



# Standard 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 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 guide is intended primarily for solutions for which 1 ng or more of any component of interest can be introduced onto a gas chromatographic column. This 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 guide, but are not a limitation of the technique. The 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 volatile/semivolatile procedures used for environmental analysis<sup>2</sup>. A detection amount of 1 ng can only be considered approximate. 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 D 6091 and D 6512.

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 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>

<sup>1</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

Current edition approved July 10, 2001. Published October 2001. Originally published as D 4128 – 82. Last previous edition D 4128 – 94.

<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 11.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 11.02.

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:*

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 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, 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 include: mass fragmentogram, extracted ion current profile, and limited mass reconstructed gas chromatogram.

3.1.9 *characteristic ion*—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 *Definitions:*

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

### 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

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

<sup>6</sup> Available from National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, VA 22161.

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

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.<sup>8</sup> 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 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 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 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

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

<sup>9</sup> *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>10</sup> These products are available from most laboratory suppliers.