~~Designation:D6520–00~~

~~An American National Standard~~ Designation: D 6520 – 06

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 D 6520; 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 microextraction (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 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~~10.

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 ~~Practice for Evaluating Laboratories Engaged in Sampling and Analysis of Water and Wastewater[3]~~ Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water

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

D 4448 Guide for Sampling Ground~~w~~-Water Monitoring Wells

3. ~~Summary of Practice~~

~~3.1This 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 HPLC.~~

~~3.2The 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.~~ Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology D 1129.

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.

---

[1] This practice is under the jurisdiction of ASTM Committee ~~D-19~~ D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

~~Current edition approved Jan. 10, 2000. Published May 2000.~~

Current edition approved July 1, 2006. Published July 2006. Originally approved in 2000. Last previous edition approved in 2000 as D 6520 – 00.

[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* ~~, Vol 11.01.~~volume information, refer to the standard's Document Summary page on the ASTM website.

The fiber is desorbed in the heated injection port of a GC or GC-MS or the injector of an 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

~~4.1This~~5.1 This practice provides a general procedure for the solid-phase microextraction 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.

~~4~~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.

~~4.3SPME~~5.3 SPME has the advantages of speed, no desorption solvent, simple extraction device, and the use of small amounts of sample.

~~4~~5.3.1 Extraction devices vary from a manual SPME fiber holder to automated commercial device specifically designed for SPME.

~~4~~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. The numbers in parentheses refer to references at the end of this standard.

Volatile Organic Compounds (1,2,3)
Pesticides, General (4,5)
Organochlorine Pesticides (6)
Organophosphorous Pesticides (7,8)
Polyaromatic Hydrocarbons (9,10)
Polychlorinated biphenyls (10)
Phenols (11)
Nitrophenols (12)
Amines (13)

~~4~~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.

~~5.~~6. Principles of SPME

~~5.1SPME~~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):

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

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

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

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

~~5~~6.1.1 Distribution of the analyte among the three phases can be calculated using the following:

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

~~5~~6.1.2 Concentration of analyte in fiber can be calculated using the following:

(5) $CF = C0VLK1K2//VG + K\,1VL + K1K2VF$

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.

6.1.1 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.

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

6.1.3 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.

6.2 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. D6520-06_5

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

~~7.1The~~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).

~~7.2In~~8.2 In the standby position, withdraw the fiber into a protective sheath. Place an aqueous sample containing organic analytes or a solid containing organic volatiles into a vial, and seal the vial with a septum cap.

~~7.3Push~~8.3 Push the sheath with fiber retracted through the vial septum and lower into the body of the vial. Inject the fiber into the headspace or the aqueous portion of the sample (see Fig. 2). Generally, when 2-mL vials are used, headspace sampling requires approximately 0.8 mL of sample and direct sampling requires 1.2 mL.

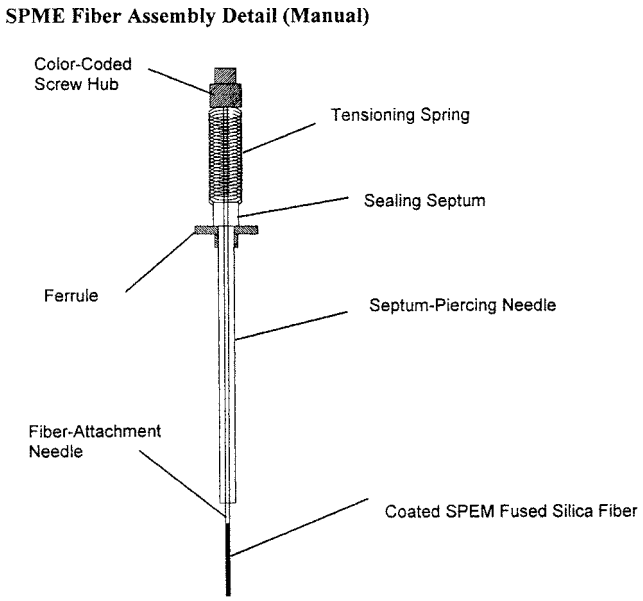
~~7~~8.4 Organic compounds are absorbed onto the fiber phase for a predetermined time. This time can vary from less than 1 min for volatile compounds with high diffusion rates such as volatile organic solvents, to 30 min for compounds of low volatility such as PAHs.

~~7~~8.5 Withdraw the fiber into the protective sheath and pull the sheath out of the sampling vial.

~~7~~8.6 Immediately insert the sheath through the septum of the hot GC injector (see Fig. 3), push down the plunger, and insert the fiber into the injector liner where the analytes are thermally desorbed and subsequently separated on the GC column.

~~7.6.1The~~8.6.1 The blunt 23-gage septum-piercing needle of the SPME is best used with a septumless injector seal. These are manufactured by several sources for specific GC injectors.

~~7.6.2A~~8.6.2 A conventional GC septum may be used with SPME. A septum lasts for 100 runs or more. To minimize septum failure, install a new septum, puncture with a SPME sheath three or four times, and remove and inspect the new septum. Pull off



NOTE 1—This figure is Fig. 5, p. 218, Vol 37, Advances in Chromatography, 1997. Used with permission.

FIG. 1 SPME Fiber Holder Assembly

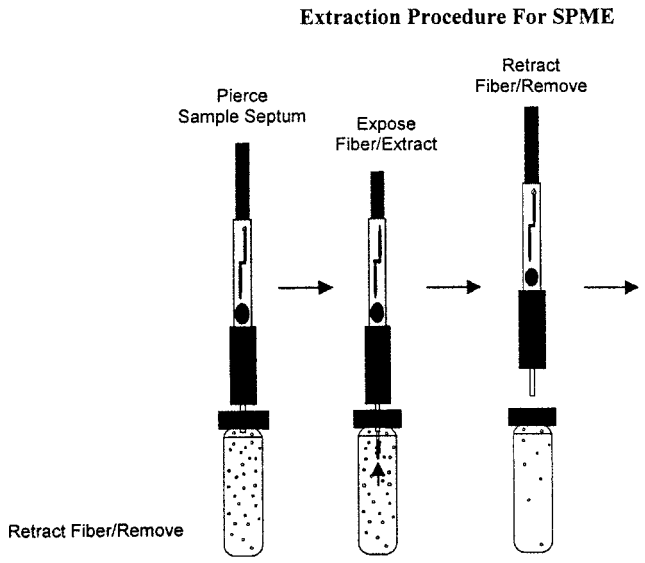


FIG. 2 Process for Adsorption of Analytes from Sample Vial with SPME Fiber

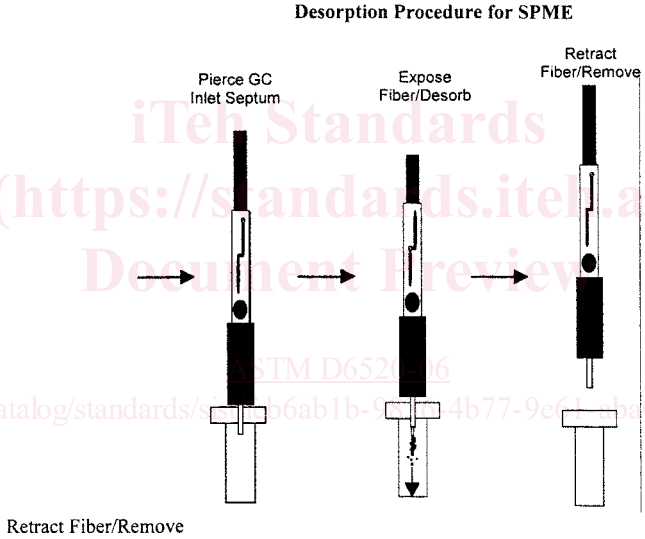


FIG. 3 Injection Followed by Desorption of SPME Fiber in Injection Port of Chromatograph

and discard any loose particles of septum material, and reinstall the septum.

~~7.6.3The~~8.6.3 The user should monitor the head pressure on the chromatographic column as the fiber sheath enters and leaves the injector to verify the integrity of the seal. A subtle leak will be indicated by unusual shifts in retention time or the presence of air in a mass spectrometer.

~~7~~8.7 Ensure that the injector liner used with SPME is not packed or contains any physical obstructions that can interfere with the fiber. The inner diameter of the insert should optimally should be about 0.75 to 0.80 mm. Larger inserts (2 to 4 mm) may result in broadening of early eluting peaks. SPME inserts are available commercially and may be used for split or splitless injection. With splitless injection, the vent is timed to open at the end of the desorption period (usually 2 to 10 min).

~~7~~8.8 Injector temperature should be isothermal and normally 10 to 20°C below the temperature limit of the fiber or the GC column (usually 200 to 280°C), or both. This provides rapid desorption with little or no analyte carryover.

~~8.~~9. Selection of Fiber Phase

~~8.1The~~9.1 The selection of the fiber phase depends on several factors, including:

~~8.1.1The~~9.1.1 The media being extracted by the fiber, aqueous or headspace,

~~8.1.2The~~9.1.2 The volatility of the analyte such as gas phase hydrocarbons to semivolatile pesticides, and

~~8.1.3The~~9.1.3 The polarity of the analyte.

~~8.2A~~9.2 A selection of fiber phases and common applications is shown in Table 1.