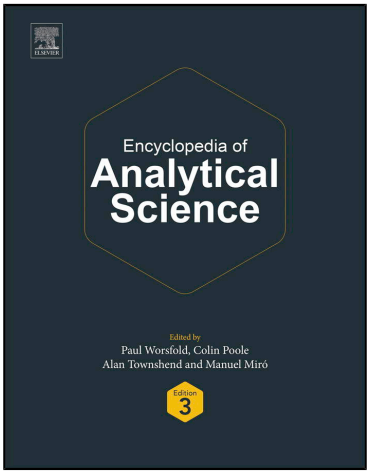

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Extraction | Magnetic Materials in Separation Science

Enrique Barrado, University of Valladolid, Valladolid, Spain
José A Rodríguez, Autonomous University of the Hidalgo State, Pachuca, Mexico

Introduction

Sample pretreatment is one of the most important steps in chemical analysis. Extensive clean-up procedures are normally required to remove matrix components which may interfere in the analysis. Some common strategies to these steps are based on the liquid–liquid extraction or solid phase extraction (SPE) techniques, in which the separation occurs by the analyte partition coefficient between the sample solution phase and the solid sorbent. SPE has several merits such as lower cost, higher enrichment factor and less consumption of organic solvents.

Several methodologies of SPE can be distinguished: dynamic solid-phase extraction, microextraction by packed sorbent, matrix solid-phase dispersion, stir-bar sorptive extraction, solid-phase microextraction; in these cases the extracting phase is retained in a support (cartridge, stir-bar or fiber). If the solid phase is suspended into the liquid sample it is denominated dispersive solid-phase extraction (DSPE). Magnetic particles (micro or nanoparticles) can be used as extracting phase, in off-line DSPE methodologies; by adding the magnetic sorbent to the sample solution to adsorb the analyte on their surface. In this case, the magnetic particles with retained analyte are separated from the sample solution by applying an external magnetic field and after elution with the appropriate solvent the analyte is analyzed. In on-line DSPE methods, the magnetic solid is magnetically immobilized in mini-columns. The sample and the different solvents flow through the column to perform retention and elution of the analytes. Magnetic materials are usually based on magnetite coated with an adequate extracting phase (silica, carbon or polymers). The synergy between both phases has been explored to develop high performance sorbents for extraction application of different analytes in complex matrices.

Theory

The separation, analyte transference from a liquid to a solid phase, is related to distribution coefficient (D), weight of the solid (w, g) and sample volume (V, mL). The fraction retained (θ) can be determined through the following expression:

$$\theta = \frac{D_w}{D_w + V}$$

On the other hand, the analyte concentration in the solid phase (mmol g^{-1}) is associated to θ according to:

$$\frac{\text{mmol}_{\text{analyte}}}{\text{g}} = \frac{[\text{Analyte}]V\theta}{w}$$

The effect of sample volume on the fraction retained (θ) is represented in Fig. 1A. The conditions employed are: initial analyte concentration of 0.01 M ([Analyte]) and amount of extracting solid phase of 1.0 g (w). θ value increases with D value and decreases with sample volume. In contrast, Fig. 1B shows that final concentration of the analyte in the solid phase increases with the sample volume. This behavior explains the increase observed in the enrichment factor when higher sample volumes are employed during analysis in solid–liquid extractions such as solid phase extraction (SPE), solid phase microextraction (SPME) and dispersive solid phase extraction (DSPE). However, the use sample volume higher than 50 mL, in DSPE mode, is laborious because of the separation of the solid phase (with the analytes) after extraction which can affect negatively the precision of the results obtained.

Magnetic Solid Phase Extraction (MSPE)

As it was previously mentioned, solid phase extraction has two principal modalities. The most common are to immobilize the extracting phase in a cartridge or on a fiber and the second one is to disperse the solid phase into the liquid sample. The latter contributes positively to the mass transference process, but separation of the solid phase involves additional steps during sample preparation. Extracting solid phases with paramagnetic properties can be easily isolated employing an external magnetic field; this property promotes the inclusion of magnetic solids (or magnetic adsorbents) in DSPE methodologies, generating a separation technique so-called magnetic solid phase extraction (MSPE).

MSPE procedure is represented in Fig. 2, initially the magnetic adsorbent is conditioned by the addition of a specific solvent in an ultrasonic bath or through a mechanical process. Subsequently the particles are magnetically isolated, washed, and the liquid phase is discarded. An adequate aliquot of sample solution is mixed with the activated magnetic adsorbent by dispersing it into the sample for a certain time; then an external magnetic field is applied in order to isolate the paramagnetic particles with the analytes retained. Once decanted the liquid phase, the solid phase is washed for the elimination of interferences. Subsequently, the analytes are eluted by addition and dispersion of an adequate solvent to the magnetic adsorbent.

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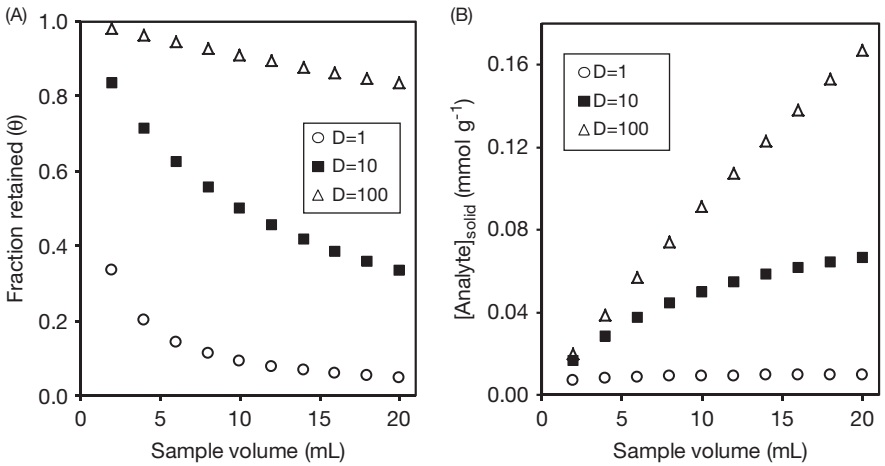

Fig. 1 Effect of the sample volume (mL) and distribution coefficient (D) on the: (A) retained fraction, θ, and concentration of the analyte in the solid phase (mmol g^{-1}). Initial analyte concentration, 0.01 M and amount of solid extracting phase, 1.0 g.

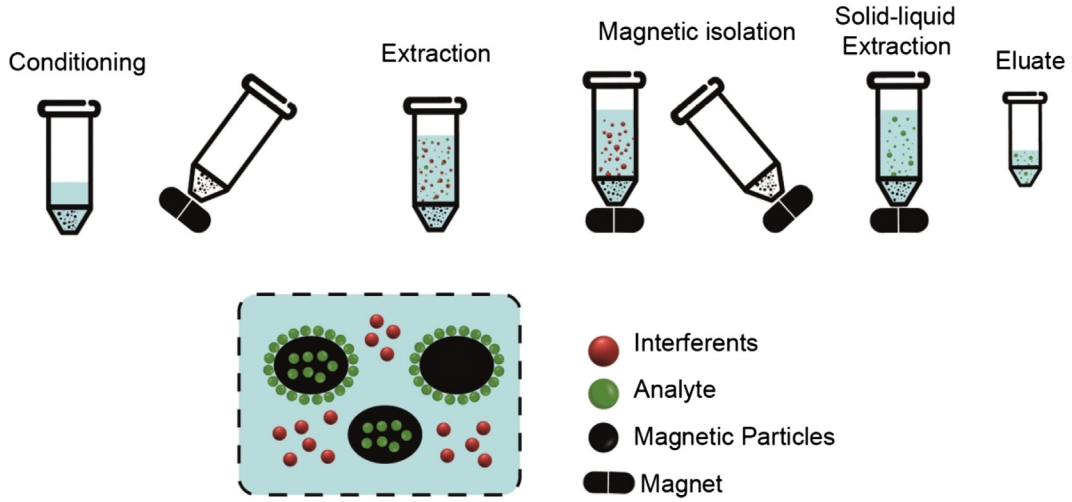

Fig. 2 Scheme of sample treatment by magnetic solid phase extraction.

The use of magnetic solids allows the separation from the liquid phase employing an external magnetic field, the composition of extracting phase is then critical to guarantee the adequate pre-concentration or the clean-up processes. The common morphology employed is the core–shell in which the core is usually an iron oxide (γ-Fe_2O_3 or Fe_3O_4) and the shell is the extracting phase, the last one can be based on carbon, polymer or silica. The desired properties of the extracting phase involve: high surface areas, homogenous size and pore distributions and the possibility to modify the magnetic solid by post-synthesis reactions.

Solids based on magnetic silica are usually synthesized through hydrolysis and condensation of tetraalkoxysilanes ($Si\text{-}(OR)_4$) in presence of γ-Fe_2O_3 or Fe_3O_4, when R = $-CH_3$ or $-CH_2CH_3$, the silica shell contains superficial silanol groups (–Si–OH) that can be used to modify the solid with different functional groups, antigens, enzymes or other recognizing agents. Another alternative synthesis involves the hydrolysis and condensation reaction in presence of other organoalkoxysilanes reagents, promoting a covalent bond and the immobilization of the functional groups of interest in the solid. The main interaction modes between the functional groups contained in the magnetic solid and the analytes are shown in Fig. 3. Hydrophobic interaction employing silica gel with octyl or octadecyl alkyl chains is commonly employed in MSPE methodologies. Particles based on magnetic silica have been employed for MSPE analysis of antibiotics, corticosteroids, non-steroidal anti-inflammatory drugs, organophosphorus pesticides, parabens, phthalate esters, polycyclic aromatic hydrocarbons and steroid hormones in biological, environmental and food samples.

Moreover, materials based on magnetic carbon have attracted the attention of the analytical community due to the chemical properties of carbonaceous materials, such as: chemical stability, high surface area and the presence of a structure rich in π electrons. The carbon forms more employed are, activated carbon, fullerene, carbon nanotubes, graphene and their oxidized forms which promote the formation of oxygen-functional groups, such as epoxy, carboxylic and hydroxyl usually employed to immobilize different extracting agents through formation of amides or esters. Despite of their advantages, the main difficult is that paramagnetic core is partially covered, the exposed iron oxide core can be then oxidized and in consequence the paramagnetic properties are lost.

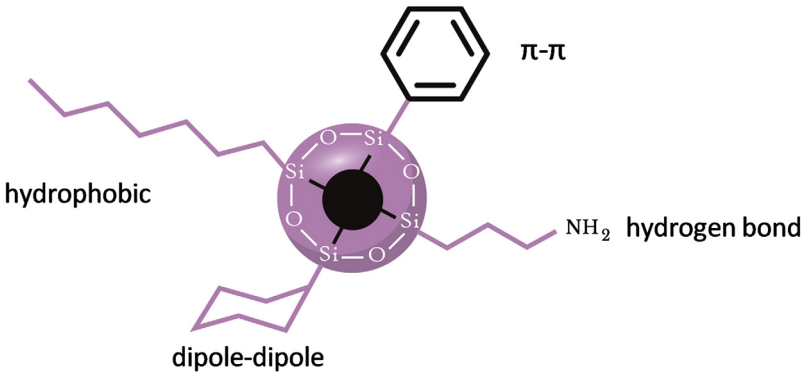

Fig. 3 Possible interaction modes using solids based on magnetic silica.

Taking into account this problem, paramagnetic core is covered with silica or compounds based on polymers previous to immobilization of carbonaceous materials. These multishell particles improve the chemical stability, biocompatibility and the possible post-synthesis modification. Application of materials based on magnetic carbon is focused on extraction of aromatic compounds in aqueous matrices, some examples include: azo dyes, methylene blue, phthalate acid esters, and polycyclic aromatic hydrocarbons.

In solid phase extraction, the use of polyacrylate or polystyrene is common. In order to promote retention of polar compounds, the polymer structure should include hydroxyl or acetyl functional groups. The retention of the analyte is a consequence of the chemical character of the functional groups; polymers can then be classified in non-polar, polar, and ion exchangers. In MSPE it has been synthesized adsorbents composed of magnetite covered with the polymeric phase, these materials are resistant to extreme pH values and are bio-compatibles. However, the use of a three phase system of Fe_3O_4/silica/polymer combines the advantages of the magnetic silica and adsorbents based on polymers.

Another alternative which has attracted the attention of the scientific community is the use of molecularly imprinted polymers, which possess a specific affinity similar to antigen-antibody. This kind of materials is synthesized by polymerization of functional and crosslinking monomers in presence of analyte (template). Once the polymer phase is obtained, the template is removed and the cavities formed interact selectively with the analyte when it is used as extracting phase. Recently, these materials have been employed to cover the paramagnetic core followed by their application in MSPE methodologies. Their applicability is focused on the analysis of organic compounds in aqueous samples such as: chlorophenols, herbicides, sulfonamides, and tetracyclines.

Other extracting phases that have been evaluated are ionic and non-ionic surfactants. The hydrophilic group of the surfactant interacts with the paramagnetic core while the hydrophobic chain interacts with the analyte contained in the liquid phase. Some applications of Fe_3O_4, modified with sodium dodecyl sulfate, cetyltrimethylammonium bromide and Triton X-100 in MSPE, are the analysis of trimethoprim, phenols and non-steroidal anti-inflammatories. In addition, surfactants are employed in three phase systems composed of Fe_3O_4/carbon/surfactant where the surfactant is employed as extracting agent and it is also employed to promote dispersion and interaction of the carbonaceous phase in the aqueous phase.

Ionic liquids (IL) are considered green solvents which can replace conventional solvents because of their properties such as low volatility, thermic stability and high ionic conductivity. Some of the most important IL are based on imidazolium salts, these ionic compounds contain in their structure an alkyl chain. Hydrophilic (imidazolium ion) and hydrophobic (alkyn chain) characters are similar to surfactants. The ionic liquid can be added during the synthesis of the paramagnetic core to promote physical adsorptions or as a monomer to generate adsorbents based on magnetic polymers. Stability and reusability of the magnetic adsorbent are associated with the employed immobilization, being the covalent inclusion through polymerization more adequate. The use of ionic liquids as extracting shell in MSPE involves different interaction mechanisms. If the alkyl chain is low ($<$C5), ion exchange mechanism between imidazolium anion and the analyte is predominant. On the other hand, when long alkyl chains are employed the adsorbents behavior is similar to the surfactants allowing their use during separation and analysis of organic molecules through hydrophobic interactions. The synthesis of three phase systems Fe_3O_4/carbon/ionic liquid or Fe_3O_4/silica/ionic liquid has been evaluated in order to include mixed mode interactions (π–π or hydrogen bond).

Some specific magnetic solids include the use of Fe_3O_4 covered with terminal NH_2 silica commonly employed for covalent immobilization of antibodies, enzymes, organic or biological ligands and metal organic frameworks. These magnetic solids are useful for selective extraction of different analytes in complex samples. Once the analyte is separated from the sample matrix, it can be eluted or analyzed directly using separation (chromatography, electrophoresis), spectroscopic (fluorescence, infrared), electrochemical or mass spectrometry techniques.

Automation

Different efforts have been made to design on-line MSPE methodologies. A first approach is the magnetic in-tube solid phase micro extraction which is based on the immobilization of magnetic silica nanoparticles inside a fused-silica capillary used as a loop in the

injection valve of a liquid chromatography system. The sample containing the analytes flows through the capillary and the analytes are retained on the magnetic solid, the internal phase is then washed and finally the analytes are eluted with an adequate solvent previous to their analysis.

Immobilization of magnetic solids in liquid chromatography and electrophoretic methods has been proposed employing permanent magnets close to the column and the capillary, respectively. The magnetic solids are then retained on the inner wall to perform the separation the analytes. Separation efficiency is a consequence of the large surface area of the magnetic particles and the magnetic field strength.

Magnetic solids have been immobilized by different protocols in order to integrate them as extraction phase in lab-on valve systems, microfluidic chip manifolds, flow injection and sequential injection protocols. In all cases, the particles are immobilized rather than being dispersed in the sample as MSPE batch mode.

Future Developments

Separation techniques based on use of magnetic solids have advantages that include: reduction of the time required for sample treatment, simultaneous separation of different analytes, easy and efficient isolation of the solid phase. These benefits promote the achievement of high enrichment factors. Additionally, the use of organic solvents is lower compared with other extraction techniques. MSPE is then considered friendly environmental.

However, the application of magnetic solids during the analysis of different analytes in ultra-trace concentration is still a challenge. Respect to the synthesis protocols, it is important to control the variables involved taking into account that the extracting phase must be homogenous, it should contain functional groups to improve dispersibility and it also must protect the paramagnetic core to promote reusability of the solids.

Finally, it is important to mention that the main challenge is the design of on-line methodologies in which the magnetic solid is dispersed into the sample. Automation of MSPE is important for routine analysis if the time required during sample treatment should be minimized.

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