Designation: D6520 – 18

Standard Practice for the Solid Phase Micro Extraction (SPME) of Water and its Headspace for the Analysis of Volatile and Semi-Volatile Organic Compounds[1]

This standard is issued under the fixed designation D6520; 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 procedures for the extraction of volatile and semi-volatile organic compounds from water and its headspace using solid phase micro extraction (SPME).

1.2 The compounds of interest must have a greater affinity for the SPME-absorbent polymer or adsorbent or combinations of these than the water or headspace phase in which they reside.

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

1.4 This practice provides sample extracts suitable for quantitative or qualitative analysis by gas chromatography (GC) or gas chromatography-mass spectrometry (GC-MS).

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

1.6 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 12.

1.8 *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:*[2]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D3370 Practices for Sampling Water from Closed Conduits
D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents
D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
D4448 Guide for Sampling Ground-Water Monitoring Wells

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

4. Summary of Practice

4.1 This practice employs adsorbent/liquid or adsorbent/gas extraction to isolate compounds of interest. An aqueous sample is added to a septum-sealed vial. The aqueous phase or its headspace is then exposed to an adsorbent coated on a fused silica fiber. The fiber is desorbed in the heated injection port of a GC or GC-MS or the injector of an high-performance liquid chromatography (HPLC).

4.2 The desorbed organic analytes may be analyzed using instrumental methods for specific volatile or semi-volatile organic compounds. This practice does not include sample extract clean-up procedures.

5. Significance and Use

5.1 This practice provides a general procedure for the solid phase micro extraction of volatile and semi-volatile organic compounds from an aqueous matrix or its headspace. Solid sorbent extraction is used as the initial step in the extraction of organic constituents for the purpose of quantifying or screening for extractable organic compounds.

[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.

5.2 Typical detection limits that can be achieved using SPME techniques with gas chromatography with flame ionization detector (FID), electron capture detector (ECD), or with a mass spectrometer (MS) range from mg/L to µg/L. The detection limit, linear concentration range, and sensitivity of the test method for a specific organic compound will depend upon the aqueous matrix, the fiber phase, the sample temperature, sample volume, sample mixing, and the determinative technique employed.

5.3 SPME has the advantages of speed, no desorption solvent, simple extraction device, and the use of small amounts of sample.

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

5.3.2 Listed below are examples of organic compounds that can be determined by this practice. This list includes both high and low boiling compounds.

Volatile Organic Compounds (**1-3**)[3]
Pesticides, General (**4, 5**)
Organochlorine Pesticides (**6**)
Organophosphorous Pesticides (**7, 8**)
Polyaromatic Hydrocarbons (**9, 10**)
Polychlorinated Biphenyls (**10**)
Phenols (**11**)
Nitrophenols (**12**)
Amines (**13**)

5.3.3 SPME may be used to screen water samples prior to purge and trap extraction to determine if dilution is necessary, thereby eliminating the possibility of trap overload.

6. Principles of SPME

6.1 SPME 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 (Phase 1), the fiber coating and aqueous sample (Phase 2), and the fiber coating and the headspace (Phase 3):

$$(\text{Phase 1})\quad K_1 = C_L/C_g \tag{1}$$

$$(\text{Phase 2})\quad K_2 = C_F/C_L \tag{2}$$

$$(\text{Phase 3})\quad K_3 = C_F/C_G \tag{3}$$

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

6.1.1 Distribution of the analyte among the three phases can be calculated using the following:

$$C_0V_L = C_GV_G + C_LV_L + C_FV_F \tag{4}$$

6.1.2 Concentration of analyte in fiber can be calculated using the following:

$$C_F = C_0V_LK_1K_2/V_G + K_1V_L + K_1K_2V_F \tag{5}$$

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

7. Interferences

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

7.1.1 Glassware should be washed with detergent, rinsed with water, and finally rinsed with distilled-in-glass acetone. Air dry or in 103°C oven. Additional cleaning steps may be required when the analysis requires levels of µg/L or below. Once the glassware has been cleaned, it should be used immediately or stored wrapped in aluminum foil (shiny side out) or under a stretched sheet of PTFE-fluorocarbon.

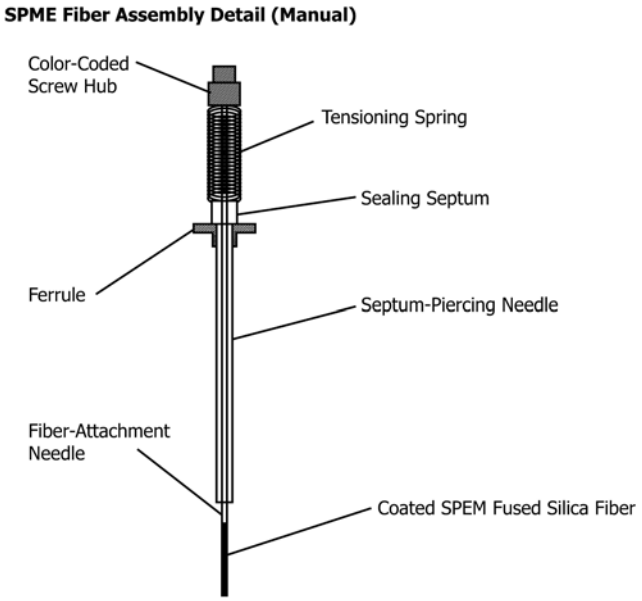
7.1.2 Plastics other than PTFE-fluorocarbon should be avoided. They are a significant source of interference and can adsorb some organics.

7.1.3 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.

7.2 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 choosing an appropriate SPME adsorbing fiber.

8. The Technique of SPME

8.1 The technique of SPME uses a short, thin solid rod of fused silica (typically 1-cm long and 0.11-µm outer diameter), coated with a film (30 to 100 µM) of a polymer, copolymer, carbonaceous adsorbent, or a combination of these. The coated, fused silica (SMPE fiber) is attached to a metal rod and the entire assembly is a modified syringe (see Fig. 1).



NOTE 1—This image originally appeared in *Advances in Chromatography*, Fig. 5, Vol 37, 1997, p. 218. Used with permission.

FIG. 1 SPME Fiber Holder Assembly