



Standard Practice for Micro-Extraction of Water for Analysis of Volatile and Semi-Volatile Organic Compounds in Water¹

This standard is issued under the fixed designation D 5241; 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 practice covers standard procedures for extraction of volatile and semi-volatile organic compounds from water using small volumes of solvents.

1.2 The compounds of interest must have a greater solubility in the organic solvent than the water phase.

1.3 Not all of the solvents that can be used in micro extraction are addressed in this practice. The applicability of a solvent to extract the compound(s) of interest must be demonstrated before use.

1.4 This practice provides sample extracts suitable for any technique amenable to solvent injection such as gas chromatography or high performance liquid chromatography (HPLC).

1.5 The values stated in SI units are to be regarded as the 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 and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 9.

2. Referenced Documents

2.1 ASTM Standards:

D 1129 Terminology Relating to Water²

D 1193 Specification for Reagent Water²

D 3370 Practices for Sampling Water from Closed Conduits²

D 3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents³

D 3856 Practice for Evaluating Laboratories Engaged in Sampling and Analysis of Water and Wastewater²

D 3973 Test Method for Low-Molecular Weight Halogenated Hydrocarbons in Water³

D 4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data²

D 4448 Guide for Sampling Groundwater Monitoring Wells⁴

D 5175 Test Method for Organohalide Pesticides and Polychlorinated Biphenyls in Water by Microextraction and Gas Chromatography³

3. Summary of Practice

3.1 This practice employs liquid/liquid extraction to isolate compounds of interest. The sample is added to an extraction device. The solvent may be added to the sample container or an extraction device and extracted for a period of 5 min. The solvent is then ready for analysis. If required, the pH may be adjusted and salt may be added prior to extraction to increase the extraction specificity and efficiency.

3.2 The solvent extract may be further processed using sample clean-up and concentration techniques. The analytes in the solvent may be analyzed using instrumental methods for specific volatile or semivolatile organic compounds. This practice does not include sample extract clean-up methods.

4. Significance and Use

4.1 This practice provides a general procedure for the solvent extraction of volatile and semi-volatile organic compounds from a water matrix. Solvent extraction is used as the initial step in the solvent extraction of organic constituents for the purpose of quantifying extractable organic compounds.

4.2 Typical detection limits that can be achieved using micro-extraction techniques with gas chromatography (GC) with flame ionization detector (FID), electron capture detector (ECD), or with a mass spectrometer (GC/MS) range from milligrams per litre (mg/L) to nanograms per litre (ng/L). The detection limit, linear concentration range, and sensitivity of the test method for a specific organic compound will depend upon the sample clean-up, injection volume, solvent to sample ratio, solvent concentration methods used, and the determinative technique employed.

¹ This practice 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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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 11.02.

⁴ *Annual Book of ASTM Standards*, Vol 11.04.

4.3 Micro-extraction has the advantage of speed, simple extraction devices, and the use of small amounts of sample and solvents.

4.3.1 Selectivity can be improved by the choice of solvent (usually hexane or pentane) or mixed solvents, extraction time and temperature, and ionic strength of the solution.

4.3.2 Extraction devices can vary from the sample container itself to commercial devices specifically designed for micro-extraction. See 7.1 and 7.2.

4.3.3 A list of chlorinated organic compounds that can be determined by this practice includes both high and low boiling compounds or chemicals (see Table 1).

5. Interferences

5.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts or elevated baselines that can cause poor precision and accuracy. See Terminology D 1129.

5.1.1 Glassware should be washed with detergent, rinsed with water, followed by a rinse with distilled in glass acetone. Final drying is done by air or 103°C oven. Additional cleaning steps may be required when the analysis requires levels of micrograms per litre or below. Once the glassware has been cleaned, it should be used immediately or stored wrapped in aluminum foil (shiny side out) or by stretching a sheet of PTFE-fluorocarbon over the top for storage.

5.1.2 Plastics other than PTFE-fluorocarbon should be avoided. They are a significant source of interference and can adsorb some organics.

5.1.3 A field blank prepared from water and carried through sampling, subsequent storage, and handling can serve as a check on sources of interferences from the containers.

5.2 When performing analyses for specific organic compounds, matrix interferences may be caused by materials and constituents that are coextracted from the sample. The extent of

such matrix interferences will vary considerably depending on the sample and the specific instrumental analysis method used. Matrix interferences may be reduced by the choice of extracting solvent, or by using a clean-up technique on the extract.

6. Selection of the Extraction Solvent

6.1 The selection of solvent for extraction will depend upon many factors, including the following:

6.1.1 Solvent compatibility with analytical instrumentation,

6.1.2 Solubility of the organic constituent in the solvent versus its solubility in water. The water/solvent ratio has been found to be critical to achieve optimum recovery of some analytes (see Test Method D 3973). Typical solvent to sample ratios are 1 to 10 or 20. The ratio should be optimized for maximum recovery or detection of an analyte, or both,

6.1.3 The availability and purity of the solvent,

6.1.4 The boiling point and viscosity of the solvent,

6.1.5 The tendency of the solvent and matrix to form emulsions, and

6.1.6 Solubility of the solvent in the water.

6.2 The analyst should analyze sample blank using the potential solvent and demonstrate a recovery using a spiking procedure in the matrix of interest before applying this procedure for sample analysis.

7. Apparatus

7.1 *Volumetric Flasks*, 110 mL.⁵

7.2 *Liquid/Liquid Extractor*.⁶

7.3 *Vials*, auto sampler with septa and caps. Vials should be compatible with the automatic sample injector and should have an internal volume of not greater than 2 mL.

7.4 *Vial*, crimper.

7.5 *Bottles*, glass narrow mouth with TFE fluorocarbon-lined septum screw caps.

7.6 *Shaker*, wrist.

8. Reagents

8.1 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Type II of Specification D 1193.

8.2 Chromatographic grade solvents that have been distilled in glass should be used in all tests. Other grades may be used, if it is first ascertained that the solvent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.3 The extraction solvent of choice should be appropriate for the matrix and compounds of interest. This choice is dependent upon the chemical properties of the organic constituents of interest and the matrix being extracted.

8.4 The spiking, standard materials and surrogates should be reagent or ACS grade or better. When they are not available as reagent grade, they should have an assay of 90 % or better.

TABLE 1 Results of Flame Ionization Detector (FID) and Electron Capture Detector (ECD) Detectability^A

NOTE 1—Lowest levels tested.

	FID (µg/L)	ECD (ng/L)
Trichloroethene	2	5
Tetrachloroethene	2	5
Monochlorobenzene	1	500
para-Chlorobenzotrifluoride	1	5
ortho-Chlorobenzotrifluoride	1	5
ortho-Chlorotoluene	1	100
meta-Chlorotoluene	1	100
para-Chlorotoluene	1	100
1,2,4-Trichlorobenzene	1	5
1,2,3-Trichlorobenzene	1	5
Hexachlorobutadiene	1	5
1,2,4,5-Tetrachlorobenzene	1	5
Hexachlorocyclopentadiene	2	5
2,4,5-Trichlorophenol	2	100
1,2,3,4-Tetrachlorobenzene	1	5
alpha-Hexachlorocyclohexane	1	5
beta-Hexachlorocyclohexane	1	5
Hexachlorobenzene	1	5
gamma-Hexachlorocyclohexane	1	5
delta-Hexachlorocyclohexane	1	5

^A Based on the injection of chlorinated compounds in pentane solution, taking into consideration the 100:1 concentration of a water sample by the microextraction technique.

⁵ Cassia, available from Baxter, 1430 Waukegan Rd., McGaw Park, IL 60085, or equivalent, has been found suitable for this purpose.

⁶ Available from J & W Scientific, 91 Blue Ravine Rd., Folsom, CA 95630, or equivalent, has been found suitable for this purpose.