methylene chloride	84	86, 49

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Naphthalene	128	-
Nitrobenzene (NB)	123	51, 77
2-Nitropropane	46	-
Pentachlororethane	167	130, 132, 165, 169
2-Picoline (2-Methylpyridine)	93	66, 92, 78
Propargyl alcohol	55	39, 38, 53
β-Propiolactone	42	43, 44
Propionitrile (Ethyl cyanide)	54	52, 55, 40
n-Propylamine	59	41, 39
n-Propylbenzene	91	120
Pyridine	79	52
Styrene	104	78
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichlororethene	95	97, 130, 132
Trichlorofluoromethane	101	103
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl acetate	43	86
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91

Table 1A

Internal Standards/Surrogates

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Benzene-d_5	84	83
Bromobenzene-d_5	82	162
Bromochloromethane-d_2	51	131
4-Bromofluorobenzene	95	174, 176
Chlorobenzene-d_5	117	-
Chloroform-d_1	84	-
Dibromofluoromethane	113	-
1,2-Dichlorobenzene-d_4	152	115, 150
1,4-Dichlorobenzene-d_4	152	115, 150
Dichloroethane-d_4	102	-
1,4-Difluorobenzene	114	-
Fluorobenzene	96	77
Pentafluorobenzene	168	-
Toluene-d_8	98	-
1,1,2-Trichloroethane-d_3	100	-

*Characteristic ion for an ion trap MS (to be used when ion-molecule reactions are observed).

Table 2

2012 DEPARTMENT OF DEFENSE LABORATORY CONTROL SAMPLE CONTROL LIMIT STUDY

Relative standard deviation of recoveries by analyte for compounds where the number of replicates, N was greater than 20 (average for all analytes: Recovery = 97%, 12% RSD).

Analyte Name	CAS #	Water RSD	Solid RSD
Acetaldehyde	75-07-0	66%	52%
Acetone	67-64-1	20%	21%
Acetonitrile	75-05-8	16%	15%
Acrolein [Propenal]	107-02-8	20%	18%
Acrylonitrile	107-13-1	12%	11%
Allyl chloride	107-05-1	11%	11%
tert-Amyl ethyl ether	919-94-8	10%	10%
tertiary-Amyl methyl ether (tame)	994-05-8	6%	10%
Benzene	71-43-2	7%	7%
Benzyl chloride	100-44-7	18%	10%
bis(2-Chloroisopropyl) ether	39638-32-9	12%	NA
Bromobenzene	108-86-1	7%	7%
Bromochloromethane	74-97-5	7%	8%
Bromodichloromethane	75-27-4	8%	8%
4-Bromofluorobenzene	460-00-4	5%	7%
Bromoform	75-25-2	11%	11%
Bromomethane	74-83-9	15%	15%
1,3-Butadiene	106-99-0	19%	10%
2-Butanone [MEK]	78-93-3	15%	16%
n-Butyl acetate	123-86-4	10%	12%
Butyl acrylate	141-32-2	72%	NA
n-Butyl alcohol	71-36-3	13%	14%
sec-Butyl alcohol	78-92-2	NA	17%
tert-Butyl alcohol	75-65-0	10%	11%
tert-Butyl formate	762-75-4	11%	NA
sec-Butylbenzene	135-98-8	8%	9%
tert-Butylbenzene	98-06-6	8%	9%
Carbon disulfide	75-15-0	12%	12%
Carbon tetrachloride	56-23-5	10%	11%
Chlorobenzene	108-90-7	6%	7%
2-Chloro-1,3-butadiene	126-99-8	12%	11%
Chlorobutane	109-69-3	NA	8%
Chlorodibromomethane	124-48-1	9%	9%
Chlorodifluoromethane	75-45-6	18%	19%
Chloroethane	75-00-3	13%	13%
2-Chloroethyl vinyl ether	110-75-8	16%	18%
Chloroform	67-66-3	7%	8%

Analyte Name	CAS #	Water RSD	Solid RSD
1-Chlorohexane	544-10-5	8%	10%
Chloromethane	74-87-3	16%	15%
1-Chloropropane	540-54-5	10%	8%
2-Chloropropane	75-29-6	12%	9%
2-Chlorotoluene	95-49-8	7%	8%
4-Chlorotoluene	106-43-4	7%	9%
2-Chloro-1,1,1-trifluoroethane	75-88-7	8%	7%
Chlorotrifluoroethene	79-38-9	22%	24%
Cyclohexane	110-82-7	10%	11%
Cyclohexanone	108-94-1	42%	22%
1,2-Dibromo-3-chloropropane	96-12-8	12%	12%
1,2-Dibromoethane (EDB, Ethylene dibromide)	106-93-4	7%	7%
Dibromofluoromethane	1868-53-7	7%	7%
Dibromomethane	74-95-3	7%	8%
1,2-Dichlorobenzene	95-50-1	7%	7%
1,3-Dichlorobenzene	541-73-1	7%	8%
1,4-Dichlorobenzene	106-46-7	7%	8%
cis-1,4-Dichloro-2-butene	1476-11-5	15%	12%
trans-1,4-Dichloro-2-butene	110-57-6	18%	13%
Dichlorodifluoromethane [Freon-12]	75-71-8	22%	23%
1,1-Dichloroethane	75-34-3	8%	8%
1,2-Dichloroethane	107-06-2	9%	9%
1,1-Dichloroethene (Vinylidene chloride)	75-35-4	10%	10%
1,2-Dichloroethene	540-59-0	7%	7%
cis-1,2-Dichloroethene	156-59-2	8%	8%
trans-1,2-Dichloroethene	156-60-5	8%	9%
Dichlorofluoromethane	75-43-4	10%	18%
1,2-Dichloropropane	78-87-5	7%	8%
1,3-Dichloropropane	142-28-9	7%	7%
2,2-Dichloropropane	594-20-7	13%	11%
1,1-Dichloropropene	563-58-6	8%	8%
1,3-Dichloropropene	542-75-6	8%	8%
cis-1,3-Dichloropropene	10061-01-5	8%	9%
trans-1,3-Dichloropropene	10061-02-6	9%	10%
1,2-Dichloro-1,1,2,2-tetrafluoroethane	76-14-2	16%	20%
1,2-Dichlorotrifluoroethane [Freon 123a]	354-23-4	11%	12%
Diethyl ether	60-29-7	10%	10%
Diethylbenzene (total)	25340-17-4	6%	6%
1,2-Diethylbenzene	135-01-3	6%	5%
1,3-Diethylbenzene	141-93-5	6%	6%
1,4-Diethylbenzene	105-05-5	6%	6%
Diisopropyl ether	108-20-3	11%	10%
Dimethyl ether	115-10-6	11%	NA

Analyte Name	CAS #	Water RSD	Solid RSD
3,3-Dimethyl-1-butanol	624-95-3	15%	14%
Dimethyldisulfide	624-92-0	15%	9%
1,4-Dioxane	123-91-1	14%	14%
Epichlorohydrin	106-89-8	13%	14%
Ethanol	64-17-5	17%	19%
Ethyl acetate	141-78-6	14%	15%
Ethyl acrylate	140-88-5	38%	49%
Ethyl methacrylate	97-63-2	9%	10%
Ethyl tert-butyl ether	637-92-3	10%	9%
Ethylbenzene	100-41-4	7%	8%
2-Ethyl-1-hexanol	104-76-7	21%	25%
4-Ethyltoluene	622-96-8	14%	13%
Fluorobenzene	462-06-6	6%	6%
Furan	110-00-9	16%	NA
Heptane	142-82-5	16%	16%
Hexachlorobutadiene	87-68-3	11%	13%
Hexachloroethane	67-72-1	10%	10%
Hexane	110-54-3	17%	17%
2-Hexanone	591-78-6	14%	16%
Iodomethane (Methyl iodide)	74-88-4	10%	10%
Isoamyl alcohol	123-51-3	14%	14%
Isobutyl alcohol	78-83-1	12%	13%
Isoprene	78-79-5	9%	18%
Isopropyl acetate [Acetic acid]	108-21-4	12%	13%
Isopropylbenzene	98-82-8	10%	11%
p-Isopropyltoluene [p-Cymene]	99-87-6	8%	9%
Methacrylonitrile	126-98-7	12%	11%
Methyl acetate	79-20-9	14%	15%
Methyl acrylate	96-33-3	12%	11%
Methyl methacrylate	80-62-6	10%	12%
Methyl sulfide	75-18-3	13%	12%
Methyl tert-butyl ether [MTBE]	1634-04-4	9%	9%
Methylcyclohexane	108-87-2	10%	11%
Methylene chloride	75-09-2	8%	10%
2-Methylnaphthalene	91-57-6	26%	27%
4-Methyl-2-pentanol	108-11-2	15%	NA
4-Methyl-2-pentanone [MIBK]	108-10-1	11%	12%
Methylstyrene	25013-15-4	8%	8%
Naphthalene	91-20-3	12%	12%
2-Nitropropane	79-46-9	16%	17%
Pentachloroethane	76-01-7	11%	11%
Pentane	109-66-0	26%	25%
2-Pentanone	107-87-9	15%	NA

Analyte Name	CAS #	Water RSD	Solid RSD
2-Propanol [Isopropyl alcohol]	67-63-0	15%	13%
Propionitrile [Ethyl cyanide]	107-12-0	12%	11%
n-Propyl acetate	109-60-4	8%	16%
n-Propylbenzene	103-65-1	8%	9%
Styrene	100-42-5	8%	8%
1,1,1,2-Tetrachloroethane	630-20-6	8%	8%
1,1,2,2-Tetrachloroethane	79-34-5	9%	9%
Tetrachloroethene	127-18-4	9%	9%
Tetrahydrofuran	109-99-9	13%	13%
1,2,4,5-Tetramethylbenzene	95-93-2	11%	11%
Toluene	108-88-3	7%	7%
1,2,3-Trichlorobenzene	87-61-6	10%	11%
1,2,4-Trichlorobenzene	120-82-1	10%	11%
1,3,5-Trichlorobenzene	108-70-3	9%	10%
2,3,4-Trichlorobutene	2431-50-7	4%	NA
1,1,1-Trichloroethane	71-55-6	9%	9%
1,1,2-Trichloroethane	79-00-5	7%	7%
Trichloroethene (Trichloroethylene)	79-01-6	7%	8%
Trichlorofluoromethane [Freon-11]	75-69-4	12%	13%
1,2,3-Trichloropropane	96-18-4	8%	9%
1,1,1-Trichlorotrifluoroethane	354-58-5	9%	7%
Trifluorotoluene	98-08-8	6%	9%
1,1,2-Trifluoro-1,2,2-trichloroethane [Freon-113]	76-13-1	11%	12%
1,2,3-Trimethylbenzene	526-73-8	6%	6%
1,2,4-Trimethylbenzene	95-63-6	8%	8%
1,3,5-Trimethylbenzene	108-67-8	8%	9%
2,2,4-Trimethylpentane [Isooctane]	540-84-1	13%	14%
Vinyl acetate	108-05-4	15%	17%
Vinyl bromide	593-60-2	13%	7%
Vinyl chloride	75-01-4	14%	14%
Xylenes [total]	1330-20-7	7%	8%
m/p-Xylene [3/4-Xylene]	179601-23-1	7%	8%
o-Xylene	95-47-6	7%	8%

Table 3

4-BROMOFLUOROBENZENE (BFB) SUGGESTED CRITERIA*

m/z	Intensity (relative abundance)
95	50-200% of mass 174
96	5 to 9% of *m/z* 95 (5 to 15% when using H_2 carrier)
173	<2% of *m/z* 174
174	50-200% of mass 95
175	5 to 9% of *m/z* 174
176	95 to 105% of *m/z* 174
177	5 to 10% of *m/z* 176

* Criteria based on EPA Method 524.4 (Reference 17), with modified *m/z* 95 and *m/z* 174 abundance criteria

Table 4

GUIDANCE RESPONSE FACTORS CRITERIA FROM EPA CONTRACT LABORATORY PROGRAM

Analyte	RF
Acetone	0.01
Benzene	0.2
Bromochloromethane	0.1
Bromodichloromethane	0.3
Bromoform	0.1
Bromomethane	0.01
2-Butanone	0.01
Carbon disulfide	0.1
Carbon tetrachloride	0.1
Chlorobenzene	0.4
Chloroethane	0.01
Chloroform	0.3
Chloromethane	0.01
Cyclohexane	0.01
Dibromochloromethane	0.2
1,2-Dibromo-3-chloropropane	0.01
1,2-Dibromoethane (EDB, Ethylene dibromide)	0.2
1,2-Dichlorobenzene	0.6
1,3-Dichlorobenzene	0.5
1,4-Dichlorobenzene	0.6
Dichlorodifluoromethane	0.01
1,1-Dichloroethane	0.3
1,2-Dichloroethane	0.07
1,1-Dichloroethene (Vinylidene chloride)	0.06
cis-1,2-Dichloroethene	0.2
trans-1,2-Dichloroethene	0.1
1,2-Dichloropropane	0.2
cis-1,3-Dichloropropene	0.3
trans-1,3-Dichloropropene	0.3
Ethylbenzene	0.4
2-Hexanone	0.01
Isopropylbenzene	0.4
Methyl acetate	0.01
4-Methyl-2-pentanone	0.03
Methyl tert-butyl ether (MTBE)	0.1
Methylcyclohexane	0.05
Methylene chloride	0.01
Styrene	0.2
1,1,2,2-Tetrachloroethane	0.2
Tetrachloroethene	0.1

Analyte	RF
Toluene	0.3
1,2,3-Trichlorobenzene	0.4
1,2,4-Trichlorobenzene	0.4
1,1,1-Trichloroethane	0.05
1,1,2-Trichloroethane	0.2
1,1,2-Trichloro-1,2,2-trifluoroethane	0.05
Trichloroethene (Trichloroethylene)	0.2
Trichlorofluoromethane	0.01
Vinyl chloride	0.01
m,p-Xylene	0.2
o-Xylene	0.2

These response factors are provided as guidance only and are not intended to be a requirement. See Appendix B for additional information.

Table 5

RECOMMENDED QUANTITY OF EXTRACT FOR ANALYSIS OF HIGH CONCENTRATION SAMPLES

Approximate Concentration Range (µg/kg)	Volume of Extract[a]
500 - 10,000	100 µL
1,000 - 20,000	50 µL
5,000 - 100,000	10 µL
25,000 - 500,000	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of solvent added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of solvent is necessary to maintain a volume of 100 µL added to the syringe.

[b] Dilute an aliquot of the solvent extract and then take 100 µL for analysis.

Table 6

VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

FLUOROBENZENE	CHLOROBENZENE-d_5	1,4-DICHLOROBENZENE-d_4
Acetone	Benzene	p-Bromofluorobenzene
Acrylonitrile	Bromodichloromethane	(surrogate)
Bromochloromethane	Carbon tetrachloride	Bromoform
Bromomethane	Chlorobenzene	*n*-Butylbenzene
2-Butanone	Cyclohexane	*sec*-Butylbenzene
Carbon disulfide	Dibromochloromethane	*t*-Butylbenzene
Chloroethane	1,2-Dibromoethane (EDB, Ethylene dibromide)	1,2-Dibromo-3-chloropropane
Chloroform	1,2-Dichloropropane	1,2-Dichlorobenzene
Chloromethane	*cis*-1,3-Dichloropropene	1,3-Dichlorobenzene
Dichlorodifluoromethane	*trans*-1,3-Dichloropropene	1,4-Dichlorobenzene
1,1-Dichloroethane	Ethylbenzene	1,2-Dichlorobenzene-d_4 (surrogate)
1,2-Dichloroethane	2-Hexanone	Hexachlorobutadiene
1,2-Dichloroethane-d_4 (surrogate)	Methyl cyclohexane	Isopropylbenzene
1,1-Dichloroethene (Vinylidene chloride)	4-Methyl-2-pentanone	Isopropyltoluene
cis-1,2-Dichloroethene	Styrene	Naphthalene
trans-1,2-Dichloroethene	1,1,1,2-Tetrachloroethane	*n*-Propylbenzene
1,4-Difluorobenzene (surrogate)	1,1,2,2-Tetrachloroethane	1,2,3-Trichloropropane
Freon 113	Tetrachloroethene	1,2,4-Trimethylbenzene
Methyl acetate	1,1,1-Trichloroethane	1,3,5-Trimethylbenzene
Methylene chloride	1,1,2-Trichloroethane	1,2,3-Trichlorobenzene
Methyl-*t*-butyl ether (MTBE)	Trichloroethene (Trichloroethylene)	1,2,4-Trichlorobenzene
Trichlorofluoromethane	Toluene	
Vinyl chloride	Toluene-d_8 (surrogate)	
	m- + *p*-Xylene	
	o-Xylene	

Please note that this list is not exhaustive of all compounds found in the table in Sec 1.1 and are suggested IS associations only.

Table 7

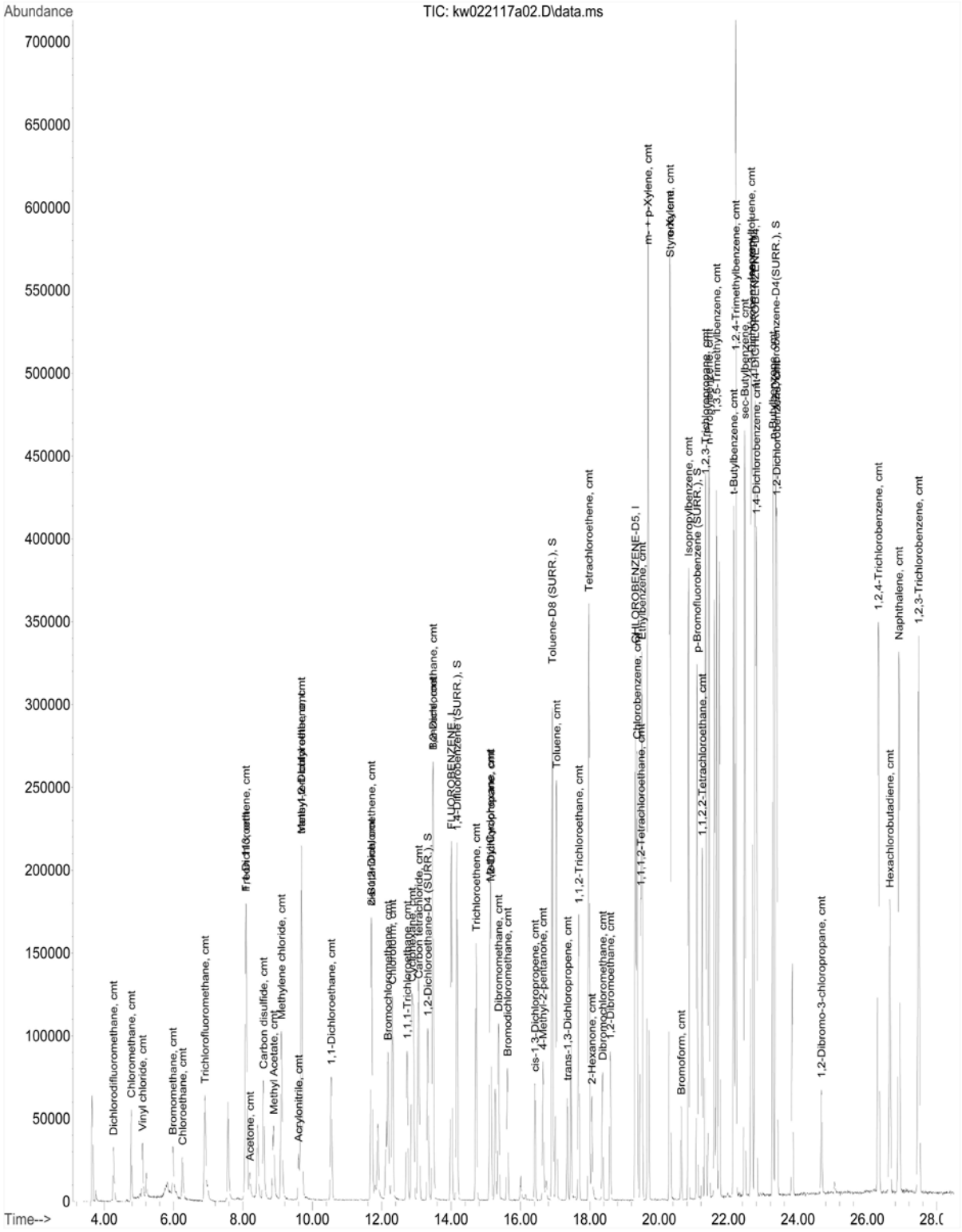
SUMMARY OF QC CRITERIA FOR USE WITH 8260D

Quality Control Type	Minimum frequency	Specification	Suggested Acceptance Criteria
Instrument performance check (Secs. 9.3.1, 11.3.1)	Prior to initial calibration	Must be verified prior to initial calibration	Meet ion ratio criteria for reference compound: 4-Bromofluorobenzene (Table 3), or alternative documented criteria
Initial Calibration (ICAL) (Secs. 9.3.2, 11.3.2-11.3.5)	Prior to analyzing samples, and as needed if continuing performance criteria cannot be met	5 points minimum for RF and linear regressions, 6 points minimum for quadratic regressions; >90% of reported target analytes meet initial calibration criteria	For average response factor (RF) calibration model: ≤20% RSD of RFs; For linear or quadratic regression model: R≥0.995, R^2≥0.99; Independent of calibration model: Lower standard (LLOQ) recalculation (refit) is within ±50% of true value; Other standards > LLOQ are within ±30% of true value; Or, relative standard error (RSE) ≤20% (Refer to Method 8000 and Reference 16 for calculation) See Method 8000 for additional criteria.
ICAL Verification (ICV) (Secs. 9.3.2, 11.3.6)	After each initial calibration, and prior to analyzing samples	Prepared from different source of target analytes than initial calibration standards	Calculated concentrations of target analytes are within ±30% of expected value
Continuing Calibration Verification (CCV) (Secs. 9.3.3, 11.4)	Once every 12 hours	>80% of target analytes meet continuing calibration verification criteria	Target analytes and surrogates are ≤20% difference or drift; internal standard responses are within 50% to 200% of mid-point of ICAL or average of ICAL internal standards; and retention times for internal standards have not shifted > 30 seconds relative to ICAL
Blanks (Secs. 9.5, 9.6.1)	One method blank per preparation batch of 20 or fewer samples; instrument blanks as needed	NA	Target analyte concentrations in blanks are < 1/2 LLOQ, or ≤ 10% of concentration in field samples
Laboratory Control Standard (LCS) (Sec 9.6.2)	One per preparation batch of 20 or fewer samples	NA	Meets recovery criteria (CCV criteria may be used if LCS and CCV are identical)

Quality Control Type	Minimum frequency	Specification	Suggested Acceptance Criteria
Duplicates and Matrix Spikes (Secs. 9.6.3)	A duplicate and matrix spike, or matrix spike/matrix spike duplicate per preparation of 20 or fewer samples (not required per batch)	NA	Meets performance-based or project-defined recovery criteria and for relative % difference between sample and laboratory duplicate or matrix spike/matrix spike duplicate;
Surrogates (Secs. 9.7)	Added to each sample	NA	Meets performance-based recovery criteria established by the laboratory or criteria chosen for the project
Internal Standards (Secs. 9.8, 11.5.6)	Added to each sample	NA	Internal standard response is within 50-200% of the response of the same internal standard in the midpoint ICAL standard (or average of ICAL) or most recent CCV
Qualitative Analyte Identification (Sec. 11.6.1)	Each target analyte	NA	RT in sample is within ±10 sec of RT in midpoint ICAL or CCV standard Characteristic ion(s) are within ±30% of expected ion ratio in reference spectrum; or, match to reference library spectra ≥0.8 (only for full mass range acquisition modes)

Figure 1

EXAMPLE GAS CHROMATOGRAM OF VOLATILE ORGANICS [a]

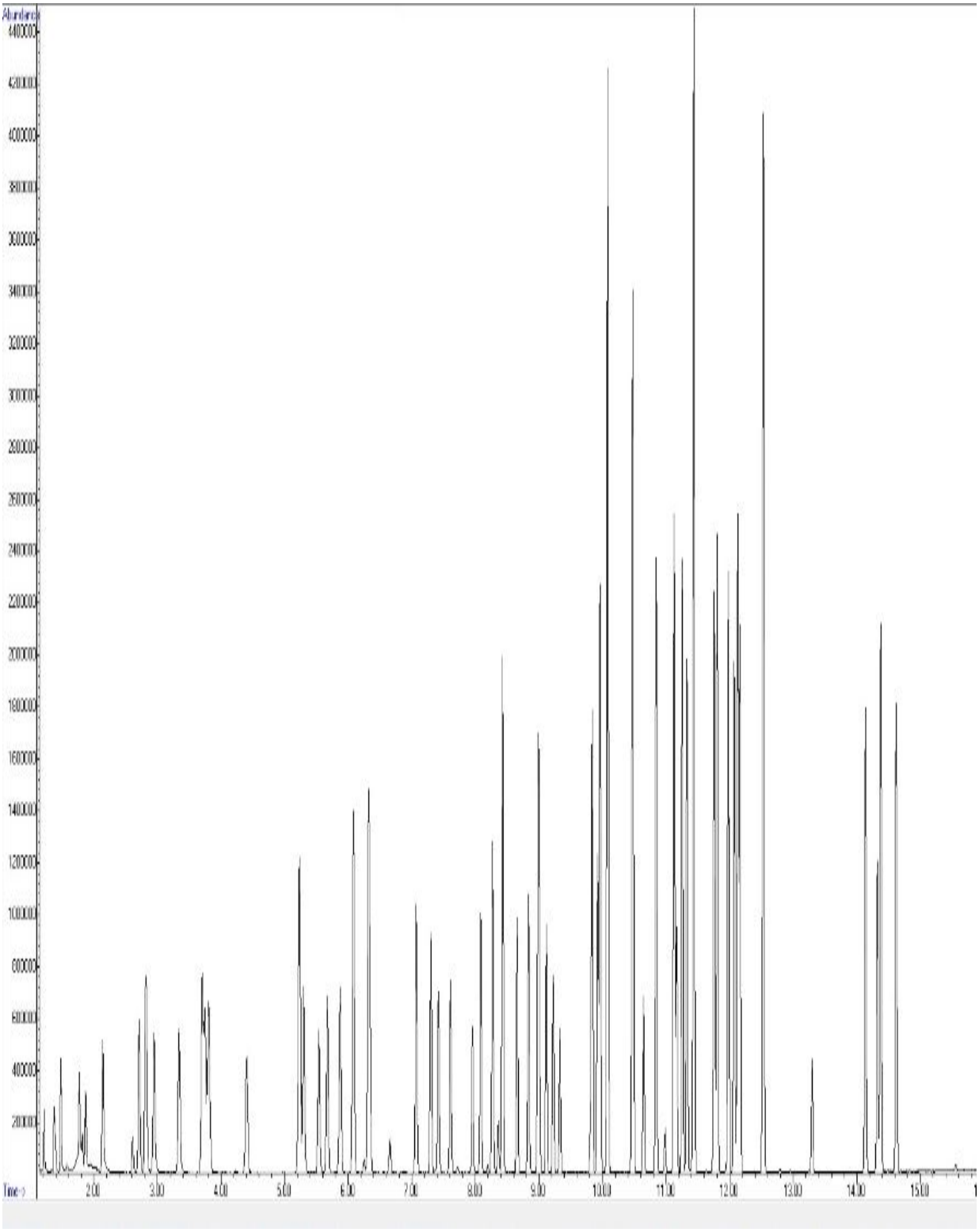


Figure

[a] Courtesy of EPA Region 10.

Figure 2

EXAMPLE GAS CHROMATOGRAM OF VOLATILE ORGANICS [a]



a. Courtesy of EPA Region 5

Appendix A: Summary of Revisions to Method 8260C (From Revision 3, August 2006)

1. Throughout the document the overall method formatting was updated for consistency with new SW-846 methods style guidance. The term mass was replaced with *m/z* to reflect what is actually being measured by the detector. Area or height was replaced with response. Language was added allowing the use of hydrogen gas as a carrier.

2. Section 1: The table (Sec. 1.1) was updated with new designations for performance (✓, *, etc.). Definitions of these symbols (Sec. 1.1) and expanded descriptions of compounds with known performance issues (Sec. 1.3) was added. Trichlorotrifluoroethane was split into two isomers: 1,1,2-Trichlorotrifluoroethane and 1,1,1-Trichlorotrifluoroethane.

3. Section 5: The designation MSDS (material safety data sheets) was updated to SDS (safety data sheets), as that is the correct term in the Global Harmonization System (GHS). A safety note was added regarding hydrogen.

4. Section 6: All vendors and product names were removed and replaced with generic terms (Sec. 6.2.1). MS acquisition rate was changed to minimum number of spectra per peak (Sec. 6.2.2.1). Subsections for tandem MS (Sec. 6.2.2.3) and SIM/CI (Sec. 6.2.2.4) were added.

5. Section 7: A paragraph was added about performing ICV with an alternate source (Sec. 7.11.3). Language was added regarding carrier gases to the reagents and standards section (Sec. 7.14).

6. Section 9: This section was completely updated and reorganized. New language and references were added from Method 8000. Sections on IDP (Sec. 9.4), blank language (Secs. 9.5 through 9.5.4), and LLOQ (Sec. 9.9) were updated and expanded. Significant revisions/additions were made to the blank section adding clarifying information about concentrations allowed in blanks (one half LLOQ), how blank concentration relates to sample concentration (<1/10), and some guidance for qualifying data. Information was added about the required frequency of LLOQ check standards (Sec. 9.9.1.2).

7. Section 11: This section was updated and reorganized. The chromatographic conditions were updated for commonly used columns (Secs. 11.2.1 through 11.2.5) and a set of conditions for hydrogen carrier gas was added (Sec. 11.2.6). The tuning criteria were updated for BFB for full scan analysis (Sec. 11.3 and Table 3), as well as other options, including SIM and/or CI analysis. Two notes were added (Sec. 11.3.1.2) regarding when each type of tune verification is appropriate. Tune verification frequency was also updated from once every 12 hours to once prior to ICAL. SIM and SRM guidance were updated (Sec. 11.3.3). A note was added regarding initial calibration curve fit when blank contamination is present and additional options for evaluation of calibration fit (Sec. 11.3.5). Updated language on ICV standards was added (Sec. 11.3.6). Clarified calibration verification frequency to allow for last initial calibration standard to be the start of 12-hour clock for samples analyzed after initial calibration (Sec. 11.4.1). Clarified that a blank is required after initial calibration and continuing calibration verification. Clarified that monitoring of ISs in CCVs is required. IS RT is now defined in absolute terms only (Sec. 11.4.4). Options to use mass spectral library searches to support qualitative identification were added (Sec. 11.6.1.3). Calculations for verifying chromatographic peak resolution were updated (Sec. 11.6.1.4). TIC interpretation language was revised (Sec. 11.6.2). Language was added regarding the analysis of TPH and GRO multicomponent mixes via total ion chromatogram (Sec. 11.7.5).

8. Section 13: Performance data listed previously in tables at the end of 8260C can now be

found at: http://www.epa.gov/hw-sw846/validated-test-method-8260d-volatile-organic-compounds-gas-chromatographymass-spectrometry.

9. Sections 14 and 15: The links to the listed safety documents were updated and replaced with the following links:
   a. http://www.acs.org/content/dam/acsorg/about/governance/committees/chemicalsafety/publications/less-is-better.pdf and
   b. http://www.labsafetyinstitute.org/FreeDocs/WasteMgmt.pdf

10. Section 16.0: Updated Reference 1 and added Reference 13 for DOD data used to populate Table 2.

11. Table 1: New analytes with suggested ions were added.

12. Table 2: LLOQ limits were removed and replaced with 2012 DOD study data.

13. Table 3: BFB criteria were updated with new criteria from Method 524.3.

14. Table 4: Min RF table was renamed as guidance and a caution statement was added below the table. Compounds are listed alphabetically by compound name.

15. Table 6: Suggested IS associations were added. Compounds are listed alphabetically by compound name.

16. Table 7: Suggested QC criteria for use with Method 8260D were added.

17. Appendix B was added discussing the use of hydrogen as a carrier gas.

18. The SW-846 Workgroup conducted a thorough review of the use of the words "must" and "should" with regards to the requirements for the frequency and type of QC samples and the associated acceptance criteria for them in this method.

19. A table of contents was added and all graphics and tables in this method were updated be 508 complaint.

B1.0 Guidance for Using Hydrogen Carrier Gas

B1.1 Hydrogen is an acceptable carrier gas to use for this analysis. However, the following modifications may be needed to make the analysis comparable to helium carrier gas:

B1.1.1 It is recommended that the highest purity (99.999% or better) hydrogen gas be used, such as from a generator or from high purity cylinders that will have minimal interferences present (e.g., hydrocarbons and water). Use of stainless steel tubing instead of copper tubing may increase the longevity of gas lines as older copper lines may become brittle over time with the use of hydrogen. MS ion source materials should be designed and approved for use with hydrogen. Contact the manufacturer of the MS to confirm the ion source is compatible with hydrogen.

Additionally, the pressure in the source should be reduced when hydrogen is used to prevent chemical ionization or other detrimental reactions from occurring. This may be done by the use of narrower bore columns (0.18 mm ID or smaller), reduction in the flow to the MS, and/or by the use of internal MS vacuum pumps (turbo pumps) with greater volumetric or pumping efficiency. Hydrogen may not be a suitable carrier gas for systems that have internal diffusion pumps.

B1.1.2 Use of hydrogen will clean (scrub) the metal surfaces of the analytical system of compounds that have adhered to the surface, generally hydrocarbons, and increase the background presence of these interferences. A bake-out of the system using high flows of hydrogen may decrease these interferences to a level that would not interfere with analysis. It is also recommended that new filters be installed on gas lines (or remove them altogether if gas purity is sufficient) to prevent the scrubbing of impurities from the filters.

B1.2 Use of hydrogen as the carrier gas may also reduce the responses of target analytes (i.e., approximately 2 - 5 times) as compared to helium. RF criteria listed in Table 4 were developed using helium carrier gas and are not appropriate for hydrogen carrier gas due to the reduced response of some analytes. If minimum RFs are used in evaluating the calibration, the laboratory should develop their own criteria or use published RFs from the instrument manufacturer. Reactivity of target analytes will vary with instrument conditions. As part of the demonstration of capability (DOC) process, evaluate target analytes for stability under the expected analytical conditions.

B1.3 As with any method modification, all QC procedures listed in Sec. 9.0 of this method should be repeated and passed using hydrogen as the carrier gas prior to the analysis of samples. Use of alternate solvents for calibration standards and extracts would also require repeating these QC procedures prior to analysis of samples.

B1.4 Hydrogen gas is highly flammable and additional safety controls may be necessary to prevent explosive levels of gas from forming. This may be accomplished by connecting vent lines from the GC inlet and MS rough pump to exhaust systems in the laboratory and leak testing all gas line connections. The flow of hydrogen should also be turned off at the source prior to opening gas lines on the GC and prior to venting the MS (such as when maintenance is performed). The user should consult additional guidelines for the safe use of hydrogen from the instrument manufacturer prior to implementing its use.