Designation: D 6889 – 03

An American National Standard

Standard Practice for Fast Screening for Volatile Organic Compounds in Water Using Solid Phase Microextraction (SPME)[1]

This standard is issued under the fixed designation D 6889; 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 a procedure for the screening of trace levels of volatile organic compounds in water samples by headspace solid phase microextraction (SPME) in combination with fast gas chromatography with flame ionization detection.

1.2 The results from this screening procedure are used to estimate analyte concentrations to prevent contamination of purge and trap or headspace analytical systems.

1.3 The compounds of interest must have a greater affinity for the SPME absorbent polymer or adsorbent than the sample matrix or headspace phase in which they reside.

1.4 Not all of the analytes which can be determined by SPME are addressed in this practice. The applicability of the absorbent polymer, adsorbent or combination to extract the compound(s) of interest must be demonstrated before use.

1.5 Where used it is the responsibility of the user to validate the application of SPME to the analytes of interest.

1.6 The values stated in SI units are to be regarded as the standard.

1.7 *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 Water[2]

D 1193 Specification for Reagent Water[2]

D 3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents[3]

D 3856 Practice for Evaluating Laboratories Engaged in Sampling and Analysis of Water and Wastewater[2]

D 4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data[2]

D 6520 Practice for the Solid Phase Micro Extraction (SPME) of Water and its Headspace for the Analysis of Volatile and Semi-Volatile Organic Compounds[3]

3. Summary of Practice

3.1 This practice employs adsorbent/gas extraction to isolate compounds of interest, see Practice D 6520. An aqueous sample is added to a small (2 mL) septum sealed vial. Salt is used to improve analyte recovery. After the addition of a surrogate standard and a short mixing cycle, a SPME fused silica fiber coated with a thick polymer film is then exposed to the aqueous headspace for a few seconds. The fiber is then desorbed in the heated injection port of a GC/FID or GC-MS and the resulting analytes chromatographed on a short narrow bore capillary column. The total analysis time is approximately 3 min.

3.2 The concentrations of the volatile organics in the water sample are estimated to determine whether the sample may be analyzed directly or first diluted prior to purge and trap or headspace analysis.

4. Significance and Use

4.1 This practice provides a general procedure for the solid-phase microextraction (SPME) of volatile organic compounds from the headspace of an aqueous matrix. Absorbent extraction is used as the initial step in the extraction of organic constituents for the purpose of screening and subsequently estimating the concentration of the volatile organic components found in water samples. This information may then be used to determine whether a sample may be analyzed directly by purge and trap or headspace or will require dilution prior to analysis.

4.2 Typical detection limits that can be achieved using SPME techniques with gas chromatography (GC) with a flame ionization detector (FlD) range from milligrams per litre (mg/L) to micrograms per litre (µg/L). The detection limit, linear concentration range, and sensitivity of this test method for a specific organic compound will depend upon the aqueous

[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] *Annual Book of ASTM Standards*, Vol 11.01.

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

matrix, the fiber phase, the sample temperature, sample volume, sample mixing, and the determinative technique employed.

4.3 Solid phase microextraction has the advantage of speed, reproducibility, simplicity, no solvent, small sample size, and automation.

4.3.1 Extraction devices vary from a manual SPME fiber holder to automated commercial devices specifically designed for SPME.

4.3.2 A partial list of volatile organic compounds that can be screened by this practice is shown in Table 1.

5. Principles of SPME

5.1 Solid phase microextraction is an equilibrium technique where analytes are not completely extracted from the matrix. With liquid samples, the recovery is dependent on the partitioning or equilibrium of analytes among the three phases present in the sampling vial: the aqueous sample and headspace (Eq 1), the fiber coating and aqueous sample (Eq 2), and the fiber coating and the headspace (Eq 3):

$$K_1 = C_L/C_g \quad (1)$$

$$K_2 = C_F/C_L \quad (2)$$

$$K_3 = C_F/C_G \quad (3)$$

where:

C_L, C_G, and C_F = concentrations of the analyte in these phases.

5.1.1 Distribution of the analyte among the three phases:

$$C_0V_L = C_GV_G + C_LV_L + C_FV_F \quad (4)$$

5.1.2 Concentration of analyte in fiber:

$$C_F = C_0V_LK_1K_2//V_G + K_1V_L + K_1K_2V_F \quad (5)$$

6. Interferences

6.1 Reagents, glassware, septa, fiber coatings and other sample processing hardware may yield discrete artifacts or elevated baselines that can cause poor precision and accuracy. See Terminology D 1129.

TABLE 1 Check Standard Composition for Screening VOCs in Water

Analyte	Sample Composition, µg/L	Detection Limit, µg/L
TBA	100 000	10 000
Methyl-t-butyl ether	1000	150
cis-1,2-Dichloroethene	3000	300
1,1,1-Trichloroethane	1000	200
Benzene	400	40
1,1,1-Trichloroethane	700	120
Toluene	200	10
Tetrachloroethene	300	50
Chlorobenzene	150	10
Ethylbenzene	100	5
m-Xylene	100	5
styrene	100	5
o-Xylene	100	5
Isopropylbenzene	100	5
2-Chlorotoluene	100	5
1,2,4-Trimethylbenzene	100	5
1,4-Dichlorobenzene-d4	150	5
1,2-Dichlorobenzene	100	5
Napthalene	100	5

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

7. Apparatus

7.1 *SPME Holder*, manual or automated sampling.

7.1.1 *SPME Fiber Assembly*—Polydimethylsiloxane (PDMS), 30uM or equivalent fiber suitable for volatiles adsorption.

7.2 *Vials with Septa and Caps*, for manual or automated SPME. Vials for automation, 2 mL.

7.3 *Gas Chromatograph*, with flame ionization detector.

7.3.1 *GC Column*, 10 m by 0.25 mm, 1uM film Methyl Silicone, or equivalent.

7.3.2 *GC Guard Column*, 1m by 0.32 mm uncoated, or equivalent.

7.3.3 *Split/splitless Injector*, with 0.75 to 1.0 mm inside diameter insert.

7.3.4 *Optional Septum Replacement Device*.

7.3.5 *Optional SPME Autosampler*.

7.3.6 *GC Compatible Workstation*.

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 Chemicals, 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.

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

8.4 *Surrogate Standard*, 30 mg/L, 1,4-dichlorobenzene-d_4 in methanol.

8.5 *Check Standard*—Prepare a check standard in methanol. Check standard should contain 30 mg/L 1,4-dichlorobenzene-d_4 plus VOCs that will be screened. A typical check standard will provide aqueous concentrations shown in Table 1 when spiking 4 µL of check standard to 700 µL water sample.

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.

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.

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-milliliter VOA vials are

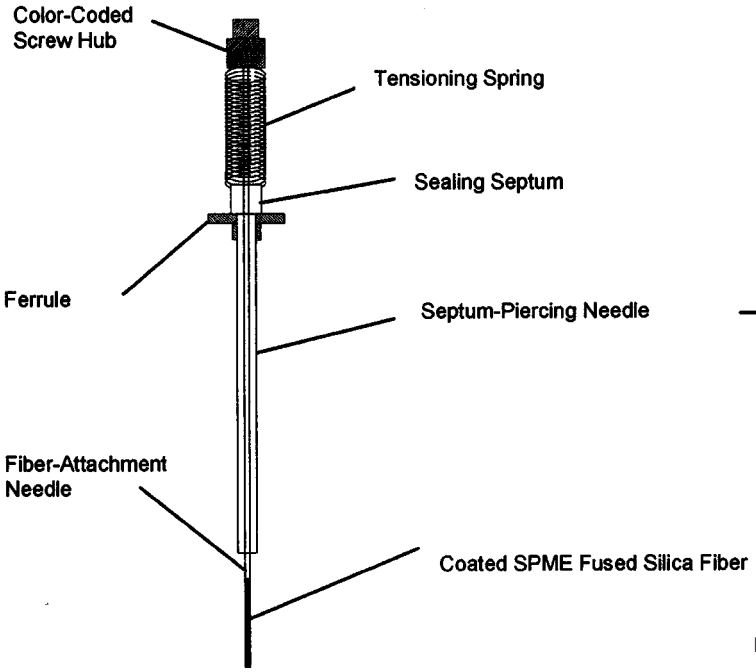

FIG. 1 Fiber Holder

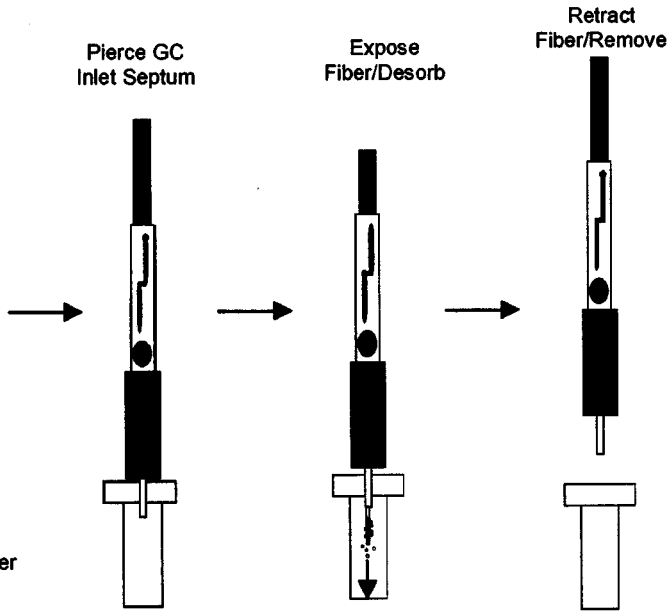

FIG. 3 Injection Followed by Desorption of SPME Fiber in Injection Port of Chromatograph

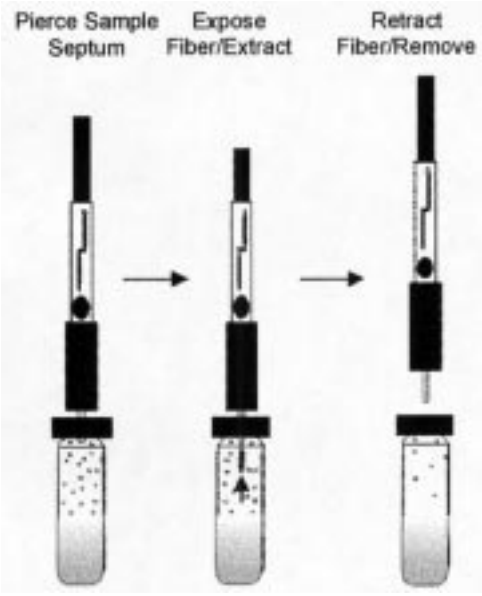

FIG. 2 Process for Adsorption of Analytes from Sample Vial with SPME Fiber

commonly used as sampling containers. Any headspace should be eliminated since 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 HCI. The constituents of concern must be stable under acid conditions. For additional information, see Practice D 3694.

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

11. Quality Control

11.1 Minimum quality control requirements include an initial demonstration of laboratory capability, analysis of method blanks and quality control check samples. For a general discussion of good laboratory practices, see Guide D 3856 and Practice D 4210.

11.2 Precision is initially determined by running at least five quality control check standards prepared by spiking reagent grade water with a methanol solution of target analytes. Subsequently, batch precision is determined by splitting spiked quality control check standards into two equal portions.

11.3 Method blanks are prepared using distilled or deionized water. The blanks must be carried through the entire analytical procedure with the samples. Each time a group of samples are run, several method blanks should be run.

11.4 A surrogate standard is added to each vial prior to SPME extraction.

11.5 Several quality control check standards should be run with each batch of samples to average one for every twenty samples. The QC check samples should demonstrate recoveries of ±30 %. Recalibration is necessary if this is not achieved.

11.6 One calibration standard at the highest concentration is required for each analyte to cover the concentration range being screened.

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

12. Procedure

12.1 Ahead of time prepare 2 mL septum-capped vials with 0.35 g NaCl.

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

12.3 Spike each vial with 4 µL surrogate standard solution (1,4-dichlorobenzene-d_4).

12.4 Remove the container cap from the sample container. Make a volumetric transfer of 0.7 mL of this sample to the 2 mL volume septum-capped vial.

12.5 Vortex each sample for approximately 5 to 10 s.

12.6 Insert SPME shaft through septum into headspace above sample.

12.7 Depress plunger either manually or automatically and expose fiber coating to headspace.

12.8 An extraction time of approximately 12 s is adequate. No mixing is required.

12.9 Following extraction, retract fiber into protective sheath and remove from vial.

12.10 Inject sheath through GC septum and in splitless mode depress plunger into a 250°C heated injector insert desorbing analytes to column. Desorption time is about 0.2 min.

12.11 Analyze desorbed analytes by GC/FID with the following parameters:

Injector, 250°C
GC Column Oven: 70°C for 0.2 min, 50°/min to 180°
Carrier Gas: Hydrogen, 12 psi head pressure
Detector: 250°C

13. Calibration, Standardization and Analysis

13.1 While the recovery of analytes with a SPME fiber is relatively low, the degree of extraction is consistent so that SPME is quantitative with linearity, precision and accuracy. Examples of upper and lower quantitation levels obtained with this screening technique are shown in Table 1.

13.2 For simple or clean sample matrices such as drinking water, external standard calibration is used.

13.3 Prepare calibration standards by spiking reagent water with a portion of the stock standard solution. Prepare a blank and a single calibration standard to cover the appropriate range. Analyze the solutions and record the readings. Repeat the operation a sufficient number of times to obtain a reliable average reading for each solution.

13.4 Construct a single point plus origin analytical curve by plotting the concentration of the standard versus its response as provided by the instrument workstation. Analyze the unknown using the same procedure and determine the approximate analyte concentration.

14. Precision and Bias

14.1 Precision and bias cannot be determined directly for this screening procedure. Precision and bias should be generated in the laboratory on the parameters of concern. Examples of this type of data may be found in the literature for volatile organic compounds; see References.

15. Keywords

15.1 screening; solid phase microextraction; SPME; volatile; water

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