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The Benefits and Limitations of Methods Development in Solid Phase Extraction: Mini Review

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Abstract

Over recent years, there has been an explosive growth of sample preparation techniques. Sample preparation is in most cases meant to be the isolation online or offline concentration of some components of interest or target analytes. Solid phase extraction (SPE) is a very popular technique nowadays in sample preparation. The principal is quite similar with liquid- liquid extraction (LLE) which involves partition of solutes between two phases. But, there are some differences between them and some benefits and limitations of difference types of SPE technique like presented in this paper.

Keywords: Solid phase extraction; benefits; limitations

1.0 INTRODUCTION

Sample preparation is in most cases meant to be the isolation online or offline concentration of some components of interest or target analytes from various matrices, making the analytes more suitable for separation and detection. Sample preparation involves extraction procedures and can also include 'clean-up' procedures for very complex 'dirty' samples [1-4]. During the separation step of the analytical process, the isolated complex mixture containing target analytes is divided into its constituents, typically by means of chromatographic or electrophoresis techniques. Quantitation is the determination of amounts of the identified compounds. Solid phase extraction (SPE) is a very popular technique nowadays in sample preparation. Over the years, SPE has undergone steady growth driven by analysis need to find sample preparation procedures that were simple and relatively inexpensive, provided good analyte recovery and adequate selectivity, reduced the use of organic solvents, and could be automated when the need arose [5]. It have various objective of usage in purification [6-8], trace enrichment [9-11], desalting [12-14] and class fractionation [15, 16]. It was widely used laboratory technique following the introduction in the 1970s of disposable sorbent cartridge containing porous particles sized to allow sample processing by gentle suction [17]. The principal is quite similar with liquid-liquid extraction (LLE) which involves partition of solutes between two phases. Both sampling methods give high recovery rate, high selectivity and robustness and low time requirements [18]. But, there are some differences between LLE and SPE like presented in the Table 1.

For solid phase extraction, the general method is by loading the solution on to the SPE solid phase, wash away the undesired component and wash off the desired one with other solvent into collection tube. But there are four SPE techniques such as using free discs, discs in syringe barrels which called catridge, 96 well SPE plates and SPE pipette tips. In addition, there are several approaches to automation SPE based on robotics, dedicated instruments using flow processing and online analyzers with direct coupling of the extraction columns to a chromatography instruments to have gained.

Numerous methods have appeared for sample preparation. It looks helpful to have an overview on them but is hard since they have been termed quite ambiguously. Various ways such as principle, configuration, scale or size, operation procedure, physical state of samples and/or solvent, and the physical or chemical nature of sampling process may be used to sort them [1]. There is no attempt to rename the methods in this paper but we aim towards an easier understanding of them.

Table 1 Differences between liquid-liquid separation (LLE) and solid phase extraction (SPE)

Differences	Liquid-liquid extraction (LLE)	Solid phase extraction (SPE)
Separation result	Two immiscible liquid phase	Involve partition between a liquid which is sample matrix or solvent with analyze and solid phase as sorbent
Price	Cheaper	Expensive cartridge
Rate of separation [19, 20]	Slower	Faster
Detection of several drugs	Cannot detect most notably, morphine and benzoylecgonine	Can detect most notably, morphine and benzoylecgonine
Handling technique [18, 19, 21]	Too labour intensive	Easier to automate and less manual effort
Solvents [19-21]	High purity solvents required	Low purity solvents still can give best separation
Selectivity [21]	Limited	High range of immiscible solvents available
"Art of extraction" [18]	More gentle extraction and give high recovery	Easily oxidized during drying
Repeatability [19]	Low	High

■2.0 BENEFITS AND LIMITATIONS OF VARIOUS METHODS OF SPE

The purpose of solid phase extraction method development is to tackle several problems that occur during sample preparation in order to get high selectivity and precise compound detection. It begins with cartridge for SPE that has been introduced for more than 20 years. Typical SPE cartridge consists of small column which generally an open syringe barrel that containing a sorbent with an average nominal particle size of about 40 µm packed between porous metal or plastics frits [22]. It comes in various sizes which available for wide range of sample volumes. It was commonly attractive for use in pesticide residue analytical method. The efficiency of extraction by cartridge depends on the quality of packing, more uniform packing will give less variation in the recoveries of samples.

Then, in early 1990s several problems encountered in the cartridges can be tackled by development of free discs technology as alternative sampling formats. It consists of variation of the extraction cartridges. It also consists of 0.5 mm thick membrane where the absorbent is immobilized in a web of microfibrils. The free discs acceptance for processing large sample volumes and small diameter discs for processing small samples [17].

Sample preparation impacts nearly all the later assayed steps and is hence critical for quantification of analytes. In common, a clean sample assists to improve separation and detection, while a poorly treated sample may invalidate the whole assay. Use of ideally cleaned samples also reduces the time to maintain instruments and in turn the cost of assay. It is because of the importance of sample preparation that some excellent reviews on this topic have appeared in 2002 in books and special journal issues.

■3.0 ASPECTS INFLUENCED THE METHOD DEVELOPMENT OF SPE

As analytical chemistry grows, sample preparation gradually becomes a major part of analysis, capable of taking up to 80% of the total time of a complete separation-based analytical process, which typically includes five steps, that is sampling, sample preparation, separation, detection and data analysis. Since then, sample preparation has developed increasingly during recent years. Environmental application is a main cause driving the development of many procedures of sample preparation due to the increased public awareness that environmental contaminants are a health risk. The increased demands in the analysis of foods and natural products have brought another pressure to develop the technologies of sample preparation. The appearance of more sensitive and reliable methodology to monitor environment is also impelled by governmental necessity to elevate public living standard and quality.

The other factor that influence the method developments are the selectivity which called extraction efficiency of the compounds. The properties and the level of the analytes should meet the demand of separation and detection. A method is always preferred which is very easy to use, has the minimum steps and uses only simple devices or systems capable of full automation. For most of the users, the method developed must be cost effectives such as consuming minimum reagents and chemical as possible with low expenses as possible on instrumentation and facilities

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Table 2 Benefits and limitations of difference type of solid phase extraction

Type of SPE	Benefits	Limitations
Free Discs [23-25]	• Can operated with smaller elution volumes • Higher flow rates (glass fibre -ticker) • Large surface area per unit bed mass • Increase in density and uniformity of packing provided by the smaller particles • may be used at fast flow rates without loss of analyte. • cleaner extracts with lower interferences due to optimization of the bed mass to reduce non-specific matrix adsorption. • ability to retain organic compounds even when high flow rates are utilized.	• Decrease in breakthrough volume • Mainly for more polar compounds • Come only in 3 diameters • Small samples would be lost • The glassware needs to be cleaned between extractions, and a test tube needs to be placed under the apparatus in the vacuum flask for extraction
Discs in syringe barrels- Cartridge [21, 26]	• Available in a wide range of sizes	• Restricted flow rates and plugging of the top frit when handling water containing suspense solid like surface water/ waste mated • Cross sectional area is small and sampling processing rates are slow and tolerance to blockage particle • Inadequate packing density • channelling reduces the capacity of the cartridge to retain analytes • incomplete reversibility of the sorption of some analytes from active sorbent sites lowers their expected recovery
96-well plates[27]	• Reduce handling errors • Limit labour outputs • Types of plates is fixed and flexible in term of volume and sorbent • Shows excellent repeatability • Compatibility with small sample volumes. • Reduced use of solvents; • Clean sample extracts minimizing the potential for ionization suppression;	• Costly wells • May use a test only a few wells used • Due to open-bed configuration, this technique is unsuitable for volatile analytes due to evaporative losses
SPE pipette tips	• Conditioning steps necessary for conventional SPE is not required • Stationary phase is washed only with 1ml of water or buffer • Faster extraction time • One extraction method for all analytes • Clean extracts • Less sample volumes • Less solvent waste	

References

[1] Chen, Y., G. Zhenpeng, W. Xianyu and Q. Changgui. 2008. Sample preparation. *Journal of Chromatography*. 1184(1–2): 191–219.

[2] Flores, É. M. M., B. Juliano., M. Marcia and K. Gunter. 2007. Sample Preparation Techniques Based on Combustion Reactions in Closed Vessels–A Brief Overview and Recent Applications. *Spectrochimica Acta Part B: Atomic Spectroscopy*. 62(9): 1051–1064.

[3] Goodwin, R. J. A. 2012. Sample Preparation for Mass Spectrometry Imaging: Small Mistakes Can Lead to Big Consequences. *Journal of Proteomics*. 5(16): 4893–4911.

[4] Nóbrega, J. A., S. Mirian, d. Rafael, C. Selange, B. Ramon and T. Mark. 2006. Sample Preparation in Alkaline Media. *Spectrochimica Acta Part B: Atomic Spectroscopy*. 61(5): 465–495.

[5] Majors, P. D., J. S. McLean and J. C. M. Scholten. 2008. NMR Bioreactor Development for Live In-situ Microbial Functional Analysis. *Journal of Magnetic Resonance*. 192(1): 159–166.

[6] Hu, G., J. S. H. Lee and D. Li. 2006. A Microfluidic Fluorous Solid-phase Extraction Chip for Purification of Amino Acids. *Journal of Colloid and Interface Science*. 301(2): 697–702.

[7] Nilsson, U. J., E. J. L. Fournier and O. Hindsgaul. 1998. Solid-phase Extraction on C18 Silica as a Purification Strategy in the Solution Synthesis of a 1-Thio-B-D-Galactopyranoside Library. *Bioorganic & Medicinal Chemistry*. 6(9): 1563–1575.

[8] Tarn, M. D., P. Giancarlo, D. Francesco, W. Paul, S. Piero and A. P. Nicole. 2013. Purification of 2-[18F]fluoro-2-deoxy-d-glucose by on-Chip Solid-phase Extraction. *Journal of Chromatography*. 1280: 117–121.

[9] Bagheri, H., A. Mohammadi and A. Salemi. 2004. On-line Trace Enrichment of Phenolic Compounds from Water Using a Pyrrole-Based Polymer as the Solid-phase Extraction Sorbent Coupled with High-performance Liquid Chromatography. *Analytica Chimica Acta*, 513(2): 445–449.

[10] Crespín, M. A., E. Ballesteros, M. Gallengo, M. Valcarcel. 1997. Trace Enrichment of Phenols by On-line Solid-phase Extraction and Gas

Chromatographic Determination. *Journal of Chromatography*. 757(1–2): 165–172.
[11] Fischer, J., M. T. Kelly, M. R. Smyth and P. Jandera. 1993. Determination of Ivermectin in Bovine Plasma by Column-switching LC Using On-line Solid-phase Extraction and Trace Enrichment. *Journal of Pharmaceutical and Biomedical Analysis*. 11(3): 217–223.
[12] Gilar, M., A. Belenky and B. H. Wang. 2001. High-throughput Biopolymer Desalting by Solid-phase Extraction Prior to Mass Spectrometric Analysis. *Journal of Chromatography*. 921(1): 3–13.
[13] Palmblad, M. and J. S. Vogel. 2005. Quantitation of Binding, Recovery and Desalting Efficiency of Peptides and Proteins in Solid Phase Extraction Micropipette Tips. *Journal of Chromatography*. 814(2): 309–313.
[14] Watkins, L. K., P. V. Bondarenko, D. C. Barbacci, S. Song, S. L. Cockrill, D. H. Russell and R. D. Macfarlane. 1999. Fast C18 Solid-Phase Desalting/Delipidation of the Human Serum Apolipoproteins for Matrix-assisted Laser Desorption Ionization and Electrospray Ionization Mass Spectrometric Analysis. *Journal of Chromatography*. 840(2): 183–193.
[15] Mulugeta, M., G. Wibetoe, C. J. Engelsen and W. Lund. 2009. Fractionation Analysis of Oxyanion-forming Metals and Metalloids in Leachates of Cement-based Materials Using Ion Exchange Solid Phase Extraction. *Talanta*. 78(3): 736–742.
[16] Zelles, L. and Q. Y. Bai. 1993. Fractionation of Fatty Acids Derived From Soil Lipids by Solid Phase Extraction and Their Quantitative Analysis by GC-MS. *Soil Biology and Biochemistry*. 25(4): 495–507.
[17] Poole, C. F., A. D. Gunatilleka and R. Sethuraman. 2000. Contributions of Theory to Method Development in Solid-phase Extraction. *Journal of Chromatography*. 885(1–2): 17–39.
[18] Lindenblatt, H., K. Edda., H. Petra., G. Euphrisyne and K. Karl-Artur. 1998. Quantitation of Psilocin in Human Plasma by High-performance Liquid Chromatography and Electrochemical Detection: Comparison of Liquid–Liquid Extraction with Automated On-line Solid-phase Extraction. *Journal of Chromatography B: Biomedical Sciences and Applications*. 709(2): 255–263.
[19] Hernanz, D., V. Gallo, A. F. Recamales, A. J. Melendez-Martinez and F. J. Heredia. 2008. Comparison of the Effectiveness of Solid-phase and Ultrasound-mediated Liquid–liquid Extractions to Determine the Volatile Compounds of Wine. *Talanta*. 76(4): 929–935.
[20] Xie, W., J. Pawlisyn, W. M. Mulle and B. K. Matuszewski. 2007. Comparison of Solid-phase Microextraction and Liquid–liquid Extraction in 96-Well Format for the Determination of a Drug Compound in Human Plasma by Liquid Chromatography with Tandem Mass Spectrometric Detection. *Journal of Pharmaceutical and Biomedical Analysis*. 45(4): 599–608.
[21] Poole, C. F., S. K. Poole, D. S. Seibert and C. M. Chapman. 1997. Determination of Kinetic and Retention Properties of Cartridge and Disk Devices for Solid-phase Extraction. *Journal of Chromatography B: Biomedical Sciences and Applications*. 689(1): 245–259.
[22] Mayer, M. L. and C. F. Poole. 1994. Identification of the Procedural Steps that Affect Recovery of Semi-volatile Compounds by Solid-Phase Extraction Using Cartridge and Particle-loaded Membrane (Disk) devices. *Analytica Chimica Acta*. 294(2): 113–126.
[23] Horne, T. and S. Holt-Larkin. 1997. Solid-phase Extraction of Phospholipids from Hemoglobin Solutions Using Empore Styrene–Divinylbenzene Disks. *Journal of Chromatography B: Biomedical Sciences and Applications*. 695(2): 259–267.
[24] Thompson, T. S. and B. D. Miller. 1998. Use of Solid Phase Extraction Disks for the GC-MS Analysis of Acidic and Neutral Herbicides in Drinking Water. *Chemosphere*. 36(14): 2867–2878.
[25] Thurman, E. M. and K. Snavely. 2000. Advances in Solid-phase Extraction Disks for Environmental Chemistry. *TrAC Trends in Analytical Chemistry*. 19(1): 18–26.
[26] Nema, T., E. C. Y. Chan and P. C. Ho. 2010. Application of Silica-based Monolith as Solid Phase Extraction Cartridge for Extracting Polar Compounds from Urine. *Talanta*. 82(2): 488–494.
[27] Vuckovic, D. 2013. High-throughput Solid-phase Microextraction in Multi-well-Plate Format. *TrAC Trends in Analytical Chemistry*. 45: 136–153.