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Nanomaterials for Elemental Speciation

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Various types of nanomaterials such as magnetic nanoparticles, carbon nanostructures, metal oxides and noble metal nanoparticles, ion imprinted polymers have been incorporated in new innovative approaches for speciation analysis. Small size, high surface to volume ratio, high chemical reactivity are the properties which makes them ideal sorbents for selective separation of chemical species. Nanostructures based on different modification of the nanoparticles and combinations between them additionally increased the nanostrategies employed for on-line or off-line determination of particular chemical species of elements.The presented review is focused on the use of nanomaterials for speciation analysis, analytical procedures developed and their application for analysis of environmental, food and biological samples. Critical view point on the current limitations as well as the future perspective are presented.

Contents

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speciation analysis, analytical procedures developed and their application for analysis of environmental, food and biological samples. Critical view point on the current limitations as well as the future perspective are presented.

1. Introduction

Trace element determination in various types of samples (industrial, environmental, pharmaceutical, biological, food, beverages) is an important field of application of modern analytical methods. Two main directions could be distinguished in this aspect: determination of total element concentrations at micro-, nano- and pico- levels and quantification of particular chemical species of the target analyte in the sample. Modern sensitive instrumental methods permit determination of total element content at extremely low levels and in rare cases preliminary separation and enrichment of trace analytes is required to overcome the most frequently observed matrix interferences. Nowadays, it is widely recognized that a large number of elements can naturally exist under various forms with considerably different behavior and properties. Due to the significant distinctions in toxicity, mobility and bioavailability of the particular chemical species, a determination of total element concentrations is generally not sufficient for comprehensive clinical and environmental considerations. Therefore, the speciation analysis has reasonably become an important topic of the present-day analytical research. According to the IUPAC guidelines, the speciation analysis includes analytical activities of identifying and/or measuring the quantities of one or more individual chemical species in a sample, where *chemical species* should be understood as a specific form of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure.[1]

Conventional analytical procedure for speciation analysis consists of several main steps: suitable quantitative extraction of chemical species of the element from the sample matrix, avoiding any interspecies changes; suitable chemical separation of extracted species and finally their sensitive detection by suitable instrumental

methods. No doubt quantitative chemical species separation is the core of the analytical methods used for speciation analysis. Modern speciation procedures are currently divided into two major groups according to the separation step: on-line chromatographic separation coupled with sensitive element detection method and non-chromatographic separation (solid phase extraction (SPE), liquid-liquid extraction (LLE), cloud point extraction (CPE) etc.) usually operated in off-line mode and followed by instrumental measurement of separated species.

Nanomaterials have been widely applied in elemental speciation due to their favorable surface-to-volume ratio, high surface chemical activity and strong adsorption capacity. Nanomaterials have been used:

- in hyphenated methods as effective interfaces between chromatographic columns and mass spectrometric detection for: (i) decomposition of metal organic complexes into ionic forms (Hg); (ii) conversion of inert element species to active hydride forming forms (prereduction of Se); (iii) photo-chemical vapor generation, replacing toxic Na/K borohydrides (Hg, Se).
- in nonchromatographic speciation approaches as effective and selective sorbents.
- in screening methods for fast, optical sensing of metal species as colorimetric nanoprobes

In the present review recent advances of the applications of various types of nanomaterials in the above mentioned directions were summarized and discussed.

2. Nanomaterials for elemental speciation analysis by hyphenated methods (on line coupled chromatographic separation and spectrometric measurement)

The hyphenated methods based on separation of the species by gas (GC) or liquid (LC) chromatography coupled on-line with highly sensitive detection system such as atomic fluorescence spectrometry (AFS), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry(ICP-MS), are the most efficient approaches for speciation analysis.[2,3,4] They are widely accepted and commonly provide high degree of automation, good precision and accuracy as well as the possibility to get exhaustive information for the particular chemical species distribution. According to author's knowledge, nanomaterials have not been used as stationary phases for chromatographic separation in elemental speciation analysis with only one exception. Molecular imprinting technology were employed to prepare a specifically affinity chromatographic stationary phase for speciation of organotin compounds by LC-ICP-MS.[5,6] Tributyltin has been chosen as the template molecule and the non-covalent approach has been applied. Three different polymerization methods have been evaluated: (i) a composite material, (ii) a polymer prepared via-Iniferter grafting; (iii) an emulsion polymer. Columns packed with

different MIPs polymers have been evaluated and compared with other commercial and not specific stationary phases. The results achieved undoubtedly confirmed the applicability of MIPs as an alternative to GC for organotin compounds speciation.

On the other hand, chromatographic speciation strategies for elemental speciation have some limitations and drawbacks mainly represented in the need of pre- and/or post-column derivatizations, possible interspecies conversions, memory effects, loss of sensitivity due to the organic solvents used, etc. Furthermore, chromatographic methods often require modification or design of interface between the column and detection system because the analytes eluted are not always suitable for direct quantification. The widest application of nanomaterials in on-line hyphenated methods is their use as interfaces between chromatographic separation and further detection of analytes by CV/HG-AFS or CV/HG-ICP-MS. Photocatalytic properties of metal oxides mainly TiO_2 are well known and widely used for UV assisted photo-oxidation or photo-reduction. Nano-sized semiconductor metal oxides have been successfully applied for both: efficient photo-oxidation of inactive organic species of determined analytes in order to ensure efficient hydride generation or photo-reduction of analyte species with the purpose of equalization of their behavior during the vapor generation step. Greener approaches for hydride generation have been also developed by replacement of commonly used reductants $NaBH_4/KBH_4$ with nanometer sized metal oxides used as UV-photo-reductant. When nanometer sized semiconductor is illuminated with UV light with suitable wavelength/energy, the absorbed photons promote electron-hole pairs, which dissociate into free photoelectrons (e^-) in the conduction band (CB) and photo holes (h^+) in the valence band (VB), which are further responsible for desired photo-reduction or photo-oxidation of target compounds. The energy gap increased as the size of the nano-TiO_2 particle decreased due to the quantum size effect, resulting in a greater reductive ability of the e^- at CB; moreover, the distance needed for the generated e^- at CB and h^+ at VB to move from the bulk to the surface is greatly shortened, remarkably reducing the probability of recombination of the generated e^-/h^+ pairs in the bulk, and resulting in more generated e^- and h^+ migrating to the surface of the nano-TiO_2 particle. Furthermore, when an h^+ scavenger is added in a reaction medium to prohibit the generated e^-/h^+ pair from rapid recombination, the remaining free e^- may serve as a reductant to reduce target analytes adsorbed on the surface of the nano-TiO_2.

Photocatalytic systems developed were used mainly as sample introduction systems for ICP-MS determination of vapor/hydride forming elements or as an interface between chromatographic separation of target species and their further detection by CV/HG AFS or CV/HG ICP-MS. An example of mechanism of photocatalytic action of ZrO_2,incorporated in hyphenatedFI HPLC-AFS system is presented in Fig. 1.
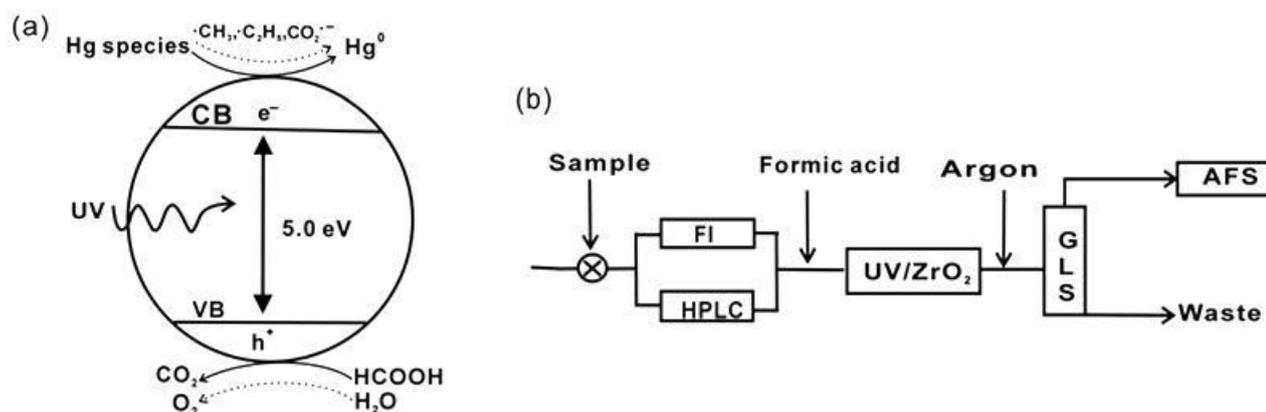
Fig. 1(a) Atomization of Hg species on the UV/nano-ZrO_2/HCOOH; (b) FI/HPLC-(UV/nano-ZrO_2/HCOOH)-AFS system. GLS: gasliquidseparator (Ref. 12).

The summary of developed photocatalytic systems and their application is presented in Table 1.

Arsenic speciation. On-line digestion device-based on the nano-TiO_2 catalyzed photooxidation of arsenic species was developed and combined with microbore anion-exchange chromatography (µ-LC) and HG ICP-MS systems for the determination of As^{III}, As^{V}, monomethylarsonate (MMA) and dimethylarsinate (DMA) in urine samples [7]. The possibility for continuous monitoring of both hydride and nonhydride (AsBet) forming arsenic species in microdialysate samples was further ensured by coupling together on-line (high performance liquid chromatography) HPLC, a post-column UV/TiO_2 film reactor, and HG ICP-MS. The UV/nano-TiO_2 film reactor was manufactured by coating nano TiO_2 onto the interior of a glass tube. The developed hyphenated method was validated by the analyses of certified reference urine and rabbit serum samples [8].

Mercury speciation by HPLC CV AFS/ HPLC CV ICP-MS. The possibility for photocatalytic reduction of Hg(II) to elemental Hg by nanometer sized TiO_2 in the presence of low molecular weight organic compounds [9] is utilized for the development of UV/TiO_2 photocatalysis reaction device as an effective sample introduction unit and an interface for mercury species determination by AFS and speciation by HPLC-CV-AFS.

Sensitive determination and speciation of Hg species in environmental and biological samples by CV-AFS and HPLC-CV-AFS has been achieved by using nano-TiO_2 stabilized on the surface of a glass fibers interface to offer active electrons under UV irradiation, while formic acid/sodium formate buffer served as a hole scavenger.[9]

A green and efficient method for post-column on-line oxidation of inactive Hg species to Hg(II), using 0.6% (v/v) H_2O_2 and Fe_3O_4 MNPs has been developed and applied for Hg speciation. Separation of mercury species was accomplished on a RP-C18 column with acetonitrile/water mixture at pH 6.8 containing 0.12% (m/v) l-cysteine as the mobile phase followed by CV-AFS quantification.[11] Inorganic mercury Hg^{II}, MeHg, EtHg and phenylmercury PhHg were selected as model compounds to validate the methodology. CRM National Research Council Canada DORM-2 fish muscle tissue and several real water samples were analyzed to confirm the accuracy of the proposed method.

The efficiency of photocatalytic systems was further improved by replacing TiO_2 with ZrO_2. Nano-semiconductors such as ZrO_2 (5.0 eV) with higher negative potentials of CB e^- facilitated the direct vapor generation of Hg species, resulting in improved VG efficiency and lowered detection limits A novel UV/nano-ZrO_2/HCOOH system was developed and fabricated as an atomization unit and as an on-line interface between HPLC and AFS for Hg speciation in seafood. The method was validated by analysis of certified reference material (CRM) and applied to Hg determination and speciation in sea food from Chinese market.[12]

Hyphenation of photo-induced chemical VG with HPLC-AFS was proposed as simple, environmentally friendly approach for the quantification of Hg^{II}, MeHg and EtHg.[10] In the developed procedure, formic acid in mobile phase was used for the photo-decomposition of organomercury compounds and reduction of Hg^{II} to Hg vapor under microwave/ultraviolet irradiation of TiO_2 nanoparticles. The developed method was validated by determination of the main analytical figures of merit and applied to the analysis of three certified reference materials.

Sellenium speciation. Photocatalysis as an environmentally friendly degradation technique has been used for the on-line prereductuion of Se^{VI} to Se^{IV}. Various types of interfaces based on TiO_2 have been combined with classic hydride generation or electrochemical hydride generation in order to achieve prereduction of Se species and further efficient VG.[13]

The photocatalytic reduction of selenate Se^{VI} has been studied using unmodified TiO_2 and Ag-loaded TiO_2 photocatalysts.[14] It has been found that in the presence of formic acid, both the TiO_2 and Ag-TiO_2 photocatalysts effectively reduced Se^{VI} to hydrogen selenide gas (H_2Se). When unmodified TiO_2 photocatalyst was used, the Se formed from the reduction of Se^{VI} was further reduced to Se^{2-} in the form of H_2Se upon the exhaustion of Se^{VI} in solution. In the presence of the Ag-TiO_2 photocatalysts, hydrogen selenide gas was generated simultaneously with the reduction of Se^{VI}. The simultaneous reduction of Se^{VI} to hydrogen selenide gas can be attributed to efficient charge separation due to the mediation of photogenerated electrons by the Ag particles.

An on-line UV photolysis and UV/TiO_2 photocatalysis reduction device combined with an electrochemical vapor generation cell (carbon fiber cathode and a platinum loop anode) have been used as an interface between HPLC and AFS for Se speciation in water-soluble extracts of garlic shoots, cultured with different selenium species.[15] The speciation of only inorganic Se species was achieved by using simple UV/nano-TiO_2 interface (formic acid as hole scavenger) between chromatographic column and ICP-MS. Proposed vapor generation device allows both Se^{IV} and Se^{VI} species in the column effluent to be converted on-line into volatile Se products avoiding application of borans. The analytical method developed has been characterized with an excellent detection limits due to the extremely fast and efficient conversion of Se species to volatile products. The method is used for the determination of inorganic Se species in water samples.

Very simple and sensitive method has been proposed for inorganic Se speciation without chromatographic separation based on Se^{IV} or Se^{VI} reaction with an organic acid under different reaction conditions using UV photochemical VG. At low temperature, only Se^{IV} can be photochemically converted to selenium volatile species, and this is used for its selective determination; however, by using boiling water bath together with nano-TiO_2 as a catalyst, both Se^{IV} and Se^{VI} can be photo chemically converted to selenium volatile species, which ensures determination of the total $Se^{IV}+Se^{VI}$. The method was validated by determining Se^{IV} in certified reference water sample and applied to real samples including commercial table salt, waste water and mineral water.[16]

Speciation of inorganic and organic Se-species was realized by anion exchange LC-ICP-MS, using on-line sequential photo catalyst-assisted digestion and VG.[17] The device operating through the nano-TiO_2 catalyzed photo-oxidation and reduction of Se species was used as an interface between anion exchange LC and VG-ICP-MS. Under the optimized conditions it has been found that Se^{IV}, Se^{VI}, and SeMet were all converted quantitatively into volatile Se products and the detection limits for Se^{IV}, Se^{VI}, and SeMet were all in the nanogram-per-liter range (based on 3σ criteria). A series of validation experiments demonstrated the applicability of the

methods to the speciation analysis of organic and inorganic Se species in the extracts of Se-enriched supplements.

In order to further improve the nanosemiconductor-based photocatalytic VG efficiency for allowing direct VG of not only selenite Se^{IV} and organic Se species such as SeMet and SeCys, but also Se^{VI}, noble metal nanoparticles were loaded onto the surface of nano-TiO_2 in order to prevent the rapid recombination of e^-/h^+ pairs, moving the Fermi level of nano-TiO_2 to a more negative potential. Detection limits achieved for Se^{IV}, Se^{VI}, SeCys and SeMet by using AFS as instrumental method have been respectively 10 μg L^{-1},14 μg L^{-1},18 μg L^{-1} and 8 μg L^{-1} and sdandard deviation has been 4.4% at 10 μg L^{-1} level for all species.[18] Alternative approach was based on nano-ZrO_2 used as photocatalyst. Nano-ZrO_2 has a large energy gap (5.0 eV), between the conduction band and valence band, greater than that (3.2 eV) of nano-TiO_2, which ensures more negative potential and thus stronger reduction ability. Detection limits achieved in this case for Se^{IV}, Se^{VI}, SeCys and SeMet by using ICP-MS as instrumental method have been respectively 6 μg L^{-1},7 μg L^{-1},10 μg L^{-1} and 15 μg L^{-1} with same RSD values. Both developed photocatalytic devices were validated and used as interfaces between HPLC and AFS or ICP-MS for Se speciation in the water- and/or enzyme-extractable Se.[18]

Table 1 Analytical procedures, using photocatalysis for chemical elements speciation

Species	Analytical Technique	NPs/process	Samples	RSD, %(at conc. μg L^{-1})	LOD μg L^{-1}	Ref
						7
As^{III}, MMA, DMA,	Microbore AE LC and (HG) ICP-MS	On-line digestion device-based on the nano-TiO_2catalyzed photooxidation, combined with on-line pre-reduction for converting the oxidized species into As^{III}	Urinary arsenic species	4.1	0.37	
				6.6	0.17	
As^V				6.0	0.18	
				5.4	0.22	
						8
As^{III},	HPLC-HG-ICP-MS	Post-column UV/TiO_2 film reactor	Dializate samples	5.3	0.46	
AsB,				5.3	0.24	
MMA				3.4	0.34	
As^V,				4.7	0.40	
DMA				3.7	0.49	
Hg^{II}, MeHg, EtHg,	HPLC-AFS	UV/TiO_2 photocatalysis reaction device for direct vapor generation of Hg species on nano-TiO_2 under UV irradiation in the presence of a formic acid and	Sediment, seafood		0.01 0.02	9

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Species	Technique	Method	Sample	Enhancement/Recovery	LOD	Ref
PhHg		sodium formate mixture.			0.03 / 0.07	
Hg^{II}, MeHg	HPLC / HG ICP-MS / HPLC-UV/nano-TiO2 HG ICP-MS	Photocatalyst-assisted VG techniques	Urine	Better than 15 (2)	0.1 / 0.03	162
Hg^{II}, MeHg, EtHg, PhHg	HPLC-HG/CV-AFS	Post-column oxidation method using Fe_3O_4 magnetic nanoparticles. On-line conversion of the organomercury species eluted from the HPLC column to Hg^{II}.	Fish muscle, waters	3.9 / 1.6 / 4.8 / 2.1	0.7 / 1.1 / 0.8 / 0.9	11
Hg^{II}, MeHg, EtHg / Hg^{II}, MeHg, EtHg	FI-CV-AFS / HPLC-CV-AFS	UV/nano-ZrO_2/HCOOH system as an online interface between HPLC and AFS. UV-generated electrons at the conduction band of nano-ZrO_2 reduce mercury species into mercury cold vapor	Seafood	Better than 4.6 (2)	0.01 / 0.006 / 0.008 / 0.024 / 0.013 / 0.016	12
Hg^{II}, MeHg, EtHg	Photoinduced HPLC-CV-AFS	Formic acid in mobile phase, used for the photodecomposition of organoHg compounds and reduction of Hg^{II} to Hg vapor under MW/UV irradiation of TiO_2 NPs.	Biological samples	3.8-115 (1-5)	0.15 / 0.15 / 0.35	10
Se^{IV}, SeMet, SeCys, Se^{VI}	VG-AFS	Nano-TiO_2 multilayer film on the surface of the glass fibre. Online pre-reduction of Se^{VI}.	Model solutions	2.4 (1000)	13	163
SeCys Se^{IV}, SeMet, Se^{VI}	HPLC-HG-AFS	An online UV photolysis and UV/TiO_2 photocatalysis reduction device and an electrochemical vapor generation cell.	Extracts of garlic shoots	5 for all species	2.1 / 2.9 / 4.3 / 3.5	15
Se^{IV}, Se^{VI}	HPLC-VG-ICP-MS	UV/nano-TiO_2 vapor generation device	Water	3.4 / 6.5 (2)	0.06 / 0.03	164
Se^{IV},	AFS/ICP MS	UV photochemical vapor generation. Nano-TiO_2 as a catalyst, both Se^{IV} and Se^{VI} are photochemically	Table salt, water	2-5	0.02 - 0.1	16

Se^{VI}		converted to selenium volatile species	samples	(1000)		
Se^{IV}, Se^{VI}	HG AFS	Nano-TiO_2 controlled volatilization system was developed for inorganic selenium speciation based on the irradiation of thiourea with ultraviolet light.	Real samples	3.7 2.7 (50)	2.39 3.38	13
Se^{IV}, Se^{VI}, SeCys, SeMet	HPLC-AFS HPLC-ICP-MS	Ag-TiO_2-based and ZrO_2-based photocatalytic vapor generation systems	Se-enriched yeast.	Varied, see text	Varied, see text	18
Se^{IV}, Se^{VI}, SeMet	Anion exchange LC-ICP-MS	On-line, sequential photocatalyst-assisted digestion and vaporization device, which operates through the nano-TiO_2-catalyzed photo-oxidation and reduction of Se species	Se-supplements	1.7	0.0039 0.007 0.008	17

3. Nanomaterials for elemental speciation analysis by nonchromatographic methods

In general, speciation analysis is often focused on the determination of the most toxic species or differentiation between inorganic and organic compounds and the quantification of all chemical forms is rarely demanded. From such view point relatively expensive hyphenated methods are not suitable for practical application especially for large number of samples from different monitoring programs. Unsurprisingly, the non-chromatographic methods have attracted tremendous attention because of their simplicity, low cost, fastness and flexibility. Based on the distinctive chemical and physical properties of the particular species, the non-chromatographic speciation strategy comprises numerous extraction methods such as conventional LLE, SPE, solid phase microextraction, single-droplet microextraction, magnetic SPE, cloud-point extraction as well as some derivatization techniques (e.g. volatilization, selective reduction) summarized in several review papers. [19-22] Undoubtedly, the quantitative and selective species separation is the core of the analytical procedures used for non-chromatographic speciation analysis. Therefore, the highest extent of selectivity at sorption or elution stage is a basic requirement for each reliable extraction technique. In this sense, combined with the well-known advantages of SPE procedures (low solvent consumption, high preconcentration factors, rapidity, simple operation in static and dynamic mode), the preparation and utilization of new functional materials as effective sorbents has reasonably become one of the current trends in the modern speciation research. Different view points on this hot topic of reseach have been presented in various review papers in the recent years. [23-32]

From an analytical point of view, utilization of various types' micro- and nano-sized materials in speciation analysis of trace elements could be branched in several major strategies, illustrated by Fig. 2
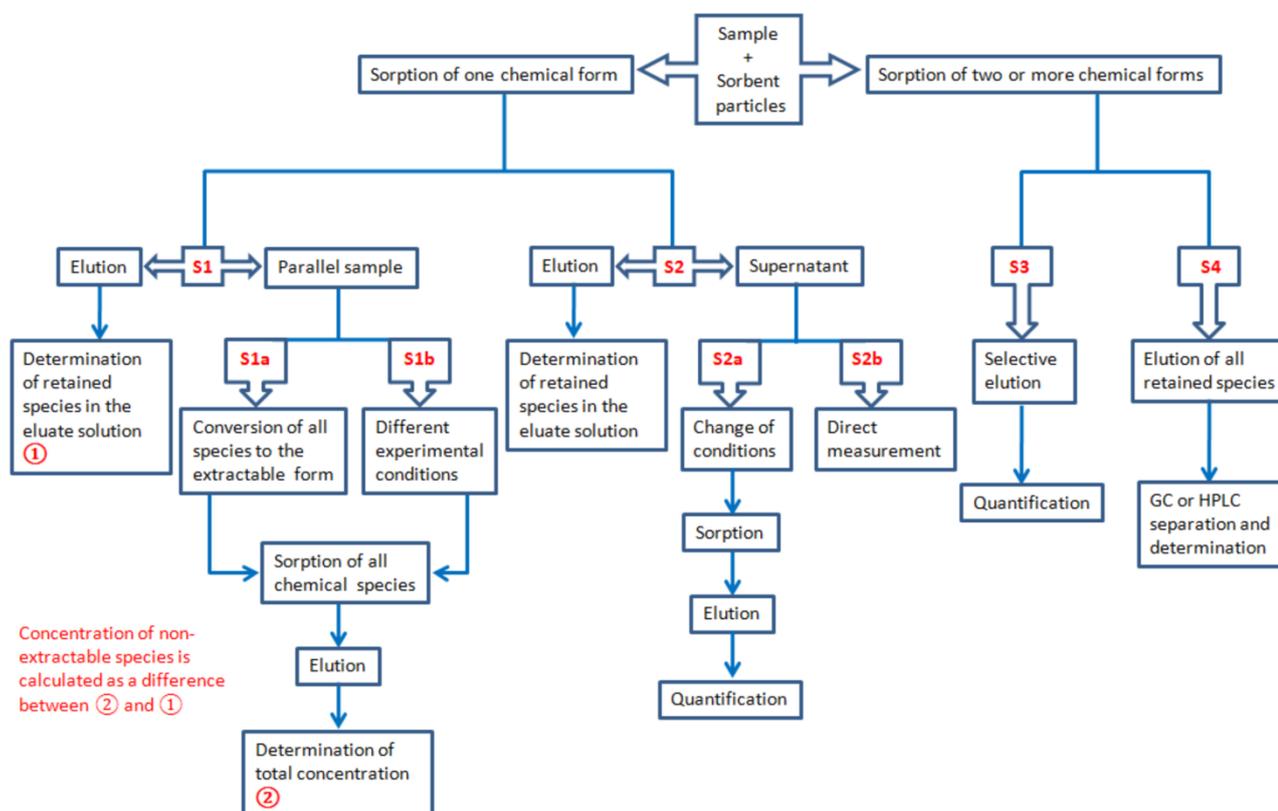
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Fig.2 Major strategies in nonchromatographic speciation analysis.

Strategy 1 (S1) Selective SPE of target chemical form of the analyte, by a nanosorbent, followed further by its measurement with an appropriate instrumental technique. A parallel sample is preliminarily treated in such a way that ensures:

> *S1a*: Conversion of all species to the extractable form, which is then determined by the same SPE procedure.
> *S1b*: Retention of all chemical species under different experimental conditions (usually pH) followed by their quantitative elution and determination.

In this way total content of the element is quantified and the concentration of non-extractable species is calculated by subtraction. This approach is widely accepted and probably the most frequently used.

Strategy 2 (S2) The target chemical form is selectively retained and after elution quantified by measurement with an appropriate instrumental technique. The supernatant solution after sorption can be treated as follow:

> *S2a:* The pH of the supernatant is adjusted to a new value in order to ensure sorption of other species of the analyte (most frequently the sorbent surface is protonated/deprotonated). After that, the retained species is eluted and instrumentally determined.

> *S2b:* Non-extractable species is directly measured in the supernatant solution by highly sensitive analytical method (e.g. ICP-MS, HG-AFS).

Strategy 3 (S3) Two or more species are retained together on the sorbent surface and then separated by selective elution. After adsorption of the analytes, an appropriate solution is passed through the column in order to ensure the quantitative elution of only one chemical species (usually the most toxic). Another option in this strategy is a sequential passing of several eluent solutions and determination of each particular species in the eluates obtained.

Strategy 4 (S4) Retention of two or more species, followed by their simultaneous elution and subsequent chromatographic separation and determination. In this case the main goal is quantitative preconcentration of the analytes in order to ensure higher sensitivity and lower limits of quantification.

The state of the art in micro- and nano-bore materials, fit for the purposes of speciation analysis and their crucial role in the efficient separation and/or enrichment of chemical species of trace elements before their instrumental determination is summarized in next paragraphs. Speciation procedures based on the application of nano-sized metal oxides, magnetic nanoparticles, carbon based nanomaterials, noble metals nanoparticles and ion imprinted polymers are presented and discussed.

3.1 Metal oxide nanopraticles (MeOxNPs)

The group of hydrous oxides of metals – SiO_2, TiO_2, ZrO_2 and MnO_2 is a group of well-known ion exchangers. They are usually described as hydrous oxides or hydrated hydroxy oxides and behave either as cation exchangers in alkaline solutions or as anion exchangers in acidic solutions, depending on the basicity of the central atom and the strength of the Me-O bond, relative to that of the O-H bond in the hydroxyl group. The exchange sites are heterogeneous. As the size of metal oxides is reduced from micrometer to nanometer level, surface area and consequently sorption activity and selectivity increased due to the size quantization effect,[33,34] however it is worth mentioning that increased surface energy inevitably leads to poor stability. Therefore as nanosorbents they are relatively rarely used alone as a column adsorbents. The size and shape of MeOxNPs are important factors, determining their adsorption performance and various forms have been applied in SPE procedures such as particles, tubes, nanospheres, nanosheets etc. Efficient synthetic methods to obtain shape-controlled, highly stable, and monodisperse MeOxNPs have been developed during the last decade. The most serious disadvantage of MeOxNPs is their low selectivity toward target analytes/species which is solved by various approaches – modification of their surface with more selective regents, preparation of combined oxides or nanocomposites with higher selectivity.

Undoubtedly nano-TiO_2 is most widely used material in SPE and speciation of chemical elements. It has been reported that bulk and nanoparticle TiO_2 anatase exhibit different chemical behavior, catalytic reactivity, and surface acidity based on their different surface planes. When adsorption capacities were normalized by mass, the nanoparticles adsorbed more than the bulk particles. However, as the results were surface normalized, the opposite tendency was observed. Adsorption kinetics as a rule followed a modified first order model, and the nanoparticles had a faster adsorption, than the bulk ones. Langmuir isotherm was most frequently suitable to characterize metal adsorption ontoTiO_2 anatase.

The summary of the analytical procedures based on separation and speciation of chemical elements on MeOxNPs is presented in Table 2.

Speciation of arsenic and antimony. Nanometer size titanium dioxide (rutile) has been used as efficient sorbent for preconcentration of Sb^{III} and Sb^V prior to their selective determination by HG-AAS. Both species have been retained on 50 mg sorbent at pH 3 and then eluted with 5 mol L^{-1} HCl: Sb^{III} is measured directly in eluent solution, Sb^V is measured after addition of KI or thiourea.[35] Almost identical procedure has been recently developed and proposed by Wang et al.[36] using selective elution with citric acid

The sorption of As^{III} and As^V on the nano-sized amorphous or crystalline TiO_2 was investigated. It was concluded that sorption capacities of the different TiO_2 polymorphs toward As^{III} and As^V depend on the sorption sites density, surface area (particles size) and crystalline structure. When normalized to surface area, As^{III} surface coverage on the TiO_2 surface remained almost constant for particles between 5 and 20 nm. However, As^V surface coverage increased with the degree of crystallinity. X-ray absorption spectroscopic analysis provided evidence of partial As^{III} oxidation on amorphous TiO_2 rather than crystalline TiO_2. The data also indicated that As^{III} and As^V form binuclear bidentate inner-sphere complexes with amorphous TiO_2 at neutral pH.[37] Speciation of inorganic As was realized by selective sorption of As^{III} on the surface of nanometer TiO_2 immobilized on silica gel at pH 9.5-10 and sorption of both

$As^{III}+As^V$ was performed within a pH range of 5.0-7.5. Electrothermal AAS was used for instrumental measurement of As species. The proposed method has been applied to the speciation of inorganic arsenic in natural water samples with satisfactory results.[38] Mesoporous TiO_2 has been chemically modified with dimercaptosuccinic acid and employed as the micro-column packing material for simultaneous separation/preconcentration of inorganic arsenic and antimony species. It was shown that total ($As^{III}+As^V$) and total ($Sb^{III}+Sb^V$) could be adsorbed quantitatively on the surface of the sorbent, within the pH range of 4–7, and only As^{III} and Sb^{III} could be selectively retained on the micro-column, within a pH range of 10–11.[39] Enrichment of several As species (As^{III}, As^V, 4-Hydroxyphenylarsonic acid (4-HPAA), 3-nitro-4-hydroxyphenylarsonic acid (3-NHPAA), MMA, DMA, 4-aminophenylarsonic acid (4-APAA) and 4-nitrophenylarsonic acid (4-NPAA) prior to HPLC-ICP-MS determination has been achieved by stir bar extraction using stir bar with disposable TiO_2 polypropylene hollow fiber coating.[40] Analytical method developed has been applied for As speciation in chicken tissue.

Speciation of Chromium. Speciation analysis of Cr^{III} and Cr^{VI} is one of the most investigated analytical problems in last years. Possible SPE strategies for inorganic Cr^{III}/Cr^{VI} speciation could be easily summarized in two alternative approaches (Fig. 1): (i) selective retention of Cr^{III} or selective retention of Cr^{VI} and selective retention of both species all at defined pH values or (ii) selective retention of Cr^{III} or Cr^{VI} and conversion respectively of Cr^{VI} or Cr^{III} to the retained one. In both cases one of the Cr species is determined by subtraction (strategy S1). The second alternative requires additional reagents for oxidation/reduction which may introduce contamination as well as incomplete conversion may degrade accuracy of Cr speciation. Relatively rarely Cr^{III} is selectively retained on the sorbent and Cr^{VI} is determined in the supernatant or the opposite (strategy S2b).

Liang et al.[41] demonstrate selective retention of Cr^{III} at pH 6 on nanometer TiO_2 micro-column or on TiO_2 nanoparticles, dynamically loaded with 8-hydroxyquinoline. The determination of Cr^{VI} has been achieved after reduction with ascorbic acid. Analogous procedures were developed by using nanometer TiO_2, TiO_2 on silica gel or TiO_2 nanotubes as column packing material.[-45] Separation and selective determination of both Cr^{III} and Cr^{VI} without interconversion between Cr species has been introduced by Wu et al.[46] On-line flow injection method based on selective sorption of Cr^{VI} at pH <2 and selective sorption of Cr^{III} at pH>7 on column packed with nanometer TiO2 immobilized on silica has been validated for Cr speciation in drinking waters.

Recently selective SPE of both Cr species has been realized using highly effective biosorbents fabricated by immobilization of three fungal strains: *Aspergillus ustus*; *Fusarium verticillioides*; *Pencillium funiculosum (Pen)* on nanosilica surface. The maximum biosorption capacity values of Cr^{III} were observed at pH 7.0, while those for Cr^{VI} were observed at pH 2.0. Potential applications for speciation and selective extraction of Cr species from real waste water samples has been successfully accomplished.[47]

Higher selectivity toward Cr^{VI} has been demonstrated for amine-functionalized bimodal mesoporous silica nanoparticles applied as a novel nanoadsorbent for preconcentration and speciation of chromium (III, VI) in water samples.[48]

Speciation of selenium. Speciation of inorganic Se^{IV} and Se^{VI} mostly in natural waters is based on their different degree of sorption on nanometer TiO_2 at different pH values. A simple and sensitive method for the selective determination of Se^{IV} and Se^{VI} in natural

water and sludge samples has been developed through selective sorption of Se^{IV} at pH 3, followed by retention of Se^{VI} at pH 0 on a nanometer-sized TiO_2 (anatase) and ETAAS or HGAAA measurement of eluted species.[,50] Quantitative sorption of both inorganic Se^{IV} and Se^{VI} on nano-TiO_2 at pH 4 has been proposed as preconcentration procedure before their speciation by ion chromatography (IC) with conductivity detection. The method has been applied for inorganic Se speciation in tap water and drink samples.[51] Speciation of dissolved inorganic and organic Se species in environmental and biological samples has been achieved by flow injection (FI) dual-column preconcentration/separation on-line coupled with ICP-MS determination. The first column packed with nanometer-sized Al_2O_3 ensures selective retention of inorganic Se^{IV} and Se^{VI}, the second column packed with mesoporous TiO_2 chemically modified by dimercaptosuccinic acid (DMSA) selectively adsorbs Se^{IV} and SeCys. Sample solution was passed through the column 1, for the separation of inorganic selenium and then, the effluent from column 1 was introduced into the column 2 for the speciation of organic selenium. The eluent from column 1 contained Se^{IV}, and Se^{VI}

was adjusted to desired pH and injected into column 2, and the speciation of Se^{IV} and Se^{VI} could also be realized thanks to their different retention on column 2. This relatively complicated analytical method has been validated by the analysis of certified reference material SELM-1 yeast.[52] Nanometer-sized Al_2O_3 loaded with Cu(II) has been proposed as packing material for micro-column for flow injection on-line speciation of organic Se species SeMet and SeCys in yeast, human urine and serum. It has been demonstrated that SeCys could be selectively retained by micro-column at pH 4.0, and eluted by 1.0 M HNO_3, while both SeMet and SeCys could be quantitatively adsorbed by the micro-column at pH 9.0, and the retained SeMet and SeCys could be easily eluted with 1.0 mol L^{-1} HNO_3.[53] Mesoporous TiO_2 loaded with Cu(II) has been proposed as efficient sorbent for L-SeMet and D-SeMet before their chiral separation and determination by micelle electrokinetic capillary chromatography. The developed procedure has been validated by analysis of certified reference material SELM-1 yeast and applied for speciation of L-SeMet and D-SeMet in selenized commercial nutrition yeast.[54]

Table 2 Application of MeOxNPs for SPE and speciation of chemical elements

Chemical species	Sorbent	Analytical Technique	Sample	EF	RSD, % (at conc. µg L^{-1})	LOD	Ref.
As^{III}, As^{V}	Nanometer TiO_2, immobilized on silica gel	ETAAS	water	50	4.8 (5)	0.024	38
As^{III}, As^{V} Sb^{III}, Sb^{V}	Mesoporous TiO_2, modified with dimercaptosuccinic acid	ICP-OES	water	50	<6.7 (20) for all species	0.11, 0.10, 0.15, 0.13	39
As^{III}, As^{V}, 4-HPAA 3-NHPAA MMA, DMA 4-APAA 4-NPAA	Stir bar with disposable TiO_2 polypropylene hollow fiber coating	HPLC-ICP-MS	Chicken tissue	8.5-22.3	6.3 - 12.6 ($As^{III/V}$at, 5), (MMA, DMA, 4-HPAA, 3-NHPAA 4-APAA, 4-NPAA at 10)	0.0114-0.0646	40
Cr^{III}, Cr^{VI}	Nanometer-sized TiO_2 micro-column	ICP-OES	water	50	2.4 (100)	0.32	42
Al^{III}, Cr^{III}	TiO_2NPs, dynamically loaded with oxin	ICP-OES	Biosamples lake water	50	3.7 (100) 2.4 (100)	1.96 Al^{III} 0.32 Cr^{III}	41
Cr^{III},	Nano-sized TiO_2 immobilized on silica gel	ICP-OES	water		3.5 (100)	0.22	43

Cr^{VI}							
Cr^{VI},	Nanometersized TiO$_2$	FI ETAAS	Drinking water		2.0 (1)	0.01	44
Cr^{III}					3.2 (0.5)	0.006	
Cr^{III}	Modified TiO$_2$ core-Au shell nanoparticles	Slurry ETAAS	Sea, tap water		-	0.34	55
Cr^{III},	TiO$_2$ nanotubes	ICP-MS	Water		3.8 (0.5)	0.23	45
Cr^{VI}							
Susp. and soluble Cr, Cr^{III},	TiO$_2$ nanotubes	ICP-MS	Tea leaves Tea infusion		3.8 (1.0)		44
Cr^{VI}						0.0075	
Cr^{III},	Amine-functionalized mesoporous silica NPs	FAAS	Water	66.7		1.2	48
Cr^{VI}							
Sb^{III},	Nanometer size TiO$_2$ (rutile)	FI HGAAS	Water		not presented	0.05	35
Sb^{V}						0.06	
Sb^{III},	Nano-sized TiO$_2$ colloids	HG AFS	Water	10	6.7	0.01	36
Total Sb					0.9	0.013	
Se^{IV},	Nanometer-sized TiO$_2$(anatase)	ETAAS	Waters sludge samles	50	0.7 (5)	0.0047	49
Se^{VI}					0.9 (5)	0.0063	
Se^{IV}, Se^{VI}, SeCys, SeMet	Nano- Al$_2$O$_3$ and mesoporous TiO$_2$, chemically modified by dimercaptosuccinic acid	FI ICP-MS	Environmental samples		3.6-9.7	0.045-0.21 Se^{IV}, Se^{VI}, Se-Met and SeCys	52
SeMet,	Cu(II) loaded nano- Al$_2$O$_3$	ICP-MS	Yeast, urine, serum	7.8	2.1 (1)	0.024	53
SeCys				7.7	1.6 (1)	0.021	
D–SeMet,	Cu(II) loaded mesoporous TiO$_2$	micelle ECC	Yeast	1400	4.4 (peak area) (10)	0.44	54
L– SeMet				1378	7.4 (peak area) (10)	0.6	
Se^{IV},	Nanometersized TiO$_2$ colloid	HG AFS	Water		7.8	0.024,	50
Se^{VI}					7.0	0.042	
Se^{IV},	Nano-TiO$_2$	IC	Water	39,	<4 (30)	0.0008	51

Se^{VI}	30	<4 (30)	0.0004

3.2 Magnetic SPE for trace element speciation

Magnetic nanoparticles (MNPs) might be accepted as an alternative to conventional SPE sorbents, as they allowed easy and fast isolation of the enriched individual compounds. Their application can significantly shorten the duration and improve efficiency of the extraction process even for a large volume of sample. Due to their small particle size, they are characterized by a high specific surface area and sorption capacity. Their application in the analytical practice increased significantly in the last decade, which is summarized in several review papers, concerning magnetic SPE (MSPE) of chemical elements and organic compounds.[56-60] The magnetic core of MNPs is usually fabricated from iron, nickel, cobalt, or their oxides, however most often these include iron oxides, such as magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3). In order to overcome difficulties, connected with easy aggregation of nanosized magnetic particles, the surface of the magnetic core is frequently coated with a suitable inorganic substances (e.g. silica, alumina or graphene) or organic substances such as molecularly-imprinted polymers, chitosan, divinylbenzene etc (see Table 3).

In a conventional batch procedure, magnetic sorbent is placed in a solution of target analytes and after completion of sorption, they are separated from the solution by using an external magnetic field, which is situated outside the extraction vessel. In this way any additional operations like centrifugation or filtration for sorbent removal are avoided and the whole sorption procedure is significantly shortened and simplified. The process of elution is also much simpler and faster based on magnetic separation of regenerated sorbent.

The summary of analytical procedures based on MSPE for chemical elements speciation is presented in Table 3.

Speciation of arsenic. Quite similar approaches have been used for inorganic As speciation by MSPE mostly based on strategy S1a. Arsenic (V) is selectively retained on: amino-modified silica-coated magnetic nanoparticles at pH 3-8[61]; cetyltrimethyl ammonium bromide immobilized on alumina-coated magnetite nanoparticles[62]; Fe_3O_4-doped Mg-Al layered double hydroxide[63] and determined respectively by ICP-MS; spectrophotometry (molybdenum blue method); chemiluminisce. As a second step, total As is determined using the same procedure after As^{III} oxidation by suitable oxidant. The analytical methods developed have been applied for inorganic As speciation in waters. The only paper for As speciation in rice samples is based on the analogous approach of MSPE, however, using a bit complicated sorbent - 3-mercaptopropionic acid coated 3-aminopropyl triethoxysilane modified Fe_3O_4.[64]

Speciation of chromium. Several papers explored different sorption behavior of Cr species on Me oxides or chitosan allowing their selective determination, e.g. selective sorption of Cr^{III} at pH around 9 and sorption of both Cr^{III}+ Cr^{VI} at pH 6-7 (strategy S1b). Various Me oxides or chitosan have been proposed as coatings for Fe_3O_4 nanoparticles: chitosan-modified magnetic nanoparticles[65]; zincon-immobilized silica-coated magnetic Fe_3O_4 nanoparticles[66]; Fe_3O_4@ZrO_2[67]. Various methods, such as ICP-OES; ETAAS and FAAS, were used for further instrumental measurement. A bit different approach has been developed by Diniz *et al.*[68] combining dispersive MSPE with CPE as a new nonchromatographic approach for preconcentration/redox speciation of Cr with FAAS detection. Chromium^{VI} is selectively retained onto mesoporous amino-

functionalized Fe_3O_4/SiO_2 nanoparticles followed by CPE of Cr^{III} as a complex with 4-(2-thiazolylazo)resorcinol.

Magnetic mixed hemimicelles SPE has been developed for Cr speciation using alumina-coated magnetite nanoparticles (Fe_3O_4/Al_2O_3 NPs), modified by the surfactant Triton X-114.[69] The enrichment procedure is based on the reaction of Cr^{III} with 1-(2-pyridilazo)-2-naphtol as a ligand, yielding a complex, which was entrapped "in situ" in the surfactant hemimicelles and determined by FAAS. After reduction of Cr^{VI} to Cr^{III} by ascorbic acid, the system was applied to total Cr determination. Authors declared that method could be used for complicated matrices, such as soil samples without any special pretreatment.

The only procedure for on-line MSPE in combination with ICP-MS, described by Huang *et al.*[70] is based on the selective retention of either Cr^{III} or Cr^{VI} under controlled pH conditions, on the inner walls of knotted reactor with magnetically immobilized, amine-functionalized magnetite microspheres. The developed method has been successfully applied to the speciation analysis of trace Cr^{III} and Cr^{VI} in drinking water samples.

Speciation of mercury. Analytical procedure for Hg speciation based on MSPE and ICP-MS measurement has been developed and successfully applied for the speciation of MeHg and Hg^{II} in human hair samples and environmental waters.[71] Both Hg^{II} and MeHg were quantitatively sorbed on Fe_3O_4@SiO_2 NPs modified with γ-mercaptopropyltrimethoxysilane. The separation of both species was achieved by selective elution of MeHg by using 1.5 mol L^{-1} HCl, containing 0.01% (m/v) thiourea and elution of total mercury by using 3% (m/v) thiourea, thus allowing selective determination of MeHg and calculation of Hg^{II} by subsequent subtraction from total Hg.

Speciation of selenium. Almost all analytical procedures devoted to Se speciation include MSPE as enrichment step for all Se species prior to their chromatographic separation rather than for selective quantitative separation and determination of individual species.

On-chip MSPE HPLC-ICP-MS method has been developed for the speciation of organic Se species.[72] An integrated microfluidic chip consisting of reaction, mixing and extraction units was designed and fabricated; sulfonated polystyrene-coated Fe_3O_4 NPs were prepared as adsorption material for MSPE of selenoamino acids and selenopeptide. Certified RM SELM-1 yeast was used to validate the accuracy of the developed analytical method. The proposed method has been successfully applied to the speciation of selenium in selenium-enriched yeast cells. The authors declared that MSPE-HPLC-ICP-MS method is sensitive, fast, easy-to-operate, and economical with unique advantages of low sample consumption consequently suitable for selenium speciation in a small number of selenium-enriched yeast cells.[70]

Kim *et al.*[73] has been proposed simple and quick MSPE technique for the determination of selenite in natural water by using TiO_2@SiO_2/Fe_3O_4 nanoparticles as sorbents. The synthesized nanoparticles were used to separate Se^{IV} in the presence of Se^{VI} or selenium anions for the photocatalytic reduction to elemental Se on the TiO_2 shell.

A new method for selenium speciation in fermented bean curd wastewater and juice, based on capillary electrophoresis(CE) separation, and on-line detection with a modified ETAAS system, has been described.[74] The separation and preconcentration of Se species has been achieved by MSPE using 5-sulfosalicylic acid functionalized silica-coated MNPs.

Speciation of tellurium Speciation of inorganic Te species has been achieved by selective sorption of Te^{IV} on gamma-mercaptopropyltrimethoxysilane modified silica-coated magnetic nanoparticles at pH 2-9. Total Te was then determined after reduction of Te^{IV} by L-cysteine using the same MSPE procedure. ICP-

MS was used as instrumental methods for Te measurement. The developed analytical method has been successfully applied to the speciation of inorganic Te in seawater.[75]

Table 3 Magnetic SPE for element speciation

Chemical species	Magnetic NPs	Analytical Technique	Sample	EF	RSD, % (at conc. µg L^{-1})	LOD, µg L^{-1}	Ref.
As^V, Total As	amino-modified $Fe_3O_4@SiO_2$	ICP-MS	water of tobacco growing area.	300	6.8 (10 ng L^{-1})	0.21 ng L^{-1}	61
A^V, Total As	CTAB immobilized on $Fe_3O_4@Al_2O_3$	Spectro Photometry	Water samples	175	2.8 (2.0 mg L^{-1})	28	62
A^V, Total As	Fe_3O_4-doped Mg-Al layered hydroxide	Chemi luminescence	Water samples	80	0.85 (0.200) 2.17 (2)	0.002	63
As^{III}, As^V	3-mercaptopropionic acid coated APTES modified Fe_3O_4	ETAAS	Water, rice	198	2.3-3.2 (0.05-25)	0.01	64
Cr^{III}, Cr^{VI}	Knotted reactor with amine-functionalized Fe_3O_4 microspheres	ICP-MS	Drinking water	96 47	1.9 (0.100) 4.5 (0.100)	1.5 ng L^{-1} 2.1 ng L^{-1}	70
Cr^{III}, Total Cr	$Fe_3O_4@ZrO_2$	FAAS	Environmental biological	25		0.69	76
Cr^{VI} Total Cr	$Fe_3O_4@Al_2O_3$	FAAS	Water, waste water	140	4.6 (5.0)	0.083	77
Cr^{III}, Cr^{VI}	Zincon-immobilized silica-coated Fe_3O_4	ETAAS	Waters	100 150	6.0 (0.1 ng L^{-1} 6.2 (0.1 ng L^{-1})	0.016 0.011	66
Cr^{III}, Total Cr	$Fe_3O_4@Al_2O_3$ modified by Triton X-114	FAAS	Water, soil			1.4-3.6(waters) 5.6 ng mg^{-1} (soil)	69
Cr^{III}, Total Cr	Chitosan-modified Fe_3O_4 nanoparticles	ICP-OES	Waters	100	4.8 (1) 5.6 (1)	0.02 0.03	65
Cr^{VI}, Cr^{III}	Mesoporous amino-functionalized Fe_3O_4(dispersive MSPE combined with CPE)	FAAS	Water, Biological samples	16 12	5.5 and 3.0 (15 and 75) 5.8 and 3.7 (15 and 165)	1.1 3.2	68

Hg^{II}, MeHg, EtHg, PhHg	Fe$_3$O$_4$ magnetic nanoparticles for green and efficient post-column oxidation	HPLC-HG/CV-AFS	Water, fish		3.9 1.6 4.8 0.9	0.7, 1.1, 0.8, 0.9	11
MeHg Total Hg	γmercaptopropyl trimethoxysilane modified Fe$_3$O$_4$@SiO$_2$	ICP-MS	Water, human hair	50 50	3.4 (0.02) 2.6 (0.05)	0.0016 0.0019	71
SeCys$_2$, SeMet SeEt, MeSeCys, GluMeSeCys	On-chip sulfonated polystyrene-coated Fe$_3$O$_4$ NPs	HPLC ICP-MS	Single cells	19 11 8 13 9	9.3 (2) 7.1 (2) 5.1 (2) 8.4 (2) 5.6 (2)	0.057 0.117 0.116 0.149 0.095	72.
Se^{IV}, Se^{VI}	TiO$_2$@SiO$_2$/ Fe$_3$O$_4$	ICP-MS	Environmental and biological analysis		remove		73
Se^{VI}, Se^{IV}, SeMet, SeCys$_2$	5-sulfosalicylic acid functionalized Fe$_3$O$_4$@SiO$_2$	CE-ETAAS	Waste water, juice	21 , 29 , 18 12	2.2 0.7 2.5 2.9	0.18 , 0.17, 0.54, 0.49	74
Te^{IV}, Total Te	gamma-mercaptopropyltrimethoxysilane modified Fe$_3$O$_4$@SiO$_2$	ICP-MS	Sea water	320	7.0 (0.01)	0.079 ng L^{-1}	75

3.3. Noble metal nanoparticles (NM-NPs) as nanosorbents for trace element speciation

Over the past 10 years, noble metal (or noble metal shell) nanoparticles have been successfully applied as a selective phase for separation and enrichment of particular element species and thus used for speciation analysis of elements existing in different oxidation states, mostly As, Cr, Sb, and Se, as well as for speciation of inorganic and organic Hg in various kind of samples. Different mechanisms have been hypothesized for the retention of metal species on NM-NPs, including selective complexation of one of the oxidation states, selective redox conversion between oxidation states before sorption on the nanoparticle surface, amalgamation, catalytic decomposition and sorption after suitable functionalization. Examples of important recent applications of NM-NPs-based nanomaterials for trace element speciation are shown in Table 4.

Determination of inorganic As species has been achieved by *in-situ* reduction and adsorption of As^{III} and As^V on Pd-NPs generated *in situ* by hydrazine and sodium borohydride as reductants.[78] It was observed that Pd-NPs obtained by reduction with sodium borohydrid allowed quantitative recovery for both As^V

and As^{III}, while Pd-NPs obtained by reduction with hydrazine could retained only As^{III}. The quantification of eluted As species was carried out using GFAAS. The proposed procedure, which can be allocated to strategy 1 (Fig. 1), was validated by analysis of total As in CRM BND301-02 (NPL, India) and was successfully applied for the determination of sub ppm to ppm levels of As^V and As^{III} in environmental water samples.

Selective determination of Cr^{III} by ETAAS has been achieved after successful transfer of Cr^{III} to the surfactant-rich phase using CPE of silver nanoparticles (AgNPs) in the presence of Triton X-114.[79]

In order to improve the transport of analytes to the detector, generation of volatile species using CVG with NaBH$_4$, has been commonly employed for elements such as As, Hg, Se, etc. Recently, three applications concerning preconcentration of MeHg[80], Sb[81], and Se[82] using the principles of HS–SDME in combination with ETAAS have been reported as examples of speciation strategy S2. The developed analytical procedures were based on the formation of hydrides, headspace sampling and trapping them onto a Pd(II)-containing aqueous drop. The sequestration mechanism proposed lied in the catalytic decomposition of the hydrides onto the elemental nano-Pd formed

in the drop as a result of the reducing action of hydrogen gas that evolves in the headspace after the sodium tetrahydroborate(III) decomposition. Pd-NPs behaved as both a trapping agent and a matrix modifier in the graphite furnace. Selective determination of MeHg has been achieved by trapping the MeHgH formed onto a drop containing Pt/Pd-NPs.[80] The drop was subsequently injected into a graphite tube for Hg determination by ETAAS. The method was validated against CRM BCR 464 Tuna fish and CRM NRCC DORM-2.

Appropriate functionalization of Ag-NPs and their immobilization on the surface of MNPs have been used in micro-SPE procedure for separation and preconcentration of Hg species, according to the strategy S2, followed by ETAAS measurement.[83] Functionalization with sodium salt of 2-mercaptoethane-sulphonate allows quantitative sorption of Hg^{II}, while functionalization with L-cysteine ensures retention of organic Hg species (MeHg, Me_2Hg, EtHg, PhHg and Ph_2Hg). After separation using magnetic field, the retained species are released from the nanocomposites by treating with a small volume of a potassium iodide solution. Mercury is measured by ETAAS using silver nitrate and potassium permanganate as chemical modifiers. The results for total mercury are verified using certified reference materials. The analysis of

edible oils was used as a test bench to check the reliability and usefulness of the proposed procedures.

Starch-stabilized Ag-NPs supported on SiO_2 submicrospheres have been proposed as a novel nanocomposite sorbent for selective sorption and enrichment of Hg^{II} in surface waters followed by ICP-MS measurement.[84] The high selectivity of SiO_2/Ag-NPs nanocomposite sorbent was explained with the selective reduction ability of immobilized Ag-NPs toward Hg^{II} compared with organic mercury and further amalgam (Ag_2Hg_3) formation. The potential of the SiO_2/Ag-NPs nanosorbent for Hg speciation and determination was approved by analysis of unpolluted surface water samples. *In situ* reduction and adsorption of Se^{IV} on Pd-NPs has been used for quantification of Se^{IV} and Se^{VI} in water samples by ETAAS.[85] Sodium borohydride was used for the simultaneous reduction of Pd(II) to Pd-NPs and Se^{IV} to elemental Se. The reduced elemental Se was adsorbed on the surface of Pd-NPs and thus separated from Se^{VI}. The method has been validated by analysis of total selenium in CRM BND701-02 (National Physical Laboratory, India) and has been successfully applied for the determination of Se^{IV} and Se^{VI} in ground water samples collected from the Nawanshahar–Hoshiarpur region, Punjab, India.

Table 4 Applications of metal (or metal shell) nanoparticles as sorbents for trace element speciation

Species	Material	Analytical technique	Sample	EF	RSD, % (at conc. µg L^{-1})	LOD µg L^{-1}	Ref.
Cr^{III} Total Cr	Ag-NPs CPE by Triton X-114	ETAAS	Water Beer Wine	1150	3.8 (0.02)	0.002	165
Cr^{VI}	Chitosan-AgNPs nanocomposite film	ICP-MS	Surface waters	-	3-5 (0.05-5)	0.02	86
As^{III} Total As	Pd-NPs Selective reduction/adsorption	GFAAS	Groundwater	50	4.2 (5 ng L^{-1})	0.029	78
MeHg Hg^{II}	Pd-NPs Pt-NPs (*In situ* synthesized)	HS-SDME-ETAAS	Fish tissue	40	≈ 7 for both materials	5 4	80
Hg^{II} Total Hg (several organic species)	Fe_3O_4@Ag-NPs (modified)	ETAAS	Water Edible oils	196	2.5-3.7 (0.03-3.5)	0.01	83
Hg^{II} Total Hg	SiO_2/Ag-NPs	ICP-MS (river water)	River waters Seawater	-	5–9 6–11	0.002 (LOQ) 0.004	84

		CV AFS (seawater)	CRM Estuarine Water BCR-505		(5-200)	(LOQ)	
Sb^{III} Total Sb	Pd-NPs (*In situ* synthesized)	HS-SDME-ETAAS	Synthetic seawater	176	4.7 (1)	0.025	81
Se^{IV} Total Se	Pd-NPs (*In situ* synthesized)	HS-SDME-ETAAS	Freshwater Seawater	25	2.5 (10)	0.15	82
Se^{VI} Total Se	Pd-NPs	ETAAS	CRM BND701-02 Groundwater	100	-	0.025	85

3.4 Carbon-based nanomaterials (CBNM)

The group of carbon-based materials includes some of carbon allotropes such as graphene, fullerenes and carbon nanotubes, composed of sp^2-hybridized C-atoms structurally organized in different ways. While graphene possesses a single or few layered planar honeycomb lattice, fullerenes are polyhedral structures with hollow spherical or ellipsoid shape where carbon atoms are connected in 5- and 6-membered cycles. Carbon nanotubes (CNTs) present a structure related to the fullerenes, so they can be considered as cylindrical fullerenes, which consists of one or more rolled graphite sheets and according to their number, CNTs can be classified as single-walled (SWCNTs) and multi-walled (MWCNTs), respectively. These materials are generally characterized with a large surface area, high mechanical strength and chemical stability as well as offer various possibilities for surface functionalization. Due to their unique structure and chemical properties, CBNM have found many applications in analytical chemistry, especially as adsorbents for SPE. There are several review articles thoroughly describing the great potential of CBNM in sample preparation, separation, speciation and detection of organic and inorganic analytes.[87-91]

The analytical application of CBNM can be considered as a promising tool for speciation analysis of trace elements, however, due to the strong van der Waals interactions the raw carbon-based materials are usually inert, hardly dispersible and insoluble in most solvents.[90] Furthermore, speciation analysis of trace elements based on SPE requires a high selectivity toward one or more ionic species, so the appropriate surface modification of CBNM is often needed. In the most common approach the sorbent is preliminarily treated with oxidizing agent such as concentrated nitric acid[92-95][87-95], or mixture of conc. sulphuric and nitric acid[96] which introduced oxygen containing functional groups. According to the type of target analytes (e.g. cationic or anionic) and correct selection of pH values, they can be selectively retained as a result of electrostatic interactions with protonated or deprotonated carboxyl, carbonyl or hydroxyl groups. For example, A. Khaligh *et al.*[91] reported a procedure for arsenic speciation based on separation of As^{III} and As^{V} by ultra sound assisted dispersive micro SPE using carboxylated nanoporous graphene as a sorbent. It was experimentally verified that at the value of pH 3.5, As^{V} was quantitatively retained due to the strong electrostatic attraction between positively charged surface (G-COOH$_2$$^+$) and H$_2AsO_4$$^-$ (the main form of As^{V} at pH 2.24–6.76), while As^{III} remain in the solution, because its major form at

these conditions is neutral H$_3$AsO$_3$. Moreover, the same experiments carried out with non-functionalized graphene showed that maximum recoveries of As^{V} were less than 35%. A similar separation scheme for speciation analysis of Cr in water samples by column SPE using oxidized MWCNTs has been proposed by Yu *et al.*[93] After adjustment of pH at 4.0, sample was passed through the column, Cr^{III} was quantitatively retained, then eluted with 10% (v/v) HNO$_3$ and measured by FAAS. The concentration of Cr^{VI} was determined according to the strategy S1a after conversion of Cr^{VI} to Cr^{III} by preliminary treatment of parallel sample with hydroxylamine hydrochloride solution.

The mechanism of separation is commonly based on electrostatic interactions, therefore the optimal pH of sorption media should be carefully defined and controlled taking into account surface properties and species distribution at different pH values. In many instances, the analytes which have to be separated and/or preconcentrated are anionic, so on the sorbent surface are reasonably grafted functional groups which can be easily protonated by simple pH adjustment. Such type of sorbent materials were made by modification of MWCNTs with 3-(2-aminoethylamino) propyltrimethoxysilane[97] and polyethyleneimine[98] and successfully applied for simultaneous multielemental speciation of As^{V}, Cr^{VI}, Se^{VI} and As^{V}, respectively. Y.-K. Tsoi *et al.*[95] have demonstrated utilization of activated carbon modified with tetrabutylammonium hydroxide as an anion exchanger for concurrent preconcentration of selenate and selenite before their chromatographic separation and determination. If the target species are cationic, their selective adsorption can be also achieved by immobilization of suitable molecules on the carbon surface. In this manner MWCNTs coated with di-(2-ethyl hexyl)-phosphoric acid[100] and L-tyrosine[101] were exploited for speciation analysis of Cr^{III} and Tl^{III}, respectively.

Islam *et al.*[102][97] have developed analytical procedure for sequential determination of Cr species in water samples by FAAS after dispersive magnetic SPE using graphene oxide decorated with magnetite modified with triethylenetetramine. Initially the retention of Cr^{VI} was accomplished at pH 2, the sorbent particles were magnetically separated and treated with 5 mL of 2 M NH$_3$. Then Cr^{VI} was measured in the eluate solution obtained, while the effluate was tunned to pH 8 and Cr^{III} was extracted and quantitatively determined as was stated in strategy S2a. The surface functionalization considerably improve extraction efficiency of carbon-based sorbent materials as well as increase their hydrophilicity.[90,103]

On the other hand, the widely used acid treatment is mainly resulted in formation of hydroxyl groups while carboxylation usually requires stronger oxidizers such as hydrogen peroxide, potassium permanganate, ammonium persulfate, etc. which could seriously damage the structure of nanoparticles.[103][98] Moreover, using of functionalized carbon-based materials as adsorbents is often followed by need of more acidic eluent solutions compared to unmodified CBNM.[104][99] A possible way to overcome such obstacles is the retention of target analytes as neutral chelate complexes onto the surface of non-functionalized SWCNTs,[105] MWCNTs,[104,106,107] fullerenes,[107-109] graphene.[110] The most frequently used ligands reported in the literature are ammonium pyrrolidinedithiocarbamate (APDC)[104-106,110] and sodium diethyldithiocarbamate (NaDDC).[107-109] Despite using of chelating agents, in some cases oxidized CBNM are preferred mainly due to their better dispersion in water samples.[92,95]

From an analytical viewpoint, CBNM-assisted speciation analysis of trace elements is mostly carried out in agreement with Strategy S1. According to the literature, this approach finds a large number of applications in speciation analysis of As,[96-98,104,111] Sb,[104,105] Cr,[93,106,112] Se,[95,110] and Tl[113] in environmental and biological samples (see Table 5). A. Afkhami et al.[114] have developed

unconventional analytical scheme for determination of selenate and selenite in natural waters after their selective reduction and collection on activated carbon (AC). Initially Se^{IV} was reduced to elemental Se by L-ascorbic acid and then determined spectrophotometrically as a result of its accelerating effect on the oxidation reaction of methyl orange with bromate in acidic media. At the second stage total amount of Se^{IV} and Se^{VI} were collected on AC after their reduction by hydrazine and concentration of Se^{VI} was calculated as a difference. The same extraction procedure was used by Bertolino et al. to determine selenate and selenite in water samples by square-wave voltammetry.[115]

Based on speciation strategy S2b, analytical procedures for As[92] and Cr[94] speciation in natural and waste water samples were realized by using of carbon nanofibers and SWCNTs, respectively.

Carbon-based nanomaterials are also used as an effective adsorbents for preconcentration of Hg,[107,108] Sn,[107,109] Pb,[107] and Se[99] species in environmental samples before their chromatographic separation and determination. Applications of CBNM in trace elements speciation analysis are summarized in Table 5.

Table 5 Carbon based materials for speciation analysis

Species	Sorbent	Modification or chelating agent	Analytical technique	Sample	EF	RSD, % (at conc. µg L^{-1})	LOD µg L^{-1}	Ref.
As^{III}	SWCNTs	APDC	HG-DC-AFS	Natural waters	25.4	4.2 (0.5)	0.0038	105
Sb^{III}					24.6	4.8 (0.2)	0.0021	
As^{III}	MWCNTs	APDC	ET-AAS	Tap, natural and bottled mineral water	250	3.5 (1.0)	0.02	104
Sb^{III}					250	3.7 (1.0)	0.05	
As^{III}	Carbon nanofibers	Oxidized	ICP-MS	Ground and lake waters	33	2.6 (1.0)	0.0045	92
As^{V}		APDC			-	1.9 (1.0)	0.240	
As^{III}	Graphene oxide	Mercapto-modified	TXRF	Natural waters	150	6.9 (4)	0.064	111
As^{V}	MWCNTs	Modified with BPEI	HG-AFS	Snow and rain water	16.3	3.6 (0.5)	0.014	98
As^{V}	MWCNTs	Modified with AAPTS	ICP-MS	Lake, river and rain water	10	7.4 (1)	0.015	97
Cr^{VI}						2.4 (1)	0.038	
Se^{VI}						6.2 (1)	0.016	
As^{V}	Nanoporous graphene	Carboxilated surface	FI-HG-AAS	Drinking, river, tap and waste water; serum, urine	50.3	3.1 (0.5)	0.0021	96

Cr^{VI}	Graphene oxide	Decorated with magnetite modified with triethylene- tetramine	FAAS	Tannery wastewater, river and industry water	10	2.99 (100)	1.4	116
Cr^{III}					10	3.36 (100)	1.6	
Cr^{III}	MWCNTs	Oxidized with conc. HNO3	FAAS	Natural water	22	1.7 (30)	1.15	93
Cr^{III}	MWCNTs	Impregnated with D2EHPA	ICP OES	Tap, well and industrial wastewater	60	< 10 (0 - 25)	0.05	112
Cr^{VI}	MWCNTs	APDC	FAAS	River and tannery wastewater	100	< 9 (50 - 200)	0.9	106
Cr^{III}	SWCNTs	Oxidized	ICP-MS	Natural and wastewater	63	2.1 (1.0)	0.01	94
Cr^{VI}						4.0 (1.0 ng)	0.024	
Hg^{II}	Fullerene C_{60}	NaDDC	GC-MS	Drinking, river, rain, sea and wastewater	250	6.3 (0.050)	0.001	108
MeHg						7.0 (0.050)	0.0015	
EtHg						7.6 (0.050)	0.0015	
Hg^{II}	MWCNTs	NaDDC	GC-MS	Water and coastal sediments	165	< 6.5 (0.1)	0.004	107
MeHg						< 6.8 (0.1)	0.003	
EtHg	C_{60} and C_{70}					< 7.2 (0.1)	0.003	
Sn^{IV}	Fullerenes					< 6.1 (0.1)	0.002	
MBT						< 7.1 (0.1)	0.003	
DBT						< 5.9 (0.1)	0.0033	
TBT						< 7.0 (0.1)	0.002	
TML						< 6.2 (0.1)	0.001	
DML						< 6.2 (0.1)	0.002	
TEL						< 6.0 (0.1)	0.001	
DEL						< 6.3 (0.1)	0.003	
Se^{IV}	Activated carbon	-	Spectropho- tometry	River and well water	50	< 7.1 (0.4-20)	12	114
Se^{IV}	Activated carbon	-	OSWV	River water	400	< 5.3 (0.4-20)	4	115
Se^{IV}	Graphene	APDC	EDXRF	Tap, lake, sea	1013	5.1	32	110

				waters				
Se^{IV}	Activated carbon	Modified with TBAH	LC-ICP-DRC-MS	Environmental waters	76	< 5 (0.05-10)	2.2	99
Se^{VI}					93	< 4.3 (0.05-10)	1.9	
Se^{IV}	MWCNTs	Oxidized APDC	XRF	Water and biological samples	-	3.2 (50)	60	95
MBT	Fullerene C$_{60}$	NaDDC	GC-MS	Marine sediments	-	7 (1)	7	109
DBT						6 (1)	9	
TBT						7 (1)	10	
Tl^{III}	MWCNTs	Modified with L-tyrosine	STPF-ETAAS	Tap water	40	3.4 (1)	3	101
Tl^{I}	MWCNTs	Oxidized	STPF-ETAAS	Tap water	20	3.9 (0.5)	9	113
V^{V}	MWCNTs	Oxidized	ETAAS	Natural waters	20	3.3 (0.2)	19	117

3.5 Polymers
3.5.1 Functionalized polymers
Polymeric sorbents are often preferred for trace element separation/preconcentration and elemental speciation due to the lack of pH limitations (stable from pH 1 to 14), higher loading capacity and selectivity than conventional functionalized silica SPE media.[118] The absence of silanol groups results in only one predominant retention mechanism, which leads to simpler extraction protocols.[119] Generally, polymeric sorbents are produced after cross-linking copolymerization of appropriate monomers. Their separation efficiency can be significantly improved by optimization of polymerization conditions, or by post-polymerization surface or/and chemical modification. Functionalization of polymer matrix is an effective approach because the functional groups grafted onto the surface are expected to provide specific interaction with the target analyte. A summary of the reported SPE methods for separation and speciation of trace elements is presented in Table 6.

Speciation of arsenic. A miniaturized SPE procedure has been developed for ultra-trace determination of inorganic arsenic species.[120] Arsenic^{III} as pyrrolidinedithiocarbamate complex was selectively adsorbed (pH 3) on poly(hydroxyethyl methacrylate) micro beads, which were packed into a micro-pipette-tip. The adsorbed arsenic was quantitatively eluted with 700 µL 0.25 M NH$_3$. Total arsenic amount was determined after reduction of As^V to As^{III} by thiourea-HCl system.

Speciation of chromium. Various polymer sorbents were prepared and evaluated for the separation of Cr^{III} from Cr^{VI} by speciation strategy S1a. Selective separation of Cr^{III} has been achieved by its complex formation and retention on chelating resins[122] or by retention of preliminary formed complex (Cr^{III}-PAR) on a cross-linked polymer,[123] while Cr^{VI} remain in the solution. Alternatively Hazer *et al.*[124] prepared poly(1,3-thiazol-2-yl methacrylamide-*co*-4-vinyl pyridine-*co*-divinylbenzene) and used them for the selective sorption of Cr^{VI} from aqueous solution. The total chromium was determined after the oxidation of Cr^{III} to Cr^{VI} by potassium permanganate.

A flow injection system with dual mini-columns packed with two cross-linked polymers – polymethacrylic acid and polyvinylimidazole and coupled to FAAS has been developed for selective retention and determination of Cr^{III} and Cr^{VI} in waters.[124] Analogous flow injection analytical procedure has been proposed from Şahan *et al.*[125]: poly 2-(5-methylisoxazol) methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinyl-benzene and Dowex 21K resins were used as chelating and ion-exchange materials for the separation/preconcentration of Cr^{III} and Cr^{VI} ions, respectively. A novel, simple and rapid method based on speciation strategy S4 was developed for the speciation of Cr in wastewater samples by short-column HPLC-ICP-MS. Both Cr^{III} and Cr^{VI} have been retained on an anion exchange column (packing material, N,N-bis(2-aminoethyl)ethane-1,2-diamine functionalized polystyrene) after transforming the cationic Cr^{III} to an anionic [Cr^{III}-EDTA] complex and then eluted rapidly (within seconds) with a very low concentration of tetrabutylammonium hydroxide solution and quantified by ICP-MS.[126]

Speciation of mercury. A new polymeric material highly specific toward both Hg^{II} and MeHg was synthesized and incorporated in effective SPE scheme for Hg speciation.[127] The polymer was prepared after copolymerization of a vinyl derivative of 8-hydroxiquinoline with 2-(methacryloylamino) ethyl 2-methyl acrylate. This sorbent enabled the separation of both mercury species (Hg (II) and MeHg) by using speciation strategy S3: first, inorganic mercury was completely recovered after elution with 3 mL of 2 M HCl in methanol and second, methylmercury was eluted with 5 mL of NaClO 20% in 1 M HCl. The proposed analytical procedure is cheap, fast, and easy to use.

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Table 6 Application of polymeric sorbents for elemental speciation by SPE

Species	Sorbent	Sample	Analytical technique	Sorption capacity, mg g^{-1}	EF	RSD, % (at conc. µg L^{-1})	LOD µg L^{-1}	Ref.
As^{III}, As^{V}	poly(hydroxyethyl methacrylate)	drinking water, snow and reference water	GFAAS	4.1 As^{III}	86	4 (0.5)	0.01	120
Cr^{III}, Cr^{VI}	poly(N,N'-dipropio-nitrile methacryl-amide-co-divinyl-benzene-co-2-acrylamido-2-methyl-1-propanesulfonic acid)	spiked water and food samples	FAAS	12.1 Cr^{III}	150	2.0	1.11	121
Cr^{III}, Cr^{VI}	β-Cyclodextrin cross-linked polymer	environmental water samples	GFAAS	0.03 Cr^{III}	25	2.5 (30)	0.056	122
Cr^{IV}, Cr^{III}	poly(1,3-thiazol-2-yl methacrylamide-co-4-vinyl pyridine-co-divinylbenzene)	stream water, wastewater	FAAS	80.0 Cr^{VI}	30	1.0 (300)	2.4	123
Cr^{III}, Cr^{VI}	poly(methacrylic acid) and poly-(vinylimidazole) cross-linked with EGDMA	tap, mineral and lake waters	FAAS	1.41 3.26	47.3 7.88	2.34 (5.0) 7.66 (5.0)	0.84 2.81	124
Cr^{III}, Cr^{VI}	poly 2-(5-methylisoxazol) methacrylamide-co-2-acryl amido-2-methyl-1-propane sulfonic acid-co-divinyl-benzene and Dowex 21K resin	tap, sea, spring, industrial waters	FAAS		48 30	2.3 (0.4) 4 (0.4)	0.05 0.3	125
Cr^{III}, Cr^{VI}	N,N-bis(2-amino-ethyl)ethane-1,2-diamine functiona-lized polystyrene	wastewater	HPLC–ICP-MS		128 105	3.6 4.3	0.004 0.007	126
Hg^{II}, MeHg	8-HQ derivate co-polymerizing with 2-(methacryloyl-amino) ethyl 2-methyl acrylate	Seawater	ICP-MS		40	–	0.01 (LOQ)	127
		Commercial fish samples	CV-AFS		-	-	0.015 mg kg^{-1}	127

3.5.2 Ion imprinted polymers

Ion imprinted polymers (IIPs) are new generation synthetic materials with artificially generated recognition sites able to specifically rebind a target ion. The synthesis approaches used for their preparation are exhaustively discussed in several reviews.[128,129] In brief, IIPs are mostly obtained by a cross-linking copolymerization of functional monomers around a template (metal ions or their complexes with specific ligands), leading to a highly cross-linked three-dimensional network polymer. Subsequent removal of the imprinted ion leaves cavities with a size, shape and chemical functionality complementary to those of the template species. When this polymer is later contacted with a solution containing different metal ions, the polymer can extract the templated ion, preferentially. High selectivity of IIPs is explained by the polymer memory effect toward the metal ion interaction with a specific ligand, coordination geometry, metal

ion coordination number, ion charge, and size. Choosing the right functional monomer and ligand is very important because this will determine, on one hand, the stability of the complex formed before and during the polymerization process and, on the other hand, the subsequent ability of the IIP to interact selectively

with the target ion. IIPs have some advantages such as stability, ease of preparation, low cost and reusability. Recently, the application of SPE with IIPs (IIP-SPE) for elemental speciation analysis attracts extensive research interest. A summary of the reported synthesis and analytical procedures for separation and speciation of chemical elements with IIP is presented in Table 7.
Speciation of antimony. A SPE method using Sb^{III}-IIP, synthesised by copolymerization of styrene and ethylene glycol dimethacrylate EGDMA in the presence of Sb^{III}-APDC complex, for the extraction and speciation of Sb combined with ETAAS has been developed.[130] The designed IIP-SPE-ETAAS procedure was applied for the speciation of the ultra trace amounts of inorganic Sb^{III} and Sb^V in natural waters. The determination of total Sb in complex matrices such as fruit juice samples is possible with developed analytical procedure.

Speciation of chromium. Different chelating reagents have been used for the synthesis of Cr^{III}-IIPs e.g. Cr^{III}–PDC complex and Cr^{III}–8-hydroxyquinoline complex as a templates and further they were incorporated in Cr speciation schemes.[131,132] The synthesized Cr^{III} IIPs showed higher selectivity towards Cr^{III} than to Cr^{VI}. Relatively fast and fully automated methods, which enabled analysis of 1 mL of sample in 4.5 min, and gave a throughput of 12 samples per hour has been developed.[132]

Several Cr^{III}-IIPs were synthesized by a surface imprinting technique[133-135]. Ion IPs prepared by this technique show many advantages including high selectivity, more accessible sites, faster mass transfer and binding kinetics, easier elution, because the imprinted cavities are located exclusively in the surface shell of the particles.[136] Zhang *et al*[133] presented surface

Cr^{III}-imprinted 3-(2-aminoethylamino)propyl trimethoxysilane functionalized silica gel sorbent as a selective SPE material for speciation analysis of Cr in environmental water samples. Due to the different mechanisms of sorption of both Cr^{III} and Cr^{VI}, the speciation analysis of Cr was performed without the use of reduction/oxidation reagent: Cr^{VI} was determined at pH 2 and total chromium – at pH 7. Sensitive and selective method for quantification of Cr^{III} and total Cr in water samples by ICP-AES with a Cr^{III}-imprinted aminopropyl-functionalized sorbent have been demonstrated.[134] Under the optimal conditions, Cr^{III} was absorbed quantitatively, but Cr^{VI} was not retained. Successful separation of Cr^{III} and Cr^{VI} has been achieved using synthesized surface Cr^{III}-IIP by an easy one step sol–gel reaction on the support of silica mesoporous material.[135]
Speciation of mercury. Mercury speciation based on IIP-SPE is usually performed by an analytical strategy S1a. Most frequently the analytical procedures developed permit separation and determination of Hg^{II} and MeHg. Various chelating agents have been used for the synthesis of the template complex of Hg(II): APDC,1-(2-thiazolylazo)-2-naphthol, dithizone, diazoaminobenzene etc. Ion IP for Hg^{II}, synthesized by copolymerizing of VP and EGDMA in the presence of Hg^{II}-diazoaminobenzene complex as a templatehas shown excellent selectivity towards Hg^{II} over mercury species as CH_3HgCl and CH_3CH_2HgCl and other alkali and alkali earth metals which normally exist in natural waters.[137] Based on the packed columns with this Hg^{II}–IIP, a highly selective SPE and preconcentration method for Hg^{II} determination from dilute aqueous solution has been developed.
Ion IPs for Hg^{II} has been prepared by cross-linking copolymerization (see Fig. 2) of methacrylic acid (MAA) and trimethylolpropane trimethacrylate in the presence of Hg complexes with two ligands: P(TAN-Hg) with 1-(2-thiazolylazo)-2-naphthol (TAN – specific chelating reagent for mercury)[138] or P(PDC-Hg) with 1-pyrrolidinedithiocarboxylic acid (PDC – non-specific reagent, forming complexes with various metals ions).[149]
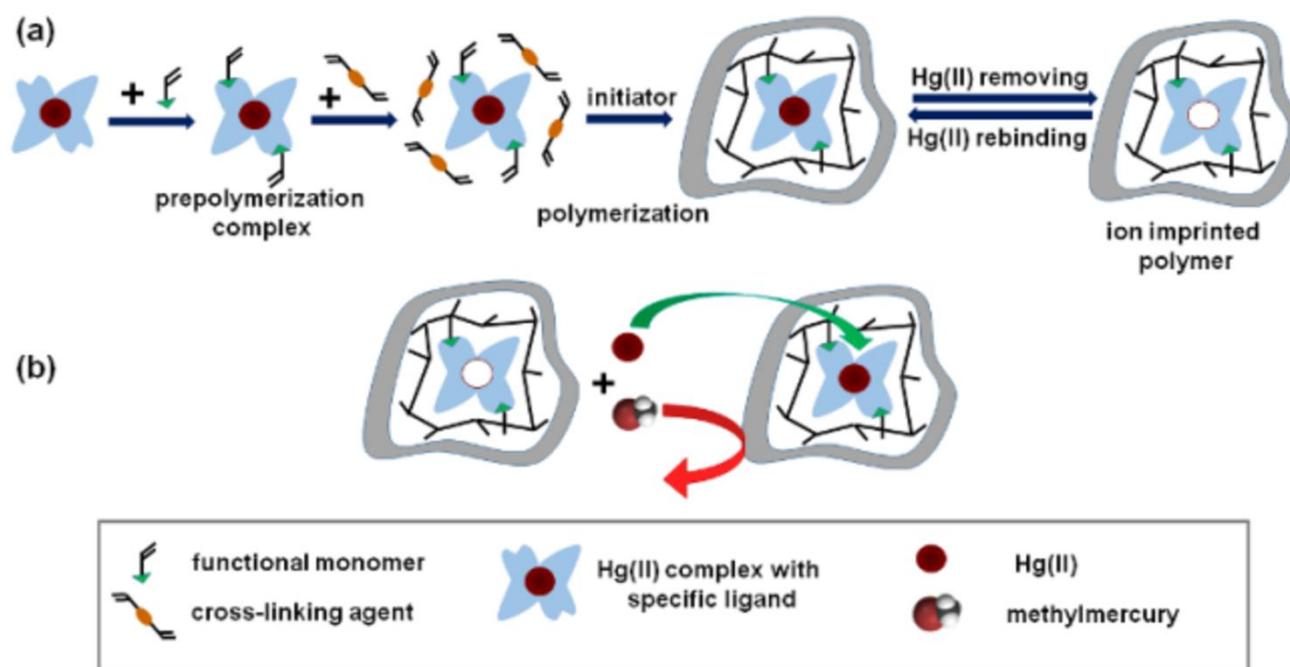
Fig. 3 Schematic illustration of the Hg(II) ion-imprinted. sorbent preparation (a) and the specificHg(II) sorption on the sorbent (b).

Both imprinted polymers, P(TAN-Hg) and P(PDC-Hg), demonstrated good selectivity toward template species Hg^{II}, which could be explained again with the assumption that configurations of ligands exhibit maximum activity for Hg^{II} complex formation because the coordination geometry is completely the same as in the complex. The optimal pH value for the quantitative sorption is 7. The P(TAN-Hg) and P(PDC-Hg) were applied for the speciation of Hg in surface waters: Hg^{II} was determined selectively in nondigested sample, while total mercury e.g. sum of inorganic and methylmercury, was determined in digested sample. A similar analytical scheme has been developed for Hg speciation analysis in wine samples by new core–shell Hg^{II} ion imprinted sorbents.[140] Recovery experiments performed for selective determination of Hg^{II} in wines showed that the interfering organic matrix did not influence the extraction efficiency when Hg-PDC complex was used as template in copolymer matrix. In comparison with other known methods for mercury determination and speciation in wine samples, the proposed method is cheaper, faster, provides comparable LODs without derivatization steps and hyphenations with GC.

Novel IIP for Hg^{II} has been prepared by a sol–gel process in the presence of dithizone–Hg^{II} chelate.[141] The optimum pH for the adsorption of Hg^{II} from aqueous solutions ranged from 7.0 to 8.0. Due to excellent selectivity of Hg^{II}–IIP toward Hg^{II} over its organic forms, Hg speciation analysis was carried out by using IIP-SPE coupled with AFS. The method developed demonstrated significant application perspectives for rapid enrichment and determination of trace Hg species in complicated matrices such as environmental and biological samples. Alternatively MeHg-IIP were synthesized by using different template complexes: monomer complex of MeHg with (4-ethenylphenyl)-4-formate-6-phenyl-2,2'-bipyridine, thermally polymerized with

divinylbenzene as crosslinker[142]; three methacryloyl-(L)-cysteine methylester monomers with one MeHg ion in a three-coordinate form.[143] Both MeHg IPs have been characterized with very high selectivity and incorporated in efficient analytical procedures for Hg speciation. Methylmercury-imprinted beads were produced by a dispersion polymerization of template complex with EGDMA as a crosslinker. Analytical procedure developed was validated by successful determination of Hg and MeHg in CRM LUTS-1 from the National Research Council of Canada and synthetic sea water using ICO-OES and HPLS-DAD as instrumental methods after SPE.

A novel adsorbent material, which contains MeHg complex with phenobarbital as a template has been synthesized by precipitation polymerization technique and has been incorporated in analytical procedure for Hg speciation by HPLC-ICP-MS according to the strategy S4.[144] Trace levels of Hg^{II}, MeHg, and EtHg have been retained on a column-packed with 200 mg of the material at pH 8.0 and at a flow rate of 2.0 ml min^{-1}. The enriched Hg species were eluted, separated on a Kinetex C18 column working under isocratic conditions and quantified by ICP-MS. The developed method was successfully applied for Hg speciation in several seawater samples from unpolluted areas.

Speciation of tin. Adsorbent, based on the imprinting technique has been synthesized for differentiation between inorganic and organotin compounds (TBT, DBT, MBT and TPhT).[145] The copolymerization was carried out in the presence of TBT (template), sodium methacrylate and cross-linker EGDMA. Tin species were quantitatively retained on this adsorbent over a wide pH range and after selective elution these compounds were determined by GFAAS. Only organotin compounds were eluted from the adsorbent with 0.1 M HCl in methanol, whereas inorganic Sn was eluted with citric acid.

The covalent imprinting approach was successfully applied for the synthesis of an IIP able to recognize organotin species.[146,147] The imprinting effect of this sorbent was evidenced within the narrow pH range 2.5–3.5, explained by a specific chemical modification, which reduces binding diversity. The IIP has been successfully evaluated in SPE procedures for the determination of organotin compounds in the certified material - mussel tissue (CRM 477) with very good recoveries.

Ion IP for Sn^{IV} has been synthesized for speciation and selective SPE of inorganic tin species from food and water samples.[148] The copolymerization of template complex (Sn^{IV}–4-(2-pyridylazo) resorcinol) was performed using MAA , EGDMA, and 2,2′ -Azobisisobutyronitrile as functional monomer, cross-linking agent, and initiator, respectively. Analytical method has been developed for selective determination of Sn^{IV} and Sn^{II} using ETAAS as instrumental method.

Table 7 Application of ion imprinted polymers for elemental speciation by SPE

Chemical species	Sorbent (template / functional monomer / cross-linker)	Sample	Analytical technique	EF	RSD, % (at conc. µg L^{-1})	LOD, µg L^{-1}	Ref.
Cr^{III}, Cr^{VI}	Cr^{III} – PDC complex / acrylamide /EGDMA	tap and river water, municipal sewage	ETAAS	10	5.8 (5)	0.018	131
Cr^{III}, Cr^{VI}	Cr^{III} – 8-HQ / styrene / divinylbenzene	CRM of waste water	FAAS	33	3.0 (2000)	2.1	132
Cr^{III}, Cr^{VI}	Cr^{III}/ 3-(2-amino-ethylamino) propyl-trimethoxysilane (on silica gel)		ICP-MS	40	4.44 (0.5) 4.41 (0.5)	0.004 0.008	133
Cr^{III}, Cr^{VI}	Cr^{III} / 3-aminopropyl-triethoxysilane on SBA-15	plating and leather wastewater	ICP-AES and UV-vis	–	<2.1 (1000)	0.53^{I}	135
Cr^{III}, Cr^{VI}	Cr^{III} / 3-aminopropyl-triethoxysilane / tetraethylorthosilicate on silica gel	lake water, tap water	ICP-AES	50	1.2 (10)	0.11	134
MeHg, Hg^{II}	MeHg / (4-ethenyl-phenyl)-4-formate-6-phenyl-2,2'-bipyridine / divinylbenzene	human hair samples	CVAAS	–	3.5	0.041	142
MeHg, Hg^{II}	MeHg / methacryloyl-(l)-cysteine / EGDMA	synthetic seawater	ICP-AES	1700 450	4.3 (50)	20 50	143
MeHg, Hg^{II}			HPLC-DAD HPLC-DAD			0.80 2.50	
Hg^{II}, MeHg, EtHg	MeHg-phenobarbital / MAA / EGDMA	seawater	HPLC-ICP-MS	50	7(0.6) 6(0.6) 5(0.6)	0.003 0.002 0.002	144
Hg^{II}, MeHg	Hg^{II}– diazoamino-benzene / VP/ EGDMA	tap water, river water, seawater	CVAAS	200	2.4 (10)	0.05	137
Hg^{II}, MeHg	Hg^{II} –1-(2-thiazolyl-azo)-2-naphthol / MAA / trimethylolpropane trimethacrylate	seawater, mineral waters	CV-AAS	–	5–9 (0.02–1)	0.006	138
Hg^{II}, MeHg	Hg^{II} – PDC / MAA / trimethylolpropane trimethacrylate	river water	CV-AAS	25	6–9 (0.03–1) 7–12 (0.03–1)	0.015 (LOQ) 0.02 (LOQ)	139
Hg^{II}, MeHg	Hg^{II} – PDC / MAA / trimethylolpropane trimethacrylate on silica gel	wine	CV-AAS.	–	6–11 (0.02–1)	0.02	140
Hg^{II}, MeHg	Hg^{II} – dithizone / 3-aminopropyltriethox	human hair, fish meat,	AFS	–	5.2 (2) 6–11(2)	0.015 0.02	141

Sb^{III}, Sb^{V}	ysilane Sb^{III}–APDC / styrene / EGDMA	seawater	ETAAS	232	3.1 (0.05)	0.004^{I}	130
Sn^{IV} Sn^{II}	Sn^{IV}–4-(2-pyridylazo) resorcinol / MAA / EGDMA	tap water, river water, food samples	GF-AAS			1.3	148
OTCs, Sn^{II}	TBT/sodium meth-acrylate / EGDMA	Sediment, sea water	GFAAS	–	<5 (0.005–0.2)	0.03 all OTCs	145
TBT, MBT, DBT, TPhT	TBT /sodium methacrylate / EGDMA	sediment and biota	LC-ICP-MS	–		LOQ: 10 all OTCs 0.004 TBT	147
		seawater	GFAAS	15			

4 Noble metal nanoparticles as optical nanosensors for trace element speciation

The unique optical properties of NM-NPs have been explored for the development of simple and fast analytical procedures for sensing of particular species of given element. The basic structure of sensor requires two components: an analyte recognizer, that binds selectively the target analyte, and a transducer, that signals this binding.

The prominent sensing approaches, supported by noble metal nanoparticles, are optical and electrochemical. The sensors employing optical feedbacks as detection signals are in the main focus of this review section,as they have wider applications in the elemental speciation.

The optical nanosensors can be classified in two main categories. The first category includes sensors based on the absorption change due to the binding of chemical species with the probe, and this absorption change could be observed by naked eyes (colorimetry) or detected by spectrophotometry. The color of plasmonic NM-NPs, such as Au-NPs and Ag-NPs, is related to the localized surface plasmon resonance phenomenon (LSPR), which occurs when the frequency of the incident light wave is in resonance with the collective oscillation of the conduction electrons of the metal. The position and intensity of this LSPR absorption band depend on the NP size and shape, as well as on the interparticle distance and surrounding environment -parameters that could be affected by the presence of analytes, which is further used for analytical purposes.

The second category includes sensors, based on the change of fluorescent signal commonly measured by fluorescence spectroscopy. The first and second types of fluorescent sensors are "on–off" (or turn-on-off) sensors, which employ an increase or a decrease of the emission intensity as a sensing signal related to the target analyte(s).

Surface enhanced Raman scattering (SERS) is a recently evolving optical modality, which is complementary to fluorescence. SERS requires the so-called SERS-active substrates, such as nanometer-sized silver or gold structures, for immobilization of the Raman reporter. The spectral change occurs upon binding with the analyte and the sensitivity and selectivity of the sensor depend on both optical reporter and nanopartricle substrate.

Analytical applications of noble metal (or noble metal shell) nanoparticles as optical nanosensors for trace element speciation are summarized in Table 8.

4.1 LSPR based nanosensors

Phosphonium ionic liquid-functionalized Au-NPs were proposed as a colorimetric probe for speciation of Asin environmental samples.[149]

Citrate capped-Au-NPs, as synthesized or functionalized with different reagents/chelating ligands (Table 8), have been most frequently used for selective Cr^{III} determination. Citrate is the preferable capping agent due to the possible coordination with Cr^{III}. In all cases, the sensing mechanism relied on the Cr^{III}-induced aggregation of surface-modified Au-NPs.[150-155 -156]

Colorimetric detection of Hg species (Hg^{II} and MeHg) has been described using Au-NPs together with a selective recognition ligand $(Cu(DDTC)_2)$.[156]Label free Ag-NPs, stabilized by gum kondagogu (GK), demonstrated high sensitivity and selectivity towards Hg^{II} without any interference from MeHg.[157] The proposed sensing mechanism is based on redox reaction between Ag-NPs and Hg^{II}.

4.2 SERS based nanosensors

A surface enhanced Raman spectroscopy cannot directly detect metal ions, but functionalization of plasmonic NPs with a ligand, that binds selectively the target metal could provide information about the chemical species. A highly sensitive SERS platform for selective detection of As^{III} in the presence of As^{V} has been reported using glutathione/4-mercaptopyridine modified Ag-NPs.[158]

The efficient speciation of Hg^{II} and MeHg has been demonstrated by using self-assembled monolayer of 4-mercaptopyridine on highly SERS-active robust hybrid plasmonic materials formed by a dense layer of interacting Au-NPs anchored onto polystyrene microbeads.[159]

4.3 Fluorescence-based nanosensors

Selective determination of Cr^{III} and Cr^{VI} in environmental water samples has been achieved for the first time by target-induced fluorescence quenching of glutathione-stabilized gold nanoclusters (NCs).[160] The speciation analysis of Cr^{III} and Cr^{VI} was based on the pH dependent fluorescence quenching capabilities of Cr^{III} and Cr^{VI}.

The feasibility of the method was approved by analysis of tap water and effluent water samples.

A fluorescence-based method using unmodified citrate-capped Au-NPs has also been reported for the determination of both Cr^{III} and Cr^{VI} in aqueous solutions.[161] Complexation of Cr^{III} with the AuNPs triggers the instantaneous aggregation, leading to the quenching of the fluorescence emission and a red-shifting of the fluorescence emission peak, which is proportional to the concentration of Cr^{III}.

Table 8 Applications of noble metal (or noble metal shell) nanoparticles as nanosensors for selective determination of chemical specie

Species	Type of NM-NPs	Functionalization	Method/Signal	Sample	LOD, µg L^{-1}	Ref.
As^{III} Total As	AuNPs	tetradecyl trihexylphosphonium chloride [C14(C6)3P]Cl] (Triton X-114)	UV-Vis/SPR band intensity	Certified reference water Ground water Lake water	7.5 As^{III}	149
As^{III} As^{V}	AgNPs	glutathione/4-mercaptopyridine (4-MPY-Raman reporter)	LRS/ SERS signal intensity	Drinking water	0.76	158
Cr^{III} Total Cr	AuNPs Citrate-capped	-	UV-Vis/SPR band intensity	Tap and river waters	15.6	150
Cr^{III} Cr^{VI}	AuNPs Citrate-capped	Tween 20	UV-Vis/SPR band intensity	Tap and river waters	0.83 0.47	151
Cr^{III}	AuNPs Citrate-capped	5,5'-dithiobis (2-nitrobenzoic acid)	UV-Vis/SPR band intensity	Standard aqueous solution	93.6	152
Cr^{III} Total Cr	AuNPs Citrate-capped	5,5'-dithiobis (2-nitrobenzoic acid)	UV-Vis/SPR band intensity HRS/HRS intensity	Vitamin supplements	20 0.025	153
Cr^{III}	AuNPs Citrate-capped	O-phospho-l-serine dithiocarbamic acid	UV-Vis/SPR band intensity	Lake water	0.22	155
Cr^{III}	AuNPs Citrate-capped	5-thio-2-nitrobenzoic acid and horseradish peroxidase	UV-Vis/SPR band intensity	Mineral, tap and lake waters	2.1	15
Cr^{III} Cr^{VI}	AuNPs Glutathione-stabilized	-	FS/FS intensity quenching	Tap water Effluent water	130 Cr^{III} 26 Cr^{VI}	160

Cr^{III}	AuNPs	-	FS/FS intensity quenching	Tap and lake waters	5.2 Cr^{III}	161
Total Cr	Citrate-capped					
Hg^{II},MeHg	AuNPs	Cu-DEDTC	UV-Vis/SPR band intensity	Drinking water	2.0 Hg^{II}	156
PhHg, EtHg	Citrate-capped				3.2 MeHg	
Hg^{II}	AgNPs	-	UV-Vis/SPR band intensity	Ground water	10 (LOQ)	157
	Gum kondagogu-stabilized					
Hg^{II}	AuNPs/PSbeads	4-Mercaptopyridine	UV/SERS signal intensity	Drinking water	0.1 Hg^{II}	159
MeHg					1.5 MeHg	

5. Conclusions and perspectives

The speciation analysis although well-established research field for almost last 20 years is still an analytical challenge. The analytical procedures developed should ensure accurate results for as many as possible species of the chemical elements in the sample, at as lower as possible detection limits and in the same time the analytical method has to be green, rapid and cheap. The separation stage as a core of these methods is the most critical step and should be characterized with high efficiency and selectivity, combined with suitability for next instrumental detection of the separated chemical species. Nanoparticle-assisted trace element speciation as an emerging topic might be accepted as a reliable answer of these requirements. The nanomaterials with their high chemical activity, high adsorption capacity and fast adsorption kinetics, unique catalytic and optical properties are in the base of new, innovative approaches for speciation analysis. The well-known strategies like selective sorption/selective elution of particular chemical species, selective redox reactions and complexation were upgraded and improved in terms of higher efficiency, sensitivity and selectivity due to the application of new nanomaterials. Even more, in order to enhance the performance of nanoscale materials, a modification with functional groups specifically binding to target metal species or additional functionalization or chelation has been introduced as effective strategies. The main drawbacks, regarding the effective application of nanomaterials, are connected with their low mechanical and chemical stability in the presence of real complicated matrices. Routine sensor applications for the most of

described analytical procedures are limited due to the relatively high detection limits achieved, much higher than relevant environmental concentrations. A serious restriction for practical employment of some nanocomposite materials is their very complicated synthesis procedure consisting of several steps, which are difficult to repeat properly. The idea to combine advantages of different types of nanomaterials does not always resulted in a more efficient sorbent. The nanoscale structure of sophisticated nanocomposites is confirmed by different methods, e. g. transmission and/or scanning electron microscopy. However, it is well known that the micrographs are representative of previously selected areas and in the some cases, they are not valid for the whole material volume. Unfortunately, quite rarely, the repeatability of synthesis procedures and the performance of nanocomposites obtained by different batches have been tested and included in the characteristics of developed analytical procedure. The future perspective of application of nanomaterials might include several new directions:

Synthesis and application of nanomaterials as stationary phases for on-line hyphenated chromatographic/instrumental detection. Evidently, an additional surface functionalization for combined improvement of mechanical stability and chemical reactivity tuning will be required.

Synthesis and application of nanomaterials as new efficient photocatalysts for photochemical vapour generation of more hydride forming elements.

Incorporation of highly reactive nanoparticles in suitable matrices for easier handling – nanocomposite films, fibers, tubes etc. preferably by using biocompatible polymers like chitosan.

Further developments in the synthesis and application of MNPs and their nanocomposites as an example of highly simple for handling SPE procedure.

Abbreviations

AAS	Atomic absorption spectrometry
AAPTS	3-(2-Aminoethylamino) propyltrimethoxysilane
ACSP	Specific affinity chromatographic stationary phase
4-APAA	4-aminophenylarsonic acid
APTES	3-aminopropyl triethoxysilane
AE LC	Anion-exchange chromatography
AFS	Atomic fluorescence spectrometry
APDC	Ammonium pyrrolidinedithiocarbamate
Asbet	Arsenobetaine
CE	Capillary electrophoresis
CL	Chemiluminescence
CNT	Carbon nanotube;
CPE	Cloud point extraction
CRM	Certified Reference Material
CTAB	Cetyltrimethyl ammonium bromide
CV	Cold vapour

CVG   Chemical vapor generation
DBT   Dibutyltin
DDTC   Diethyldithiocarbamate
DMA   Dimethylarsinate
DMSPE   Dispersive microsolid-phase extraction
ECC   Electrokinetic capillary chromatography
EDTA   Ethylendiaminetetraacetic acid
EF   Enrichment factor
EGDMA   Ethylene glycoldimethacrylate
ETAAS   Electrothermal-atomic absorption spectrometry
EtHg   Ethylmercury
FAAS   Flame-atomic absorption spectrometry
FS   Fluorescence spectrometry
FRET   Fluorescence Resonance Energy Transfer mechanism
FI   Flow injection
GC-MS   Gas chromatography-mass spectrometry
GFAAS   Graphite furnace atomic absorption spectrometry
HG   Hydride generation
HPLC   High performance liquid chromatography
HRS   Hyper Rayleigh Scattering
HS   Headspace
4-HPAA   4-Hydroxyphenylarsonic acid,IC   Ion chromatography
ICP-AES   Inductively coupled plasma-atomic emission spectrometry
ICP-MS   Inductively coupled plasma mass spectrometry
IIP   Ion imprinted polymer
IIP-SPE   Solid phase extraction with ion imprinted polymer
IST   Intramolecular Charge Transfer mechanism
LC   Liquid chromatography;
LC-MS/MS   Liquid chromatography–tandem mass spectrometry
LLE   Liquid-liquid extraction
LLLME   Liquid-liquid-liquid microextraction
LOD, LOQ   Limit of detection, limit of quantification
LRS   Laser Raman spectrometry
LSPR   Localized surface plasmon resonance
MAA   Methacrylic acid
MBT   Monobutyltin
MCFA   Multi-commutation flow analysis
MeHg   Methylmercury
MMA   Monomethylarsonate
MNPs   Magnetic nanoparticles
MSPE   Magnetic solid phase extraction
MW   Microwave
MWCNTs   Multi-walled carbon nanotubes
NaDDC   Sodium diethyldithiocarbamate
3-NHPAA   3-nitro-4- hydroxyphenylarsonic acid
4-NPAA   4-nitrophenylarsonic acid
NP   Nanoparticle
PDC   1-Pyrrolidinedithiocarboxylic acid
PET   Photo-induced Electron Transfer mechanism
PhHg   Phenylmercury
RSD   Relative standard deviation
SDME   Single-drop microextraction
SeCys   Selenocystine
SeMet   Selenomethionine
SERS   Surface enhanced Raman spectroscopy
SPE   Solid phase extraction
SWCNTs   Single-walled carbon nanotubes
OTCs   Organotin compounds
TBAH   Tetrabutylammonium hydroxide
TBT   Tributyltin

TPhT   Triphenyltin
TXRF   Total reflection X-ray fluorescence
UV-Vis   Ultraviolet-visible spectrometry
VG   Vapour generation.

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