

Review Article

An Overview about Recent Advances of Micro-Solid Phase Extraction in Flow Based Techniques

Warunya Boonjob*

Department of Analytical Chemistry, Charles University,
Czech Republic

*Corresponding author: Warunya Boonjob,
Department of Analytical Chemistry, Charles
University in Prague, Heyrovského 1203, 500 05,
Hradec Králové, Czech Republic

Received: July 02, 2014; Accepted: July 13, 2014;

Published: July 16, 2014

Most of samples such as environmental or biological samples are usually not ready for direct introduction into the analytical instruments [1]. Sample preparation is an important and essential step which aimed to transform target compounds to a form and concentration suitable for analysis. In the analytical procedures, sample preparation is the slowest and the most costly part of the analytical process. Particularly multi-step procedures are utilized which takes about 50-75% of the total time of the analysis [2]. For this reason, the faster sample preparation can be done, the more quickly the analysis will be completed. Thus, sample preparation is required highly reproducibility and without considerable loss of the analyses.

Solid Phase Extraction (SPE)

Solid phase extraction (SPE) is a widely sample preparation method prior to chromatographic technique [3] which based on transfers of analyses from the liquid sample matrix to the solid sorbent. Knowledge of the hydrophobic, polar and/or ionogenic properties of both analyses and sorbent due to the selection of appropriate conditions of the liquid matrix and the sorbent according to the physico-chemical properties of the analyses, namely van der Waals forces (non-polar interactions), hydrogen bonding, dipole-dipole forces (polar interactions) and action-anion interactions (ionic interactions) are required.

A typical SPE procedure involves the following steps

Conditioning - the sorbent is activated by wetted with a suitable solvent to activate the functional groups on its surface, afterward followed by water.

Loading - the sample is percolated through the sorbent.

Washing - interfering or non specific components of the matrix are removed while taking care not to elude the analytes as well.

Elution - analytes of interest are eluted with an appropriate solvent and further pre-concentration takes place by evaporation with N₂ gas and reconstitution in desired medium prior to analysis.

Retention and capacity are more relevance parameters influencing the efficiency of the SPE process. In this context, retention of analyses on the sorbent should be maximum during the loading and washing steps but minimal during the elution step. Method development in

Abstract

Sample preparation makes appearance on faster and more reliable sample preparation method with suitable and selectivity up to limit of legislation. The article presents an overview of the miniaturized and automated sample preparation method development in micro-SPE using flow based techniques.

SPE is accomplished by investigating different stationary phase and their masses, volumes of conditioning, sample loading, wash, and elution solvents, and amount of sample used in the experiment.

Mixed

Each of mixed-mode and multidimensional SPE, analysts retain through a primary mechanism such as by Van der Waals interactions, polar dipole-dipole forces, hydrogen bonding, or electrostatic forces. However, sorbents often exhibit retention by a secondary mechanism as well. Bonded silica ion-exchange sorbents primarily exhibit electrostatic interactions, but the analysis also experiences non polar interaction with the bonded legend. Non polar bonded silica primarily retain analyses by hydrophobic interactions but exhibit a dual-retention mechanism, due to the silica backbone and the presence of un reacted surface silanol (-SOH) groups [4].

A mixed-mode sorbent is designed chemically to have multiple retentive sites on an individual solid sorbent particle. These sites exploit different retention mechanisms by chemically incorporating different ligands on the same sorbent. For example, sorbents have been manufactured that contain hydrophobic alkyl chains and cation-exchange site on the same sorbent particle useful for the exchange of the extraction of polar organic analyses from bio fluids [5]. Alternatively, there are several approaches to achieving mixed-mode or multi-dimensional mode (Figure 1). Sorbent particles of different types (i.e., a hydrophobic sorbent and an ion-exchange sorbent) that exhibit separate mechanisms of retention can be homogeneously admixed, or blended in the same column, or they can be layered into the same column by packing one phase over another. Additionally, multi-dimensional phases can be stacked by arranging in tandem series sorbents of different retention mechanisms contained in separate columns [6]. The technique of stacking or sequencing sorbents in tandem columns, termed *chromatographic mode sequencing* (CMS), can afford very selective isolation of analyses [7]. Multi-dimensional SPE mode approaches.

Comparison of off-line Versus On-line SPE Methods

In general, off-line methods provide a larger flexibility. Since they do not suffer from the constraint that the final elution conditions from

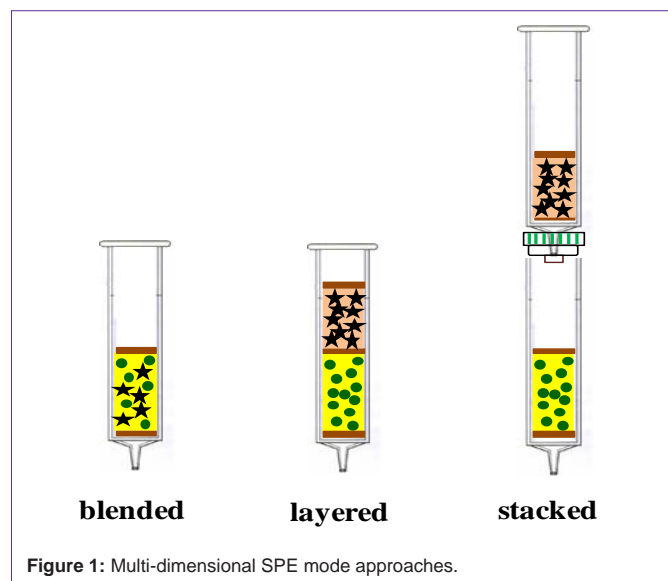


Figure 1: Multi-dimensional SPE mode approaches.

the SPE cartridge need to be compatible with the detection system. On-line SPE approaches are that: samples and SPE cartridges are processed in a completely enclosed system, the operator is protected from working with hazardous and/or volatile organic solvents, and there is less handling and manipulation involved with no transfer loss of analyses. Direct elution is performed from the extraction cartridge into the detection instrument via transfer line. The time consuming in evaporation and reconstitution steps of off-line SPE prior to analysis are eliminated, making on-line SPE more efficient and fully automated (Figure. 2).

Flow based techniques for automatic SPE

An ideal of sample preparation should be involving a minimum number of working steps and environmental friendly concern. Due to the number of samples grow high-throughput and fully automated analytical techniques become required. An automation and/or on-line SPE for sample preparation is of great value in order to maximize throughput and minimize costs, time, and analyst risks due to

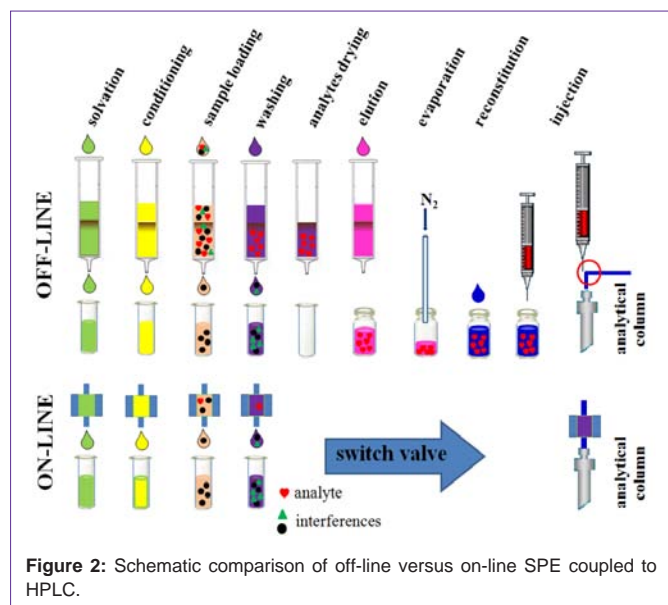


Figure 2: Schematic comparison of off-line versus on-line SPE coupled to HPLC.

chemicals exposure since the entire process of tropical SPE take place in close system, which eliminates error-prone steps like evaporation and reconstitution. In this context, online proper design of the extraction devices and procedures facilitates rapid and convenient implementation couple with separation and quantification in automation for sample preparation. Flow based techniques are established techniques for making it possible. Advantages of flow based techniques are to reduce the amount of solvents and time-reduction and can design manifold for exhaustive or non-exhaustive extraction methods. To this end, the flow based techniques involving SPE, namely sequential injection analysis-SPE, sequential injection analysis-bead injection-SPE and sequential injection analysis-bead injection Lab-on-Vale-SPE will be described.

Sequential Injection Analysis (SIA)

Sequential injection analysis (SIA) was introduced by Ruzicka and Marshall [8]. SIA is a second generation of flow injection analysis (FIA). SIA is outstanding techniques for performing solution chemistry, its most significant potential lies in that offers versatile schemes for the more complicated on-line sample manipulation steps (e.g. SPE methods) before the actual measurement. SIA is based on continuous bi-directional pumping of carrier and reagent streams as precisely coordinated and controlled by computer software [9-11]. A typical SIA manifold is illustrated in Figure 3. A basic SIA manifold composes of a multi-position selection valve (6-port valve), furnished with a central communication port (CC) that can rotate to address each one of the peripheral ports of the valve, a central communication line (CL) together with a holding coil (HC) is connected to a syringe pump. The ports of the selection valve are connected to reservoirs of sample, reagents, detector and other peripheral units (e.g., a sorbent column), respectively. A typical operational procedure is described as follows; firstly the CC is directed to the port connected to the sample line (port 1) and a well-defined volume of sample zone is aspirated into the HC. Then, the valve is redirected to the port connected to the reagent line (port 2) and a reagent zone is aspirated into the HC adjacent to the sample zone. Afterwards, the selection valve is turned to the port connected to the detector (port 4), and the sample and reagent zones are propelled forward through the reaction coil where zone dispersion occurs, resulting in the formation of detectable species which subsequently is monitored by the detector [10]. The ports of the multi position selection valve can be coupled to various

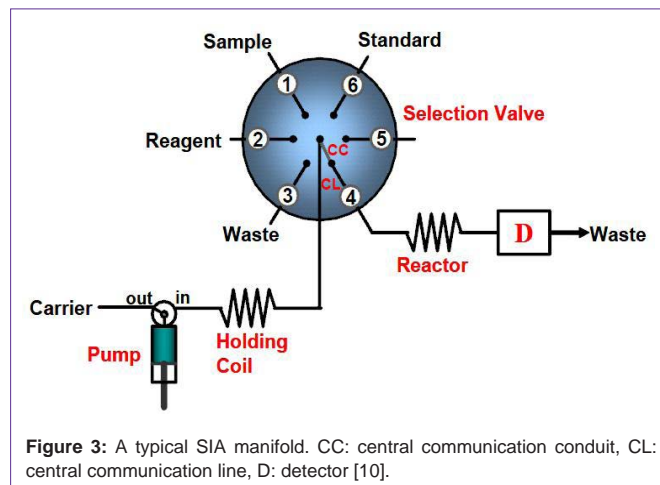


Figure 3: A typical SIA manifold. CC: central communication conduit, CL: central communication line, D: detector [10].

units including reservoirs, detectors, pumps, reactors, separators, special cells, and other manifold. As illustrated in Figure 4.

The most notable advantage of SIA is the drastic reduction in the consumption of sample and reagents, hence resulting in less waste production which is more and more important nowadays due to the increasing costs in the disposal of chemical wastes. In addition, the accurate handling of sample and reagent zones is readily controlled by a computer within the single-channel manifold, allowing full automation. It is easy to reprogram the method and shift from one application to another. By employing solvent resistant materials for the conduits, SIA system can virtually handle any kind of reagents.

Sequential Injection Analysis-solid Phase Extraction (SIA-SPE)

Sequential injection analysis implemented to SPE (SIA-SPE) system involves the permanent packed column, bead injection-SPE, and bead injection lab-on-valve-SPE. SIA-SPE- permanent packed column is an appropriate solid material permanently packed in a proper column or design to be able to integrate with the SIA manifold prior to detection and for reliable application. Breakthrough capacity of the column, the column dimension and the particle size of the sorbent material must be carefully balanced. Although smaller particles sizes resulted in higher breakthrough capacities, and tended to cause progressively tighter packing and hence created flow resistance in the column and flow network.

The repeated use of permanent packed SPE column in the flow network might give rise to several problems. Some sorbent materials undergo volume changed because of swelling or shrinking, at different conditions which caused problem of irreversible changes such as contamination, deactivation of the surface or even loss of active sites. Furthermore, incomplete elution of the retained species from the sorbent medium leads to carry-over effects between consecutive runs. To this end, sequential injection analysis-bead injection-solid phase extraction (SIA-BI-SPE) with the renewable surface sorbents is created to overcome those mentioned drawbacks of SIA-SPE.

Sequential Injection Analysis-bead Injection SPE (SIA-BI-SPE)

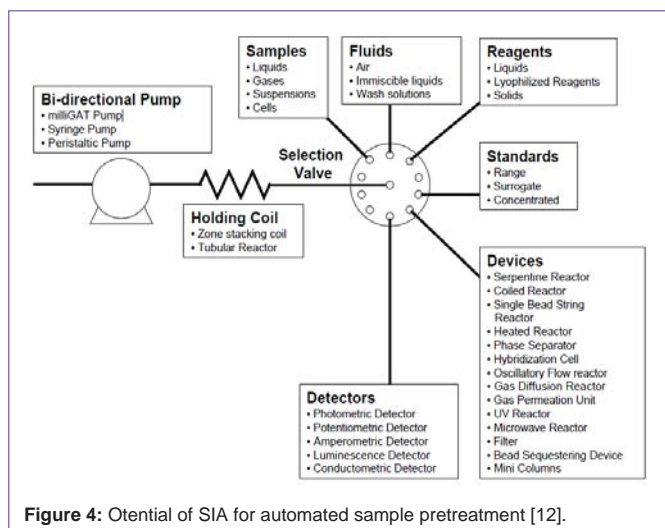


Figure 4: Ontient of SIA for automated sample pretreatment [12].

SIA-BI-SPE technique is based on the aspiration of a precise volume of beads (solid sorbent particles) suspension and retaining beads within special flow cell so called "a jet ring cell", which consists of a tube positioned perpendicular to a flat surface, leaving a narrow circular gap, to achieve the consistency in the bead packing and the mechanical and/or chemical stability of the bead layer (Figure 5). The liquid can escape through the gap in a radial fashion, while the beads are retained and per fused. At the end of the analysis cycle, the jet ring cell is emptied, and the spent beads are removed into waste [13].

The typical SIA-BI-SPE procedure comprises of

Bead packing; an exact volume of a bead suspension is aspirated through the selection valve *via* a syringe pump and loaded into a flow cell to trap into a jet ring cell or special configuration flow cell (Figure 5).

Bead condition; the beads are perfused with an appropriate of organic solvent and wetted by water.

Sample loading; a sample is injected through SPE bead column, and the analysis is trapped on the bead surfaces.

Washing; the analyses is treated with very mind organic solvent to remove interferences.

Elution; the analyses is eluted from the bead using small amount of an appropriate organic solvent prior to detection without evaporation and reconstitution unlikely classical SPE.

Bead discarding; the beads are automatically discarded from the flow cell into waste at the end of analysis cycle. (Figure 5)

SIA-BI-SPE improved assay sensitivity and lower limits of detection due to the analyses can accumulate on the beads. New trend in automatic SIA-SPE is directed to couple BI with the new generation of miniaturized flow systems, the so-called *bead injection*

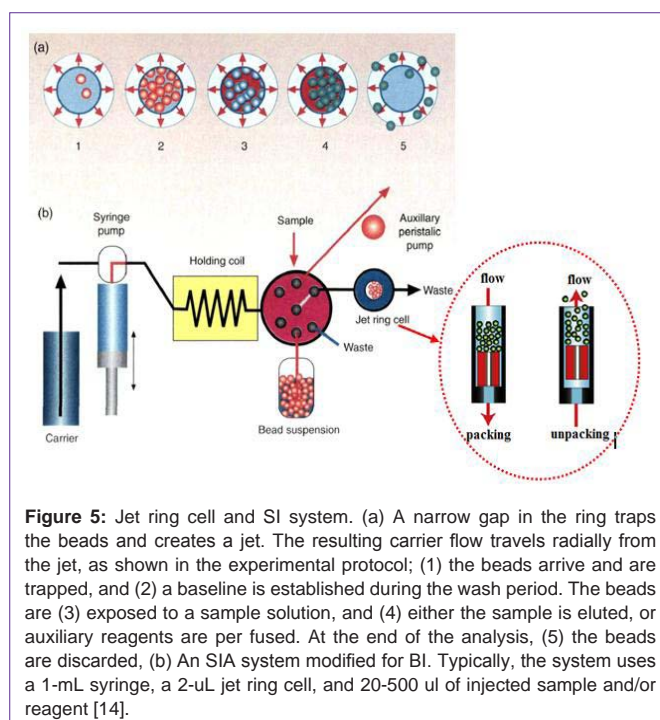


Figure 5: Jet ring cell and SI system. (a) A narrow gap in the ring traps the beads and creates a jet. The resulting carrier flow travels radially from the jet, as shown in the experimental protocol; (1) the beads arrive and are trapped, and (2) a baseline is established during the wash period. The beads are (3) exposed to a sample solution, and (4) either the sample is eluted, or auxiliary reagents are per fused. At the end of the analysis, (5) the beads are discarded, (b) An SIA system modified for BI. Typically, the system uses a 1-mL syringe, a 2-uL jet ring cell, and 20-500 ul of injected sample and/or reagent [14].

lab-on-valve SPE (SIA-BI-LOV-SPE).

Sequential Injection Analysis-bead Injection Lab-on-valve-SPE (SIA-BI-LOV-SPE)

SIA-BI-LOV was introduced by Ruzicka in 2000 [15] as a supplement for SIA manifold. Besides the common components of SIA systems (a multi-position selection valve, a holding coil and a syringe pump), an integrated micro conduit, which is normally fabricated by hard PVC or more chemically resistant Ultem, furnished with micro-channels corresponding to the ports of selection valve, is mounted on top of the multi-position selection valve. A basic BI-LOV-SPE manifold for μ SPE is depicted in Figure 6.

SIA-BI-LOV-SPE is actually extended to constitute a small laboratory, potentially allowing a multitude of unit operations for a given assay to be executed in an on-line SPE. The SIA-BI-LOV-SPE can be operated within a wide range of sample and reagent expenditure, from as low as microliter and sub microliter levels to normal ranges that are employed in conventional SIA operation. As a result of its versatility SIA-BI-LOV-SPE may contain solid column reactors packed with small beads furnished with active groups and even detection facilities. Whatever the bead material applied, the analysis protocol is similar to SIA-BI-SPE but the bead column of SIA-BI-LOV-SPE takes place in a channel of LOV.

SIA-BI-LOV-SPE with renewable solid sorbent materials employing mixed-mode SPE for automated determination of trace level concentrations of polychlorinated pollutants has been investigated for the first time allied to GC for on-line μ SPE in a mesofluidic Lab-on-a-Valve (LOV) format [17]. This new approach fostered the determination of PCBs in landfill leachate samples in a fully automated fashion with the advantages over traditional online SPE-GC methods of simplicity, versatility, and cost-effectiveness as compared to commercially available robotic systems (e.g., Propekt, Propekt-2 from Spark Holland) and negligible cross-contaminations as a consequence of the renewal of the sorbent material in each analysis cycle. The automated SIA-BI-LOV-SPE-GC method was highly sensitive (LOQs between 0.5 and 6.1 ng L⁻¹), accurate (recovery percentages >81%), and reproducible with RSD values lower than 13% for real leachate samples.

In order to handle the bead material reproducibly within the

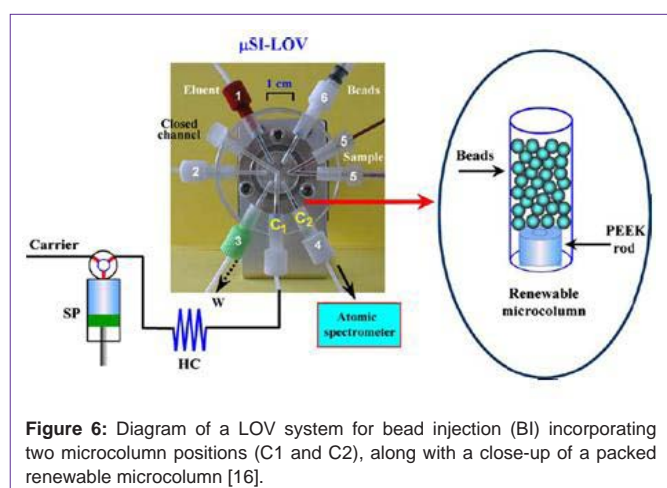


Figure 6: Diagram of a LOV system for bead injection (BI) incorporating two microcolumn positions (C1 and C2), along with a close-up of a packed renewable microcolumn [16].

automatic SIA-BI-LOV-SPE system, bead-size homogeneity and the spherical shape are required to prevent compact settlement into the conduits of the flow set-up. Hence, chemically-modified silica-gel lumps are not really suited for this purpose as a result of their irregular shape and size distribution. However, bead material with a backbone of poly (styrene-divinylbenzene), poly (vinylpyrrolidone) (e.g., Oasis-type beads) or agarose (e.g., Sephadex or Sepharose-type beads) fulfills the foregoing demands, because they are perfectly spherical and have a uniform size. The use of either micellar media or ancillary continuous recirculation schemes for the bead suspension might be needed for reliable manipulation of hydrophobic sensing entities with higher density than water within the flow manifold. Commercially available sepharose beads, mostly stored in 20% ethanol, can be used directly, while dry beads need to be suspended in an appropriate amount of water or buffer solution before use. Hydrophobic sorbents are often wetted with organic solvent (methanol) before dilution by water to obtain beads suspension within the range of 1:10-1:20 (m/v).

Selective Sorbent Materials Using in Automated SPE

Molecularly imprinted polymer

Molecular imprinted polymers (MIPs) are synthetic crosslink polymers with artificially generated recognition sites which able to specifically rebind a target molecule in preference to other closely related compounds as an attempt to synthesize antibody mimics [18]. These materials are obtained by polymerising functional and cross-linking monomers around a template molecule, leading to a highly cross-linked three-dimensional network polymer. The monomers are chosen considering their ability to interact with the functional groups of the template molecule. Once polymerisation has taken place, template molecule is extracted and binding sites with shape, size and functionalities complementary to the target analyte are established (Figure. 7).

Nowadays MIPs use in SPE, *molecularly imprinted polymer solid-phase extraction (MIP-SPE)*, is by far the most advanced technical application of MIPs. The MIPs offer the advantages of an easy, low cost, rapid preparation, and high thermal and chemical stability although early analyses breakthrough might be an issue. In addition, increased selectivity relative to other sorbents because larger sample volumes can be extracted. MIPs have recently been proven to have

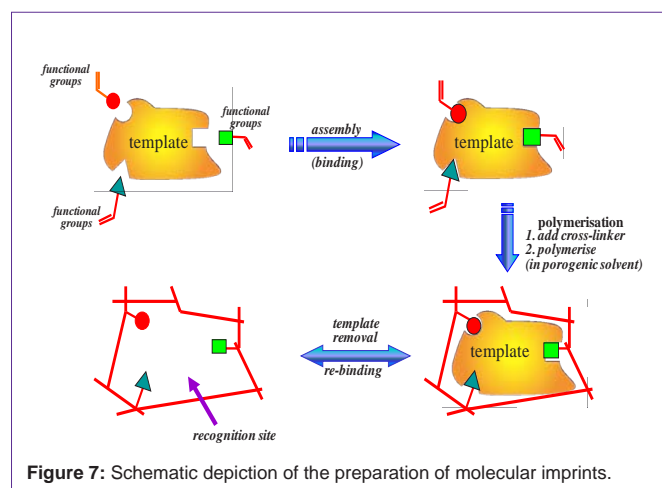


Figure 7: Schematic depiction of the preparation of molecular imprints.

high chemical robustness, providing the opportunity to clean and reactivate them for multiple uses in SPE especially for the analysis in the presence of complex biological or environmental matrix interferences.

Retention of the analyte on these sorbents is due to shape recognition, however other physico-chemical properties including hydrogen bonding, ionic interactions, and hydrophobic interactions are important to retention as well. However, desorption is usually more difficult if any sorbent has increased affinity for the analyte. One problem noted in MIP-SPE is incomplete removal of the template molecule from the polymer, resulting in leaching of the analyte (bleeding) during subsequent analyses. Stringent cleaning of the sorbent and analytical confirmation of the lack of interfering compound can reduce this problem. The use of MIPs as selective sorbent materials allows performing a customized sample treatment step prior to the final determination. This is of special interest when the sample is complex and the presence of interferences could prevent final quantification by typical chromatographic techniques coupled to common detectors. On-line hyphenation of multimodal micro-solid phase extraction involving renewable molecularly imprinted and reversed-phase sorbents to liquid chromatography for automatic multi residue assays has proved the concept of using MIP together in Oasis HLB in mixed-mode SPE for pre concentration and isolation of organic pollutants in complex matrices as crude soil extracted [19].

Carbon nano materials

Carbon nano tubes (CNTs) represent the novel carbon-based nano materials with unique properties such as high surface areas, large aspect ratios, remarkably high mechanical strength as well as high electrical and thermal conductivities. They can be described as a graphite sheet rolled up into a nano scale-tube. Two structural forms of CNTs exist single-walled (SWCNTs) and multi-walled (MWCNTs) carbon nano tubes. CNTs length can be as short as a few hundred nanometers or as long as several micrometers. SWCNTs have diameters between 1 and 10 nm and are normally capped at the ends. In contrast, MWCNTs diameters are much larger (ranging from 5 nm to a few hundred nanometers) because their structure consists of many concentric cylinders held together by van der Waals forces [20]. The characteristic structures and electronic properties of carbon nano tubes allow them to interact strongly with organic molecules, *via* non-covalent forces, such as hydrogen bonding, π - π stacking, electrostatic forces, van der Waals forces and hydrophobic interactions. These interactions along with their hollow and layered nano-sized morphology make them a good candidate for application as a SPE sorbent.

Zhou et al [21] compared the trapping efficiency of CNTs and C18 packed cartridge using sulfonyleurea herbicides as the model compounds. When the matrices of the samples were very simple, such as tap water and reservoir water, the enrichment performance between these two adsorbents had no significant difference. However, carbon nano tubes become much more suitable to extract herbicides from complex matrices (such as seawater and well-water). Carbon nano tubes could be also used in a format of disk [22]. Incorporating sorbents of small particle size, the disk format provided a larger surface area than the cartridge, resulting in good mass transfer and fast flow rates [23]. To enhance the sorption capacity of the disks,

double or even triple disks have been used together. A comparison study showed that the double-disk system (comprising two stacked disks with 60 mg of CNTs) exhibited extraction capabilities that were comparable to those of a commercial C18 disk with 500 mg sorbent for non polar or moderately polar compounds. The triple layered CNTs disk system showed good extraction efficiency with sample volumes up to 3000 ml [24].

Other application was using carbon nano-materials as sorptive surfaces for SPE in automatic flow-mode in the in-house special reactor so-called a stirred-flow micro-column. Designed stirred-flow micro-column was proved to minimise nano particle agglomeration and negligible pressure drop for cleanup and pre concentration of triazine herbicides in waters and soil extracted samples [25].

On-line Coupling of SPE with HPLC

A typical on-line SPE arrangement prior to HPLC separations is easy to perform in any laboratory using simple switching valves and commercial pre-columns and their holders (Figure 8). This system is also named *column-switching liquid chromatography* [26]. The SPE column is located in the loop position of the injection valve. The column-switching valve was used to direct the flow from the extraction column either to waste or to the HPLC analytical column. At the beginning of each run, the SPE column was conditioned. In the load position, sample was directly loaded onto the sorbent and then pre concentrated, while matrix components were removed during the washing step. The valve was then switched to the inject position, so that appropriate solution (normally HPLC mobile phase) eluted the analyses from the extraction column toward the analytical column, wherein they were separated prior detection. After elution, the valve was switched back to its original position to wash and re-equilibrate the extraction column.

Conclusion

Automatic sample preparation methods are nowadays imperative to meeting compressed analytical timeline. As a result, mechanized sample preparation methods with different proper design hyphenated with analytical techniques were developed for determination of target compound at level below those endorsed in current Directives.

On-line/automation method is become more relevance to eliminate errors and time associated with manual sample preparation

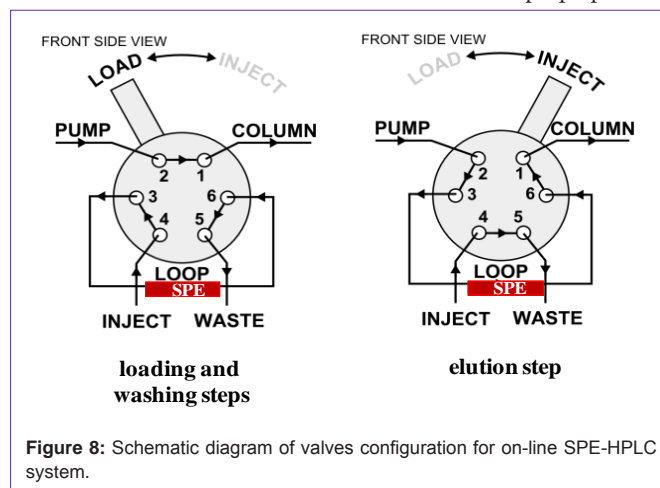


Figure 8: Schematic diagram of valves configuration for on-line SPE-HPLC system.

steps and therefore results in more accurate and faster analytical data. Although such a device has not yet been built, today flow based techniques are able to couple with varieties of detectors. Sample preparation and determination were able to perform in parallel.

References

1. Mitra S, BRUKH R. *Sample Preparation Techniques in Analytical Chemistry*: John Wiley & Sons, Inc. 2003.
2. Prabu SL, Suriyaprakash TNK. Extraction of Drug from the Biological Matrix: A Review. *InTech*. 2012; 479-506.
3. Chen L, Wang H, Zeng Q, Xu Y, Sun L, Xu H, et al. On-line coupling of solid-phase extraction to liquid chromatography-a review. *J Chromatogr Sci*. 2009; 47: 614-623.
4. M.J.M. W. *Essential guides to method development in solid-phase extraction*: Encyclopedia of Separation Science, Academic Press, London; 2000.
5. Law B. *Solid-phase extraction: Principles, techniques, and applications*. New York: Marcel Dekker; 2000.
6. Georgi K, Boos KS. Multidimensional on-line SPE for undisturbed LC-MS-MS analysis of basic drugs in biofluids. *Chromatographia*. 2006; 63: 523-531.
7. S.J. R, T.J. G. Use of chromatographic mode sequencing for sample preparation in the analysis of caffeine and theobromine from beverages. *Journal of agricultural and food chemistry*. 1982; 30: 775-778.
8. Ruzicka J, Marshall GD. Sequential injection: A new concept for chemical sensors, process analysis and laboratory assays. *Analytica Chimica Acta*. 1990; 237: 329-343.
9. Hansen EH, Wang J. Implementation of suitable flow injection/sequential injection-sample separation/preconcentration schemes for determination of trace metal concentrations using detection by electrothermal atomic absorption spectrometry and inductively coupled plasma mass spectrometry. *Analytica Chimica Acta*. 2002; 467: 3-12.
10. Hansen EH, Miró M. How flow-injection analysis (FIA) over the past 25 years has changed our way of performing chemical analyses. *TrAC - Trends in Analytical Chemistry*. 2007; 26: 18-26.
11. Lenehan CE, Barnett NW, Lewis SW. Sequential injection analysis. *Analyst*. 2002; 127: 997-1020.
12. Marshall G, Wolcott D, Olson D. Zone fluidics in flow analysis: Potentialities and applications. *Analytica Chimica Acta*. 2003; 499: 29-40.
13. Ruzicka J, Scampavia L. From flow injection to bead injection. *Anal Chem*. 1999; 71: 257A-263A.
14. Ruzicka J, Pollema CH, Scudder KM. Jet ring cell: a tool for flow injection spectroscopy and microscopy on a renewable solid support. *Anal Chem*. 1993; 65: 3566-3570.
15. Ruzicka J. Lab-on-valve: Universal microflow analyzer based on sequential and bead injection. *Analyst* 2000; 125: 1053-1060.
16. Miró M, Hansen EH. Solid reactors in sequential injection analysis: Recent trends in the environmental field. *TrAC - Trends in Analytical Chemistry*. 2006; 25: 267-281.
17. Quintana JB, Boonjob W, Miró M, Cerdà V. Online coupling of bead injection lab-on-valve analysis to gas chromatography: Application to the determination of trace levels of polychlorinated biphenyls in solid waste leachates. *Analytical Chemistry*. 2009; 81: 4822-4830.
18. Tamayo FG, Turiel E, Martín-Esteban A. Molecularly imprinted polymers for solid-phase extraction and solid-phase microextraction: Recent developments and future trends. *Journal of Chromatography A*. 2007; 1152: 32-40.
19. Boonjob W, Yu Y, Miró M, Segundo MA, Wang J, Cerdà V. Online hyphenation of multimodal microsolid phase extraction involving renewable molecularly imprinted and reversed-phase sorbents to liquid Chromatography for Automatic multiresidue assays. *Analytical Chemistry*. 2010; 82: 3052-3060.
20. An X, Zeng H. Functionalization of carbon nanobeads and their use as metal ion adsorbents. *Carbon*. 2003; 41: 2889-2896.
21. Zhou Q, Xiao J, Wang W. Comparison of multiwalled carbon nanotubes and a conventional adsorbent on the enrichment of sulfonylurea herbicides in water samples. *Anal Sci*. 2007; 23: 189-192.
22. López-Lorente AI, Simonet BM, Valcárcel M. The potential of carbon nanotube membranes for analytical separations. *Anal Chem*. 2010; 82: 5399-5407.
23. Niu H, Cai YQ, Wei FB, Jiang G. Solid-phase extraction of sulfonylurea herbicides from water samples with single-walled carbon nanotubes disk. *Microchimica Acta*. 2009; 164: 431-438.
24. Niu HY, Cai YQ, Shi YL, Wei FS, Liu JM, Jiang GB. A new solid-phase extraction disk based on a sheet of single-walled carbon nanotubes. *Anal Bioanal Chem*. 2008; 392: 927-935.
25. Boonjob W, Miró M, Segundo MA, Cerdà V. Flow-through dispersed carbon nanofiber-based microsolid-phase extraction coupled to liquid chromatography for automatic determination of trace levels of priority environmental pollutants. *Analytical Chemistry*. 2011; 83: 5237-5244.
26. Hennion MC. Solid-phase extraction: method development, sorbents, and coupling with liquid chromatography. *J Chromatogr A*. 1999; 856: 3-54.