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Standard Guide for Identification and Quantitation of Organic Compounds in Water by Combined Gas Chromatography and Electron Impact Mass Spectrometry[1]

This standard is issued under the fixed designation D4128; 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 (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This 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. This guide can be used to provide 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 guide, but are not a limitation of the technique. The guide is written for 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 volatile/semivolatile procedures used for environmental analysis[2]. The actual detection limits for each component must be determined in each laboratory. Actual detection amounts will vary with the complexity of the 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 D6091 and D6512.

1.3 The 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 guide is applicable to capillary column gas chromatography.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1066 Practice for Sampling Steam

D1129 Terminology Relating to Water

D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)[4]

D1193 Specification for Reagent Water

D2908 Practice for Measuring Volatile Organic Matter in Water by Aqueous-Injection Gas Chromatography

D3370 Practices for Sampling Water from Flowing Process Streams

D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents

D3871 Test Method for Purgeable Organic Compounds in Water Using Headspace Sampling

D3973 Test Method for Low-Molecular Weight Halogenated Hydrocarbons in Water

D5175 Test Method for Organohalide Pesticides and Polychlorinated Biphenyls in Water by Microextraction and

[1] 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

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[2] EPA Methods 624 and 8260C (volatiles) and EPA Methods 625 and 8270D (semivolatiles) are suitable for quantitation.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] The last approved version of this historical standard is referenced on www.astm.org.

Gas Chromatography
D5316 Test Method for 1,2-Dibromoethane and 1,2-Dibromo-3-Chloropropane in Water by Microextraction and Gas Chromatography
D5317 Test Method for Determination of Chlorinated Organic Acid Compounds in Water by Gas Chromatography with an Electron Capture Detector
D5789 Practice for Writing Quality Control Specifications for Standard Test Methods for Organic Constituents (Withdrawn 2002)[4]
D6091 Practice for 99 %/95 % Interlaboratory Detection Estimate (IDE) for Analytical Methods with Negligible Calibration Error
D6512 Practice for Interlaboratory Quantitation Estimate
E260 Practice for Packed Column Gas Chromatography
E355 Practice for Gas Chromatography Terms and Relationships

2.2 *EPA Documents:*
EPA Method 524.2–1995 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry[5]
EPA Method 624–1984 Purgeables[5]
EPA Method 625–1984 Base/Neutrals and Acids[5]
SW-846 Method 8270D Semivolatile Organic Compounds by Gas Chromatography (GC-MS)[6,7]
SW-846 Method 8260C Volatile Organic Compounds by Gas Chromatography (GC-MS)[6,7]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms relating to water used in this standard, refer to Terminology D1129. For definitions of terms relating to gas chromatography used in this standard, refer to Practice E355.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *characteristic ion, n*—usually the primary ion in the mass spectrum used to measure response for quantitation purposes. When there are interferences in the mass chromatogram of a primary ion, a secondary characteristic ion must be used for quantitation.

3.2.2 *confirmed identification, n*—in order to confirm a tentative identification, both the GC retention 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.

3.2.3 *mass chromatogram, n—(see Discussion)*—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.

3.2.3.1 *Discussion*—There are several synonyms in current use for mass chromatogram. These include: mass fragmentogram, extracted ion current profile, and limited mass reconstructed gas chromatogram.

3.2.4 *match, n*—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 ±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.

3.2.5 *reconstructed gas chromatogram (RGC), n—(see Discussion)*—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.

3.2.5.1 *Discussion*—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.

3.2.6 *reference compounds, n*—these are authentic materials used to obtain mass 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.

3.2.7 *semi-volatile organic compound, n*—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.

3.2.8 *tentative identification, n*—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.)

[5] Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http://www.epa.gov.
[6] Available from National Technical Information Service (NTIS), 5301 Shawnee Rd., Alexandria, VA 22312, http://www.ntis.gov.
[7] SW 846 can be found online at https://www.epa.gov/hw-sw846.

3.2.9 *volatile organic compound, n*—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.

4. Summary of Practice

4.1 The 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 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 are not true interferences, but are a source of trouble in 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 guide. 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.[8] Most modern GC-MS systems are typically controlled by a data system for computerized instrument control of data acquisition and data reduction. 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 D3973.

7.3 *Apparatus for Purge-and-Trap GC-MS Sample Introduction*—See Test Method D3871 or EPA Methods 524.2 or 8260C.

7.4 *Microsyringe,* 10-µL.

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.[9] 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.[10] In all cases, sufficient reagent blanks must be processed with the samples to ensure that all compounds of interest are not present 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 that meets

[8] Consult operation manuals from manufacturers of GC-MS or GC-MS/DS systems.

[9] *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.

[10] These products are available from most laboratory suppliers.

the purity specifications of Type I or Type II water presented in Specification D1193. This water must be shown not to 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.[11] Many 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 under the same conditions. User libraries 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 1). Bonded phase fused silica capillary columns are commonly used. For examples, consult other ASTM test methods, such as Test Methods D5175, D5316, D5317, or EPA methods. Liquid phases for GC columns used in direct aqueous injection analysis shall conform to Practice D2908.

NOTE 1—General guidelines for column selection can be found in GC or column suppliers' literature and textbooks.

8.6 The following chemicals may be used in this guide.

8.6.1 *Methyl Stearate.*

8.6.2 *Malathion.*[12]

8.6.3 *bis-(pentafluorophenyl)Phenyl Phosphine.*

8.6.4 *decafluorotriphenyl phosphine (DFTPP).*

8.6.5 *bromofluorobenzene (BFB).*

8.6.6 *Isopropyl Alcohol.*

8.6.7 *Methylene Chloride.*

8.6.8 *Methyl Hexanoate.*

8.6.9 *N-Methyl-2-Pyrrolidone.*

9. Hazards

9.1 **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 D1066, Guide D1192, Practices D3370, or Practices D3694.

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.[13] Among the more widely used techniques are:

10.2.1.1 Direct aqueous injection (see Practice D2908).

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 D3871).

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 D3973 and EPA Methods 524.2 or 8260C).

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 D3694 will apply.

10.4 *Sample Introduction*—Sample introduction into the chromatograph shall follow the precautions described in Practice E260.

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, 11.1.2, or as specified in the test method can 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**).[14] 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] Reference spectra are published by the American Society for Mass Spectrometry (*A Guide to Collection of Mass Spectral Data*, 2nd ed., 1978), East Lansing, MI; the American Petroleum Institute (Project 44), Washington, DC; the National Institute of Standards and Technology, Gaithersburg, MD; and Wiley Interscience, John Wiley and Sons, New York, NY.

[12] Malathion is a trademarked product from American Cyanamid, Agricultural Research Division, Princeton, NJ.

[13] Useful references for these techniques may be found in the bi-annual review issues of *Analytical Chemistry*.

[14] The boldface numbers in parentheses refer to a list of references at the end of this standard.