Recent advances in speciation analysis of mercury, arsenic and selenium

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Mercury (Hg), arsenic (As) and selenium (Se) are ubiquitous in the environment and exist in a variety of species, which have great influence on their transport, bioaccumulation and toxicity. This review presents the recent research progress in speciation analysis of Hg, As, and Se, with emphasis on enhanced cold vapor generation as interface for liquid chromatography and atomic spectrometry, speciation of volatile species in gas phase, and isotope dilution technique to improve the precision and accuracy of speciation. Hyphenated techniques to characterize the complexes of Hg and As with phytochelatin and chromatographic separation coupled with multi-collector-inductively coupled plasma mass spectrometry to measure species-specific isotopic ratios, are also briefly discussed.

speciation, mercury, arsenic, selenium, chromatographic separation, atomic spectrometry

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Mercury (Hg) and arsenic (As) are among the most highly toxic elements for humans and ecosystems and can cause serious environmental and human health problems even at low concentrations [1,2]. Selenium (Se) is an “essential toxin” for human health. It has been recognized as an important antioxidant and anti-cancer element. However, Se can also pose negative impact such as defective skin and hair loss [3]. The adsorption/uptake, transport, bioaccumulation, metabolism and toxicity of these elements strongly depend on their chemical species present in environmental and biological samples. In the environment, one species can transform to another through chemical or biological processes. For example, in anaerobic sediments, sulfur-reducing or iron-reducing bacteria can methylate inorganic mercury into highly toxic methylmercury (MeHg) [4,5]. Therefore, speciation analysis of Hg, As and Se is of great importance in order to elucidate the biogeochemical cycle and toxicology of these elements.

Speciation analysis mainly involves chromatographic

separation (gas chromatography (GC) or high performance liquid chromatography (HPLC)) hyphenated with element-specific spectrometry or molecular mass spectrometry. This review presents the recent advances in speciation analysis of Hg, As, and Se based on chromatographic separation, with emphasis on enhanced cold vapor generation (CVG) as interface for LC and atomic spectrometry, speciation of volatile Hg, As and Se in gas phase, and isotope dilution technique to improve the precision and accuracy of speciation. Hyphenated techniques to characterize the complexes of Hg and As with phytochelatin and chromatographic separation coupled with multi-collector-inductively coupled plasma mass spectrometry (MC-ICP-MS) to measure species-specific isotopic ratios, are also briefly introduced.

1 Synopsis of recent advances in speciation of Hg, As and Se

1.1 Speciation of Hg

Liquid chromatography hyphenated with atomic spectrometry

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has been widely used in speciation of Hg in environmental and biological samples and was reviewed recently [6]. Successful determination of ultra-low concentration of MeHg is mainly carried out using purge and trap pre-concentration followed by gas chromatography-atomic spectrometry detection. Aqueous ethylation by NaBEt₄-purge and trap-GC-atomic fluorescence spectroscopy (AFS) or ICP-MS is becoming a routine method for determination of ultra-low MeHg in environmental or biological samples. However, sulphide [7], dissolved organic matter (DOM) [7] and chloride [8] present in sample matrix interfere with the ethylation reaction, decreasing the derivatization efficiency [7] or transforming of MeHg into elemental mercury (Hg⁰) [8]. Although aqueous propylation of MeHg by NaBPr₄ does not cause any transformation of MeHg [8], artifact of MeHg and EtHg may form as side products of the propylation of Hg²⁺ in the propylation reaction [9]. Aqueous phenylation by NaBPh₄ is a good alternative to ethylation and propylation. The advantages of phenylation include: (1) Chloride, DOM and sulphide do not interfere with the derivatization [10]. (2) Unlike ethylation, it can be used to distinguish between Hg²⁺ and EtHg [11], as the derivatization products are different. (3) The lower volatility of the derivatization product of Hg²⁺, Hg(Ph)₂, minimizes its interference on quantitative determination of MeHg and possible contamination of GC and detector by Hg²⁺. By using the developed phenylation-purge and trap preconcentration coupled with GC-AFS/ICP-MS [10] and GC-MS [11], the occurrence of EtHg in the Florida Everglades was verified, which confirmed the previous finding of EtHg in soils and sediments of the Florida Everglades [12].

1.2 Speciation of As

Various As species, including inorganic arsenate (As(V)), inorganic arsenite (As(III)), monomethylarsonic acid (MMA(V)), monomethylarsonous acid (MMA(III)), dimethylarsinic acid (DMA(V)), dimethylarsinous acid (DMA(III)), trimethylarsine oxide (TMAO), tetramethylarsonium (Me₄As⁺), arsenobetaine (AsB) and arsenocholine (AsC), have been widely observed in biological and environmental samples. A number of reviews focusing on the speciation analysis of these As species have been published in recent years [13–17].

Arsenosugars, a kind of As-containing carbohydrates, widely present in freshwater, marine biota and terrestrial organism. A comprehensive introduction of the method for sample pre-treatment, extraction, separation and detection of arsenosugars can be found in a recent review [18].

In addition to the aforementioned As species, the fat-soluble As, so-called arsenolipids, are also widely present in organism but their structure are largely unknown. Recently, 14 arsenolipids, including 11 new compounds, were identified and quantified in brown algae, wakame (*Undaria pinnatifida*) and hijiki (*Hizikia fusiformis*), by HPLC-MS and

GC-MS [19]. Both algal species contained arsenosugar-phospholipids as the major type of arsenolipid, and arsenic-hydrocarbons were also detected, especially in Hijiki, suggesting that algae are the possible origin of these arsenolipids in marine ecosystems. Two arsenolipids, 1-dimethylarsinoylpentadecane and 1-dimethylarsinoyl *all-cis*-4,7,10,13,16,19-docosahexane were indentified in Sashimi tuna, together accounted for as high as 20% of total As [20]. Combined use of elemental and molecular mass spectrometry is helpful to identify the arsenic-containing non-polar compounds and elucidate their structure. By using combined HPLC-ICP-MS and HPLC-electrospray ionization (ESI)-MS, novel arsenic-containing long-chain fatty acids [21] and hydrocarbons [22] were identified in fish oil. Furthermore, the response factor of known concentration of arsenic (e.g. As(III)) obtained by using ICP-MS could be used to determine species-specific response factors for other unknown arsenolipids [23]. These results demonstrated that arsenolipids are important organic As species in marine organism and illustrate the importance of these studies on understanding metabolism of arsenolipids and the consequently health effect on human. After alkaline hydrolysis, sub-structure of AsC and DMA was indentified in the arsenolipids of starspotted shark *Mustelus manazo* [24]. This finding was later partially demonstrated by investigating the human metabolism of arsenolipids in cod liver [25]. The arsenolipids could be rapidly metabolized to water-soluble compounds in the urine, including DMA and arsenic-containing fatty acids.

4-Hydroxy-3-nitrobenzene arsenic acid (roxarsone, ROX) and 4-aminophenyl arsenic acid (p-arsanilic acid, p-ASA) have been widely used as coccidiosis prevention and animal growth promotion in the poultry and swine industry [26]. Development of chromatographic method to simultaneously monitoring ROX, p-ASA and their more toxic As metabolites is urgent for food safety and for evaluating the environmental impact of poultry litter application. Dionex AS16 and AS7 columns can well separate ROX and p-ASA from the more common and more toxic As species including As(III), As(V), MMA and DMA [27]. By using HPLC-ICP-MS and HPLC-ESI-MS/MS, chlorinated phenylarsonic acids and phenylarsine oxide derivatives were indentified in chlorine-containing water [26]. Under visible light, ROX can be decomposed to more toxic inorganic arsenic [26]. Poultry feather meal contains high concentration of inorganic As (30–1500 µg kg⁻¹) (account for 37%–83% of total As) [28], possibly as the result of metabolism of organic arsenic feed additives. These findings highlight the importance of management of poultry litter and poultry-source meal.

1.3 Speciation of Se

Speciation analysis of Se species, such as inorganic selenite (Se(IV)), inorganic selenate (Se(VI)), selenomethylselenocysteine (SeMSeCys), selenocystine (SeCys) and seleno-

methionine (SeMet), using various instrumental techniques have been published in recent years [29–33].

Selenosugars, Se-containing carbohydrates, are a group of important metabolites in animals besides trimethylselenium. Currently, four selenosugars were identified in liver, serum and urine of quail [34], turtle [35], rat [36], porcine [37], and human [38], including methyl-2-acetamido-2-deoxy-1-seleno- β -D-galactopyranoside (selenosugar 1) [39,40], methyl-2-acetamido-2-deoxy-1-seleno- β -D-glucopyranoside (selenosugar 2) [40], and methyl-2-amino-2-deoxy-1-seleno- β -D-galactopyranoside (selenosugar 3) [40] and selenosugar A [41]. In urine samples, selenosugar 1 is the major metabolite. It is proposed that active Se metabolite, GS-SeH is transferred to the sugar moiety to form selenosugar A, and then it is methylated to selenosugar 1 [41]. Instable selenosugar 1 could be oxidized by air or H_2O_2 to methylseleninic acid [42]. Selenosugar 1 in urine is also sensitive to temperature and light with volatile DMeSe, DMeDSe, and MeSeSMe being the major transformation products [43]. This work suggests that urine samples should be cooled immediately after collection to prevent transformation of selenosugars. For longer-term storage, urine samples should be kept at -80°C or at -20°C after lyophilisation. Recently, Aureli et al. [44] found some new selenosugar compounds in grains of wheat, rice and maize, including methylseleno-Se-pentose-hexose, deaminoselenocysteine-Se-hexose, cyclic selenomethionine-Se-hexose, and methylseleno-Se-deoxypentose-hexose.

2 Analysis of volatile species of Hg, As and Se in gas phase

Detection of volatile species of Hg, As and Se is important for understanding the transformation and global cycle of these elements in the environment. However, speciation of gaseous species released from real environmental samples is always challenging.

2.1 Speciation of volatile Hg species

The volatile Hg species in atmosphere mainly include Hg^0 , MeHg (as chloride or hydroxide) and dimethylmercury ($(Me)_2Hg$) [45]. Hg^0 can be well concentrated on a gold trap [45, 46]. Volatile MeHg can be on-line ethylated by passing through a $0.45\ \mu\text{m}$ Millex-HA filter impregnated with $50\ \mu\text{L}$ of $NaBEt_4$ (1% in Milli-Q water), then trapped on Tenex trap and analyzed by thermally desorbed-GC-AFS [45]. Gaseous MeHg can also be sampled by refluxing mist chamber with chelating agent solution (ammonium pyrrolidine dithiocarbamate, APDC) as the scrubbing solution, followed by ethylation-purge and trap-GC-AFS analysis [47]. $(Me)_2Hg$ can be trapped directly by activated-carbon [46] or Tenex trap [45], then analyzed by thermally desorbed-GC-AFS or ICP-MS.

2.2 Speciation of volatile As species

Headspace injection coupled with GC-MS [48,49] and GC-ICP-MS [49] has been used for study the volatile arsine species formed by intestinal microorganisms [49] and the stability of arsine [48]. By combining the strengths of element-specific detection using ICP-MS and molecular identification using ESI-MS, six mixed arsenic/sulfur or arsenic/selenium compounds (Me_2AsSH , Me_2AsSMe , $Me_2AsSSMe$, $(Me_2As)_2S$, $MeAs(SMe)(SEt)$, $Me_2AsSeMe$) formed by intestinal microorganisms were identified and verified. However, these direct headspace injection methods often suffer from high detection limits and are not sensitive enough for real sample analysis. Solid phase micro-extraction (SPME), cryotrapping and chemotrapping can be utilized to pre-concentrate the volatile arsenic before detection to improve analytical sensitivity. SPME fiber (PDMS, PDMS-CAR, and PDMS-CAR-DVB) were recently used to sample and concentrate volatile arsenic followed by GC-MS analysis [50]. Me_2AsCl , followed by Me_3As , Me_2AsSMe and $MeAsCl_2$ were identified in the gas from the Yellowstone National Park. Yuan et al. [51] described an integrated cryotrapping-GC-ICP-MS system incorporating the bacterial incubation and volatile arsenic species analysis, which enabled to on-line determine the volatile arsenic species produced by bacteria. The headspace of the bacterial cultures was purged with He gas, and the volatile arsenic species were trapped in a chromatographic column (100 cm PTFE tubing packed with 10% OV-101) immersed in liquid N_2 . The cryogenically trapped arsines (AsH_3 , $MeAsH_2$, Me_2AsH , and Me_3As) were then separated and detected by GC-ICP-MS. The arsine standards for quantitative calibration were prepared by reactions between As(III), MMA(V), DMA(V), and TMAO and tetrahydroborate(III) and oxalic acid. However, purging after cryogenically trapping always results in a sudden increase of system pressure, causing ICP plasma shutdown. An AFS detector was coupled with a cryogenical trap to solve this problem [52]. In this novel setting, a short packed cotton U column was utilized to rapidly separate volatile arsenicals [52]. Compared with cryotrapping, chemotrapping is more suitable for field studies. Recently, a silver nitrate impregnated silica gel filled tubes was developed for chemotrapping arsines [53]. Boiling water was used to elute the arsenicals from the trap before HPLC-ICP-MS detection. This chemotrapping method can concentrate these highly volatile arsine species present in diluted gas samples on solid supporting materials and is readily deployable in laboratory and field studies.

2.3 Speciation of volatile Se species

Volatile Se species can be directly injected using headspace mode followed by gas chromatographic separation [54,55]. SPME is widely used to determine volatile Se including $(Me)_2Se$, $MeSeSMe$, $(Me)_2Se_2$, $(MeS)_2Se$ and $(MeSe)_2S$. Tedlar bags sampling-cryotrapping-GC-ICP-MS has been

used for volatile selenium species determination in fermentation gases [56] and human breath [57]. Recently, a simple and easily transportable chemotrapping technique was developed for volatile $(\text{Me})_2\text{Se}$ and $(\text{Me})_2\text{Se}_2$ [58]. Concentrated HNO_3 can trap and oxidize $(\text{Me})_2\text{Se}$ and $(\text{Me})_2\text{Se}_2$ to

stable and non-volatile dimethyl selenoxide and methylseleninic acid. Quantitative recovery of $65.2\%\pm 1.9\%$ for $(\text{Me})_2\text{Se}$ and $81.3\%\pm 3.9\%$ for $(\text{Me})_2\text{Se}_2$ could be achieved.

The current analytical methods for volatile species of Hg, As and Se are summarized in Table 1.

Table 1 Analytical methods for volatile species of Hg, As and Se

Sample	Analyte	Sampling method	Separation and detection	Reference
Arsine standards	AsH_3 , MeAsH_2 , Me_2AsH , Me_3As	Headspace	GC-MS	[48]
Volatile arsenic compounds formed by intestinal microorganisms	Me_2AsSH , Me_2AsSMe , Me_2AsSSMe , $(\text{Me}_2\text{As})_2\text{S}$, $\text{MeAs}(\text{SMe})(\text{SEt})$, Me_2AsSeMe	Headspace	GC-MS GC-ICP-MS	[49]
Volatile arsenicals in air	AsH_3 , MeAsH_2 , Me_2AsH , Me_3As	Tedlar bags sampling-cryotrapping	GC-ICP-MS	[59]
Volatile arsenicals in natural gas	Me_3As	Chemotrapping by silver nitrate impregnated silica gel tubes	UV-HG-AFS	[60]
Volatile arsenicals in natural gas	Me_3As	Cryotrapping	GC-ICP-MS	[61]
Volatile arsenicals from paddy soil	AsH_3 , MeAsH_2 , Me_2AsH , Me_3As	Chemotrapping by silver nitrate impregnated silica gel tubes	HPLC-ICP-MS	[53]
Volatile arsenicals from lake sediment	AsH_3 , MeAsH_2 , Me_2AsH , Me_3As	Cryotrapping	GC-AFS with packed cotton column	[52]
Volatile arsenicals from hot spring	Me_2AsCl , Me_3As , Me_2AsSMe , MeAsCl_2	SPME	GC-MS	[50]
Volatile arsenicals released from bacteria	AsH_3 , MeAsH_2 , Me_2AsH , Me_3As	Cryotrapping	GC-ICP-MS with column of 100 cm PTFE tubing packed with 10% OV 101	[51]
Mercury in landfill gas	Me_2Hg	Trapping with Carbotrap TM	TD-GC-AFS	[62]
Mercury in ambient air	MeHgCl or MeHgOH	High-flow mist chamber with APDC solution	Ethylation-purge and trap-GC-AFS	[47]
Volatile Hg in digester and deposit gases	Hg^0 and Me_2Hg	Gold trap and activated-carbon trap	Thermally desorbed-GC-AFS	[46]
Volatile Hg in Hg-contaminated water-sediment microcosms	Hg^0 , MeHg (MeHgCl or MeHgOH) and Me_2Hg	Au/Pt trap for Hg^0 ethylation-Tenax trap for MeHg Tenax trap for Me_2Hg	Thermally desorbed-GC-AFS or ICP-MS	[45]
Volatile selenium species in fermentation gases	Me_2Se , SeEtMe , $\text{Se}(\text{Et})_2$, $\text{Se}_2(\text{Me})_2$ and other unidentified Se species	Tedlar bags sampling-cryotrapping	GC-ICP-MS	[56]
Volatile selenium in atmosphere	Me_2Se	Cryofocusing on a small glass wool-packed column	GC-ICP-MS	[63]
Volatile selenium in environmental and biological samples	Me_2Se and $\text{Se}_2(\text{Me})_2$	Headspace hollow fiber protected liquid-phase microextraction	GC-MS	[64]
Volatile selenium standard	Me_2Se and $\text{Se}_2(\text{Me})_2$	Concentrated nitric acid trapping	HPLC-ESI-MS	[58]
Volatile selenium in <i>in vitro</i> metabolism models	MeSeH , Me_2Se and $\text{Se}_2(\text{Me})_2$	Headspace	GC-MS	[54]
Volatile selenium from beers, wines and spirits	Me_2Se and $\text{Se}_2(\text{Me})_2$	SPME	GC-AES	[65]
Volatile selenium from intestinal microorganisms	MeSeH , Me_2Se and $\text{Se}_2(\text{Me})_2$	Headspace	GC-ICP-MS	[55]
Volatile selenium from green onions	$\text{Se}_2(\text{Me})_2$, MeSeSMe , $\text{Se}_2(\text{Me})_2$, $(\text{MeS})_2\text{Se}$, $(\text{MeSe})_2\text{S}$ and other unidentified Se species	SPME	GC-ICP-MS	[66]
Volatile selenium in human breath	Me_2Se	Tedlar bags sampling-cryotrapping-cryofocussing	GC-ICP-MS	[57]
Volatile selenium in production and gastric digestion processes of selenized yeast	Me_2Se , $\text{Se}_2(\text{Me})_2$ and other unidentified Se species	SPME	GC- microwave induced plasma (MIP)-optical emission spectrometry (AES)	[67]
Volatile selenium in roasted coffee	MeSeH , Me_2Se , $\text{Se}_2(\text{Me})_2$, MeSeSEt , MeSeSMe , MeSeSeEt , $\text{Se}_2(\text{Et})_2$, Et_2Se	SPME	GC-ICP-MS	[68]
Volatile selenium from Se accumulating plants	Me_2Se , $\text{Se}_2(\text{Me})_2$, MeSeSMe	SPME	GC-MS or ICP-MS	[69]

3 Complexation of Hg and As with phytochelatin

Phytochelatin (PC) play an important role in metal detoxification in plants through forming metal-PC complexes [70]. Reversed phase (RP)-HPLC-ESI-MS was used to monitor the complexes of Hg with phytochelatin in Hg-exposed Alfalfa [71], maize [71], rice plants [72] and Chinese cabbage [70]. Simultaneous detection *via* ICP-MS and ESI-MS after RP-HPLC separation could provide the information of both elemental content and molecular structure. A variety of novel Hg-phytochelatin complexes were identified in rice plants exposed to Hg^{2+} , including (Ser)PC₂Hg, (des-Gly)PC₂Hg and (Glu)PC₂Hg [72].

Similarly, RP-HPLC-ESI-MS/ICP-MS was widely applied for the determination of As-phytochelatin in plants. When using HPLC-ICP-MS, the measured As:S ratios are often misleading in the identification of As-phytochelatin complexes due to the relatively low resolution of the chromatography system [73]. Therefore, parallel use of ESI-MS/ICP-MS detection is necessary to prove the occurrence of As-phytochelatin complexes. Another study emphasized the importance of on-line separation and detection of As-phytochelatin complexes because pre-cleaning step using size-exclusion chromatography (SEC) with subsequent fraction collection and freeze-drying prior to the analysis using RP-HPLC-ICP-MS/ESI-MS often lead to decomposition of the As-phytochelatin complexes. Extraction using formic acid and subsequent analysis using RP-HPLC-ICP-MS/ESI-MS with low pH mobile phase (0.1% formic acid) are helpful for stabilization of the As-phytochelatin complexes [74].

Examples of complexes of Hg and As with phytochelatin are listed in Table 2.

4 Enhanced cold vapor generation as interface for LC and atomic spectrometry

Although ICP-MS could be coupled with liquid chromatography directly with a nebulizer, chemical-vapor generation (CVG) as interface of HPLC-ICP-MS is helpful to increase the sensitivity for volatile-species-forming elements (volatile element or hydrides) as well as decrease the interference of non-hydride-forming species. When using anion exchange or ion pairing mode LC directly coupled with ICP-MS, elevated concentration of AsB in urine sample could interfere the accurate quantification of As(III). Incorporating KBH_4 -HCl hydride generation (HG) system between HPLC and ICP-MS could improve sensitivity and specificity since AsB is not a hydride-forming arsenic species. The hydride generation process converts As(III), As(V), MMA(V), and DMA(V) to volatile arsines (AsH_3 , MeAsH_2 , Me_2AsH), but leaves AsB in chromatographic elution. Hence, by separating the gaseous arsines from liquid phase, the interference from AsB could be eliminated and the quantitative determination of As(III) can be improved significantly [79]. However, this hydride generation system cannot be used to determine non-hydride-forming arsenic species. When characterizing all arsenic-containing compounds becomes necessary, converting non-hydride-forming arsenic species to hydride-forming arsenic species is required. Photooxidation of the arsenic species before HG has been used for this purpose. Nakazato et al. [80] developed a post-column high-efficiency photooxidation (HEPO) reactor, in which LC eluent was passed into a reaction tube through a low pressure mercury lamp. The HEPO reactor provides efficient irradiation with 185 nm vacuum ultraviolet light, and can oxidize "persistent" organic arsenicals (e.g.

Table 2 Complexes of Hg and As with phytochelatin

Plant species	Complexes with phytochelatin	Analytical method	Reference
Alfalfa and maize	HgGC_2 , HgPC_2 , HghPC_2 , $\text{Hg}(\text{hPC}_2)_2$, $\text{Hg}_2(\text{hPC}_2)_2$ and $\text{Hg}_3(\text{hPC}_2)_3$, HghPC_3 , $\text{Hg}(\text{hPC}_3)_2$, $\text{Hg}_2(\text{hPC}_3)_2$, HghPC_4 , Hg_2hPC_4 , HgPC_4 , Hg_2PC_4 , MeHg-hPC_2	RP-HPLC-ICP-MS RP-HPLC-ESI-MS	[71]
Rice plants	PC_2Hg , (des-Gly) PC_2Hg , (Glu) PC_2Hg , (Ser) PC_2Hg	RP-HPLC-ICP-MS RP-HPLC-ESI-MS	[72]
Chinese cabbage	HgPC_2 , HgPC_3 , HgPC_4 and Hg_2PC_4	RP-HPLC-ESI-MS	[70]
Standard of As-phytochelatin	As(III)(OH)-PC_2 , As(III)-PC_3	RP-HPLC-ICP-MS RP-HPLC-ESI-MS	[75]
<i>Thunbergia alata</i>	$\text{As(III)-(PC}_2)_2$, As(III)-PC_3 , As(III)-PC_4 , As(III)-PC_3	RP-HPLC-ICP-MS RP-HPLC-ESI-MS	[73]
<i>Arabidopsis</i>	As(III)-PC_4 , As(III)-PC_3 , $\text{As(III)-(PC}_2)_2$, As(III)-(GS)_3	RP-HPLC-ICP-MS RP-HPLC-ESI-MS	[76]
<i>Brassica juncea</i>	As(III)-(GSH)_3 , As(III)-PC_3	SEC-ICP-MS SEC-ESI-MS	[77]
<i>Thunbergia alata</i>	As(III)-PC_3 , $(\text{GS})\text{As(III)PC}_2$, As(III)-PC_4 , $\text{As(III)-(PC}_2)_2$	RP-HPLC-ICP-MS RP-HPLC-ESI-MS	[74]
<i>Holcus lanatus</i> and <i>Pteris cretica</i>	$\text{As(III)-(PC}_2)_2$, GS-As(III)-PC_2 , As(III)-PC_3 , As(III)-(GS)_3 , As(III)-PC_2 , GS-As(III)-PC_3	RP-HPLC-ICP-MS RP-HPLC-ESI-MS	[78]

arsenobetaine) to arsenate in 3.5 s without using any oxidizing agents. As peak broadening and dilution of the LC-separated peaks caused by mixing with the oxidant solution (peroxodisulfate) were minimized, the detection limits for 10 arsenic species tested were improved significantly. The developed interface is useful to screen trace unknown non-hydride-forming arsenic species. Additionally, quantification of unidentified arsenic species was made possible using the calibration curve of As(V) on the basis of complete decomposition of most organic arsenic species. The proposed method revealed for the first time the occurrence of 20 arsenic species, including some unknowns, in human urine, some of which were undetectable by conventional LC-ICP-MS and LC-HG-ICP-MS.

In elemental speciation using hydride generation, the conversion efficiencies of species into corresponding hydrides are dependent on various factors. For example, the concentration of HCl required to convert As(V) to its hydride is much higher than that for DMA(V) [81]. Thus, optimized experimental conditions for DMA(V) is not necessary suitable for As(V). Accordingly, a gradient hydride generation interface between LC and atomic absorption spectroscopy (AAS) was developed by Tian et al. [81] for speciation of As(V), As(III), MMA, DMA and TMAO. Six mol/L HCl was used for the hydride generation of As(V), As(III) and MMA and then the valve was switched to introduce 0.6 mol/L HCl as hydride generation medium for DMA and TMAO. This setting realized simultaneous determination of As(V), As(III), MMA, DMA and TMAO with high sensitivity. Gradient HG is also a promising interface for Hg^{2+} and MeHg determination, as the concentration of KBH_4 for converting MeHg to MeHgH is much higher than that for converting Hg^{2+} to elemental Hg [82].

Vapor generation for Se(VI) analysis by conventional KBH_4 -HCl reduction is usually not as effective as that for Se(IV). Usually, pre-reduction of Se(VI) to Se(IV) is necessary before HG procedure. Pre-reduction procedures of Se(VI) by thiourea at 100 °C [83] or UV/ TiO_2 photocatalysis [84] followed by conventional KBH_4 -HCl HG were developed. After on-line pre-reduction, the HG efficiency of Se(VI) was greatly improved. Sun et al. [85] developed a novel UV/nano- TiO_2 photo-chemical vapor generation (PCVG) device to couple between LC and ICP-MS for the determination of Se(IV) and Se(VI) without using conventional KBH_4 -HCl HG techniques. After HPLC separation and mixing with formic acid and nano- TiO_2 suspension, both Se(IV) and Se(VI) can be transformed to volatile Se species under UV irradiation. Recently, a nano-semiconductor-based photocatalytic vapor generation was developed as an interface of HPLC and AFS or ICP-MS [86]. Different PCVG systems, including UV/HCOOH, UV/ TiO_2 -HCOOH, UV/Ag- TiO_2 -HCOOH, and UV/ ZrO_2 -HCOOH, were compared for HG of Se species. UV/ ZrO_2 -HCOOH PCVG system as HPLC-ICP-MS interface provided high sensitivity for Se(VI) (0.016 ng mL^{-1}), Se(IV)

(0.014 ng mL^{-1}), (SeCys) $_2$ (0.018 ng mL^{-1}), and SeMet (0.007 ng mL^{-1}) with lower RSDs (<4.4%). The volatile Se species generated in the UV/ ZrO_2 -HCOOH systems was also identified as H_2Se by cryogenically trap-GC-MS.

Photo-induced chemical vapor generation has also been used as an interface between LC and AFS/ICP-MS for mercury speciation. Under UV irradiation, the chromatographic eluent was firstly mixed with formic acid. Then, under UV irradiation, organomercurials (MeHg, EtHg and PhHg) can be transformed to elemental Hg vapor and then detected by AFS [87,88] or ICP-MS [89]. Nano- TiO_2 photocatalysis can catalyze the reductive decomposition of organomercurials to elemental Hg [87,89]. A much simpler interface of HPLC and AFS by using formate buffer in mobile phase as photo-reaction reagent was developed recently [90]. Using this interface, no post-column reaction reagent was needed and the flow injection system used in traditional procedure is also omitted, which significantly simplifies the instrumentation and reduces the analytical cost.

Wang et al. [91] recently found that MeHg can be transformed to Hg^0 directly by reacting with KBH_4 and HCl in the presence of *L*-cysteine. This *L*-cysteine-induced degradation of organomercurials was used in the HPLC-CVG-AFS hyphenated system for speciation of mercury. In this procedure, *L*-cysteine in the mobile phase of chromatography was complexed with MeHg and EtHg, and after chromatographic separation and mixed with KBH_4 and HCl, MeHg and EtHg were reduced to Hg^0 directly. The proposed HPLC-CVG-AFS system is very simple and bears low cost, as no strong oxidant and additional post-column interface (e.g. ultraviolet or microwave) were needed.

In addition to UV [92] and ultrasonic [93] irradiation, solution cathode glow discharge (SCGD) can also promote the CVG of Hg species within formic acid [94]. A novel SCGD induced CVG was developed as interface to on-line couple LC with AFS for the speciation of Hg^{2+} , MeHg and EtHg [95]. The decomposition of organomercurials and the reduction of Hg^{2+} could be completed in one step with SCGD induced vapor generation system in the presence of formic acid without using any other redox reagents ($\text{K}_2\text{S}_2\text{O}_8$ or KBH_4).

5 Using isotope dilution analysis to improve the precision and accuracy of speciation

Isotope dilution analysis is often the preferred choice to improve the accuracy and precision of elemental speciation. Although As has only one stable isotope (^{75}As), the isotope dilution analysis of AsB can be performed by using ^{13}C enriched AsB spike and HPLC-ESI-MS detection [96]. ^{13}C isotope labeled SeMet spike was also reported for isotope dilution using LC-ESI-MS [97] and GC-MS [98]. There are 5 stable isotopes (^{74}Se , ^{76}Se , ^{77}Se , ^{78}Se , and ^{80}Se) for Se and 7 stable isotopes (^{196}Hg , ^{198}Hg , ^{199}Hg , ^{200}Hg , ^{201}Hg , ^{202}Hg ,

Table 3 Examples of using isotope dilution for the speciation of Hg, As and Se

Sample	Analyte	Isotope-labeled spike	Analytical method	Reference
Fish tissue	AsB	^{13}C -AsB	LC-LTQ-Orbitrap-MS	[96]
Human serum	Selenoprotein P, albumin and glutathione peroxidase	^{77}Se	Affinity chromatography-ICP-MS	[102]
Protein tryptic digests	Selenium-containing peptides	^{76}Se	Nano-HPLC-ICP-MS	[103]
Edible wild mushrooms	Water soluble selenium	^{77}Se	Size exclusion, RP and anion exchange chromatography-ICP-MS	[104]
Human plasma	Selenoprotein P, albumin and glutathione peroxidase	^{77}Se	Anion exchange chromatography-ICP-MS	[105]
Biofortified Products	SeMet, SeCys, Se (VI), Se (IV), SeOMet	^{76}Se	RP-Ion Pairing-ICP-MS	[106]
Petroleum refinery wastewaters	Se (IV), Se (VI), selenocyanate	^{77}Se	Ion chromatography -ICP-MS	[107]
Human serum	Se (IV), Se (VI), Se(Cys) ₂ , SeMet, selenoprotein P selenoalbumin, and glutathione peroxidase	^{78}Se	Ion-pair-RPLC and affinity chromatography-ICP-MS	[108]
Yeast	SeMet	^{13}C -SeMet	GC-MS and LC-MS	[98]
Acid hydrolysis of selenium-enriched yeast	SeMet	^{74}Se -SeMet, ^{13}C -SeMet	LC-MS and LC-ICP-MS	[97]
Mouse plasma	d- and l-enantiomers of SeMet	d, l- $^{13}\text{C}_3$, ^{82}Se SeMet	GC-MS	[109]
Yeast	SeMet after CNBr derivatization	^{74}Se -SeMet	GC-ICP-MS and GC-MS	[110]
Yeast	SeMet	^{77}Se -SeMet	HPLC-ICP-MS	[111]
Human serum	SeMet	^{77}Se -SeMet	SEC-capillary HPLC-ICP-MS	[112]
Yeast	SeMet	^{76}Se -SeMet	HPLC-ICP-MS	[113]
Food	γ -glutamyl-SeMC	^{77}Se - γ -glutamyl-SeMC	HPLC-ICP-MS	[114]
Garlic extract and rat urine	SeMC, selenosugar, methylselenonic acid, methylseleninic acid, SeMet, Se(VI), Se(IV)	^{76}Se -SeMC, ^{76}Se -selenosugar, ^{76}Se -methylselenonic acid, ^{77}Se -methylseleninic acid, ^{77}Se -SeMet, ^{78}Se -Se(VI), and ^{82}Se -Se(IV)	HPLC-ICP-MS	[115]
Soils and sludges	Hg^{2+}	$^{204}\text{Hg}^{2+}$	Methylation-SPME-GC-MS	[116]
Fish tissue	MeHg	Me^{198}Hg	Propylation-SPME-GC-MS	[117]
Biological certified reference materials	MeHg	Me^{201}Hg	Ethylation-GC-MS	[118]
Fish	MeHg	Me^{202}Hg	Propylation-SPME-GC-MS	[119]
Soils and sediments	MeHg	Me^{201}Hg	LC-ICP-MS	[120]
Fish tissue	MeHg	Me^{202}Hg	Ethylation or phenylation-GC-ICP-MS	[121]
Zooplankton and fish	MeHg	Me^{201}Hg	Ethylation -GC-ICP-MS	[122]
Mouse tissues	MeHg and EtHg	Me^{200}Hg and Et^{199}Hg	Butylation-GC-ICP-MS	[123]
Fish tissue	MeHg	Me^{200}Hg	HPLC-ICP-MS	[124]
Biological materials	MeHg and Hg^{2+}	^{200}Hg	Solid sampling-electrothermal vaporization-ICP-MS	[125]
Water, biotissues and sediment	Hg^{2+} and MeHg	Me^{201}Hg and $^{199}\text{Hg}^{2+}$	Propylation or ethylation-GC-ICP-MS	[126]
Invertebrates and plant	MeHg	Me^{201}Hg	Ethylation-GC-ICP-MS	[127]
Rat tissues	Mercury-containing proteins by isotope-enriched MeHg	Hg^{2+} with natural abundance	SEC-ICP-MS	[101]
Biological sample	MeHg	Me^{201}Hg	Ethylation-GC-MS	[128]
Natural gas condensate	Me_2Hg , MeHg and Hg^{2+}	$\text{Me}_2^{198}\text{Hg}$, Me^{198}Hg and $^{198}\text{Hg}^{2+}$	GC-ICP-MS or GC-furnace atomization plasma ionization-MS	[129]
Freshwaters	MeHg	Me^{201}Hg	Ethylation-GC-ICP-MS	[130]
Biological samples	MeHg and Hg^{2+}	Me^{201}Hg and $^{199}\text{Hg}^{2+}$	Ethylation-purge and trap-GC-ICP-MS	[131]
Biological tissues	MeHg and Hg^{2+}	Me^{198}Hg and $^{201}\text{Hg}^{2+}$	HPLC-ICP-MS	[100]
Whole blood	MeHg	Me^{198}Hg	Ethylation-purge and trap-GC-ICP-MS	[132]
Natural waters and snow	MeHg and Hg^{2+}	Me^{201}Hg and $^{199}\text{Hg}^{2+}$	Propylation-GC-ICP-MS	[133]
Gaseous samples	Hg^0 , Me_2Hg , MeHg and Hg^{2+}	$^{201}\text{Hg}^{2+}$, $^{202}\text{Hg}^0$, Me^{200}Hg and $\text{Me}_2^{198}\text{Hg}$	Ethylation-purge and trap-GC-ICP-MS or purge and trap-gold trap-GC-ICP-MS	[99]
Gaseous samples	Hg^0 , Me_2Hg , MeHg	$^{199}\text{Hg}^0$, $\text{Me}_2^{198}\text{Hg}$ and Me^{200}Hg	Carbotrap TM -GC-ICP-MS	[134]
Fish tissue	MeHg	Me^{199}Hg	HPLC-CVG-MC-ICP-MS	[135]
Natural water	MeHg	Me^{200}Hg	Ethylation-purge and trap-GC-ICP-MS	[136]
River water and snow sample	MeHg	Me^{201}Hg	Ethylation or propylation-purge and trap-GC-ICP-MS	[8]

and ^{204}Hg) for Hg. A variety of isotopes can be selected for the preparation of the isotope-enriched species. For example, ^{198}Hg , ^{199}Hg , ^{200}Hg , ^{201}Hg and ^{202}Hg were all reported for synthesizing the isotope-enriched MeHg. Additionally, a variety of multiple spike species-specific isotope dilution procedure [99, 100] can be used to simultaneously measure different species of Hg and Se in order to correct for the analyte loss and the inter-conversion of species in sample preparation and analysis. When the isotope-enriched species is not available, species-unspecific isotope dilution can be performed by post-column spiking one isotope tracer [101]. The species-unspecific isotope dilution can correct the instability of the ICP-MS detector, useful for the quantitative determination of metal-containing proteins in organism.

Examples of using isotope dilution for speciation of Hg, As and Se are summarized in Table 3.

6 Chromatographic separation coupled with MC-ICP-MS to measure species-specific isotopic ratios

The measurement of stable Hg isotopic ratio in different environmental samples has shown significant Hg isotope variations [137]. Species-specific Hg isotope fractionation of MeHg has recently been observed in biological samples [138,139] and in chemical transformation processes such as methylation [140] and demethylation [138,141,142]. The fingerprint of mass-dependent and -independent fractionation of MeHg in natural environmental samples was suggested to be a good indicator of important processes in the global cycle of MeHg and will be helpful to understand and quantify these processes [138]. However, the conventional measurement of Hg isotope fractionation of MeHg usually involved MeHg extraction, purification and offline MC-ICP-MS determination [138,140], which is tedious and time-consuming. Recently, precise online measurement of isotopic ratios of MeHg was realized by on-line coupling of GC and MC-ICP-MS [143–145]. In addition to on-line introduction of the GC separated Hg species, introduction of Tl standard solution to ICP torch is needed for mass bias correction [143,144]. This hyphenated system has been successfully used to determine the mass-dependent and mass independent fractionation of MeHg in environmental samples [143]. Species-specified Se isotope fractionation of Se(IV) in lake sediments and lake water was also determined by using thiol cellulose pre-concentration and subsequent off-line HG-MC-ICP-MS determination [146].

7 Concluding remarks

Hg, As and Se are ubiquitous in the environment. Speciation in environmental, food, and biological samples plays an important role in understanding the biogeochemical cycle, exposure, metabolism, and toxicological effects of Hg, As

and Se. The complementary use of elemental and molecular mass spectrometry hyphenated with GC and LC is important to screen and identify new species. Chemical vapor generation is an effective interface between liquid chromatography and atomic spectrometry. The performance of hyphenated systems could be further improved by utilizing enhanced chemical vapor generation. Isotope dilution analysis has been proven an important tool for speciation, owing to its high accuracy and small uncertainties. Development of commercially available isotope-enriched species will highly promote the popularity of this technology. MC-ICP-MS hyphenated with LC and GC could be a novel approach to study the isotopic composition of species, which will play important roles in the research of species-specific fractionation of Hg and Se in the future.

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