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An American National Standard

Standard Practice for Micro-Extraction of Water for Analysis of Volatile and Semi-Volatile Organic Compounds in Water[1]

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:* [2]

D 1129 Terminology Relating to Water

D 1193 Specification for Reagent Water

D 3370 Practices for Sampling Water from Closed Conduits

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

D 3856 Guide for Good Laboratory Practice in Laboratories Engaged in Sampling and Analysis of Water and Wastewater

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

D 4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data[3]

D 4448 Guide for Sampling Groundwater Monitoring Wells

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

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.

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

[1] This practice 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] 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.

[3] Withdrawn

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 microextraction. 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.

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

NOTE—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.

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.[4]

7.2 *Liquid/Liquid Extractor*. [5]

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.

8.5 *Hydrochloric Acid (HCl) or Sulfuric Acid Solution*—(H_2SO_4) (1:1 v:v), prepared by slowly adding 50 mL of acid to 50 mL of water.

8.6 *Sodium Hydroxide Solution* (NaOH), prepared by dissolving 40 g NaOH in water and diluting to 100 mL.

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

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

8.7 *Sodium Sulfate* (Na_2SO_4), reagent grade, granular, anhydrous, prepared by heating to 300°C under a flow of nitrogen.

NOTE 1—Nitrogen is only required when trace work using ECD is required.

8.8 *Magnesium Sulfate* ($MgSO_4$), reagent grade, granular, anhydrous, prepared by heating at 400°C for a minimum of 4 h in a shallow tray to eliminate interfering organics.

8.9 *Sodium Chloride* (NaCl), reagent grade, granular.

8.10 *Sodium Thiosulfate*—($Na_2S_2O_3$), reagent grade, granular.

9. Hazards

9.1 The toxicity and carcinogenicity of chemicals used or that could be used in this practice have not been precisely defined. Each chemical should be treated as a potential health hazard. Exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this practice.

9.2 If using ether solvents, the hazard of peroxides formation should be considered by testing for the presence of peroxide prior to use.

10. Sample Handling

10.1 There are many procedures for acquiring representative samples of water. The procedure chosen will be site and analysis specific. There are several guides and practices for sampling listed in the ASTM subject index under **Sampling-Water Applications**. Two good sources are Practices D 3370 and Guide D 4448.

10.2 The recommended sample size is 40 to 100 mL. More or less sample can be used depending upon the sample availability, detection limits required, and the expected concentration level of the analyte. Forty millilitre VOA vials are commonly used as sampling containers. Head space should be eliminated if volatiles analysis is required.

10.3 *Sample Storage*:

10.3.1 All samples must be iced or refrigerated to 4°C from the time of collection until ready for extraction.

10.3.2 Samples should be stored in a clean dry place away from samples containing high concentrations of organics.

10.4 *Sample Preservation*:

10.4.1 Some compounds are susceptible to rapid biological degradation under certain environmental conditions. If biological activity is expected, adjust the pH of the sample to about 2 by adding HCl. The constituent of concern must be stable under acid conditions. For additional information, see Practices D 3694.

10.4.2 If residual chlorine is present, add sodium thiosulfate as a preservative (30 mg/4 oz bottle).

NOTE 2—Any reagents added to the sample at the time of collection or before analysis must be added to the laboratory blank and standard. See 11.3.

11. Quality Control

11.1 Minimum quality control requirements are an initial demonstration of laboratory capability, analysis of method blanks, a laboratory fortified blank, a laboratory fortified sample matrix and, if available, quality control samples. For a general discussion of good laboratory practices, see Guide D 3856 and Practice D 4210.

11.2 Select a representative spike concentration (about three times the estimated detection limit or expected concentration) for each analyte. Extract according to Section 12 and analyze.

11.3 Method blanks must be prepared using reagent grade water and contain all the reagents used in sample preservation and preparation. The blanks must be carried through the entire analytical procedure with the samples. Each time a group of samples are run that contain different reagents or reagent concentrations, a new method blank must be run.

11.4 All calibration and quality control standards must be extracted using the same reagents, procedures, and conditions as the samples.

11.5 Precision and bias must be established for each matrix and laboratory analytical method.

11.5.1 Precision should be determined by splitting spiked samples or analytes in the batch into two equal portions. The replicate samples should then be extracted and analyzed.

11.5.2 Bias should be determined in the laboratory by spiking the samples with the analytes of interest at a concentration three times the concentration found in the samples or less.

NOTE 3—The bias may be decreased by keeping the temperature, shaking speed and time, ionic strength, and solvent and sample volumes constant.

12. Procedure

12.1 Remove samples from storage and allow them to equilibrate to room temperature.

12.2 Remove the container cap from the sample container. Withdraw and discard a pre-selected volume of sample to allow adequate volume for the addition of the solvent and space for adequate mixing during shaking. Five to 10 mL of sample is typically removed from a 40 mL vial.

12.3 Replace the container cap and weigh the container and its contents to the nearest 0.1 g. Record the weight for subsequent sample volume determinations (see 12.7). If a commercial device is to be used instead of the sample vessel for the extraction, make a volumetric transfer of the volume of the sample specified by the manufacturer to the extraction device and utilize this volume in 13.2, omitting the calculation in 13.1 and the weight measurements in 12.2 and 12.7.

12.4 Remove the container cap. If acid neutral or base compounds are of interest, adjust the pH to <2 for acid neutral and >11 for base compounds. Add the preselected volume of solvent to each extraction vessel (typically 1 to 2 mL of solvent per 40 mL of sample volume) and recap. Shake vigorously by hand for 5 min. Allow the water and solvent phases to separate. If ionic strength needs to be increased add approximately 0.1 g NaCl per 1 mL of sample before shaking.

NOTE 4—If the J&W liquid/liquid extractor [5] is used, water is added after the solvent and aqueous solutions are shaken and centrifuged. This forces the lighter-than-water sample/solvent layer into the graduated capillary tube. The sample/solvent is then recovered with a syringe and is ready for analysis.

NOTE 5—If the Cassia [4] is used, recap or crimp the TFE-fluorocarbon

coated disc in place before shaking.

12.5 Remove the cap and carefully transfer by disposable glass pipet approximately 0.5 mL of the solvent layer into an autosampler vial for analysis. If needed, sodium sulfate or magnesium sulfate may be used to dry the solvent.

12.6 Transfer the remaining solvent phase into a second autosampler vial; be careful not to include any of the water phase. Preserve this second vial at 4°C for an immediate reanalysis if necessary.

12.7 If further extraction is required under different pH conditions (acid neutral or base), carefully remove the remaining solvent from the sample, adjust the pH, and add the necessary fresh solvent volume. Repeat 12.4 and 12.5.

12.8 Discard the contents of the sample bottle in an environmentally safe manner. Shake off the remaining few drops using short, brisk wrist movements, replace the cap, and weigh the empty bottle to the nearest 0.1 g.

12.9 Analyze the extracts by the appropriate method(s) and correct the results for volume according to Section 13.

13. Calculation

13.1 Calculate the sample volume (V_s) in mL as equal to the net sample weight in grams as follows:

$$V_s = \textit{grossweight}\ (11.2) - \textit{tare weight}\ (11.7)$$

NOTE 6—Brine samples will require a correction for density if high accuracy is required. Samples with a high sediment content should be calculated based on weight to weight.

13.2 Calculate the corrected sample concentration as follows:

13.2.1 When uncorrected analyte concentration is known:

$$C = C_i \frac{X\ 1000}{V_s}$$

where:

C = concentration in µg/L,
C_i = uncorrected analyte concentration in µg/mL, and
V_s = volume of the sample in mL.

13.2.2 When only areas or peak heights are known:

$$C = S_c \times \frac{A_r}{S_r} \times \frac{E_x}{V_s} \times 1000$$

where:

C = concentration, in µg/L,
S_c = concentration of analyte in the standard, in µg/mL,
A_r = response in area or peak height of the analyte in the sample,
S_r = response in area or peak height of the standard for the analyte to be determined,
E_x = mL of extract, and
V_s = volume of sample extracted, in mL.

14. Precision and Bias

14.1 Precision and bias cannot be determined directly for this practice. However, this procedure was used in the determination of organohalide pesticides, polychlorinated biphenyls, and chlorinated organics. See Test Method D 5175.

14.2 Precision and bias should be generated in the laboratory on the parameters of concern.

14.3 Precision may be improved by the use of an internal standard. Where internal standards are utilized, add the internal standard to the extraction solvent container prior to aliquoting the solvent to the extraction vessel.

NOTE 7—The results of one laboratory determining chlorinated organics listed in Tables 1-3 are being included as information. A Cassia volumetric flask containing 100 mL of acidified sample was extracted with 1 mL of pentane solvent and analyzed using a gas chromatograph with flame ionization and electron capture detectors. The injection volume was 1 µL. Note that the bias information determined from the data will be greater than would be expected from this practice. The standard was not processed through the entire practice, which would minimize the bias of the practice.

15. Keywords

15.1 extraction; microextraction; sample preparation; semivolatile; volatile; water

TABLE 2 Recovery Data for Pentane Microextraction of 10 µg/L Spiked Field Samples

NOTE—Based on the Extraction of Six Spiked Water Solutions

	Average % Recovery	% Relative Standard Deviation
Trichloroethene	69	4
Tetrachloroethene	72	4
Monochlorobenzene	82	3
para-Chlorobenzotrifluoride	68	4
ortho-Chlorobenzotrifluoride	76	4
ortho-Chlorotoluene	88	4
meta-Chlorotoluene	88	4
para-Chlorotoluene	88	4
1,2,4-Trichlorobenzene	91	4
1,2,3-Trichlorobenzene	95	4
Hexachlorobutadiene	78	4
1,2,4,5-Tetrachlorobenzene	94	4
Hexachlorocyclopentadiene	84	4
2,4,5-Trichlorophenol	65	9
1,2,3,4-Tetrachlorobenzene	92	4
alpha-Hexachlorocyclohexane	94	5
beta-Hexachlorocyclohexane	87	5
Hexachlorobenzene	94	6
gamma-Hexachlorocyclohexane	96	4
delta-Hexachlorocyclohexane	91	5

TABLE 3 Summary of Recovery Data for the Pentane Microextraction of Spiked Field Samples [A]

	Average % Recovery	% Relative Standard Deviation
Trichloroethene	71	6
Tetrachloroethene	68	4
Monochlorobenzene	85	3
para-Chlorobenzotrifluoride	63	5
ortho-Chlorobenzotrifluoride	74	2
ortho-Chlorotoluene	88	2
meta-Chlorotoluene	90	4
para-Chlorotoluene	89	2
1,2,4-Trichlorobenzene	89	5
1,2,3-Trichlorobenzene	93	5
Hexachlorobutadiene	64	16
1,2,4,5-Tetrachlorobenzene	93	4
Hexachlorocyclopentadiene	75	10
2,4,5-Trichlorophenol	60	6
1,2,3,4-Tetrachlorobenzene	91	5
alpha-Hexachlorocyclohexane	95	2
beta-Hexachlorocyclohexane	86	2
Hexachlorobenzene	95	2
gamma-Hexachlorocyclohexane	97	2
delta-Hexachlorocyclohexane	90	3

[A] Average of five replicate spiked water solutions each at 20, 50, and 100 µg/L and six replicate spiked water solutions at 10 µg/L.