Analytica Chimica Acta 875 (2015) 7–21

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Review

Vapor generation – atomic spectrometric techniques. Expanding frontiers through specific-species preconcentration. A review

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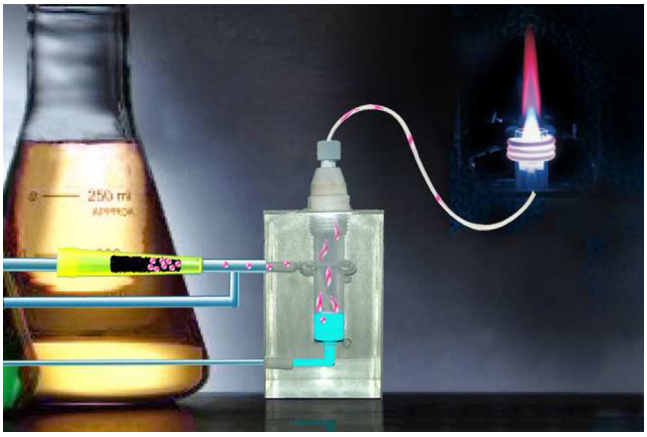
HIGHLIGHTS

- Recent advances in vapor generation and atomic spectrometry were reviewed.
- Species-specific preconcentration strategies after and before VG were discussed.
- New preconcentration and speciation analysis were evaluated within this framework.

GRAPHICAL ABSTRACT

This article reviews 120 articles found in SCOPUS and specific Journal cites corresponding to the terms 'preconcentration'; 'speciation'; 'vapor generation techniques' and 'atomic spectrometry techniques' in the last 5 years.



Abbreviations: AAS, atomic absorption spectrometry; AFS, atomic fluorescence spectrometry; APDC, ammonium pyrrolidine dithiocarbamate; BI, bead injection; CF, continuous flow; CPE, cloud point extraction; CV AAS, cold vapor atomic absorption spectrometry; CVAFS, cold vapor atomic fluorescence spectrometry; CVG, chemical vapor generation; CVG-AFS, chemical vapor generation atomic fluorescence spectrometry; Cys, cysteine; DDTC, diethyldithiocarbamate; DLLME, dispersive liquid liquid microextraction; SDME, single drop microextraction; DMA, dimethylarsinic acid; DPC, 1,5-diphenylcarbazide; EPT, 1,3-bis(2-ethoxyphenyl)triazene; ESMs, eggshell membranes; ETAAS, electrothermal atomic absorption spectrometry; ETV, electrothermal vaporization; EVA, ethyl vinyl acetate; FIA, flow injection analysis; GFAAS, graphite furnace atomic absorption spectrometry; HG, hydride generation; HG-AAS, hydride generation atomic absorption spectrometry; HG-AFS, hydride generation atomic fluorescence spectrometry; HPLC, high performance liquid chromatography; HS-SDME, headspace single drop microextraction; HSSPME, headspace solid phase microextraction; ICP-MS, inductively coupled plasma mass spectrometry; ICP-OES, inductively coupled plasma optical emission spectrometry; IL, ionic liquids; LDHs, layered double hydroxides; LLE, liquid–liquid extraction; LOV, lab-on-a-valve; MBT, mercaptobenzothiazole; ME, microextraction; MMA, monomethylarsonic acid; MSPE, magnetic solid phase extraction; NP, nanoparticles; PADAP, (pyridylazo)-5-(diethylamino)phenol; PTFE, polytetrafluoroethylene; PVG, photocatalytic vapor generation; QFAAS, quartz flame atomic absorption spectrometry; RC-GLS, reaction chamber/gas liquid separator; RTILs, room temperature ionic liquids; SIA, sequential injection analysis; SPE, solid phase extraction; SPME, solid phase microextraction; TESMs, thioglycolated eggshell membranes; TSIL, task specific ionic liquid; TRXRF, total reflexion X-ray fluorescence; UV, ultraviolet; UVG, ultraviolet vapor generation; VGT, vapor generation techniques.

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http://dx.doi.org/10.1016/j.aca.2014.12.040
0003-2670/

ARTICLE INFO

Article history:
Received 2 July 2014
Received in revised form 9 December 2014
Accepted 17 December 2014
Available online 30 December 2014

Keywords:
Vapor generation techniques
Atomic spectrometry
Specific species preconcentration before VG
Specific species preconcentration after VG
Speciation analysis

ABSTRACT

We review recent progress in preconcentration strategies associated to vapor generation techniques coupled to atomic spectrometric (VGT-AS) for specific chemical species detection. This discussion focuses on the central role of different preconcentration approaches, both before and after VG process. The former was based on the classical solid phase and liquid–liquid extraction procedures which, aided by automation and miniaturization strategies, have strengthened the role of VGT-AS in several research fields including environmental, clinical, and others. We then examine some of the new vapor trapping strategies (atom-trapping, hydride trapping, cryotrapping) that entail improvements in selectivity through interference elimination, but also they allow reaching ultra-low detection limits for a large number of chemical species generated in conventional VG systems, including complete separation of several species of the same element. This review covers more than 100 bibliographic references from 2009 up to date, found in SCOPUS database and in individual searches in specific journals. We finally conclude by giving some outlook on future directions of this field.

Contents

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1. Introduction

The vapor generation techniques (VGT) have progressed to reach a noticeably maturity, standing out as a preference choice among the most popular techniques for trace analysis like arsenic (As) and mercury (Hg) determination in a variety of samples [1–7]. The popularity of VGT arises from several reasons remarking its relative simplicity and low cost of apparatus. Perhaps the incomplete vapor generation reaction as consequence of sample matrix constituents is the main drawback of VG methods. This situation is usually easy to deal with compared to those occurring in electrothermal atomization atomic absorption spectrometry (ETAAS) or inductively coupled plasma mass spectrometry (ICPMS). However, the main reason lies on the generic principle of the technique involving analyte preconcentration and separation from the sample matrix resulting in a superior sensitivity and mainly, in a striking suppression of interferences during atomization [8].

The former definition of VG confined to the generation of volatile hydrides after the reaction between tetrahydroborate (THB) and the elemental species has been expanded in recent years. Some other transition and noble metals have been tested with THB-based reactions, and volatile species were generated [9–11]. In spite of the sensitivity and selectivity achieved, different sample pretreatments are often needed in order to either adequate it for the VG process, eliminate interferences (sample clean up) or preconcentrate analyte(s) [6,12–15]. Since only few atomic spectrometric techniques are selective for the determination of species, sample pretreatments becomes a prominent feature that enables the possibility to discriminate between total content of a trace element and the content of each individual chemical form in which it occurs. The quantitation of individual forms of an analyte is termed speciation analysis (specific-species determination); and most analytical methods employed for speciation involve the hyphenation of an atomic spectrometric detector with a separation technique, namely chromatography (LC or GC) [7,12,16–24], capillary electrophoresis (CE) [25–27], solid phase extraction (SPE) [13,28–37], liquid–liquid extraction (LLE) with its variants [38–43], among others. Roughly speaking, VGT are thus derivatization steps after the separation process itself that preconcentrate further the analyte(s) with considerable improvements in selectivity [6]. Preconcentration strategies have also been described for the volatile species generated in the VG technique resulting in the so called gas-phase trapping [44–54].

This article critically reviews the progress, limitations, and research conducted in the last 5 years and covers developments in specific-species preconcentration strategies associated to vapor generation technique with atomic spectrometry detection. The documented preconcentration strategies are solid phase extraction and liquid–liquid extraction (LLE) – species preconcentration before vapor generation – and gas phase trapping in atomizer, cryotrapping and gas-solid phase trapping – species preconcentration after vapor generation. Chromatographic techniques for species preconcentration and separation after or before vapor generation are not discussed in this review.

2. Species preconcentration before VG

As already mentioned, direct and accurate determination of target analytes at trace levels by any vapor generation-analytical atomic spectrometric approach is quite challenging as consequence of possible matrix interferences faced in trace elemental analysis. Several ways to overwhelm these issues have been studied, being the most effective approaches those based on combinations between preconcentration and/or separation methodology with VG. They generally include solid-phase extraction or liquid–liquid extraction. In the two following sections, SPE and LLE techniques are discussed in detail as strategies to preconcentrate and separate selected species analytes prior to VGT. In this fashion, new approaches for elemental preconcentration and speciation and interferences elimination of VG processes will be critically reviewed and compared.

2.1. Solid phase extraction

Solid phase extraction is one of the most important sample pretreatment techniques for trace analysis. Separation procedures based on SPE have been widely used to retain selectively one of the components of sample onto a solid-phase in order to eliminate interferences before analyte determination. In preconcentration and speciation techniques, elution or desorption procedure follows to separation procedure, featuring high enrichment factors, and reduced solvents consumption, and high sampling rate. In terms of selectivity, improvements can be easily achieved through thorough selection of analyte–sample–adsorbent sets (Table 1).

2.1.1. Batch solid phase extraction (SPE)

As demonstrated in the last decades, SPE techniques are versatile analytical approaches that can be easily driven in discontinuous schemes (batch), but are readily adapted to continuous flow systems (Fig. 1). To apply batch SPE, the analytes should be retained on a solid material quantitative and reproducibly, and readily eluted by a known amount of suitable eluents. For preconcentration purposes, the eluent volume should be as small as possible.

In this matter, the available bibliography of the latest 5 years shows that recent developments in elemental preconcentration still take advantage of the batch configuration of SPE. New preconcentration and speciation methods with modified octadecylsilane (C-18) have been documented. For instance, a selective method toward Hg species using 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene – 4-BDPB – and supported on C-18 was described [54]

Table 1
Summary of SPE-vapor generation strategies associated to atomic spectrometries reported in the last 5 years.

Preconcentration technique	Preconcentrated species	Detection limit and other figures of merit[a] ($\mu g\,L^{-1}$)	References
Octadecyl silica modified by 4-bpdb (1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene	Hg(II)	DL: 0.00187 (RSD[b]: 2.98–4.45; EF[d]: 128. 320 mL sample volume; 2.5 mL eluate volume)	[54]
Octadecyl silica modified by 1,3-bis(2-ethoxyphenyl)triazene	Hg(II)	DL: 0.0106 (RSD: 2.9; EF: 380; breakthrough volume: 1900 mL; final elution volume: 5.0 mL)	[55]
Silica gel modified with L-cysteine	Hg(II), $CH_3Hg(I)$	DL: 0.0015, 0.005 (RSD: 7–12; 200 mL sample volume; 5 mL final elute with recoveries ranging 95 and 105%)	[56]
Staphylococcus aureus loaded Dowex Optipore V-493 resin	Hg(II), $CH_3Hg(I)$	DL: 0.0025, 0.0017 (RSD: 6.0; EF: 25. 250 and 10 mL sample and eluent volumes)	[57]
Streptococcus pyogenes immobilized on Dowex Optipore SD-2 resin	Hg(II), $CH_3Hg(I)$	DL: 0.0021, 0.0015 (EF: 25. 250 and 10 mL sample and eluent volumes)	[58]
Ag NPs onto nano-TiO_2; nano-ZrO_2	Se(IV), Se(VI), $(SeCys)_2$, SeMet	1.2, 1.8, 7.4, 0.9 (UV/Ag–TiO_2–HCOOH system); 0.7, 1.0, 4.2, 0.5 (UV/ZrO_2–HCOOH) (RSD: 5.1).	[60]
Nano-TiO_2	Se(IV)	DL: 0.0006 (RSD: 2.1; EF: 17)	[61]
Rhodamine hydrazide modifying Fe_3O_4 microspheres	Hg(II)	DL: 1.5×10^{-7} (RSD: 2.2)	[63]
Fe_3O_4 doped with 1,5-diphenylcarbazide	Hg(II)	DL: 0.16 (RSD: 2.2; EF: 100. 200 mL initial volume, 2.0 mL final volume)	[64]
Amino-modified $CoFe_2O_4/SiO_2$particles	Cd	DL: 0.00315 (RSD: 4.9; EF: 50)	[65]
Au–Fe_3O_4microspheres	Hg(II)	DL: 0.0015 (RSD: 3.7; EF: 10, 30 and 80 for 2 mg, 5 mg, and 10 mg sorbent material)	[66]
C-18 modified with sodium diethyldithiocarbamate	Hg	DL: 0.00003–0.00008 (RSD: 5.0)	[67]
Amberlite XAD-16 resin	As(III)	DL: 0.26[c] (RSD: 6.2)	[69]
Ethyl vinyl acetate	Zn	DL: 0.06 (EF: 230. 16 mL sample volume)	[70]
Activated carbon	Sc	DL: 4.0240 (25 mL sample volume)	[71]
Manganese dioxide and cellulose fiber (As(III))	As(III)), As(V), MMA, DMA	DL: 0.019, 0.33, 0.39, 0.62 (RSD better than 4.2; EF: 14.0–19.2. 2 mL sample volume)	[72]
Agar modified with 2-mercaptobenzimidazole	Hg(II)	DL: 0.02 (RSD: 1.9–2.6; EF: 100)	[73]
Sulfur powder modified with *N*-(2-chloro benzoyl)-*N*-phenylthiourea	Hg(II)	DL: 0.012 (RSD: 1.2–3.9; EF: 333. 1000 mL sample volume, 60 min)	[74]
Thioglycolated eggshell membranes	Se(IV), Se(VI)	DL: 0.06 (RSD: 3.3; EF: 17.2. 1.0 and 0.05 mL sample and eluent volumes)	[76]
C-18 phase, 717 anionic-exchange resin	As(III), As(V)	DL: 0.02, 0.03 (RSD: 2.8, 2.9; EF: 7.0, 8.2. Sampling volume of 1.0 mL and an eluent volume of 100 μL for both species)	[78]
Cigarette filter	As(III)	DL: 7.4 (RSD: 2.6; EF: 26. 180 s preconcentration time)	[79]
Thiocarbonohydrazide immobilized on aminopropyl-controlled pore glass resin, XAD type anion exchanger	Sb(III) and Sb(V)	DL: 0.013, 0.021 (RSD: 4.6, 3.0; EF: 5.5, 3.9)	[80]
Yttrium hydroxide deposited onto cellulose fiber	As(III), As(V)	DL: 0.017 (RSD:2.6; EF: 16.4. 1.0 mL sample volume)	[82]
Co-polymeric Oasis HLB	Hg(II)	DL: 0.04 (RSD: 3.8. 9 mL sample volume, 1.5 mL final volume)	[88]
Bare poly-copolymer sorptive beads	Hg(II)	DL: 0.012 (RSD: 9.0; EF: 17)	[89]

[a] DL: detection limit.
[b] Percent relative standard deviation.
[c] $\mu g\,g^{-1}$.
[d] $mol\,L^{-1}$.

for analysis of real samples, prior to cold vapor atomic absorption spectrometry. Similar to this method, C-18 membrane disks were modified with 1,3-bis(2-ethoxyphenyl)triazene – EPT – for selective retention of Hg. After elution, CV-AAS was also used as detection technique in its conventional mode [55]. Despite preconcentration factors above 380 could be achieved (1.9 L sample volume), the membrane lifetime was very short (3 cycles).

Like this last, other methods using modified silica have been also described recently in batch SPE schemes. A method with L-cysteine immobilized on silica for Hg speciation and preconcentration was proposed [56]. The modified silica was easily regenerated, demonstrating that chemical and mechanical stability were maintained even after several SPE cycles. Besides, high adsorption capacity with consequent favorable enrichment factors were claimed. Differential atomization behavior of inorganic mercury and organic species allowed different measurements conditions; *i.e.*, while inorganic and total Hg were measured without heat, CH_3Hg^+ was completely atomized if heated the atomizer at 920 °C. A distinguishable feature of this method lies on the possibility for field treatments for speciation determination and enrichment of Hg species during sampling ("on-site" approach), and the possibility of analyzing samples within 48 h.

A batch SPE method for trace Hg(II) and methyl-Hg speciation was optimized with the bacterium *Staphylococcus aureus* immobilized on the resin Dowex Optipore V-493 prior to CV-AAS [57]. An interesting feature of this method is that both mercury species are retained under the same experimental conditions, but selective and sequential elution with varying HCl concentrations could be performed easily. Besides the speciation ability and the excellent sensitivity achieved (preconcentration factor of 25-fold), the stability of the biosorbent was excellent for more than 50 cycles without detriment in the adsorption capacities. Later on, the same authors, developed a similar solid phase extraction protocol based on speciation of Hg(II) and methyl-Hg, with *Streptococcus pyogenes* bacteria immobilized on Dowex Optipore SD-2 [58]. Similar preconcentration factors and detection limits were obtained.

New functional adsorbents have been designed to extend applications of SPE techniques. In this way, nanomaterials are attractive substrates due to their particular structure and high surface. Typically, carbon nanotubes (CNTs) and oxides of Al, Si and transition metals have been employed to assist chemical vapor generation by converting chemical vapor generation-inactive species into active ones [59]. Li et al. [60] studied new improvements in this field (photocatalytic vapor generation). In this way, they could applied PVG to the determination of Se-methionine and Se-cystine, for instance. Information about preconcentration factors was not available from their work.

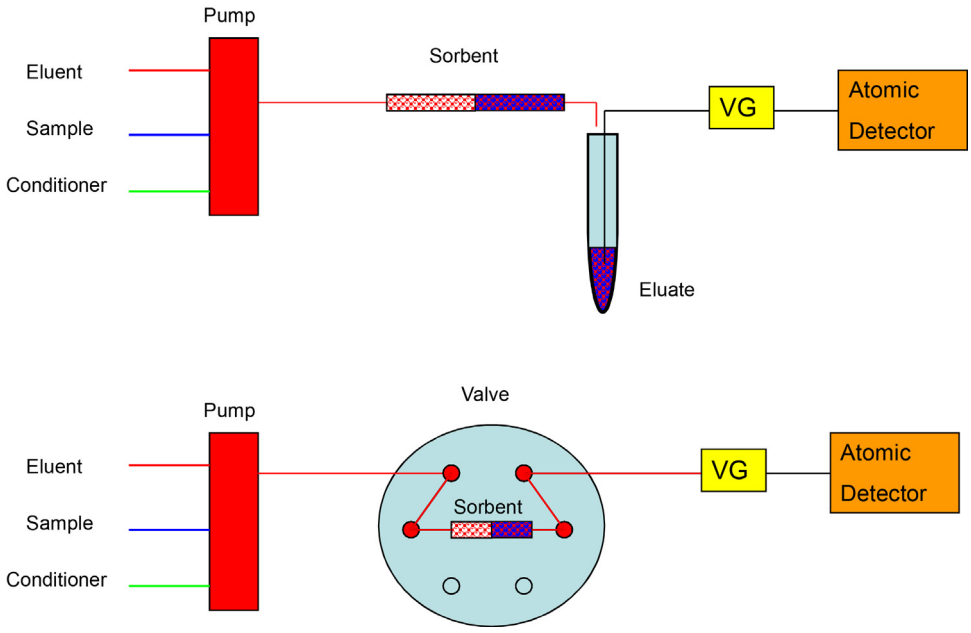

Fig. 1. Schematic flowing diagrams of batch and on-line SPE techniques with peristaltic pumps.

Adsorption of Se from the samples with high concentrations of transition/noble-metal ions by nano-TiO_2 at low pH have been demonstrated, and this procedure was combined with *in situ* slurry hydride generation as a novel highly efficient sampling method [34]. In brief, the method involved reducing all Se species to Se(IV) form which was then selectively retained onto TiO_2 nanoparticles, and then they were separated and stripped with a solution of potassium THB. After that, SeH_2 was generated in HCl media within the GLS of an AFS instrument. Compared to the conventional HG method, the sensitivity and the limit of detection were improved 17- and 16-folds, respectively. In addition, besides the high sample throughput, this method may be used for the determination of other hydride-forming elements in complex samples containing heavy metals at high concentrations. Further studies demonstrated that improvements in stability of slurried samples could be achieved with colloidal TiO_2 [61]. Features remarked of this method included the possibility of determination inorganic Se species (*i.e.*, Se^{IV} and Se^{VI}) separately without desorption step. The preconcentration factors were not mentioned as such in this work, but calculations can be made considering the 100 mL initial sample volume and the 5 mL final volume.

Magnetic solid phase extraction (MSPE) is an interesting variant of SPE that uses magnetically active materials as adsorbents. MSPE is operated with the aid of an external magnetic field to separate the adsorbent (with the corresponding adsorbed analytes) from the sample matrix. A recent work in this matter has been published by Fu et al. [62]. They used microspheres of Fe_3O_4 with its surface modified with Rhodamine hydrazide for preconcentration of inorganic mercury prior to CV-AAS determination in natural water. This method achieved excellent selectivity toward Hg even with high levels of other metal ions present. Reusability was achieved with the application of rinsing steps at the end of each preconcentration cycle. Magnetic Fe_3O_4 modified with 1,5-diphenylcarbazide (DPC) was also assayed in a similar scheme for Hg determination [63]. In this case, the magnetic adsorbent could be used for 8 cycles or recycled during 6 months.

Other application was reported by Zhai et al. [64] that synthesized magnetic nanoparticles of amino $CoFe_2O_4/SiO_2$ core shell. This material was used to preconcentrate Cd in MSPE mode. HCl was used to elute Cd and reaction with THB was assured in this media allowing complete CVG process prior to AFS detection. The authors claimed that this material could be reused for more than 45 SPE cycle.

Other use of Fe_3O_4 magnetic microspheres was described for MSPE of Hg(II). These nanoparticles were modified with Au and after magnetic separation, they were slurried reducing the risk of analyte loss or sample cross contamination prior to CVG. The overall procedure lasted 15 min and the calculated enrichment factors were 10, 30, and 80 for 2 mg, 5 mg, and 10 mg sorbent, respectively [65].

2.1.2. Flow injection-solid phase extraction (FI-SPE)

Solid phase extraction techniques advantage other sample pretreatments in terms of ease of operation, mainly as consequence of its possibility to be incorporated within automated schemes of analysis. Also, SPE systems are readily combined with different atomic detectors both in off-line or on-line modes (Fig. 1). Automatic transport of fluids and in-line sample handling, offers innovative means to execute sample pretreatment with achievement [54]. They likewise permit accurate means to introduce analytes into gas–liquid separator of different VG system.

New advances in the field of flow injection analysis (FIA) have been introduced recently to improve the sensitivity toward Hg and to remove interferences [66]. A FI approach that coupled on-line solid phase extraction enrichment with ultraviolet vapor generation atomic fluorescence spectrometry (UVG-AFS), was proposed for mercury. Quantitative retention efficiency and maximum exclusion of inorganic and organic matrix in water samples were achieved with a C-18 mini cartridge modified with sodium diethyldithiocarbamate (DDTC). Quantitative elution was observed by using HCOOH and L-cysteine mixing solution. Quartz tubing was sintered into the UV lamp to enlarge VG efficiency.

Also, advances in this field were conducted by Qin et al. [67]. In a recent article, they showed a method for mercury preconcentration in a PTFE coil after chelation with diethyldithiocarbamate (DDTC). Differential behavior between inorganic and organic species of Hg with DDTC allowed its separation and further detection by AFS. The claimed detection limits were 0.004 mg L^{-1}

or 0.0008 mg L^{-1} for Hg^{2+} for 40 or 200 s of sample loading time, respectively. This procedure was applied for speciation analysis of Hg^{2+} and $MeHg^{+}$ by controlling the desorption and photochemical vapor generation conditions. The accuracy was checked with the CRMs waters (GBW 080392 and GBW 080393), fish muscle (GBW 10029), and human hair (GBW 09101b), as well as National Research Council Canada DORM-2 fish muscle tissue.

Similar to partition chromatography, the chemical processes in the extraction and elution stages depend on the partition coefficient of analytes between the extractant material and the mobile fluid [54,68]. Consequently, new and efficient materials have been introduced (including modification of existing materials) for SPE, with noticeably improvements in the technique performance.

Other kind of adsorbent materials used as solid phase in SPE techniques are classic polymeric solid supports (resins, cellulose and others) that are readily obtained by means of functionalization. Fit for purpose functional groups that are added to add selectivity through species-specific complex formation are discussed next.

In this fashion, Liu et al. [69] reported a new method to determine trace As(III) species with Amberlite XAD-16. Covalent $AsCl_3$ formation was induced by addition of concentrated HCl and then retained quantitatively by the resin. The main achievement of this method is the matrix interferences reduction. This can be advised from the application that authors published in their work where this approach was successfully applied to the determination of As in a high purity Sb_2O_3 material, taking into account the matrix Sb(III) interferences.

Recently, our group reported a preconcentration procedure for trace Zn determination using SPE in association with VG-ICP-OES [70]. The SPE occurred into a minicolumns filled with ethyl-vinyl acetate (EVA) turnings. Selective Zn retention was documented and elution was accomplished with HCl solutions. Volatile species of this metal were generated on-line by merging the acidified eluent and sodium THB. A total enhancement factor of 230 for 16 mL of sample processed (time-based sampling) was achieved. An advisable sampling frequency of 17 h^{-1} was thus obtained. The same scheme was adapted for CVG of Sc with ICP-OES detection [71]. The analysis of natural waters was successful with this method that reached an enhancement factor of 240-fold (25 mL of sample processed). On the other hand, the certain formation of a Sc vapor and, as a consequence, the absent transport of Sc to the ICP-torch in the form of an aerosol, was demonstrated for the first time.

As inexpensive and suitable SPE materials, mineral and insoluble inorganic salt have been used. It has been documented that MnO_2 serves as water healthier for arsenic removal since it displays high adsorption capacity toward As species. A recent work [72] took advantage of those facts and employed MnO_2 as adsorbent material for column SPE of arsenic species (As(III), As (V), monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA)). The basic procedure involved As(III) oxidation to As(V) by MnO_2, whereas other species remained unaffected. Elution took place with tetramethylammonium hydroxide, which promotes stripping of retained species. After reversed phase liquid chromatography separation (C30 column), the eluted arsenic species were subject to gradient HG-quartz flame atomizer-AAS detection.

A SPE method in which chemically modified agar was used as adsorbent material has been recently described also for Hg(II) preconcentration [69]. This was done through addition of 2-mercaptobenzimidazole to agar. The retained Hg(II) ions were eluted with HCl and measured by CV-AAS. The mercury vapors were generated by a homemade reaction cell-gas liquid separator, which provided high sensitivity. The preconcentration factor of this method was 100. Hereafter, these authors developed a SPE method based on a minicolumn filled with sulfur powder modified with *N*-(2-chloro benzoyl)-*N*-phenylthiourea for preconcentration of mercury ions [70]. The retained Hg(II) ions were eluted with HCl solution and measured by CV-AAS. Due to the relatively high sample flow rate allowed (16 mL min^{-1}), 1000 mL sample could be processed and a preconcentration factor of 333-fold was achieved. This situation lasted however, several minutes with deteriorate the final performance in terms of concentration efficiency. Although improvements are needed, this was the first application of modified sulfur as a solid phase extractor. The limit of detection of the method was comparable to or better than some of the previously reported methodologies.

Alternative ways of modification of solid phase extraction materials to allow desired selectivity toward specific chemical species include the use of biomaterials. Their chemical reactivity originated from the presence of various functional groups has attracted the attention of researches in this field. Biomaterials host specific functional groups and they can provide alternatives to improve the metal-binding capacity and sorption selectivity SPE adsorbents [75–77]. Former works in this field have used living and dead bacteria, cell membrane fragments, biomolecules such as aminoacids, peptides, and even nucleic acids immobilized on suitable supports (*e.g.*, controlled pore glass); but routine applications were hampered due to the need of manipulation under biosafety conditions. New trends (including the concepts of green analytical chemistry) have driven the research to new, safe and economic materials that fulfill the requirements of SPE for trace analysis.

Eggshell membranes are a particular biomaterial that possess a disulfide bond-rich surface. Free thiol groups can be generate through adequate reduction with thioglycolate [76]. Consequently, this unique material is particularly attractive to retain chemical species that bond with sulfide under certain circumstances. Eggshell membranes treated this way have been recently used as SPE adsorbent material for both Se(IV) and Se(VI) that were retained differentially; Se(VI) was retained reversibly through ionic interactions, and Se(IV) was reduced to Se(0) and further deposited. The enrichment factor was 17.2 for reduced sample volume (1 mL) but with incomplete analyte elution. Consequently, samples were treated with $KMnO_4$ before preconcentration for total Se determination. A second cycle was thus needed where samples without any pretreatment were processed allowing measuring Se(VI). Subtraction of this result to that obtained for total Se yielded the original concentration of Se(IV).

Simple alternatives for speciation analysis have been described consisting in multiple-column manifolds. A dual column method was described by Chen et al. [78] for preconcentration and speciation of As species. This method invovled complexation of As (III) with ammonium pyrrolidine dithiocarbamate and retention on C-18. A second SPE phase with an anionic exchanger was used to retain As(V). The retained species were then eluted sequentially with HCl directly to the HG system. In this context, Li et al. [79] took also advantage of the PDC–As(III) complex, which was this time retained on a cigarette filter for better As(III) preconcentration. The consumption of 22 mL of sample yielded an enrichment of 26-fold (preconcentration time of 180 s).

Fornieles et al. [80] settled an automated method for the determination of Sb(III) and Sb(V) by HG-ICP-MS. In this case a multiple column system was designed, involving two consecutive columns; one column was filled with 1,5-bis(2-pyridyl)-3-sulfophenyl methylene thiocarbohydrazide immobilized on aminopropyl-controlled pore glass resin for retention of Sb(III), and other consisting on a XAD type anion exchanger for retention of Sb(V). It is undoubtedly that selectivity was achieved with success in a relatively simple and fast way, but however, poor enrichment factors were obtained (5.5 and 3.9; for Sb(III) and Sb (V), respectively). Regarding to detection limits (0.013 μg L^{-1} for Sb

(III) and 0.021 $\mu g\,L^{-1}$ for Sb(V)), it must be stressed that sensitive conditions could be achieved anyways (considering 2 min sample loading time or 2.2 mL sample consumption).

2.1.3. Sequential injection-solid phase extraction (SIA-SPE)

In sequential injection analysis (SIA), the sample and reagents are sequentially pumped (time-based) into a reaction coil; the mixture is then delivered counter-flow toward the detection system. Automation is allowed through software-controlled hardware, ensuring the reproducibility. A multi-port rotary valve is the main component allowing sequential selection of solutions and redirection of fluids toward a suitable detector. Even more, the possibility of having all solutions on the ports, enabled various determinations with the same manifold [81]. The survey of research articles published in the last 5 years shows that several methods for VGT have been adapted with success to SIA schemes. In the following section, a series of results in this matter are discussed.

Inorganic arsenic speciation was accomplished in a SIA approach that used a minicolumn filled with cellulose fiber particles modified with an $Y(OH)_3$ thin layer on the surface [82]. Precise pH adjustment sufficed to retain As(V) selectively in presence of As(III). Alkaline eluents were assayed instead of acids solutions to prevent dissolution of $Y(OH)_3$ precipitate. In this sequence, the eluate was transferred to a centrifuge tube from where As(V) was reduced to As(III) and after the solution was pumped toward the GLS of the HG system of the AFS instrument. The sample volume processed was 1 mL, allowing a enrichment factor of 16.4 compared to conventional HG-AFS. After this work, this group synthesized a layered double hydroxides cellulose fiber particles for inorganic Se speciation [83]. Experimentally, a PTFE minicolumn filled with these particles was incorporated into a SIA system for selenite retention. Total inorganic Se determined after previous reduction to selenite. As mentioned in previous work, alkaline stripping reagents were used for the recovery of the adsorbed analytes to avoid the dissolution of the sorbent medium. A sample volume of 1.0 mL yielded a satisfactory enrichment factor of 13.3-fold.

In other approach [19], unmodified cellulose fiber was used as SPE adsorbent in a SIA manifold to preconcentrate As(III) previously masked with the reagent APDC. Selectivity was thus assured even in presence of the other arsenic species. The processed sample was of 2 mL which yielded enrichment factors of 14.0 and 19.2 for As(III) and As(total). The authors claimed that by coupling this sequential injection system based on solid phase extraction with chromatographic separation gradient hydride generation-quartz flame atomic absorption spectrometry further improved the sensitivity for arsenic speciation as compared to previously reported procedures [72] based on merely gradient hydride generation.

Immobilization of amino acids on suitable materials gives advantageous features by misuse of coordination ability of amino-, carboxyl- and sulfur-groups with heavy metal species [84]. The functionalization of cellulose fiber with L-cysteine (Cys-fiber) for instance has improved significantly the adsorption capacity toward mercury and methyl-mercury [85].

Chen et al. employed a Cys-fiber minicolumn (10 mg sorbent material) for on-line separation and preconcentration of Hg species in a sequential injection system. The inorganic mercury was selectively quantified using CV-AAS, while the total amount of mercury was determined by adopting the flame/heat atomization mode, and thus the concentration of methyl-mercury was achieved by the difference. The optimization of the $NaBH_4$ concentration as reducing reagent was crucial to achieve the above mentioned speciation/detection. Quantitative Hg preconcentration/speciation was attained.

2.1.4. Lab-on-a-valve-solid phase extraction (LOV-SPE)

The 'lab-on-a-valve' (LOV) concept was introduced since more than 10 years, and joints selected characteristics of FIA and SIA. LOV include a selection valve as the main component of the structure, a holding coil and a propulsion unit, usually a syringe pump [54]. It can be designed to undertake all laboratory needed to carry a particular chemical analysis. The integrated flow cell can be configured adapted to accomplish SPE procedures by means of the possibility to incorporate a renewable microcolumn. This approach is named 'bead-injection (BI) analysis' [86,87]. In BI, bead suspensions are processed akin to solutions, trapped as microcolumns, and used to preconcentrate target species followed by on-line disposal after certain number of SPE cycles. Despite of its attractive features, miniaturized LOV setups do not cope with the characteristics of VGT.

Modification of the LOV unit for in-line VG and membraneless gas–liquid separation was introduced to preconcentrate/determine Hg species [88]. The uptake of Hg(II) was accomplished onto the surface of a microcolumn packed with co-polymeric Oasis HLB beads. The preconcentrated analyte was eluted with $HCl–HNO_3$ solutions, merged downstream with tin(II) chloride, and swept into the integrated reaction chamber/gas liquid separator (RC-GLS) furnished with a particular gas dryer membrane purged with nitrogen gas, to prevent humidity in the gaseous phase.

In the same context, a pressurized BI-SPE method with an integrated GLS for on-line VG and determination of inorganic Hg was described [89]. In this scheme, beads of poly(divinylbenzene-*N*-vinylpyrrolidone) were placed to form the integrated microcolumn and uptake Hg(II) in the solution. The LOV manifold was configured to discard the beads after each adsorption/elution cycle and new aliquots of beads were used each time. In tis sense, the analytical performance of the extraction system was maintained. The global time of analysis for the sequence sequence including sample aspiration, analyte retention, elution and quantification by AFS was about 11 min. The maximum enrichment factor was 17. Due to differences in the eluent volume, the proposed method featured a better enrichment factor than that previously reported in Ref. [88].

2.2. Liquid–liquid extraction (LLE)

Liquid–liquid extraction (LLE) has evolved from a time and reagents consumption technique into a miniaturized and on line technique encompassing Green Chemistry principles. From this evolution, techniques like cloud point extraction (CPE) and microextraction (ME) have aroused. The latest involve dispersive liquid liquid microextraction (DLLME), single drop microextraction (SDME) and headspace single drop microextraction (HS-SDME) among others. These techniques contribute to VG in different configurations as observed in Fig. 2. CPE, DLLME and SDME deliver elemental species in a suitable form for VG. HS-SDME introduces *in situ* VG during the extraction process. Advantages and drawbacks of each configuration will be discussed in the following sections with special focus on ionic liquids (IL), a new family of extractants (Table 2).

2.2.1. Cloud point extraction (CPE)

CPE is a sensitive extraction method based on formation of a cloudy phase during extraction by micelle formation containing the target element by surfactant molecules after temperature changes. As observed in Fig. 2a, after centrifugation surfactant rich phase is collected. CPE configuration delivers the target element to VG. However, some drawbacks have to be attended previous CPE-VG coupling. The most important is difficulties of elements to form vapor in the micellar phase. Recent papers involving CPE-VG describes different strategies to overcome this problem. Ulusoy

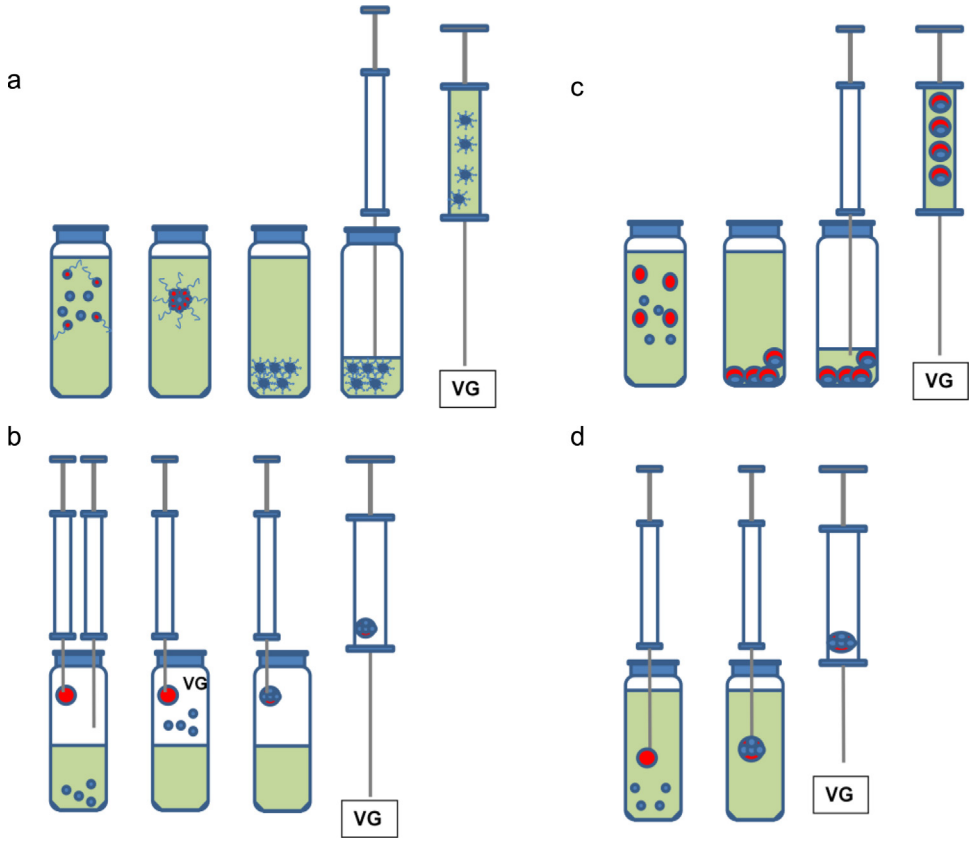

Fig. 2. Schematic diagram of LLE configurations. (a) DLLME, (b) HS-SDME, (c) DLLME, and (d) SDME.

et al. [43] acidified and add antifoam to the surfactant-rich phase to quench foaming of surfactant during hydride generation. This research was applied to specific As(III) extraction differentiating As (III) from As(V). Addition of an ion-pairing complex provides specificity to the extraction and solubility to As(III) into the surfactant-rich phase since inorganic ions have low solubility in the mentioned phase. Another interesting approach has been reported by Yuan et al. [90]. There is practically no antecedent of coupling CPE with CVAFS for Hg determination. This is probably because of the foam produced during the vapor mercury generation process in the medium of surfactant, which may interfere with the determination of Hg and then inhibit the application of CPE for Hg determination. By introduction of $SnCl_2$ and a home-made gas–liquid separator foaming, which is always observed when generating vapor mercury in the presence of surfactant, was strongly reduced.

From the mentioned above CPE as an extraction technique certainly reduces matrix effects on VG process and achieves lower detection limits. However, difficulties of VG in the surfactant phase limits its application to VG coupling. Recently a novel solution to this problem has been proposed by Deng et al. [91]. They proposed the introduction of graphene oxide to form a well-dispersed colloid in aqueous phase for quantitative extraction of heavy metal. However, the complete uptake of graphene oxide colloids from water is not practically possible. Through the introduction of NaCl, graphene oxide aggregation could be caused by neutralizing the excessive negative charges on the surface of graphene oxide sheets, eliminating repulsion. Conventional (Pb, Bi, Sn) and non-conventional (Cd) VG elements were determined. In addition, an organic reagent free method was developed reaching a greener analytical chemistry.

2.2.2. Dispersive liquid–liquid microextraction (DLLME)

DLLME is a LLE technique that serves elements to VG as observed in Fig. 2. DLLME consists in the dispersion the high viscosity extracting solvent within the aqueous sample solution.

Table 2
Liquid–liquid extraction methods coupled to vapor generation.

Preconcentration technique	Preconcentrated species	Enrichment factor	References
CPE-HG AAS	As(II)	60	[43]
CPE-CV AFS	Hg(II)	29	[94]
CPE-AFS/ICP OES	Pb, Cd, Bi, Sb	35, 8, 36, 37	[95]
RTIL-LLE-FI-CV AAS	Hg	36	[96]
TSIL-USA-DLLME-CV AAS	Hg(II), $(CH_3)_2Hg$	310	[97]
HS-SDME-ETAAS	Sb(III)	176	[42]
HS-SDME-ETV-ICP MS	As, Sb, Bi, Pb, Sn	9, 85, 138, 130, 37, 72	[38]
IL-HS-SDME-ETAAS	Hg(II)	75	[40]
TSIL-PTFE-SPME-CV/UV-AAS	Hg	21	[39]
IL-SPE-CV AAS	Cd	80	[98]

This turbid solution is centrifuged and the viscous phase containing the target element collected. The major problem of coupling DLLME to VG is this viscous phase indeed. Turning this phase more fluidic and suitable for VG requires a "back extraction" that depletes the enrichment factor achieved by DLLME. For this reason DLLME has been readily associated to different combinations of atomic spectrometry techniques, but however, just few are devoted to VG.

The high consumption of dispersing solvents, decrease in partition coefficient along with toxic, flammable and environment damaging characteristics of these solvents has encouraged the search for new alternatives. In this context, room temperature ionic liquids (RTILs) appeared as an alternative to regular solvents in a wide range of applications due to the stability they posse in aqueous media, insignificant vapor pressure, the fact that they remain liquid at room temperature, and their relatively favorable viscosity and density characteristics. In addition they present lower toxicity and volatility, greener chemistry, good solubility in organic solvents, higher thermal stability compared to conventional solvents as well as good extractability for various organic compounds and metal ions.

Literature revision of the last 5 years showed that most of the research coupling DLLME to VG introduces RTILs. Martinis et al. [92] introduced the RTIL 1-butyl-3-methylimidazolium hexafluorophosphate ([C4mim][PF6]) for preconcentration of Hg [17,18] as it forms a biphasic liquid system with water. However, many drawbacks were attended before determination. To improve Hg solubility in RTILs a complexing agent was added, 5-Br-PADAP. To prevent the precipitation of the formed complex in water media, addition of ethanol was recommended as co-solvent, with consequent dilution. Once the Hg-5Br-PADAP was adsorbed on RTILs, the formed dispersion was centrifuged and the sample extracted. However, since the presence of organic matter can negatively affect cold VG a back-extraction with HCl was needed, with consequent dilution. Nevertheless to counter this dilution steps that detriments preconcentration factors an FI system configuration was designed reaching satisfactory results.

Undoubtedly back-extraction represents a serious inconvenient in DLLME-VG procedures. For this reason Stanisz et al. [93] developed a procedure with no need of back-extraction. It consisted in a task specific ionic liquid-based ultrasound-assisted dispersive liquid–liquid microextraction (TSIL USA DLLME) combined with cold vapor atomic absorption spectrometry (CV AAS) for determination of mercury species in water and biological samples. TSILs are ionic liquids modified with thiol or urea groups generally used as extraction solvents for Hg determination. Methyltrioctylammonium thiosalicylate was the TSIL employed and Hg^{2+} and CH_3Hg^+ the species determined. Retro-extraction, after centrifugation and aqueous phase extraction, was avoided by diluting the organic phase with only a few microliters of ethanol. Cold VG was achieved with $SnCl_2$ and HCl. Another remarkable advantage of the proposed method was that no complexing reagent was needed.

2.2.3. Head space single drop micro-extraction (HS-SDME)

Head space single drop micro-extraction is a family of preconcentration strategies for gas-phase analyte separation that are particularly suitable to extract gaseous analyte species generated in VGT. Although the preconcentration step occurs just after the VG process, HS-SDME is included here for convenience, as it is derived from SDME techniques that are discussed in this section.

HS-SDME introduces *in situ* VG during the extraction process as can be observed in Fig. 2b. This is a one-step method for sampling, sample cleaning-up, analyte preconcentration and elution. Non sophisticated instrumentation is required for microextraction, only a high precision syringe. Unlike SPME, memory effects are eliminated in HS-SDME since a fresh drop of solvent is always used for extraction. The major advantage of HS-SDME over direct-SDME is the freedom of interferences from the sample matrix since these are less likely to reach the drop during *in situ* VG, although this principle is shared by all VG procedures. This statement was confirmed by Pena-Pereira et al. [42] after the selective preconcentration of Sb^{3+} employing a single drop of Pd^{2+}. Total antimony ($Sb^{3+} + Sb^{5+}$) was determined after pre-reduction of Sb^{5+} to Sb^{3+}, reaching speciation. Determinations were performed in this case by ETAAS. This types of detectors are preferred in HS-SDME since requires microliters volumes to be introduced in the graphite oven and no back-extraction of the vapor forming element from the drop is required.

The multielemental nature of ICP MS was exploited by Gil et al. [38] to determine As, Sb, Bi, Pb, Sn and Hg employing a single drop of Pd^{2+}. Since the single drop cannot be introduced in conventional ICP MS autosamplers, an ETV configuration was used as sample requirements are similar to those mentioned for graphite furnace in ETAAS. The authors claim that interferences from other non-hydride forming elements or matrix interferences are avoided because only volatile compounds reach the microdrop situated in the headspace above the sample solution.

Synergy between RTILs and HS-SDME converge in the method developed by Martinis and Wuilloud [40] when 6 μL of CYPHOS® IL 101 was employed as single drop for Hg retention. Determination of Hg^{2+} and organic Hg was achieved by selective reduction with $SnCl_2$. This research represents an advantageous alternative by offering inexpensive RTILs to form the single drop instead of expensive Pd^{2+} solutions, along with the well know speciation possibility.

HS-SDME with *in situ* VG has shown in the last 5 years potential to substitute DLLME for the reasons mentioned above. These last researches add a solution to the problem presented by back-extraction by direct introduction of the single drop into atomizers, previous optimization. Some new features have been added like multielemental analysis and the introduction of RTILs to avoid Pd drops. However, more research is needed to evaluate speciation and miniaturization possibilities and to overcome some drawbacks like low sample throughput and relatively elevated sample volume consumption.

2.2.4. Alternative techniques introducing ILs

A new combination involving ILs adsorbed on a solid support has been proposed for extraction of vapor forming elements. Despite of being interesting alternatives to conventional procedures employing ILs that deserves discussion, no significant advantages to the previous discussed techniques have been demonstrated at this time.

The first procedure has been described by Gündogdu and Ay [39] involving using TSIL coated PTFE tube for solid phase microextraction of mercury. The retained Hg on TSIL was eluted with ethanol and two strategies were evaluated for VG: reduction with $SnCl_2$ and UV reduction with formic acid. Despite novelty and the fact that no centrifugation step is required compared to DLLME, the method presents some weak points like PTFE coating with TSIL before each determination and the introduction of excessive sample volumes (200 mL). It is noticeable the introduction of UV reduction for vapor generation. The introduction of a TSIL avoided the introduction of a complexing reagent for Hg retention.

Developments on elemental absorption on solid supports employing ILs coating were also presented by Pourreza and Ghanemi [94]. They retained Cd ions, a non convetional vapor forming element) on a column packed with sulfur powder modified with 2-mercaptobenzothiazole (2-MBT) in the medium of 1-butyl-3-methylimidazolium hexafluorophosphate

([bmim]$^{+}$PF6^{-}) ionic liquid. The presence of ionic liquid during modification of sulfur enhanced the retention of cadmium ions on the column. The major advantage of this method is the HCl elution, being the Cd readily for VG. The employed sample volume is elevated, 200 mL, limiting the applicability of this method.

Despite the strength and weakness of these alternative techniques introducing ILs, present the first steps into a long path of development involving ILs and solid supports, a combination with high potential.

3. Species preconcentration after VG: gas-phase trapping

In a regular setup, the volatile chemical species generated in a VG system are determined with a suitable atomic detector based on absorption (AAS), emission (AFS or ICPOES) and even mass spectrometry (ICPMS). In all cases, the conventional configuration involves introducing the generated vapors to the atomizer in a very simple scheme (sample conditioning > chemical or electrochemical vapor generation > atomic absorption spectrometry detection). In this section, progress and new trends in this application of VGT is discussed [95–120]. A comparision among some remarkable advances are shown in Table 3. Several issues regarding contamination, memory effects, and sensitivity and selectivity losses have been well documented, and recent reviews can be consulted for detailed discussions [6,12,13,24,95].

3.1. In atomizer trapping

3.1.1. Quartz tube atomizers (QTA)

Although firstly designed for liquid sample introduction and flame atomization atomic absorption spectrometry (FAAS), atom trapping (AT) techniques have been now associated to VG-AAS as prominent alternatives to enhance analytical performance (sensitivity and selectivity) [96], allowing detection limits at the pg L^{-1} levels for several analytes (which are increasingly). The basic scheme involves generation of gaseous species of the analyte, trapping them on the surface of a pre-heated quartz cylinder, and revolatilizing them by sudden application of heat to the trap. Different trapping approaches have been developed, being the externally heated quartz tube (QT) perhaps the most studied. In this configuration, the trap process may occur on the quartz surface [46,48,52,97] or on a tungsten-coil [49,103–105].

Recent advances in quartz tube atomizer hydride generation atomic absorption spectrometry (QTA-HGAAS) technique for lead (Pb) determination have been extensively studied by Kratzer and co-workers [98,99,102]. They introduce a compact trap-and-atomizer

Table 3
Gas phase trapping for species preconcentration after VGT.

Preconcentration tecnique	Preconcentrated species	Detection limit and other figures of merit	References
MSPE-QTA-AAS	Hg°	90 and 300 pg mL^{-1} for Pd and SiO_2 coated with Pd, respectively (the repeatability expressed as %RSD was 4.3)	[108]
VG-W coil-AAS	BiH_3	DL: 25 ng L^{-1} (the enhancement factor was 21 when compared with the regular system without trap, by using peak height values)	[109]
HG-HR-CS-STAT-FAAS	As, Bi, Cd, In, Pb, Se, Te, Tl	DL: 25, 10, 5, 80, 10, 10, 20 and 40 ng mL^{-1} for As, Bi, Cd, In, Pb, Se, Te and Tl, respectively (RSD ranged from 6 to 11% for liquid and slurry samples)	[105]
HG-QT-FAAS	Ge and inorganic Sn species	DL: 25 and 8 ng mL^{-1} for Ge and Sn, respectively (2 min *in situ* preconcentration time, sensitivity enhancement, compared to FAAS, were 10- and 14-folds for Ge and Sn, respectively)	[52]
VG-QT-AAS	Ag	DL: 1.0 ng mL^{-1} (nolinear relationship between Ag concentration and measured absorbance as peak height is advised. An empirical equation was thus proposed $y = 0.044 \times 1.423$)	[119]
HG-W coil-AAS	TeH_2	DL: 0.08 ng mL^{-1} (1 min trapping and 1.5 mL sampling volume. The enhancement factor was 28 compared to conventional HG-AAS)	[49]
Thin film HG-ETAAS	CuH_2	DL: 0.1 ng mL^{-1} (sample volume of 1 mL and the precision expressed as RSD was 4.0%. Lower DL were also informed for higher sample volumes)	[45]
HG-CT-AAS	Arsine and methyl-substituted arsines (iAsIII, MAsIII, and DMAsIII)	DL: less than 6 ng As/g of biological tissue (iAsV, MAsV and DMAV could be determined with the same DLs after complete reduction with L-cysteine)	[50]
HG-ETAAS	SbH_3	DL: 0.03 ng mL^{-1} (the repeatability at the concentration level of 1 ng mL^{-1} was 1.6% RSD)	[120]
VG-QT-AAS	Ni	DL: 1.0 ng mL^{-1} (the calibration function (the correlation coefficient was 0.99218)). The linear range: 1–50 ng mL^{-1}. Precision was in the range of 9.0% for 25 ng min^{-1} of Ni (evaluated as peak area)	[46]
HG-ETAAS	Se	DL: 30 ng L^{-1} (QL: 101 ng L^{-1}. The calibration curve for Se showed reasonable linearity $r^2 = 0.988$. The characteristic mass, m_0 was found as 95 pg)	[117]
HG-ETAAS	As	DL: 6.4 ng mL^{-1} (collection time of 30 s. The characteristic mass was 24 pg)	[115]
HG-QT-AAS	PbH_2	DL: 0.21 ng mL^{-1} Pb (30 s preconcentration, sample volume 2 mL)	[102]
HG-CT-AAS	iAs(III), iAs(V), MAs, DMAs, and TMAsO	DL: 70 ng L for inorganic arsenate, 42 ng L for mono- and dimethylarsenates and 30 ng L for all the other determined species (sensitivity of trivalent species, found in measurements performed with solutions in the absence of L-cysteine, was the same as that of pentavalent species found in measurements performed with measured solutions treated with L-cysteine; and the generation efficiency of corresponding arsines from pentavalent As species was negligible)	[47]
HG-ETAAS	TeH_2	DL: 0.086 ng mL^{-1} (QL: 0.29 ng mL^{-1}. With Ru modified graphite tube 173-fold enhancement was obtained over 180 s trapping period with respect to ETAAS; the tubes could be used for 250 cycles. DLs were 0.0064 and 0.0022 ng mL^{-1} for Pd and Ru treated ETAAS systems, respectively, for 180 s collection of 9.6 mL sample solution)	[53]
HG-SPE-ETAAS	AsH_3	DL: 1 ng L^{-1} (QL: 5 ng L^{-1} and the characteristic mass, 5.8 pg could be achieved. $r = 0.9993$, from the limit of quantification up to 500 ng L^{-1}, RSD = 6.3%. A sensitive enhancement factor of 38 was reached when 2 mL of sample were processed and 50 mL of HNO_3 were used as eluent)	[44]
HG-CT-ICPMS	Arsine and methyl-substituted arsines (iAsIII, MAsIII, and DMAsIII)	DLs: 3.4, 0.06, 0.14 and 0.10 pg mL^{-1} were achieved for inorganic As, mono-, di- and trimethylated species, respectively, from a 500 mL sample	[51]
HG-QT-AAS	Sn	DL: 0.029 ng mL^{-1} and 0.14 ng mL^{-1} with and without preconcentration (preconcentration efficiency of 95 ± 5% was found for 120 s preconcentration period)	[48]
FI-HG-W coil-AAS	Cd	DL: 0.003 ng mL^{-1} (sample volume: 5 mL; the sensitivity and the LOD were improved by 58- and 66-folds compared to conventional direct injection W-coil AAS)	[107]

device (Fig. 3), based on quartz multi-atomizer for the determination of hydride forming elements at ultratrace levels, with its inlet arm being resistively heated. Excess of hydrogen gas evolved in the VG process is taken out in an oxygen atmosphere. Alternatively, hydrogen is used to volatilize the trapped species.

Among the documented advantages of this approach, the low and controlled analyte losses and the lack of temperature gradients between the trap and the optical arm are highlighted; *i.e.*, the inherent advantage of the preconcentration procedure and apparatus design described in the work of Kratzer is complete analyte trapping and succeeding volatilization. Trapping and volatilization temperatures were 290 and 830 °C, respectively; and further analyte losses are possible. Despite the fact that about 100% of trapped plumbane is released when employing H_2 from TBA decomposition (30 mL min^{-1} H_2), extra H_2 was added (100 mL min^{-1} H_2) to prevent peak dispersion (tailing), but the method efficiency was not affected (Fig. 3). Ultratrace levels of Pb can thus be determined above the detection limits (0.21 ng mL^{-1} for 30 s preconcentration, and a sample volume of 2 mL). Bismuth interfere over plumbanne retention in the preconcentration mode in a QTA device, but in the on-line atomization mode no significant interferences were documented. The logical explanation was that Bi interference took place in the preconcentration or subsequent atomization step. These experimental observations were further studied [100] through quantification of trapping and volatilization efficiencies of plumbanne by an independent radiotracer method employing the ^{212}Pb radioactive indicator. Besides, the trap capacity and the nature of the Bi interference were examined using that radiotracer approach. Although 1–10 ng of analyte is typically preconcentrated in ultratrace analysis, the QT was capable to efficiently trap and volatilize around 200 ng Pb (Table 3).

Alternatively, tungsten coil traps (Fig. 4) have demonstrated superior performance in preconcetrating volatile species generated from VGT. A W-coil trap is resistively heated unlike quartz trap, achieving high heating rates. The W-coil is adapted from a commercially tungsten lamp; used and readily replaced. The tungsten trap is located in the inlet arm of a conventional T-tube atomizer (Fig. 5).

After the pioneer studies in hydride trapping with tungsten coils [106,107], this technique was further investigated for different VG systems and with different modifications including coating of tungsten surface with noble metals [96,108]. Xi et al. [49] carried out a comprehensive study on TeH_2 preconcentration on a W-coil with deposition of Au, Re, Ir and Pt. The method detection limit was 0.08 ng mL^{-1} with 1.0 min for preconcentration. This is to say, the obtained enhancement factor of 28-fold (compared to conventional HG-AAS) which could be increased at higher trapping times. A linear dynamic range between 0.5 and 20 ng mL^{-1} was achieved. The repeatability expressed as relative standard deviation (RSD) was 5.8% ($n = 11$) for 1 min collection of 2 ng mL^{-1} Te solution. Analysis of three standard reference materials (GBW 07311, stream sediments; and GBW 07404 and GBW 07429, soil) confirmed the accuracy.

A FI-HG-W-coil-AAS method for on-atomizer trapping of Cd (Fig. 5) was developed more recently by Chen et al. [103]. Volatile species of Cd were produced using a FI-HG system consisting of a six port rotary valve, two three-channel peristaltic pumps and a gas liquid separator which end tip was inserted into the atomizer manually. The generated volatile species of Cd were swept by an Ar stream and directed toward the W-coil atomizer for on-atomizer trapping (more details on this design can be found in Ref. [103]). Compared to conventional direct injection W-coil AAS, the DL (0.003 ng mL^{-1}) was improved 66-fold for 5 mL of sample. Higher sample volumes would lead to more sensitive determinations. In this case the repeatability calculated as relative standard deviation ($n = 11$) was 2.6% for a 0.5 μg L^{-1} Cd standard. Spike-recovery studies confirm that no analyte loses during validation.

Alternatively, volatile species generated in a VG system can be firstly preconcetrated in a micro-solid phase extraction septum and then desorbed within the QTA. In spite of the discontinuous nature and the tedious operation, low detection limits and excellent accuracy can be achieved. A recent article published by C. Romero et al. [108] demonstrated the applicability of this principle for the ultra-trace Hg determination in two biological samples (NRCC CRM TORT-2, lobster hepatopancreas and CRM BCR-278, mussel tissue). The basic principle involves mercury cold

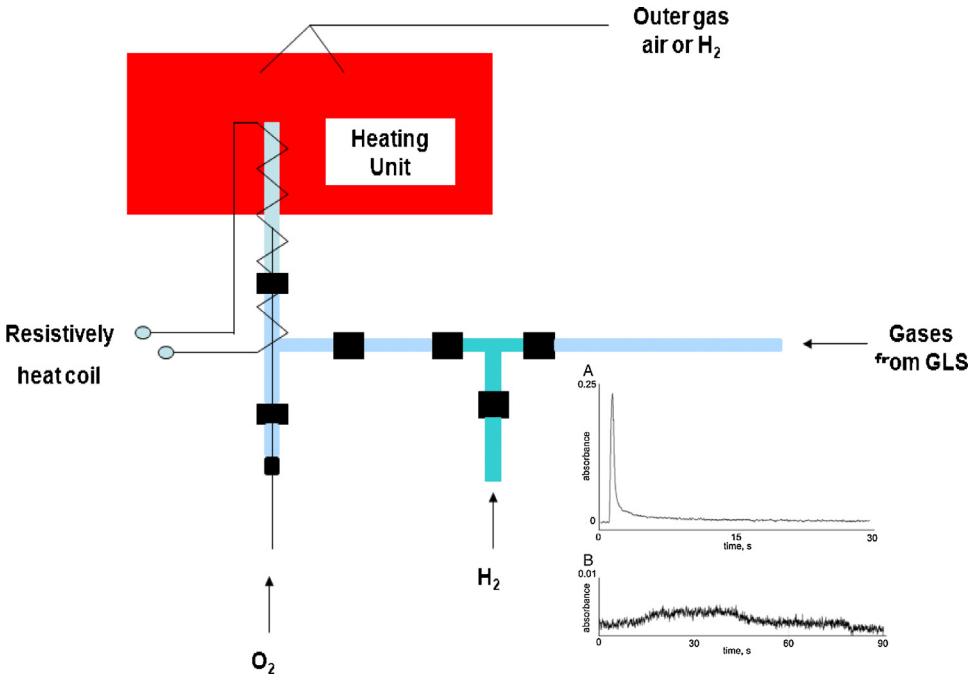

Fig. 3. Compact trap-and-atomizer device based on quartz multi-atomizer (adapted from Ref. [98]).

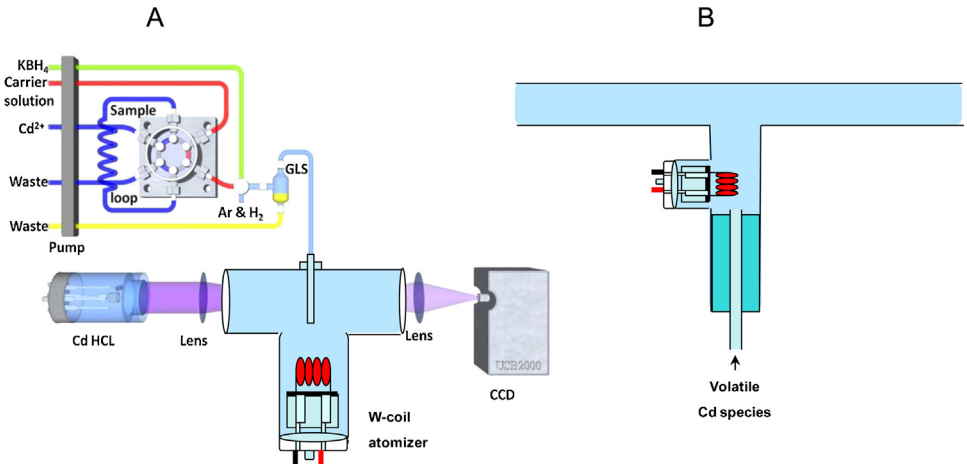

Fig. 4. (A) Scheme of flow injection hydride generation for on-atomizer trapping by tungsten coil and AAS (adapted from Ref. [103]) and (B) conventional W-coil.

vapor generation in THB media, collecting the evolved Hg° vapors in the surface of a Pd-coated fiber, to finally introduce the septum into the QTA. Finally, external resistive heating is applied and the retained analyte is desorbed and determined by AAS. The analytical characteristics indicated good linearity (linear regression coefficient of 0.998) up to an 80 ng mL^{-1}. The detection limits were 90 and 130 pg mL^{-1} Hg with the Pd wire and the Pd-coated SiO_2 fiber, respectively. The repeatability expressed as relative standard deviation for seven replicates was 4.3%.

3.1.2. Graphite tube atomizers

Adequate modification of the graphite surface of an ETAAS enables the retention of volatile hydrides. To this aim, it was suggested using graphite tubes coated with permanent modifiers, such as metals of the platinum group (PGMs) or metals with high boiling points [110]. Iridium was found as one of the most economic modifiers; tubes treated with this modifier could be used for several hundred measurements without any re-coating. Once the VG process is optimized, special care must be taken on other critical variables of the trapping process, *i.e.*, the trapping temperature and the atomization temperature of the graphite furnace. Typical values are between ambient temperature and several hundred °C for trapping conditions; and values above 1200 °C for atomization. Remarkable contributions have been done by Professor B. Welz in this field [111,112]. Both batch and flow-injection approaches for chemical vapor generation can be easily adapted as described below.

Batch hydride generation technique was adapted to preconcentrate arsine (AsH_3) in an Ir-coated graphite tube [111]. This approach enabled the accurate quantification of As in gasoline samples after acid digestion. A collection time of 30 s in a graphite tube coated with 150 μg of Ir as permanent modifier and pre-heated to 250 °C was proposed. The DL and QL values were 0.43 and 1.4 μg L^{-1}, respectively with an adequate precision of 5.3%. The characteristic mass was 24 pg, practically the same as for direct As determination by ETAAS. The extremely low limits of detection, allowed treating samples in a digestion procedure with no practical limitations with the final dilution factor.

Other batch-vapor generation approach has also been described in association with ETAAS trapping. A method for trace Sn(II) determination with electrochemical (Ec) HG-ETAAS with *in situ* trapping was described by Masrournia and Shadmehri [113]. The

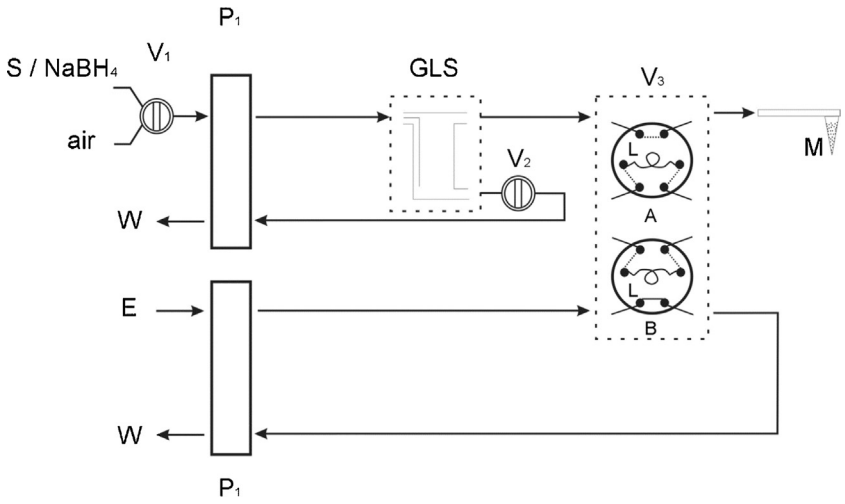

Fig. 5. Schematic diagram of the instrumental set up. S: sample; E: eluent; L: loop 50 mL volume; W: waste; P: peristaltic pump; M: minicolumn packed with oxidized multiwall carbon nanotubes mounted on the arm of ETAAS autosampler; V1, V2 and V3: valves; GLS: gas–liquid separator. Injection valve positions (a) sample loading and (b) injection (taken from Ref. [44]).

permanent chemical modifiers, Pd, W, Ir, and Pt were evaluated for graphite coating. This method worked over a linear range from 1 to 200 $\mu g\,L^{-1}$, with a detection limit of 0.8 $\mu g\,L^{-1}$ and a relative standard deviation of 6.2% ($n = 3$) for 100 $\mu g\,L^{-1}$ Sn(II). This method was applied to the analysis of real water samples and reference materials; and adequate recoveries over the range of 93.1–115.0% were documented.

Other application was also described by Shaltout et al. [112]. They applied the trapping technique to preconcentrate Se_2H after VG onto an Ir-coated graphite tube. This research added new insights to the Se determination in vegetal tissues by ETAAS, where Fe and P are spectral interferences affecting the accuracy in trace Se analysis. The method involved a microwave-assisted acid digestion for soybean and soil samples, with further reduction of Se(VI) to Se (IV) in HCl media. The VG was a continuous system for hydride generation with an outlet tip introduced into the dosing hole of the Ir-coated graphite tube that was pre-heated to 500 °C. The limits of detection and quantification of the method were 30 $ng\,L^{-1}$ Se and 101 $ng\,L^{-1}$ Se, respectively, corresponding to about 3 $ng\,g^{-1}$ and 10 $ng\,g^{-1}$, respectively in the solid samples. Analysis of two food CRM, soybean and rice, and soil and sediment CRM confirmed the validity of the method.

It must be stressed that experimental evidence showed that high levels of more than one hydride-forming species entail loses of sensitivity. An interference study of As, Sb and Bi hydrides in collection of H_2Se within an Ir-modified transversally-heated graphite tube atomizer (THGTA) was undertaken by Furdíková and Dočekal [97]. The effect of addition of air (from 0.03 to 12 $mL\,min^{-1}$) into the gaseous phase in the collection of SeH_2 at temperatures of 400 °C and 900 °C in presence of arsine (AsH_3), bismuthine (BiH_3) and stibine (SbH_3) was evaluated. Corrosion of graphite, and consequently reduction in tube life time, was observed at elevated temperatures when air was mixed beyond the stoichiometric ratio. The determination of Se can be performed preferably at 400 °C (below 600 °C) under addition of air corresponding at optimum in stoichiometry to 50–70% of generated hydrogen. Standard tube life time is preserved under these conditions.

In these and other former studies [14,96], it has been also documented that using Ir as modifier enhances the sensitivity [111]. Besides, low background can be obtained; but however, possible transfer loss of volatile species and tube damage by reaction with HG by-products can be advised.

3.2. Other trapping approaches

To this point, it has been discussed the advance and new developments in trapping of volatile species with vapor generation techniques. In this fashion, only in-atomizer hydride trapping approaches have been reviewed. In this section, the discussion is extended to other approaches including preconcentration of volatile species previous to the atomizer through cryogenic trapping (cryotrapping) or gas–solid phase trapping process.

Cryotrapping also accomplishes the required goals of a preconcentration technique: analyte enrichment and interference (and matrix effects) elimination. This approach may be used as a separation technique, where the analytes desorb from the trap in accordance with their boiling points. Typical trapping temperatures are in the range −150 to −196 °C. In contrast to typical absorbing media, consisting of solutions of $AgNO_3$, dithiocarbamate or KI, water has been recently used to collect elemental vapors as well as other noble metal species arising from VGT. Unlike collection *via* decomposition and formation of a soluble salt or complex, the solubility of the target specie is the limiting for the preconcentration efficiency.

All recent applications of cryotrapping take advantage of the specific-species desorption principle and are devoted to speciation studies consequently. A series of studies have been undertaken by Dědina and co-workers in the last 5 years [47,50,51] in the matter of arsenic speciation. The applicability of a cryotrapping automatic device developed some years ago [114] was demonstrated. Speciation analysis of As was carried out to determine methylated As(III) in mouse liver by HG-cryotrapping-AAS [50]. Adequate sample preparation allowed discriminating between As(V) and As (III) species; *i.e.*, strong acidic conditions to generate hydrides of As (V) and As(III) species; and pH 6 to selectively generate hydrides of As(III) species. The overall procedure was as follows: fresh (undigested) homogenates prepared from 4 sections of the liver of a mouse exposed to inorganic As(III) (50 ppm) for 9 days were divided into two aliquots. To begin, hydrides from the trivalent As species (iAsIII, MAsIII, and DMAsIII) are generated at pH 6 and measured directly without sample pretreatment. After that, a second sample aliquot was added with 2% L-cysteine to reduce the pentavalent As species (iAsV, MAsV, and DMAsV); thus, arsines generated from this sample aliquot represent both tri- and pentavalent As species – iAs(III + V), MAs(III + V), and DMAs(III + V) – present in the sample. The concentrations of the pentavalent As species are then determined by subtracting the results of analysis in the first sample aliquot.

A recent study described an As speciation analysis in pharmaceutical samples [47]. This method involved also selective generation of substituted arsines species. The reported detection limits were 70 $ng\,L^{-1}$ for inorganic arsenate, 42 $ng\,L^{-1}$ for mono- and dimethylarsenates and 30 $ng\,L^{-1}$ for all the other determined species. The accuracy was assessed through comparison with ICP-MS. Further improvements in sensitivity could be achieved through association of this HG-cryotrapping technique to ICP-MS detection. Lately, this approach was applied for As speciation [51] by selective HG without prereduction or with L-cysteine prereduction. Methylated species desorbed differentially after collection at −196 °C. Limits of detection of 3.4, 0.06, 0.14 and 0.10 $pg\,mL^{-1}$ were achieved for inorganic As, mono-, di- and trimethylated species, respectively, from a 500 mL sample. Speciation analysis of river water (NRC SLRS-4 and SLRS-5) and sea water (NRC CASS-4, CASS-5 and NASS-5) reference materials certified to contain 0.4–1.3 $ng\,mL^{-1}$ total As was performed. Sums of calculated concentration for selected species agreed well with the total certified As content. The HG-CT-ICP-MS method was successfully used for analysis of microsamples of exfoliated bladder epithelial cells isolated from human urine.

Complete separations were plausible using this HG-cryotrapping technique. Despite some interferences have been documented due to low HG yield, adequate separation for As species of toxicological and biological interest could be reached. The main drawback compared to chromatographic methods is that the study of error propagation involves the combination of two responses; *i.e.*, subtractions of signals are proposed to measure As(V) species. This is in detriment of evaluated sensitivity and precision.

Recent research has shown that carbon nanotubes are adequate sorbents for CO, CO_2, Ar, N_2, CH_4 and others [115–117]. In a recent work, we demonstrated [44] that selective and quantitative retention of arsine occurred on CNTs by van der Waals interactions. This was a discontinuous configuration (Fig. 5) of hydride trapping to enhance sensitivity without sophisticated systems. After preconcentration, elution was accomplished with nitric acid directly onto the graphite atomizer. A high enhancement factor of 38 was reached for 2 mL of sample and 50 µL of HNO_3 were used as eluent. The quality of results was assessed in terms of accuracy, sensitivity and precision. A detection limit of 1 $ng\,L^{-1}$, quantification limit of 5 $ng\,L^{-1}$ and the characteristic mass, 5.8 ± 0.4 pg were thus achieved. A satisfactory correlation between concentration of

arsine and absorbance ($r = 0.9993$) from the limit of quantification up to 500 ng L^{-1}, with a relative standard deviation of 6.3% were obtained. A certified water sample (QC metals in natural waters) and real tap water were also analyzed.

The group of C. Bendicho published a trapping method for hydrides and vapors generated in THB media [118]. The principle involved using nanoparticles of silver that were used as retaining substrates. They were previously fixed onto quartz reflectors of an X-ray spectrometer. The informed detection limits and enrichment factors for Se and Hg were 0.18 and 0.55 μg L^{-1}, and 265 and 175, respectively. Method validation took place through analysis of three biological CRM.

4. Future trends

Despite the assumed maturity of vapor generation techniques, new frontiers are observed in this field as a consequence of new developments aided by preconcentration strategies. Beyond the obvious increase in sensitivity and selectivity toward specific chemical species, these techniques still have a large number of undescribed applications. In this revision, we have showed the actual state of vapor generation associated to analytes preconcentration before and after VGT.

To explore the future of VGT, a number of directions should be considered. Beyond the intrinsic advantages of VG as a consequence of associations with preconcentration approaches, the most important improvements have been reported in the analytical performance of AAS. This technique becomes this way advantageous and compete with sophisticated technologies. New field applications are thus observed from ultra-trace analysis of several analytes to speciation and fractionation of metallic and non-metallic species in samples of different origins and interests. New directions point toward new analytes (unconventional; *i.e.*, noble metals, REE, halogens, *etc.*). Further applications of these preconcentration techniques are expected.

Regarding productivity of VGT-AAS systems, miniaturization and automation are important topics that are being discussed. Current developments are toward portable and low consumption devices that are aligned with the green chemistry concepts; and new improvements are expected in this matter.

Acknowledgments

This work was supported by Universidad Nacional de San Luis through the research project PROICO 2-1512; Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) through the research project PIP11220110100123; and Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT) through the research project PICT-2010-1899.

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