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## Standard Practice Guide for Identification and Quantitation of Organic Compounds in Water by Combined Gas Chromatography and Electron Impact Mass Spectrometry<sup>1</sup>

This standard is issued under the fixed designation D 4128; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This ~~practice guide~~ covers the identification and quantitation of organic compounds by gas chromatography/mass spectrometry (GC-MS) (electron impact) that are present or extracted from water and are capable of passing through a gas chromatograph without alteration. The ~~practice guide~~ is intended primarily for solutions for which ~~10~~ 1 ng or more of any component of interest can be introduced onto a gas chromatographic column. This ~~practice guide~~ has the advantage of providing tentative identifications of volatile and semi-volatile organics, but is restricted to (a) compounds for which reference spectra can be obtained and (b) compounds that can be separated by gas chromatography (GC). These restrictions are imposed on the ~~practice guide~~, but are not a limitation of the technique. The ~~practice guide~~ is written for, but not restricted to, analysis using automated data acquisition and handling.

1.2 Guidelines have been included for quantitation using ASTM Test Methods D3871, D3973, and other GC-MS

<sup>1</sup> This ~~practice guide~~ is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water

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volatile/semivolatile procedures used for environmental analysis<sup>2</sup>. A detection amount of ~~10~~ 1 ng is suggested for the practice, this amount can only be considered an approximate guide; approximate. The actual detection limits for each component must be determined in each laboratory. Actual detection amounts will vary with the complexity of the ~~sample, matrix,~~ the kind and condition of the GC/MS system, the sample preparation technique chosen, and the application of cleanup techniques to the sample extract, if any. Lower levels of detection can be achieved using modern sensitive instruments or with selected ion monitoring (SIM). To determine the interlaboratory detection estimate (IDE) and the interlaboratory quantitation estimate (IQE), follow Practices D 6091 and D 6512.

1.3 The ~~practice guide~~ is applicable to the identification of many organic constituents of natural and treated waters. It includes all modes of sample introduction, including injection of organic extracts, direct aqueous injection, and purge and trap techniques.

1.4 The ~~practice guide~~ is applicable to either packed or capillary column gas chromatography, including wide-bore capillary columns. Because of their greatly enhanced resolution, capillary columns are strongly recommended.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 1066 Practice for Sampling Steam<sup>3</sup>

D 1129 Terminology Relating to Water<sup>3</sup>

D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits<sup>3</sup>

D 1193 Specification for Reagent Water<sup>3</sup>

D 2908 Practice for Measuring Volatile Organic Matter in Water by Aqueous-Injection Gas Chromatography<sup>4</sup>

D 3370 Practices for Sampling Water from Closed Conduits<sup>3</sup>

D 3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents<sup>4</sup>

D 3871 Test Method for Purgeable Organic Compounds in Water Using Headspace Sampling<sup>4</sup>

D 3973 Test Method for Low-Molecular Weight Halogenated Hydrocarbons in Water<sup>4</sup>

D 5175 Test Method for Organohalide Pesticides and Polychlorinated Biphenyls in Water by Microextraction and Gas Chromatography<sup>4</sup>

D 5316 Test Method for 1,2-Dibromoethane and 1,2-Dibromo-3-Chloropropane in Water by Microextraction and Gas Chromatography<sup>4</sup>

D 5317 Test Method for the Determination of Chlorinated Organic Acid Compounds in Water by Gas Chromatography with an Electron Capture Detector<sup>4</sup>

D 5789 Practice for Writing Quality Control Specifications for Standard Test Methods for Organic Constituents<sup>4</sup>

D 6091 Practice for 99%/95% Interlaboratory Detection Estimate (IDE) for Analytical Methods with Negligible Calibration Error<sup>3</sup>

D 6512 Practice for Interlaboratory Quantitation Estimate<sup>3</sup>

E 260 Practice for Packed Column Gas Chromatography<sup>5</sup>

E 355 Practice for Gas Chromatography Terms and Relationships<sup>5</sup>

### 2.2 U.S. Environmental Protection Agency:

SW-846 Method 8270c Semivolatile Organic Compounds by Gas Chromatography (GC-MS)<sup>6,7</sup>

SW-846 Method 8260b Volatile Organic Compounds by Gas Chromatography (GC-MS)<sup>6,7</sup>

Methods for the Determination of Organic Compounds in Drinking Water-Supplement I, EPA/600/4-90/020, July 1990<sup>6</sup>

Methods for the Determination of Organic Compounds in Drinking Water-Supplement II, EPA/600/R-92/129, August 1990<sup>6</sup>

## 3. Terminology

### 3.1 Definitions of Terms Specific to This Standard:

#### Annual Book of ASTM Standards, Vol 11.01.

<sup>2</sup> U.S. EPA Methods 624 and 8260 (volatiles) and U.S. EPA Methods 625 and 8270 (semivolatiles) are suitable for quantitation.

<sup>3</sup> Annual Book of ASTM Standards, Vol 11.02.

<sup>4</sup> Annual Book of ASTM Standards, Vol 14.1.02.

<sup>5</sup> Available from National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, VA 22161.

<sup>5</sup> Annual Book of ASTM Standards, Vol 14.02.

<sup>6</sup> Consult operation manuals

<sup>6</sup> Available from manufacturers of GC/MS or GC/MS/DS systems; National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, VA 22161.

*Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see Analar Standards for Laboratory Chemicals, BDH Ltd., Poole, Dorset, U.K., and the United States Pharmacopeia and National Formulary, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.*

<sup>7</sup> SW 846 can be found online at <http://www.epa.gov/epaoswer/hazwaste/test/main.htm>.

3.1.1 *volatile organic compound*—an organic compound that can be readily separated from water by inert gas sparging and thermally desorbed onto a GC column or is readily amenable to direct aqueous injection GC. The compounds must elute from the column within its temperature range without alteration of the structure of the compound.

3.1.2 *semi-volatile organic compound*—an organic compound that can be separated from water by extraction, either liquid/liquid or solid phase, undergo volume adjustment, and be injected onto a GC. The compounds must elute from the column within its temperature range without alteration of the structure of the compound.

3.1.3 *tentative identification*—all identifications are considered tentative until confirmed by co-injection of an authentic reference compound showing identical retention time and similar mass spectra. (Tentative identification based on library matches only are subjected to false positives.)

3.1.4 *match*—two criteria must be satisfied to verify a comparison of a sample component to a standard match: (1) elution of the sample component at the same retention time as the standard component as shown by co-injection or standard addition, and (2) correspondence of the sample component and the standard component mass spectrum. If co-elution of interfering components prohibits accurate assignment of the sample component retention time from the total ion chromatogram, the retention time should be assigned by using extracted ion current profiles for ions unique to the component of interest. To meet the second criteria, all ions present in the authentic mass spectra at a relative intensity greater than 10 % (whereas the most abundant ion in the spectrum equals 100 %) must be present in the sample spectrum; the relative intensities of these ions must agree within  $\pm 20$  % between the standard and sample spectra. (As an example, for an ion with an abundance of 50 % in the standard spectra, the corresponding sample abundance must be between 30 % and 70 %.) However, there may be additional peaks in the sample mass spectrum caused by co-eluting interfering components that are not present in the reference mass spectrum.

3.1.5 *confirmed identification*—in order to confirm a tentative identification, both the GC retention ~~data~~ time and the mass spectrum of a compound shall uniquely match those of a reference compound as demonstrated by co-injection of the authentic standard with the tentatively identified compound.

3.1.6 *reconstructed gas chromatogram (see Note 1) (RGC)*—an RGC is the computer output representing either the summed intensities of all scanned ion intensities or a sample of the total current in the ion beam for each spectrum scan plotted against the corresponding spectrum number. Generally, it can be correlated with a flame ionization detector gas chromatogram.

NOTE 1—There are many synonyms in common use for RGC. These include: total ionization plot, total ionization current trace, reconstructed ion chromatogram, total ion current profile, and total ion chromatogram.

3.1.7 *reference compounds*—these are authentic materials used to obtain mass ~~spectra and spectra~~, gas chromatographic retention data, and response factors. The operator can prepare the standards or they can be prepared commercially. Quality control solutions should be prepared independently from the calibration solutions. Quantitation methods may also require surrogate spiking solutions to determine extraction efficiency.

3.1.8 *mass chromatogram (see Note 2)*—a limited mass RGC, or mass chromatogram, represents the intensities of ion currents for only those ions having particular mass to charge ratios. It is a means of quickly scanning a complex RGC plot to locate peaks which could be specific compounds or types of compounds. However, a complete mass spectrum is required for tentative identification.

NOTE 2—There are several synonyms in current use for mass chromatogram. These includes: mass fragmentogram, extracted ion current profile, and limited mass reconstructed gas chromatogram. ~~—GC/MS/DS stands~~

3.1.9 *characteristic ion*—usually the primary ion in the mass spectrum used to measure response for gas chromatograph-mass spectrometer data system quantitation purposes. When there are interferences in the mass chromatogram of a primary ion, a secondary characteristic ion must be used for quantitation.

### 3.2 Definitions:

3.2.1 For definitions of terms relating to water used in this ~~practice~~, guide, refer to ~~D~~ definitions in D 1129. For definitions of terms relating to gas chromatography used in this ~~practice~~, guide, refer to Practice E 355.

## 4. Summary of Practice

4.1 The ~~practice guide~~ consists of the introduction of organic compounds from water into a GC-MS for mass spectral identification and guidelines to determine concentration. Volatile organic compounds are typically introduced through a purge-and-trap sample introduction device, although volatile compounds can also be introduced by direct aqueous injection. Semi-volatile compounds are typically introduced as organic extracts from an extracted sample by syringe. A component's spectrum is recorded as the component elutes from the chromatographic column. The tentative identification of a sample component is ~~determined~~ based on its mass spectrum and supported by its GC retention data. This tentative identification may be confirmed by co-injection of an authentic standard yielding an identical retention time and a similar mass spectrum.

## 5. Significance and Use

5.1 With the common occurrence in water of organic compounds, some of which are toxic, it is often necessary to identify the specific compounds present and to determine the concentration.

## 6. Interferences

6.1 Sample alteration and losses of the component of interest ~~losses~~ are not true interferences, but are a source of trouble in ~~d~~

performing a qualitative GC/MS analysis. Examples of component loss are: decomposition, polymerization, adsorption, and both volatilization prior to introduction into the GC and non-volatilization after introduction into the GC. In addition, GC/MS interface plugging can lead to apparent losses.

6.2 Chromatographically unresolved compounds or instrumental background which co-elutes with the compounds of interest can interfere with this practice. These interferences can change the apparent mass spectrum of the compound of interest, thereby making tentative identification difficult.

6.3 Other interferences, such as background GC peaks due to contaminated sample preparation reagent blanks, GC columns, instrumentation or column bleed, are common problems that the analyst must strive to understand and eliminate.

6.4 Isomeric compounds may be difficult to separate by GC and the mass spectra of isomers are frequently identical within experimental error. This could lead to either ambiguity in identification or to actual incorrect identification in some cases. The analyst must be aware of this potential problem.

6.5 When attempting to identify compounds in water samples containing large numbers of compounds, particularly complex mixtures such as petroleum products, great care must be exercised to determine that candidate unknown mass spectra are free of interfering peaks as possible. Judicious background-subtraction can assist in this endeavor. Additional information can be gathered by examining the extracted ion current profiles of the major mass spectral peaks in the candidate spectrum. Frequently, the occurrence of contaminated spectra can be determined by noting differences in the profiles of several mass chromatograms that do not exactly fit the profiles of the peaks of the compound of interest. These may be co-eluting interferences. However, it is rarely possible to completely eliminate all interferences from complex samples, and the analyst must be aware of this in interpreting unknowns against reference spectra.

## 7. Apparatus

7.1 GC/MS/DS—A gas chromatograph interfaced to a mass spectrometer having electron impact ionization capability is used. Although not required, most modern GC/MS systems are typically controlled by a data system for computerized instrument control of data acquisition and data reduction. Packed or capillary Capillary columns are preferred with most GC-MS systems although packed GC columns may be used.

7.2 Apparatus required to extract organic compounds from water and concentrate them in a small volume of organic solvent—This apparatus includes a 2-L separatory funnel for batch extractions or 1-L continuous liquid-liquid extractor and facilities for Kuderna-Danish concentration. Liquid-liquid extraction for volatile organic constituents can be conducted using the apparatus specified in Test Method D 3973.

7.3 Apparatus for purge-and-trap GC/MS sample introduction—See Test Method D 3871 or EPA Method 524.2.

7.4 Microsyringe, 10- $\mu$ L.

## 8. Reagents and Materials

8.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.<sup>9</sup> For trace analysis using organic solvents for liquid-liquid extraction or elution from solid sorbents, solvents specified as distilled-in-glass, nano-grade, or pesticide-grade frequently have lower levels of interfering impurities.<sup>10</sup> In all cases, sufficient reagent blanks must be processed with the samples to ensure that all compounds of interest are not present as in blanks due to reagents or glassware. Other grades of reagents may be used, providing it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type II. This water must be shown to not contain contaminants at concentrations sufficient to interfere with the analysis.

8.3 Reference compounds shall be of known purity; impurity peaks shall not interfere with the compound of interest.

8.4 Reference spectra for tentative identifications may be obtained from commercially available mass spectral libraries such as the electronic EPA/NIST/NIH Mass Spectral Library or from various publications.<sup>11</sup> Many GC/MS/DS systems GC-MS/DS contain libraries of reference spectra as well as software required to match unknown spectra to these libraries. User libraries of compounds of interest may be generated from reference compounds run on the same instrument used for unknown analysis and

<sup>8</sup> These products are available

<sup>8</sup> Consult operation manuals from most laboratory suppliers; manufacturers of GC-MS or GC-MS/DS systems.

<sup>9</sup> Reference spectra are published by the

<sup>9</sup> Reagent Chemicals, American Chemical Society for Mass Spectrometry (A Guide to Collection of Mass Spectral Data Specifications, 2nd ed., 1978), P.O. Box 1508, East Lansing, MI 48826; the American Petroleum Institute (Project 44), 1220 "L" St., N.W., Chemical Society, Washington, DC 20005, DC. For suggestions on the National Institute testing of reagents not listed by the American Chemical Society, see Analard Standards for Laboratory Chemicals, BDH Ltd., Poole, Dorset, U.K., and Technology, Gaithersburg, MD 20899; the United States Pharmacopeia and Wiley-Interscience, John Wiley and Sons, 605 Third Ave., New York, NY 10158; National Formulary, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

<sup>10</sup> Malathion is a trademarked product

<sup>10</sup> These products are available from American Cyanamid, Agricultural Research Division, P.O. Box 400, Princeton, NJ 08540; most laboratory suppliers.

<sup>11</sup> Useful references

under the same conditions. ~~Such User libraries should result in~~ allow faster and more accurate tentative identifications than large generalized libraries. Reference spectra for confirmed identifications are determined under the same conditions for sample analysis by co-injecting the reference compounds with the sample extract, or adding the reference compounds to aqueous samples, and confirming both the co-elution of the unknown and reference compounds and their matched mass spectra.

8.5 *Gas Chromatography Column*—All-inclusive guidelines for GC column selection do not exist. Each analysis requires careful consideration of the column used (see Note 3). Bonded phase fused silica capillary columns have proven remarkably popular and successful. For examples, consult other ASTM test methods, such as Test Methods D 5175, D 5316, D 5317, or US EPA methods. Liquid phases for GC columns used in direct aqueous injection analysis shall conform to Practice D 2908.

NOTE 3—General guidelines for column selection can be found in GC or column suppliers' literature and textbooks, and ASTM Atomic/Molecular Data Series AMD 25A and AMD 25A S-1, Gas Chromatographic Data Compilation (and supplement), ASTM, 1971.

~~8.6 textbooks.~~

8.6 The following chemicals may be used in this guide.

8.6.1 Methyl Stearate.

~~8.76.2 Malathion<sup>12</sup>.~~

~~8.8~~

8.6.3 bis-(pentafluorophenyl)Phenyl Phosphine.

~~8.96.4 decafluorotriphenyl phosphine (DFTPP).~~

8.6.5 bromofluorobenzene (BFB).

8.6.6 Isopropyl Alcohol.

~~8.10~~

8.6.7 Methylene Chloride.

~~8.11~~

8.6.8 Methyl Hexanoate.

~~8.12~~

8.6.9 N-Methyl-2-Pyrrolidone.

## 9. Hazards

9.1 **Caution:** Isomeric compounds may be difficult to separate by GC and the mass spectra of isomers are frequently identical within experimental error. This could lead to either ambiguity in identification or to actual incorrect identification in some cases. The analyst must be aware of this potential problem.

9.2 **Caution:** When attempting to identify compounds in water samples containing large quantities of compounds, particularly complex mixtures such as petroleum products, great care must be exercised to determine that candidate unknown mass spectra are as devoid of interfering peaks as possible. Judicious choice of background subtracting routines can assist in this endeavor. Additional information can be gathered by examining the extracted ion current profiles of the major mass spectral peaks in the candidate spectrum. Frequently, the occurrence of contaminated spectra can be determined by noting differences in the profiles of several mass chromatograms that do not exactly fit the profiles of the peaks of the compound of interest. These may be co-eluting interferences. However, it is rarely possible to completely eliminate all interferences from complex, low-level analyses, and the analyst must be aware of this in interpreting unknowns against reference spectra.

9.3 **Warning:** Due care shall be exercised in handling samples to minimize operator exposure to all chemicals including solvents, standards, and reagents. Solvents are a particular source of hazard because of the large quantities used in many sample preparation procedures. General practice regarding the proper use of a gas chromatograph/mass spectrometer system can be found in the manufacturer's operation manual. Since potentially toxic materials may be handled, all effluent and vent gases from any source should be vented in an environmentally safe manner. Possible sources to be considered include split gas from GC exhaust, gas from vacuum pumps, and waste containers.

## 10. Sample Handling, Preparation, Preservation, and Introductions

10.1 Collect the sample in accordance with Practice D 1066, Specification D 1192, Practices D 3370, or Practices D 3694.

10.2 *Sample Preparation:*

10.2.1 *Techniques of Sample Preparation*—There are many techniques of sample preparation, and the most appropriate to the application should be used.<sup>13</sup> Among the more widely used techniques are:

<sup>11</sup> Reference spectra are published by the American Society for these techniques may be found in *Mass Spectrometry (A Guide to Collection of Mass Spectral Data, 2nd ed., 1978)*, P.O. Box 1508, East Lansing, MI 48826, the bi-annual review issues American Petroleum Institute (Project 44), 1220 "L" St., N.W., Washington, DC 20005, the National Institute of Analytical Chemistry, Standards and Technology, Gaithersburg, MD 20899, and Wiley Interscience, John Wiley and Sons, 605 Third Ave., New York, NY 10158.

<sup>12</sup> The boldface numbers in parentheses refer to the references at the end of this practice.

<sup>12</sup> Malathion is a trademarked product from American Cyanamid, Agricultural Research Division, P.O. Box 400, Princeton, NJ 08540.

<sup>13</sup> This guide is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water

10.2.1.1 Direct aqueous injection (see Practice D 2908).

10.2.1.2 Liquid-liquid extraction (acid, base, neutral), followed by concentration adjustment and injection. Extraction of a 1-L sample is typically accomplished by methylene chloride batch extraction using either a 2-L separatory funnel or a 1-L continuous extractor at both high and low pH. Liquid-liquid extraction can also be used for volatile compounds (see Test Method D 3871).

10.2.1.3 Purge-and-trap, which consists of sparging volatile organic compounds from water with an inert gas, collecting the compounds on a trap, and then thermally desorbing them onto the head of a GC column (see Test Method D 3973 and EPA Method 524.2).

10.3 *Sample Preservation*—There may be existing methodology for preservation of specific analytes. If so, that methodology should be followed; if not, then the appropriate sections of Practices D 3694 will apply. ~~Volatil samples will be preserved according to EPA Method 524.2. apply.~~

10.4 *Sample Introduction*—Sample introduction into the chromatograph shall follow the precautions described in Practice E 260.

## 11. GC/MS System Performance

11.1 Depending on the sample matrix (water or organic solvent), identification of the solutes in one of the following solutions in 11.1.1 or 11.1.2 shall be used to establish the satisfactory performance of the GC/MS system before proceeding to analyze unknown solutions. The RGC generated by the test solution should give GC peaks with a signal to background ratio greater than four-to-one. A representative mass spectrum corresponding to each GC peak should be identified in accordance with criteria in use in the operator's laboratory. Such criteria should include reference to literature spectra or matching and interpretation techniques described in the literature (1).<sup>14</sup> Each component shall be present at 25 µg/mL. Inject 2 µL of either solution.

11.1.1 Methylene chloride—methyl stearate, bis-(pentafluoro-phenyl)phenyl phosphine, Malathion.

11.1.2 Water—isopropyl alcohol, methyl hexanoate, N-methyl-2-pyrrolidone.

Each component shall be present at ~~25 ng/µL.~~ µg/mL. Inject ~~2 µL.~~ µg of either solution.

11.2 *Preparation of Performance Check Solution—Methylene Chloride Solution:*

11.2.1 Weigh 125 mg each of methyl stearate, bis-(pentafluorophenyl)phenyl phosphine, and Malathion into separate 100-mL volumetric flasks using an analytical balance accurate to 0.0001 g. Dilute each to volume with methylene chloride and mix well.

11.2.2 Pipet 2 mL of each solution into the fourth volumetric flask and dilute to volume with methylene chloride. This solution contains ~~25 ng/µL.~~ µg/mL of each component.

11.2.3 Transfer the contents of each flask to a separate 120 mL screw cap brown glass bottle with a polytetrafluoroethylene (PTFE)-lined septum cap and store at 4°C. Storage lifetime is not known, but should be enhanced by maintaining the solutions at 4°C in the dark. Transferring approximately 1 mL of the ~~25-n~~ µg/mL solution to a 2-mL screw-cap vial with a polytetrafluoroethylene (PTFE)-lined septum cap is convenient. This 1-mL solution can be readily replaced weekly.

11.3 *Direct Aqueous Injection Water Solution:*

11.3.1 Clean a 1-L volumetric flask with chromic acid cleaning solution.

11.3.2 Rinse thoroughly and fill with clean water to the mark.

11.3.3 Insert PTFE-covered stirring bar and chill in an ice bath for at least 40 min with stirring.

11.3.4 Inject 25 µL each of N-methyl-2-pyrrolidone, methyl hexanoate, and isopropyl alcohol into the volumetric flask below the surface of the water.

11.3.5 Stir approximately 10 min.

11.3.6 Remove the stirring bar.

11.3.7 The final concentration of each compound is as follows based on correction for density:

~~N-methyl-2-pyrrolidone = 25.7 ng/µL~~

~~N-methyl-2-pyrrolidone = 25.7 mg/L~~

~~Methyl hexanoate = 22.1 ng/µL~~

~~Methyl hexanoate = 22.1 mg/L~~

~~Isopropyl alcohol = 19.6 ng/µL~~

~~Isopropyl alcohol = 19.6 mg/L~~

11.3.8 Cap the flask and seal with PTFE tape and store at 4°C. Storage lifetime is not known. Weekly preparation is recommended.

11.4 For volatile samples to be analyzed by purge-and-trap, follow the system performance procedures listed in Test Method D 3973 or the appropriate EPA Method 524.2. method.

11.5 Other system performance procedures are acceptable for use in this guide as long as the performance criteria have been documented and meet applicable regulatory requirements.

## 12. Data Acquisition

12.1 A method blank should be prepared with organic free water using the same sample preparation technique as the unknown sample. Compounds detected in the method blank should be reported. For compounds detected in both the blank and the samples,

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<sup>14</sup> The boldface numbers in parentheses refer to the references at the end of this guide.

provide an estimate of the relative concentrations.

12.2 *Tuning*—The GC/MS system shall be adjusted in accordance with the manufacturer’s instructions. This shall be done through adjustment of mass spectrometric conditions (drawout potential, emission current, etc.) to optimize mass spectral peak shapes and relative peak intensities for a calibration compound or mixture. Because the relative peak intensities for some quadrupole mass spectrometers are very sensitive to these tuning parameters, tuning criteria in the form of target peak intensity ratios have been established. However, these differ for volatile versus semi-volatile compounds. For volatile compounds, bromofluorobenzene is used as the check compound in EPA Method 524.2, while for semi-volatile compounds bis-(pentafluorophenyl)phenylphosphine (or compounds, decafluorotriphenyl phosphine (DFTPP)) is used (2). The ion abundance criteria should be met as directed by the instrument manufacturer or as cited in the applicable test method. Note that systems tuned to one criteria will not typically meet the other criteria.

#### 12.3 *Data System Calibration:*

12.3.1 The data system sensitivity and zero are adjusted in accordance with the manufacturer’s recommendations.

12.3.2 The mass scale of the data system is established by assignment of known masses in the spectra of calibration standards. Depending on the overall system, the assignment may either be made automatically by the computer or require manual assignment of three or more peaks by the operator. The manufacturer’s instructions should be followed.

#### 12.4 *GC/MS Conditions:*

12.4.1 Gas chromatographic conditions are determined by previously established methods, if available, that have been shown to provide the desired separation of the compounds of interest. Carrier gas is typically ultra-high purity (UHP) helium.

12.4.2 *GC/MS Interface Conditions*—~~Common practice for packed columns and wide-bore capillary columns is to use a molecular separator at 20°C higher temperature than final column temperature.~~ For narrow-bore capillary columns, common practice is to terminate the column as close to the mass spectrometer source as possible with a transfer line temperature near the final column temperature. Common practice for packed columns and wide-bore capillary columns is to use a molecular separator at 20°C higher temperature than final column temperature.

12.4.3 *Mass Spectrometer Conditions*—Ionizing voltage should be 70 eV, and a minimum of three scans (preferably 5 to 10 scans) should be obtained from each chromatographic peak. Instruments should be operated following manufacturer’s recommendations.

### 13. Data Reduction

13.1 *General*—The GC effluent enters the MS continuously in the course of a GC/MS run and mass spectra are obtained as individual scans from one extreme of the mass range to the other. The scanning process ~~may be triggered manually or may be~~ preferably scanned continuously under computer control. ~~This practice is directed toward computer control.~~ The immediate objective is to obtain the best possible mass spectrum of each compound that has been resolved by the GC. The investigator should be aware of background peaks arising from sources such as air or column bleed or coeluting peaks.

13.2 *Computerized Scans*—The data acquired during a GC/MS run are acquired by cyclically scanning the mass spectrometer throughout the GC run so that scan numbers directly correlate with retention times. ~~Data from each scan are typically stored on a magnetic disk in the form of mass/intensity pairs following conversion from time, voltage, or magnetic field/intensity pairs.~~ Each scan consists of a set of mass/intensity pairs covering the entire mass range of the scan.

13.2.1 The spectral numbers are correlated with elapsed GC time. The RGC is reconstructed from stored data and serves as a guide to the user in selection of stored spectra for data processing. If desired, retention time, or scan number ranges and attenuation factors for the display, can be changed for more detailed views of the RGC. In addition, intensity values can be limited to those of a few selected masses in order to sort out specific peaks in a complex chromatogram. The associated dialogs for these displays may be found in the user’s manuals.

13.2.2 *Spectra Selection*—Selection of spectra based on the RGC or on extracted ion current profiles is accomplished by use of interactive graphical displays, or by automated peak detection procedures. Instructions for these procedures can be found in the manufacturer’s manuals, tutorials, or in user courses offered by the manufacturers.

13.2.3 *Background Correction*—Typically, the data processing system will permit background correction of selected spectra. Background correction can produce cleaner spectra which may be considerably easier to interpret or match with library spectra. These routines typically operate in one of two manners: (1) specific background spectra can be selected and subtracted from the candidate spectrum, or (2) a candidate spectrum may be “enhanced” by directly calling a routine which automatically selects only those peaks in a spectrum which maximize at or very near the candidate spectrum number. The user is strongly encouraged to completely investigate the background subtraction routines for his the particular system to become familiar with the strengths and weaknesses of all possible options. Consult the manufacturer’s manuals and courses for details.

13.2.4 *Saturation*—Although most systems contain software flags which indicate when a particular mass intensity has exceeded the dynamic range of the detector system and become saturated, these routines may not operate with background subtracted spectra. Before calling the subtraction routine, the user of the system should check the spectra of both the GC-peak and the background to determine if either contains saturated peaks. The user must be aware that, when the data system subtracts an unsaturated intensity from a saturated one, it will give an intensity that appears to be a normal unsaturated one. In fact, such an intensity is meaningless.

13.2.5 *Data Presentation*—Computerized GC/MS data outputs include bar graphs, tabulated spectra, overlaying mass

chromatograms having different masses, and multiplication of all intensities within a selected range by a multiplication factor. Typically, these results may be called through automated procedures and queued to permit unattended operation.

### 13.3 *Data Presentation for Matching:*

13.3.1 *Computerized Matching*—Many computer spectra matching programs use some form of spectral abbreviation to reduce both the time for transmission to:

13.3.1 Most GC-MS systems contain a central computer and the storage space of the database with a spectral library needed for matching. Various schemes for abbreviation are in use, but the most popular one (3) involves consideration of only the two most intense peaks in each 14-amu window starting at mass 6. If two intensities in the window are equal, the first is arbitrarily chosen. Table 1 shows the results of such an abbreviation for ASTM Spectrum No. 1, allyl amine. The original 52 peaks are abbreviated matching system to 8 peaks by this process. tentatively identify compounds.

### 13.4 *Compound Identification:*

13.4.1 *General*—There are three principal means of compound identification from mass spectra (4). These are: computerized spectral matching, manual searching of mass/intensity tabulations, and interpretation based on knowledge of fragmentation processes of organic molecules (1). The latter approach requires an expert knowledge of mass spectral fragmentation processes and is beyond the scope of this practice guide and will not be treated here.

13.4.2 *Computerized Spectral Matching*—Computerized spectral matching includes several approaches. All require an appropriate library of reference spectra. As a minimum, this reference file should contain spectra of all organic compounds that may be present in the water sample. For best performance, a reference file should be developed from standards run on the same instrument and under the same conditions as the unknown. This will result in the most precise spectral matches obtained in the minimum time because there will be a limited number of spectra in the reference file. However, this approach is not practicable for true unknown matching where the largest library of possibilities is desired. Under this condition, the tuning criteria of 12.2 are relied upon to produce spectra which are standardized.

13.4.2.1 Most modern GC/MS/DS systems GC-MS/DS contain a large spectral library and the associated software for matching routines, either interactively (one at a time) or in procedures which can be called for unattended operation. Combining automated peak detection methods with automated spectral matching and automatically printed results can result in a highly automated system capable of unattended operation. However, the user is strongly encouraged to become familiar with the details of how the spectral matching routines are accomplished so as to be more capable of evaluating the information provided with the matches. Frequently, the system will provide one or more indexes for how well the unknown matches a reference spectra, and how well the reference spectra matches the unknown. The user can select how the system will order and present these indexes, and the quality of the matches is greatly dependent on several parameters set by the user. Again, details of the operation of the matching routines are found in the manufacturer's manuals and training courses.

13.4.2.2 If spectral matching routines are not available, automatic transmission of spectra data to a central computer for matching may be accomplished. In this routine, either the abbreviated spectrum or the entire spectrum is sent from the GC/MS to another computer for matching without user interaction. Certain of these programs also give the user an index that indicates how well the sample matches the reference.

13.4.2.3 *Manual Searching*—There are several collections of mass spectral data (5) that are listed by masses with the most intense peak first, the second most intense peak second, etc. A widely used collection (6) contains masses and intensities for the eight most intense peaks of 31 101 spectra. It is indexed by each of the three most intense peaks. Searching of tables is governed by the intensity ranking of peaks. Generally the tabulation is entered in the part indexed by the mass number of the most intense peak in the unknown. The other masses given are scanned to see how well they agree with the masses of the unknown.

13.4.2.4 *Automated Manual Searching*—This approach is particularly useful when a terminal connection to a central computer is available, but no computer is available on the GC/MS system. The analyst selects mass peaks from a spectrum and manually enters their mass/intensity values through the remote terminal. As the peaks are entered, the spectra in the data base are screened to see which contain that combination of peaks. Frequently, only five peaks are required to reduce the possibilities to ten or less. This technique relies on the skill of the analyst to select mass peaks which are unique to the compound of interest. The user is cautioned that one mass peak that is not associated with the compound of interest will eliminate that compound from consideration in this technique. However, the skilled analyst can use this system to obtain information about compounds which do not exist in the data base by selecting masses which are characteristic of classes of compounds instead of particular compounds.

13.4.3 *Supporting Information*—Mass spectra are highly distinctive, but are not unique, nor are all possibilities of unknowns present in any database. Therefore, all other possible information should be used to support the tentative identifications made by this practice guide. Such information includes the GC retention time (7) and the peak-by-peak comparison of the complete mass spectrum of the unknown with the spectrum of an authentic sample of the suspected compound run on the same system. If the compound is not available, the appropriate spectrum in one of the available compilations (8) of mass spectral data should be compared, but the identification must be considered tentative until an authentic sample is available. In addition, all other information about the sample and the compounds that may be present in it needs to be available to the analyst. In addition, any pre-treatment or cleanup procedures applied to the sample need to be communicated. Frequently, information about polarity or solubility of possible compounds present can be of great help to the analyst.

### 13.5 *Guidelines for Quantitation:*

13.5.1 There may be instances when the operator may need to determine the concentration of the identified compound(s) from this guide. For compliance monitoring, follow the method that is approved by the regulatory authority or meets the project requirements.

13.5.2 Prepare calibration solutions containing the appropriate internal standards as described in the corresponding method. A minimum of five standards bracketing the entire concentration range of interest should be prepared and injected into the GC-MS system. The response of the base peak or designated characteristic ion should be compared against that of the nearest internal standard to determine a response factor. The average of response factors should be employed when the RSD is less than 15 percent. The response factor (RF) can be calculated as follows:

$$RF = \frac{(A^x)(C^{is})}{(A^{is})(C^x)} \quad (1)$$

where:

$A^x$  ≡ area of the characteristic ion for the compound being measured,  
 $A^{is}$  ≡ area of the characteristic ion for the internal standard,  
 $C^x$  ≡ concentration of the compound being measured, and  
 $C^{is}$  ≡ concentration of the nearest internal standard.

NOTE 4—If the compound is not a target compound and can be qualified as an estimated concentration, only one standard is necessary to determine the response factor; however, the response should be within ±30 percent of that found in the sample since the range of linearity may be unknown. The estimate can also be determined by assuming an RF equal to 1 (having the same response as the corresponding internal standard); however, the estimate will likely be much less accurate. Estimates cannot be used for compliance reporting but may be useful for characterizing the content of the sample.

13.5.3 If the response factor RSD is greater than 15 %, then the calibration curve is generated based on regression analysis, which usually can be performed by the data analysis system. The R value should be greater than 0.99.

13.5.4 For purge and trap, calculate the concentration of the sample as follows:

$$Conc., \mu\text{g/L} = \frac{(A^x)(C^{is})}{(A^{is})RF} \quad (2)$$

where:

$A^x$  ≡ the response of the characteristic ion of the sample,  
 $C^{is}$  ≡ the concentration of the internal standard,  $\mu\text{g/L}$ , and  
 $A^{is}$  ≡ the response of the characteristic ion of the internal standard.

13.6 For semi-volatiles, calculate the concentration of the sample as follows:

$$Conc., \mu\text{g/L} = \frac{(A^x)(C^{is})(V^f)}{(A^{is})(V^i)(RF)} \quad (3)$$

where:

$A^x$  ≡ the response of the characteristic ion of the sample,  
 $C^{is}$  ≡ the concentration of the internal standard,  $\mu\text{g/L}$ ,  
 $A^{is}$  ≡ the response of the characteristic ion of the internal standard,  
 $V^f$  ≡ the final volume of the extract (mL), and,  
 $V^i$  ≡ the initial extraction volume (L).

## 14. Precision and Bias

14.1 This practice guide is a qualitative test that includes guidelines for quantitation from a variety of test methods. Precision and bias data are not applicable.

## 15. Evaluation of Practice

15.1 To help evaluate the practice, an interlaboratory test was carried out by eight participants. A three-component test solution was distributed as an unknown (2-methylthiobenzothiazole, a trichlorobiphenyl isomer, and n-docosane each at 50 ng/ $\mu\text{L}$  in methylene chloride).

15.2 To establish performance of their GC/MS/DS systems, the participants were instructed to analyze the methylene chloride performance check solution (described in the practice) according to this practice.

15.3 The unknown solution was then analyzed using the same conditions to identify the components.

15.4 *Summary of Results (see Table 2):*

15.4.1 2-methylthiobenzothiazole was correctly identified by the eight participants. The principal method of identification was

computerized library search (used by six of the participants):

15.4.2 Trichlorobiphenyl was correctly identified by seven participants. The erroneous identification was another chlorobiphenyl homolog. The principal method of identification was computerized library search; the erroneous identification was done using a matched eight-peak index.

15.4.3 *n*-Docosane was correctly identified by six participants. One erroneous identification was a C<sub>22</sub>H<sub>46</sub> hydrocarbon (manual interpretation) and the other was a C<sub>19</sub> to C<sub>25</sub> hydrocarbon (automatic library search). Identification methods were equally split between computerized library search and manual inspection.

## 16. Keywords

165.1 gas chromatography; GC-MS; mass spectrometry; organic compounds

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