TRENDS IN SORBENTS FOR SOLID PHASE EXTRACTION

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The determination of organic compounds in areas such as environmental, biological or food analyses, at low levels requires efficient sample preparation techniques prior chromatographic techniques, to preconcentrate and/or clean-up the sample.

Solid-phase extraction (SPE) has become one of the most important sample pre-treatment techniques. In SPE, the analytes to be extracted are portioned between the solid-phase and a liquid phase (samples matrix), and analytes must have greater affinity for the solid-phase than for the sample matrix. The choice of sorbent is therefore a key point in SPE to obtain selectivity and capacity. Numerous materials can be used as SPE sorbents. Thus, the research in SPE is mainly focused on the development of new sorbents to enhance the extraction of polar compounds and to obtain selective sorbents for specific applications [1,2]. Several examples of new synthesised materials that are either commercially available or "in-house" prepared and their application to SPE are described.

Classically, they are divided into silica-based, carbon-based and macroporous polymeric sorbents. Of these, polymeric sorbents are the most suitable because of their chemical stability and broad range of physico-chemical characteristics. The type of sorbent, its structure and its interactions with the solute are clearly related to the efficiency of the extraction process. Thus, when new materials are being developed, it is equally important to define both their chemical structure, which determines the type of interactions, and their morphology (i.e. specific surface area, porosity, particle size, etc.), which determines the mechanical properties and, eventually, the stability of the resin.

One of the general features of the macromolecular polymeric sorbents is its porous structure and high specific surface area, which is essential to increase the retention capability towards the compounds. These sorbents are known as highly crosslinked sorbents, which are macroporous styrene-divinylbenzene (St-DVB) polymers with specific surface area up to 800 m^2 g^{-1}. A step further are hypercrosslinked resins, which posse a significant content in microporous and

therefore, display an extremely high specific surface area (up to 2000 m^2 g^{-1}) and hence excellent sorption properties. Some studies have shown that recoveries are best when hypercrosslinked sorbents are used and not sorbents with a lower crosslinking degree (and therefore with a lower specific surface area). For instance, the hypercrosslinked resin Hysphere-SH gave better recoveries than conventional macroporous resin PRLP-S in the on-line SPE of substituted phenols [3].

Other options to enhance the extraction of polar compounds are copolymers with a polar monomer and chemically modified polymers.

Commercial sorbents based on copolymers with a polar monomer include, for instance, OASIS HLB (from Waters), Abselut Nexus (from Varian) and efficient extraction of polar compounds have been obtained from these sorbents [4,5]. Examples of in-house sorbents are those of the Trockimzuck group [6], based on several polar monomers, and those of our group, using 4-vinylpyridine-divinylbenzene (4VP-DVB) [7], N-vinylimidazole-divinylbenzene [8] or hypercrosslinked resins which have different hydroxyl group contents [9] and good recoveries for polar compounds, such as phenol, were obtained in all cases, being the best one for the hypercrosslinked resin.

Chemically modifying existing polymers is another method for obtaining polar sorbents. This option has been adopted by either research groups to improve the available sorbents or manufacturers. In our research group a commercial St-DVB resin was modified with such moieties as o-carboxybenzoyl [10], 2-carboxy-3/4-nitrobenzoyl and 2,4-dicarboxybenzoyl [11]. When these resins were tested by on-line SPE, the recoveries were higher than their unmodified analogues. Examples of commercially available chemically modified resins are: Isolute ENV+ (modified with hydroxyl groups) from IST, Strata X (with vinylpyrrolidone) from Phenomenex or Speed-Advanta (with carboxyl moieties) from Applied Separations.

As regards to increase the selectivity, in the last few years molecularly imprinted polymers (MIPs) have been increasingly used as sorbents in solid-phase extraction [2]. MIPs are tailor-made materials which have specific cavities for a template molecule and they can be synthesised by several techniques. The simplest one is polymerisation in solution, which gives rise to a monolith which must be crushed before use. Other techniques are precipitation, which gives rise to spherical particles with the advantages that these have for applications such as chromatography, suspension, two-step swelling, emulsion core-shell, etc. [2]. At present there are already some commercial MIPs but most of the published results are obtained with “in house” prepared MIPs.

Molecularly imprinted solid-phase extraction (MISPE) has mainly been used in environmental [2,12,13] and biological samples [2,14]. Of the latter, biological fluids such as urine, serum or plasma have been the most frequently analysed samples, but relatively few studies focus on tissue samples. MISPE has been used in both on-line and off-line mode, coupled to liquid chromatography.

In this lecture we also present an overview of the various MIP applications developed by our group. All MIPs have been synthesised by using polymerisation in solution and, when possible, MISPE has been on-line connected to liquid chromatography. The synthetic procedure and the different steps for solid-phase extraction are described and examples are given of the MIPs synthesised using as templates different environmental pollutants or drugs. For instance, naphthalenesulfonic acids can be extracted from 500 ml of sample without interference from other compounds in the sample, using an MIP synthesised with 1-naphthalenesulfonic acid as template [12]. Anti-inflammatory drugs such as ibuprofen, naproxen, diclofenac or fenoprofren can be also extracted from river and waste water samples by using ibuprofen as the template of the MIP, because of its crossreactivity [15].

As regards biological samples, urine and tissue samples have been analysed. It is interesting to use MIPs to analyse tissue samples because their matrix is complex. The use of an MIP for the enrofloxacin enables two fluoroquinolones to be selectively extracted from pig liver after a two-step SPE, using an OASIS cartridge and the MIP, at the levels required by the EU legislation [16], which states that the total sum of both fluoroquinolones should not exceed 200 $\mu g\ kg^{-1}$.

In urine samples, the high selectivity of an MIP for ciprofloxacin, a fluoroquinolone used in human medicine, enables the chromatographic separation to be eliminated and the urine extract to be directly determined with mass spectrometry after a two-step SPE (using OASIS and the MIP), which involves a significant decrease in analysis time [17].

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