Speciation of trace metals and metalloids by solid phase extraction with spectrometric detection: a critical review

ALİ REHBER TÜRKER

Review Article

Speciation of trace metals and metalloids by solid phase extraction with spectrometric detection: a critical review

Ali Rehber TÜRKER[*]

Department of Chemistry, Faculty of Science, Gazi University, Ankara, Turkey

Abstract: Considerable interest is continuing to be shown in the speciation of metals, metalloids, and organometals due to the dependence of their toxicity and mobility on their chemical form. This review focuses on the speciation analysis of metals, metalloids, and organometals by solid phase extraction before spectrometric detection, and all aspects of analytical speciation such as determination of oxidation states and organometallic compounds. Some applications of speciation of metals and metalloids are also presented and discussed in this review. Fractionation, which is used sometimes as speciation, and chromatographic detection are not discussed. This review covers approximately the last four years (2012–March 2016), offering a critical review of the speciation of metals, metalloids, and organometals.

Key words: Solid phase extraction, speciation, spectrometry, trace elements

1. Introduction

As in the last several decades, considerable interest has continued to be shown in the speciation of trace metals and metalloids due to the difference in their toxicity and mobility according to their chemical form. Some trace elements are required for basic physiological and metabolic processes such as enzyme processes and therefore they are essential for humans.[1] However, some of them have toxic effects and may cause some diseases.[1] Individual species of an element might possess different chemical, physical, and biological properties. The well-known examples are chromium (Cr), arsenic (As), mercury (Hg), and selenium (Se). For example, Cr presents in nature generally as Cr(III) cations and Cr(VI) anions (CrO_4^{2-}, $Cr_2O_7^{2-}$) that are relatively stable oxidation states having quite different effects on biological systems. Since Cr(VI) penetrates more easily than Cr(III) from biological membranes, Cr(VI) compounds are more toxic than Cr(III).[2] In fact, Cr(III) ions help to adjust cholesterol and fatty acid metabolism.[3] Therefore, it may be regarded as an essential trace element. Similarly, organo-mercury compounds such as methylmercury are more toxic than inorganic Hg(II). Conversely, while organo-arsenic compounds such as arsenobetaine are not toxic, other As species are generally toxic. Although tributyltin is toxic for various organisms and is used as a biocide, inorganic Sn(IV) is not toxic.[4] Therefore, the total concentration of an element, in general, cannot reflect the hazard or benefit of different species. Because of this, studies about elemental speciation and speciation analysis in a wide range of applications and matrices continue to increase.[5] Therefore, developing a simple, rapid, and efficient method for monitoring the species of elements found in the environment is still very important.

Identifying and/or measuring the quantities of one or more individual chemical species in a sample is

[*]Correspondence: aturker@gazi.edu.tr

defined as speciation analysis.[6] Chemical species of an element may be isotopic compositions, oxidation states, and/or molecular structures. Speciation analysis is also an analytical activity to determine an element among defined chemical species in a system.[6] The characterization of the bioavailability of an element from complex matrices may also be considered speciation analysis. Speciation analysis is more difficult than total analysis. In many detection techniques, especially atomic spectrometric techniques, such as AAS, OES, and ICP-MS, only total metal concentrations can be determined directly. For speciation analysis, additional sample preparation procedures such as masking and separation should be performed prior to detection. One sample preparation procedure that is widely applied prior to detection is solid phase extraction (SPE).[7]

By applying SPE, (i) one species is usually selectively adsorbed on a SPE adsorbent or (ii) both species are retained on the same sorbent under different experimental conditions (different pH, different complexing agent etc.).[8,9] The other approach for speciation is applying sequential extraction using different solid phases for both species.[10,11] In some speciation analysis, a reagent is added to the sample for obtaining a compound of one species that will be adsorbed by the sorbent selectively.[12] In some studies, the adsorbent is chemically or physically loaded by a reagent or microorganisms to produce binding sites on the solid surface for the selective retention of one species.[13] Many different solid phases have been used in speciation studies to separate individual species selectively. Among these solid phases, nanometal oxides, microorganism loaded materials, chelating agent loaded materials, and ion imprinted materials have found wide applications.[14−20] The sorption procedure is followed by elution and quantification of sorbed species in speciation and/or preconcentration studies. SPE may be carried out by applying continuous and batch systems. In the continuous system, column techniques usually consist of a micro- or minicolumn loaded with a solid phase as an appropriate sorbent has been used.[21] The batch system is usually carried out in a beaker containing solid sorbent. The sorbent retaining an analyte is separated usually by filtration before elution. If the sorbent has magnetic properties, it can be separated by using an external magnet.

Some reviews have been published about elemental speciation using SPE over the last four years.[5,22−27] In recent years, SPE has been the most often used method in trace metal analysis in the environment for separation, preconcentration, and speciation purposes. Various solid phases were developed for column SPE. Column SPE can be used conveniently for on-line preconcentration/separation system and easily automated. SPE has many advantages over classical liquid–liquid extraction techniques. Some of these are lower solvent use, isolation of analytes from large sample volumes, higher efficiency, low disposal costs, short extraction times, minimal evaporation losses, and higher reproducibility.[7]

In SPE a wide range of natural materials such as silica[28] and cellulose[29] and various synthetic materials such as ion-imprinted polymers,[30] carbon nanotubes,[31] metal oxides,[32] Amberlite XAD resins,[33] ion exchange resins,[34] functionalized materials with chelating reagents,[35,36] functionalized organic or inorganic materials with microorganisms,[37] high-surface-area nanometal oxides,[38,39] and magnetic sorbents[40] have been used as solid phase materials.

This paper provides a review of articles involving speciation of metals and metalloids in various sample matrices. This review focuses primarily on trace metals, SPE, and atomic spectrometry. Instrumentation for speciation, including detection methods, is also reviewed and a detailed discussion of a particular application is included.

In most studies related to preconcentration and speciation, the optimum experimental parameters that influence the retention of chemical species onto the SPE sorbent has been studied. These experimental parameters are generally pH of sample solution, concentration of analyte, volume of sample, type and concentration

of eluent, sample flow rate (for column procedure), and contact time (for batch procedure). In a speciation analysis, the analytical performance of the method is also evaluated in detail. For this purpose, accuracy, precision, LOD, LOQ, and linear working range are usually determined, and, furthermore, interference effects of sample matrices or foreign ions are investigated. In some studies, sorption capacity and sorption kinetics are also studied. Speciation studies of trace elements available in the period covered by this review are mostly related to again As, Cr, and Hg and dominate the current literature.

2. Elemental speciation analysis

2.1. Arsenic

Researchers studying the speciation of As continued to determine As species in many fields such as the environment and food in the last four years. The published papers on As speciation in this period were discussed and some analytical parameters are summarized in Table 1. A method based on selective extraction of As species by SPE was presented.[41] In that study, functionalized aluminum oxide nanoparticles were used without applying any oxidation or reduction steps, and 1 mol L^{-1} HCl was used for the elution of adsorbed As from the sorbent. GFAAS was used as the detection technique. Under optimized experimental conditions LODs were found as 1.81 and 1.97 ng L^{-1} for As(III) and total As, respectively, with preconcentration factors up to 750. Linear working ranges were 5.0–280 ng L^{-1} and 8.0–260 ng L^{-1} for As(III) and total As, respectively.[41]

Table 1. Summary of analytical parameters of As speciation.

Sorbent	Sample	Analytes	Analytical technique	LOD ng L^{-1}	PF	Ads. capacity mg/g	Ref.
Functionalized aluminum oxide nanoparticles	Environmental, food, and biological samples	As(III) As	GFAAS	1.81 1.97	750	-	41
Iminodiacetate chelating disks and cation-exchange disks	Spring water and well water	As(III) As(V)	WDXRF	800 600	- -	-	43
Carboxylated nanoporous graphene	Drinking water wastewater, well water, human serum, and urine	As(V)	FI-HG-AAS	2.1	50.3	125.4	44
Methyl esterified egg-shell membrane	Tap water, lake water, spring water, and wastewater	As(V)	FAAS	15	-	-	45
Membrane filter	River water	As(III)	visual comparison	2000	-	-	46
Molecular recognition technology	Natural water samples and vegetables	As(V)	GFAAS	60	-	18.7	47
Amberlite IRA 900	Tap water, thermal water	As(V)	ETAAS	126	-	229.9	48
Poly(hydroxyethyl methacrylate) microbeads	Drinking water and snow	As(III)	GFAAS	10	86	-	49
Modified multiwall carbon nanotubes	Human hair	As(V)	HGAFS	14	16.3	26.2	50

In another method based on dispersive microsolid phase extraction and total-reflection X-ray fluorescence spectrometry (TXRF), As species were determined together with other heavy metal ions. In this method a novel

mercapto-modified graphene oxide (GO-SH) as an adsorbent was synthesized by grafting 3-mercaptopropyl trirnethoxysilane on a graphene oxide (GO) surface. It was shown that GO-SH adsorbs As(III) selectively in the presence of As(V).[42] The adsorption of As(III) as nonionic As (H_3AsO_3) was performed at pH 3–8. Adsorption of As(III) at pH above 8 decreases due to the formation of anionic As species ($H_2AsO_3^-$). Because predominant As(V) species also exist as anionic $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-} at this pH range, adsorption of As(V) on the sorbent was also very low. The authors explained that these anionic species were not retained on the sorbent due to electrostatic repulsion between anionic species and the negatively charged thiolates formed via the dissociation of the thiol groups. The speciation of As was checked by spiking water samples with various As species. As(III) was determined using the proposed procedure, whereas the sum of As(III) and As(V) was determined after reduction of As(V) to As(III) with L-cysteine. The concentration of As(V) was calculated as the difference.

Hagiwara et al.[43] suggest a method based on wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) after applying in situ SPE for the speciation of As(III) and As(V) in drinking water. In this method iminodiacetate chelating disks and cation-exchange disks placed on a Zr and Ca (ZrCa-CED) and hydrophilic PTFE membrane filters were used. To avoid spectral interference of Pb(II), it was removed before speciation analysis of As. For this purpose, 50 mL of water sample (pH 5–9) was passed through a chelating disk. Then, after adjusting pH of the solution passed through the chelating disk to 2-3, APDC solution was added to obtain As(III)-APDC complex. This solution containing As(III)-APDC and As(V) was passed through a PTFE filter placed on a ZrCa-CED. As(III)-APDC complex was retained by the upper PTFE filter, while As(V) ions were collected on the lower ZrCa-CED. The disks were washed, separated, and analyzed to determine As species by WDXRF spectrometry. The LODs for As(III) and As(V) were 800 and 600 ng L^{-1}, respectively. As speciation was carried out by the proposed method in spring water and well water.[43]

Khaligh et al.[44] suggested the use of two types of ultrasound assisted-dispersive microsolid phase extraction (US-D-mu-SPE) for the speciation of inorganic As. Carboxylated nanoporous graphene (G-COOH) was used as SPE adsorbent. Flow injection hydride generation atomic absorption spectrometry (FI-HG-AAS) was used as the detection method. High (H-US-D-mu-SPE) and low (L-US-D-mu-SPE) sample volume techniques for ultrasound assisted-dispersive microsolid phase extraction were applied to extract the analytes. While As(V) ions were recovered on G-COOH at pH 3.5 ($>95\%$), As(III) ions were not recovered ($<5\%$). Total As content was determined after oxidation of As(III) to As(V) using potassium permanganate. As(III) was calculated from the difference between total As concentration and As(V) concentration. The LOD for As(V) was 2.1 ng L^{-1} in H-US-D-mu-SPE and 24.8 ng L^{-1} in L-US-D-mu-SPE. The preconcentration factor for As(V) was 50.3 in H-US-D-mu-SPE and 5.1 in L-US-D-mu-SPE. The accuracy of the method was checked by analyzing the spiked samples and spiked CRM (NIST, SRM 2669 frozen human urine) with known As(III) and As(V) concentrations. The proposed speciation method was applied for the determination of As(III) and As(V) in real samples, such as drinking water, tap water, petrochemical factory wastewater, well water, human serum, and human urine.[44]

For the speciation analysis of inorganic As by SPE in environmental waters, thiol- and amine-bifunctionalized mesoporous silica materials were synthesized as a sorbent.[28] Characterization of synthesized sorbents was carried out by using SEM, TEM, XRD, IR, TGA, nitrogen gas adsorption, and elemental analysis. Adsorption isotherms and adsorption kinetics of As(V) and As(III) were also investigated by batch system. For the speciation analysis of As by SPE, a sequential elution strategy was applied for effective separation of As(III) and

As(V). For this purpose, firstly As(V) was eluted with 0.1 mol L^{-1} HNO_3 selectively. Then As(III) was eluted using 1 mol L^{-1} HNO_3 with 0.01 mol L^{-1} KIO_3.[28]

Methyl esterified egg-shell membrane (MESM) as a green sorbent was prepared for As speciation by esterification of egg-shell membrane (ESM). The sorption capacity of MESM for arsenate was higher than that of bare ESM (about 200-fold). MESM selectively adsorbed As(V) at 100% sorption efficiency in the presence of As(III) at pH 6. As(III) was not retained by MESM under these conditions. As(V) was eluted with 1.5 mol L^{-1} HCl. The LOD and RSD% for As(V) were 15 ng L^{-1} and 3.5%, respectively. Total inorganic As was determined by applying the same sorption process after oxidizing As(III) to As(V).[45]

A new visual method based on SPE for inorganic As speciation has been presented.[46] In this procedure, As(III) was treated with sodium dibenzyldithiocarbamate (DBDTC) to obtain a colorless complex. When the solution of As(III)-DBDTC complex was passed through the membrane filter, it retained As(III)-DBDTC complex quantitatively. Then As(III)-DBDTC complex was treated with a Cu(II) solution to obtain yellowish Cu(II)-DBDTC complex. The As(III) concentration was determined by comparing the color of the solution visually with the color standard. The LOD for As(III) was 2000 ng L^{-1} for visual comparison. The linear range and LOD of the reflection spectrometric method were 0–20,000 ng L^{-1} and 200 ng L^{-1}, respectively. In order to determine the concentration of As(V), it was first reduced to As(III) using L-cysteine and the above method applied. In order to eliminate the interference of heavy metal ions, metal-DBDTC complexes were removed by filtering the solution at pH 7.0 prior to extraction of As(III)-DBDTC complex. It was shown that the concentrations of As(III) and As(V) in river water samples could be determined by the proposed method.[46]

A simple SPE method based on molecular recognition technology (MRT) gel was developed for the selective separation of As(III) and As(V). While As(V) was selectively retained on the MRT–SPE cartridge system at pH 4–9, As(III) was passed without retention. As species were determined with GFAAS. The adsorption capacity of the MRT–SPE, precision as RSD%, and the LOD for As(V) were 0.25 ± 0.04 mmol g^{-1}, 2.9% (n = 10, C = 1 μmol L^{-1}), and 60 ng L^{-1}, respectively. The reusability of the MRT–SPE system was about 100 cycles with the sample solution spiked with 100 μmol L^{-1} As(V) ions. The proposed method was validated by analyzing CRMs such as BCR-713 effluent wastewater and BCR-610 groundwater. The speciation analysis of As(III) and As(V) in tap water, lake water, and river water samples collected from local sources was carried out with recoveries >98.7%.[47]

Tunçeli et al.[48] proposed a SPE method using Amberlite IRA 900 resin as an adsorbent for the speciation of As(III) and As(V) and total As. ETAAS with Ni chemical modifier was used for detection. Experimental parameters for As(V) were optimized. While As(V) was recovered quantitatively at pH 4.0, total As (III and V) was recovered at pH 8.0. The recovery of As(V) was 98.0 ± 1.9%. Adsorption capacity and the LOD for As(V) were 229.9 mg g^{-1} and 126 ng L^{-1}, respectively. Total inorganic As was determined at pH 8.0 and the concentration of As(III) was calculated by the difference between As(V) concentration and total inorganic As concentration. The accuracy of the proposed method was checked by analyzing SRM (CWW-TM-D wastewater) and spiked water samples with recoveries >95%. Determination of As(III), As(V), and total As could be carried out in thermal water and tap water samples with a relative error of about 3%.[48]

A minicolumn SPE procedure was used for the determination of ultratrace As(III) and As(V).[49] To obtain the mini-SPE column 30 mg of poly(hydroxyethyl methacrylate) microbeads as a sorbent was packed into a micropipette tip. The As(III)-pyrrolidinedithiocarbamate complex was selectively retained on the sorbent,

while As(V) ions were not. The retained As(III) was eluted by 700 μL of 0.25 mol L^{-1} NH$_3$ quantitatively and determined by GF-AAS. Mg(NO$_3$)$_2$ was used as chemical modifier to improve the signal intensity of atomic absorption. Precision (RSD%) and characteristic mass were 2.6% and 25 pg, respectively. As(V) ions were reduced to As(III) by thiourea–HCl for the determination of the total As. Then the concentration of As(V) was calculated from the difference. The LOD and preconcentration factor of As(III) were 10 ng L^{-1} and 86, respectively. The application of the method was demonstrated by analyzing a reference water sample (SEM-2011) and drinking water and snow samples. The recoveries were between 96% and 100% with the spiked samples (0.5 and 1.0 μg L^{-1} for As(III) and As(V), respectively).

Modified multiwall carbon nanotubes (MWCNT) were used as a new solid phase for the selective adsorption of As(V) in SPE.[50] MWCNTs were modified with cationic polyethyleneimine to increase selectivity. In this study, a minicolumn containing about 5 mg of the sorbents was used for As determination for on-line SPE-HG-AFS. Eighty percent sorption efficiency corresponding a sorption capacity of 26.2 mg g^{-1} was obtained for As(V) at pH 5.8. The sorption efficiency for As(III) was below 5% at this pH. As an eluent 100 μL of 0.6% (m/v) NH$_4$HCO$_3$ was used for As(V). Enrichment factor and LOD of As(V) were 16.3 and 14 ng L^{-1}, respectively. The linear working range and RSD% (at 0.5 mg L^{-1} As(V)) were 50–1500 ng L^{-1} and 3.6%, respectively. Total As concentration was determined after oxidizing As(III) to As(V). The validation of the proposed method was carried out by analyzing a human hair certified reference material (GBW09101).

In recent decades, solid phase microextraction (SPME) has been widely used for speciation and/or preconcentration together with HPLC. In one of these studies, amine-functionalized SPME was developed by sol–gel method and used for the speciation of DMA, MMA, and As(V) from aqueous solutions. HPLC-ICP-MS was used as the detection technique.[51] The optimum pH of the solution, shaking speed, extraction time, and temperature were 5.0, 700 rpm, 30 min, and 20 °C, respectively. The extraction performance of the coating was affected negatively by the addition of NaCl. The reason for this interference was concluded to be that anionic As species may compete with chloride anions for retaining on the active sites of anion exchange resin.

Other novel materials for solid phase adsorbents are nanomaterials. Titanium dioxide nanotubes are one of the examples of nanoadsorbents. Chen et al. used titanium dioxide nanotubes for on-line speciation of inorganic As ions (As(III) and As(V)). ICP-MS was used for the analytical detection of As species.[52] Speciation analysis based on the different pH requirement for As species could be performed successfully. All of the As species were adsorbed quantitatively at the range of pH 3.0–6.0. However, As(III) ions were only retained quantitatively at the range of pH 6.0–10.0. Under the optimal conditions, the LOD, enrichment factor, and RSD were 1.9 ng L^{-1}, 75, and 2.5% (C = 1.0 ng mL^{-1}) for As(III), respectively. As(III) and As(V) ions in spiked water samples were determined with recoveries of 95.5%–102%.

Speciation of As(III), As(V), MMA, and DMA in synthetic landfill leachate was performed using a strong cation exchange disk modified with sulfonic groups as solid phase sorbent. WDXRF has been used as a detection technique.[53] While DMA was retained selectively onto the cation exchange disk inorganic As ions and MMA were not adsorbed under the same conditions. The LOD for DMA was 218 ng L^{-1}. It was found that Pb interferes with the As signal due to the closeness of the As and lead X-ray fluorescence lines (As-K-α and Pb-L-α). This spectral interference of lead was eliminated by applying a correction factor. By analyzing spiked synthetic landfill leachate samples containing As(III), As(V), MMA, and DMA, recoveries of 98%–105% were obtained after the elimination of Pb interference.

A fast and selective SPE technique using a thiol-modified sand for the removal and speciation of As(III) from aqueous matrices has been developed.[54] While As(III) was retained on the thiol-modified sand placed in a disposable cartridge, As(V) was not retained. As(V) and As(III) were separated in 23 groundwater samples. The method was verified by analyzing the urine certified reference material (GBW09115).

Modified multiwall carbon nanotubes with 3-(2-aminoethylamino) propyltrimethoxysilane (AAPTS) were used as a sorbent for As speciation. As species and other elements present in environmental samples were determined by ICP-MS after microcolumn SPE separation.[31] While AAPTS-MWCNTs adsorbent selectively adsorbed As(V), Cr(VI), and Se(VI), at about pH 2.2, they did not adsorb As(III), Cr(III), or Se(IV) under the same conditions. For the determination of total Cr, Se, and inorganic As, As(III), Cr(III), and Se(IV) were first oxidized to As(V), Cr(VI), and Se(VI) with 10.0 μmol L^{-1} KMnO$_4$ and then determined in a similar way. The concentrations of As(III), Cr(III), and Se(IV) were calculated by subtracting the concentrations of As(V), Cr(VI), and Se(VI) from the total concentrations. The LOD and RSD% for As(V) were 15 ng L^{-1} and 7.4% (c = 1 μg L^{-1}, n = 7). The developed method was validated by analyzing in CRMs GSBZ50009-88 environmental waters for total Cr and GSBZ50027-94 for Cr(VI), and GBW3209 for As (III) and GBW3210 for As(V). It was found that the suggested adsorbent was stable up to 100 adsorption/elution cycles when 0.8 mol L^{-1} HNO$_3$ was used as eluent.[31]

A new sorbent, a N-(betaaminoethyl)-gamma-aminopropyltriethoxysilane, was synthesized in situ by sol–gel method for selective adsorption of As(V). Amino active sites of the sorbent packed in a fused capillary column were effective for extraction of As(V). For speciation of inorganic As species a dual column and an oxidation coil configuration were designed as an on-line SPE system. When passing the solution containing As(III) and As(V) through the dual column, As(V) was adsorbed by the first column quantitatively while As(III) present in the output solution of the first column was oxidized to As(V) with KMnO$_4$ solution and then adsorbed quantitatively as As(V) by the second column. To determine the As species by ICP-MS, the retained As species As(V) were then sequentially eluted by diluted HNO$_3$. The enhancement factor, RSD%, and LOD for As(III) were 60, 3.2% (n = 6, c = 1 mg L^{-1}), and 5 ng L^{-1}, respectively. The enhancement factor, RSD%, and LOD for As(V) were 60, 3.8% (n = 6, c = 1 mg L^{-1}), and 5 ng L^{-1}, respectively.[55]

A single-celled microorganism, thermoacidophilic iron-oxidizing archaeon *Acidianus brierleyi* was used for the removal of inorganic As from wastewater. As(III) and Fe(II) ions in an acidic culture medium were first simultaneously oxidized to higher oxidation states of the elements, i.e. As(V) and Fe(III), respectively, and As(V) was immobilized as FeAsO$_4$. Then *A. brierleyi* containing As species was passed through a minicolumn packed with an anion-exchange resin and the analytes were determined successively by ICP-OES.[56] For the speciation analysis, pH of the sample was adjusted to 5.0 and it was passed through the column containing adsorbent. As(V) ions were selectively retained on the sorbent, while As(III) was not adsorbed at this pH. The retained As(V) was eluted from the column with 1 mol L^{-1} HNO$_3$. Total As was determined directly by ICP-OES without applying any column SPE procedure. The LODs of As(III), As(V), and total As were 1.58 $\times$ 10^5, 8.6 $\times$ 10^4, and 2.11 $\times$ 10^5 ng L^{-1}, respectively. It was observed that Fe(II) ions interfere with the oxidation of As(III) (increase the oxidation) in the culture medium.

2.2. Chromium

In order to demonstrate the performance of a novel adsorbent synthesized or prepared, authors widely continue to apply it as SPE of individual Cr species. Most of the SPE methods for Cr speciation published in 2012–2016 were applied for environmental samples. Many papers focused on the separation, speciation, and preconcentration of Cr by applying column or batch SPE systems. The published papers on Cr speciation in this period were discussed and some analytical parameters are summarized in Table 2.

In one of these studies, unmodified graphene membranes was first synthesized as a sorbent for Cr(VI).[57] Multilayer graphene membranes were prepared on a glass substrate from graphene oxide (GO) by applying drop-casting. The characterization of membranes was performed by using AFM, TOF-SIMS, and XPS. It was shown that the height of graphene membranes was 122 nm. The characterization also showed that membranes contain functional groups that were nonreduced, causing the lattice defects. From the adsorption isotherms and characterization of adsorption sites it was concluded that adsorption sites were uniformly distributed on graphene membranes and bind Cr(VI) ions as a monolayer, and there were both electrostatic interactions and chemisorption. Cr concentration was determined by TXRF. LOD and RSD% were 80 ng L^{-1} and 3% (N = 5) for Cr(VI), respectively. Accuracy was checked by analyzing CASS-4 seawater and NWTM-27.2 lake water certified reference materials. It was stated that the suggested SPE method could be successfully used for the speciation analysis of Cr in high salinity water samples. The method was simple, solvent-free, and sensitive.[57]

In order to obtain a selective sorbent (XAD-16-XO) for the speciation of Cr(III) and Cr(VI) by SPE, Amberlite XAD-16 was functionalized by xylenol orange. A flow-injection on-line SPE system with FAAS was used for speciation. The Cr(III) ions were selectively adsorbed on the XAD-16-XO chelating resin, while Cr(VI) ions were not. The optimized experimental parameters of pH and eluent were 5 and 0.5 mol L^{-1} HNO$_3$. The linear working range for Cr(III) was up to 600 μg L^{-1}. The enrichment factor, precision (RSD%), and LOD for Cr(III) were 73, 1.08% (at 100 μg L^{-1}), and 110 ng L^{-1}, respectively. In order to determine the total Cr, Cr(VI) was first reduced to Cr(III) using hydroxylamine hydrochloride. Then Cr(VI) concentration was calculated by subtraction of Cr(III) concentration from the concentration of total Cr. The influence of foreign ions on Cr speciation was also investigated. The validation was performed by analyzing water standard reference material, SRM 1643e (NIST).[58]

Diniz and Tarley[40] have suggested the combination of two preconcentration methods for the speciation of Cr. In their study, dispersive magnetic solid phase extraction (DMSPE) and cloud point extraction (CPE) were combined into a new nonchromatographic preconcentration/speciation method for Cr. The detection method was FAAS. Mesoporous amino-functionalized Fe$_3$O$_4$/SiO$_2$ nanoparticles were used as solid phase adsorbent, and 4-(2-thiazolylazo)resorcinol (TAR) was used as complexing agent for CPE. Batch SPE was applied first for sequential preconcentration of Cr(VI) at pH 5.0 and followed by cloud point extraction of Cr(III) as metallic complex. The optimized conditions were 45.0 mL of sample solution, 25 mg of magnetic nanoparticles, 1 min extraction period, and 0.5 mL of 2.5 mol L^{-1} HCl as eluent. The remaining Cr(III) in the solution was then subjected to CPE. The preconcentration factors for Cr(VI) and Cr(III) were 16 and 12, respectively. The LODs were 1100 ng L^{-1} for Cr(VI) and 3200 ng L^{-1} for Cr(III), respectively. There is a high tolerance toward potentially interfering ions (cations and anions) and humic acid. Precisions (RSD%) were 5.8 and 3.7% for Cr(III) using solutions at 15.0 and 165.0 μg L^{-1} and 5.5 and 3.0% for Cr(VI) using solutions at 15.0 and 75.0 μg L^{-1} concentrations (n = 10), respectively. The accuracy of the method was checked by using a DORM-3 (Fish Protein Certified Reference Material for Trace Metals).[40]

Table 2. Summary of analytical parameters of Cr speciation.

Sorbent	Sample	Analytes	Analytical technique	LOD ng L^{-1}	PF	Ads. capacity mg/g	Ref.
Cellulose acetate membrane filter	Wastewater and lake water	Cr(III)	FAAS	1400	94	-	29
Dowex Optipore L493 functionalized with dithizone	Water	Cr(III)	FAAS	130	82	-	36
Mesoporous amino-functionalized Fe$_3$O$_4$/SiO$_2$ nanoparticles	Fish Protein Certified Reference	Cr(III) Cr/VI)	FAAS	3200 1100	16 12		40
Unmodified graphene membranes	High salinity water samples	Cr(VI)	TXRF	80	-	-	57
Amberlite XAD-16 functionalized by xylenol orange	Water standard reference material	Cr(III)	FAAS	110	73	-	58
Magnetic nanoparticles modified by chitosan	Lake water and tap water	Cr(III) Total Cr	ICP-OES	20 30	-	-	59
Multiwalled carbon nanotube	Phosphate rock	Cr(III)	FAAS	0.288 mg/kg	-	-	60
Nanostrontium titanate	Natural river water, lake water, and tap water samples	Cr(III) Cr(VI)	FAAS	-	-	16.08 5.86	61
Chitosan (CTS) grafted with 2-hydroxyethyltrimethyl ammonium chloride	Pond water, lake water, tap water	Cr(VI)	FAAS	20	-	205	62
Nanometer sized zirconium phosphate	Natural water samples	Cr(III)	ETAAS	1.5	300	9.34	63
Poly-2-(5-methylisoxazole) methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene)	Various water and food samples	Cr(III)	FAAS	10	200	34.3	64
Montmorillonite saturated with potassium ions	Water samples	Cr(VI)	ICP-OES	200	-	-	65
Multiwalled carbon nanotubes	Electroplating wastewater samples	Cr(III)	FAAS	1150	22	7.1	66
Poly(N,N-dipropionitrile methacrylamide-co-divinylbenzene-co-2-acrylamido-2-methyl-1-propanesulfonic acid) chelating resin	Various water and food samples	Cr(III)	FAAS	1110	150	12.1	67
Ion imprinted polymer	Tap water, river water, and municipal sewage	Cr(III)	ETAAS	18	-	-	68
Poly(methacrylic acid) and polyvinylimidazole	Different kinds of water samples	Cr(III) Cr(VI)	FI-FAAS	840 1580	47.3 8.6	1.42 3.24	69
Poly-2-(5-methylisoxazole)methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene and Dowex 21K	Wastewater	Cr(III) Cr(VI)	FAAS	50 300	48 30		70
Alumina-coated magnetite nanoparticles	Water and soil samples	Cr(III)	FAAS	1400– 3600 for water (5.6 ng/mg for soil)	-	-	71
Poly(1,3-thiazol-2-yl methacrylamide-co-4-vinylpyridine-co-divinylbenzene)	Seawater	Cr(VI)	FAAS	2400	30	80	72

Another sensitive and selective SPE method was presented by Habila et al. for the speciation analysis of Cr ions.[29] The speciation was based on the addition of cochineal red A to the sample solution to obtain of Cr(III)-cochineal red A complex and passing sample solution through the cellulose acetate membrane filter. Cr(III)-cochineal red A complex was selectively retained on a cellulose acetate membrane filter, while Cr(VI) ions were not retained on the filter. The total concentration of Cr was determined after conversion of Cr(VI) to Cr(III) with hydroxylamine hydrochloride. The concentration of Cr(VI) was calculated from the difference between total Cr concentration and Cr(III) concentration. The preconcentration factor and LOD for Cr(III) were 94 and 1400 ng L^{-1}, respectively. The method was validated by analyzing various CRMs such as fortified lake water (TMDA-54.4), water (TM-25.3), Montana soil (SRM 2710), and sewage sludge (BCR-144 R) and employed for the speciation of Cr in wastewater and lake water.[29]

In order to overcome the drawbacks of conventional techniques, biosorption with SPE has been proposed for the removal and preconcentration of Cr ions.[37] *Aspergillus ustus* (Asp), *Fusarium verticillioides* (Fus), and *Pencillium funiculosum* (Pen) fungal strains were used as microorganisms. These microorganisms were immobilized on a nanosilica (NSi) surface to obtain NSi-Asp, NSi-Fus, and NSi-Pen biosorbents. These biosorbents were used for selective and effective removal of both Cr(III) and Cr(VI) ions from environmental samples. The obtained biosorbents were characterized by SEM and FTIR analysis. The batch technique was used for biosorption experiments. The biosorbents retained Cr(III) at pH 7.0, while they retained Cr(VI) at pH 2.0. The sorption capacity of NSi-Asp, NSi-Fus, and NSi-Pen biosorbents for Cr(III) was about 2467, 2667, and 1867 μmol g^{-1}, respectively, at optimum pH 7.0. The sorption capacity of NSi-Asp, NSi-Fus, and NSi-Pen for Cr(VI) was about 6467, 6400, and 3800 μmol g^{-1}, respectively, at pH 2.0. Sorption reached equilibria at about 15 min. The method was applied to real wastewater samples.[37]

An on-line flow injection SPE technique for the speciation of Cr(III) and Cr(VI) was presented.[36] Dowex Optipore L493 was functionalized with dithizone and applied as a new solid phase adsorbent. A batch SPE system was used for speciation with a contact time of 120 s. The resin retained Cr(III) ions selectively from the solution containing both species. Cr species were determined by FAAS. Retained Cr(III) ions were eluted with 0.1 mol L^{-1} HNO$_3$ from the resin and aspirated directly to the flame of FAAS. A preconcentration factor of 82 and LOD of 130 ng L^{-1} were found for Cr(III). The precision as RSD% was 1.13% for 100 μg L^{-1} Cr(III). Concentration of Cr(VI) ions was determined after reduction of Cr(VI) to Cr(III) using hydroxylamine hydrochloride and determination of total Cr as Cr(III). Cr(VI) content was calculated from the difference between the contents of total Cr and Cr(III). The accuracy of the suggested method was verified by analyzing NIST SRM 1643e, Trace Elements in Water.[36]

Cui et al. proposed magnetic nanoparticles as a solid phase adsorbent for the speciation of Cr(III) and Cr(VI). Magnetic nanoparticles were synthesized and modified by chitosan by an emulsion method. Cr(III) ions were retained by the sorbent at pH 9, while total Cr was retained at pH 6. Cr species were determined by ICP-OES in environmental water samples. Under the optimized conditions, 100-fold preconcentration was reached. The LODs and RSD% for Cr(III) were 20 ng L^{-1} and 4.8%, and for total Cr were 30 ng L^{-1} and 5.6%, respectively. The proposed speciation method was applied to analyze lake water and tap water. The accuracy of the proposed method was checked by analyzing the CRM GSBZ50009-88.[59]

A cation-exchange disk (CED) and an anion exchange disk (AED) were proposed as solid phase extractant for the separate determination of Cr(III) and Cr(VI).[34] pH of a water sample containing both species was

adjusted to 5.6 and passed through a column packed with CED and AED. The CED was placed on the AED in the column. Under these conditions Cr(III) acetylacetonate [Cr(acac)(3)] and Cr(III) were retained on the CED, while Cr(VI) was adsorbed on the AED. The retained Cr(acac)(3) was eluted first with CCl_4 and then Cr(III) and Cr(VI) were eluted with 3 mol L^{-1} nitric acid. Cr species were determined by metal furnace atomic absorption spectrometry (MFAAS) in the eluates after diluting with CCl_4 and water, respectively. The linear working range for the Cr(acac)(3) aqueous solutions was 0.1 to 1 ng. The LOD of Cr was 20 pg. The recoveries for Cr(III), Cr(VI), and Cr(acac)(3) were 96.0%–107% for spiked water samples (c = 50 μg L^{-1}) such as tap water, rainwater, and bottled drinking water. In a humic acid solution, quantitatively recovery (103%) for Cr(acac)(3) was obtained but lower recoveries, i.e. 84.8% and 78.4%, were obtained for Cr(III) and Cr(VI), respectively.[34]

The speciation of Cr(III) and Cr(VI) in phosphate rock is regarded as a difficult task due to the possibility of mutual conversion of Cr species during sample preparation such as digestion/leaching.[60] In this study, a multiwalled carbon nanotube (MWCNT) was used as a SPE adsorbent to remove Cr(III) from the solution at pH 9. Phosphate rocks were digested by applying ultrasound digestion (USD) by using 300 mg of phosphate rock and 4.0 mL of 4.0 mol L^{-1} nitric acid and by applying 15 min sonication. The results were compared with the results obtained with classical digestion (CD). FAAS was used for the determination of Cr species. Total concentration of Cr was determined after reducing Cr(VI) to Cr(III). The LOD of Cr(III) was 0.288 mg kg^{-1}. The accuracy of the method was checked by analyzing LKSD-4 lake sediments. Total Cr and Cr(III) concentrations in Jordanian PR samples were 29.1–122.0 mg kg^{-1} and 23.8–101.7 mg kg^{-1}, respectively.[60]

Nanostrontium titanate for the SPE of Cr species was synthesized by sol–gel method. Characterization of the sorbent was carried out by using XRD and SEM. The nanostrontium titanate was a new block adsorbent like a leaf. The selective retention of Cr species was provided at different pH values, i.e. Cr(VI) ions retained at pH 1–3, while Cr(III) ions were retained at pH 7–14. Retained Cr(III) and Cr(VI) ions at different pH values were eluted with 1 mol L^{-1} HCl and 2 mol L^{-1} NaOH, respectively. The method was applied for Cr speciation in a natural river water sample, a lake water sample, and a tap water sample. Cr determination was performed by AAS.[61]

As a new type of adsorbent for Cr speciation, chitosan (CTS) was grafted using 2-hydroxyethyltrimethyl ammonium chloride (HGCTS). It was shown that the HGCTS could adsorb Cr(VI) selectively at pH 4.0. The equilibrium time for adsorption and adsorption capacity was 80 min and 205 mg/g, respectively. The adsorption isotherm was found to fit the Langmuir model and the kinetic model agreed with the pseudo-second–order model. FAAS was used as the determination technique. The LOD, RSD, and recovery were 20 ng L^{-1}, 1.2%, and 99% to 105%, respectively.[62]

A nanometer sized zirconium phosphate was used as adsorbent in a microcolumn for the selective separation of Cr(III) from Cr(VI). After SPE of the sample solution, Cr(III) ions in the eluate were determined by ETAAS. Cr(VI) ions were reduced to Cr(III) by 10% (m/v) of aqueous ascorbic acid to determine total Cr as Cr(III). The LOD for Cr(III) was 1.5 ng L^{-1} with a preconcentration factor of 300. The adsorption capacity and precision as RSD% for Cr(III) were 9.34 mg/g and 3.2% (c = 10 ng/mL, n = 7), respectively. The method was applied to natural water samples for the speciation of Cr(III) and Cr(VI).[63]

As a new SPE sorbent for the speciation of Cr(III) ions, a chelating resin poly-2-(5-methylisoxazole) methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene) (MAD) was synthesized.

Cr(III) ions were almost quantitatively retained on the resin at pH range of 1.5–4.5, while Cr(VI) was not retained at this pH. Under the optimized conditions, adsorption capacity, the preconcentration factor, LOD, and binding equilibrium constant were 34.3 mg g^{-1}, 200, 10 ng L^{-1}, and 1.5 L mg^{-1} for Cr(III), respectively. The method was verified by analyzing SPS-WW2 Batch 108 wastewater and GBW 07402 soil as CRMs. Cr species in various water samples such as electroplating wastewater, well water, tap water, dirty water, and refining water and various food samples such as green tea, black tea, flour, rosemary, bean, and pomegranate flower were determined by the proposed method.[64]

In the present work, a low cost sorbent montmorillonite as a solid phase was proposed for the separation of Cr(III) from Cr(VI) in water samples by SPE prior to quantification of Cr(VI) in aqueous sample by ICP-OES. The batch system was applied for the removal of Cr(III) ions completely from the sample. Only a contact time of 1 min between the adsorbent and the aqueous sample was sufficient for quantitative removal of Cr(III) ions. The Cr(VI) ions that remained in solution were quantified by ICP-OES. The LOD of Cr(VI) was 200 ng L^{-1}. Mineral montmorillonite saturated with potassium ions (MTK) could be used as an adsorbent for speciation of Cr.[65]

Once again multiwalled carbon nanotubes as a solid phase adsorbent were proposed for the on-line speciation and preconcentration of Cr.[66] The nanotubes selectively retained Cr(III) at pH 3.0–6.0 due to the functional groups and negative charges on its surface, while it did not retain Cr(VI). Cr(III) was determined by FAAS in the elution solution after eluting by 10% (v/v) HNO$_3$. Enrichment factor, LOD, precision (RSD%), and linear working range for Cr(III) were 22, 1150 ng L^{-1}, 1.7%, and 5–200 mg L^{-1}, respectively. After reduction of the Cr(VI) to Cr(III) with hydroxylamine hydrochloride, total Cr concentration was determined as Cr(III). Cr(VI) content was calculated from the difference between the concentrations of total Cr and Cr(III).

As a SPE sorbent, poly(N,N-dipropionitrile methacrylamide-co-divinylbenzene-co-2-acrylamido-2-methyl-1-propanesulfonic acid) chelating resin was prepared and used for the Cr speciation. Cr(III) content of water and food samples was determined by FAAS after applying SPE and elution.[67] The sorption capacity, preconcentration factor, LOD, and RSD% for Cr(III) were 12.1 mg g^{-1}, 150, 1110 ng L^{-1}, and 2.0% (n = 10), respectively. The method was validated by analyzing CRMs of TMDA-70 lake water and SRM 1568a rice flour.

An ion imprinted polymer for Cr(III) separation has been synthesized by Lesniewska et al.[68] Cr(III)-pyrrolidinedithiocarbamate, ethylene glycol methacrylate, and acrylamide functional monomer were used as components of imprinted polymer. ETAAS was used as the detection technique. The retention efficiency of Cr(III) ions was 87% on the Cr(III)-imprinted polymer at pH 3.50–4.75 and the precision was 3.2% (RSD). Retained Cr(III) was eluted with 0.2 mol L^{-1} HNO$_3$. It was found that there was no interfering effect of Ni(II) or Cu(II) ions on the selectivity of the sorbent towards Cr(III) ions, while Fe(III) ions (at higher than 0.5 mg mL^{-1}) interfered with the retention of Cr(III). The LOD for Cr(III) was 18 ng L^{-1}. The method was applied to tap water, river water, and municipal sewage for Cr determination.

For the speciation of Cr(III) and Cr(VI) by a flow-injection (FI)-SPE system cross-linked polymers were used as adsorbent.[69] For this purpose a dual minicolumn packed with poly(methacrylic acid) and polyvinylimidazole was designed and used. FAAS was used in the on-line detection system. The pH of the solutions containing Cr(III) and Cr(VI) ions was adjusted to 4.0 and the solutions were passed through the dual mini-columns at a flow rate of 3.0 mL min^{-1}. The poly(methacrylic acid) phase retained Cr(III) ions selectively, while the polyvinylimidazole phase retained Cr(VI). Then both of the retained ions were sequentially eluted

with 2.5 mol L^{-1} HNO$_3$ from the columns and the eluates were analyzed to determine the analyte ions by FAAS. The LODs and preconcentration factors for Cr(III) and Cr(VI) were 840 and 1580 ng L^{-1} and 47.3 and 8.6, respectively. The recoveries were 90%–108% for spiked samples containing 40 mg L^{-1} Cr(III) and Cr(VI).

In order to determine Cr(III) and Cr(VI) in water samples an on-line SPE-FAAS method was proposed.[70] Two minicolumns were fitted in parallel to a flow injection manifold. The first column was filled with poly-2-(5-methylisoxazole)methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene and the second column was packed with Dowex 21K. The first column was used to retain Cr(III) while the second column was used to retain Cr(VI). Both Cr species retained on the sorbents were eluted with 3 mol L^{-1} HNO$_3$ and the elution solutions obtained from each column were directly aspirated to the flame of a FAAS. In order to determine total Cr content, Cr(III) ions were first converted to Cr(VI) ions by a hot procedure and the Cr(VI) ions obtained were retained by passing the solution through the second column. The enrichment factors (48 and 30) and the LOD values (50 ng L^{-1} and 300 ng L^{-1}) were obtained for Cr(III) and Cr(VI), respectively. The method was verified by analyzing CRM (CWW-TM-D, wastewater).

Alumina-coated magnetite nanoparticles (Fe$_3$O$_4$/Al$_2$O$_3$) as nanomaterial were synthesized for speciation of Cr(III) and Cr(VI) in various samples. The nanoparticles were modified by Triton X-114 and used for SPE.[71] In this procedure Cr(III) was complexed with 1-(2-pyridilazo)-2-naphtol and then the complex obtained was retained in situ in the hemimicelles of Triton X-114. The detection technique was FAAS for Cr(III). Total Cr was determined after converting Cr(VI) ions to Cr(III) ions by the addition of ascorbic acid and by applying the method described above. Concentration of Cr(VI) was calculated by subtracting the Cr(III) concentration from total Cr concentration. The recoveries and LOD of Cr(III) were in the range of 98.6%–100.8% and 1400–3600 ng L^{-1}, respectively. The method could be used for complicated matrices such as soil samples without applying any special pretreatment procedures.

Poly(1,3-thiazol-2-yl methacrylamide-co-4-vinylpyridine-co-divinylbenzene) was synthesized and proposed as an adsorbent for SPE of Cr ions.[72] It was stated that Cr(III) and Cr(VI) were retained on the adsorbent at different pH values. The adsorbent selectively retained Cr(VI) ions at pH 2, while it did not retain Cr(III) ions. Total Cr content was determined after oxidization of Cr(III) to Cr(VI) with KMnO$_4$. Preconcentration factor and LOD for Cr(VI) were 30 and 2400 ng L^{-1}, respectively.

2.3. Iron and manganese

Only two papers were published about the speciation of iron (Fe) and manganese (Mn) by SPE since 2012 (Table 3). For the speciation of Fe ions in estuarine and coastal waters, a portable automatic flow injection (FI) system was used. As an adsorbent C18 SPE cartridges were used with a liquid waveguide capillary cell (LWCC). SPE–LWCC enhanced the sensitivity of the ferrozine method for the determination of Fe(II). In the proposed method, first Fe(II) ions were complexed with ferrozine and then retained onto a C18 cartridge as Fe(II)-ferrozine complex. The adsorbed complex was eluted with HCl–ethanol solution and determined by spectrophotometrically. Fe(III) ions were converted to Fe(II) ions with ascorbic acid to determine total Fe concentration. In the optimization of the FI-SPE-LWCC system a univariate experimental design was used. The interfering effect of salinity on the determination of Fe(II) and on the sensitivity of the method was also studied and no significant effect was observed. Therefore, it was concluded that the method could be applied for both estuarine and coastal waters without applying any procedure. The LOD of Fe(II) and total Fe was

3.12 ng L^{-1} and 5.36 ng L^{-1}, respectively. The linear working range for Fe was 0.5–50 nmol L^{-1}. Dissolved Fe species were monitored continuously for 20 h by the proposed method.[73]

Table 3. Summary of analytical parameters of Hg, Se, and Tl speciation.

Sorbent	Sample	Analytes	Analytical technique	LOD ng L^{-1}	PF	Ads. capacity mg/g	Ref.
Modified mesoporous silica	Seawater samples	Hg(II) MeHg	ICP-MS	4 2	11.0 4.7	0.035	74
Hg(II) ion-imprinted polymers (IIPs)	Spiked seawater, lake water, human hair and fish meat samples	Hg(II) Org.Hg	AFS	15 20	-	-	75
Ion-imprinted polymer (IIP)	Seawater, river water, and mineral water	Hg(II) MeHg	FAAS with QT atomizer	20 20	-	-	76
Amberlyst 36	Water and fish samples	Hg(II) MeHg	CVAAS	440 560	-	-	77
Multiwall carbon nanotubes functionalized with 3-(2-aminoethylamino) propyltrimethoxysilane	Rain water, lake water, and river water	Se(VI) Se(IV)	ICP-MS	16,000	-	-	80
XAD resin	Edible oils	SeMet, MeSeCys SeCys	UPLC-ESI-MS/MS	0.01 mg/kg	-	-	82
Alumina functionalized with sodium dodecyl sulfate	Wastewater sample	Tl(I) Tl(III)	ICP-MS	25 160	-	-	83

Shirkhanloo et al.[38] proposed a novel SPE method for rapid speciation/preconcentration of Mn(II) and Mn(VII) ions. In this study, amine-functionalized mesoporous silica UVM-7 as nanoadsorbent was synthesized and used in ultrasound assisted-dispersive-microsolid phase extraction (US-D-mu-SPE). After separation and preconcentration by US-D-mu-SPE, Mn species were determined by atom trapping-flame atomic absorption spectrometry (AT-FAAS). Experimental parameters affecting the recoveries of Mn(II) and Mn(VII) were investigated and optimized. Preconcentration and speciation of Mn(II) and Mn(VII) ions with NH$_2$-UVM-7 were obtained in water samples due to the formation of NH-Mn^{2+} and –NH$_3^+$-MnO$_4^-$ at pH 8 and 5, respectively. The batch adsorption capacity of NH$_2$-UVM-7 for Mn(II) and Mn(VII) ions was 1733 μmol g^{-1} and 570 μmol g^{-1}, respectively. Under the optimized conditions, LOD (3s/m) and LOQ (10s/m) were 7 ng L^{-1} and 30 ng L^{-1} for Mn(II) and 8 ng L^{-1} and 40 ng L^{-1} for Mn(VII). The preconcentration factors and RSD% for Mn(II) and Mn(VII) were 102.3 and 98.8 and 2.3% and 2.8% (n = 10, C = 10 μg L^{-1}), respectively. The accuracy of the developed method was verified by analyzing NIST-SRM 1640a. The method was successfully applied to various water samples, such as drinking water, well water, river water, and wastewater samples.

2.4. Mercury

Mercury speciation is still one of the most important speciation analyses in foods and environmental samples such as soil, water, atmosphere, and biota due to the toxicity of Hg. Various analytical techniques, such as atomic absorption spectrometry, UV-VIS spectrophotometry, spectrofluorometry, voltammetry, chromatography, ICP-MS, and ICP-OES have been used for quantification. In speciation analysis, Hg species are generally separated

each other and also from the matrix by using SPE prior to quantification. For this purpose, researchers continued to synthesize and develop various solid phase adsorbents such as nanosorbents and magnetic sorbents during the period covered by this review. The published papers on Hg speciation in this period were discussed and some analytical parameters are summarized in Table 3.

In one of the studies, modified mesoporous silica as a new nanosorbent was synthesized, characterized, and used for the Hg speciation and/or preconcentration. Mesoporous silica was modified with 1,5-bis(2-pyridyl) methylene thiocarbohydrazide. Speciation analysis was performed by applying column SPE and a flow injection technique-cold vapor generation procedures prior to ICP-MS detection. This nanosorbent retained Hg(II) ions at pH 5 with an adsorption capacity of 173.1 μmol g^{-1}. The developed method was used for the on-line preconcentration and sequential determination of Hg(II) and MeHg in various samples. Sequential elution of Hg species was performed by using 0.2% HCl for CH_3Hg^+ and 0.1% thiourea in 0.5% HCl for Hg(II). Under the optimized conditions by applying a preconcentration time of 120 s, the enrichment factors were 4.7 and 11.0, the LODs were 2 and 4 ng L^{-1}, and the precisions (RSD%, n = 10, at 2 mg L^{-1} for both species) were 2.8% and 2.6% for MeHg and Hg(II), respectively. LGC 6016 estuarine water and SRM 2976 mussel tissue as certified materials were used in order to the check the accuracy of the method. Hg speciation was successfully performed in Malaga Bay seawater samples.[74]

In recent years, to increase selectivity ion imprinted polymers have been widely used as SPE adsorbent. Zhang et al.[75] proposed the use of Hg(II) ion-imprinted polymers (IIPs) as a novel adsorbent for speciation of Hg in environmental and biological samples. A sol–gel process was used for preparing Hg ion-imprinted polymers (Hg-IIPs). Dithizone was used as a chelating agent and dithizone-Hg(II) chelate was used as a template. 3-Aminopropyltriethoxysilane was used as a functional monomer in this process. After preconcentration and/or separation of Hg species by SPE, atomic fluorescence spectroscopy (AFS) was used for detection. It was shown that the Hg-IIPs have high binding capacity and fast kinetics for Hg(II) adsorption. The adsorption process fitted a Langmuir isotherm. The kinetic model of Hg-IIPs was found to be suitable for the pseudo-second–order kinetic model. The proposed IIP showed a good reusability (10 adsorption-desorption cycles) and excellent selectivity (selectivity factors, 19–34) toward Hg(II) over organic Hg compounds and other metal ions. Thus, by using IIPs-SPE-AFS, LOQ for Hg(II) and organic Hg were 15 ng L^{-1} and 20 ng L^{-1}, respectively. This method was validated by using two CRMs and spiked samples. The recoveries of Hg(II) were in the range of 93.0%–105.2% for spiked seawater and lake water samples. The proposed speciation analysis was applied for human hair and fish meat after spiking with Hg species. The IIPs-SPE-AFS could be used for speciation analysis of trace Hg species in various matrices with high-effective enrichment.[75]

Another SPE procedure based on ion-imprinted polymer (IIP) for the speciation of Hg in surface waters for Hg(II) was developed.[76] The IIP was synthesized by co-polymerization of methacrylic acid monomer and Hg(II)-1-pyrrolidinedithiocarboxylic acid complex. In the co-polymerization process trimethylolpropane trimethacrylate and 2,20-azo-bis-isobutyronitrile were used as cross-linking agent and initiator, respectively. Hg(II)-IIP was characterized by various techniques. The proposed speciation method was applied for the analysis of a CRM (BCR 505, estuarine water). As a detection technique FAAS with QT atomizer was used. Total Hg was determined after degrading the organic Hg (MeHg). By subtracting the Hg(II) value from the total Hg value, organic Hg interpreted as methyl mercury was calculated. Recoveries of MeHg were in the range of 92%–96% for spiked CRM and seawater, river water, and mineral water. The LOQs for Hg(II) and MeHg were 15 and 20 ng L^{-1}, respectively.

In our study,[77] for speciation of inorganic mercury (Hg^{2+}) and monomethylmercury (CH_3Hg^+) ions Amberlyst 36 was used as column SPE adsorbent. A simple and selective procedure for speciation was proposed. Hg species were determined by CVAAS. As optimum experimental parameters, flow rate of 3 mL min^{-1}, pH 4.0, and 50 mL of sample solution were found for both Hg(II) and CH_3Hg^+ ions. Because both species were retained at pH 4.0, the speciation could be provided by using different eluents. CH_3Hg^+ ions were eluted with 10 mL of 0.1 mol L^{-1} HCl solution, while Hg(II) ions were eluted with 10 mL of 0.2 mol L^{-1} thiourea solution in 3 mol L^{-1} HCl. The LODs for Hg(II) and CH_3Hg^+ were 440 ng L^{-1} and 560 ng L^{-1}, respectively. The accuracy of the proposed method was checked by analyzing a certified reference material (ERM-CE464), spiked water samples, and spiked fish samples. CH_3Hg^+ could be determined with a relative error below 10%. There was no significant difference between the found (5.0 ± 0.3 mg kg^{-1}) and certified values (5.5 ± 0.17 mg kg^{-1}) with 95% confidence level.[77]

2.5. Selenium

As is known, Se is considered both a toxic and an essential element for humans. There is a specific concentration range that is beneficial for humans. It is toxic above the upper limit of this concentration range. Se comes into drinking and wastewaters from mines, oil refineries, coal-fired power plants, and agriculture processes. Se deficiency is an important problem as well as its toxicity. Therefore, to maintain human health and ecotoxicity, Se level has to be controlled in environmental samples such as drinking water. This review article includes the studies about Se speciation (Table 3). Recently published papers showed that the studies continue to develop effective adsorbents, including nanomaterials for Se speciation. Binary metal oxides in raw or modified forms have been used for Se speciation.[78] Latorre et al.[79] published a review article in 2013 about the speciation and preconcentration of inorganic Se by using SPE. In this review, by evaluating the published papers, different speciation strategies and the applicability of different solid phase adsorbents, such as graphene, nanoparticles, and carbon nanotubes, have been evaluated and discussed.

Peng et al.[80] proposed multiwall carbon nanotubes (MWCNTs) functionalized with 3-(2-aminoethylamino) propyltrimethoxysilane (AAPTS) as SPE adsorbent (AAPTS-MWCNTs) for speciation of inorganic Se and inorganic As and Cr simultaneously in various water samples. The microcolumn SPE was applied prior to ICP-MS detection. It was found that higher oxidation state analytes [Se(VI), As(V), and Cr(VI)] were selectively retained by AAPTS-MWCNTs at pH 2.2, while lower oxidation state analytes [As(III), Cr(III), and Se(IV)] were not adsorbed at this condition. Total inorganic analytes was determined after the oxidation of lower oxidation states of the analytes to the higher oxidation states of the analytes with 10.0 μmol L^{-1} KMnO$_4$. The concentration of lower oxidation states of the analytes was calculated from the difference. Under the optimized conditions, the LODs were 15, 38, and 16 ng L^{-1} for As(V), Cr(VI), and Se(VI), respectively. Precision of the method as RSD% was 7.4%, 2.4%, and 6.2% (c = 1 μg L^{-1}, n = 7) for As(V), Cr(VI), and Se(VI), respectively. Validation was performed by analyzing reference materials of GSBZ 50009-88, GSBZ 50027-94, GBW 3209, and GBW 3210 environmental waters. The method was applied for the speciation of analytes in various water samples, such as rain water, lake water, and river water.[80]

As an example of mixed oxide sorbent materials $TiO_2@SiO_2/Fe_3O_4$ nanoparticles were used for the extraction of Se(VI) selectively from natural waters.[81] Inorganic Se speciation was based on the separation of Se(IV) from Se(VI) and organic Se. The separation was carried out by photocatalytic reaction with TiO_2 under UV radiation (6 W) for 3 h. TiO_2 shell of the nanoparticles with UV irradiation causes photocatalytic

reduction of Se(VI) and Se(IV) ions to Se(0) atoms. Fe_3O_4 core serves to collect particles due to its attractive superparamagnetic force. It was concluded that UV radiation power and reaction time affected the efficiency of the photocatalytic reduction process.

Extraction of Se species such as SeMet, MeSeCys, and SeCys in edible oils by SPE was performed by Torres et al.[82] XAD resin was used as SPE adsorbent. Se species were determined by UPLC-ESI-MS/MS. In this study liquid–liquid extraction was performed by using water/methanol (80/20 v/v) solution to extract organic Se compounds from olive oil. Then SPE was performed using an XAD resin. As eluent 0.5 mol L^{-1} formic acid was used. Se species in the elution solutions were determined using a RP C8 column coupled to ESI-MS/MS. An enrichment factor of 60 and a LOD of 0.01 mg kg^{-1} were obtained. MeSeCys was found in olive oil samples in the range of 2.0 to 8.3 mg kg^{-1}.

2.6. Thallium

It is known that thallium exists as Tl(I) and Tl(III) ions in environments having different toxicity, stability, and reactivity. Depending on stability properties, most of the dissolved thallium in aqueous samples is present as Tl(I). However, the toxicity of Tl(III) ions is higher than that of Tl(I) ions. Therefore, speciation of thallium is also important in various matrices. During the period covered by this review only two papers were published on the speciation of thallium by using SPE (Table 3). In one of them, alumina (63 μm, particle size) was functionalized with sodium dodecyl sulfate (an anionic surfactant) and used as a SPE adsorbent for the speciation of Tl(I) and Tl(III) in wastewaters. For this purpose Tl(III) was complexed with diethylenetriaminepentaacetate (DTPA) treated with the sorbent. Tl(III)-DTPA complex was retained on the sorbent, while Tl(I) was not retained. The retained Tl(III) ions were eluted with 40% nitric acid and quantified by ICP-MS. The LODs for Tl(I) and Tl(III) were 2.5 pg mL^{-1} and 16.0 ng L^{-1}, respectively. The interfering effect of other ions on thallium speciation was also studied. It was found that Pb(II) and Cd(II) up to 500-fold excess and Zn(II) up to 2000-fold excess do not interfere with Tl speciation.[83]

3. Conclusion

This critical review focuses on the use of various adsorbents for SPE for the speciation of trace elements. Among the preconcentration and/or speciation methods, SPE is still the most favorable. SPE can be used both for on-line and off-line speciation. Most researchers continue to synthesize and/or develop novel adsorbents that have high acid and base resistance, large surface area, selectivity for analytes, high adsorption capacity, and easy regeneration facilities. Many selective SPE adsorbents such as nanometal oxides, magnetic adsorbents, chelating polymers, ion or molecularly imprinted polymers, biosorbents, chemically modified resins, and natural low-cost adsorbents have been developed and characterized for speciation trace elements in various samples. As can be seen from the articles reviewed above, trace element speciation has been realized generally by applying two different strategies. These strategies involve (1) the retention of all species (ions of trace element or organometals) on the same sorbent, then elution by the different elution solution, and determination of each species in different eluates, or (2) preferential one species is retained by an adsorbent, while the others are not retained. The second strategy needs a prereduction or preoxidation step in order to convert all species to the oxidation state of ionic form retained by the adsorbent to determine total concentration. In general, the concentration of nonadsorbed species is calculated from the difference between total concentration and determined concentration of adsorbed ions. Therefore, since the first strategy does not require a reduction

or oxidation step prior to SPE, avoiding excessive sample manipulation, it has an advantage over the second strategy. Pretreatment steps involve using additional reagents that may contain impurities and reduction or oxidation may not be completed quantitatively. However, with the same adsorbent, the possibility of obtaining different retention and elution conditions for all species is generally low. In order to increase the selectivity of SPE, different procedures such as chelating procedure and chemical modification of the sorbents with specific organic substances imprinting polymer with an analyte have been applied. In a chelation procedure, a species that is not retained normally onto the adsorbent alone is converted to its chelates. Using ion imprinted or molecularly imprinted polymers increases the selective retention of imprinted ions or molecules. In a chemical modification, adsorbent is functionalized with a complexing agent to increase the affinity, metal uptake recoveries, capacities, and stabilities of adsorbents. Functionalized CNTs, metal oxides, and nanomagnetic adsorbents are examples of chemical modification. This review demonstrates that SPE with novel sorbents is still effective for the speciation of dissolved components with different oxidation states in water.

Abbreviations

AAS	Atomic absorption spectrometry
AB	Arsenobetaine
AC	Arsenocholine
AEC	Anion exchange chromatography
AFM	Atomic force microscopy
AFS	Atomic fluorescence spectrometry
APDC	Ammonium pyrrolidine dithiocarbamate
CPE	Cloud point extraction
CRM	Certified reference material
CNT	Carbon nanotube
CV-AAS	Cold vapor atomic absorption spectrometry
DMA	Dimethylarsenic
ESI-MS/MS	Electrospray ionization mass spectrometry/mass spectrometry
ETAAS	Electrothermal atomic absorption spectrometry
EtHg	Ethylmercury
FAAS	Flame atomic absorption spectrometry
FTIR	Fourier transform infrared
GFAAS	Graphite furnace atomic absorption spectrometry
HPLC	High performance liquid chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
IR	Infrared
LOD	Limit of detection
LOQ	Limit of quantification
MeHg	Methyl mercury
MetSeCys	Methioneinselonocysteine
MMA	Monomethylarsenic
MMMTA	Monomethylmonothioarsonic acid
MS	Mass spectrometry
NIST	National Institute of Standards and Technology
PTFE	Poly(tetrafluoroethylene)
PF	Preconcentration factor
RSD	Relative standard deviation
SeCys	Selenocysteine
SEM	Scanning electron microscopy

SeMet	Selenomethionein
SPE	Solid phase extraction
SPE-HG-AFS	Solid phase extraction-hydride generation-atomic fluorescence spectrometry
SPME	Solid phase microextraction
SRM	Standard reference material
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TMSe	Trimethylselenium
TOF-SIMS	Time-of-flight secondary ion mass spectrometry
TRIS	Tris(hydroxymethyl)aminomethane
TXRF	Total reflection X-ray fluorescence
UPLC	Ultra performance liquid chromatography
WDXRF	Wavelength dispersive X-ray fluorescence
WHO	World Health Organization
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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