Review

Solid phase extraction of trace elements

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Abbreviations: AAS, Atomic absorption spectrometry; ACN, Acetonitrile; AES, Atomic emission spectrometry; APDC, Ammonium pyrrolidine dithiocarbamate; BAS, Bis[l-hydroxy-9,10-anthraquinone-2-methyl]sulfide; 5-BrPADAP 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol; BSQ, 8-(Benzenesulfonamido)quinoline; 18C6, 18-Crown-6; CA, Chromotropic acid; CTA, Cetyltrimethylammonium; CV-AAS, Cold vapour atomic absorption spectrometry; DAD, Diode array detector; DDQ, 7-Dodecenyl-8-quinolinol; DDTC, Diethylthiocarbamate; DDP, 0,0-Diethyl-dithiophosphate; DEBT, N,N9-Diethyl-N9-benzoylthiourea; DMS, Diethyl selenide; DMBS, Dimethyglyoxal bis(4-phenyl-3-thiosemicarbazone); DMDS, Dimethyl diselenide; DMG, Dimethylglyoxime; DMS, Dimethyl selenide; DPC, Diphenylcarbazide; DPCO, Diphenylcarbazone; DPD, N,N-Dimethyl-p-phenylenediamine; DPTH, l,5-bis(di-2-pyridyl) methylene dithiocarbohydrazide; DVB-VP, Divinylbenzene-vinylpyrrolidone; DZ, Dithizone; DzS, Dithizone sulfonic acid; ECD, Electron capture detection; EDTA, Ethylene diamine tetracetic acid; ERT, Erichrome black-T; ETAAS, Electrothermal atomic absorption spectrometry; Et, Ethyl; EtOH, Ethanol; F-AAS, Flame atomic absorption spectrometry; FI, Flow injection; FPD, Flame photometric detection; FZ, Ferrozine; GC, Gas chromatography; GCB, Graphitized carbon black; HDEHP, Bis(2-ethylhexyl) hydrogen phosphate; HMDIC, Hexamethylenedithiocarbamate; H2MEHP, 2-Ethylhexyl dihydrogen phosphate; 8-HQ, 8-Hydroxyquinoline; 8-HQ-5-SA, 8-Hydroxyquinoline-5-sulfonic acid; HT18C6, Hexathia-18-crown-6; HT18C6TO, Hexathia-18-crown-6-tetraone; IBMK, Isobutyl methyl ketone; ICP, Inductively coupled plasma; IDA, Iminodiacetate; IP, Ion-pair; KR, Knotted reactor; LC, Liquid chromatography; LLE, Liquid–liquid extraction; LOD, Limit of detection; MBT, 2-Mercaptobenzoiazole; Me, Methyl; MeOH, Methanol; MPSP, 3-Methyl-l-phenyl-4-stearoyl-5-pyrazolone; MPT, Microwave plasma torch; MS, Mass spectrometry; NCH, Neocuproine; NDSA, 2-Naphthol-3,6-disulfonic acid; NN, 1-Nitroso-2-naphthol; ODETA, 4-(N-octyl)diethylenetriamine; PA, Polyaclate; PAA, Picolinic acid amide; PADMAP 2-(2-pyridylazo)-5-dimethylaminophenol; PAN, 1-(2-pyridylazo)2-naphthol; PaPhA, Polyaminophosphonic acid; PAR, 4-(2-pyridylazo)resorcinol; PC, Pyrocatechol; PDATA, Proplyenediaminetetraacetic acid; PDT, 3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine; PDC, Poly(dithiocarbamate); PE, Polyethylene; PGC, Porous graphitized carbon; Ph, Phenyl; PIPDTC, Piperidine dithiocarbamate; PS-DVB, Polystyrene-dicylambenzenz; PTFE, Polytetrafluoroethylene; PUF, Polyurethane foam; PV, Pyrocatechol violet; ROMP, Ring-opening metathesis polymerisation; SA, Salicylic acid; SDS, Sodium dodecylsulfate; SFE, Supercritical fluid extraction; SGBM, Silica gel bound macrocycles; SPE, Solid phase extraction; SPS, Solid-phase spectrophotometry; TAN, 1-(2-tiazolylazo)-2-naphthol; TBP, Tri-n-butyl phosphate; TBP, Tetra-(4-bromophenyl)-porphyrin; TBT, Tributyltin; TCPP, Carboxyphenyloporphyrin; THF, Tetrahydrofuran; TOPO, Tri-n-octylphosphine oxide; TPhT, Triphenyltin; TS, Methylthiosalicylate; TSA, Thiosalicylic acid; TTA, 2-Thenoyltrifluoroacetone; UV, Ultraviolet; XO, Xylenol orange.

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1. Introduction

Despite the selectivity and sensitivity of analytical techniques such as atomic absorption spectrometry, there is a crucial need for the preconcentration of trace elements before their analysis due to their frequent low concentrations in numerous samples (especially water samples). Additionally, since high levels of non-toxic components usually accompany analytes, a clean-up step is often required. Liquid–liquid extraction is a classical method for preconcentrating metal ions and/or matrix removal. Solid phase extraction (SPE) is another approach that offers a number of important benefits. It reduces solvent usage and exposure, disposal costs and extraction time for sample preparation. Consequently, in recent years SPE has been successfully used for the separation and sensitive determination of metal ions, mainly in water samples. After outlining the theory of this technique, guidelines are given for the development of SPE-based methods for preconcentration of many trace elements. Finally, examples of applications are presented.

2. Theory

The principle of SPE is similar to that of liquid–liquid extraction (LLE), involving a partitioning of solutes between two phases. However, instead of two immiscible liquid phases, as in LLE, SPE involves partitioning between a liquid (sample matrix) and a solid (sorbent) phase. This sample treatment technique enables the concentration and purification of analytes from solution by sorption on a solid sorbent. The basic approach involves passing the liquid sample through a column, a cartridge, a tube or a disk containing an adsorbent that retains the analytes. After all of the sample has been passed through the sorbent, retained analytes are subsequently recovered upon elution with an appropriate solvent. The first experimental applications of SPE started fifty years ago [1,2]. However, its growing development as an alternative approach to liquid–liquid extraction for sample preparation started only in the mid-1970s. It has been extensively used in the past fifteen years for the preconcentration of organic micropollutants, especially pesticides, in water samples [3]. However, numerous studies have also shown the great potential of this technique for speciation studies.

2.1. Presentation of the technique

2.1.1. Basic principles

An SPE method always consists of three to four successive steps, as illustrated in Fig. 1. First, the solid sorbent should be conditioned using an appropriate solvent, followed by the same solvent as the sample solvent. This step is crucial, as it enables the wetting of the packing material and the solvation of the functional groups. In addition, it removes possible impurities initially contained in the sorbent or the packaging. Also, this step removes the air present in the column and fills the void volume with solvent. The nature of the conditioning solvent depends on the nature of the solid sorbent. Typically, for reversed phase sorbent (such as octadecyl-bonded silica), methanol is frequently used, followed with water or aqueous buffer whose pH and ionic strength are similar to that of the sample. Care must be taken not to allow the solid sorbent to dry between the conditioning and the sample treatment steps, otherwise the analytes will not be efficiently retained and poor recoveries will be obtained. If the sorbent dries for more than several minutes, it must be reconditioned.

The second step is the percolation of the sample through the solid sorbent. Depending on the system used, volumes can range from 1 ml to 1 l. The sample may be applied to the column by gravity, pumping, aspirated by vacuum or by an automated system. The sample flow-rate through the sorbent should be low enough to enable efficient retention of the analytes, and high enough to avoid excessive duration. During this step, the analytes are concentrated on the sorbent. Even though matrix components may also be retained by the solid sorbent, some of them pass through, thus enabling some purification (matrix separation) of the sample.

The third step (which is optional) may be the washing of the solid sorbent with an appropriate solvent, having a low elution strength, to eliminate matrix components that have been retained by the
solid sorbent, without displacing the analytes. A drying step may also be advisable, especially for aqueous matrices, to remove traces of water from the solid sorbent. This will eliminate the presence of water in the final extract, which, in some cases, may hinder the subsequent concentration of the extract and/or the analysis.

The final step consists in the elution of the analytes of interest by an appropriate solvent, without removing retained matrix components. The solvent volume should be adjusted so that quantitative recovery of the analytes is achieved with subsequent low dilution. In addition, the flow-rate should be correctly adjusted to ensure efficient elution. It is often recommended that the solvent volume be fractionated into two aliquots, and before the elution to let the solvent soak the solid sorbent.

2.1.2. Retention of trace elements on the sorbent

Adsorption of trace elements on the solid sorbent is required for preconcentration (see Fig. 2). The mechanism of retention depends on the nature of the sorbent, and may include simple adsorption, chelation or ion-exchange. Also, for trace elements, ion-pair solid phase extraction may be used.

2.1.2.1. Adsorption. Trace elements are usually adsorbed on solid phases through van der Waals forces or hydrophobic interaction. Hydrophobic interaction occurs when the solid sorbent is highly non-polar (reversed phase). The most common sorbent of this type is octadecyl-bonded silica (C_{18}-silica). More recently, reversed polymeric phases have appeared, especially the styrene-divinylbenzene copolymer that provides additional π-π interaction when π-electrons are present in the analyte [4]. Elution is usually performed with organic solvents, such as methanol or acetonitrile. Such interactions are usually preferred with online systems, as they are not too strong and thus they can be rapidly disrupted. However, because most trace element species are ionic, they will not be retained by such sorbents.

2.1.2.2. Chelation. Several functional group atoms are capable of chelating trace elements. The atoms most frequently used are nitrogen (e.g. N present in amines, azo groups, amides, nitriles), oxygen (e.g. O present in carboxylic, hydroxyl, phenolic, ether, carbonyl, phosphoryl groups) and sulfur (e.g. S present in thiols, thiocarbamates, thioethers). The nature of the functional group will give an idea of the selectivity of the ligand towards
trace elements. In practice, inorganic cations may be divided into 3 groups:

- **group I-‘hard’ cations**: these preferentially react via electrostatic interactions (due to a gain in entropy caused by changes in orientation of hydration water molecules); this group includes alkaline and alkaline-earth metals (Ca\(^{2+}\), Mg\(^{2+}\), Na\(^{+}\)) that form rather weak outer-sphere complexes with only hard oxygen ligands.

- **group II-‘borderline’ cations**: these have an intermediate character; this group contains Fe\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), Pb\(^{2+}\), Mn\(^{2+}\). They possess affinity for both hard and soft ligands.

- **group III-‘soft’ cations**: these tend to form covalent bonds. Hence, Cd\(^{2+}\) and Hg\(^{2+}\) possess strong affinity for intermediate (N) and soft (S) ligands.

For soft metals, the following order of donor atom affinity is observed: 0<N<S. A reversed order is observed for hard cations. For a bidentate ligand, affinity for a soft metal increases with the overall softness of the donor atoms: (0, 0)<(0, N)<(N, N)<(N, S). The order is reversed for hard metals. In general, the competition for a given ligand essentially involves Group I and Group II metals for O sites, and metals of Group II and Group III for N and S sites. The competition between metals of Group I and Group III is weak.

Chelating agents may be directly added to the sample for chelating trace elements, the chelates being further retained on an appropriate sorbent. An alternative is to introduce the functional chelating group into the sorbent. For that purpose, three different means are available: (1) the synthesis of new sorbents containing such groups (new sorbents); (2) the chemical bonding of such groups on existing sorbents (functionalized sorbents); and (3) the physical binding of the groups on the sorbent by impregnating the solid matrix with a solution containing the chelating ligand (impregnated, coated or loaded sorbents). The latter remains the most simple to be used in practice. Its main drawback is the possible flush of the chelating agent out of the solid sorbent during sample percolation or elution that reduces the lifetime of the impregnated sorbent.
Different ligands immobilized on a variety of solid matrices have been successfully used for the preconcentration, separation and determination of trace metal ions. Chelating agents with an hydrophobic group are retained on hydrophobic sorbents (such as C\textsubscript{18}-silica). Similarly, ion-exchange resins are treated with chelating agents containing an ion-exchange group, such as a sulfonic acid derivative of dithizone (i.e. diphenylthiocarbazone) (DzS), 5-sulfo-8-quinolinol, 5-sulfosalicylic acid, thiosalicylic acid, chromotropic acid, or carboxyphenyl-porphyrin (TCPP) [5–8].

Binding of metal ions to the chelate functionality is dependent on several factors: (1) nature, charge and size of the metal ion; (2) nature of the donor atoms present in the ligand; (3) buffering conditions which favor certain metal extraction and binding to active donor or groups; and (4) nature of the solid support (e.g. degree of cross-linkage for a polymer). In some cases, the behavior of immobilized chelating sorbents towards metal preconcentration may be predicted using the known values of the formation constants of the metals with the investigated chelating agent [9]. However, the presence of the solid sorbent may also have an effect and lead to the formation of a complex with a different stoichiometry than the one observed in a homogeneous reaction [10,11]. In fact, several characteristics of the sorbent should be taken into account, namely the number of active groups available in the resin phase [7,10], the length of the spacer arm between the resin and the bound ligand [12], and the pore dimensions of the resin [13].

2.1.2.3. Ion-pairing. When a non-polar sorbent is to be used, an ion-pair reagent (IP) can be added to the sorbent [14]. Such reagents contain a non-polar portion (such as a long aliphatic hydrocarbonated chain) and a polar portion (such as an acid or a base). Typical ion-pair reagents are quaternary ammonium salts and sodium dodecylsulfate (SDS) [15,16]. The non-polar portion interacts with the reversed-phase non-polar sorbent, while the polar portion forms an ion-pair with the ionic species present in the matrix (that could be either free metallic species in solution or complexes).

2.1.2.4. Ion exchange. Ion-exchange sorbents usually contain cationic or anionic functional groups that can exchange the associated counter-ion. Strong and weak sites refer to the fact that strong sites are always present as ion-exchange sites at any pH, while weak sites are only ion-exchange sites at pH values greater or less than the pK\textsubscript{a}. Strong sites are sulfonic acid groups (cation-exchange) and quaternary amines (anion-exchange), while weak sites consist of carboxylic acid groups (cation-exchange) or primary, secondary and tertiary amines (anion-exchange). These groups can be chemically bound to silica gel or polymers (usually a styrene-divinylbenzene copolymer), the latter allowing a wider pH range.

An ion-exchanger may be characterized by its capacity, resulting from the effective number of functional active groups per unit of mass of the material. The theoretical value depends upon the nature of the material and the form of the resin. However, in the column operation mode, the operational capacity is usually lower than the theoretical one, as it depends on several experimental factors, such as flow-rate, temperature, particle size and concentration of the feed solution. As a matter of fact, retention on ion-exchangers depends on the distribution ratio of the ion on the resin, the stability constants of the complexes in solution, the exchange kinetics and the presence of other competing ions. Even though ion-exchangers recover hydrated ions, charged complexes and ions complexed by labile ligands, they are of limited use in practice for preconcentration of trace elements due to their lack of selectivity and their retention of major ions [17]. Yet, for some particular applications they may be a valuable tool. Hence, iron speciation was possible through selective retention of the negative Fe(III)-ferron complex on an anion-exchanger [18]. Selenium speciation was also feasible by selectively eluting Se(IV) and Se(VI) retained on an anion-exchanger [19].

2.1.3. Elution of trace elements from the sorbent

The same kind of interactions usually occur during the elution step. This time, the type of solvent must be correctly chosen to ensure stronger affinity of the trace element for the solvent, to
ensure disruption of its interaction with the sorbent (as illustrated in Fig. 2). Thus, if retention on the sorbent is due to chelation, the solvent could contain a chelating reagent that rapidly forms a stronger complex with the trace metal. Elution may also be achieved using an acid that will disrupt the chelate and displace the free trace element. Similarly, if retention is due to ion exchange, its pH dependence enables the use of eluents with different pH to be used, such as acids.

Of prime importance is to selectively elute only the target species. So, if they are more strongly retained on the sorbent than the interferent compounds, a washing step with a solvent of moderate elution strength is highly advisable before elution of the target species with the appropriate solvent.

2.2. Operation

The sorbent may be packaged in different formats: filled micro-columns, cartridges, syringe barrels and discs [2,20,21]. The disposable sorbent containers are illustrated in Fig. 3.

2.2.1. Micro-columns

The use of a micro-column is a common procedure for extraction of trace elements from various samples. It affords the opportunity of packing the column with the desired sorbent, so that a broader choice than the commercially disposable containers is available. In addition, the size of the column (i.e., the sorbent weight) may be adapted to the sample volume. In particular, it allows larger sample volumes, thus enabling the preconcentration of metal ions at very low concentration levels. However, such columns must be reused, so that careful blank washings should be conducted to avoid cross-contamination. In addition, columns with a narrow internal diameter limit usable flow-rates to a range 1–10 ml/min that necessitates long trace-enrichment times for large sample volumes [22].

As will be discussed later, micro-columns are frequently used in systems affording the on-line coupling of SPE to analytical techniques. However, in that case, the size of the column is limited to achieve acceptable analytical performance.

2.2.2. Disposable cartridges and syringe barrels

Nowadays, the most frequently used design in off-line SPE is the cartridge or the syringe barrel. They are usually made of polypropylene or polyethylene and filled with packing material having different functional groups. The solid sorbent is contained between two 20 μm polypropylene frits (in some cases they may be made of glass). They afford great selectivity due to the broad types of sorbents contained in commercially available systems with different column volume available. In addition, their disposable character prevents possible cross contamination.

Cartridges vary from as little as 100 mg to 1 g or more. Syringe barrels range in size from 1 to 25 ml and packing weights from 50 mg to 10 g. Solvent reservoirs may be used at the top of the syringe barrels to increase the total volume (50–100 ml). The barrel of the syringe terminates in a male Luer tip, which is the standard fitting to be used with various SPE vacuum manifolds available. For cartridges, both a female and male Luer tips are present, to enable use of either a positive or negative pressure.

The major disadvantages of cartridges and syringe barrels are slow sample-processing rates and a low tolerance to blockage by particles and adsorbed matrix components, due to their small cross-sectional area. Channeling reduces the capacity of the cartridge to retain analytes and results
in contamination of the isolated analytes with impurities originating from the manufacturing and packing process. Such contaminants were evident for C<sub>18</sub>-silica cartridges, while less contaminants were observed with C<sub>18</sub>-silica disks [23,24].

2.2.3. Disks

The use of flat disks with a high cross-sectional area may largely prevent all the problems encountered with columns, cartridges and tubes [21]. The packing material is usually embedded in an inert matrix of polytetrafluoroethylene (PTFE) microfibris, with a typical composition of 90% w/w sorbent and 10% w/w PTFE fibers [25]. Other types of disks use a glass-fibre matrix to hold the sorbent particles, in order to enable a higher flow-rate. The disks are available in different diameters from 4 to 90 mm, the size most frequently used being 47 mm. They are designed to be used in conjunction with a filtration apparatus connected to a water aspirator [25]. In order to remove potential interferences and to ensure optimal extraction of the analyte of interest, disk cleaning and conditioning should be done before its use.

Due to a lower void volume and a higher surface area associated with small particles as compared to cartridges, partitioning of the analytes is favored. Hence, a smaller mass of sorbent is required to process a similar volume of sample. Disks thus present the advantage of reducing solvent volumes for both the conditioning and elution steps. Additionally, the decreased back-pressure encountered with these devices enables the use of high flow-rates, and their wide bed minimizes the chance of plugging. In addition, new technology for embedding the stationary phase prevents channeling and improves mass transfer. As classical disks are dedicated to the SPE of large-volume samples, new systems have very recently emerged that enable the use of disks for small-volume samples: the extraction disk cartridge (the disk is placed in a syringe-barrel format), and the 96-well microtiter plate configuration [20,21,26]. Such systems are primarily dedicated to biological samples.

One of the drawbacks of using disks is the decrease in the breakthrough volume (which is the volume that can be percolated without analyte losses). In addition, disks have lower capacity than cartridges, so that for real samples (e.g. high content of natural organic matter in river water) incomplete retention of the target metal species may result [27]. As a consequence, disks are recommended when there is a strong interaction between the analyte and the sorbent.

2.3. Advantages of the technique

Classical liquid–liquid extractions of trace elements are usually time-consuming and labor-intensive. In addition, they require strict control of extraction conditions, such as temperature, pH and ionic strength. For all these reasons, several procedures tend to be replaced by SPE methods. This technique is attractive as it reduces consumption of and exposure to solvents, their disposal costs and extraction time [28]. It also allows the achievement of high recoveries [29], along with possible elevated enrichment factors. However, as different results between synthetic and real samples may be observed [30], recoveries should be estimated in both cases as far as possible. In addition, SPE can be interfaced on-line with analytical techniques, such as liquid chromatography (LC) or atomic absorption spectrometry (AAS). Its application for preconcentration of trace metals from different samples is also very convenient due to sorption of target species on the solid surface in a more stable chemical form than in solution. Finally, SPE affords a broader range of applications than LLE due to the large choice of solid sorbents.

2.3.1. Preconcentration

LLE requires the use of large volumes of high-purity solvent, thereby affording limited preconcentration factors. The use of SPE enables the simultaneous preconcentration of trace elements and removal of interferences, and reduces the usage of organic solvents that are often toxic and may cause contamination. Upon elution of the retained compounds by a volume smaller than the sample volume, concentration of the extract can be easily achieved. Hence, concentration factors of up to 1000 may be attained.

2.3.2. Preservation and storage of the species

SPE allows on-site pre-treatment, followed by simple storage and transportation of the pre-treated
samples with stability of the retained metallic species for several days [21,24,31,32]. This point is crucial for the determination of trace elements, as the transport of the sample to the laboratory and its storage until analysis may induce problems, especially changes in the speciation. In addition, the space occupied by the solid sorbents is minimal and avoids storage of bulky containers and the manpower required to handle them.

2.3.3. High selectivity

SPE offers the opportunity of selectively extracting and preconcentrating only the trace elements of interest, thereby avoiding the presence of major ions. This is crucial in some cases, such as with spectrophotometric detection, since the determination of heavy metals in surface waters may necessitate the removal of non-toxic metals, such as Fe or Zn, when they occur at high concentrations [33]. It may also be possible to selectively retain some particular species of a metal, thereby enabling speciation. For example, salen I modified C_{18}-silica is quite selective towards Cu(II) [34], while chemical binding of formylsalicylic acid on amino-silica gel affords selectivity towards Fe(III) [35]. This high selectivity may also be used to remove substances present in the sample that may hinder metal determination, such as lipid substances in the case of biological samples [36].

2.3.4. Automation and possible on-line coupling to analysis techniques

SPE can be easily automated, and several commercially available systems have been recently reviewed [26]. Home-made systems have also been reported [37]. In addition, SPE can be coupled on-line to analysis techniques. On-line procedures avoid sample manipulation between preconcentration and analysis steps, so that analyte losses and risk of contamination are minimized, allowing higher reproducibility [38]. In addition, all the sample volume is further analyzed, which enables smaller sample volume to be used. However, in the case of complex samples, off-line SPE should be preferred due to its greater flexibility, and the opportunity to analyze the same extract using various techniques.

2.3.4.1. On-line coupling to liquid chromatography

On-line systems mainly use a micro-column. The sorbent is chosen not only for its efficiency in trapping analytes, but also for its compatibility with the stationary phase packed into the chromatographic column. Indeed, it is highly recommended to use the same packing in the precolumn and the chromatographic column to prevent losses in efficacy upon analysis. For the case of two different sorbents being used, the retention of the analytes in the precolumn should be lower than in the analytical column to ensure band refocusing at the head of the chromatographic column. On-line systems with several detectors have been reported, such as ultraviolet (UV) detector [39] or inductively coupled plasma mass spectrometer (ICP-MS) [40], with detection limits in the 0.05–50 µg/l range. Detection limits as low as 0.5 ng/l could even be achieved by detection at the maximum absorption wavelength using a photodiode array UV detector [41]. Additional coupling may be feasible, such as the on-line coupling of supercritical fluid extraction (SFE) with an on-line SPE–LC system [42]. The coupling of SPE to LC via flow injection has also been reported using cold vapour AAS (CV-AAS) as the detection, enabling enrichment factors approximately 850 [43].

2.3.4.2. On-line coupling to atomic absorption spectrometry

Olsen et al. [44] and Fang et al. [45,46] were the first to describe an on-line flow-injection (FI) sorbent extraction preconcentration system for flame AAS (F-AAS) using micro-columns packed with a cation-exchanger. Later, they also proposed a system for on-line flow-injection sorbent extraction preconcentration with electrothermal vaporization AAS (ET-AAS) using lead as a model trace element [47]. Since then, numerous papers reported FI with on-line preconcentration followed by AAS, as exemplified by determination of Cu, Cr(VI) or Pb [48–50]. Selected applications are reported in Table 1. The sorbent should provide for rapid sorption and desorption of the analytes to be used in FI systems [65]. In addition, it should be provided for a high selectivity. In practice, C_{18}-silica is very frequently used as organic solvents (such as methanol) can
**Table 1**
Applications of SPE to FI on-line preconcentration systems

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Trace elements</th>
<th>Chelating agent added</th>
<th>Sorbent</th>
<th>Eluent</th>
<th>Analysis method</th>
<th>Recovery (%)</th>
<th>Loading time (volume)</th>
<th>Preconcentration factor</th>
<th>LOD (ng/l)</th>
<th>Sampling frequency (h⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic sorbents</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sea and waste waters</td>
<td>Cd</td>
<td>None</td>
<td>DPTH-functionalized-SiO₂</td>
<td>HNO₃–HCl</td>
<td>ICP–AES</td>
<td>97.5–104</td>
<td>1 min</td>
<td>86</td>
<td>1100</td>
<td>40</td>
<td>[51]</td>
</tr>
<tr>
<td>Sea and waste waters</td>
<td>Cd</td>
<td>None</td>
<td>TS-functionalized-SiO₂</td>
<td>Thiourea</td>
<td>ICP–AES</td>
<td>95.2–103.3</td>
<td>2 min</td>
<td>62</td>
<td>4300</td>
<td>24</td>
<td>[51]</td>
</tr>
<tr>
<td>Sea waters</td>
<td>Fe</td>
<td>None</td>
<td>8-HQ-functionalized-SiO₂</td>
<td>HCl</td>
<td>Spectro-photometry</td>
<td>106.3</td>
<td>2 min</td>
<td>—</td>
<td>0.016 nM</td>
<td>—</td>
<td>[52]</td>
</tr>
<tr>
<td>Geological sample, Cu metal, Pb nitrate</td>
<td>Ag</td>
<td>None</td>
<td>MBT-functionalized-SiO₂</td>
<td>Thiourea</td>
<td>F-AAS</td>
<td>93.5–101</td>
<td>1 min</td>
<td>—</td>
<td>660</td>
<td>60</td>
<td>[53]</td>
</tr>
<tr>
<td>Certified ore samples, Ni alloy, anode slime, electrolytic solution</td>
<td>Ag, Au, Pd</td>
<td>None</td>
<td>Amidino-thioureido-SiO₂</td>
<td>Thiourea</td>
<td>F-AAS</td>
<td>98.7–101.4</td>
<td>1 min (4.5 ml)</td>
<td>—</td>
<td>1100–17 000</td>
<td>—</td>
<td>[54]</td>
</tr>
<tr>
<td>Fish, human urine</td>
<td>MeHg, EtHg, PhHg, Hg(II)</td>
<td>APDC C₁₈-silica</td>
<td>MeOH-ACN-water</td>
<td>LC–CV-AAS</td>
<td></td>
<td>92–106</td>
<td>20 min (58.5 ml)</td>
<td>750–950</td>
<td>5.5–10.4</td>
<td>2.3</td>
<td>[43]</td>
</tr>
<tr>
<td>Sea water</td>
<td>MeHg, Hg(II)</td>
<td>DDTC C₁₈-silica</td>
<td>EtOH</td>
<td>CV-AAS</td>
<td></td>
<td>85–107.5</td>
<td>(25 ml)</td>
<td>500</td>
<td>16</td>
<td>—</td>
<td>[55]</td>
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<td>MeOH</td>
<td>ET-AAS</td>
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<td>104 s</td>
<td>25–100</td>
<td>6.5–1.26</td>
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<td>Cu, Cd, Co 1,10-Phenan-throline</td>
<td>APDC C₁₈-silica</td>
<td>EtOH</td>
<td>F-AAS</td>
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<td>88.9–100.5</td>
<td>30 s</td>
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<td>300–6000</td>
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<tr>
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<td>Cd</td>
<td>PAR or PADMAP C₁₈-silica</td>
<td>MeOH</td>
<td>ET-AAS</td>
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<td>82.5–111.2</td>
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Table 1 (Continued)

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<th>Sorbent</th>
<th>Eluent</th>
<th>Analysis method</th>
<th>Recovery (%)</th>
<th>Loading time (volume)</th>
<th>Preconcentration factor</th>
<th>LOD (ng/l)</th>
<th>Sampling frequency (h⁻¹)</th>
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<td>Cr(III), Cr(VI), Cr(total)</td>
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<td>MeOH</td>
<td>F-AAS</td>
<td>95–105</td>
<td>60–300 s</td>
<td>90–500</td>
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<td>ET-AAS</td>
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<td>Analysis method</td>
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</tbody>
</table>
be used as eluting solvents leading to a high sensitivity in flame AAS. Complexing reagents are, therefore, added for efficient retention of trace metals. Their choice is based on their fast reaction with metals, such as diethyl-dithiocarbamate (DDTC) and ammonium pyrrolidine dithiocarbamate (APDC) [56,59,60,62,91]. In addition, both reagents are water soluble and do not adsorb on C$_{18}$-silica so that it does not overload with the reagent itself. However, these reagents lack selectivity, so that other reagents have been used for particular applications, like 1-10-phenanthroline [57], 4-(2-pyridylazo)resorcinol (PAR) or 2-(2-pyridylazo)-5-dimethylaminophenol (PADMAP) [58], 0,0-diethyl-dithiophosphate (DDTP) [63], 1-nitroso-2-naphthol (NN) [61], 1-(2-tiazolyazo)-2-naphthol (TAN) [66]. The microcolumn can be inserted into the tip of the PTFE capillary in the autosampler arm of a graphite furnace atomic absorption spectrometer [56].

Even though C$_{18}$-silica has been the most frequently used sorbent for FI preconcentration, other sorbents were found satisfactory for some applications as shown in Table 1, such as functionalized silica [51–53], alumina [70–73], activated carbon [63,87–90], polyurethane foam (PUF) [63,92], or PTFE turnings [48–50]. A particular knotted reactor (KR) has been recently developed, which consists of a long tube properly knotted usually made of PTFE. The trace element species are adsorbed on the inner wall of the tubing as indicated by scanning electron microscopy [77]. This reactor allows higher sample loading volumes than micro-columns due to its lower back-pressure. In addition, the inner wall may be precoated with a hydrophobic ligand for subsequent retention of trace elements [93]. However, on the other hand, lower enrichment factors are attained as compared to micro-columns [75]. For that reason, in case of trace metals, micro-columns are usually preferred for the achievement of low levels of determination.

2.3.4.3. On-line coupling to ICP–AES or ICP–MS. The first report of FI on-line preconcentration coupled to ICP-atomic emission spectrometry (AES) appeared nearly twenty years ago [94]. Since then, several studies have used this coupling with different sorbents such as ZrO$_2$ or function-alyzed silica gel for example [51,69]. Similarly, numerous studies have reported on-line coupling to ICP–MS, as noted earlier [95]. A few examples are given in Table 1 [82,84].

2.3.4.4. On-line coupling to spectrophotometry. Spectrophotometry offers the advantage of requiring inexpensive and very common instrumentation. In addition, by choosing a non-selective chromogenic reagent, multi-metal determinations may be possible [33]. Its coupling to FI analysis is well suited for monitoring purposes and a few studies present such systems as indicated in Table 1 [33,52,68,86]. Solid-phase spectrophotometry (SPS) has also been reported with FI systems due to its simplicity and low detection limits. The solid sorbent is packed in either commercially available or customized flow cells. With such systems the retained analytes are periodically removed from the flow cell using an acid or a complexing solution [67,83,85]. On-line FI sorbent extraction procedures have several advantages over the corresponding off-line methods: higher sample throughput (increased by 1 to 2 orders of magnitude), lower consumption of sample and reagent (also reduced by 1 to 2 orders of magnitude), better precision (with relative standard deviations approx. 1–2%), lower risk of loss or contamination and easy automation. However, the FI method by using column extraction has some disadvantages. In particular, it may suffer from insufficient adsorption on the resin and clogging of the column when insoluble ligands are used [96].


Development of an SPE method can be considered as a two-step procedure. First, the most appropriate sorbent for the application should be chosen (the following is intended to help the reader in choosing a solid sorbent for trace element determination). Optimization of the most influential parameters should then be undertaken. Obviously, optimization should initially be performed using spiked synthetic solutions, but it must be followed by the use of certified reference materials or spiked real samples, as matrix components
(such as ligands or other ions) may change the trace element retention on the sorbent, thereby decreasing recoveries of the target species.

3.1. Selection of solid sorbent

Solid sorbents may be hydrophobic or polar. It is common to call reversed-phase sorbents the packing materials that are more hydrophobic than the sample, which are frequently used with aqueous samples. On the other hand, normal-phase sorbents refer to materials more polar than the sample and they are used when the sample is an organic solvent containing the target compounds. When hydrophobic supports are used, retention of ionic metal species will require the formation of hydrophobic complexes. This can be achieved through addition of the proper reagent to the sample or thorough immobilization of the reagent on the hydrophobic solid sorbent. Addition of reagent to the sample is appropriate for the fixation of unstable metal species (such as Cu(I) and Fe(II)) to maintain speciation, while immobilization offers the convenience of having a prepared cartridge or disk before analysis. Immobilization may also provide a significant development in speciation analysis, because metal equilibrium in the sample may not be affected by reaction on the cartridge.

The nature and properties of the sorbent are of prime importance for effective retention of metallic species. Careful choice of the sorbent is thus crucial to the development of SPE methodology. In practice, the main requirements for a solid sorbent are: (1) the possibility to extract a large number of trace elements over a wide pH range (along with selectivity towards major ions); (2) the fast and quantitative sorption and elution; (3) a high capacity; (4) regenerability; and (5) accessibility. In particular, sorbents that allow fast reaction rates are preferred to achieve faster extraction as well as higher loading capacities. Hence, sorbents based on hydrophilic macroporous polymers and cellulose or on fibrous materials provide excellent kinetic properties [97].

The broad variety of sorbents available explains one of the most powerful aspects of SPE, which is selectivity. Sorbents can be mainly categorized as organic based ones (natural polymers, as well as synthetic polymers) and inorganic based ones (silica gel SiO$_2$, alumina Al$_2$O$_3$, magnesia MgO and other oxide species). Immobilization of organic compounds on the surface of the solid support is usually aimed at modifying the surface with certain target functional groups for a higher selectivity of the extraction. The selectivity of the modified solid phases towards certain metal ions is attributed to several well-known factors, such as the size of the organic compound used to modify the sorbent, the activity of the loaded surface groups, and the type of the interacting functional group. However, the selective extraction of a single trace element from other interfering ion(s) represents a direct challenge for finding a suitable phase capable of exhibiting a sufficient affinity to selectively bind that metal ion. For particular applications, the combination of two sorbents may thus be advisable. As an example, the passage of water samples through two successive chelating resins enabled the determination of trace and major elements [98]. Similarly, the combination of an anion and a cation-exchange resin enabled the speciation of Cu and Mn in milk samples [99].

3.1.1. Inorganic based sorbents

Inorganic based sorbents are mainly made of silica gel even though other inorganic oxides may be used, as discussed later (cf. Fig. 4). Silica gel based sorbents present the advantages of mechanical, thermal and chemical stability under various conditions. They frequently offer a high selectivity towards a given metal ion. However, all silica-based sorbents suffer from different chemical limitations, namely the presence of residual surface silanol groups (even after an end-capping treatment) and a narrow pH stability range. Applications of such sorbents to off-line SPE are presented in Tables 2 and 3.

3.1.1.1. Silica gel. Silica gel can be used as a very successful adsorbing agent, as it does not swell or strain, has good mechanical strength and can undergo heat treatment. In addition, chelating agents can be easily loaded on silica gel with high stability, or be bound chemically to the support, affording a higher stability.
The surface of silica gel is characterized by the presence of silanol groups, which are known to be weak ion-exchangers, causing low interaction, binding and extraction of ionic species [131]. In particular, silica gel presents high sorption capacity for metal ions, such as Cu, Ni, Co, Zn or Fe [132]. Retention is highly dependent on sample pH with quantitative retention requiring pH values over 7.5–8, as under acidic conditions silanol groups are protonated and the ion-exchange capacity of the silica gel is greatly reduced or even reduced to zero at low pHs. In addition, this sorbent has a very low selectivity, and is prone to hydrolysis at basic pH. Consequently, modification of the silica gel surface has been performed to obtain solid sorbents with greater selectivity. Two approaches are used for loading the surface with specific organic compounds, chemical immobilization and physical adsorption. In the first case, a chemical bond is formed between the silica gel surface groups and those of the organic compound (functionalized sorbent). In the second approach, the organic compound is directly adsorbed on the silanol groups of the silica gel surface (impregnated or loaded sorbent), either by passing the reagent solution through a column packed with the adsorbent, or by soaking the adsorbent in the reagent solution.

Impregnating reagents are ion-exchangers or chelating compounds. Numerous reagents have been investigated for impregnation of silica gel as a means of increasing retention capacity and selectivity of the sorbent for trace elements, namely thionalide (2-mercapto-N-2-naphthylacetamide) [101,102], 2-mercaptobenzothiazole (MBT) [133], NN [103], 8-hydroxyquinoline (8-HQ) [134,135], 3-methyl-1-phenyl-4-stearoyl-5-pyrazolone (MPSP) [100], salicylaldoxime [132], dimethylglyoxime (DMG) [13], Aliquat 336 (methyltricaprylammonium chloride) and Calcon (hydrophobic sodium sulfonate) [136]. Examples of applications are given in Table 2. Increased stability of the sorbent is obtained by the chemical binding of chelating functional groups on silica gel [104]. Applications to the determination of trace elements have been reported for more than twenty years with several functional groups, such as amines, dithiocarbamates, iminodithiocarbamates or dithioacetals [13,105,106,137,138]. Careful choice of the bound chelating groups enables speciation studies. Hence, dithizone-functionalized silica gel was reported selective towards Hg(II).
Table 2
Applications of off-line SPE to water samples using inorganic supports

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Trace elements</th>
<th>Sorbent</th>
<th>Operation</th>
<th>Experimental conditions</th>
<th>Analysis method</th>
<th>Recovery (%)</th>
<th>Adsorptive capacity</th>
<th>Preconcentration factor</th>
<th>LOD (µg/l)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Silica</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tap water</td>
<td>Cu/Co/Ni</td>
<td>MPSP-loaded- SiO₂</td>
<td>Glass column</td>
<td>Sample pH: 4.5</td>
<td>F-AAS</td>
<td>94.6–101</td>
<td>43/45/49 µmol/g</td>
<td>40</td>
<td>60/40/70</td>
<td>[100]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Elution: HCl 1 M</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sea water</td>
<td>Pd</td>
<td>Thionalide-loaded-SiO₂</td>
<td>Glass column (1 cm i.d.)</td>
<td>Sample pH: 4</td>
<td>F-AAS</td>
<td>83–99</td>
<td>0.8 mg/g</td>
<td>3200</td>
<td>0.03</td>
<td>[101]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Washing elution: thioxurea 0.2 M + HCl 0.1 M</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sea water</td>
<td>As(III)</td>
<td>Thionalide-loaded-SiO₂</td>
<td>Glass column (1 cm i.d.)</td>
<td>Sample pH: 7</td>
<td>Spectrophotometry</td>
<td>92–95</td>
<td>5.6 µmol/g</td>
<td>—</td>
<td>0.12</td>
<td>[102]</td>
</tr>
<tr>
<td>River and sea water</td>
<td>Co</td>
<td>NN-loaded-SiO₂</td>
<td>Glass column</td>
<td>Sample pH: 3.5</td>
<td>γ-Emission</td>
<td>96–98 mmol/g</td>
<td>0.03</td>
<td>10–100</td>
<td>—</td>
<td>[103]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Washing elution: acetic acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spiked tap water</td>
<td>Hg(II)</td>
<td>Dithizone-functionalized-SiO₂</td>
<td>Column</td>
<td>Elution: HCl 10 M</td>
<td>CV-AAS</td>
<td>99–99.5</td>
<td>300 µmol/g</td>
<td>200</td>
<td>3.96</td>
<td>[104]</td>
</tr>
<tr>
<td>Tap and sea waters</td>
<td>Hg(II)</td>
<td>Dithioacetal-functionalized-SiO₂</td>
<td>Column</td>
<td>Elution: water</td>
<td>CV-AAS</td>
<td>91–100</td>
<td>917–1100 µmol/g</td>
<td>5</td>
<td>—</td>
<td>[105]</td>
</tr>
<tr>
<td>Spiked tap and sea waters</td>
<td>Hg(II)</td>
<td>Dithiocarbamate-functionalized-SiO₂</td>
<td>Glass column</td>
<td>Elution: water</td>
<td>CV-AAS</td>
<td>88–100</td>
<td>0.6–0.983 mmol/g</td>
<td>—</td>
<td>—</td>
<td>[106]</td>
</tr>
<tr>
<td>Matrix</td>
<td>Trace elements</td>
<td>Sorbent</td>
<td>Operation</td>
<td>Experimental conditions</td>
<td>Analysis method</td>
<td>Recovery (%)</td>
<td>Adsorptive capacity</td>
<td>Preconcentration factor</td>
<td>LOD (μg/l)</td>
<td>Ref.</td>
</tr>
<tr>
<td>------------------</td>
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<td>-------</td>
</tr>
<tr>
<td>Sea water</td>
<td>V/Co/Ni/Ga/Y/Mo/Cd/Cr/Pr/Nd/Sm/Eu/Gd/Tb/Dy/Mo/Er/Tm/Yb/Lu/W/U</td>
<td>8-HQ-functionalized-fluorinated metal alkoxide glass</td>
<td>Column (6 mm i.d., 30 mm bed height)</td>
<td>Washing sample pH: 5 Washing elution: HNO₃ 0.5 M backflush</td>
<td>ICP-MS</td>
<td>85–116</td>
<td>—</td>
<td>10</td>
<td>0.00037–2200 ng/l</td>
<td>[107]</td>
</tr>
<tr>
<td>Other oxides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rain, river, sea, tap waters</td>
<td>Cr(III)/Cr(VI)</td>
<td>TiO₂</td>
<td>Glass column (1 cm i.d.)</td>
<td>Sample pH: 2 or 8 Elution: HNO₃ 0.5 or 1 M</td>
<td>ET-AAS</td>
<td>78.4–99.2</td>
<td>8125/6983 μg/g</td>
<td>100</td>
<td>0.030/0.024</td>
<td>[108]</td>
</tr>
<tr>
<td>Natural, waste, sea waters</td>
<td>Cd/Co/Cu/Fe/Mn/Ni/Pb</td>
<td>TiO₂</td>
<td>Glass column (1 cm i.d.)</td>
<td>Sample pH: 8 Elution: HNO₃ 1 M and/or EDTA 0.1 M</td>
<td>F-AAS</td>
<td>89–100</td>
<td>5000 μg/g</td>
<td>300</td>
<td>0.01–0.04</td>
<td>[109]</td>
</tr>
<tr>
<td>Tap, ground waters</td>
<td>Cr(III)/Cr(VI)</td>
<td>Neutral Al₂O₃</td>
<td>Column (1 cm i.d.)</td>
<td>Sample pH: 6.5–7 Elution: NH₃ 1 M + HNO₃ 4 M</td>
<td>ET-AAS</td>
<td>99–100</td>
<td>—</td>
<td>25</td>
<td>0.01</td>
<td>[110]</td>
</tr>
<tr>
<td>Tap, ground waters</td>
<td>Se(IV)/Se(VI)</td>
<td>Acidic Al₂O₃</td>
<td>Teflon column (1 cm i.d.)</td>
<td>Sample pH: 2–8 Elution: NH₃ 0.1 M and 4 M</td>
<td>ET-AAS</td>
<td>90–98</td>
<td>23.2/2.0 μg/g</td>
<td>16/100</td>
<td>0.049/0.80</td>
<td>[111]</td>
</tr>
</tbody>
</table>
Table 3
Applications of off-line SPE to water samples using C<sub>18</sub>-silica based supports

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Trace elements</th>
<th>Reagent</th>
<th>Operation Conditions</th>
<th>Analysis Method</th>
<th>Recovery (%)</th>
<th>Adsorptive capacity</th>
<th>Preconcentration factor</th>
<th>LOD (µg/l)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>No reagent</strong></td>
<td>Sea water</td>
<td>TBT</td>
<td>None Cartridge or Empore disk (25 mm) or Bond Elut cartridge</td>
<td>Conditioning sample drying elution: acidified ethyl acetate</td>
<td>GC–ECD</td>
<td>93.5–111.5</td>
<td>1000</td>
<td>—</td>
<td>[24]</td>
</tr>
<tr>
<td>Spiked sea waters</td>
<td>TPhT</td>
<td>None Bond Elut cartridge</td>
<td>Conditioning: MeOH + NaCl Sample Washing</td>
<td>Fluorimetry</td>
<td>81–89</td>
<td>100</td>
<td>—</td>
<td>—</td>
<td>[112]</td>
</tr>
<tr>
<td>Sea water</td>
<td>TPhT None</td>
<td>Bond-Elut cartridge (40 µm) Washing sample, Washing air drying elution: MeOH</td>
<td>Fluorescence (after addition of flavonol to the eluate)</td>
<td>—</td>
<td>250</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>[113]</td>
</tr>
<tr>
<td><strong>Addition of the reagent to the sample</strong></td>
<td>Sea water</td>
<td>Se/Sb</td>
<td>APDC Glass column (1.4 cm i.d)</td>
<td>Sample pH: 1.2 Washing elution: MeOH</td>
<td>ET-AAS</td>
<td>94–97</td>
<td>40–75</td>
<td>0.007/0.05</td>
<td>[114]</td>
</tr>
<tr>
<td>Sea water</td>
<td>Cd/Zn/Cu/Mn/Fe/Ni/Co</td>
<td>8-HQ</td>
<td>Glass column (1.4 cm i.d)</td>
<td>Sample pH: 8.9 Washing (water + oxine) elution: MeOH</td>
<td>ET-AAS</td>
<td>67–108</td>
<td>50–100</td>
<td>—</td>
<td>[115]</td>
</tr>
</tbody>
</table>
Table 3 (Continued)

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Trace elements</th>
<th>Reagent</th>
<th>Operation</th>
<th>Experimental conditions</th>
<th>Analysis method</th>
<th>Recovery (%)</th>
<th>Adsorptive capacity</th>
<th>Preconcentration factor</th>
<th>LOD (µg/l)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>River water</td>
<td></td>
<td>Cu</td>
<td>Neocuproine</td>
<td></td>
<td>Washing conditioning: MeOH</td>
<td>Spectrophotometry (454 nm)</td>
<td>99.7–102.6</td>
<td>940 µg Cu²⁺</td>
<td>50–100</td>
<td>0.12</td>
</tr>
<tr>
<td>CRM water (SLRS-3), lake, river, drinking waters</td>
<td>Cu(I)</td>
<td>Bathocuproine</td>
<td>Bond Elut cartridge</td>
<td>Washing conditioning: MeOH + water Sample pH: 4.3 Elution: MeOH-water 90:10 (v/v)</td>
<td>Spectrophotometry (484 nm)</td>
<td>—</td>
<td>—</td>
<td>20–40</td>
<td>0.40–3.8</td>
<td>[27]</td>
</tr>
<tr>
<td>Tap waters, well water</td>
<td>Fe</td>
<td>Bathophenanthroline</td>
<td>Empore disks (47 mm)</td>
<td>Washing activation: MeOH + water Sample pH: 4–7 Elution: EtOH</td>
<td>Spectrophotometry (533 nm)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.080</td>
<td>[117]</td>
</tr>
<tr>
<td>Synthetic seawaters</td>
<td>MeHg/PhHg/Hg(II)</td>
<td>Dithizone</td>
<td>Sep Pak cartridge</td>
<td>Sample pH: 4 + EDTA 0.001 M Washing</td>
<td>LC–DAD</td>
<td>95–104</td>
<td>200</td>
<td>0.14/0.16/0.14</td>
<td>[31]</td>
<td></td>
</tr>
<tr>
<td>Rain, lake, river waters</td>
<td>MonoBT/DiBT/TBT/MonoPhT/DiPhT/TPhT</td>
<td>Tropolone</td>
<td>Sep-Pak cartridge</td>
<td>Ethylation-GC–FPD</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>[118]</td>
<td></td>
</tr>
<tr>
<td>Tap, well and river waters</td>
<td>Cu</td>
<td>Quinone derivative</td>
<td>Empore disks (47 mm)</td>
<td>Washing Conditioning: buffer sample pH: 7.0 Drying Elution: HNO₃ 0.1 M</td>
<td>F-AAS</td>
<td>98.4–102</td>
<td>360 µg Cu²⁺</td>
<td>400</td>
<td>0.2</td>
<td>[119]</td>
</tr>
<tr>
<td>Matrix</td>
<td>Trace elements</td>
<td>Reagent</td>
<td>Operation</td>
<td>Experimental conditions</td>
<td>Analysis method</td>
<td>Recovery (%)</td>
<td>Adsorptive capacity</td>
<td>Preconcentration factor</td>
<td>LOD (μg/l)</td>
<td>Ref.</td>
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</tr>
<tr>
<td>Tap, rain, snow and sea waters</td>
<td>Cu(II)</td>
<td>Schiff’s base (salen I)</td>
<td>Empore disk (47 mm)</td>
<td>Washing sample pH: 5.5–6 Air drying elution: HNO₃ 0.1 M</td>
<td>AAS</td>
<td>—</td>
<td>396 μg Cu²⁺</td>
<td>≥ 500</td>
<td>0.004</td>
<td>[34]</td>
</tr>
<tr>
<td>Synthetic and spring waters</td>
<td>Pb(II)</td>
<td>Schiff’s base</td>
<td>Empore disk</td>
<td>Washing sample pH: 2–8 Air drying elution: HNO₃ 0.5 M</td>
<td>F-AAS</td>
<td>97.1–100.2</td>
<td>700 μg/disk</td>
<td>50</td>
<td>16.7</td>
<td>[120]</td>
</tr>
<tr>
<td>River water</td>
<td>Pb(II)</td>
<td>BAS</td>
<td>Empore disk (47 mm)</td>
<td>Washing sample pH: 2–7 Air drying elution: acetic acid 1 M</td>
<td>F-AAS</td>
<td>—</td>
<td>476 μg Pb²⁺</td>
<td>≥ 300</td>
<td>0.050</td>
<td>[121]</td>
</tr>
<tr>
<td>Sea waters</td>
<td>Fe(II)</td>
<td>Ferrozine</td>
<td>Sep Pak cartridge</td>
<td>Conditioning: MeOH + water sample pH: 6.8–8.3</td>
<td>Spectro-photometry (562 nm)</td>
<td>91</td>
<td>—</td>
<td>40</td>
<td>0.6</td>
<td>nmol/l [122]</td>
</tr>
<tr>
<td>Rain, sea waters</td>
<td>Fe(II)</td>
<td>Ferrozine</td>
<td>Sep Pak cartridge</td>
<td>Elution: MeOH Conditioning: MeOH + water Sample</td>
<td>LC–UV (254 nm)</td>
<td>92–99</td>
<td>—</td>
<td>100–500</td>
<td>0.1</td>
<td>nmol/l [123]</td>
</tr>
<tr>
<td>Certified sea waters (NASS-2 and SLEW-1)</td>
<td>Cu/Cd</td>
<td>APDC</td>
<td>Teflon cartridge (0.94 mm i.d)</td>
<td>Washing Elution: MeOH Conditioning: MeOH + water Sample: 6–8 Air drying Elution: MeOH</td>
<td>ET-AAS</td>
<td>95.8–103.3</td>
<td>—</td>
<td>25–50</td>
<td>0.0024/0.00018</td>
<td>[124]</td>
</tr>
<tr>
<td>Tap and Spring waters</td>
<td>U(IV)</td>
<td>TOPO</td>
<td>Empore disk (47 mm i.d)</td>
<td>Washing conditioning sample elution: MeOH</td>
<td>Spectro-photometry</td>
<td>85</td>
<td>4033 μg/disk</td>
<td>8</td>
<td>0.1</td>
<td>[125]</td>
</tr>
<tr>
<td>Matrix</td>
<td>Trace elements</td>
<td>Reagent</td>
<td>Operation</td>
<td>Experimental conditions</td>
<td>Analysis method</td>
<td>Recovery (%)</td>
<td>Adsorptive capacity</td>
<td>Preconcentration factor</td>
<td>LOD (μg/l)</td>
<td>Ref.</td>
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</tr>
<tr>
<td>Sea waters</td>
<td>La/Ce/Pr/Nd/Sm/Eu/Gd/Tb/Dy/Ho/Er/Tm/Yb/Lu</td>
<td>HDEHP/H$_2$ME HP</td>
<td>Sep Pak cartridge</td>
<td>Sample pH: 3–3.5, Washing elution: HCl 6 M</td>
<td>ICP–MS</td>
<td>88.8–99.8</td>
<td>—</td>
<td>200–1000</td>
<td>—</td>
<td>[126]</td>
</tr>
<tr>
<td>Spiked natural waters</td>
<td>Bi</td>
<td>Cyanex 301</td>
<td>Cartridge (0.5 g)</td>
<td>Conditioning: HCl 0.1 M, Sample pH: 1, Air drying, Elution: HNO$_3$ 3 M</td>
<td>ET-AAS</td>
<td>98.5–100</td>
<td>—</td>
<td>10–100</td>
<td>10$^5$</td>
<td>[127]</td>
</tr>
<tr>
<td>Sea, well and tap waters</td>
<td>Be</td>
<td>Quinalizarin</td>
<td>Sep pak cartridge</td>
<td>Washing conditioning sample pH: 6–6.6, Elution: HNO$_3$ 0.5 M</td>
<td>F-AAS</td>
<td>98–101</td>
<td>200 μg</td>
<td>200</td>
<td>0.2</td>
<td>[128]</td>
</tr>
<tr>
<td>Tap, spring waters</td>
<td>Ag$^+$</td>
<td>HT18C6</td>
<td>Empore disk</td>
<td>Conditioning: MeOH + water, Sample elution: Na$_2$S$_2$O$_3$ 0.1 M</td>
<td>AAS</td>
<td>996–100.3</td>
<td>210 μg/disk</td>
<td>200</td>
<td>0.050</td>
<td>[129]</td>
</tr>
<tr>
<td>Tap, river, well and spring waters</td>
<td>Hg(II)</td>
<td>HT18C6TO</td>
<td>Empore disk (47 mm i.d)</td>
<td>Washing sample pH: &lt;7, Air drying, Elution: HBr 1 M</td>
<td>CV-AAS</td>
<td>97.1–101.3</td>
<td>241 μg Hg$^+$</td>
<td>50</td>
<td>0.006</td>
<td>[130]</td>
</tr>
</tbody>
</table>

[126] [127] [128] [129] [130]
[104], even though dithizone was reported to react with many trace elements [139]. Similarly, purpurrogallin-bound silica gel enabled selective extraction of Fe(III) [140]. Simultaneous retention of trace elements is possible by choosing a non-selective chelating group, such as N-propylsalicylaldimine [141] or Bismuthol I (2,5-dimercaptol,3,4-thiadiazole) [142]. Acidic groups can also be used for further chelation of trace elements, such as phosphonic acid [143] and calixarene tetrahydroxamic acid [144]. Alternatively, macrocycles may be bound to silica (SGBM) [145], such as 18-crown-6 (18C6) [146].

It must be kept in mind that despite chemical bonding of functional groups on the silica gel surface, free silanol groups still remain [143]. Their number can be minimised by end-capping the sorbent, but some will still be present. As a consequence, they will participate in the retention of trace elements somewhat, especially at pHs above their pKₐ (ionized form).

3.1.1.2. C₁₈-bonded silica gel. Despite the large variety of bonded phases available, octadecyl-bonded silica has currently become the most popular phase used. Numerous applications report the use of C₁₈-silica, as indicated by the studies reported for water samples in Table 3. In particular, organometallic compounds (e.g. tributyltin (TBT), triphenyltin (TPhT), alkylselenides) can be retained on this sorbent due to possible hydrophobic interaction [19,24,112,113]. Bare C₁₈-silica can also retain a fraction of inorganic trace elements, probably due to the presence of silanol groups on its surface [34]. However, in practice, due to its hydrophobic character, C₁₈-silica is not well suited for retention of trace element species, as the latter are often polar or ionic. Retention on C₁₈-silica may be improved by addition of a ligand reagent to the sample before its percolation through the sorbent. The hydrophobic part of the ligand will thus have hydrophobic interaction with the C₁₈-silica and be retained on the sorbent, while the functional group of the ligand will ensure chelation of the trace element. Among reagents, one can cite 8-HQ [115], APDC [114], 1,10-phenanthroline [18], or bathocuproine [27].

An alternative approach is to form the complex by passing the sample through a C₁₈-silica containing the immobilized reagent. Octadecyl bonded silica, modified by suitable ligands has been successfully used for the separation and sensitive determination of metal ions. Examples are given in Table 3. The careful choice of the ligand may add selectivity to the extraction step, favoring speciation. For example, salen I-modified C₁₈-silica was found selective for Cu(II) [34], while impregnation of C₁₈-silica with neocuproine was suitable for Cu(I) [116]. C₁₈-silica coated with bis [1-hydroxy-9,10-anthraquinone-2-methyl]sulfide (BAS) was preferred for Pb(II) retention [121], while coating with N,N'-diethyl-N'-benzoylthiourea (DEBT) was recommended for Pd [147]. Macrocycles may also be loaded on C₁₈-silica and efficiently used for the retention of trace metals, such as hexathia-18-crown-6 (HT18C6) [129] or calixarene hydroxamate [144].

For some particular applications, mixed ligand complexes may be used to ensure synergistic adsorption of the metal complex on the solid sorbent. Thus, while Cu(II) ions cannot complex with neutral tri-n-butyl phosphate (TBP) molecules adsorbed on C₁₈-silica, the form of Cu(TTA) complex (TTA being 2-thenoyltrifluoroacetone) was retained at approximately 80% [148]. Alternatively, in some cases, loading the chelating agent on C₈-silica instead of C₁₈-silica may give better results as observed for the retention of bismuth on oxinate-loaded reversed phase [149].

Despite their broad application to trace element preconcentration, bonded silica phases (either C₁₈-silica or functionalized-silica gel) present the drawback of a limited range of pH that can be used, as in acidic (below 2 to 4) and basic (above 8) pHs hydrolysis may occur, which changes the interactions that occur between the sorbent and the trace elements. As a consequence, polymeric sorbents may be preferred.

3.1.1.3. Other inorganic oxides. Apart from silica other inorganic oxides have been tested for the adsorption of trace elements as shown in Tables 1 and 2. Whereas SiO₂, due to its acidic properties, is expected to adsorb only cations, basic oxides (such as magnesia MgO) should adsorb only
anions. As a matter of fact adsorption of ions on oxide surfaces is believed to proceed with participation of hydroxyl groups. These groups are negatively charged (deprotonated) under basic conditions, thereby retaining cations and positively charged (protonated) under acidic conditions, thereby retaining anions. Consequently, on amphoteric oxides (namely titania TiO₂, alumina Al₂O₃, zirconia ZrO₂), cations are adsorbed under basic conditions (pH above the isoelectric point of the oxide which was reported to be 6.2 for TiO₂ [109]) while anions are adsorbed under acidic conditions (pH below the isoelectric point of the oxide). For example, chromium speciation may be achieved by careful adjustment of the sample pH: pH 2 and 7 for retention of Cr(VI) (anionic) and Cr(III) (cationic), respectively, on acidic alumina [70,71]; pH 2 and 8 for retention of Cr(VI) and Cr(III) on titania, respectively [108]. The concurrent adsorption of H⁺ is responsible for the absence of retention of cationic species at very low pHs. However, changing the sample pH may affect speciation and should be avoided as far as possible. So it may be preferred to find a suitable sorbent for retaining the targeted species with subsequent selective elution for further speciation studies. With regards to chromium speciation, neutral alumina has been used for that purpose [110,150].

The preparation technique is of prime importance [109], as the adsorption properties of many oxides strongly depend on the characteristics of the solid, namely crystal structure, morphology, defects, specific surface area, hydroxyl coverage, surface impurities and modifiers. Thus, the coating of acidic alumina with an anionic surfactant allowed the selective retention of Cr(VI) in very acidic solutions [151]. Adsorption on inorganic oxides may also be influenced by the presence of salts in the matrix. In particular, high concentrations of phosphates and sulfates may decrease trace element retention on titania [152]. On the opposite, major cations (Na⁺, K⁺, Ca²⁺, Mg²⁺) are weakly adsorbed on titania [152,153].

3.1.2. Organic based sorbents

Organic based sorbents may be divided into polymeric and non-polymeric sorbents, as shown in Fig. 5. Polymeric sorbents have been, by far, the most used for trace element preconcentration having the advantage over bonded silica in that they can be used over the entire pH range. Their
disadvantage is that the conditioning step is more time consuming as they require extensive cleaning before use. Comprehensive reviews on polymeric phases have been published [97,154]. Masqué et al. published an extensive review on sorbents used for the SPE of polar organic micropollutants from natural waters [155]. The purpose of this section is to summarize the most frequently used organic based sorbents for trace elements, as well as the more recently reported ones.

In most applications, new sorbents have been synthesized by chemically bonding chelating groups to polymeric cross-linked chains and characterizing their ability to selectively adsorb trace elements. Most of the chelating groups reported have low water solubility to avoid their leaching from the sorbent, as most applications deal with aqueous samples. At the same time, a too hydrophobic group will hinder wettability of the sorbent by the aqueous sample, resulting in poor retention efficiency. A compromise is thus necessary. In addition to the functional group, the efficiency of polymeric sorbents depends on various physicochemical parameters, such as particle size, surface area, pore diameter, pore volume, degree of cross-linking and particle size distribution.

3.1.2.1. Polystyrene-divinylbenzene based sorbents. Macroporous hydrophobic resins of the Amberlite XAD series are good supports for developing chelating matrices. Amberlite XAD-1, XAD-2, XAD-4 and XAD-16 are poly styrene-divinylbenzene (PS-DVB) resins with a high hydrophobic character and no ion-exchange capacity. In addition to the hydrophobic interaction that also occurs with C$_{18}$-silica, such sorbents allow $\pi-\pi$ interactions with aromatic analytes.

Due to the hydrophobic character of PS-DVB, retention of trace elements on such sorbents requires the addition of a ligand to the sample. Inorganic ligands may be used [156], but organic ligands are preferred, such as APDC [157,158], 8-quinolinol [166], APDC [167] or 5-BrPA-DAP (2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol) [168]. Macrocycles can also be adsorbed, such as calixarene hydroxamate [144]. However, in practice, the resins prepared by impregnation of the ligand are difficult to reuse, due to partial leaching of the ligand (thus resulting in poor repeatability). To overcome this problem, the resin may be chemically functionalized. Several chemical modifications of PS-DVB have recently been reviewed [169], but only a few are commercially available. The ligands are generally coupled to a methylene or an azo spacer on the matrix. Among ligands, one can cite Alizarin Red-S [170], salicylic acid (SA) [171], thiosalicylic acid (TSA) [172], pyrocatechol violet (PV) [173], chromotropic acid (CA) [174], pyrocatechol (PC) [175,176], Tiron (disodium salt of 1,2-dihydroxybenzene-3,5-disulfonic acid) [177], quinalizarin (1,2,5,8-tetrahydroxy-anthraquinone) [22], bicine [N,N-bis(2-hydroxy-ethyl) glycine] [178], and poly(dithiocarbamate) (PDT) [179].

Of great interest are also the sulfonated PS-DVB resins, as they show excellent hydrophilicity and high extraction efficiencies for polar organic compounds [154,155]. In the case of rapid sulfonation under mild conditions, a mixed-mode retention can be observed: adsorption of neutral compounds on the polymeric resin, and cation exchange of ionic species on sulfonate groups [180]. The use of a particular sulfonated PS-DVB resin has been recently reported to enable chromium speciation [181]. 2-Naphthol-3,6-disulfonic acid (NDSA) has been coupled to the PS-DVB through an azo function. In that way, the formation of an azo cation at very low pHs enabled retention of the anionic Cr(VI), whereas the sulfonate group enabled retention of Cr(III) in neutral and basic media [181]. For particular applications, trimethylammonium functionalized PS-DVB may also be used with anion-exchange properties.

As summarized in Table 4, which presents selected applications of polymeric sorbents for the preconcentration of trace elements from water samples, even though PS-DVB has been probably the most widely used of polymers, others also have been successfully used as detailed below.
Table 4
Applications of off-line SPE using polymeric sorbents to water samples

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Trace elements</th>
<th>Sorbent</th>
<th>Operation</th>
<th>Experimental conditions</th>
<th>Analysis method</th>
<th>Recovery (%)</th>
<th>Adsorptive capacity (mg/g)</th>
<th>Preconcentration factor</th>
<th>LOD (µg/l)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Adsorptive resins</strong></td>
<td></td>
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<tr>
<td>Tap water</td>
<td>Cd/Cu/Mn/Ni/Pb/Zn + 8-HQ</td>
<td>XAD-2</td>
<td>Polypropylene column</td>
<td>Conditioning sample pH: 8–9, Elution: HCl 2 M</td>
<td>ICP–AES</td>
<td>82.3–97.2</td>
<td>—</td>
<td>100</td>
<td>—</td>
<td>[160]</td>
</tr>
<tr>
<td>Tap water</td>
<td>Cr(VI), total Cr + DPC</td>
<td>XAD-16</td>
<td>Glass column (1 cm i.d)</td>
<td>Washing sample pH: 1, Elution: H2SO4 0.05 M/MeOH</td>
<td>F-AAS</td>
<td>97.3–99.0</td>
<td>0.4 mg/g</td>
<td>5.25</td>
<td>45</td>
<td>[161]</td>
</tr>
<tr>
<td>Drinking and sea waters</td>
<td>Bi/Cd/Cu/Fe/Ni/Pb+APDC</td>
<td>Chromosorb-102</td>
<td>Glass column (0.9 cm i.d)</td>
<td>Washing conditioning sample pH: 6, Elution: acetone</td>
<td>F-AAS</td>
<td>95–110</td>
<td>—</td>
<td>300</td>
<td>0.10–11</td>
<td>[158]</td>
</tr>
<tr>
<td>Tap, mineral, river waters</td>
<td>Co + 8-HQ</td>
<td>Chromosorb-105</td>
<td>Column (4 mm i.d)</td>
<td>Washing sample pH: 8, Elution: EtOH/ HNO3 2 M</td>
<td>ET-AAS</td>
<td>95.2–99.2</td>
<td>—</td>
<td>80</td>
<td>0.0134</td>
<td>[182]</td>
</tr>
<tr>
<td>Tape, lake, waste waters</td>
<td>Cr(III)</td>
<td>Cellulose</td>
<td>Syringe barrel</td>
<td>Purification sample pH: 11, Elution: HCl 2 M</td>
<td>ET-AAS</td>
<td>98–99.3</td>
<td>—</td>
<td>100</td>
<td>0.0018</td>
<td>[183]</td>
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<tr>
<td><strong>Chelating resins</strong></td>
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<tr>
<td>Waters</td>
<td>TBT</td>
<td>Tropolone-loaded-XAD-2</td>
<td>Glass column (1.5 cm i.d)</td>
<td>Sample + 0.8% H2SO4, Washing HCl</td>
<td>ET-AAS</td>
<td>104</td>
<td>—</td>
<td>80</td>
<td>0.0144</td>
<td>[164]</td>
</tr>
<tr>
<td>Matrix</td>
<td>Trace elements</td>
<td>Sorbent</td>
<td>Operation</td>
<td>Experimental conditions</td>
<td>Analysis method</td>
<td>Recovery (%)</td>
<td>Adsorptive capacity</td>
<td>Preconcentration factor</td>
<td>LOD (µg/l)</td>
<td>Ref.</td>
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<tr>
<td>Sea water</td>
<td>Co/Cu/Fe/Ni/Zn</td>
<td>PDT-loaded-XAD-2</td>
<td>Column</td>
<td>Washing elution: MeOH in Soxhlet apparatus</td>
<td>F-AAS</td>
<td>96.3–103.5</td>
<td>—</td>
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<td>[4]</td>
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<td>(0.9 cm i.d)</td>
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<tr>
<td>Well water,</td>
<td>Cu/Cd/Co/Pb/Zn/Mn</td>
<td>Quinalizarin-functionalized-XAD-2</td>
<td>Glass column (1 cm i.d)</td>
<td>Washing sample pH: 5–7, Elution: ( \text{HNO}_3 ) 4 M</td>
<td>F-AAS</td>
<td>91–98</td>
<td>3.15/1.70/1.62/5.28/1.42/0.94</td>
<td>100/50/40/50/100/65/65</td>
<td>2.0/1.3/5.0/15.0/1.0/1.6</td>
<td>[22]</td>
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<tr>
<td>river water</td>
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<tr>
<td>Well waters</td>
<td>Zn/Cd/Pb/Ni</td>
<td>PV-functionalized-XAD-2</td>
<td>Glass column (1 cm i.d)</td>
<td>Washing sample pH: 3–7, Elution: ( \text{HNO}_3 ) 4 M</td>
<td>F-AAS</td>
<td>98</td>
<td>1410/1270/620/1360</td>
<td>60/50/23/18</td>
<td>—</td>
<td>[173]</td>
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<td>Zn/Pb</td>
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<tr>
<td>Salicylic acid-functionalized-XAD-2</td>
<td>Glass column (1 cm i.d)</td>
<td>Washing sample pH: 5.0, Elution: ( \text{HCl} 1 \text{ M} ) 2–4 M</td>
<td>F-AAS</td>
<td>98–100</td>
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<td>[171]</td>
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<tr>
<td>Well waters</td>
<td>Zn/Pb</td>
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<tr>
<td>Well waters</td>
<td>Zn/Cd/Pb/Ni</td>
<td>Alizarin Red-S-functionalized-XAD-2</td>
<td>Glass column (1 cm i.d)</td>
<td>Washing sample pH: 4–6, Elution: ( \text{HNO}_3 ) 1–4 M or ( \text{HCl} 4 \text{ M} )</td>
<td>F-AAS</td>
<td>95–100</td>
<td>511/124/306/124</td>
<td>40</td>
<td>10</td>
<td>[170]</td>
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<tr>
<td>River waters</td>
<td>Cu/Cd/Co/Ni/Pb/Zn/Mn/Fe</td>
<td>Tiron-functionalized-XAD-2</td>
<td>Glass column (1 cm i.d)</td>
<td>Washing sample pH: 4–7.5, Elution: ( \text{HNO}_3 ) 4 M</td>
<td>F-AAS</td>
<td>91–99</td>
<td>25–200</td>
<td>0.5–24</td>
<td>[177]</td>
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<tr>
<td>Matrix</td>
<td>Trace elements</td>
<td>Sorbent</td>
<td>Operation</td>
<td>Experimental conditions</td>
<td>Analysis method</td>
<td>Recovery (%)</td>
<td>Adsorptive capacity</td>
<td>Preconcentration factor</td>
<td>LOD (µg/l)</td>
<td>Ref.</td>
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<tr>
<td>River waters</td>
<td>Cd/Co/Cu/Ni/Fe/Zn</td>
<td>CA-functionalized-XAD-2</td>
<td>Glass column (1 cm i.d.)</td>
<td>Washing sample pH: 4–7 Elution: HNO₃ or HCl 2 M</td>
<td>F-AAS</td>
<td>95–100</td>
<td>9.35/3.84/8.50/3.24/6.07/9.65</td>
<td>100–200</td>
<td>—</td>
<td>[174]</td>
</tr>
<tr>
<td>River and tap</td>
<td>Pb</td>
<td>CA-functionalized-XAD-2</td>
<td>Glass column (1 cm i.d.)</td>
<td>Washing sample pH: 3–8 Elution: HNO₃ 2–10 M</td>
<td>F-AAS</td>
<td>97</td>
<td>186.3 µmol/g</td>
<td>200</td>
<td>4.06</td>
<td>[176]</td>
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<tr>
<td>waters</td>
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<tr>
<td>River and tap</td>
<td>Cd/Co/Cu/Fe/Ni/Zn</td>
<td>PC-functionalized-XAD-2</td>
<td>Glass column (1 cm i.d.)</td>
<td>Washing sample pH: 3–6.5 Elution: HNO₃ 2 M</td>
<td>F-AAS</td>
<td>—</td>
<td>0.023–0.092 mmol/g</td>
<td>80–200</td>
<td>—</td>
<td>[175]</td>
</tr>
<tr>
<td>waters</td>
<td></td>
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<td>River and tap</td>
<td>Pb</td>
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<td>Glass column (1 cm i.d.)</td>
<td>Washing sample pH: 5–7.5 Elution: HNO₃ 1 M</td>
<td>F-AAS</td>
<td>94</td>
<td>104.7 µmol/g</td>
<td>100</td>
<td>3.80</td>
<td>[176]</td>
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<td>River and tap</td>
<td>Pb</td>
<td>TSA-functionalized-XAD-2</td>
<td>Glass column (1 cm i.d.)</td>
<td>Washing sample pH: 4 Elution: HNO₃ 0.5–2 M</td>
<td>F-AAS</td>
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<td>89.3 µmol/g</td>
<td>100</td>
<td>4.87</td>
<td>[176]</td>
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<td>Tap, river</td>
<td>Cd/Co/Cu/Fe/Ni/Zn</td>
<td>TSA-functionalized-XAD-2</td>
<td>Glass column (1 cm i.d.)</td>
<td>Washing sample pH: 3.5–7 Washing elution: HNO₃ 2 M</td>
<td>F-AAS</td>
<td>92–98</td>
<td>197.5/106.9/214.0/66.2/309.9/47.4</td>
<td>180–400</td>
<td>0.48/0.20/4.05/0.98/1.28/3.94</td>
<td>[172]</td>
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Table 4 (Continued)

| Matrix                        | Trace elements | Sorbent         | Operation      | Experimental conditions                  | Analysis method | Recovery (%) | Adsorptive capacity | Preconcentration factor | LOD (μg/l) | Ref. |
|-------------------------------|----------------|-----------------|----------------|------------------------------------------|-----------------|--------------|---------------------|------------------------|------------|      |
| Artificial sea water, natural waters | Cd/Cu/Mn/Ni/Pb/Zn | APDC-loaded-XAD-4 | Glass column (0.9 cm i.d) | Sample pH: 5.0 Washing elution: HNO₃ 4 M | ICP–AES         | 98.2–99.6     | 9.47/11.08/8.62/7.21/10.25/10.62 mg/g | 150/200/140/120/150/200 | 0.1/0.4/0.3/0.4/0.6/0.5 | [167] |
| Artificial sea water, natural waters | Cd/Cu/Mn/Ni/Pb/Zn | pipDTC-loaded-XAD-4 | Glass column (0.9 cm i.d) | Sample pH: 5.0 Washing elution: HNO₃ 4 M | ICP–AES         | 97.6–99.1     | 9.18/10.76/8.17/7.46/9.86/10.28 mg/g | 150/200/140/120/150/200 | 0.7/1.0/0.8/0.9/1.7/1.2 | [167] |
| Sea water                     | Ag/Al/Bi/Cd/Cu/Fe/Ga/Mn/Ni/Pb/Ti | DDQ-loaded-XAD-4 | Teflon column (8 mm i.d) | Washing sample pH: 8 Washing elution: HCl 2 M Backflush Sample pH: 8.5 Elution: acidified water (pH 2.0) | F-AAS or ET-AAS | 73–107         | 0.55 mmol/g          | 62.5                   | 0.00016–0.3 | [166] |
| Tap water                     | Cu/Mn/Zn        | Calixarene Tetrahydroxamate-loaded-XAD-4 | Plastic cartridge (0.9 cm i.d) | Conditioning sample pH: 10 Elution: HNO₃ 8 M | F-AAS           | —             | —                  | 25                     | —          | [144] |
| Tap and mineral waters        | Mn              | PDTC-functionalized-XAD-4 | Glass column (1 cm i.d) | Conditioning sample pH: 5.5–7 Elution: HCl 1 M | F-AAS           | 97.2           | 9.1 μmol/g         | 20                    | 0.5        | [179] |
| Spiked solutions              | Co/Cu/Fe/Hg/Ni/Pb/Zn | Bicine-functionalized-XAD-4 | Glass column | Conditioning sample pH: 5.5–7 Elution: HCl 1 M | ET-AAS          | 97.6–99.1      | 0.32–0.44 mmol/g | 40–50                | —          | [178] |
### Table 4 (Continued)

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<th>Matrix</th>
<th>Trace elements</th>
<th>Sorbent</th>
<th>Operation</th>
<th>Experimental conditions</th>
<th>Analysis method</th>
<th>Recovery (%)</th>
<th>Adsorptive capacity</th>
<th>Preconcentration factor</th>
<th>LOD (µg/l)</th>
<th>Ref.</th>
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<td>Waste waters Cr(III)/Cr (VI)</td>
<td>Cr</td>
<td>NDSA-functionalized-PS-DVB</td>
<td>Glass column (1 cm i.d)</td>
<td>Sample pH: 1.5 or 6</td>
<td>F-AAS</td>
<td>85.9–96.1</td>
<td>0.40/1.18 mmol/g</td>
<td>20</td>
<td>—</td>
<td>[181]</td>
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<td>River water Hg(II)</td>
<td>Hg</td>
<td>PAA-functionalized-PS-DVB</td>
<td>Glass column (1 cm i.d)</td>
<td>Conditioning sample pH: 5.4</td>
<td>Spectrophotometry</td>
<td>96</td>
<td>0.6 mmol/g</td>
<td>30</td>
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<td>[184]</td>
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<td>River and tap waters Pb</td>
<td>Pb</td>
<td>XO-loaded-XAD-7</td>
<td>Glass column (1 cm i.d)</td>
<td>Washing Sample pH: 5</td>
<td>F-AAS</td>
<td>91</td>
<td>16.9 µmol/g</td>
<td>100</td>
<td>2.44</td>
<td>[176]</td>
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<td>River waters Cd/Co/Cu/Fe/Ni/Zn</td>
<td>Cd/Co/Cu/Cu/Fe/Ni/Zn</td>
<td>XO-loaded-XAD-7</td>
<td>Glass column</td>
<td>Sample pH: 4–5</td>
<td>F-AAS</td>
<td>96–100</td>
<td>1.6–2.6 mg/g</td>
<td>10–200</td>
<td>9/24/6/6/3/21</td>
<td>[185]</td>
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<tr>
<td>River and reservoir waters Cr(III)</td>
<td>Cr</td>
<td>8-HQ-functionalized-polyacrylonitrile</td>
<td>Glass column (4 mm i.d)</td>
<td>Washing Sample pH: 6</td>
<td>ICP–MS</td>
<td>98–105</td>
<td>41.7 µmol/g</td>
<td>5</td>
<td>0.06</td>
<td>[186]</td>
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<td>Aqueous sample from a non-ferrous metal smelter Au/Pt/Pd/Ir</td>
<td>Au/Pt/Pd/Ir</td>
<td>Aminothiourea-functionalized-polyacrylonitrile</td>
<td>Glass column (0.5 cm i.d)</td>
<td>Washing sample pH: 2</td>
<td>ICP–AES</td>
<td>97–99</td>
<td>2.80/1.75/1.56/1.15 mmol/g</td>
<td>6–65</td>
<td>—</td>
<td>[187]</td>
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<td>Sea water Be/Bi/Co/Ga/Ag/Pb/Cd/Cu/Mn/In</td>
<td>Be/Bi/Co/Ga/Ag/Pb/Cd/Cu/Mn/In</td>
<td>Aminophosphonic-dithiocarbamate-functionalized-polyacrylonitrile</td>
<td>Glass column (4 mm i.d)</td>
<td>Sample pH: 6</td>
<td>ICP–MS</td>
<td>93–104</td>
<td>0.83–74.1 µmol/g</td>
<td>200</td>
<td>0.002–0.601</td>
<td>[188]</td>
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<td>Sorbent</td>
<td>Operation</td>
<td>Experimental conditions</td>
<td>Analysis method</td>
<td>Recovery (%)</td>
<td>Adsorptive capacity</td>
<td>Preconcentration factor</td>
<td>LOD (µg/l)</td>
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<td>River, lake and rain waters</td>
<td>Hg(II)/MeHg</td>
<td>Dithiocarbamate-functionalized-polyvinyle</td>
<td>Column (1.5 cm i.d)</td>
<td>Washing Sample pH: 1–11 Elution: thiourea 5% in HCl</td>
<td>CV-AAS</td>
<td>91–95</td>
<td>—</td>
<td>667</td>
<td>0.0002</td>
<td>[189]</td>
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<tr>
<td>Sea water</td>
<td>Cd/Cu/Mn/Ni/Pb/Zn</td>
<td>Chelamine</td>
<td>Column</td>
<td>Washing sample pH: 6.5 Washing elution: HNO₃ 2 M</td>
<td>ET-AAS</td>
<td>91–102</td>
<td>1 mmol/g</td>
<td>200</td>
<td>0.0023–0.033</td>
<td>[190]</td>
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<tr>
<td>Sea water</td>
<td>Cd/Co/Cu/Mn/Ni/Pb/Zn</td>
<td>Chelex-100</td>
<td>Column</td>
<td>Sample pH: 6.5 Washing elution: HNO₃ 2 M</td>
<td>ET-AAS or F-AAS</td>
<td>&gt; 98</td>
<td>—</td>
<td>50</td>
<td>0.001–0.1</td>
<td>[191]</td>
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<td>River water, seawater</td>
<td>Cd/Pb/Zn</td>
<td>Amberlite IRC-718</td>
<td>Glass column (0.5 cm i.d)</td>
<td>Washing conditioning sample washing elution: HNO₃</td>
<td>F-AAS</td>
<td>63–104</td>
<td>1.06/0.096/1.77 mmol/g</td>
<td>10</td>
<td>—</td>
<td>[192]</td>
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<td>Ground and fresh waters</td>
<td>Se(IV)/Se(VI)/SeCyst</td>
<td>Amberlite IRA-743</td>
<td>Glass column (1 cm i.d)</td>
<td>Washing conditioning sample elution: HClO₄ 1 M + water</td>
<td>LC–ICP–MS</td>
<td>93–97</td>
<td>—</td>
<td>55</td>
<td>0.010</td>
<td>[193]</td>
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<td>Ion exchangers</td>
<td>Waste water</td>
<td>Cr</td>
<td>Cartridge (0.5 g)</td>
<td>Activation: MeOH + buffer Sample pH: 4.5 Elution: Na₂SO₄ 0.5 M</td>
<td>Spectrophotometry (544 nm) after reaction DPC</td>
<td>80–98.8</td>
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<th>Experimental conditions</th>
<th>Analysis method</th>
<th>Recovery (%)</th>
<th>Adsorptive capacity</th>
<th>Preconcentration factor</th>
<th>LOD (μg/l)</th>
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<td>Sea, river, tap waters</td>
<td>Se(IV)/Se(VI)</td>
<td>Anion exchanger (SAX)</td>
<td>Cartridge</td>
<td>Conditioning Sample</td>
<td>GC–MS</td>
<td>91–99</td>
<td>—</td>
<td>40–500</td>
<td>1600/1400</td>
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<td>Elution: HCOOH 1 M + HCl 3 M</td>
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<tr>
<td>River, spring, waste waters</td>
<td>Be</td>
<td>Anion exchanger</td>
<td>Column (1 cm i.d)</td>
<td>Conditioning: HCl + H₂O + NaOH Sample pH: 6–8 Elution: HCl 1.5 M</td>
<td>F-AAS</td>
<td>95–102.5</td>
<td>—</td>
<td>125</td>
<td>0.045</td>
<td>[195]</td>
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3.1.2.2. Divinylbenzene-vinylpyrrolidone copolymers. Sorbents made of divinylbenzene-vinylpyrrolidone (DVB-VP) copolymers have recently been developed, such as Oasis HLB [154]. The hydrophilic N-vinylpyrrolidone affords good wetting ability of the resin, while the hydrophobic divinylbenzene provides reversed-phase retention of analytes. This sorbent has been successfully applied to the determination of polar organic compounds in water samples. It is more convenient to use, compared to classical sorbents, as it can dry out during the extraction procedure without reducing its ability to retain analytes. In addition, it is stable over the entire pH range. However, until now, no application related to the preconcentration of trace elements has been reported. Similarly, the use of Oasis MCX, a sulfonated divinylbenzene-vinylpyrrolidone copolymer [154], may be useful for the retention of trace element species, as this sorbent combines the properties of the previous sorbent with those of a strong cation-exchanger. Application to the preconcentration of triphenyltin has been reported [36].

3.1.2.3. Polyacrylate polymers. Amberlite XAD-7 and XAD-8 are ethylene-dimethacrylate resins. They are non-aromatic in character and possess very low ion-exchange capacity. Due to the polarity of acrylates, such resins enable the recovery of hydrophilic compounds. Such loaded sorbents are stable over the entire pH range. However, until now, no application related to the preconcentration of trace elements has been reported. Similarly, the use of Oasis MCX, a sulfonated divinylbenzene-vinylpyrrolidone copolymer [154], may be useful for the retention of trace element species, as this sorbent combines the properties of the previous sorbent with those of a strong cation-exchanger. Application to the preconcentration of triphenyltin has been reported [36].

3.1.2.4. Polyurethane polymers. Due to its sorption capacity for several trace elements polyurethane foam has been tested for use in SPE. Most of the time complexing reagents are added to enhance the sorption capacity. Hence, PUF coated with DMG, NN, DDTC or hexamethylene-dithiocarbamate (HMDC) was found efficient in retaining trace elements [198–200]. The chelating reagent can also be directly added to the sample, and the metal chelates further retained on PUF, as observed with thiocyanate complexes [92,201,202] and DDTP complexes [63]. Very recently, the immobilization of an enzyme (alkaline phosphatase) has been reported on PUF with further application as an enzymatic procedure for Pb(II) determination [203].

3.1.2.5. Polyethylene polymers. Polyethylene is also attractive for SPE of trace elements as this support adsorbs several metal complexed with hydrophobic ligands. Additionally, the adsorbed complexes can be eluted with a small volume of organic solvents permitting high enrichment factors. Polyethylene can also be used in strongly acidic and basic media and for that reason, it has been used as a sorbent for the retention of chromium in an acidic medium after the addition of DPC [204].

3.1.2.6. Polytetrafluoroethylene polymers. PTFE can retain trace elements after addition of a chelating reagent to the sample such as APDC, DDTC or dithizone (DZ) [48–50,74,76]. PTFE may also be precoated with a suitable ligand, like 2-methyl-8-hydroxyquinoline [93]. The sorbent can be used as PTFE turnings [48–50], PTFE beads [75], or as a PTFE tubing in a knotted reactor [74,76].

3.1.2.7. Polystyrene polymers. Polystyrene polymers may be an interesting alternative to common sorbents (namely Amberlites XAD-2 and XAD-8, C18-silica) when they have a hyper cross-link structure. The addition of a reagent to the sample is required to form complexes that are further retained on the hydrophobic sorbent [79].

poly(ethylene glycol dimethacrylate-hydroxyethylmethacrylate) microbeads [197].
3.1.2.8. Polyamide polymers. Polyamide polymers have been used for the retention of rare earth elements [205]. A chelating reagent was added to the sample for complexing the trace elements. This reagent Thorin (α-[3,6-disulfo-2-hydroxy-l-naphthylazo]benzenearsonic acid) was chosen to enable interaction with the sorbent through electrostatic forces and non-hydrophobic interaction.

3.1.2.9. Imidodiacetate-type chelating resins. Polymeric resins containing iminodiacetate groups [−CH₂−N(CH₃)COO−]ₓ as active sites (IDA resins) have been widely used for the retention of trace elements. They have been synthesized by bonding the iminodiacetate functional groups to several polymeric sorbents, such as polystyrene (Chelex-100) [10,29,30,191,206–209] or a highly crosslinked agarose gel (IDA-Novarose) [80]. The spacer arm length was found to have an effect on the formation of metal complex species in the chelating resin [12].

A major drawback of such sorbents is that, due to the weak acid character of the functional group, the degree of protonation will critically affect the ability of the resin to retain metal cations. Hence, for Chelex-100, protonation of the carboxylates and the donor N atom are reported to be complete at pH 2.21, while a completely deprotonated form is reached at pH 12.30. Also, such sorbents are non-selective, so that trace element retention may be reduced due to retention of major ions (namely Ca(II) and Mg(II)) [96,191]. Besides, the presence of ligands in the sample may prevent trace element retention on the sorbent due to their complexation as observed in real waters due to the presence of organic matter [80,210].

3.1.2.10. Propylenediaminetetraacetic acid-type chelating resins. The synthesis of a fine-particle macroporous polymer-based propylenediaminetetraacetic acid (PDATA) type resin has been recently reported [211]. The structure of this sorbent is very similar to that of ethylene diamine tetraacetic acid (EDTA) with a spacer arm enabling the retention of several trace elements upon chelation.

3.1.2.11. Polyacrylonitrile based resins. Polyacrylonitrile fibers have been functionalized to obtain ion-exchange chelating sorbents with aminophosphonic, dithiocarbamate or aminothiourea groups [187,188]. However, as such synthesis are time-consuming an alternative is to coat the polyacrylonitrile fiber with a proper reagent for further trace element retention such as 8-HQ [186,212].

3.1.2.12. Ring-opening metathesis polymerisation-based polymers. A high-capacity carboxylic acid-functionalized resin has been prepared using ring-opening metathesis polymerisation (ROMP) [213]. Electron microscopy revealed that the obtained material consists of irregularly shaped, agglomerated particles having a non-porous structure with diameter and specific surface area dependent on the polymerisation sequence and the stoichiometries. This material was pH stable and could be reused. The presence of the carboxylic groups confers an excellent hydrophilic character to the sorbent (ensuring a high wettability of the sorbent by water), while the polyunsaturation of the carrier chain, as well as the entire backbone provides for a significant reversed-phase character. The carboxylic acid groups provide weak coordination sites enabling the retention of rare earth elements. Similarly, dipyridyldiamide-functionalized resins have been reported to allow the extraction of ‘soft’ metals such as Pd(II) and Hg(II) [214].

3.1.2.13. Carbon sorbents. Activated carbon is prepared by low-temperature oxidation of vegetable charcoals. Due to their large surface areas (300–1000 m²/g), these sorbents are well-recognized for their very strong sorption both for trace organic compounds and trace elements. There is evidence of two types of adsorption sites on activated carbons: (1) graphite-like basal planes that enable adsorption through van der Waals forces, especially π-electron interactions, and (2) polar groups like carbonyls, hydroxyls and carboxyls, that may interact via ionic interaction of hydrogen bonding [215]. Consequently, trace elements may be directly adsorbed on activated carbon [19,216]. Metal chelates may also be retained on this sorbent after addition of a proper chelating agent to the sample [17] such as amino acids [217], dithizone [218], APDC [88,219], PAN [220], 8-HQ [221], cupferron [221], Bismuthiol II
(3-phenyl-5-mercapto-1,3,4-thiadiazole-2(3H)-thione) [222], or DDTP [63,87]. The ligand should be chosen to avoid a strong interaction with the activated carbon otherwise complete dissociation of the metal chelate would be observed [215].

The main drawback when using activated carbons is their heterogeneous surface with active functional groups that often lead to low reproducibility. In addition, these sorbents are very reactive and can act as catalysts for oxidation and other chemical reactions. Fortunately, along with the development of polymer materials and bonded phases, a new generation of carbon sorbents appeared in the 1970s and 1980s with a more homogeneous structure and more reproducible properties. Graphitized carbon blacks (GCB) are obtained from heating carbon blacks at 2700–3000 °C in an inert atmosphere [155]. They are non-specific and non-porous sorbents (surface area approx. 100 m²/g), and are considered to be both reversed-phase sorbents and anion-exchangers due to the presence of positively charged chemical heterogeneities on their surface. Such sorbents have been extensively used in the past few years for the SPE of polar organic pollutants from water samples [183,224]. In particular, the selective retention of Cr(III) was reported thereby enabling chromium speciation [183]. This sorbent may also be functionalized to increase the SPE selectivity. Thus, selenium speciation has been reported on cellulose functionalized with quaternary amine due to the selective elution of the retained Se(IV) and Se(VI) species using nitric acid at two different concentrations [225].

3.1.2.15. Naphthalene based sorbents. Retention of trace elements on microcrystalline naphthalene is also feasible, either after addition of a ligand to the sample [226], or after functionalization of the solid to ensure better adsorption characteristics towards trace elements [227,228]. However, the use of this solid support is rather uncommon. In addition, until now it has been reserved to batch experiments.

3.2. Influential parameters

The main experimental variables that affect analyte recovery by SPE have been extensively reported by Poole et al. [2,229]. They are briefly discussed below and illustrated with reported applications.

3.2.1. Conditioning parameters

3.2.1.1. Washing step. A washing step is highly recommended, especially when ultratrace elements are to be determined. Thus, blank extracts containing trace levels of Zn, Cu and Fe were suspected to be due to contaminants from C₁₈-silica [115].

3.2.1.2. Conditioning solvent. Even though some sorbents have been used without a conditioning step this is not recommended. This step will at least remove possible remaining contaminants and air from the sorbent bed. Additionally, in some cases, this step is crucial for successful retention of the analytes. The nature of the conditioning solvent must be appropriate to the nature of the solid sorbent to ensure good wettability of the functional groups. As an example with hydrophobic supports such as C₁₈-silica or PS-DVB, quite polar organic solvents such as methanol should be used. The sorbent should further be conditioned by a solvent whose nature is similar to that of the sample. Thus, for aqueous samples, the solvent will be water with a pH and ionic strength similar to that of the sample.
3.2. Loading parameters

3.2.1. Sample volume to be percolated. An important parameter to control in SPE is the breakthrough volume, which is the maximum sample volume that should be percolated through a given mass of sorbent after which analytes start to elute from the sorbent resulting in non-quantitative recoveries (Fig. 6). The breakthrough volume is strongly correlated to the chromatographic retention of the analyte on the same sorbent and depends on the nature of both the sorbent and the trace element, as well as on the mass of sorbent considered and the analyte concentration in the sample [3]. In addition, it depends on the sorbent containers, as disks usually offer higher breakthrough volumes than cartridges. This volume may be determined experimentally or estimated using several methods [229]. For that purpose the nature of the sample has to be taken into account, as the possible presence of ligands may dramatically reduce the breakthrough volume [230].

3.2.2. Sample flow-rate. The sample flow-rate should be optimized to ensure quantitative retention along with minimization of the time required for sample processing. This parameter may have a direct effect on the breakthrough volume, and elevated flow-rates may reduce the breakthrough volume [4,229]. As a rule, cartridges and columns require lower maximum flow-rates than disks ranging typically from 0.5 to 5 ml/min. This value may be increased by a factor of 10 using disks.

3.2.2.3. Sample pH. Sample pH is of prime importance for efficient retention of the trace elements on the sorbent. Its influence strongly depends on the nature of the sorbent used. Careful optimization of this parameter is thus crucial to ensure quantitative retention of the trace elements and in some cases selective retention. In particular with ion-exchangers, correct adjustment of sample pH is required to ensure preconcentration. Thus, in the case of cationic-exchangers, low pH usually results in poor extraction due to competition between protons and cationic species for retention on the sorbent.

When retention of trace elements is based on chelation (either in the sample or on the solid sorbent), the sample pH is also a very important factor as most chelating ligands are conjugated bases of weak acid groups and accordingly, they have a very strong affinity for hydrogen ions. The pH will determine the values of the conditional stability constants of the metal complexes. By contrast, pH may have no influence with some non-ionizable organic ligands [130].

For inorganic oxides, pH is also of prime importance. In particular, on amphoteric oxides such as TiO₂ or Al₂O₃, cations are adsorbed at elevated pHs due to the deprotonation of functional groups, whereas anion retention requires acidic conditions for the protonation of functional groups.

3.2.2.4. Sample matrix. The presence of ligands in the sample matrix may affect trace element retention when stable complexes are formed in the sample with these ligands, as trace elements are less available for further retention. Thus, if metals are present in the sample as strong complexes, they may not dissociate resulting in no retention of the free metal on the sorbent. As an example, reduction in the retention of Cu(II) on Amberlite CG50 occurs in the presence of ligands such as glycine [230]. In the case of real samples, the presence of natural organic matter is of great concern as it may complex trace elements as observed for Cu(II) [231,232]. Yet, in some cases
the presence of ligands may be a valuable tool for adding selectivity to the SPE step. This requires that the added ligands be correctly chosen to complex only the elements that are not of interest, so that they are not retained on the sorbent [31].

The presence of ions other than the target ones in the sample may also cause problems during the SPE step. In particular, due to their usually high levels (e.g. Ca(II)), they may hinder the preconcentration step by overloading the sorbent or cause interferences during spectrophotometric analysis. Therefore, their influence should be studied before validating a SPE method. Sometimes the addition of a proper masking agent (such as EDTA, thiourea or ethanolamine for example) may prevent the formation of interferences due to ions present in the sample [128].

Finally, the ionic strength of the sample is another parameter to control for an efficient SPE, as it may influence the retention of trace elements, and thus the value of the breakthrough volume for a given sorbent [122,195].

3.2.3. Elution parameters

3.2.3.1. Nature of the solvent. The nature of the elution solvent is of prime importance and should optimally meet three criteria: efficiency, selectivity and compatibility, as discussed below. In addition, it may be desirable to recover the analytes in a small volume of solvent to ensure a significant enrichment factor. The eluent may be an organic solvent (when reversed-phase sorbents are used), an acid (usually with ion-exchangers), or a complexing agent.

Firstly, the eluting solvent should be carefully chosen to ensure efficient recovery of the retained target species and quantitative recovery as far as possible. As an example among several solvents tested for the elution of TPhT from C_{18}-silica (namely a Triton X-100 surfactant aqueous solution, acetonitrile, tetrahydrofuran (THF), methanol–water 80:20, methanol), only methanol enabled the achievement of acceptable recoveries (approx. 85%) [112].

A further characteristic of the elution solvent arises with the possibility of introducing selectivity. Using a solvent with a low or moderate eluting power, the less retained analytes can be recovered without eluting the strongly retained compounds. Thus, if the elements of interest are those that remain on the sorbent another elution step with a more eluent solvent will ensure their quantitative recovery. In that way interferent analytes were removed during the first eluting step (also called washing step). On the opposite, if the compounds of interest are the less retained on the sorbent their elution with a low or moderate eluting solvent ensures their selective recovery, as the interferent compounds will remain on the sorbent due to stronger interactions with the solid support. In some cases, this selectivity may authorized speciation. For example, 1 M HCOOH removed only Se(IV) from an anion-exchange resin, leaving Se(VI) retained on the sorbent, which was further eluted using 2 M HCl [19].

Finally, the elution solvent should be compatible with the analysis technique. In particular, when using both flame and electrothermal AAS, HNO₃ should be preferred to other acids (namely H₂SO₄, HCl), as nitrate ion is a more acceptable matrix [128].

3.2.3.2. Solvent pH. As retention of trace elements on solid sorbents is usually pH-dependent, careful choice of the elution solvent pH may enhance selectivity in the SPE procedure. As an example, once retained on eriochrome black-T (ERT)-functionalized-silica gel, Mg(II) could be eluted first at a pH approximately 4, while increasing the pH to 5–6 was required for eluting Zn(II) [9].

3.2.3.3. Elution mode. Most of the time, for practical reasons, sample loading and elution steps are performed in a similar manner. However, to avoid irreversible adsorption and ensure quantitative recoveries, elution in the backflush mode is recommended in some cases. This means that the eluent is pumped through the sorbent in the opposite direction to that of the sample during the preconcentration step. This is especially crucial when carbon-based sorbents have to be used due to possible irreversible adsorption of the analytes.

3.2.3.4. Solvent flow-rate. The flow-rate of the elution solvent should be high enough to avoid
excessive duration, and low enough to ensure quantitative recovery of the target species. Typical flow-rates are in the range of 0.5 to 5 ml/min for cartridges and of 1 to 20 ml/min for disks [34]. As a rule, the higher the flow-rate, the larger the solvent volume required for complete elution [119,121,129,130].

3.2.3.5. Solvent volume. Similar to the breakthrough volume, the elution volume may be determined either experimentally or estimated theoretically [229]. Minimum elution volume for a cartridge is defined as 2 bed volumes of elution solvent. Bed volume is typically 120 µl/100 mg of sorbent. For classical disks, the minimum solvent volume required is approximately 10 µl/mg of sorbent [20]. Consequently, larger elution volumes would be required for disks. The elution volume can usually be reduced by increasing the concentration of the eluting solvent (e.g. acid). However, in this case, problems with subsequent analysis may be encountered (e.g. F-AAS). Alternatively, the use of micro-sized disks may allow reduced solvent volume [20].

The elution step should enable sufficient time and elution volume to permit the metallic species to diffuse out of the solid sorbent pores. As a rule, 2 elution cycles are usually recommended as compared to a single step (e.g. 2 × 5 ml elution should be preferred to a single 10 ml elution). Soaking time is also critical and 2 to 5 min soak is most of the time allowed before each elution.

4. Applications of SPE to the determination of selected trace elements

4.1. Cadmium

Cadmium is known to be a highly toxic trace metal. Owing to its very low concentrations in the environment, a preconcentration is usually required for its determination. This can be performed on an anion-exchange resin, after reaction of Cd(II) with chloride and the formation of the anionic CdCl$_4^{-}$ complex [86]. Yet, Cd(II) retention generally occurs through chelation, either by adding a chelating agent to the sample, by impregnation of the sorbent, or by the synthesis of new chelating resins. Hence, a FI preconcentration on-line with F-AAS has been reported for the determination of Cd(II) [77]. Cadmium complexed with DDTC was sorbed on the inner walls of a PTFE knotted reactor, and further on-line eluted with isobutyl methyl ketone (IBMK) giving a detection limit of 0.1 µg/l. However, very acidic pHs (lower than 2) were required for optimum sensitivity and collection efficiency. In addition, DDTC is rather non-selective, so that retention of other trace elements may occur. This drawback maybe overcome by adding masking agents, such as thiourea and ascorbic acid/phenanthroline for copper and iron, respectively, or by choosing a more selective reagent, such as DDTP [233]. Still very acidic pHs were required for optimum sensitivity and collection efficiency. APDC offers the advantage of a broader pH range without decomposition. Hence, Cd(II) complexed with APDC was stable for pHs between 4 and 8, and could be efficiently retained on C$_{18}$-silica [56,124]. Further elution with methanol and FI on-line ET-AAS analysis enabled detection limits of 0.178 ng/l or 1.26 ng/l depending on the system used. Other chelating reagents may be used, such as PAR or PADMAP [58], or tetra-(4-bromophenyl)-porphyrin (T$_4$BPP)[41].

Impregnation of the sorbent with a chelating reagent has been reported for the preconcentration of Cd(II). In that case, the choice of a chelatant that have a high affinity for cadmium is preferred to ensure high selectivity. For example, BSQ has been immobilized on Amberlite XAD-7 and used in a FI system giving a detection limit of 1.9 µg/l [78]. However, Zn(II) was also retained, while other ions were found to interfere (namely Mg(II), Cu(II), Fe(III)). Amberlite XAD-7 coated with DMBS also enabled the retention of Cd(II) from neutral medium with simultaneous retention of Pb(II) [196].

When ICP–AES is used as the analysis technique, the use of organic solvents should be avoided as they may generate strong turbulence in the ICP. So, new chelating resins were developed for the Cd(II) preconcentration in a FI–ICP–AES system, such as 1,5-bis(dl-2-pyridyl) methylene dithiocarbohydrazide (DPTH)- or methylthiosalicylate (TS)-functionalized silica gel leading to detection limits of 1.1 and 4.3 µg/l, respectively.
They offer the advantage of having no affinity for sodium, potassium, calcium and magnesium, enabling the Cd(II) analysis in real water samples. However, other trace elements reduced Cd(II) retention on both resins, such as Zn(II) or Cu(II). In some cases, the interfering effect of Zn(II) can be avoided by careful adjustment of the sample pH, as observed on the Lewatit TP807'84 resin that contains a phosphonic derivative as extractant [33]. Nevertheless, other ions were still co-extracted with Cd(II), namely Cu(II) and Pb(II).

4.2. Chromium

Chromium species enter the environment as a result of effluent discharge from steel industries, electroplating, tanning industries, oxidative dyeing, chemical industries and cooling water towers. They may also enter drinking water supply systems from the corrosion inhibitors used in water pipes and containers or by contamination of the underground water from sanitary landfill leaching. Therefore, it is of major concern to study the characteristics of chromium in aquatic systems. Chromium occurs mainly in (III) and (VI) oxidation states. While Cr(III) is an essential trace element, Cr(VI) is highly carcinogenic and mutagenic due to its high oxidative character. So, it is important to develop analytical methods that enable analysis of chromium in its different oxidation states. However, sampling and preconcentration steps might disturb the redox equilibrium between Cr(III) and Cr(VI), thereby affecting the original speciation state of the sample.

Most SPE methods are based on the high reactivity of Cr(VI), due to the relatively inert nature of Cr(III). Many methods are thus based on the determination of Cr(VI) and total chromium. FI on-line preconcentration procedures reported for chromium species were exhaustively reviewed up to 1992 by Sperling et al. [71], and later (until 1998) by Prasada Rao et al. [59].

4.2.1. Cr(VI)

The determination of chromium is frequently achieved by spectrophotometry after derivatisation with a reagent such as DPC. The reaction of DPC is very selective for Cr(VI) so it can be performed directly without a separation step. The chromate oxidizes DPC to diphenylcarbazone (DPCO) to form a soluble strongly red–violet compound with Cr(III) (Cr(III)-DPCO\(^{3-n^+}\)). A large excess of DPC is essential as compounds present in the sample may consume the reagent. The Cr(III)-DPCO complex can be retained on polyethylene packed in a column and subsequently eluted with methanol before being analyzed by LC [204]. This procedure was applied to the determination of chromium in geological samples. The determination of total chromium may also be achieved after preliminary oxidation of Cr(III). Elements posing interference with this method are mainly Mo(VI), Fe(III) and V(V), and their separation using SPE with an anionic-exchanger (SAX) has been performed for the subsequent spectrophotometric determination of chromium [194]. The Cr(III)-DPCO complex was also found to be retained on cation-exchange (SCX) membrane disks [234]. The color intensity of the membrane was then correlated to the Cr(VI) concentrations by visual analysis. This simple procedure was found to provide a highly sensitive semi-quantitative field test for the determination of Cr(VI) in aqueous samples. A cation-exchange resin was also used for the FI on-line preconcentration of the Cr(III)-DPCO complex [83], which can be retained at pH 1 on Amberlite XAD-16 resin and then eluted using 0.05 M H\(_2\)SO\(_4\) solution in methanol [161]. In this way, Cr(VI) can be determined in tap water samples, as total chromium after oxidation of Cr(III) into Cr(VI) using potassium permanganate.

Cr(VI) may also be chelated by DDTC, and subsequently retained on C\(_{18}\)-silica [60]. Total chromium may be estimated using the same procedure with prior oxidation of Cr(III) to Cr(VI). The FI on-line preconcentration systems enabled detection limits of 16 ng/l for Cr(VI) and 18 ng/l for total Cr. Very recently, selective retention of Cr(VI), compared to Cr(III) was obtained using PTFE turnings packed in the micro-column of a FI manifold. APDC was used for complexation of Cr(VI) in the samples before preconcentration, and elution was achieved with IBMK before analysis using F-AAS [49]. Similarly, after reaction with APDC, the Cr(VI) complex could be retained...
on the PTFE inner wall of a knotted reactor or on PTFE beads packed into a column, and subsequently eluted with ethanol [74,75]. Also, acidic alumina enables selective retention of Cr(VI) [70] and a micro-column was used in a FI manifold to separate and preconcentrate Cr(VI) from Cr(III) in water samples. However, it was later reported that between pH 3 and 6 Cr(III) could also be retained on that sorbent [235].

4.2.2. Cr(III)

Very recently, selective preconcentration of Cr(III) on a cellulose micro-column has been reported to be highly dependent on sample pH [183]. Below pH 8, very low retention occurred, while at pH 11 almost quantitative adsorption could be achieved. Elution of the retained Cr(III) species with 5 ml of HCl (2 M) enabled its subsequent determination by ET-AAS with a 1.8 ng/l limit of detection. This method also enabled the determination of total chromium following initial reduction of Cr(VI) to Cr(III) with hydroxylamine.

The coating of the positively charged acidic alumina with an anionic surfactant, SDS, has been reported to enable selective retention of Cr(VI) in strongly acidic solution, while the cationic Cr(III) remains unabsorbed [151]. Separation of the two species could thus be obtained and Cr(III) determined by ET-AAS. However, this method presents two major limitations: no analyte enrichment and the need to adjust sample pH to 0.6, which may affect chromium speciation. In another study, basic alumina has been shown to selectively retain Cr(III) at pH 2–7 [73], permitting elution with nitric acid.

Selective retention of Cr(III) was also reported with a macroporous PS-DVB resin (CHP-20P) after complexation in solution with 8-HQ at 85 °C [159]. The use of hydroxylamine as a reductant was found efficient for the reduction of Cr(VI) to Cr(III) without affecting Cr(III) retention as it does not complex this species. 8-HQ-immobilized-polyacrylonitrile fiber has been recently reported to selectively retain Cr(III) at pH 6, enabling its preconcentration from river and reservoir water samples, while Cr(VI) was unretracted [186]. Selective retention of Cr(III) (cationic) was also achieved on a chelating ion-exchange column packed with poly(aminophosphonic acid) (PaPhA) resin [81]. By using on-line FI preconcentration coupled to F-AAS, a detection limit of 0.2 μg/l could be obtained with a sample throughput of 30 h⁻¹.

4.2.3. Cr(VI)/Cr(III)

A procedure based on the reaction of chromium species with APDC and subsequent retention of the complexes on SPE permitted a subsequent on-line LC–UV analysis [39]. The Cr(III) reacts with the chelating agent under relatively mild conditions to give only one product, i.e. tris[pyrrolidine-l-dithioato-S,S']chromium(III), whereas Cr(VI) reacts to give two products, one being the former complex. Thus, the concentration of Cr(VI) needs to be corrected for the Cr(III) complex. The automated SPE system was optimized to yield detection limits of 0.2 μg/l for Cr(III) and 0.06 μg/l for Cr(VI). A FI on-line preconcentration procedure followed by F-AAS detection has been reported to allow determination of both chromium species in water samples based on selective formation of DDTC complexes of Cr(VI) in the pH range of 1–2, and of Cr(III) in the 4–9 pH range [59]. A detection limit of 0.02 μg/l could thus be achieved. Cr(III) could also be retained in the presence of Mn(II), which enhances the Cr(III) signal [59].

TiO₂ has been recently reported to be very promising for chromium speciation [108]. Indeed, this sorbent can selectively adsorb Cr(III) or Cr(VI) depending on the pH of the sample. At pH 2, Cr(VI) is the sole chromium species retained, while at pH 8 it is Cr(III). Nitric acid (0.5 or 1 M) allows quantitative elution of the retained species. Acidic alumina has also been reported to retain both Cr(III) and Cr(VI) [235]. However, careful adjustment of the pH was of prime importance as below pH 3 and above pH 6 retention of Cr(III) and Cr(VI), respectively, decreased [235]. Hence, a FI on-line preconcentration method has been reported on activated acidic alumina with buffering of the sample before retention either at pH 7 (for Cr(III)) or pH 2 (for Cr(VI)) [71]. Cr(III) exhibited a typical cationic sorption (it increased with pH and decreased when competing...
cations are present), whereas Cr(VI) exhibited a typical anionic sorption (it decreased with increasing pH and in the presence of competing dissolved anions). Thus, the use of neutral alumina seems more appropriate for chromium speciation since it offers the advantage of requiring no adjustment of the water sample pH. Hence, both Cr(III) and Cr(VI) can be quantitatively retained on neutral alumina with speciation being achieved using selective elution of the species, i.e. 1 M ammonia solution for Cr(VI) followed by 4 M HNO₃ for Cr(III) [110]. This method affords a 25-fold pre-concentration factor with a limit of detection of 10 ng/l. A similar preconcentration on alumina followed by selective elution for separation of the two chromium species has been reported [72].

A new resin that consists of PS-DVB functionalized with NDSA enabled the retention of Cr(VI) at sample pH of 1.5, and of Cr(III) at pH 6.5 [181]. Thus, speciation of chromium was accomplished by adjustment of the pH along with the percolation of two sub-samples at the desired pH. The selective retention of both chromium species could also be achieved on a polymeric sorbent containing aminocarboxylic groups at pH 3 and 7, for Cr(VI) and Cr(III), respectively [236]. Microwave heating was found to promote the sorption. Chromium species may also be retained on an anionic-exchanger (SAX) after their complexation with EDTA [237]. Controlled elution of the analytes with 0.5 M NaCl enables their speciation. In this manner, detection limits of 0.4 and 1.1 μg/l were obtained for Cr(III) and Cr(VI), respectively.

4.3. Iron

Iron is widely distributed in nature and is one of the most important elements in biological systems. Its biological effectiveness is influenced by its chemical properties, such as valence, solubility and the degree of chelation or complex formation. Several methods have been proposed for the determination of Fe(III) and Fe(II) species.

4.3.1. Fe(III)

Some solid phases have been synthesized to enable high selectivity towards Fe(III). Thus, the chemical bonding of formylsalicylic acid on amno-silica gel enabled the preconcentration of Fe(III) from a mixture containing other trace elements in batch experiments [35]. The capacity of this sorbent for Fe(III) was 0.95 mmol/g. This high selectivity was attributed to the presence of two chelating oxygen atoms. The selective SPE of Fe(III) on purpurogallin chemically immobilized on silica gel has also been reported [140]. Once eluted from the sorbent the iron species were analyzed using AAS. Due to strong affinity of Fe(III) to the bound organic compound, as compared to Fe(II) (the distribution coefficient, Kᵢₒ, was found to be 120 500 for Fe(III) and 12 700 for Fe(II)), speciation of iron could be achieved using this procedure. Only minor Fe(III) (2.1%) was found to be reduced to Fe(II) upon interaction with the sorbent. Using batch experiments, Fe(III) could be selectively extracted from tap water as well as from a soft drink sample (7-Up).

Yamini and Amiri [117] developed an efficient method for the selective extraction, concentration and determination of trace amounts of Fe(III) in aqueous media, enabling determination of iron in a 500 ml water sample in less than 30 min with a reproducibility better than 3%. Iron(III) was initially reduced to Fe(II) by addition of hydroxylamine (NH₂OH) and the bathophenanthroline complex Fe(bathophenanthroline)²⁺ was analyzed by the use of C₁₈-silica membrane disks and spectrophotometry. The ligand was added to the sample before SPE, and the solution heated to enhance formation of the complex. By comparison with AAS and ICP emission spectrometry, this method offers simplicity and applicability to field determination of iron. However, pure solvents eluted only a fraction of the complex and addition of NaClO₄ to the elution solvent was required for complete removal of the retained complex, indicating that interactions between the complex and the C₁₈-silica are dispersive or ionic. At sample pH below 2.5 recovery decreased probably due to competition of H⁺ with Fe(II) for reaction with bathophenanthroline. The influence of several ions was investigated, most were tolerated at high levels without interfering with the determination of iron. However, some species such as Co²⁺, Ni²⁺, VO₃⁻ and especially Cu²⁺, interfered. The interference effect of Cu²⁺ is due to the preferential
formation of a very stable, almost colorless, complex between Cu(I) and bathophenanthroline. Its effect was eliminated by the addition of excess amounts of thiourea, as a masking agent, while the effect of the other ions was eliminated by use of excess amounts of bathophenanthroline. A FI catalytic spectrophotometric method has also been developed for the shipboard determination of iron in sea water samples [52]. Retention was achieved using 8-HQ-functionalized silica gel. After elution with HCl mixing with the reagents (H$_2$O$_2$ and N,N-dimethyl-p-phenylenediamine (DPD)) was performed to ensure the formation of the color. A detection limit of 0.016 nM could thus be achieved.

4.3.2. Fe(II)
Iron(II) is thermodynamically unstable in sea water containing dissolved oxygen due to its rapid oxidation to Fe(III) (half-life being approx. 4–10 min depending on the pH). Yet, the determination of Fe(II) in sea water is important because of its role in the solubility, speciation and biological utilization of iron in oceanic surface waters; in addition Fe(II) may reduce oxygen, thereby producing radicals in the water.

The colorimetric reagent ferrozine (FZ) [3-(2-pyridyl)-5,6-bis(4-phenylsulfonic acid)-2,4-triazine] forms a stable, colored complex with Fe(II) in a pH range of 4–10, but not with Fe(III) [238]. Interferences are also possible due to complexation of Cu(I), and to a lesser extent of Co(II) and Ni(II) by FZ. Thus, a procedure has been developed enabling the preconcentration of Fe(II) from sea water, thanks to its retention as the Fe(FZ)$_3$ complex on a C$_{18}$-silica cartridge and subsequent elution with methanol [122]. Iron was then analyzed directly by spectrophotometry (562 nm). C$_{18}$-silica was loaded with FZ by passing a FZ solution through the cartridge (the retention capacity of the cartridge for FZ increased with increasing ionic strength of the solution). Once the sea water has been passed through the cartridge, washing was performed with 5 ml of 0.1 M NaCl–0.005 M NaHCO$_3$ to remove sea salts and prevent precipitation of Mg$^{2+}$ and Ca$^{2+}$ in methanol upon elution. Cu(I) interference was minimised by adding neocuproine (NCH) to the methanol extract avoiding the presence of the Cu(FZ)$_2$ complex. However, in this method both the Fe(FZ)$_3$ complex and the excess FZ were eluted and contributed to the absorbance measurement, which may result in unreliable determination of low Fe(II) concentrations. Therefore, this procedure was further improved by performing a chromatographic separation of the two species after the SPE step. In addition, 254 nm was found more suitable for detection than 562 nm. In this way, ultratrace amounts of Fe(II) could be determined in several samples (aerosols, rainwater and sea water) [123].

A procedure, similar to that reported by King et al. [122] has been used for the on-line FI preconcentration of Fe(II) from sea water samples [68]. It could be extended to Fe(III) determination based on its initial reduction by addition of ascorbic acid to the sample. Copper interference could be suppressed by loading the C$_{18}$-silica with a mixture of FZ and NCH, but at the same time the column capacity was lower than when loaded with FZ alone.

4.3.3. Fe(III)/Fe(II)
Most of the methods report the determination of only one of the two iron species mainly by selective complexation. However, this can cause a shift in the Fe(II)/Fe(III) equilibrium in the solution as a result of redox reactions. To prevent such problems, a procedure has been reported that enables the simultaneous complexation of both Fe(II) and Fe(III) in the sample followed by retention of the complexes on selective solid sorbents [18]. Fe(II) was complexed by addition of 1,10-phenanthroline, while Fe(III) formed a complex with ferron (8-hydroxy-7-idoquinoline-5-sulfonic acid). The solution was thus passed successively to an anion-exchange resin and a reversed-phase sorbent. Since the Fe(III)-ferron complex is negatively charged, it was retained by the first solid phase (for sample pH 3–6), while the Fe(II)-phenanthroline was passed through due to its non-polar character. This complex was then retained by the second solid sorbent (C$_{18}$-silica). This method enabled the determination of both labile Fe(II) and Fe(III) species in wine samples.
4.4. Lead

Lead is a toxic metal, which accumulates in the vital organs of man and animals. Its cumulative poisoning effects are serious haematological damage, anaemia, kidney malfunctioning, brain damage, etc. Lead is still emitted into the biosphere in considerable amounts owing to its application as a fuel additive, mainly as tetraethyllead and tetramethyllead. It is also present in many industrial streams. Due to the presence of lead in environmental samples at low levels, its separation from other elements present and the use of a preconcentration step prior to lead determination are usually necessary. All the studies reported until now focused on the preconcentration of inorganic lead Pb(II). The performances of Pb determination using different sorbent materials have been reviewed recently [50,176]. Some examples are given below. Firstly, as a cationic species, Pb(II) can be retained on cation-exchangers, such as basic alumina [239]. However, such sorbents are rather non-selective. So, other strategies have been used that are the retention of Pb complexes on hydrophobic sorbents, the retention of Pb(II) on sorbents coated with a chelating reagent and the synthesis of new chelating resins.

Lead complexed with DDTP could be retained on C₁₈-silica, activated carbon and PUF [63]. In that way analysis through a FI system coupled to F-AAS was performed with limits of detection of 0.3, 1.2 and 3 µg/l for C₁₈-silica, PUF and activated carbon, respectively. In another FI system Pb(II) was complexed with APDC retained on PTFE turnings and further eluted with IBMK leading to 0.8 µg/l as a limit of detection [50]. This method enabled the determination of Pb(II) in various environmental and biological samples. Complexes can be formed with DDTC in acidic medium, further retained on C₁₈-silica and eluted with IBMK or methanol before F-AAS, enabling the detection of 3 to 10 µg/l [62,233]. Alternatively, the sorbent can be impregnated with the chelating reagent. Hence, the SPE of lead on C₁₈-silica disks has been reported after impregnation of the sorbent with a S-containing Schiff’s base to enable Pb(II) chelation [120]. After elution with nitric acid lead was further analyzed by F-AAS with a limit of detection of 16.7 µg/l. Retention of lead was quite selective even in the presence of other ions. The addition to the sample of ammonia as a masking agent was recommended to suppress the interfering effect of some cations, namely Cu(II), Zn(II) and Hg(II). Similarly, the coating of C₁₈-silica with BAS was found highly selective in retaining Pb(II) with subsequent elution using acetic acid and F-AAS analysis leading to 50 ng/l as a limit of detection [121]. Pb(II) could also be retained on Amberlite XAD-7 coated with DMBS [196] or XO [176], Amberlite IRA-904 impregnated with TCPP [8], or PUF coated with 2-(2-benzothiazolylazo)-2-p-cresol [240].

Chelating resins have also been synthetized for the selective preconcentration of Pb(II). For example, Amberlite XAD-2 was functionalized through an azo spacer by several chelating agents, such as CA, PC and TSA, and used for the retention of Pb(II) from water samples [176]. Similarly, this sorbent functionalized with SA also enabled the retention of Pb(II), along with Zn(II) [171]. In each case nitric acid enabled lead desorption. Limits of detection in the 2.4–4.9 µg/l range were obtained. Amberlite XAD-7 functionalized with a crown ether was also found suitable for the preconcentration of Pb(II) [241].

Very recently, an attractive test procedure has been reported that enables the determination of as low as 20 ng/l of Pb(II) [203]. It is based on the immobilization of an enzyme, alkaline phosphatase on PUF.

4.5. Mercury

The presence of mercury species in aquatic food chain is of great concern as it is well-known that inorganic mercury (Hg²⁺) is converted into highly toxic methylmercury (MeHg⁺) by aquatic organisms. Due to the presence of mercury in environmental samples at low levels, its separation from other elements present and the use of a preconcentration step prior to the determination is usually necessary.

4.5.1. Hg(II)

Mercury can be preconcentrated from aqueous samples using a chelating ion-exchange resin con-
taining histidine covalently bound to its carboxyl group [242]. A chelating PS-DVB-based resin with picolinic acid amide (PAA) as the functional group was also found efficient for Hg(II) retention from water samples [184]. Several functional groups chemically bound to silica gel have also been reported to afford selective sorbents for preconcentration of Hg(II) during adsorption. This was the case with DZ [104] and dithioacetal derivatives [105]. Another procedure involving the use of C\textsubscript{18}-silica disks impregnated with hexathia-18-crown-6-tetraone (HT18C6TO), was shown to quantitatively extract Hg(II) from natural waters in less than 15 min [130]. Recovery was nearly independent of pH (in the range of 1 to 7) as already reported for the solvent extraction of metals with crown ethers. Before eluting Hg\textsuperscript{2+} with 1 M HBr, a washing step with 1 M HNO\textsubscript{3} was recommended to remove small amounts of retained Cu\textsuperscript{2+}, Zn\textsuperscript{2+}, Pb\textsuperscript{2+} and Cd\textsuperscript{2+}.

4.5.2. Hg(II)/organic Hg

A chelating resin based on vinyl polymer and containing dithiocarbamate groups was found efficient for retention of inorganic and organic mercury from water samples over a broad range of pHs (1 to 11) [189]. The species were eluted using an acidic aqueous solution of 5% (w/v) thiourea, enabling a preconcentration factor of 666 and the determination of mercuric species with a limit of detection of 0.2 ng/l. The use of another chelating resin containing dithiocarbamate groups was also found effective in retaining inorganic as well as organic mercury in the pH range 1-4 resulting in limit of detection of 0.5 ng/l [243]. The on-line FI preconcentration of mercury species (Hg(II), methylmercury, ethylmercury) on a dithiocarbamate resin has also been reported [244]. Detection limits of 0.05 ng/l and 0.15 ng/l for organic and inorganic mercury, respectively, could be obtained. However, this method involved manual steps once the species were eluted with thiourea, extraction into toluene as the diethyl dithiocarbamate complexes, butylation with a Griegard reagent and subsequent gas chromatography (GC) analysis. In addition, preconcentration failed in the presence of high amounts of humic substances in the water samples.

Complexation of mercuric species with APDC, FI on-line preconcentration on C\textsubscript{18}-silica, further separation with LC, and analysis by CV-AAS has been reported [43]. In this manner, Hg species (methylmercury, ethylmercury, phenylmercury and Hg(II)) in fish and human urine could be analyzed at the ng/l level. Chelation with DDTD and preconcentration on C\textsubscript{18}-silica in a FI–CV-AAS system resulted in detection limits of 10 ng/l for methylmercury and Hg(II) with an enrichment factor of 20 [64]. Several ligands were tested: DDTC, APDC and DZ (or diphenylthiocarbamate) [55]. Results showed the superiority of carbamate type reagents for the preconcentration of Hg(II) and methylmercury using this system. With DDTC, detection limits of 16 ng/l of Hg could be obtained.

4.6. Selenium

Selenium is present in the environment from both natural and anthropogenic inputs. This element has been recognized as an essential nutrient. However, at concentrations higher than 130 µg/l it becomes toxic. Se(IV) and Se(VI) are the predominant species in natural waters. Biomethylation may also occur, leading to the formation of organic species such as dimethyl selenide (DMSe), dimethyl diselenide (DMSe) and diethyl selenide (DESe), and detoxification. Therefore, a reliable speciation procedure is required to evaluate toxicity of samples. An overview of SPE procedures developed for selenium has been recently given [193] and some are detailed below. It appears that most methods were dedicated to the determination of inorganic selenium.

4.6.1. Se(IV)

APDC has been loaded on C\textsubscript{18}-silica and used for the preconcentration of Se from sea water prior to ET-AAS [114]. Speciation of inorganic Se(IV) and Se(VI) was possible since APDC selectively chelates Se(IV). A reduction of Se(VI) to Se(IV) prior to chelation is required for the determination of total inorganic Se. However, this method was not selective as other trace elements were retained on the sorbent (such as Bi, Pb, Zn, As, Sn, V). Complexation of Se(IV) could also be obtained
Both forms of inorganic selenium can be retained on acidic alumina and extracted from natural waters without any pH adjustment [111]. Selective elution is achieved using ammonia at different concentrations for eluting Se(VI) and then Se(IV) enabling speciation of inorganic selenium in natural waters. Quantitative recoveries from spiked tap water and ground water were obtained except for one tap water, where 42 and 154% of Se(IV) and Se(VI), respectively, were recovered possibly due to oxidation of Se(VI) by residual chlorine. Similar observations were made in another study [40].

Dowex-IIX8 ion-exchanger enabled preconcentration of both Se(IV) and Se(VI) [246]. The species were then separated during elution with two different concentrations of HCl. Inorganic selenium species were also retained on several anion-exchange resins based on either cellulose or PS-DVB copolymer [225]. Despite a lower affinity, the functionalized cellulose sorbent was preferred, as it enabled a better separation of Se(IV) and Se(VI) during elution with different concentrations of nitric acid. Traces of Se(IV) and Se(VI) could also be retained on a molybdate-form anion-exchange resin in batch experiments [247], permitting speciation of inorganic selenium in natural waters except sea water (where foreign ions interfered).

The coupling of SPE to LC–ICP–MS enabled the speciation of inorganic selenium in natural water samples by ion-pairing (with tetrabutylammonium phosphate as the reagent) and sorption on C18-silica, subsequent elution and separation in the chromatographic column by anion-exchange [40]. However, sample volumes were limited to 10 ml due to the limited capacity of the preconcentration column.

4.6.3. Organic Se

Tanzer and Heumann [248] developed a method for the selective determination of acidic/neutral and basic organoselenium species in water samples based on the selective retention of the species on Amberlite XAD-2 at different sample pHs (3 and 8, respectively). However, this method was found questionable by other authors who noted partial retention of Se(IV) on that sorbent [225].

4.6.4. Se(IV)/Se(VI)/organic Se

Simultaneous preconcentration of inorganic and organic selenium species is a more difficult task. A combined SPE method has been reported to enable preconcentration of both inorganic and organic species of selenium [19]. An anion-exchanger cartridge was placed on the top of a C18-silica cartridge so that inorganic selenium was retained on the first cartridge, while organic species were retained on the reversed-phase sorbent. The cartridges were then separated and the species eluted: 1 M HCOOH for Se(IV), 3 M HCl for Se(VI), CS2 for organic compounds. In another recent procedure, simultaneous determination of organic (selenocystine) and inorganic selenium (Se(IV) and Se(VI)) species was achieved using off-line preconcentration on Amberlite IRA-743 followed by separation of the species and analysis using LC–ICP–MS [193]. No adjustment of the sample pH was required. However, the sorbent was not selenium selective, and selenomethionine could not be retained under the conditions developed due to strong competition with hydrogen carbonate.

4.7. Tin

Organotin compounds have found widespread industrial applications as biocides, antifouling paints, catalysts and polyvinyl chloride stabilizers. So, there are a variety of pathways for their entry into the environment. Whereas inorganic tin is basically harmless, some organotin compounds are highly toxic, especially tri-substituted organotin species. Therefore, there is a need for sensitive methods that enable the determination and speci-
nation of these compounds. Several studies report the use of SPE for organotin determination [249–251].

4.7.1. Butyltins

Tributyltins have been used as insecticides, fungicides, acaricides and preservatives for many different types of materials. In particular, they have been used as antifouling paints (as biocides) on ships, boats and dock resulting in release of TBTs directly into the aquatic environment where they are non-specific and extremely toxic to non-target animal and plants species. C18-silica, either in cartridges or in PTFE disks, has been found effective in preconcentrating TBTs from aqueous solutions [24]. Enrichment factors up to 1000 can be obtained enabling the quantification of TBTs at the 0.1 µg/l level. In addition, TBTs can be stored on such solid supports at room temperature for at least 1 month. Amberlite XAD-2 impregnated with tropolone has also been reported to retain TBT and dibutyltin, while monobutyltin was not retained [164]. The addition of 0.8% sulfuric acid to the water sample enabled the selective retention of only TBT on the resin. This species was subsequently eluted with IBMK and analyzed by ET-AAS enabling quantitative determination of TBT in water samples with a limit of detection of 14.4 ng/l and a preconcentration factor of 80.

4.7.2. Phenyltins

Triphenyltin is retained on C18-silica cartridges, even though a fraction of the compound cannot be recovered [112]. Hence, best recoveries (between 81 and 89%) were obtained by elution in the backflush mode with 10−4 M 3-hydroxyflavone in methanol. Retention of TPhT on other silica-based sorbents (octyl, phenyl and cyanopropyl) has also been reported [112].

4.7.3. Butyltins/phenyltins

A semi-automated system was reported that enabled organotin speciation [251], wherein pre-concentration was performed using a microcolumn of C18-silica placed in a FI manifold. Percollation of a derivatising reagent (sodium tetraethylborate) through the column enabled derivatisation of the organotin compounds. Elution of the derivatised species (monobutyltin, monophenyltin, dibutyltin, diphenyltin, TBT and TPhT) was achieved using methanol and their separation and analysis was performed using GC–AES. In this manner, with rather small sample volumes (10–50 ml) detection limits in the range of 0.10–0.17 ng/l could be obtained. Application of the method was tested with real river water samples, and results were consistent with those obtained using classical liquid–liquid extraction. Similarly, in an off-line system, organotins derivatised by sodium tetraethylborate could be retained on C18-silica disks, and further eluted with supercritical CO2 [252].

The use of tropolone-loaded C18-silica has also been used for the retention of several butyltins and phenyltins (mono-, di-, tri- and some tetra-substituted compounds) [118]. However, selectivity could not be achieved using SPE only. Organotins were separated by subsequent GC analysis after their ethylation with Grignard reagent. This method affords a sensitivity of low ng/l in surface waters and mg/kg in sewage sludges.

Speciation of tin has also been reported using both graphitized carbon black and silica gel as sorbents [223]. Water samples were first passed through GCB, allowing the retention of TBT and TPhT, while inorganic tin passed unimpeded and was analyzed directly. The organic species were subsequently eluted with a mixture of methanol/dichloromethane (4:1), and separated on silica gel. The overall method provided an enrichment factor of up to 80 000, but required the complete evaporation of the organotin fraction eluted from GCB, and the dissolution of the solid residue in hexane before separation on silica gel.

Finally, organotins can be efficiently retained on strong cation-exchange silica-based bonded phases (Bond-Elut SCX) and strong cation-exchange polymeric-based phase (Oasis-MCX). The presence of NH4+ was essential for elution of the compounds. Recoveries were lower with the polymeric phase particularly for TPhT, probably because of strong interaction of the aromatic rings with the N-vinylpyrrolidone-divinylbenzene support [36].
5. Conclusion

The use of SPE procedures has been growing in the past few years due to their advantages offered for trace element determinations, namely conservation of species, good preconcentration factors (thus enabling the achievement of very low limits of detection), ease of automation, and possible online coupling to instrumental techniques.

Despite the numerous steps and parameters used to enable efficient extraction and recovery of the target analytes, the choice of the solid sorbent is the most critical step. Among the numerous sorbents that have been used, it clearly appears that the initial use of ion-exchangers is being replaced by more selective supports containing chelating functional groups. Such sorbents are frequently based on hydrophobic supports namely C₁₈-silica or PS-DVB copolymer, the latter affording a broader pH range. The simplest procedure consists of adding the chelating reagent directly to the sample. A more suitable way of proceeding is to load the reagent on the solid sorbent. The coated sorbent thus obtained may usually be used several times, or PS-DVB copolymer, the latter affording a broad-

Alternatively, the reagent may also be chemically bound to the sorbent leading to the synthesis of new phases, and thus avoiding any leaching of the reagent. Promising results have also been recently obtained with inorganic oxides such as titania and alumina, as retention of some trace elements could be achieved with the raw sample (i.e. no reagent addition nor pH adjustment), thereby avoiding possible speciation changes in the sample.

Examples given in this review for several trace elements show the high potential of SPE, especially its possible high selectivity (by choosing the nature of the sorbent and/or the chelating agent, as well as the nature of the eluent). In fact, in some cases, differentiation of species may be achieved, thereby offering new opportunities for speciation. There is thus no doubt that this technique will face a growing interest for trace element determination and speciation in the future, as already evidenced for organic micropollutant determinations in the recent years.

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