

Determination of BTEX in Water By SPME-GC/MS

Introduction

An analytical process usually consists of sampling, sample preparation, sample analysis, data interpretation, and report generation steps. Each step is critical for obtaining accurate and reproducible results. A sample preparation step is necessary to isolate the components of interest from a sample matrix since most analytical instrument can not handle the matrix directly. Sample preparation step sometimes includes "clean up" procedures, especially for very complex "dirty" samples. This step must also bring the analytes to a suitable concentration level. For example, before the determination of trace components present in soil or water can be determined, they must be isolated from the matrix, then concentrated, and often subjected to clean up. If the mixture is heterogeneous, mechanical procedures such as filtration and centrifugation may be necessary to separate the various phases. To separate the components of homogeneous mixture one must take advantage of the differing physical-chemical properties of the individual components. Such method as distillation, absorption, crystallization, and extraction are then applied. Sample preparation normally remains a bottleneck in analytical process, despite advances in instrumentation and computer technology. Sample preparation typically account for at least 30% of the errors encountered in the performance of analytical methods. Analysts sometimes may require 10 times as long as to prepare the sample for analysis than to perform the actual analysis. The biggest sources of error in sample preparation result from sample processing, operator error, and contamination. Improving these three sources alone can improve the quality of analytical results by 50%. Clearly, sample preparation is the most error-prone, tedious, and time-consuming step in analytical process. Many traditional techniques, like liquid / liquid extraction, are associated with problems such as the use of toxic, ozone depleting or carcinogenic organic solvents. Renewed awareness of the pollution and hazard caused by these compounds has resulted activities to eliminate and use of these organic solvents, and hence inducing a major change in sample preparation methodology. Sample preparation techniques that minimize the use of toxic, ozone depleting or carcinogenic organic solvents will therefore be welcome. Furthermore, if the new technique can also be simpler, faster and easy to automate, thereby increasing throughput, reducing errors and sample preparation step, its value would be enhanced even more. Among sample preparation techniques, solid phase microextraction (SPME) is one of the most attractive sample preparation techniques because SPME is a solvent-free and enrichment technique alternative to classical extraction and also liquid injection for a wide variety of analytes.

SPME was first developed in 1989 at the University of Waterloo (Ontario, Canada) by Pawliszyn and his group and has been marketed since 1993 by Supelco (Bellefonte, PA). Since then the technique has grown enormously.

In this extraction technique, analytes of interest are allowed to adsorb onto a small microfiber made of a fused silica coated with a thin-film of stationary phase.

Analytes either in the air or in an aqueous sample come into equilibrium with the fiber according to their affinity for the solid phase. The microfiber, which is incorporated into a gas chromatography (GC) syringe, is directly injected into the GC either manually or by automated system. Because the SPME fiber is heated at the GC injection port to allow the analytes to be desorbed from the fiber, the injection is directly to the GC without solvent.

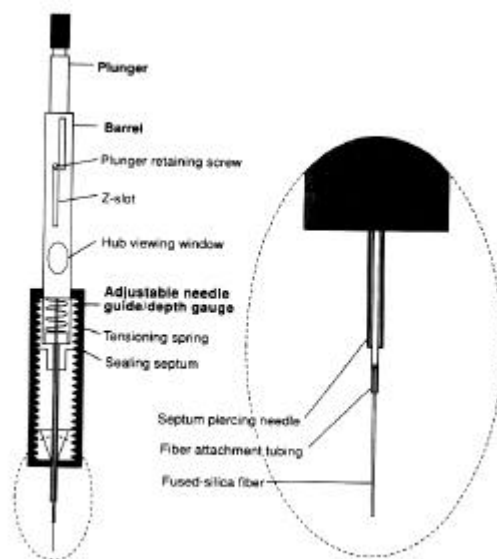


Figure 1 SPME device (taken from Ref.2).

A typical SPME, shown in Figure 1, is a syringe-like unit containing a fiber assembly that enables the analyst to retract and expose the fiber. To use the unit, the analyst first draws the coated fiber into the needle, passes the needle through the septum that seals the sample vial. Then pushing down on the plunger and locking the fiber in place can expose the fiber. The depth of the fiber can be adjusted by turning the black depth gauge for either direct fiber immersion in the solution or exposing the fiber to the headspace above solution. After a given amount of time, the analyst will sorb to the phase coated on the fused-silica fiber, aided by stirring of the sample solution. The sorption step typically reaches equilibrium about 2 to 30 minutes. It is not necessary that the analytes reach equilibrium; however, the extraction time between samples must be consistent. After sample sorption, the fused-silica fiber is withdrawn into the needle, and the needle is removed from the sample vial and introduced into an analytical instrument where analytes are removed by either thermal desorption typically in GC injector, or solvent desorption in HPLC system via SPME/HPLC interface. The fiber assembly is reusable. Currently, the commercial available fibers are polydimethylsiloxane (PDMS), PDMS/divinylbenzene (DVB), polyacrylate, Carbowax /DVB, DBV-carboxenTM-PDMS. The fiber will be selected according to the molecular weights and the polarity of the analytes. For examples, 100 μm polydimethylsiloxane (PDMS)-coated fiber for low molecular weight or volatile compounds, 30 μm or 7 μm for larger molecular weight or semivolatile compounds, 85 μm polyacrylated-coated fiber for very polar analytes from

polar samples, polydimethylsiloxane/divinylbenzene(PDMS/DVB)-coated fiber for volatile polar analytes (such as alcohols or amines), and 50/30 DVB/Carboxen on PDMS fiber for an expanded range of analytes (C3-C20).

Theoretical aspects of SPME

SPME is a two-step process, including the absorption of analytes onto the fiber and the desorption of analytes into an analytical instrument. Absorption is an equilibrium extraction technique, achieved through fiber immersion either directly into the liquid sample or in the headspace. The mass of an analytes extracted by the polymeric coating is related to the overall equilibrium of the analyte in the three-phase system described by the following expression:

$$n = [K_{fs}V_f C_0 V_s] / [K_{fs}V_f + K_{hs}V_h + V_s] \quad (1)$$

where n is the mass of analyte adsorbed by the coating; C_0 is the initial concentration of the analyte in the matrix; V_f , V_h and V_s are the volumes of the fiber coating, the headspace, and the matrix, respectively; K_{fs} is the fiber/sample matrix partition coefficient, and K_{hs} is the headspace/sample matrix partition coefficient.

If we assume that the vial containing sample is fully filled with the aqueous matrix (no headspace), the term $K_{hs}V_h$ can be eliminated leading to the simplified equation:

$$n = [K_{fs}V_f C_0 V_s] / [K_{fs}V_f + V_s] \quad (2)$$

Both Equations 1 and 2 clearly indicates that linear relationship between the amount of analytes absorbed by the fiber coating and the initial concentration of these analytes in a sample. In addition, Equation 2 also indicates that if V_s is very large ($V_s \gg K_{fs}V_f$), the amount of analyte extracted by the fiber coating

$$n = K_{fs}V_f C_0 \quad (3)$$

is not related to the sample volume. This feature, combined with its simple geometry, makes SPME ideally suited for field sampling and analysis. Because the fiber can be exposed to air or immersed directly into a well, lake, or river, for instance, SPME reduces field analysis time by combining sampling, extraction, concentration, and injection into a single uninterrupted process.

The speed of extraction is controlled by the mass transport of the analytes from the sample matrix to the coating. Agitation method such as magnetic stirring will increase the mass transport of the analytes. For volatile compounds, the headspace extraction method is preferred since the mass transfer of volatile compounds from the headspace to the fiber coating is very fast due to the large diffusion coefficient of analytes in the gas phase; volatile compounds transfer more efficiently than from water directly to coating. Generally, placing a fiber directly into a sample to extract relatively polar compounds and semivolatile compounds works well for relatively clean water samples. In the case of a

solid matrix or wastewater sample with grease, oil, and high molecular weight humic acid, however, direct sampling may not work well; sampling analytes from the headspace above the matrix is recommended.

Although SPME is mainly an equilibrium extraction technique, it has the ability to perform exhaustive extraction. If the coating/matrix partition coefficient, K_{fs} , is very large ($K_{fs}V_f \gg V_s$), the amount of analyte absorbed by the coating is $n = C_0V_s$, and exhaustive extraction can be achieved. Precision in SPME technique is typically about 5% RSD for manual operation and can be as low as 1% using an autosampler.

Several factors can influence the amount of analytes extracted by SPME, including the volume of the coating, the coating characteristics, derivatization of target analytes, modification of matrices, and heating the sample.

SPME has been applied to the analysis in various fields, such as environmental chemistry, forensic chemistry, pharmaceutical, food, beverage, and flavor.

In this experiment SPME will be used as sample preparation and enrichment technique that allows you to analyze BTEX (benzene, toluene, ethylbenzene, and xylenes) directly from a water sample.

Reagents

- 100 ppm BTEX methanolic stock solution.
- A BTEX unknown solution.

Procedure

GCD GC/MS which is based on a quadrupole mass analyzer will be used for collecting the data in this experiment. Please consult the instrument manual for operation of the GCD. Methods will also be provided to save your time. We will acquire the calibration data and an unknown sample in the scan mode. In experiment we will use special SPME insert of 0.75 mm i.d. This narrow insert will ensure the linear flow rate of the GC carrier gas can be obtained for efficient desorption during splitless injection mode.

1. Load method CH424SPM.M
2. From the data acquisition window, set up a sample run. Make a folder and use it to store the data for all the runs
3. Check that the split flow is approx. 20 mL (± 5 mL). You will be injecting in splitless mode. The purge time will be set to 1 minutes.
4. Condition the SPME fiber by desorption for 5 minutes in a GC injector. The GC column should then be temperature programmed to flush out the fiber impurities.
5. Prepare a series of standards 50, 100, 200, and 400 ppb solutions of BTEX in water by injecting, respectively 12.5, 25, 50, and 100 μ L of 100 ppm BTEX in methanol to the 25 mL water initially in the sample vial.

6. Beginning from standard 50 ppb BTEX in water put a stir bar in the vial. Then place the vial on a magnetic stirrer and set the revolutions to a moderate speed.
7. With the fiber retracted, pierce the vial septum with the SPME needle and lock it in the bottom position, then fasten the SPME device with a clamp.
8. Start the extraction by depressing the SPME plunger to expose the fiber to the headspace above the water sample. The position of the needle tip should be about 1 cm below the vial septum.
9. Allow the analytes absorb on the fiber for exactly 10 minutes.
10. Retract the fiber back to the needle and remove the needle from the vial.
11. Insert the needle of the SPME device into the GC injector, and quickly depress the plunger (and again lock it in the bottom position) to expose the SPME fiber in the heated zone of the injector to thermally desorb the analytes onto the GC column, and start the analysis.
12. After exactly 2 minutes desorption time, retract the fiber back to the needle and remove the needle from the GC injector.
13. Repeat steps 6-12 for other BTEX standards
14. Construct the calibration curves by plotting peak area vs. Concentration and obtain the best straight line based on linear regression.
15. Obtain BTEX unknown sample from your instructor. Pipet a 25-mL aliquot of this into the sample vial, then follow with the same procedure as the standards.
16. Estimate the concentrations of BTEX as they were supplied to you, and report the result in terms of 95% confidence limits.

References

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- (3) Pawliszyn, J. "Solid Phase Microextraction: Theory and Practice"; Wiley-VCH: New York, 1997; pp 193-204.