Article

Solid phase extraction

Christie Lombardi

Department of Chemistry, University of Otago, PO Box 56, Dunedin 9054, and Department of Chemistry, University of Victoria, Victoria, BC V8P 5C2, Canada (email: *lombardi@uvic.ca*)

Keywords: *analytical chemistry, chromatography, sample preparation*

Christie is visiting the University of Otago as a summer research intern from the University of Victoria, Canada, where she is about to enter her final year of undergraduate chemistry studies towards a BSc(Hons) degree. Her research at Otago with Dr Kim Hagemann concerns a multi-residue pesticide analysis of regional honey bee populations.

Introduction

Sample preparation is a critical step in the analysis of environmental and biological samples. This transformation of the bulk sample to a form suitable for analysis has been estimated to take 80% of the typical total analysis time.[1] In analytical chemistry, an important part of sample preparation is the quantitative extraction of the compounds of interest (analytes) from the other components of the sample (the matrix) which may interfere with instrumental analysis.

Historically, liquid-liquid extraction has been widely used in analytical chemistry for the extraction of analytes from environmental samples. In recent decades, however, solid phase extraction (SPE) has rapidly developed as a useful alternative technique. In solid phase extraction, a liquid sample is passed through sorbent particles (the solid phase) to which the analytes have a greater affinity than the bulk liquid. The analytes are selectively retained by the sorbent and subsequently extracted from those particles by elution with an appropriate liquid solvent. This method of extraction simplifies the analysis through removal of much of the sample matrix.[2]

Although the technique of solid phase extraction was first applied experimentally in the late 1940s,[3] the developments leading to its widespread use and adoption into current analytical methods started in the 1970s. Solid phase extraction techniques were initially used to concentrate small amounts of organic pollutants from water, but its use has now extended to a wide variety of matrices including serum, blood, urine, milk, oils, sediments, soils, plant and animal tissues, and pharmaceutical preparations.[1,4,5]

Solid phase extraction modes and sorbents

The main modes of solid phase extraction are reversed phase, normal phase, and ion exchange. These methods differ in how the compound of interest is retained. Reversed phase SPE aims to remove nonpolar analytes from a polar matrix. A hydrophobic solid phase is used to retain the analytes and organic solvents are used for elution. Normal phase SPE uses a polar solid phase to extract polar compounds from a nonpolar sample matrix. Typically a solvent that is more polar than the sample's original matrix is then used to elute the analytes. Ion exchange SPE is used for compounds that are charged when in a solution. In this case, sample pH may be adjusted before extraction and organic solvents are used for elution.

Solid phase extraction sorbents are available in a variety of formats: contained in cartridges, in columns similar to syringe barrels, in disks, or in bulk. Typical sorbents are based on either functionalised silica or polymers, but carbon nanotubes, biosorbents, and nanoparticles have also recently come into use.[6]

Typical materials for column housings are made of glass or polypropylene with the sorbent contained by polyethylene, stainless steel, or Teflon frits. Samples may be extracted using individual columns (Fig. 1), vacuum manifolds accommodating 12-24 samples, using a vacuum flask assembly, or large volume samplers. When selecting the appropriate solid phase extraction mode and equipment, the sample volume, matrix, and anticipated concentration of analytes must all be considered.

General procedure for solid phase extraction

There are four typical steps for solid phase extraction: sorbent conditioning, sample loading, washing, and elution (Fig. 2). Once the extraction is complete, the eluate is ready for instrumental analysis.

The conditioning step prepares the sorbent by making it compatible with the liquid solution, promoting better surface contact, and removing any impurities or contaminants present. Typically, a volume of 5-60 mL of solvent[7] is adequate for a sorbent in an SPE tube or disk.

Once the sorbent has been conditioned, the sample is quantitatively transferred onto the column and allowed to pass through using vacuum, applied pressure, or a pump. The flow rate depends on the analytes, column dimensions, and the sorbent particle size. In all cases flow rate should be kept reasonably constant and, although dropwise flow is ideal, flow rates from 2-50 mL/min are typical.[7] As the sample passes through the column, the analytes are retained while undesired matrix components pass through.

Once the sample has passed through the column the sorbent is washed by passing a carefully chosen solution or solvent through the column. The aim of this step is to re-

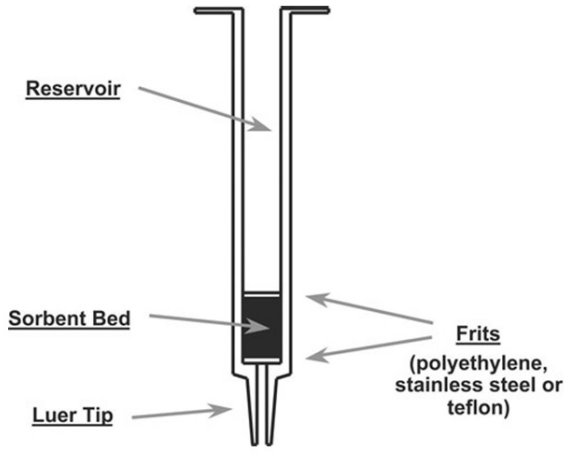

Fig. 1. Typical SPE column [adapted from ref. 7]

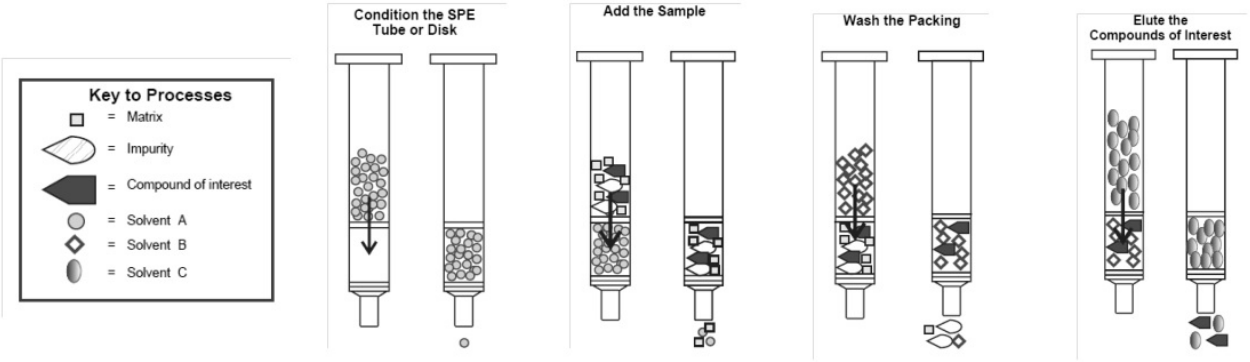

Fig. 2. The solid phase extraction process [adapted from ref. 5]

move undesired matrix components while retaining the analytes. Typically, volumes of 5-60 mL of solvent[7] for SPE tubes or disks are used for the wash step.

The final step in the extraction process is to recover the analytes using an elution solvent. The analytes are removed from the sorbent and returned to a liquid phase appropriate for analysis while undesired components, which were not removed in the wash step, are left behind. The elution solvent, typically 200 µl to 10 mL of an organic liquid,[7] is added to the column and collected. A well-chosen elution solvent will use as small a volume as possible to completely extract the analytes from the solid phase.

Prior to extraction, additional sample pretreatments such as pH adjustment, filtration or addition of organic solvents may be required to enhance the retention of the analytes on the solid phase. The sample volume, matrix, sorbent type, and analytes will dictate the necessary sample preparation.

Advantages of solid phase extraction

Solid phase extraction has a number of advantages over liquid-liquid extraction that have led to its rapid development and increasing usefulness as a sample preparation technique. These benefits include faster, less labour intensive sample manipulation, reduced solvent use, and higher concentration factors.[1,4,5]

Rapid, easily performed extractions make solid phase extraction an attractive alternative to liquid-liquid extraction. Large volume samples can easily be accommodated, multiple extractions can be carried out simultaneously, and the process can be readily automated. Liquid-liquid extraction, by contrast, requires significant and labourious manipulation of the sample, the automation of which is difficult.

Reduced solvent use is another advantage of solid phase extraction. The large volumes of organic solvents required for liquid-liquid extraction pose issues concerning its appropriate disposal, analyst exposure, and potential contamination of sample extracts. Solid phase extraction uses significantly less organic solvents than liquid-liquid extraction, reducing both costs and exposure.

Solid phase extraction achieves a concentration of analytes due to the small elution volumes used for extraction from the sorbent material. Liquid-liquid extraction concentration factors (a measure of how much more concentrated an analyte is in the extract than in the sample) are limited by the volume ratio of the sample and solvent. Concentration factors of 1000 or more are possible using solid phase extraction, where a highly efficient liquid-liquid extraction may only achieve a concentration of 100.[8]

SPE in action

While solid phase extraction may be used as a stand-

alone method for sample preparation, in recent years it has also proven to be useful as a pre-concentration step in other analytical procedures. For example, capillary electrophoresis (CE) is a valuable analytical method which provides high resolution separation with small sample volumes, but has low sensitivity when used with relatively dilute samples. Coupling solid phase extraction with capillary electrophoresis allows for the simultaneous concentration and clean-up of large sample volumes before injection on the CE instrument, resulting in improved sensitivity and lower detection limits.[9] This particular application of solid phase extraction has been used in capillary electrophoretic analyses of acidic pharmaceuticals in river water,[10] the detection of amines in wine,[11] the determination of insulin derivatives in biological fluids,[12] antioxidants in olive oil,[13] and melamine residues in milk.[14]

Conclusions

Solid phase extraction techniques, methods, and materials are continually being refined and developed. Innovations in sorbent materials and miniaturisation techniques such as solid phase microextraction and hyphenated capillary electrophoresis,[10] liquid chromatography,[15] and NMR techniques[16] indicate that solid phase extraction will continue to offer new solutions to the challenges facing analytical chemists.

References

1. Buszewski, B.; Szultka, M. *Crit. Rev. Anal. Chem.* **2012,** *42*, 198-213.
2. Harris, D. *Quantitative Chemical Analysis*, W.H. Freeman and Company: New York, 8th edn. 2010.
3. Liška, I. *J. Chromatogr. A* **2000,** *885*, 3-16.
4. Mitra, S. *Sample Preparation Techniques in Analytical Chemistry*, John Wiley & Sons, Inc.: Hoboken, New Jersey, 2003.
5. Supelco, *Guide to Solid Phase Extraction*, Bulletin 910, Sigma-Aldrich Co.: 1998.
6. Wan Ibrahim, W. A.; Abd Ali, L. I.; Sulaiman, A.; Sanagi, M. M.; Aboul-Enein, H. Y. *Crit. Rev. Anal. Chem.* **2014,** *44*, 233-254.
7. Fritz, J. S. *Analytical Solid-Phase Extraction*, Wiley-VCH: New York, 1999.
8. Biotage, www.biotage.se (accessed 1/09/2012).
9. Puig, P.; Borrull, F.; Calull, M.; Aguilar, C. *Anal. Chim. Acta* **2008,** *616*, 1-18.
10. Maijó, I.; Borrull, F.; Calull, M.; Aguilar, C. *Electrophoresis* **2011,** *32*, 2114-2122.
11. Arce, L.; Ríos, A.; Valcárcel, M. *J. Chromatogr. A* **1998,** *803*, 249-260.
12. Visser, N. F. C.; Van Harmelen, M.; Lingeman, H.; Irth, H. *J. Pharm. Biomed. Anal.* **2003,** *33*, 451-462.
13. Nevado, J. J. B.; Robledo, V. R.; Callado, C. S. C. *Food Chem.* **2012,** *133*, 497-504.
14. Sun, H.; Liu, N.; Wang, L.; He, P. *J. Chromatogr. Sci.* **2010,** *48*, 848-853.
15. Christophoridou, S.; Dais, P.; Tseng, L. I. H.; Spraul, M., *J. Agric. Food Chem.* **2005,** *53*, 4667-4679.
16. Jaroszewski, J. W. *Planta Med.* **2005,** *71*, 795-802.