Liquid-Phase Headspace Micro-extraction Into a Single Drop

by Alexander Y. Nazarenko

Sample preparation is a necessary part of any analytical procedure. The continuous search for better sample preparation procedures has led to new methods, the main advantages of which are short processing time and negligible quantity of solvents used. Indeed, in many common analytical methods, the volume of the analyte is very small. In gas chromatography, this volume is around 1–3 µL, while in HPLC and graphite furnace atomic adsorption spectrometry (GFAAS), it is usually around 5–20 µL. Therefore, the traditional sample preparation procedures resulting in volumes of several milliliters may lead to unnecessary dilution of the analyte and waste of time and reagents.

Among the microextraction procedures developed in recent years, the most well known and efficient is solid-phase microextraction (SPME).[1] Some difficulties are still present when the extraction of highly hydrophilic volatiles is attempted. The liquid-phase analogue (liquid-phase microextraction, LPME) has also been developed. Most LPME designs include liquid–liquid extraction from the bulk aqueous phase into a small volume of organic solvent immiscible with water.[2,3] Single-drop microextraction (SDME) was employed to transfer hydrophobic analytes into a drop of organic solvent with further GC or HPLC determination.[4]

For many complex samples, headspace extraction is the fastest and cleanest method for analyzing volatile components in dirty matrixes.[5] The possibility of applying headspace microextraction into a single drop of ethylene glycol has been demonstrated.[6] Another design, in which extraction occurs inside the syringe, was suggested for chlorobenzenes.[7]

The flame ionization detector (FID) is insensitive to nonhydrocarbons such as water and carbon disulfide. Thus, they are attractive solvents for microextraction (no blank signal). This paper suggests the use of ultrapure water as a solvent for headspace microextraction of hydrophilic volatiles and carbon disulfide as a possible medium for hydrophobic volatiles.

Instrumentation

An HP5890 gas chromatograph (**Agilent Technologies Inc.,** Palo Alto, CA) with FID and nitrogen as a carrier gas was used throughout this work.

Procedure

A sample (usually 5–10 mL) was placed into a 25-mL vial covered with a membrane (*Figure 1*). The needle of a 10-µL GC syringe (**Hamilton Co.,** Reno, NV) containing water was introduced into the vial; the plunger was gently pushed to create a 1-µL drop (*Figure 2*). Volatile compounds first evaporated from the
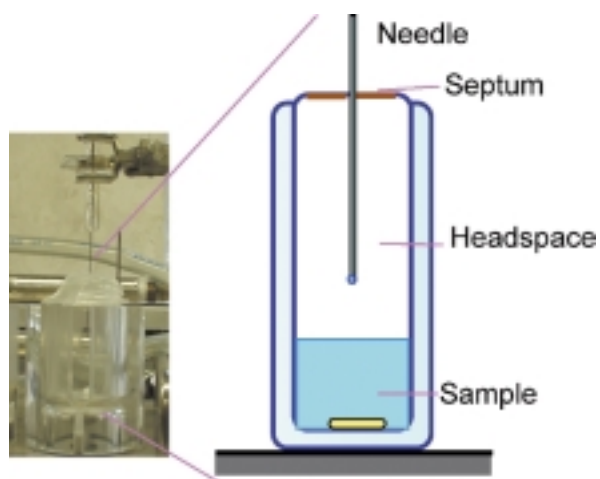

Figure 1   *Simple device for headspace LPME. Stirring and thermostating are optional.*
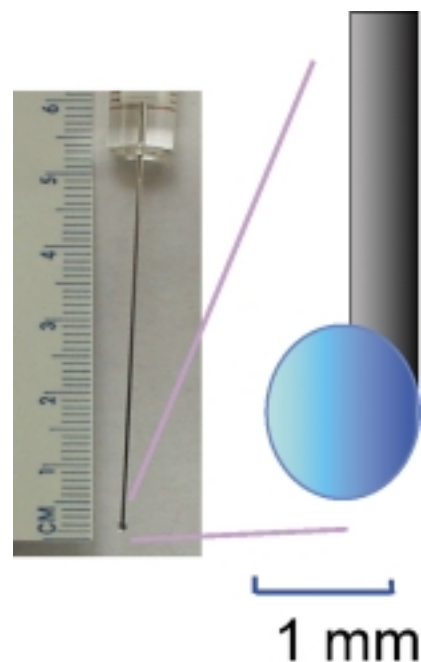

Figure 2   *A 1-µL water drop at the end of a syringe needle.*

sample into headspace and were then extracted from the headspace into a drop of water. After 2–3 min, the drop was retracted into the needle
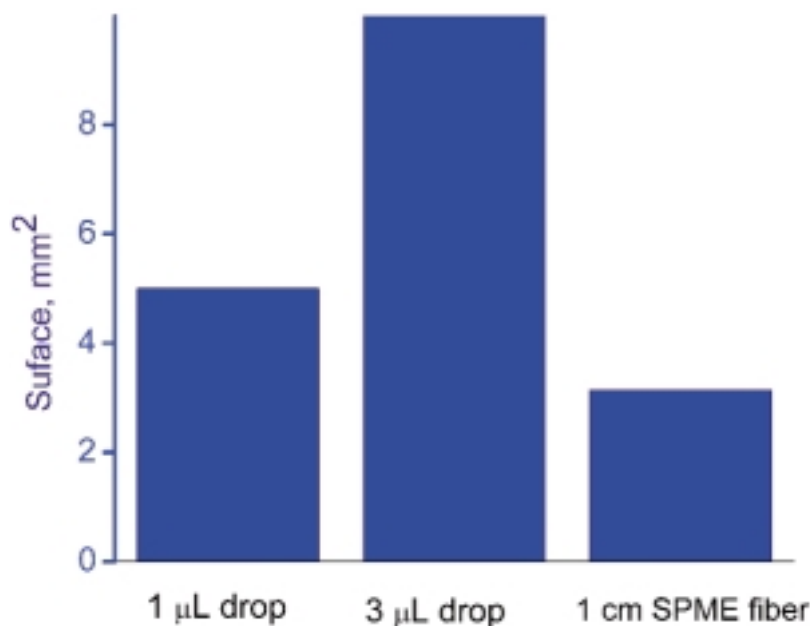
Figure 3   Surface area of 1- and 3-μL liquid drops and of a 1-cm-long SPME fiber (diam 100 μm).
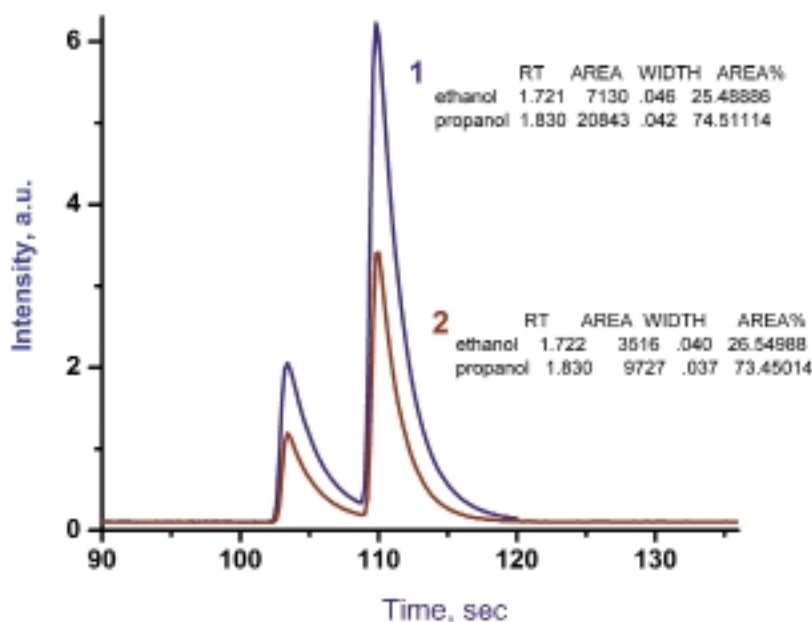

Figure 4   Chromatograms of source (1) and receiving (2) aqueous samples containing ethanol and propanol. Because of the short extraction time, the equilibrium is not reached, and the concentration of alcohols in a drop is visibly smaller than in a source solution. Nevertheless, it does not affect the results if an internal standard is employed.

and then injected into the GC instrument for further separation and determination. Adjusting the temperature and mixing improved the transfer of volatile analytes from the sample into the headspace of the vial.

Results and discussion

The natural limitation of headspace LPME is the rapid evaporation of small amounts of volatile liquids. Simple tests show that even in open air, the 1-μL water drop is stable for more

than 7 min at 25 °C. Inside the vial with an aqueous sample, no change in drop volume was visible after 20 min. Therefore, a 2–3 min extraction does not affect the water drop. Because of faster evaporation of volatile solvents, larger drop volumes and strict time control may be suggested for non-aqueous extraction. Presaturation of headspace volume with a small, calculated amount of extractant is another possible solution.

The surface area of a liquid drop is visibly larger than that of an SPME fiber (*Figure 3*), resulting in a relatively fast extraction process. Because a new drop is employed for each consecutive extraction, no memory effects are observed.

As an example, the results of alcohol determination in an aqueous sample are presented in *Figure 4*. Propanol or *t*-butanol was employed as an internal standard. Separate peaks for all propanols and butanols were easily achieved. The determination of 0.16 mg/mL ethanol showed a relative standard deviation of 10%, which is similar to most SPME procedures. Minimal extraction of hydrophobic hydrocarbons was detected in appropriate tests.

It has been shown[8] that injecting water does not harm the stationary phase of most capillary columns. Many of the problems associated with water injections are caused by other phenomena, such as backflash. To minimize these problems, it is important to use liners with large volumes, lower the injector temperature, and maintain a high column head pressure and carrier gas flow rate.

To extract hydrophobic hydrocarbons, carbon disulfide was tested. Shorter extraction times (80–100 sec) and a larger starting drop volume (3 μL) resulted in the reproducible extraction of aromatic hydrocarbons such as toluene, ethylbenzene, and xylenes with only a

small solvent peak visible from the FID. The extraction of hydrophilic compounds (ethanol, propanol, etc.) was reduced by two orders of magnitude relative to extraction in water.

Conclusion

Headspace liquid-phase microextraction provides a simple, low-cost alternative method for the analysis of volatile compounds. It is amenable to future developments with methods other than GC-FID. The use of water, a 100% "green" solvent, is an attractive, albeit risky, approach for the extraction of hydrophilic volatiles.

References

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