



# Magnetic graphene oxide as a valuable material for the speciation of trace elements

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## ABSTRACT

Magnetic solid phase extraction (MSPE) has been explored for the application in preconcentration processes to achieve highly sensible analytical methods. Attending to the different magnetic adsorbent materials used in this field, functionalized magnetic graphene oxide (MGO) has proven to be effective for selective analysis and speciation of metals, metalloids, and derivatives in combination with several analytical techniques. Despite the increasing number of articles on speciation of trace elements using functionalized MGO as solid phase adsorbent, there are no dedicated reviews that cover the application of this novel nanomaterial, being this work pioneer in this area. This article provides a comprehensive review of the relevant literature related to the speciation of Al, Cr, As, Se, Ag, Cd, Hg, Tl and Pb, with special focus on species determined, toxicity, MGO functionalization, analytical performance, and applications, mainly to environmental and food samples. Finally, future challenges and trends related to this topic are shown.

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## 1. Introduction

Trace elements (TEs) are present in the environment with concentrations under 0.01% or 100 mg L<sup>-1</sup>. This group includes heavy metals (density >5 g cm<sup>-3</sup> and metallic nature), metalloids and non-metals (low atomic density). While some TEs are essential for the correct metabolism function, others such as mercury and lead may be toxic or harmful to humans, even at low concentrations [1–3]. Anthropogenic activities increase TEs concentrations in the environment, being currently cause of concern [4]. Besides, these elements can present several chemical forms or compounds with different toxicities. For example, As<sup>III</sup> is considered much more toxic than As<sup>V</sup>. The different chemical forms (isotopic composition, electronic or oxidation states, inorganic complex, organometallics, etc) of a particular element or its compounds are called species [5,6], and the separate determination of them, speciation. In the speciation analysis, the modification of the species throughout the analytical process must be avoided to get a high sensibility and selectivity [7,8].

The concentration of relevant chemical species in the environment is in the ng·L<sup>-1</sup>–μg·L<sup>-1</sup> range, and these low levels make the analysis process tedious and susceptible to critical errors [9]. Real samples have very low concentrations of TEs, even lower than the detection limits of usual analytical techniques such as atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP MS). Moreover, an additional problem is samples with complex matrices. For these reasons the quantification, and even more the speciation of TEs, are very difficult processes to deal with, if only these techniques are used. To solve this, separation and preconcentration methodologies are applied prior to the determination of an analyte in real samples [10,11].

Solid phase extraction (SPE), which has been used as a sample pre-treatment for decades, is one of the most popular extraction strategies due to its advantages such as precision, automation, low consumption of organic solvents and high extraction capacity [12,13]. SPE has been previously used in combination with conventional techniques for the extraction and preconcentration of analytes prior to analysis [14]. Once the analyte has been adsorbed and separated from the matrix, the species of interest can be eluted in a reduced volume. This allows a selective extraction and preconcentration of analytes, making the procedure useful in

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complex matrices. In addition, it can be coupled with the detection techniques on-line and can be automated, reducing analysis times considerably [14,15]. Improvement in SPE techniques and the quest for new SPE adsorbents has never ceased.

Magnetic solid phase extraction (MSPE) with magnetic particles as the adsorbents is an improved SPE technique that has aroused great interest in recent years. MSPE presents reduced analysis times, less reagents consumption, and is environmentally friendly [16]. Magnetic nanoparticles (MNPs) are one of the sorbent materials commonly used due to their magnetic properties and nanometric size [17]. Compared with micrometer-sized particles, nanometer-sized particles offer a significantly higher surface area-to-volume ration and a short diffusion route, resulting in higher extraction capacity, rapid extraction dynamic and high extraction efficiencies. The most relevant MNPs are magnetite ( $\text{Fe}_3\text{O}_4$ ) and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), thanks to their biocompatibility, biodegradability, physiological and chemical stability, low toxicity, and strong magnetic response [18,19]. The use of MSPE avoids common SPE problems with other nanoparticles, such as clogging of filters. For the extraction process, MNPs are suspended in the sample containing the analyte and, after a suitable adsorption time, an external magnetic field is applied for the rapid separation of the MNPs that have retained the analyte. Then, the matrix is eliminated after decantation of the magnetic nanoparticles and subsequently the analytes are eluted with a small volume of a suitable solvent. Finally, the MNPs are separated with the aid of a magnet and the eluted species are analysed [16,20]. In addition, MSPE can be carried out automatically and on-line with the usual atomic spectrometry techniques, as the MNPs can be immobilised inside a microcolumn or a knotted-reactor with the aid of an external magnetic field during the adsorption and elution processes [21,22].

Graphene oxide (GO) belongs to the graphene-derived materials family, in fact, it is the main raw material in graphene synthesis. This nanomaterial consists in a spatial two-dimensional single-layer structure with excellent mechanical, thermal and electrical properties [23,24]. GO has a laminar structure of hexagonal lattices, formed by the bonds between  $\text{sp}^2$  carbons. This structure provides a large surface area, resulting in a high adsorption capacity of the material. Each carbon atom has also a  $\pi$  orbital perpendicular to the sheet, contributing to the existence of an electronic cloud. Various oxygen functional groups (epoxy, carbonyl, and hydroxyl) are distributed on the surface of the GO film, with carboxylic acid and carbonyl groups at the limits [25]. Functional groups with oxygen allow a stronger interaction with the adsorbed analytes, thanks to the van der Waals forces and hydrogen bonds generated. Furthermore, oxygen containing functional groups on the surface provide a hydrophilic character to the material and allow the introduction of alternative functional groups on the surface [26,27].

MNPs and GO present very good characteristics as adsorbents, but both materials present some limitations such as: aggregates formation that decrease the active surface of pure inorganic MNPs, loss of the magnetic properties when  $\text{Fe}_3\text{O}_4$  (magnetite) is oxidized to  $\text{Fe}_2\text{O}_3$  (maghemite) form, whose magnetic capacities are considerably lower [28] and the SPE process with GO is tedious, slow and requires high sample volumes [29]. The GO-MNPs coupling solves all these drawbacks. The agglomeration of nanoparticles is avoided due to their dispersion on GO, which also prevents oxidation of the MNPs with atmospheric oxygen. The extraction process is no longer tedious and takes much less time than using only GO, thanks to the magnetic separation, which means that filtering or centrifuging is not necessary. The obtained material of the GO-MNPs coupling is called magnetic graphene oxide (MGO) and presents excellent characteristics as a magnetic adsorbent for use in MSPE [30].

Despite all its advantages, MGO presents one limitation: it is not

a selective material. This fact can be easily solved by adding functional groups (GP) on the surface of the material. This functionalization will depend on the analyte to be extracted and can be highly selective towards it. A fast and selective MSPE can be achieved with functionalized MGO, without the need to carry out a sample pre-treatment [31]. The MGO functionalization reported in the literature can be carried out in two main ways. Some authors carry out a functionalization of silica-coated MNPs and subsequently disperse them on the GO film [32]. Other authors synthesise MNPs by coprecipitation on the GO and then functionalize via the carboxyl groups of the GO films [33]. A third way to synthesise the MGO is a combination of the two previous routes, achieving a higher functionalization rate by the introduction of GP into the MNPs and GO, and by the incorporation of chemical anchors between them [34].

In this review article, the main purpose is to collect the last trends in the field of speciation analysis using MGO as sorbent. A comparison and discussion of the relevant literature related to the speciation of Al, Cr, As, Se, Ag, Cd, Hg, Tl and Pb, with special focus on the determined species, toxicity, functionalization, and analytical performance of the methods and applications, mainly to environmental and food samples.

## 2. Speciation of TEs using MGO as sorbent

### 2.1. Aluminium

Aluminium is one of the most abundant elements of the Earth crust, and it can be found in plants and underground water, including drinking water. Al is usually present as oxides and aluminosilicates that are non-toxic to plants. However, as soil pH drops down ( $\text{pH} < 5$ ), Al transforms to  $\text{Al}^{\text{III}}$ , which is considered a toxic chemical easily absorbable by plants. Industrial food packaging represents 20% of Al global consumption, and industrial products and processed foods are considered a major source of Al intake and environmental contamination [35]. Besides, the composites based on the coupling of polysaccharides and aluminosilicates are considered as promising materials for the preparation of drug delivery systems [36].

The most common species are  $\text{Al}^{\text{III}}$  and organic forms such as triisobutyl aluminium (TiBA) and trimethylaluminium ( $\text{Al}_2\text{Me}_6$ ) [37]. This element can be found in low concentrations, but over 0.3% of intake is bioaccumulated in human tissues like brain or bones, producing Alzheimer, muscle fibrosis and cancer [38,39]. The toxicity of Al is dependent on the chemical form, being more toxic the aqua- or hydroxy complexes due to their lability [40]. Several analytical techniques have been previously used for Al determination: ICP OES, flame AAS (FAAS), photoluminescence, graphite furnace AAS (GFAAS), etc. [41–44]. However, prior to analysis of trace amounts, an additional preconcentration step is needed to ensure a suitable selectivity and sensitivity of the analysis.

A novel methodology for the speciation of aluminium based on a microwave assisted solid phase microextraction (MDM- $\mu$ -SPE) with detection by FAAS, was developed by Shir Khanloo et al. [37]. In this work, a magnetic graphene oxide functionalized with 4-(phenyl) methanethiol ( $\text{Fe}_3\text{O}_4@4\text{-PhMT-GO}$ ) was used as adsorbent. Inorganic aluminium was adsorbed by this material, and only  $\text{Al}^{\text{III}}$  was determined when a non-digested sample was analysed. In order to determine total aluminium (organic and inorganic), the samples were digested at pH 6 prior to analyse, and the concentration of organic aluminium could be obtained by subtracting the inorganic to the total (Fig. 1). The selectivity of the material can be explained by electrostatic interactions of thiol groups (C-SH) and Al. Under acid conditions ( $\text{pH} < 6$ ), thiol groups are protonated ( $\text{C-SH}_2^+$ ), then repulsions between the functional group and the inorganic species are produced ( $\text{C-SH}_2^+ \text{---} \text{Al}^{3+}$ ). On the other hand, the groups are

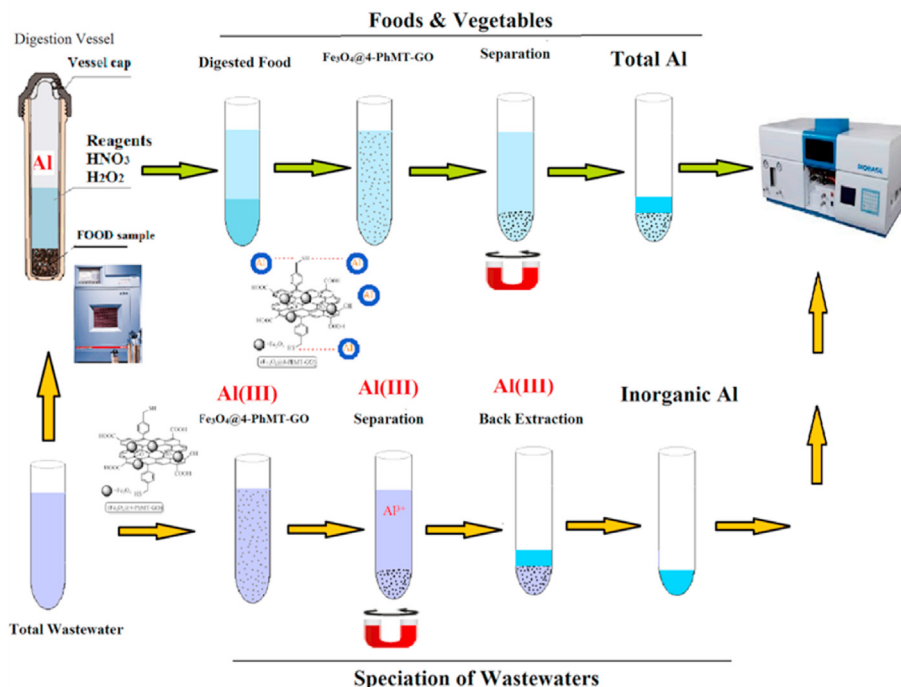


Fig. 1. MDM- $\mu$ -SPE process for the extraction and speciation of aluminium in food and water samples [37].

negatively charged when  $\text{pH} \geq 6$ , increasing the electronic interactions ( $3\text{C}-\text{S}^{2-}-2\text{Al}^{3+}$ ). The method presents an excellent analytical performance: linear range  $5-1600 \mu\text{g L}^{-1}$ , LOD  $1.5 \mu\text{g L}^{-1}$ , enrichment factor (EF) 48.8 and standard deviation 2.5% [37]. This method was applied to the speciation of aluminium traces in foods, vegetables, and wastewater with good representativity. The conclusion of this work was that foods cooked with aluminium pots or conserved in aluminium foil content more amounts of Al than those cooked with PTFE.

## 2.2. Chromium

Chromium is a worldwide TE used at the metallurgy field due to the anti-corrosive properties, being also applied in tannery, paint, and catalysis industries [45,46]. This metal can be found mostly as  $\text{Cr}^{\text{II}}$ ,  $\text{Cr}^{\text{III}}$  and  $\text{Cr}^{\text{VI}}$ , being the trivalent form the most stable one. Concerning the divalent specie, several  $\text{Cr}^{\text{II}}$  compounds exists, but they oxidize to  $\text{Cr}^{\text{III}}$  derivatives easily in atmospheric conditions, so this specie is not considered in chromium speciation analysis [47]. Then,  $\text{Cr}^{\text{III}}$  and  $\text{Cr}^{\text{VI}}$  are considered the most interesting species, which present different sources and opposite effects at the organism. Meanwhile  $\text{Cr}^{\text{III}}$  can be found naturally in minerals and plants, also can be considered an essential nutrient involved in the lipids and proteins metabolism [48,49],  $\text{Cr}^{\text{VI}}$  is primarily synthetic, useful in several industrial processes, and can be considered a human carcinogen [50]. The different behaviour of both species is due to  $\text{Cr}^{\text{III}}$  exhibits very low solubility (in its oxide form) resulting in low toxicity and mobility in the environment [51] while  $\text{Cr}^{\text{VI}}$  ( $\text{Cr}_2\text{O}_7^{2-}$ ) is a powerful oxidant with high capacity to go through biological cell membrane easily [52,53]. World Health Organization (WHO) establishes a maximum amount of total chromium in drinking water of  $0.05 \text{ mg L}^{-1}$  [54].

Diverse sources of Cr in the environment are reported, leading to a large variability of complex matrixes where this metal coexists usually at low concentrations. On this way, a previous separation step is mandatory to decrease the matrix interferences [55]. Cloud point extraction (CPE) [56], membrane extraction (ME) [57], liquid

phase microextraction [58–60], SPE [61–63], coprecipitation [64] and ionic exchange separation [65] are the most used techniques for chromium separation and preconcentration. In the bibliography, several nanomaterials based on functionalized MGO for Chromium speciation can be found with different selectivity toward  $\text{Cr}^{\text{III}}$  or  $\text{Cr}^{\text{VI}}$ . The functionalization with poly(2-aminothiazol) was applied by Sarikhani et al. ( $\text{PAT@Fe}_3\text{O}_4\text{/GO}$ ) for the extraction and removal of  $\text{Cr}^{\text{VI}}$  from water samples by MSPE prior to GFAAS detection. The presence of the polymer layer enhanced the  $\text{Cr}^{\text{VI}}$  selectivity by ionic exchange and high recovery yields for  $\text{Cr}^{\text{VI}}$  were obtained even in the presence of other potentially interferent ions. Under the optimized conditions, RSD 8.5% and LOD  $1.0 \text{ ng} \cdot \text{L}^{-1}$ , being this method successfully applied for the determination of trace  $\text{Cr}^{\text{VI}}$  in water samples [66].

Seidi et al. synthesized magnetic graphene oxide functionalized with polyaniline ( $\text{MGO@PANI}$ ), which was applied in a magnetic dispersive solid phase extraction (MDSPE) with detection by GFAAS to achieve the selective  $\text{Cr}^{\text{VI}}$  extraction. PANI has high electrical conductivity, excellent environmental stability, relatively low density, ease of preparation and low cost. This polymer can be found in three oxidation states: leucoemeraldine, pernigraniline and emeraldine. The third one is the most stable at room temperature in addition to the fact that its conductivity can be regulated by adjusting the pH (in this work the pH was adjusted to 5.6). The anionic exchange between  $\text{Cr}^{\text{VI}}$  and aniline counterion is the reason for the excellent adsorption capacity of this material. Several ions were tested as interferents and a high selectivity toward  $\text{Cr}^{\text{VI}}$  species was obtained due to the anion-exchange mechanism. The LOD and LOQ were calculated as  $5.0$  and  $15 \text{ ng L}^{-1}$ , respectively, and the developed method showed a good linear range ( $15-300 \text{ ng} \cdot \text{L}^{-1}$ ) and good precision RSD 5.3%, being applied for the analysis of water samples [67].

Kazemi et al. employed MDSPE for the separation, preconcentration and speciation of  $\text{Cr}^{\text{VI}}$  coupled to FAAS for the quantification. MGO was used due to its selectivity to  $\text{Cr}^{\text{VI}}$  at low pH, in the pH range 2.0–3.0. This behaviour is easily explained because, at acid pH, chromium forms ( $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$ ) whose negative charges

interact efficiently with the positively charged surface of MGO at this pH range. Total Cr was obtained by oxidation from Cr<sup>III</sup> to Cr<sup>VI</sup> with KMnO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>. Cr<sup>III</sup> concentration can be determined by the difference. The best eluent was found to be nitric acid in methanol. The method showed high selectivity for Cr<sup>VI</sup>. Under the optimized conditions, the method exhibited a linear dynamic range of 0.5–50.0 µg L<sup>-1</sup>, LOD 0.1 µg L<sup>-1</sup>, and RSD 3.8%. The method was successfully applied for the speciation and determination of Cr<sup>VI</sup> and Cr<sup>III</sup> in environmental water samples [68].

Recently, Cang et al. developed an ionic liquid as extractant for a MSPE coupled ICP OES method. In this work, MGO was coated with amino acid ionic liquid (Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>-GO-AAIL) for the determination and quantification of both Cr species. The extractant was selective to Cr<sup>III</sup> at pH 9, and this behaviour could be explained attending to the chemical forms of Cr<sup>III</sup> and Cr<sup>VI</sup> at pH ≥ 9, Cr(OH)<sub>3</sub> and CrO<sub>4</sub><sup>2-</sup>, respectively. Cr<sup>III</sup> interacts easily with Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>-GO-AAIL, meanwhile the anionic form suffers a strong electrostatic repulsion, being not adsorbed. First, total Cr was directly quantified without sample pre-treatment. Afterwards, the quantification of Cr<sup>III</sup> was performed by MSPE using HCl 1 M as eluent. Analytical performance under optimal conditions for Cr<sup>III</sup> and Cr<sup>VI</sup> in water samples were the following: linear range 6–650 and 3–350 µg L<sup>-1</sup>, LOD 0.406 and 0.186 µg L<sup>-1</sup>, RSD 7% and 4.9%, respectively. EF obtained for Cr<sup>III</sup> was 25.7 [69].

As can be observed in the reported methods mentioned above, chromium speciation methods were usually based on the inter-conversion between species for total quantification, obtaining the remaining one by difference. This methodology carried some drawbacks such as incomplete conversion, time consumption and contamination risk, which could affect the sample preparation. In order to avoid these problems, a novel MSPE-FAAS method was developed by Islam et al. The sorbent used for this purpose was MGO functionalized with triethylenamine (mf-GO), whose selectivity can be switched by pH modulation. At low pH values, amine groups were protonated and interacted with Cr<sup>VI</sup> anions (available at this pH too). At neutral and basic pH, a stable chelate was formed through N atoms with Cr<sup>III</sup> ions, meanwhile the anionic form suffers a strong electrostatic repulsion. The optimal pH for Cr<sup>VI</sup> adsorption was found to be 2.0, 10 min of adsorption time, and ammonia solution was employed for the elution process. On the other hand, the optimal conditions for Cr<sup>III</sup> were pH 8.0, 30 min of adsorption time and the elution was performed with NH<sub>4</sub>NO<sub>3</sub> [70].

### 2.3. Arsenic

Arsenic is a ubiquitous element in the environment, which arises from natural and anthropogenic sources. As is considered a highly polluting metal, being harmful for human health even at low exposure levels. Some serious diseases such as diabetes and cancer are associated to the exposure of As, including neurological damage [71]. The toxicity of this element depends on the chemical form, being the inorganic species (As<sup>III</sup>, As<sup>V</sup>) 100 times more toxic than the organic species such as cacodylate, arsenobetaine (AsBet), arsenocholine and arsenosugars. Besides, inorganic trivalent form is 60 times more toxic than the pentavalent species [72–74]. The WHO guideline value for As in drinking water is 10 ng mL<sup>-1</sup> [75]. Moreover, As<sup>III</sup> and As<sup>V</sup> are the most common arsenic species in nature, being the most relevant target analytes for As monitoring [76,77]. GFAAS, ICP OES and ICP MS have been previously reported for the determination of traces and ultratracés of As in different samples [78]. However, the separation or identification of the different As species is not possible using these atomic analytical techniques, obtaining the signal of As total. In order to achieve speciation, some authors use pre-treatments to preconcentrate, separate or eliminate As species such as adsorption [79,80],

electrocoagulation [81], hydride generation [82], HPLC [83] or pH treatments [84,85].

Saçmaci et al. developed a speciation method of As<sup>III</sup> and As<sup>V</sup> in water and food samples via zeta potential analysis based on MSPE. Functionalized MGO with reduced L-Glutathione was used as adsorbent (GO/Fe<sub>3</sub>O<sub>4</sub>@GHS). This material presented high affinity towards arsenic due to the charges. The pH was studied, being As<sup>III</sup> quantitatively recovered with the magnetic nanomaterial at in 0.5–1.5 mol L<sup>-1</sup> HNO<sub>3</sub> concentration range, while As<sup>V</sup> was not quantitatively recovered at any pH. Finally, the pH was optimized, being pH 1 the best conditions to generate the highest number of bonds between the sulphur group from GO/Fe<sub>3</sub>O<sub>4</sub>@GHS and As<sup>III</sup>. For As<sup>V</sup> determination, this species was reduced to As<sup>III</sup> and analysed, obtaining the total As signal. Finally, the As<sup>V</sup> concentration was calculated by subtracting As<sup>III</sup> from total As. The optimized procedure showed an enrichment factor of 5, linear range from 0.125 to 4.0 mg L<sup>-1</sup>, LOD and LOQ were found to be 0.11 and 1.1 µg L<sup>-1</sup>, respectively, and RSD value of 1% for As<sup>III</sup> determination [72].

Nodeh et al. also reported a speciation method for the determination of inorganic As species in water. In this work, graphene oxide modified with silica coated magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/GO) was applied in a MSPE process, and ICP MS was used as detector. The pH was optimized to 4.0, and HCl was finally selected as eluent after comparing the elution capacity of this acid with other acid solutions (HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>). The system presented better adsorption efficiency towards As<sup>III</sup>, and this arsenic species was initially determined. Later, As<sup>V</sup> was reduced using L-Cysteine prior to analysis to determine total As. Finally, As<sup>V</sup> concentration was calculated by subtracting the initial As<sup>III</sup> to the total As. The reusability of the material was studied, and possible ion interferences were tested. As a result, this material can be reused 12 times, and the developed method did not suffer from interferences. Moreover, suitable RSDs (0.1–4.3%, n = 3) and extended linear calibration were obtained for both species (0.05–2.0 ng mL<sup>-1</sup>). The LODs obtained were 7.9 pg mL<sup>-1</sup> for As<sup>III</sup> and 28.0 pg mL<sup>-1</sup> for As<sup>V</sup> [86].

A novel nanocomposite based on magnetic graphene oxide was reported by Saçmaci et al. [87]. The synthesis steps are shown in Fig. 2. First, tiopronin (TSH) was used as functionalization of magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>-TSH) to improve the selectivity of the material to metal ions. Separately, GO layer was functionalized by covalent bonds with the dendrimer PAMAM-G4 (GO-PG4). The dendrimer was used due to its capacity to be functionalized through the multiple amine bonds located on its surface. Then, Fe<sub>3</sub>O<sub>4</sub>-TSH and GO-PG4 were coupled through amide bond to prepare the magnetic nanocomposite (GO-PG4@Fe<sub>3</sub>O<sub>4</sub>-TSH). As<sup>III</sup> concentration was directly measured via zeta potential analysis at pH 4.5 and using 0.2 mL HCl as eluent, while the determination of total As was carried out using KI and L-(+)-Ascorbic as reductants. This method was applied in baby food samples, presenting the following analytical performance for As<sup>III</sup> determination: linear range 0.01–5 mg L<sup>-1</sup>, LOD and LOQ 0.11 and 0.37 µg L<sup>-1</sup>, respectively, and RSD <1.6% [87].

Montoro-Leal et al. developed a MSPE method to enrich both, inorganic and organic arsenic species (AsBet, cacodylate, As<sup>III</sup> and As<sup>V</sup>) in biological samples and environmental waters [88]. A novel MGO functionalized with [1,5-bis (2-pyridyl) 3-sulfophenylmethylene] thiocarbonohydrazide (MGO-PSTH) was used as solid phase adsorbent. In this work, the simultaneous preconcentration and elution of the arsenic species was achieved using a magnetic knotted-reactor coupled with a flow injection (FI) system, while the ultra-trace separation and determination of the analytes were achieved by high performance liquid chromatography combined with inductively coupled plasma mass spectrometry (HPLC-ICP MS). When a chelating

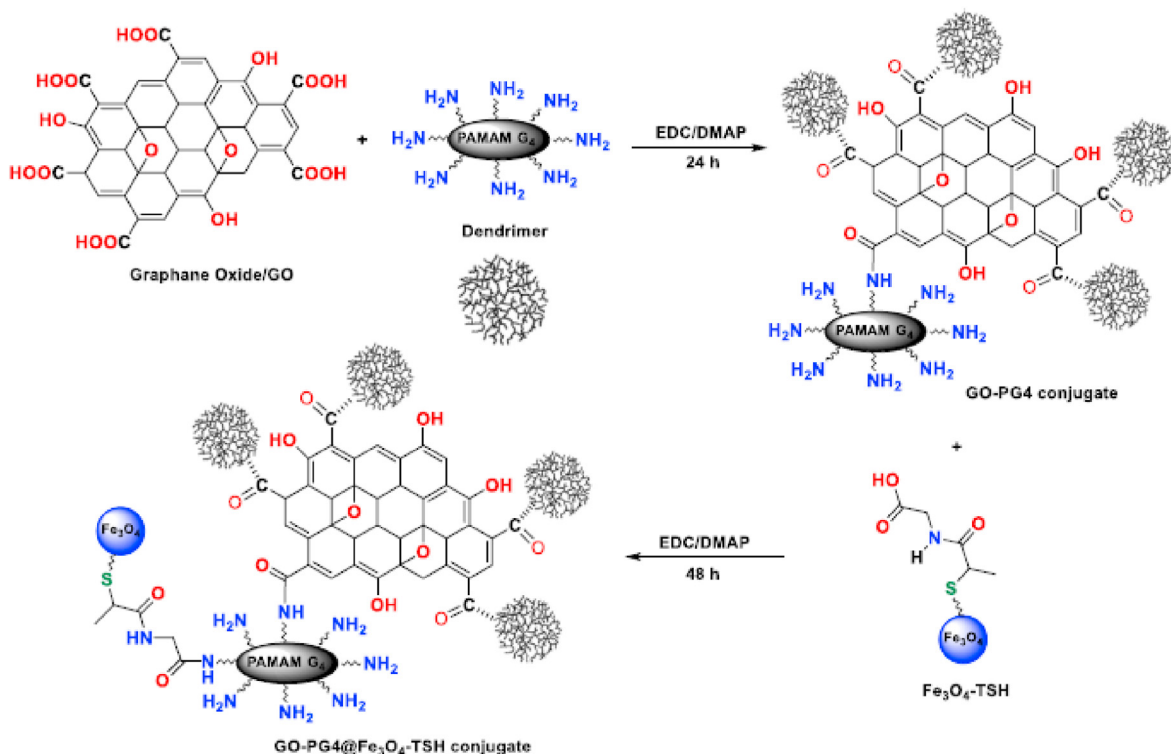


Fig. 2. Synthesis route for the preparation of GO-PG4@Fe<sub>3</sub>O<sub>4</sub>-TSH [87].

agent is used, pH highly affects the complexation of the analytes. Therefore, pH was studied in order to find the best conditions to retain the arsenic species, being finally optimized to pH 1. First, the standard or sample was introduced in the FI system at pH 1, being eluted with 0.1% m/v thiourea + 0.1% m/v L-cysteine solution in NaOH pH 12.0. Then, 1 mL of eluent was collected in a chromatographic vial, which was introduced in the autosampler of HPLC-ICP MS for the separation and determination of the species using a gradient of NaHCO<sub>3</sub> 0.005 M, Na<sub>2</sub>CO<sub>3</sub> 0.1 M and NaOH pH 12 as mobile phase. In this kind of methods, the adequate selection of the eluent/mobile phase is crucial because similar matrix solutions are necessary to ensure the compatibility of MSPE and HPLC-ICPMS systems. It was demonstrated that the adsorption process was mainly based on the formation of coordinated species of arsenic and the functional group. Under the optimized conditions, the LODs and EF for the arsenic species were 3.8 ng L<sup>-1</sup> As<sup>Bet</sup>, 0.5 ng L<sup>-1</sup> cacodylate, 1.1 ng L<sup>-1</sup> As<sup>III</sup> and 0.2 ng L<sup>-1</sup> As<sup>V</sup> with RSDs <5%. Urine, well-water, and seawater samples were analysed, showing promise for routine monitoring of arsenic species in biological fluids and environmental samples [88].

Attending to the analytical techniques, ICP MS and zeta potential were used. While better RSD values were calculated using zeta potential analysis [72,87], lower LODs and LOQs were obtained by using ICP MS [86,88]. In order to achieve inorganic arsenic speciation (As<sup>III</sup> and As<sup>V</sup>), both analytical techniques can be used, and most of the methods were also based on the interconversion between species for total quantification, or the selective adsorption of one of the species. Moreover, ICP MS can be coupled with separation modules to perform the speciation of organic and inorganic species. Therefore, atomic techniques can be considered the most suitable option to develop arsenic speciation methods.

#### 2.4. Selenium

Selenium is an essential element with antioxidant and antitumor effects [89], but the excess of this element can produce

serious damage in the organism [90]. The toxicity of Se depends on the concentration and the chemical form, being more toxic selenite and selenate than the organic compounds such as selenoaminoacids, selenopeptides, selenoproteins, etc. The separation techniques and sensitive detection are usually combined to achieve Se determination. However, when biological samples are analysed, additional preconcentration steps are needed due to the low concentration of this element [91,92]. Guo et al. reported a MSPE combined with a hole fibre liquid-liquid microextraction (HF-LLLME), using MGO (Fe<sub>3</sub>O<sub>4</sub>@GO) modified with polyaniline (PANI) and Cu<sup>II</sup> as sorbent (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PANI@GO/Cu) and ICP MS as detector. Coordinated complexes of polar selenoaminoacids and Cu<sup>II</sup> were formed, allowing the speciation [90]. In order to avoid the alteration of the sample during the preconcentration process, a solution of ethylenediamine was used as eluent. This method showed the following analytical performance for the analysis of Se compounds (SeCys<sub>2</sub>, MeSeCys, SeMet, and SeEt) in rice: linear range 158–278 μg L<sup>-1</sup>, LOD 0.0075–0.013 μg L<sup>-1</sup> and standard deviation 6.8–10.2% [90].

#### 2.5. Silver

Ag can be found in the environment as a metal ion (Ag<sup>I</sup>) and silver nanoparticles (AgNPs). When Ag<sup>I</sup> is bioavailable, the toxicity is higher than any other metal, except Hg. Besides, the AgNPs are considered an emerging pollutant widely extended in nature due to their industrial application in cosmetics, biomedicine, and food packaging [93,94], being harmful for living beings even at low concentrations [95–98]. Some studies have demonstrated that Ag<sup>I</sup> is more toxic than others chemical forms like AgNPs [95], so the determination and speciation of both is crucial to evaluate adequately the pollution caused by this element. When Ag is found in μg·L<sup>-1</sup> - ng·L<sup>-1</sup> concentration range, the analysis by standard analytical techniques such as AAS or ICP MS is not always possible [99,100]. Moreover, it is well known that the toxicity of

nanoparticles depends on the particle size, being crucial the size characterization. Single particle inductively coupled plasma spectrometry mass (SP-ICP MS) is an effective technique to determine the size distribution and particles concentration in water [101–103]. However, the discrimination of nanoparticles and solvated metals is not possible with this technique, producing the overlap of particles signal by the continuous signal of solvated ionic metal. To avoid this interference, some authors use sorbents to separate the ionic metal from the nanoparticle form [104].

Luo et al. used magnetic reduced graphene oxide (M-rGO) as sorbent to separate selectively  $\text{Ag}^{\text{I}}$  from the sample matrix, allowing the AgNPs size characterization in natural waters [105]. The 98% of  $\text{Ag}^{\text{I}}$  was eliminated in tap water, river water and wastewater, and small AgNPs (<50 nm) were adequately characterized. This method was successfully applied in tap water, river water and wastewater, eliminating the 98% of  $\text{Ag}^{\text{I}}$ . The influence of pH was studied because the properties of sorbent and the target species depended on this parameter [106]. The proposed mechanism for the adsorption was the formation of coordination complexes of  $\text{Ag}^{\text{I}}$  and the oxygen containing functional groups from M-rGO [107]. When pH was upper to 9, the adsorption increased due to the formation of  $\text{AgOH}$ , producing the deposition of this species over the surface of the material. The process for the magnetic separation of  $\text{Ag}^{\text{I}}$  and AgNPs can be observed in Fig. 3 [105].

## 2.6. Cadmium

Cadmium is a relatively low-cost metal obtained as a subproduct from copper and zinc processing. It is employed in several products such as anticorrosive materials, polymer stabilizers, dyes, and Ni–Cd batteries. In the environment, Cd is not found as a metal but forming complex oxides, sulphides and carbonates in zinc, lead, and copper ores; on the other hand, in the organism is available as  $\text{Cd}^{\text{II}}$  and organic derivatives. Cadmium easily slides into organism by water, food or air (being smoking one of the main sources) and interacts with proteins, enzymes and sulphur-derivative biological structures [108–112]. At human matrixes, such as blood, serum and urine; cadmium organic derivatives are formed by linking of Cd to some molecules as glutathione (GSH–Cd), cysteine (Cys–Cd), metallothionein (MT–Cd) and acetate (AC–Cd) [108–110]. Usually cadmium is carried to liver, kidney, brain, and bones. The presence of this metal in the organism could develop several diseases like multiple sclerosis, liver dysfunction, lung cancer, and osteoporosis

[113,114].

As different Cd organic derivatives can be found in the organism, the development of speciation methods is crucial. To achieve this goal, Khaleghi et al. designed a new ultrasound-assisted dispersive magnetic micro solid-phase extraction (USA-DM- $\mu$ -SPE) method, coupled to a GFAAS for the quantification step. The SPE was developed with a naphthalene-1-thiol functionalized GO, modified with magnetite MNPs ( $\text{Fe}_3\text{O}_4@\text{NpSH-GO}$ ). The optimal pH found was settled at 6.0, allowing covalent interactions between  $\text{Cd}^{\text{II}}$  and thiol groups from the sorbent. Besides, organic derivatives such as Cys–Cd or GSH–Cd in blood samples were not extracted by thiol groups from  $\text{Fe}_3\text{O}_4@\text{NpSH-GO}$ . In order to obtain total Cd concentration, organic Cd was transformed into inorganic Cd by acid digestion, performed at high temperatures so, total Cd was afterwards extracted by USA-DM- $\mu$ -SPE and determined. Organic Cd was obtained by difference, and the analytical process is shown in Fig. 4. This way, the analytical performance, working with the optimal conditions for Cd speciation in blood samples were the following: linear range 30–1520  $\text{mg L}^{-1}$ , LOD 10  $\text{ng L}^{-1}$ , enrichment factor 4.88 and RSD 1.1%. This method was successfully applied with rapid separation (4 min), repeatability, low LOD, efficient extraction and high recuperation rate [112].

## 2.7. Mercury

Mercury is one of the most toxic pollutants in the world which arises from anthropogenic and natural sources [115]. When humans are exposed to this element, serial damage is caused to vital organs such as brain, heart, stomach, kidneys, and lungs even at trace concentration [116]. The toxicity, solubility and bioavailability of Hg depend on the chemical form, being elemental ( $\text{Hg}^0$ ), inorganic ( $\text{Hg}^{\text{I}}$  y  $\text{Hg}^{\text{II}}$ ) and organic mercury species such as methylmercury ( $\text{MeHg}^{\text{I}}$ ), ethylmercury ( $\text{EtHg}^{\text{I}}$ ), phenylmercury ( $\text{PhHg}^{\text{I}}$ ) the most common Hg species in the environment [117,118].  $\text{MeHg}^{\text{I}}$  is considered the most dangerous species of mercury due to the liposolubility, bioaccumulation, neurotoxicity, and its easy transmission through the human food chain [118]. Besides, inorganic mercury can transform into  $\text{MeHg}^{\text{I}}$  in environment. The maximum Hg concentration allowed in surface water by the European Union is 0.07  $\mu\text{g L}^{-1}$  [119]. Therefore, the development of simple and sensitive analytical methods for the determination of traces and ultratraces of Hg in wastewater, environmental samples and food is crucial [119,120]. Cold vapor coupled with atomic spectrometry

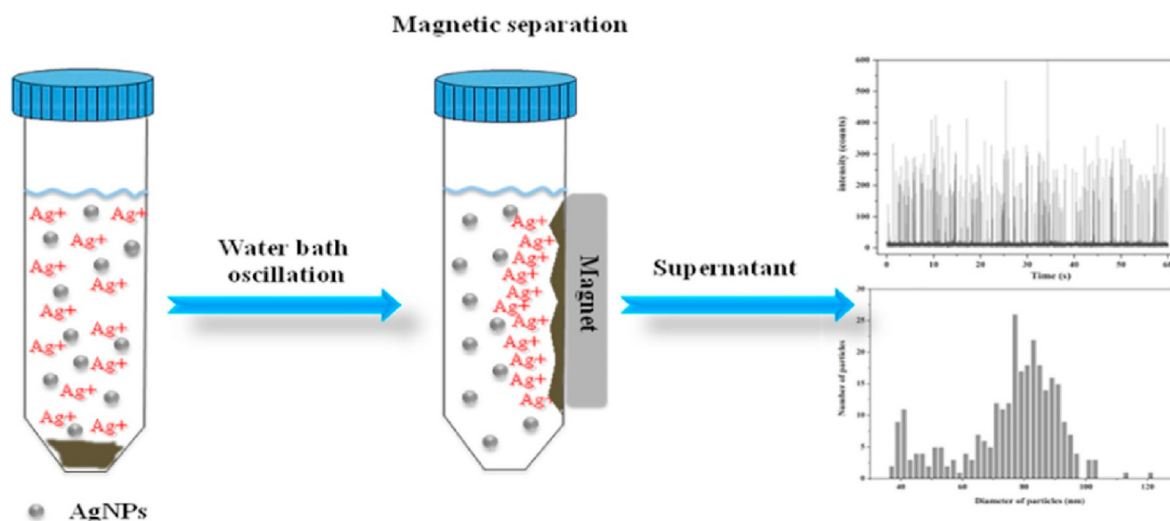


Fig. 3. Magnetic solid phase extraction process for the separation of  $\text{Ag}^{\text{I}}$  and AgNPs in water samples [105].

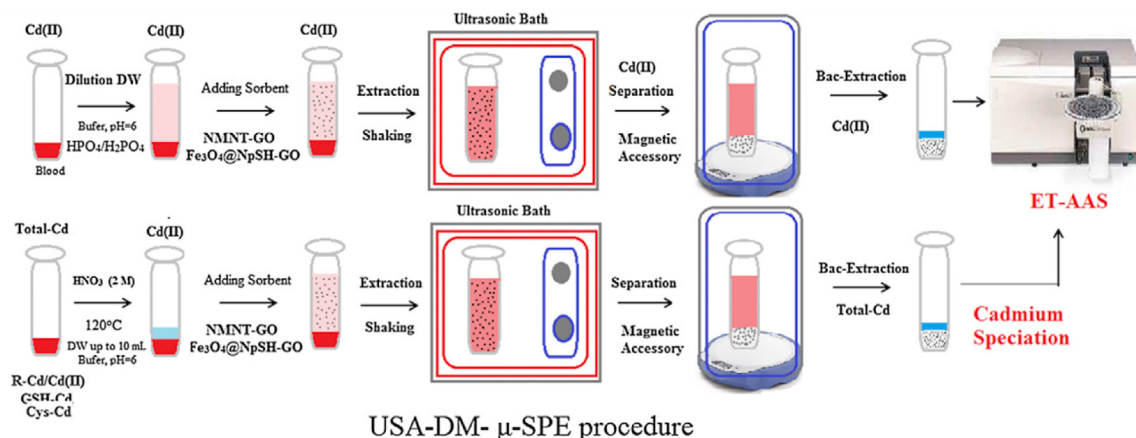


Fig. 4. Cadmium speciation in blood samples by USA-DM-m-SPE applying Fe<sub>3</sub>O<sub>4</sub>@NpSH-GO as sorbent [112].

(CV-AS): AAS, AFS, ICP OES e ICP MS are the most common analytical techniques used for this purpose [121–125]. However, due to the low concentration of this element and the complex matrix of several samples, additional pre-treatments are often necessary even when a sensitive technique is used [126]. Some authors have reported the application of MGO to develop MSPE methods for the preconcentration and determination of Hg [127–129]. However, the use of this kind of materials to develop a speciation method of mercury is quite recent.

A speciation method based on a MSPE prior to detection by HPLC/ICP MS was developed by Li et al. As can be observed in Fig. 5, functionalized MGO with dithizone (D@RGO-Fe<sub>3</sub>O<sub>4</sub>) was used as solid phase sorbent, retaining two species of mercury, inorganic mercury (IHg) and methylmercury (MeHg). A mix of L-Cysteine, HCl and methanol was used for the elution of the Hg species. The resultant preconcentrated solution was introduced in HPLC/ICP MS to separate and determine both, IHg and MeHg. The optimized method presented excellent analytical performance for the analysis of Hg species in water and fish samples: linear range 1.6–500, 0.6–500 ng L<sup>-1</sup>, LOD 0.48, 0.17 ng L<sup>-1</sup>, high enrichment factor 400, 380, RSD 4.2, 3.8% for IHg and MeHg, respectively [130].

## 2.8. Thallium

Thallium is a rare element that can be more toxic than arsenic, cadmium, lead and mercury [131,132]. The United States Environmental Protection Agency (EPA) has considered Tl as a dangerous

pollutant, setting a maximum permissible level of 2  $\mu\text{g L}^{-1}$  [133]. This element can be found in two oxidation states, Tl<sup>I</sup> and Tl<sup>III</sup>, being the monovalent the less toxic and the predominant form in aqueous media. The trivalent form is stable under strong oxidative conditions, but also its presence has been reported in photochemical reactions and biological processes [134]. Tl<sup>III</sup> can be stabilized by interactions with aminopolycarboxylic acids and humic species [135]. Therefore, the speciation of Tl in environmental samples is of importance [133,136]. Atomic analytical techniques such as ICP MS and GFAAS have been reported for Tl determination [137,138], and their combination with MSPE to achieve the speciation of this element [139,140]. For example, a nanocomposite based on aminodibenzo-18-crown-6 magnetite nanoparticles was applied by Rezabeyk et al. for the selective retention of Tl<sup>I</sup>, and the determination was carried out by GFAAS [139].

In the study developed by López-García et al. a composite of graphene oxide coupled with ferrite nanoparticles was prepared and used for the determination and speciation of Tl. The addition of graphene-Fe<sub>3</sub>O<sub>4</sub> composite, potassium iodide and Aliquat® 336 (a commercial mix of quaternary ammonium species in which methyltrioctylammonium represents 88–93%) into the sample at pH 2, resulted in the retention of both Tl<sup>I</sup> and Tl<sup>III</sup>. After, the material was decanted using an external magnetic field, and the retained species were eluted with sodium ethylenediaminetetracetate solution at pH 9. The addition of iodide in the extraction of total Tl is explained due to the capacity of graphene oxide to retain this halide [141], presenting a double function: facilitating the adsorption of

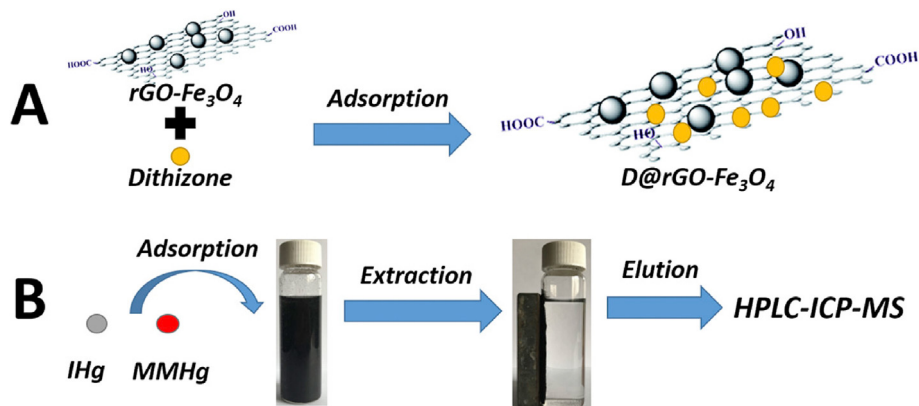


Fig. 5. Magnetic solid phase extraction of Hg species in water samples [130].

Tl<sup>I</sup>, and the reduction of Tl<sup>III</sup> to Tl<sup>I</sup> [142]. For speciation, a previous liquid-liquid extraction stage with methanol/chloroform in the presence of cetylpyridinium and bromide was carried out in a second aliquot of the sample to retain the trivalent form. Then, the protocol was followed as explained above and the signal corresponding to Tl<sup>I</sup> is obtained. The concentration of Tl<sup>III</sup> is calculated by difference. This method was validated with five certified samples and real water samples were analysed, including seawater. The optimized procedure showed an enrichment factor of 185, LOD 0.01 µg L<sup>-1</sup> and the RSD <5% [143].

### 3. Trends and future challenges

The relevance of MGO for the development of MSPE speciation methods is increasing, even at ultra-trace levels. However, the application of this material presents some disadvantages. As has been said before, MGO is based on the coupling of GO and MNPs, being GO normally synthesized by authors following non-green routes such as Hummer's or modified Hummer's synthesis. Long reaction times, aggressive and toxic chemicals are used often, and the fabrication of GO at industrial scale is complex and expensive. For this reason, some researchers are developing novel 2D carbon materials through more sustainable synthesis routes. For example, mechanochemical milling has been recognized as a viable approach to quickly promote reactions of solids, without added solvents or only under substoichiometric amounts. Research groups have already applied mechanochemical methods to produce GO from graphite with a lower environmental footprint [144,145]. Ahmad et al. also proposed the preparation of ultra-thin carbon sheets from waste, using onion covers as carbon source and no need for solvents (Fig. 5). This novel material was applied for the adsorption of arsenic species [146]. Therefore, a future challenge would be the preparation of alternative materials for the substitution of GO as sorbent, using new 2D materials with similar properties and fabricated through rapid, simple, cheap, and environmentally friendly synthesis routes. Besides, Daneshvar et al. also proposed the use of IL to functionalize the material due to their stability

under strict chemical and thermal conditions, low vapor pressure and no flammable, being environmentally friendly compounds [147].

Other improvements that some authors are trying to implement are related to the experimental procedure of speciation. There are mainly four speciation procedure (P1, P2, P3 and P4), which are shown in Fig. 6. As can be observed in this work, P1 and P2 are the most general procedures, where just one of the chemical forms of the analyte is adsorbed. For the determination of the other chemical form, this second one is turned into the detectable form and the analysis is performed to obtain the total concentration. Then, in order to calculate the concentration of the non-detectable species, the concentration of one analyte is subtracted to the total concentration. The strategy P3 shows an alternative to carry out the speciation. In this case, all species are retained and eluted simultaneously in the MSPE system, which is combined with separation techniques like HPLC to achieve speciation. In P4, the chemical forms are also retained simultaneously, but the analytes are eluted separately using different eluent solutions. This last alternative is difficult to develop because high selectivity of the chosen solution to elute each analyte is needed. However, M4 is also the most effective, simple, and rapid procedure, because interconversion of one chemical form in another or the use of additional analytical instrumentation is not necessary. Therefore, the errors caused by conversion yields are avoided and the analysis time is optimized. Each species must be eluted separately, then there are the same number of analytes than elution steps. Despite not being the most extended procedure, this strategy can be more present in future research lines due to the excellent advantages.

Recently, the concept of speciation has been updated due to the presence in nature of NPs and the ions released from them. The distinction of both is crucial because NPs and the ionic form present different behaviour and toxicity. These nanomaterials arise from the industrial human activity and their use has increased in the last few years. The novelty of this research field and the lack of NPs certified samples also limit the development of these studies. However, although there is not many reported analytical methods

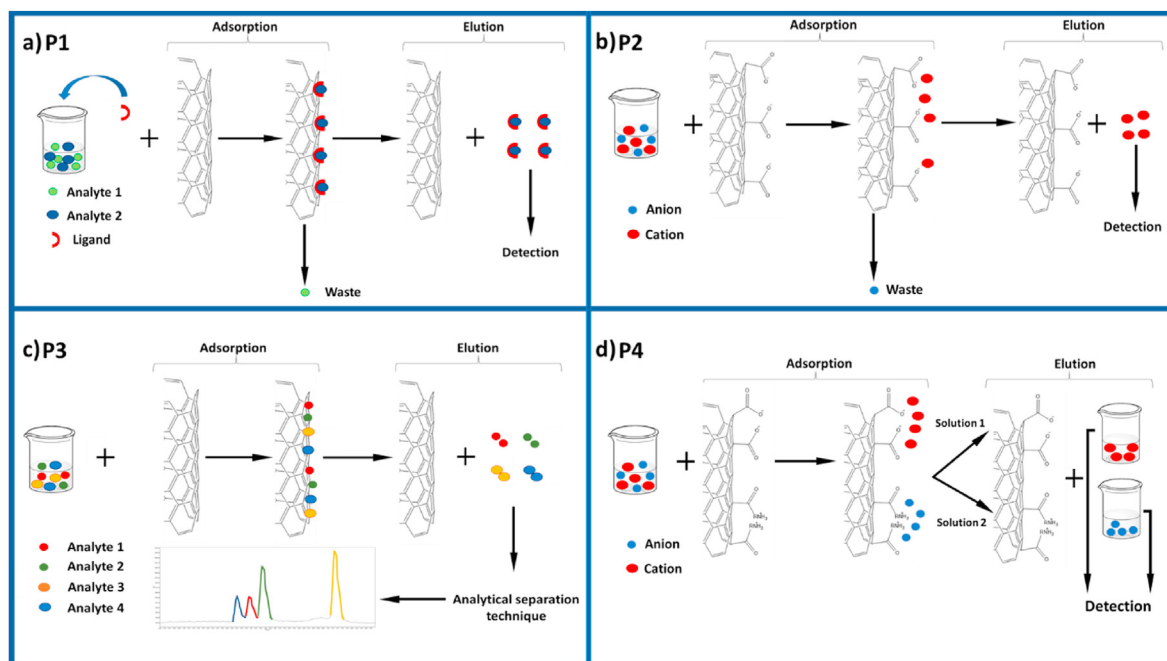


Fig. 6. Different speciation strategies a) P1, b) P2, c) P3 and d) P4.



**Table 1**  
Speciation of metals and metalloids by MSPE using MGO as solid phase adsorbent.

Material	Analytes	Technique	Samples	LOD ( $\mu\text{g}\cdot\text{L}^{-1}$ )	EF	Speciation mechanism	Ref.
Fe <sub>3</sub> O <sub>4</sub> @4-PhMT-GO	Al <sup>III</sup> /OrgAl	AT-FAAS	Wastewater, vegetables, food	1.5	48.8	P1/P2	[37]
PAT@Fe <sub>3</sub> O <sub>4</sub> @GO	Cr <sup>VI</sup>	ETAAS	Wastewater, well water, mineral water	0.001	182	P1/P2	[66]
MGO@PANI	Cr <sup>VI</sup>	GFAAS	Wastewater, river water	0.005	40	P1/P2	[67]
MGO	Cr <sup>VI</sup>	FAAS	Drinking, river and sea water	0.1	200	P1/P2	[68]
Fe <sub>3</sub> O <sub>4</sub> -SiO <sub>2</sub> -GO-AAIL	Cr <sup>III</sup>	ICP-OES	Lake water and industries effluents	0.406	25.7	P1/P2	[69]
mf-GO	Cr <sup>VI</sup>	FAAS	Environmental water	0.186	–	P4	[70]
	Cr <sup>III</sup>			1.6	10		
GO/Fe <sub>3</sub> O <sub>4</sub> @GHS	As <sup>III</sup> /As <sup>V</sup>	Zeta potential	Tap water, hot spring water, tea samples	0.1	5	P1/P2	[72]
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> /GO	As <sup>III</sup> As <sup>V</sup>	ICP-MS	spring water, lake, river, and tap water	0.0079	23	P1/P2	[86]
				0.028	23		
GO-PG4@Fe <sub>3</sub> O <sub>4</sub> -TSH	As <sup>III</sup> /As <sup>V</sup>	Zeta potential	Baby food	0.11	125	P1/P2	[87]
MGO-PSTH	As <sup>III</sup> As <sup>V</sup> Cacodylate AsBet	HPLC-ICP-MS	Urine, well-water, seawater	0.0011	6	P3	[88]
				0.0002	19		
				0.0005	12		
				0.0038	4		
				0.013	29		
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PANI@GO/ Cu	SeCys, MeSeCys SeMet SeEt	HPLC-ICP-MS	Rice, yeast cells	0.011	22	P3	[90]
				0.0085	29		
				0.0075	38		
				<50 nm <sup>a</sup>	–		
M-rGO	AgNPs	SP-ICP-MS	Tap water, river water and wastewater	0.01	4.88	P1/P2	[105]
Fe <sub>3</sub> O <sub>4</sub> @NpSH-GO	Cd <sup>II</sup>	GFAAS	Blood	0.00048	400	P1/P2	[112]
D@RGO-Fe <sub>3</sub> O <sub>4</sub>	IHg MeHg	HPLC-ICP-MS	Fish, river water, ground water, sea water and sewage effluents	0.00017	380	P3	[130]
				0.01	185		
GO-Fe <sub>3</sub> O <sub>4</sub>	Tl <sup>I</sup> /Tl <sup>III</sup>	ETAAS	Bottled water, rain, surface water	0.01	185	P1/P2	[143]

<sup>a</sup> Small AgNPs (<50 nm) were characterized following the analytical procedure.

dedicated to this kind of speciation, nanomaterials based on electrostatic interactions have been applied. For example, it has been pointed out that MGO is an adequate material in this field because the Ag<sup>I</sup> and AgNPs speciation has been already achieved using this material as solid phase adsorbent [105]. A future challenge would be the application of MGO in speciation studies on NPs other than AgNPs. Finally, a miniaturized and semiautomated system based on MGO has been also reported in this work for arsenic speciation [88]. This kind of works are expected to be more present in the following years due to their rapidity and reproducibility. In general, completely automated speciation studies where MSPE is coupled with the detection technique are scarce, and there is no report of this kind of analytical method using MGO as sorbent. So, this combination should be prioritized for speciation analysis.

#### 4. Conclusions

Since it was launched, MGO has demonstrated to be a valuable tool in a huge number of applications. In this work, it has been proven its applicability as a solid phase adsorbent in MSPE for the speciation of trace elements. High EFs, regeneration and easy functionalization capacity make MGO a promising material, being usually fabricated by authors, which often hinders intercomparison studies of results. The extended  $\pi$ - $\pi$  system, the oxygen containing functional groups and the presence of MNPs on the surface allows different interactions with molecules, including ions and organic derivatives. Moreover, the modification of the surface is possible by functionalization with well-known chemicals such as chelating groups or polymers. The electrostatic interactions between MGO and the analytes are highly dependent on the conditions of the medium, being pH one of the most critical parameters to be studied and optimized. The analytical performance, application, functionalization, analysed species and analytical techniques of the reported methods have been summarized in Table 1. As can be observed, the most extended application is the analysis of

environmental samples, mainly water samples, and the procedure based on the selective adsorption is the most extended (P1 and P2). This highlights the special concern trace metals, and their derivatives produce in modern society. Finally, possible improvements of the application of MGO as sorbent have been indicated and discussed such as the use of ecologic MGO synthesis routes and more efficient speciation mechanisms, demonstrating that the topic presented in this work offers many alternatives and prospect that can be exploited in future research works.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

No data was used for the research described in the article.

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