TECHNIQUES IN ON-LINE SAMPLE PREPARATION FOR BOTH GAS AND LIQUID CHROMATOGRAPHY

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Introduction

The off-line automation of many sample preparations has become possible with the development over the past two decades of robust Solid-Phase Extraction (SPE) products and methods. While the chemistry of extraction is now well described for many different sample types, conventional SPE devices do not lend themselves to simple on-line use with gas or liquid chromatographic systems.

Micro-solid-phase Extraction (µ-SPE)

µ-SPE columns (Figure 1) are miniaturized SPE columns that are suitable for the processing of very small samples (< 30µL of sample is required) and the minimization of reagent and solvent consumption. Because the devices retain the original chemistries of conventional SPE devices, chemistries and methods are directly transferable from conventional devices. The scale of the devices means that only the quantity of sample required for analysis need be prepared and extracted. Because the SPE column is incorporated directly into an autosampler needle, void volumes are reduced to the needle volume (Figure 2).

The effectiveness of the µ-SPE column is demonstrated for the extraction of caffeine and its metabolites from urine in a scaled version of a convention SPE method (Figure 3). The µ-SPE is particularly useful for on-line matrix exchange and desalting of biological specimens prior to LC or LCMS analysis.

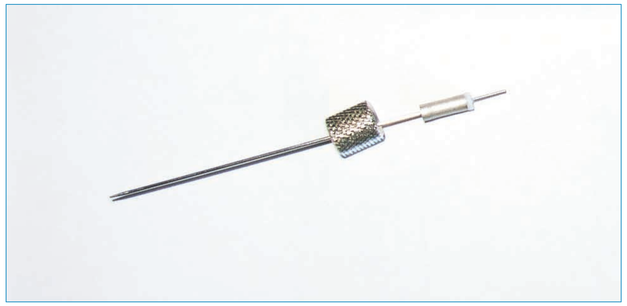

Figure 1. *A µ-SPE column ready to be fitted to a gas-tight syringe (total void volume < 10µl).*

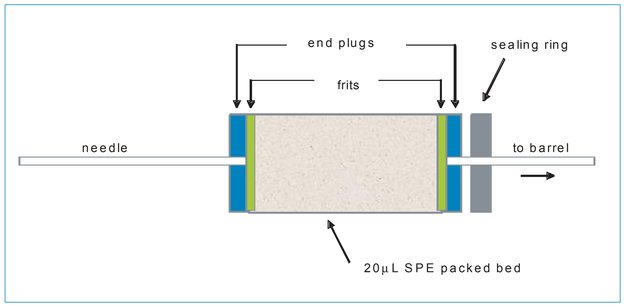

Figure 2. *A schematic view of a µ-SPE column.*

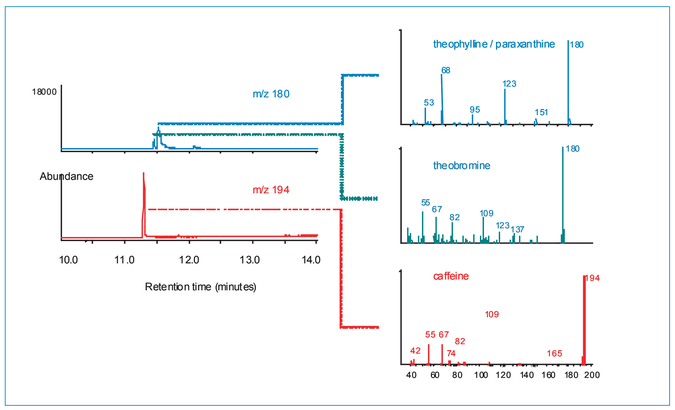

Figure 3. *Caffeine and metabolites in human urine by µSPE and GCMS.*

Conditions: 100µL human urine on a 40µm µC18 column that was conditioned with . Methanol (30µL) and water (30µL). After sample loading, the column was washed with water (30µL) and eluted with methanol (30µL). A 2µL portion of sample was analysed by GCMS on a BPX5 column without further preparation.

Conclusion

- In-syringe micro solid-phase (µSPE) is a method for purification or speciation of small samples that may be used both online with automated injector systems and as a standalone sample preparation device.

- The small bed volumes and low backpressures make the packed bed cartridges particularly useful for LC and LCMS applications that require solvent exchange, desalting and preconcentration.

In-needle Immobilized Liquid Phase Extraction (iLPE)

iLPE is based on a phase-coated headspace needle and is designed for use primarily with GC. The devices may be used for sampling both headspace and liquid samples but are more robust than SPME fibres. Extraction efficiency is determined primarily by partition-coefficients and is influenced by temperature and surface area of the liquid-phase. Selection of different immobilized liquid phases makes iLPE a useful way to achieve selective sampling for specific applications. The needle and capillary are excellent thermal conducts allowing sampling at ambient temperature followed by rapid desorption into a GC injector port.

The iLPE needles can be fitted to a conventional autosampler syringe or gas-tight syringe for use with headspace samples (Figure 4). Solvent desorption is also possible for on-line use with LC inlets.

The effectiveness of the iLPE needle is demonstrated for the extraction of volatile esters alcohols and aldehydes from ripe banana peel as a small volume alternative to a convention headspace method (Figure 5).

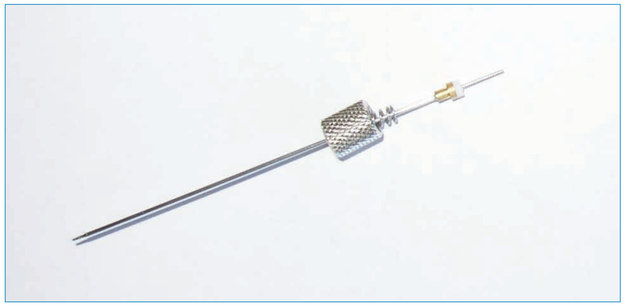

Figure 4. : *A picture of the iLPE needle ready to be fitted to a gas-tight GC syringe*

Conclusion

iLPE sampling devices are suitable for the on-line preparation of gas or liquid samples down to a sample size of a few microlitres. The sorbents described have well established chemistries, are resistant to fouling by macromolecules in biological samples and may be used in either solvent elution or thermal desorption modes or a combination of both. The devices are ideal for use with autosamplers for on-line use.

- iLPE is an alternative to traditional headspace and SPME enhanced headspace analysis.

- The temperature and surface area dependence of extraction rate offers the opportunity for focusing or concentration of particular analytes in a way that is not possible with conventional headspace techniques.

- Trapping and desorption allows the analysis of headspace samples with small gas volumes using conventional GC inlet methods.

- Because the liquid phase is not a bonded sorbent, iLPE is not affected by secondary retention of analytes, inorganic or highly polar organic materials by polar support materials.

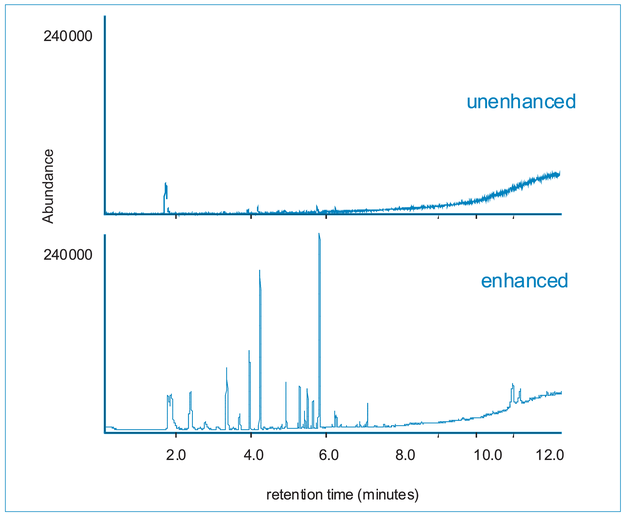

Figure 5. *Volatile esters in banana skin sampled by conventional headspace and iLPE technique.*

Conditions were 100mg of the ripe banana peel at 25°C in a sealed 1mL vial. Sampling for iLPE included 10 x100µL fill strokes at 25µL/s on a 3 µm film of BPX5 phase. Injection was 20µL headspace using a hot needle injection at 190 °C with 3s preheating and an injection speed of 2uL/sec.

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