

## Recent advances in flow-based sample pretreatment for the determination of metal species by atomic spectrometry

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During the last few years, various flow-based separation/preconcentration methodologies have gained pertinent novel advances and exhibited powerful capability in the field of sample pretreatment and their hyphenation with detection by atomic spectrometry. The present mini-review presents and discusses the progress of flow-based sample processing approaches commonly used for the assay of trace elemental species with detection by atomic spectrometry, including preliminary sample pretreatment, solid phase extraction (including solid phase microextraction), liquid-liquid extraction, vapor generation and dialysis techniques. Special emphasis has been paid on the novel applications and analytical procedures hyphenated with atomic spectrometry. The future perspectives of flow-based sample pretreatment protocols in the determination of trace elements and their speciation are also discussed.

### flow system, sample pretreatment, atomic spectrometry

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The determination of trace elements in different types of samples plays an important role in the field of analytical chemistry, especially to those of the highly toxic metal/metalloid species, e.g.  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cr(VI)}$ ,  $\text{As(III)}$ ,  $\text{Se(IV)}$ . The existence of these elemental species has significant impact on the ecological system, biological organisms as well as human health [1]. Various atomic spectrometric procedures have inherently presented themselves as the most attractive option, due to their excellent sensitivity and precision for the determination of trace levels of elemental species, these include flame atomic absorption spectrometry (FAAS), electrothermal/graphite furnace atomic absorption spectrometry (ETAAS/GFAAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma-atomic/optical emission spectrometry (ICP-AES/OES), microwave induced plasma-optical emission spectrometry (MIP-OES), inductively coupled plasma-mass spectrometry (ICP-MS). However, the direct application of

these analytical techniques to real sample analysis is frequently restricted because they are generally very sensitive to the complex sample matrix compositions and the variations of sample matrixes tend to cause significant effect on the analysis results. Particularly, the accurate determination of ultra-trace amount of metal species in highly complex sample matrixes is always a real challenge in practical applications. In these cases, the direct determination of the analytes is generally not possible or not reliable by atomic spectrometry. Thus it is imperative to apply appropriate sample pretreatment processes for the removal of interfering sample matrix components and in the mean time increasing the concentration of the analytes by appropriate preconcentration [2]. As automatic operation platforms for fluidic delivering and on-line sample processing, the three generations of flow injection techniques, e.g. flow injection (FI), sequential injection (SI) and lab-on-a-valve (LOV), provide ideal alternatives to perform sample pretreatment successively in a cyclic mode and accurately introduce the analytes into the detector in a liquid or gas flow [3]. During the

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last few years, various novel flow-based sample pretreatment methodologies have exhibited powerful capability and gained extensive attentions in the field of sample separation/preconcentration and their hyphenation with different detection techniques including atomic spectrometry [4].

The aim of this mini-review is to present and discuss the state-of-the-art progress of flow-based sample pretreatment protocols in the period of 2010–2012 commonly applied for the quantification of trace level of elemental (heavy metal) species hyphenating with atomic spectrometry. In the meantime, the future perspectives of this field are also depicted. These are discussed separately in the following sections.

## 1 Preliminary sample pretreatment

Generally, the metal species can only be determined by atomic spectrometric techniques when the analytes are existing in an aqueous medium. Therefore, the analytes/metal species in real samples should be first transferred into aqueous solution. In this respect, microwave-assisted digestion is normally used to release the analytes/metal species from solid or organic matrix into aqueous solution. A procedure for the determination of 12 elements in sediments was developed by microwave digestion in aqua regia with ensuing detection by ICP-AES [5]. As an alternative to complete wet digestion, the extraction of metal species by using acids or water provides a simple and rapid approach for leaching the analytes, as recently illustrated by the determination of trace elements in mastic gum of pistacia lentiscus by ICP-AES [6] and the quantification of water-soluble zinc in airborne particulate matters by FAAS [7]. As an effective sampling protocol, slurry sampling has the advantages of eliminating the need for a sample pretreatment step and reducing the risk of analyte loss or sample cross contamination. This has been demonstrated by several novel methods proposed for the determination of trace elements in environmental matrixes such as boron carbide powders [8], estuarine sediments [9], coal samples [10], etc. However, the analysis of ultra-trace level of analytes generally runs into problem due to the interfering effects of complex sample matrix components.

It is worth mentioning that the low viscosity and high stability of microemulsion make it a suitable approach for the preparation of samples. Thus microemulsion has been increasingly exploited in the analysis of fuels. For instance, an automatic microemulsion preparation approach was recently developed for the determination of metal species in fuel samples with detection by GFAAS [11]. It should be emphasized that after these simple or preliminary sample processing, the sample matrix components are generally not eliminated, and thus their potential interfering effects on the determination of analytes of interest are often problematic in practices. When concerning highly complex sample matrixes, various separation/preconcentration procedures are

required. The approaches based on solid phase extraction (solid phase microextraction), liquid-liquid extraction, vapor generation and dialysis are the common alternatives for improving the sensitivity and selectivity of the available atomic spectrometric techniques.

## 2 Solid phase extraction/microextraction

Solid phase extraction (SPE) including solid phase microextraction (SPME) is one of the most important sample pretreatment techniques. It can generally provide rapid phase separation and offer high enrichment factors. In addition, it is ease of operation and automation. It is known that the most important part of SPE/SPME is the features of the sorbent materials and their effectiveness in interactions with the analyte of interest. Therefore, in order to achieve better performance on the separation and ensuing determination of trace elements or metal species by atomic spectrometric detectors, it is highly desirable to develop novel and efficient adsorbent materials or modify the existing materials for the extraction and isolation of target elemental species from complex sample matrixes. Table 1 summarizes the important recent advances in flow-based SPE for the separation and preconcentration of trace elemental species followed by detection with various atomic spectrometric techniques.

The most interesting SPE materials reported in the literatures for the separation and preconcentration of target elements are those based on activated carbon, silica, resin, cellulose fibre, mineral, insoluble inorganic salt, biomaterial, etc. Activated carbon is an excellent collector for a wide range of metal ions or species, but it provides no selectivity. In fact, it is generally modified by attaching or immobilizing various functional groups to create desired selectivity for specific metal species, e.g. sodium diethyldithiocarbamate for arsenite [12], 4-(8-hydroxyquinoline-azo) benzamide for Pb(II) [13], benzoyl hydrazine for Er(III) [14] and ethyl-3-(2-aminoethylamino)-2-chlorobut-2-enoate for Au(III), Pd(II) and Pt(IV) [15]. It is known that silica has favorable mechanical and thermal stability and lower susceptibility to swelling and shrinking, which can also be modified by various functional groups to improve its selectivity toward metal species [16–24]. As an alternative to SPE column, sorbent materials based on silica can be readily made into membranes for the extraction of metal ions [25–27]. Some functionalized polymeric solid supports such as resin and cellulose are also good alternatives to facilitate SPE process. These are readily available by the functionalization or modification of polymers [28–40] or commercial products, e.g. HyperSep SCX [41], Oasis-HLB [42] and Amberlite XAD-7 [43]. As a cheap and useful alternative for the general sorbent material, mineral and insoluble inorganic salt materials have recently been used for solid phase extraction of various metal species. In this respect,

**Table 1** Flow-based solid phase extraction for the determination of trace elements by atomic spectrometry

Analyte	Sorbent material	Sample	Detector	Enrichment factor	LOD <sup>a)</sup> ( $\mu\text{g L}^{-1}$ )	RSD (%)	Ref.
As	Activated carbon modified with sodium diethyldithiocarbamate	Water	GFAAS	100	0.04	1.58	[12]
Pb	Activated carbon modified with 4-(8-hydroxyquinoline-azo) benzamidine	Water, river sediment, soil	ICP-AES	100	0.43	<2.1	[13]
Er	Activated carbon modified with benzoyl hydrazine	Sediment, orange and balsam pear leaves	ICP-OES	100	73 <sup>c)</sup>	<2.0	[14]
Au, Pd, Pt	Activated carbon modified with ethyl-3-(2-aminoethylamino)-2-chlorobut-2-enoate	Plainpalladium ore, auto catalyst	ICP-AES	125	5, 11, 9	<3.0	[15]
Pb	Silica modified with ionic liquid	Soil, river water	FAAS	185	0.7	4.2	[16]
Cd, Cu	Nanoporous silica modified with diphenylcarbazide	Water, soil, ore, sediment, fish	FAAS	294, 291	0.15, 0.45	<4	[17]
Au, Cu, Ag	Mesoporous silica modified with 3-aminopropyl, 3-mercaptopropyl and <i>N</i> -[2-aminoethyl]-3-aminopropyl groups, respectively	NR <sup>b)</sup>	ETAAS	10	0.14, 0.02, 0.025	3.4, 2.7, 3.1	[18]
Pd	Silica gel-polyethylene glycol	Water, dust, ore	FAAS	125	0.54	<4	[19]
Co, Cr, Ni, Cd, Mn, Zn	Silica gel modified with 1-(di-2-pyridyl) methylene thiocarbonohydrazide	Water	ICP-MS	3.5, 7.2, 2.3, 11.3, 9.9, 32.9	0.006, 0.530, 0.130, 0.240, 0.004, 0.030	1.4, 1.2, 0.3, 2.6, 0.3, 4	[20]
Pd	Silica gel modified with diphenyldiketone-monothiosemicarbazone	Tap water, catalytic converter	FAAS	335	5	<2	[21]
Hg	Octadecyl silica	Water, fish, milk, sausage	VG-AAS	128	0.00187	2.98–4.45	[22]
Cr	SBA-15 mesoporous silica modified with $\gamma$ -aminopropyl-trimethoxysilane	Waste water, riverine water	FAAS	44	0.2	2.1	[23]
Cu	Silica gel modified with dithizone	Water	FAAS	42.6	0.2	1.7	[24]
Cu	Octadecyl silica membrane disks modified with oxime ligands	Water	FAAS	>400	0.25, 0.29	NR <sup>b)</sup>	[25]
Cu	Octadecyl silica membrane disks modified with a Schiff base	Water	FAAS	>400	0.0102	NR <sup>b)</sup>	[26]
Hg	Octadecyl silica membrane disks modified with 1,3-bis(2-ethoxyphenyl)triazene	Water	VG-AAS	74	0.0106	1.1, 2.9	[27]
Cd, Co, Ni	8-Hydroxyquinoline chelating resin	Water	ICP-MS	NR <sup>b)</sup>	0.008, 0.006, 0.009	2.47, 2.09, 3.03	[28]
As	Cellulose fibre modified with yttrium hydroxide	Water, human hair	HG-AFS	16.4	0.017	2.6	[29]
Cu	Chloromethylated polystyrene modified with 1-phenyl-1,2-propanedione-2-oxime thiosemicarbazone	Water, soil, milk	FAAS	41	0.56	2.0	[30]
Cr(III), Cr(VI)	Chloromethylated polystyrene modified with <i>N,N</i> -bis(naphthylideneimino)diethylenetriamine	Water	FAAS	70, 30	0.6, 2.5	2.55, 0.8	[31]
Se	Cellulose fibre modified with Mg-FeCO <sub>3</sub> layered double hydroxides	Water, rice	HG-AFS	13.3	0.011	3.3	[32]
Hg, MeHg	Cellulose fibre modified with L-cysteine	Water, seaweed, cosmetic	HG-AFS	9.8, 10	0.001, 0.003	1.5, 2.6	[33]

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Analyte	Sorbent material	Sample	Detector	Enrichment factor	LOD <sup>a)</sup> (µg L <sup>-1</sup> )	RSD (%)	Ref.
Cr	Polyvinyl chloride modified with <i>N</i> -methylimidazolium	Water	ETAAS ICP-MS	23.4 23.7	0.003 0.0032	2.9 0.5	[34]
Fe, Cu, Pb	Amberlite IR-120 modified with 8-hydroxyquinoline	Water	FAAS	166, 200, 250	1.6, 0.7, 2.2	<4.4	[35]
Cu, Co, Ni, Zn, Cr, Cd, Pb	Amberlite XAD-16 modified with salicylamide	Water, mango pulp, leafy vegetables, fish	FAAS	440, 380, 360, 280, 280, 260	0.56, 0.64, 0.65, 0.70, 0.75, 0.88, 1.17	<5	[36]
Cd, Cu, Ni, Pb	Amberlite XAD-2 modified with 3-(2-nitro-phenyl)-1 <i>H</i> -1,2,4-triazole-5(4 <i>H</i> )-thione	Water, food	ICP-AES	60	0.22, 0.18, 0.20, 0.16	<4	[37]
Bi	Ethylenediaminetriacetic acid chelating resin	Seawater	ICP-MS	NR <sup>b)</sup>	10 <sup>-6c)</sup>	<4	[38]
Cd, Pb, Ni, Zn, U, Mo, Fe, Co, V, Mn	Toyopearl AF-Chelate-650M iminodiacetate resin; Toyopearl 8-hydroxyquinoline resin; silica immobilized 8-hydroxyquinoline resin	High-salinity petroleum	ICP-MS	NR <sup>b)</sup>	0.0007, 0.009, 0.017, 0.024, 0.0002, 0.047, 0.058, 0.002, 0.013, 0.041	NR <sup>b)</sup>	[39]
Cu, Pb, Ni	Amberlite XAD-4 modified with <i>N,N</i> -bis(salicylidene)cyclohexanediamine	Water	FAAS	200	0.11, 1.91, 0.43	1.0–2.48	[40]
Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	HyperSep SCX	Water, sediment, mussel, tuna	ICP-AES	10.7, 13.2, 12.8, 9.4, 13.1, 13.1, 12.7, 14.3, 14.0, 8.4	0.09, 0.07, 0.06, 0.2, 0.08, 0.05, 0.1, 0.07, 0.2, 0.08	4.1, 4.5, 3.7, 3.9, 4.5, 5.1, 3.7, 4.2, 2.5, 4.2	[41]
Cr, Cu	Oasis-HLB	Water	FAAS	70, 195	0.8, 0.1	3.5, 2.7	[42]
Ni	Amberlite XAD-7	Water	FAAS	125	0.44	2.8	[43]
Cr, Hg, Pb	Bentonite modified with 4-aminoantipyrine	Water	ICP-AES	100	0.12, 0.09, 0.23	2.7, 2.1, 1.6	[44]
Cu, Mn, Ni	Alumina hollow fiber	Water	ICP-OES	10	0.88, 0.61, 0.38	7.9, 6.2, 7.2	[45]
Cr	Iron phosphate	Water	ETAAS	8.7	0.02	2.5	[46]
As(V), MMA, DMA, As(III)	MnO <sub>2</sub>	Water, Hijiki	HPLC-HG-AS	17.0, 16.7, 14.0, 19.2	0.33, 0.39, 0.62, 0.019	4.2, 2.9, 3.9, 2.7	[47]
Cr(III), Cr(VI)	Fe <sub>3</sub> O <sub>4</sub> magnetite microspheres modified with amine group	Drinking water	ICP-MS	96, 47	0.0015, 0.0027	1.9, 4.5	[48]
Ru, Rh, Pd, Ir, Pt, Au	Fe <sub>3</sub> O <sub>4</sub> magnetite microspheres modified with mercapto group	Rock, human hair	ICP-MS	46, 32, 43, 38, 44, 46	2.1, 1.9, 2.5, 1.8, 1.9, 1.2, 1.9, 2.1, 1.4, 1.7	1.2, 1.3	[49]
Ag	Moringa oleifera seeds	Water	FAAS	35	0.22	3.8	[50]
Pb	Filamentous fungal biomass-loaded TiO <sub>2</sub> nanoparticles	Water	FAAS	868	0.78	<9	[51]
Ag	Eggshell membrane	Polymetallic ore, sediment	FAAS	NR <sup>b)</sup>	27	<4.95	[52]
Rare earth	Walnut shell	Sediment, copper ore, tea leaf, human hair, agricultural and food products	ICP-MS	79–102	0.002–0.034 <sup>c)</sup>	0.5–2.0	[53]
Cd	Mungbean-coat	Water, city waste incineration ash	ETAAS	19.8	0.0014	2.4	[54]

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Analyte	Sorbent material	Sample	Detector	Enrichment factor	LOD <sup>a)</sup> ( $\mu\text{g L}^{-1}$ )	RSD (%)	Ref.
Cd	Surface-engineered yeast cells	Water, soil	GFAAS	30	0.0011	3.3	[55]
As	Bacillus subtilis cells modified with Iron(III)	Water, human hair	GFAAS	9.2	0.08	4	[56]
Cd	Surface-engineered yeast cells	Water, soil	GFAAS	30	0.0011	3.3	[57]
Mn	Multiwalled carbon nanotubes modified with 1-(2-pyridylazo)-2-naphthol	Water, aluminum alloy	FAAS	100	0.058	0.41	[58]
Fe, Cu, Mn, Pb	Multiwalled carbon nanotubes	Lake water, sediment, plant, food	FAAS	20	4.9, 6.5, 3.5, 8.0	<2.5	[59]
Pb, Cd	Multiwalled carbon nanotubes modified with manganese dioxide	Water, human hair	ETAAS	100	0.0044, 0.0015	3.2, 2.5	[60]
Pd	Oxidized multiwalled carbon nanotubes	Water, fly ash, road dust	FAAS	165	0.3	5.3	[61]
Cd	Multiwalled carbon nanotubes modified with iron phosphate	Water, soil	ETAAS	31.2	0.0013	2.2	[62]
Cr	Multiwalled carbon nanotubes modified with poly(diallyldimethylammonium chloride)	Water	ETAAS	8.6	0.016	3.9	[63]
Cr	Graphene	Water	FAAS	125	0.5	4.3, 3.4	[64]
Cd	Graphene oxide modified with cyanobacterium metallothionein	Water, soil	GFAAS	14.6	0.0012	3.2	[65]
Pb	Titanium dioxide nanoparticles modified with coliform bacteria	Tea, river water, wine, baby food	FAAS	1300	0.9	<4	[66]
Cd, Pb	Nano-alumina modified with sodium dodecyl sulfate-1-(2-pyridylazo)-2-naphthol	Water, lettuce, valeriana officinale	FAAS	250	0.15, 0.17	2.8, 3.2	[67]
Cu	Nano-alumina modified with sodium dodecyl sulfate	Oyster tissue, tap water, black tea, mushroom	FAAS	25	2.5	3.3	[68]
Pb	Silver nanoparticles	Human urine, blood	GFAAS	61	0.068	4.1	[69]
Pd	Pd-dimethylglyoxime-4-vinylpyridine imprinted polymer	Tap water	FAAS	33.3	5	NR <sup>b)</sup>	[70]
Ru	Ru-allyl acetoacetate-methacrylic acid imprinted polymer	Water, grass	ETAAS	20	0.32	2.5	[71]
Pt	Pt-acetaldehyde thiosemicarbazone-methacrylic acid imprinted polymer,	Tap water, tunnel dust, anode slime	ETAAS	2.5	0.16	4.5	[72]
Ru	Ru-thiosemicarbazide-methacrylic acid imprinted polymer, Ru-acetaldehyde thiosemicarbazone-methacrylic acid imprinted polymer	Water, hair, grass	ETAAS	3-4	0.16, 0.25	<5	[73]

a) LOD: limit of detection; b) NR: not reported; c)  $\text{ng g}^{-1}$ .

bentonite [44], alumina [45], iron phosphate [46],  $\text{MnO}_2$  [47] and  $\text{Fe}_3\text{O}_4$  [48,49] have been successfully used for specific purposes. In particular,  $\text{Fe}_3\text{O}_4$  as a special supporter provides a magnetic immobilization procedure for on-line SPE without the need for any frits or plugs. Recently, the characteristic biomaterials have attracted increasing attention in SPE because of their chemical reactivity originated from the presence of various functional groups on the surface of the sorbent materials. A lot of efforts have been dedicated to selective retention of some metal species with moringa oleifera seeds [50], filamentous fungal biomass [51], egg-shell membrane [52], walnut shell [53] as well as mung-bean-coat [54] as adsorbent. By introducing some specific selective functional groups on the surface of biomaterials via the approach of surface engineering technique provides an alternative to improve the metal-binding capacity and sorption selectivity of biomaterials toward some biologically and environmentally significant metal species [55–57].

As emerging functional materials, various nanomaterials and ionic imprinted polymeric materials have been paid extensive attention in the field of SPE process for the selective separation and preconcentration of metal species. Compared with micrometer-sized sorbent, nanomaterials have a significantly higher surface area, resulting in a favorable extraction capacity and in many cases provide satisfactory extraction efficiency. In addition, ionic imprinted materials offer better selectivity toward the imprinted metal or metal species. The commonly encountered nanomaterials serve as SPE sorbents or supporting materials are those based on carbon and metal oxides or other related materials, such as carbon nanostructures including carbon nanotubes [58–63] and graphene based structures [64,65], titanium dioxide [66], alumina [67,68] as well as silver [69]. In practice, the ion-imprinted materials offer high selectivity towards the imprinted metal ions or species. This feature makes it possible to selectively bind the target metal species in the presence of other metal cations [70–73]. However, when treating real biological or environmental samples, the presence of very complex sample matrix components frequently blocks the successful separation of the target metal species. In this respect, extensive efforts should be made in the future studies.

### 3 Liquid-liquid extraction

Liquid-liquid extraction (LLE) has been traditionally and widely used for the separation and preconcentration of metals and metal species for a long time. Nowadays, the trend of liquid-liquid extraction has been directed to the avoidance of the consumption of large amount of organic solvents in order to protect the operator and the environment. In this respect, various extraction approaches with very limited consumption of organic solvents have been developed and widely employed for the pretreatment of various sample

matrixes. These protocols include dispersive liquid-liquid microextraction (DLLME), cloud point extraction (CPE), solidified floating organic drop microextraction (SFODME), in situ solvent formation microextraction (ISFME) as well as hollow fiber supported liquid membrane extraction (HF-SLME), etc.

Among these extraction approaches, DLLME has been widely employed during the recent years. One of the most important key issues for the success of DLLME is the choice of solvent for performing the extraction. Solvents of higher densities than water are preferred as they are readily separated from the water phase via centrifugation after extraction. Very recently a novel extraction method has been developed for the separation of cadmium, lead and bismuth, followed by flow injection sample introduction and detection by ICP-MS [74], where the metal species of interest were effectively transferred into carbon tetrachloride by DLLME after complexation with sodiumdiethyldithiocarbamate. In order to reduce the environmental effect to the extent possible, the substitution of toxic solvents with green alternatives for performing DLLME attracted extensive attentions. In this respect, fatty alcohols [75,76] as well as ionic liquids [77,78] have been employed for this purpose. When using a microcolumn packed with a sorbent material such as poly(etheretherketone)-turnings [75] or florisil [77], the extraction solvent can be on-line separated from the aqueous phase instead of centrifugation.

CPE is an impressive alternative to conventional LLE and very recently some novel applications of CPE have been developed for the determination of trace level of metals with detection by atomic spectrometry. Some of the important procedures include the preconcentration of vanadium via the isolation of its complex with 2-(2'-thiazolylazo)-*p*-cresol in Triton X-100 surfactant and the determination is facilitated by GFAAS [79]; the separation/preconcentration of bismuth in the form of its 8-hydroxyquinoline complex in Triton X-114 surfactant prior to its determination by ICP-OES [80]. In order to improve the traditional CPE pattern, rapid synergistic CPE procedure was proposed by using octanol as cloud point revulsant of Triton-114 and synergistic reagent for extraction. The extraction could be accomplished within a very short time at room temperature (without heating) in a water bath [81].

The progress of SFODME was exhibited on the evaluation of the performance for separation/preconcentration and determination of copper by means of flow injection sample introduction and FAAS detection [82,83]. In this case, a free microdrop of 1-undecanol was adopted and 3-amino-7-dimethylamino-2-methylphenazine or 1,5-diphenyl carbazide were used as complexing reagent. Subsequently, a ligandless SFODME approach was proposed by using 1-dodecanol for the preconcentration of trace level of cadmium in the absence of chelating reagent [84].

It is known that one of the major advantages of ISFME is its compatibility with high content of salt. This feature was

recently further demonstrated by the extraction of trace level of cadmium in saline samples [85]. In addition, HF-SLME was successfully hyphenated with a portable W-coil ETAAS for the determination of trace lead in water samples [86].

#### 4 Vapor generation

Vapor generation (VG) provides an effective scheme for the isolation of hydride or vapor forming elements or metal species from complex sample matrixes. By using this approach, the analyte of interest could be readily isolated from sample matrix components, and in the mean time appropriate preconcentration of the analyte could be achieved. The hyphenation of VG with various atomic spectrometric techniques remains an alternative approach for selective and sensitive determination of trace metal species, and a considerable number of papers appear each year devoted to this subject [87].

Nowadays, chemical VG is quite commonly used for the determination of some biologically and environmentally significant metal species. Among these metals, Se, Te, As, Sb, Bi, Ge, Sn, Pb were separated via hydride generation (HG) while Hg and Cd were isolated via cold vapor generation (CVG). A lot of attentions have been directed to the automation of the sample processing system aiming at obtaining optimal analytical performance. A multicommutated flow system was designed and evaluated for the determination of total arsenic and selenium in natural and drinking water samples by HG-AAS [88]. Factorial design has been demonstrated to be helpful to characterize the effects of reagent conditions. This was characterized by the determination of lead with detection by a high-resolution continuum source HG-AAS [89].

During the last few years, efforts have been made to enhance the analytical throughput of the traditional approach generally used for the determination of single element. Simultaneous multi-element determination has been employed for the measurement with atomic spectrometry by introducing the gaseous species (hydride/vapor) of the analyte into an atomizer or an excitation source. These approaches include fast sequential AAS [90], multi-channel AFS [91,92], ICP-OES [93] and MIP-OES [94]. In comparison with single-element quantification, the feature of multi-element determination is also characterized by an obvious advantage, i.e. the reduction of reagents and sample consumption as well as the minimization of waste generation.

Traditionally, HG or CVG is used for a limited number of elements. Nowadays, the scope of hydride/vapor generation through the reaction with  $\text{NaBH}_4$  as the reducing reagent has been expanded to transition and noble metals, i.e. Fe, Co, Ni, Cu, Ag, Au and other elements. Significant efforts have thus been invested to overcome the shortcoming of low HG efficiency in rapid gas-liquid phase separation of

the generated hydride/vapor. The use of enhancement reagents or modifiers was also demonstrated to be effective. A simple and cost-effective thin film hydride generator has been successfully used for HG and the determination of trace copper by flow injection in situ hydride trapping GFAAS [95]. This approach possessed the advantages of rapid generation and fast separation of the unstable gaseous copper species from the liquid phase. It was demonstrated that room temperature ionic liquid combined with ammonium pyrrolidinedithiocarbamate (APDC) could synergistically enhance the HG efficiencies of iron, cobalt and nickel to 2.5-, 3.2- and 3-fold respectively [96]. It has been verified that the optimization of reagents and operation conditions was also important to improve the HG efficiency, as demonstrated in the vapor generation process of nickel [97].

Based on the different reaction conditions or the introduction of chromatographic separation, chemical VG can be further applied in the field of speciation analysis. A simple non-chromatographic method for the determination of mercury, methylmercury, dimethylmercury and phenylmercury was developed by means of AFS [98]. The determination is performed on the basis of the singular behavior of mercury species versus the different reagents/approaches involved in the CVG such as sodium borohydride, stannous chloride, potassium persulfate, and UV radiation. An automated chromatographic method for the speciation of inorganic and methylated arsenic species was achieved by HG-cryotrapping-gas chromatography-AAS [99], where the arsines were preconcentrated and separated in a chromosorb filled U-tube. Arsenic speciation was also performed based on liquid chromatographic separation followed by gradient hydride generation with detection by quartz tube AAS [100].

Besides the conventional chemical VG, other VG procedures have gained some novel advances. Photochemical VG is based on the exposure of sample to UV radiation in the presence of low molecular weight organic acids [101], which provides a powerful alternative with detection by AFS. This has been demonstrated in the direct determination of mercury in ethanol biofuel or white vinegar [102,103]. A novel VG technique for iodine determination by ICP-OES was developed based on solution cathode glow discharge induced advanced redox processes of iodide and iodate [104]. The *in-situ* produced highly reactive chemical species in the discharge eliminated the need for externally supplied sources of any redox reagents. Electrolytic CVG as a sample introduction technique in atomic spectrometry was further studied by the determination of mercury [105]. It was found that phosphate buffer solution increased the signal intensity of Hg vapor from electrolytic generation on Pt cathode and reduced the impact of cathode erosion on the stability of signal intensity. By using the electrothermal vaporization technique, it has been successfully used for the quantification of a series of trace elements, e.g. As, Co, Cu, Fe, Mn, Ni, Se and V, in biological samples with formic

acid as the vapor forming reagent and with detection by ICP-MS [106]. In comparison with acid digestion, electrothermal vaporization for sample treatment is a simple and cost effective process, and it also minimized the environmental effect.

## 5 Dialysis

Dialysis technique permits continuous monitoring of the variation of low molecular weight species with respect to time or sampling site. Thus, this technique helps to reveal the behavior of species migration. A hyphenated approach was developed for studying the bioaccessibility of arsenic in shrimp based on continuous-flow dialysis and on-line detection with ICP-MS [107]. It was found that half of the arsenic in shrimp was bioaccessible and most was contributed from organic arsenic species. Furthermore, the arsenic bioaccessibility in shrimp was not increased with the addition of ascorbic acid or fruit juices. An ultrasonic dialysis and capillary electrophoresis system with detection by ICP-OES was developed for the identification and determination of calcium species in human red blood cells [108]. Ultrasound dialysis enhances the movement of liquids and facilitates mass transfer which results in rapid equilibrium. Eight primary different calcium-containing species were found in human red blood cells. It was demonstrated that the calcium species with the greatest mobility was not free  $\text{Ca}^{2+}$  action, but a calcium-erythrocyte membrane species of 50–100 kD.

## 6 Conclusions and perspectives

For the analysis of trace metal species, ICP-AES, AAS, AFS and ICP-MS are currently the major detection techniques. Various sample pretreatment procedures play an important role in the elimination of matrix interferences and in the meantime to improve the analytical performance via the preconcentration of ultra-trace level of metal species. It should be emphasized that from the view point of biological and environmental sciences, the quantification of total amount is no longer sufficient for many of the metals, especially arsenic, selenium, mercury, etc. In this respect, it is highly desirable to develop selective sample pretreatment procedures for the isolation of some specific metal species. The functionalization of adsorbents or solvents with selective functional groups provides a promising approach for maintaining selectivity of solid phase extraction and solvent extraction. On the other hand, the improvement on the vapor generation efficiency of copper, iron and some other elements is the major issue in order to enhance the sensitivity for these metal species. The development of green adsorbents or solvents with desired selectivity is also a key issue for future studies in the field of sample pretreatment.

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