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# Non-chromatographic hydride generation atomic spectrometric techniques for the speciation analysis of arsenic, antimony, selenium, and tellurium in water samples—a review

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Hydride generation (HG) coupled with AAS, ICP–AES, and AFS techniques for the speciation analysis of As, Sb, Se, and Te in environmental water samples is reviewed. Careful control of experimental conditions, offline/online sample pretreatment methods employing batch, continuous and flow-injection techniques, and cryogenic trapping of hydrides enable the determination of various species of hydride-forming elements without the use of chromatographic separation. Other non-chromatographic approaches include solvent extraction, ion exchange, and selective retention by microorganisms. Sample pretreatment, pH dependency of HG, and control of  $\text{NaBH}_4/\text{HCl}$  concentration facilitate the determination of As(III), As(V), monomethylarsonate (MMA), and dimethylarsinate (DMA) species. Inorganic species of arsenic are dominant in terrestrial waters, whereas inorganic and methylated species are reported in seawater. Selenium and tellurium speciation analysis is based on the hydrides generation only from the tetravalent state. Se(IV) and Se(VI) are the inorganic selenium species mostly reported in environmental samples, whereas speciation of tellurium is rarely reported. Antimony speciation analysis is based on the slow kinetics of hydride formation from the pentavalent state and is mainly reported in seawater samples.

*Keywords:* Non-chromatographic hydride generation techniques; Speciation analysis; Arsenic; Antimony; Selenium; Tellurium

## 1. Introduction

Assessment of environmental risk caused by metalloids such as As, Sb, Se, and Te is widely recognized to be dependent upon speciation. According to the latest IUPAC [1] guidelines, the term ‘speciation analysis’ refers to analytical activities of identifying and/or measuring the quantities of one or more chemical species in a sample. The term chemical species refers to the specific form of an element, defined as molecular, complex, or nuclear structure or oxidation state. It is now well established that information about the speciation of an element is required for understanding the

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reaction of many elements. For example, the inorganic forms of arsenic and selenium exhibit different toxicities, i.e. As(III) is more toxic than As(V), and Se(IV) is more toxic than Se(VI). However, methylated forms of these elements are relatively less toxic than their inorganic forms, and organic forms of arsenic, like arsenobetaine and arsenocholine, are virtually non-toxic. In addition, knowledge of speciation could help to explain the mobility, bioavailability, storage, and retention of elemental species in different environmental matrices including the human body.

Speciation analysis usually involves two steps: (1) separation of different forms and (2) their subsequent quantification. A wide variety of techniques, based on liquid chromatography interfaced with atomic spectrometric techniques, known as hyphenated techniques, i.e. HPLC–HGAAS [2], HPLC–HGAFS [3], HPLC–HG–ICP–mass spectrometry (MS) [4], etc., have been proposed for the speciation of hydride-forming elements and reviewed recently [5]. The primary advantage of this approach is the unequivocal species separation and specific online detection. Unfortunately, most of these techniques have significant disadvantages [6]: increased complexity, co-elution of species of the same element [7], problems associated with the stability of plasma due to the use of organic solvents, and interference arising from polyatomic ions in conventional ICP–MS [8]. Additionally, these types of hyphenated instruments are not standard equipment in most laboratories engaged in water-quality monitoring. Further considerations to be taken into account are the acquisition and running costs, analysis time, and ease of handling, especially for routine analysis.

HG coupled with atomic spectrometric techniques is a sensitive analytical tool for the determination of trace levels of As, Sb, Se, and Te. The popularity of HG, nearly 30 years since its introduction as an analytical technique, is still increasing because of its ability in differentiating different oxidation states of these elements by simple procedures, without the use of chromatographic separation. By applying suitable separation techniques, elemental species which form the corresponding hydrides can be quantitated. The separation techniques include selective hydride formation based on pH adjustment, buffer, reaction media, matrix modification, complexation-extraction, selective retention, etc. Another approach is to collect the hydrides in a cold trap and their sequential release to the detection system. In addition, a variety of modern automated flow-injection (FI) and continuous flow (CF) approaches utilizing efficient hyphenations with online sample/analyte treatment (pre- or post-HG or both) such as sample introduction, decomposition, prereduction, ultraviolet photo oxidation, microwave decomposition, enrichment, solid-phase extraction, etc. constitute the various approaches for elemental speciation.

## 2. Previous reviews

We refer readers to the references listed in table 1 for recent general reviews focused on speciation analysis of metalloids by HG coupled with various detectors. The other complementary reviews include new developments, extraction techniques, stability studies, etc. More information on speciation analysis of arsenic, antimony, selenium, and tellurium can be found in the articles listed in tables 2 and 3.

Table 1. General reviews on HG techniques in speciation analysis and other complementary reviews.<sup>a</sup>

Title	Comments	Year	Reference
Hydride generation atomic absorption spectroscopy	Excellent monograph on HGAAS; discusses fundamentals, applications and other aspects of HG technique	1995	[9]
Extraction techniques in speciation analysis of environmental samples	Reports species selective extraction techniques like LLE, SPE for As, Se, and Sb	1995	[10]
Atomic absorption spectrometry (AAS), a versatile and selective detector for trace-element speciation	Reports speciation methods by FAAS, HGAAS, ETAAS, and hyphenated techniques, sampling, and sample preparation	1996	[11]
Chemical speciation by flow-injection analysis: a review	Reports applications of FI coupled with various detectors for speciation analysis of several elements including As	1996	[12]
New developments in FI-VGAAS	Reports new developments in FI-HGAAS-improvements in speciation analysis, interferent removal, matrix modification, and preconcentration	1996	[13]
Chemical speciation by hydride generation atomic spectrometry	Speciation analysis of As, Bi, Ge, Pb, Sb, Se, Sn, and Te by HGAAS techniques and hyphenated techniques	1997	[14]
Borohydride techniques in trace-element speciation	Overview of speciation analysis by HGAAS, HGAFS and hyphenated techniques with online/offline redox systems	1997	[15]
Hyphenated vapour-generation atomic absorption spectrometric techniques	An extensive review about VGAAS. Discusses flow techniques, online sample decomposition, on/off-line prereduction, preconcentration, separation coupled with HGAAS, ETAAS, hyphenated techniques-VG-CT/GC-AAS, HPLC-VGAAS, HPLC-UV-VGAAS, etc.; LODs of various methods	1999	[16]
Speciation and analysis of mercury, arsenic, and selenium by atomic fluorescence spectrometry	Compares HGAAS and HGAFS in terms of figures of merit for As and Se	2000	[17]
Vapour generation or electrothermal AAS? Both!	Overview of VG-AAS and VG-GFAAS for the speciation analysis of As, Bi, Sb, and Se—relative merits and limitations	2000	[18]
Literature survey of on-line elemental speciation in aqueous solutions	Reports separation/pre-treatment techniques coupled with AAS, AFS, ICP, ICP-MS for the speciation analysis of As, Sb, Se, and other elements	2001	[19]

(Continued)

Table 1. Continued.

Title	Comments	Year	Reference
Determination of different forms of As, Sb, and Se in water samples using hydride generation	A mini-review covers the speciation analysis of As, Sb and Se in water samples by HGAAS	2002	[20]
Atomic absorption spectrometry in determination of As, Sb, and Se in environmental samples	Reports methods of total and speciation analysis of As, Sb, and Se by HGAAS and HG-GFAAS	2002	[21]
Analytical applications of volatile metal derivatives	Reviews various vapour generation techniques in Atomic spectrometric techniques	2002	[22]

<sup>a</sup> AAS: atomic absorption spectrometry; AFS: atomic fluorescence spectrometry; CF: continuous flow; Coppt: co-precipitation; CT: cryogenic trapping or cold trapping; DCP: direct-current plasma; DPCSV: differential pulse cathodic stripping voltammetry; Ec: electrochemical; ETAAS: electrothermal AAS; FAAS: flame atomic absorption spectrometry; FI: flow injection; GC: gas chromatography; GF: graphite furnace; HG: hydride generation; HPLC: high-performance liquid chromatography; ICP-AES: inductively coupled plasma-atomic emission spectrometry; ICP-MS: inductively coupled plasma-mass spectrometry; ITP: isotachopheresis; LOD: limit of detection; LC: liquid chromatography; LLE: liquid-liquid extraction; IC: ion chromatography; MIP: microwave-induced plasma; NAA: neutron activation analysis; QF: quartz furnace; SPE: solid-phase extraction; SPME: solid-phase microextraction; UV: ultraviolet; VG: vapour generation.

Table 2. Arsenic speciation analysis reviews.

Title	Comments	Year	Reference
Analytical methodology for speciation of arsenic in environmental and biological samples	Reports various As species, speciation analysis by HGAAS, HGAFS, HG-GFAAS, ICP-AES, ICP-MS, HPLC-ICP-MS, NAA, and electrochemical methods	1997	[23]
Speciation of methyl arsenic, methyl and butyl tin, methyl mercury compounds, and their inorganic analogues by hydride derivatization	Discusses As speciation chemistry, speciation analysis of methylated species and interference problems	1997	[24]
Determination of As species in environmental samples; use of the alga, <i>Chlorella vulgaris</i> , for As(III) retention	Overview of existing speciation methodologies and micro-organisms for selective retention	1998	[25]
Arsenic: occurrence, toxicity and speciation techniques	Reports summary of occurrence, toxicity, and speciation techniques	2000	[26]
Arsenic speciation analysis	Reports As species, chromatographic techniques for separation, detection by atomic spectrometric methods, and sample preservation	2002	[27]
Arsenic contamination in groundwater; some analytical considerations	Discussion on improvement in development of field testing kit based on Gutzeit method	2002	[28]
Arsenic speciation in environmental samples	Reports As species, sample preparation, separation techniques, hyphenated techniques, and LODs of methods	2003	[29]
Advances in As speciation techniques	Speciation techniques based on hyphenated techniques	2004	[30]
Analytical methods for inorganic arsenic in water: a review	Reports speciation analysis based on HG-AAS, AFS, HG-GFAAS, HG-ICP-AES, ICP-MS, and hyphenated techniques	2004	[31]
Determination As species: a critical review of methods and applications 2000-2003	Extensive review: reports As species in environmental, biological, marine and food samples; speciation methods based on HGAAS, AFS, ICP-MS, hyphenated techniques, advances in detection techniques, and species stability	2004	[32]
Arsenic speciation analysis in water samples; a review of hyphenated techniques	Reports As speciation techniques such as HPLC-HGAAS, LC-HGAAS, HPLC-ICP-MS, and species distribution in environmental water samples	2005	[5]

Table 3. Antimony, selenium, and tellurium speciation analysis reviews.

Title	Comments	Year	Reference
Analytical methods for antimony speciation in waters at trace and ultra-trace levels; a review	Reports on/offline separation techniques coupled to HGAAS hyphenated techniques, detector and interferences studies	1998	[33]
Methods for determination of antimony in terrestrial environmental samples	Extensive review on antimony speciation methods, HG techniques, hyphenated techniques, detectors, and interferences studies	2000	[34]
Speciation of antimony for the 21st century: promises and pitfalls	Focuses on Se speciation in various matrices, analytical problems; HGAAS, AFS and hyphenated techniques	2001	[35]
Analytical techniques applied to the speciation of selenium in environmental matrices	Reports Se species, distribution, methods based on AAS, AFS, ETAAS, DPCSV and hyphenated techniques	1994	[36]
Analytical methods for the speciation of selenium compounds: a review	Extensive review on inorganic and organic Se speciation methods in environmental matrices	1994	[37]
Speciation of organoselenium compounds	Reports organoselenium species and methods of speciation	1996	[38]
Determination of selenium and tellurium in environmental samples	Critical review on Se and Te determination; reviews sample collection, preservation, pretreatment, interferences, speciation, and hyphenated techniques	1997	[39]
Speciation of selenium compounds	Reports Se species and speciation methods	1998	[40]
Determination of selenium species in environmental samples	Overview of Se species, stability, sample preparation, and speciation methods	2002	[41]
Modern preconcentration methods for the determination of selenium species in environmental water samples	Overview of preconcentration techniques such as CT, SPE, SPME, ITP, and co-precipitation techniques	2004	[42]
Trends in selenium determination/speciation by hyphenated techniques based on AAS and AFS	Reports preservation, sample collection and speciation methods based on HGAAS and HG-ETAAS	2005	[43]

### 3. Aims and scope

Although this review deals primarily with recent developments in HG techniques based on non-chromatographic methods, it is not aimed solely at an analytical audience but is intended for all scientists with an interest in speciation analysis. It is hoped that the information will be accessible to, and useful for, scientists in interdisciplinary fields such as environmental science and toxicology. The aim of this review is to highlight the developments, achievements, current state, analytical scope, performance characteristics, advantages, limitations, and prospects of HG coupled with various atomic spectrometric detectors for the speciation analysis of As, Sb, Se, and Te in environmental water samples. Emphasis is placed on the methods reported after the year 2000, although some previous publications are considered for performance evaluation. As we focus on simple procedures based on HG, hyphenated techniques involving MS are not discussed.

The concentrations of several arsenic, antimony, and selenium species in different environmental water samples are reported in tables 4–6.

### 4. Arsenic speciation analysis

#### 4.1 Development of HG as a speciation technique

In 1973, Braman and Foreback [87] reported the first method of arsenic speciation, i.e. arsenite, arsenate, monomethylarsonate (MMA), and dimethylarsinate (DMA) based on selective HG and sequential volatilization. The evolved arsenicals were collected in a liquid nitrogen trap, warmed, and sequentially released according to their boiling point (arsine  $-55^{\circ}\text{C}$ , methylarsine  $2^{\circ}\text{C}$ , dimethylarsine  $55^{\circ}\text{C}$ ) and determined by the DC arc emission method. The work of Braman and Foreback may be seen as heralding in the field of speciation analysis, in particular, arsenic speciation. In subsequent years, research in speciation analysis grew steadily, exploiting the pH dependency of HG. In the last two decades, interest in arsenic speciation has been heightened by toxicological issues, in particular the carcinogenic effects of inorganic arsenic in drinking water and the worldwide human-health implications [88, 89]. In addition, arsenic is also attracting renewed clinical interest and is currently posting some remarkable success in the treatment of a certain type of leukemia [90].

#### 4.2 Speciation analysis based on selective HG

The reaction between tetrahydroborate (THB) and an oxyion in solution is sensitive to pH, and for the reaction to proceed rapidly, the analyte species must be fully protonated. As  $\text{p}K_1$  for arsenic acid is 2.3, the reaction must therefore be carried out at very low pH, i.e.  $1\text{--}2\text{ mol L}^{-1}$  HCl is generally employed. Arsenite ( $\text{p}K_1$  9.2), on the other hand, is protonated under natural water conditions, and reacts with THB under mild acidic conditions. Thus, differentiation of As(III) and As(V) could be achieved simply by exploiting the pH dependency of THB reduction.



Table 4. Concentration of arsenic species in environmental samples.<sup>a</sup>

Sample/source	Conc. units	As <sub>T</sub> <sup>a</sup>	As(III)	As(V)	MMA	DMA	Org-As	Technique	Reference
GW/China	µg L <sup>-1</sup>	509.8 <sup>b</sup>	287.5 <sup>b</sup>	141.2 <sup>b</sup>				SPE-FI-HGAAS	[44]
TW/Philippines	µg L <sup>-1</sup>	0.4	0.1	0.3				SPE-FI-HGAAS	[45]
MW/Philippines	µg L <sup>-1</sup>	0.3	0.3	–				SPE-FI-HGAAS	[45]
RW/Greece	µg L <sup>-1</sup>	3.42	1.2	2.22				FI-HGAAS	[46]
LW/Greece	µg L <sup>-1</sup>	2.25	0.95	1.3				FI-HGAAS	[46]
TW/Greece	µg L <sup>-1</sup>	0.86	–	0.86				FI-HGAAS	[46]
RW/Japan	µg L <sup>-1</sup>	0.97	0.3	0.67				SPE-ICP-AES	[47]
TW/Japan	µg L <sup>-1</sup>	0.53	–	0.53				SPE-ICP-AES	[47]
MW/Japan	µg L <sup>-1</sup>	3.97	0.5	3.47				SPE-ICP-AES	[47]
RW/Chile	µg L <sup>-1</sup>	289	53.3	201	nd	nd		SPE-HG-CT-ICPAES	[48]
RW/Chile	µg L <sup>-1</sup>	358	145	176	4.6	2.4		SPE-HG-CT-ICPAES	[48]
GW/Argentina	%	30–308	36					FI-HGAAS	[49]
LW/China	µg L <sup>-1</sup>	2.2	0.72	1.48				FI-HGAFS	[50]
RW/China	µg L <sup>-1</sup>	2.08	0.18	1.90				FI-HGAFS	[50]
GW/WB, India	µg L <sup>-1</sup>	54.2–415	54–395	0.2–167				CF-HGAAS	[51]
Rainwater/Brazil	µg L <sup>-1</sup>	5.5–6.7	5.5–6.7	nd				FI-HGAAS	[52]
GW/Solvenia	µg L <sup>-1</sup>	0.417						Coppt-HGAFS	[53]
SW/Mediterranean	%	30	5					FI-HGAAS	[54]
MW/Spain	µg L <sup>-1</sup>	0.34–0.52	0.34–0.52					CF-HG-AFS	[55]
TW/Spain	µg L <sup>-1</sup>	0.30–1.17	0.03–0.21	0.14–1.17				CF-HG-AFS	[55]
GW/WB, India	mg L <sup>-1</sup>	0.03–3.7	0.01–2.5	0.016–1.2				FI-HGAAS	[56]
RW/Venezuela	µg L <sup>-1</sup>	5.40	1.20	4.20				FI-HG-CT-AAS	[57]
SW/Venezuela	µg L <sup>-1</sup>	12.90	1.90	8.50	–	1.80		FI-HG-CT-AAS	[57]
DW/Denmark	µg L <sup>-1</sup>	9.09	9.09		0.70			FI-HG-AAS	[58]
GW/Germany	µg L <sup>-1</sup>	4.1	1.9	–				EcHG-FI-HGAAS	[59]
PW/Netherlands	µg L <sup>-1</sup>	55.9 <sup>c</sup>	28.5 <sup>c</sup>	26.8 <sup>c</sup>	0.60 <sup>c</sup>	nd		HG-CT-AAS	[60]
RW/Brazil	µg L <sup>-1</sup>	1.47	–	1.47				HG-AAS	[61]
RW/France	µg L <sup>-1</sup>	2300	nd	2300	nd	nd		HG-CTAAS	[62]
SW/Macedonia	µg L <sup>-1</sup>	1.95	1.8	<0.1	0.15	<0.1		HG-AAS	[63]
LW/Australia	µg L <sup>-1</sup>	34.8	1.1	35.5	41.5	1.1		HG-AAS	[64]
GW/Bangladesh	µg L <sup>-1</sup>	66.6–239.4	<0.1–38.2	62.1–211.6	<0.1			CF-HGAAS	[65]
GW/Poland	µg L <sup>-1</sup>	0.40–2.04	0.21–0.80	0.19–1.24				HG-GFAAS	[66]

<sup>a</sup>As<sub>T</sub>: total arsenic; GW: ground water; RW: river water; SW: sea water; LW: lake water; TW: tap water; MW: mineral water; DW: drinking water; PW: pore water; SPE: solid-phase extraction; Coppt: co-precipitation.

<sup>b</sup>Average of six samples and As<sub>T</sub> includes 81.1 µg L<sup>-1</sup> of particulate As.

<sup>c</sup>Average of three samples.

nd: not detected.

Table 5. Concentration of selenium species in environmental samples.

Sample	Source	Conc. units	Se <sub>T</sub> <sup>a</sup>	Se(IV)	Se(VI)	Se <sub>org</sub> <sup>b</sup>	Technique	Reference
Water-treatment plant	Spain	µg L <sup>-1</sup>	58.8	2.6	56.2		FI-HGAFS	[67]
Water-treatment plant	Spain	µg L <sup>-1</sup>	35.2	0.5	34.7		FI-HGAFS	[67]
Tap water	Canada	ng L <sup>-1</sup>	392.7	76.4	210	106.3	CF-HGAFS	[68]
Lake water	Canada	ng L <sup>-1</sup>	273.1	66.7	—	214.8	CF-HGAFS	[68]
Lake water	Canada	ng L <sup>-1</sup>	589.9	208.1	—	329.8	CF-HGAFS	[68]
Rain water	China	µg L <sup>-1</sup>	0.66	0.36	0.27		FI-HGAFS	[69]
River water	China	µg L <sup>-1</sup>	0.38	0.18	0.20		FI-HGAFS	[69]
Lake water	China	µg L <sup>-1</sup>	0.22	0.07	0.15		FI-HGAFS	[69]
River water	Japan	µg L <sup>-1</sup>	0.24	0.13	0.11		LLE-HG-ICPAES	[70]
River water	Japan	µg L <sup>-1</sup>	0.09	0.01	0.08		LLE-HG-ICPAES	[70]
Sea water	France	ng L <sup>-1</sup>	44	10	21	13	FI-HG-GFAAS	[71]
Drinking water	Argentina	ng L <sup>-1</sup>	55	—	55		SPE-FI-GFAAS	[72]
Sea water	Spain	µg L <sup>-1</sup>	5	<0.07	5		FI-HGAFS	[73]
Sea water	Spain	µg L <sup>-1</sup>	10	<0.07	10		FI-HGAFS	[73]
Sea water	Japan	µg L <sup>-1</sup>	0.07–0.11	0.03–0.05	0.07–0.04		SPE-HGAAS	[74]
Drinking water	Sweden	ng L <sup>-1</sup>	199	62	137		SPE-FI-HGAAS	[75]
Ground water	Sweden	ng L <sup>-1</sup>	182	52	130		SPE-FI-HGAAS	[75]
Lake water	Sweden	ng L <sup>-1</sup>	192	52	140		SPE-FI-HGAAS	[75]
Sea water	Spain	µg L <sup>-1</sup>	3.78	1.8	0.98		SPE-FI-HGAAS	[76]
Ground water	Wyoming	µg L <sup>-1</sup>	20+2	8	7	5	Coppt-HGAAS	[77]
Ground water	Wyoming	µg L <sup>-1</sup>	127+24	9	87	31	Coppt-HGAAS	[77]
Ground water	Wyoming	µg L <sup>-1</sup>	95+12	7	70	15	Coppt-HGAAS	[77]
Mineral water	Italy	µg L <sup>-1</sup>	2.11	nd	2.11		CF-HGAAS	[78]
Mineral water	Italy	µg L <sup>-1</sup>	0.97	0.34	0.63		CF-HGAAS	[78]
Mineral water	Italy	µg L <sup>-1</sup>	0.36	nd	0.36		CF-HGAAS	[78]
Sea water	California	ng L <sup>-1</sup>	80.2	<5	80.20		HG-CT-AAS	[79]
Lake water	California	ng L <sup>-1</sup>	17.70	<5	17.70		HG-CT-AAS	[79]
Rainwater	California	ng L <sup>-1</sup>	52.4	52.4	<5		HG-CT-AAS	[79]

<sup>a</sup>Total selenium;

<sup>b</sup>Organic selenium.

nd: not detected.

Table 6. Concentration of antimony species in environmental water samples.

Sample	Source	Conc. units	Sb <sub>T</sub> <sup>a</sup>	Sb(III)	Sb(V)	Technique	Reference
Tap water	—	µg L <sup>-1</sup>	0.18	nd	0.18	SPE-GFAAS	[80]
Snow	—	µg L <sup>-1</sup>	0.11	0.038	0.072	SPE-GFAAS	[80]
Sea water	Atlantic Ocean	µg L <sup>-1</sup>	0.20	0.01	0.19	CF-HG-GFAAS	[81]
Tap water	—	ng L <sup>-1</sup>	132	< 7	132	SPE-GFAAS	[82]
Lake water	Canada	ng L <sup>-1</sup>	119.3	—	39.6	CF-HGAFS	[83]
Lake water	Canada	ng L <sup>-1</sup>	141.2	21.4	72.5	CF-HGAFS	[83]
Lake water	Poland	µg L <sup>-1</sup>	0.51	0.33	0.18	CF-HGAAS	[84]
Lake water	Poland	µg L <sup>-1</sup>	0.62	0.26	0.36	CF-HGAAS	[84]
Natural river water	China	µg L <sup>-1</sup>	0.26	< 0.01	0.26	SPE-HGAAS	[85]
Polluted lake water	China	µg L <sup>-1</sup>	1.20	0.10	1.10	SPE-HGAAS	[85]
Polluted lake water	China	µg L <sup>-1</sup>	1.70	1.05	0.65	SPE-HGAAS	[85]
Tap water	Poland	µg L <sup>-1</sup>	0.44	0.05	0.39	HG-GFAAS	[86]
Mineral water	Poland	µg L <sup>-1</sup>	0.22-0.72	< 0.01-0.44	0.22-0.62	HG-GFAAS	[86]

<sup>a</sup>Total antimony.  
nd: not detected.

Aggett and Aspell [91] first reported the determination of As(III) and total As by determining As(III) at a pH of 4–5 and total As with  $5 \text{ mol L}^{-1}$  HCl. Nakashima [92] reported the determination of As(III) in presence of As(V) at  $0.25 \text{ mol L}^{-1}$  HCl with  $3\text{--}5 \text{ mg mL}^{-1}$  of Zr(IV) and 2% KI. Total As was determined in  $2 \text{ mol L}^{-1}$  HCl containing 1% KI. The Zr(IV), along with 2% KI, selectively suppressed the signal of As(V) in As(III) determination. Based on the pH dependency of arsine generation, several workers reported the speciation of inorganic arsenic [93–96]. Soon it was realized that methylated species also form their corresponding methylated arsines and could be determined in the same way as their inorganic forms [97].

Hinners [98] pointed out the major drawback of this procedure. He reported that if methylated arsenic is present, it could also contribute to the signal of As(III) and total As, and suggested that buffer solutions having a sufficient buffer capacity could minimize this error, and species-specific standards should be used for calibration. Lopez *et al.* [99] determined As(III) in citrate buffer and total As in  $6 \text{ mol L}^{-1}$  HCl without prereduction. They [99] reported that MMA and DMA interfered in the determination of As(III) and total As. Other workers suggested that not only does the pH affect the speciation but other factors such as kinetics and complexation are also involved [99, 100]. Several authors [101–104] reported the use of acetate and citrate buffers for As(III) determination at  $\text{pH} \approx 5$  and total arsenic at higher acidities, i.e.  $1\text{--}5 \text{ mol L}^{-1}$  acid with KI/KI-ascorbic acid prereduction. However, all these studies continued to report only the inorganic As speciation analysis.

Anderson *et al.* [105] reported a selective reduction method to speciate inorganic and methylated forms using different buffer matrices. One important finding of this work was that in mercaptoacetic acid medium, the four arsenic species (As(III), As(V), MMA, and DMA) showed similar response profiles. They proposed that the sulfur-containing ligand must play a significant role in effecting rapid hydride generation, probably, by altering reaction mechanism. Brindle *et al.* [106] and Chen *et al.* [107] introduced the use of L-cysteine as a prereductant for As(V) and reported that it reduces the acid concentration required for hydride formation and minimizes interferences from transition metals [108]. The use of L-cysteine gained popularity as a prereductant, and many procedures have included its use for As speciation analysis. Following the method of Anderson *et al.* [105], several articles were published on arsenic speciation analysis utilizing different acids, buffers, and redox media to determine inorganic [109–111] and methylated species [61–64, 112–117]. Typical procedures include the work of Torralba *et al.* [112, 113], Yano *et al.* [114], Rude and Puchelt [115], Quinaia *et al.* [116], and Shraim *et al.* [64, 117]. Shrim *et al.* [64] proposed the use of  $\text{HClO}_4$  and claimed that it is the only acid that facilitates the determination of total inorganic As without the interference from methylated species.

Selective hydride generation offers a simple and inexpensive practical tool for As speciation analysis. However, there are several inherent disadvantages: long reaction times, allow sample throughput, and an increased use of chemicals besides the strict control of reaction conditions are required.

Another approach for As speciation analysis is based on the use of appropriate concentration of acid and THB for selective generation of hydrides. However, this approach is limited to the determination of inorganic As species only. Most procedures use a low concentration of acid/THB to generate  $\text{AsH}_3$  from As(III) and a higher concentration of acid/THB for total As determination. This approach is based on the redox property of THB, which acts as a reductant and hydride source.

Narsito and Agterdenbos [100] observed a significant difference in the reduction efficiency between As(III) and As(V) at THB concentrations <1% and strongly acidic media. They suggested that As(III) is converted to AsH<sub>3</sub> more efficiently than As(V) under these conditions. Borho and Wilderer [118] reported the use of low THB concentrations under highly acidic conditions, i.e. pH < 0 to generate AsH<sub>3</sub> only from As(III). This is particularly useful for acid-preserved samples. Muller [119] reported the selective AsH<sub>3</sub> formation from As(III) using a low THB concentration. Sigrist and Beldomenico [49] reported a similar procedure using the FI-HGAAS system for samples containing <1 µg L<sup>-1</sup> of methylated As.

This approach is found to introduce serious errors, if methylated arsenicals are present. In addition, the use of low concentrations of THB decreases the sensitivity, and so the limit of detection (LOD) would be affected. In contrast, this approach offers an extended linear working range.

Other approaches for selective determination of As species include selective extraction and co-precipitation techniques [10]. These techniques allow the separation of one or more species of interest and subsequent HG. One important advantage of this approach is that interference from methylated species is greatly minimized. Generally, ammonium pyrrolidinedithiocarbamate (APDC) [120–124] or ammonium sec-butyl-dithiophosphate [125] is used to selectively complex As(III) at pH 3.5–5.5.

Yu *et al.* [85] reported selective retention of As(III) on thiol cotton (cotton treated with thioglycolic acid), which was eluted by hot HCl. As(V) was determined after KI-thiourea prereduction. Bombach *et al.* [126] reported the selective retention of As(V) by an anion-exchange column for on-site species separation. Okumura *et al.* [127] reported a zirconium loaded sorbent for the retention of As(III) and As(V), which were selectively eluted with 0.5 mol L<sup>-1</sup> of HCl and NaOH, respectively. Chatterjee *et al.* [128] described a method to specifically extract As(III) with sodium diethyldithiocarbamate at pH 5.5 in CCl<sub>4</sub> and subsequent determination by HGAAS. Samanta *et al.* [56] followed the same procedure to speciate inorganic arsenic. Dapaah and Ayame [129] extracted As(III) with zinc hexamethylenedithiocarbamate complex in 2,6-dimethyl-4-heptanone. The organic phase was back-extracted with Cu(II) and determined by FI-HGAAS. Van Elteren *et al.* [130] determined As(V) and As(III) by co-precipitating As(V) as molybdate complex with tetraphenylphosphoniumchloride and As(III) with dibenzylidithiocarbamate.

### 4.3 HG-CT techniques

The discovery of dissolved methylated arsenic species in the marine environment and most of the subsequent work which has been carried out to understand the presence and significance of related antimony, selenium, and tellurium species has resulted from the development of cryogenic-trap hydride methods. Cryogenic trapping of the volatile hydrides at liquid-N<sub>2</sub> temperatures results in a focusing of the products as a narrow plug of material which can then be separated either by a distillation mechanism using glass beads or a chromatographic material packed column. The collected arsines differ significantly in their boiling points (b.p. AsH<sub>3</sub> -55°C, CH<sub>3</sub>AsH<sub>2</sub> 2°C and (CH<sub>3</sub>)<sub>2</sub>AsH 55°C) and can be sequentially evolved from the trap by heating. With a glass-bead trap, this is simply achieved by removing it from liquid N<sub>2</sub>, but, if a chromatographic

material packing is involved, it must be heated electrically. The arsines are then detected with different atomic spectrometric methods.

The first reported As speciation method by Braman and Foreback [87] utilized the trap-speciation method. They utilized a 'U' tube packed with glass beads. Subsequently, several improvements to this trap system have been reported [131, 132]. Andreae [133] described a method with considerable improvement in the system with air-H<sub>2</sub> flame AAS and attained LODs in ng L<sup>-1</sup> levels. The glass beads were replaced by silanized glass wools, which gave quantitative recovery compared with silanized glass beads (80%). Howard and Arbab-Zavar [134] utilized a continuous flow hydride generator with CT-QFAAS detection. This greatly improved the performance and minimized transition metal interferences. Van Cleuvenbergen *et al.* [135] determined As(III) in Tris buffer (pH 7.5) and total arsenic at pH 0.8. Anderson *et al.* [136] used phthalate buffer for As(III) reduction and oxalic acid for determining other species. Ryu *et al.* [137] determined As(III) at pH 6, and total arsenic and methylated species were determined at pH 1.5 using oxalic acid.

Howard and Comber [138] obtained an improved sensitivity by changing the CF manifold geometry, etching the glass beads with HF instead of silanization used previously, and obtained an LOD of 19–61 ng L<sup>-1</sup> using 1 mL of sample. Michel *et al.* [139] reported an improvement in the technique with the use of H<sub>2</sub>SO<sub>4</sub> instead of HCl and progressive addition of THB. According to these authors [139], this resulted in a smoother and efficient response, and an LOD of 10 ng L<sup>-1</sup> was reported. A further remarkable improvement in species separation was reported by van Elteren [60], by coprecipitation of As(III) with sodium dibenzylthiocarbamate and As(V) with tetraphenylephosphoniumchloride as molybdate complex and determined separately. The methylated arsines were passed through a novel perma-pure filter, collected in a stainless steel trap, and determined by QFAAS. The advantage of this trap is faster heating and cooling, thus yielding a better species separation. The reported LOD was 0.16 µg L<sup>-1</sup>. Burguera *et al.* [140] reported arsine generation by Fleitmann reaction, i.e. using Al-NaOH for inorganic arsenic speciation analysis. The advantage of this procedure is the use of low-cost, stable, and easily stored reagents compared with the THB/HCl system.

Howard and Salou [141] applied cysteine pretreatment method, which led to a sensitivity enhancement and better interference control, and attained an LOD of 50 ng L<sup>-1</sup>. In another study [142], they investigated various prereductants for use in HG-CT-QFAAS and reported that thiglycolic acid also produced the same effect as that of cysteine. Burguera *et al.* [57] reported a fully automatic FI-HG-CT-AAS. The trap was made of PTFE coil and heated by microwave radiation. The reported LODs were 20, 24, 35, and 60 ng L<sup>-1</sup> for As(III), As(V), MMA, and DMA, respectively. Molenat *et al.* [62] used phosphate buffer (pH 6.8) for As(III) and oxalic acid for As(III) + As(V), MMA, DMA, and trimethylarsine oxide (TMAO) determination. Narvaez *et al.* [48] reported the online removal of copper as iminodiacetate complex using a microcolumn prior to HG. As(III) was determined selectively using acetate buffer (pH 4.5), and As(III) + As(V), MMA, and DMA were determined at pH 1.

Another remarkable achievement in the CT technique was the determination of methylated species of As(III) and As(V). Hasegava *et al.* [143] reported a solvent extraction procedure using the diethylammonium diethyldithiocarbamate (DDDC) procedure to determine the methylated trivalent arsenic species and methylated pentavalent arsenic species, in addition to inorganic species. In another study [144], they

described a method to determine the non-hydride fraction, in addition to the hydride reactive species. According to them, the non-hydride fraction may be divided into ultraviolet (UV)-labile and UV-inert fractions based on their conversion into hydride active species. Cabon and Cabon [145] determined hydride active species by alkaline persulfate digestion, whereas the same matrix after UV irradiation converted the inactive species to hydride active species and quantified by FI-CT-HGAAS. Recently, Hsiung and Wang [146] reported a novel packed cold finger trap (PCFT) packed with 10% OV-101 on chromosorb W-HP. This led to a better performance in terms of species separation than the 'U' trap. LODs of 0.047, 0.042, 0.0045, and 0.0063  $\mu\text{g L}^{-1}$  were reported for As(III), As(V), MMA, and DMA, respectively.

Cryogenic trapping methods offer efficient species separation and improved LOD to  $\text{ng L}^{-1}$  levels. The methods reported earlier used glass beads as packing material, which led to incomplete species recovery and separation. These drawbacks are minimized in the chromatographic material filled traps. However, the complexity of the system as a whole makes this method less attractive for routine monitoring.

#### 4.4 FI-HGAAS techniques

The introduction of FI principles and techniques into HG methods in AAS, pioneered by Astrom's [147] work in 1982, established an important milestone in the development of HGAAS. The topic has been reviewed by several authors [12, 13, 16]. FIA offers many advantages; the main features include a shorter analysis time, less consumption of sample/reagents, reduced human intervention, better sensitivity and precision, and increased tolerance to interference. The flexibility of this approach to include online separation techniques based on ion exchange, complexation/solvent extraction, solid-phase extraction (SPE), oxidation/reduction, etc. enabled its applicability as a powerful tool in speciation analysis.

Differentiation of As(III) and As(V) was performed by online pH-dependent arsine generation either utilizing varying acid/THB concentration or using appropriate buffers. Determination of As(III) and total As after online reduction using KI/KI-ascorbic acid [148–150], thiosulfate [124], and L-cysteine [151–154] was reported by many workers. Stopped flow techniques were developed to allow the reduction of As(III) species utilizing KI [155] and 4  $\text{mol L}^{-1}$  HCl [156]. The use of L-cysteine avoids the problems faced with other reductants such as KI and HCl. Lee *et al.* [157] showed that L-cysteine is an effective pre-derivatizing agent for inorganic as well as methylated arsenic species. Carrero *et al.* [158] studied the pre-derivatization of As species with L-cysteine and reported that at low acid concentrations, arsine is formed by the action of THB with analyte-thiolate complex, and at high concentration of acid, arsine is produced by a nascent hydrogen mechanism. Nielsen and Hansen [58] reported an online reduction of As(V) with KI-ascorbic acid in a heated knotted reactor. Torralba *et al.* [159] determined As(III) selectively in citrate buffer and total arsenic with 6  $\text{mol L}^{-1}$  HCl. Online co-precipitation with  $\text{La}(\text{OH})_3$  in a knotted reactor for selective As(III) determination was also reported [160], with an LOD of 3  $\text{ng L}^{-1}$ .

In contrast to the online reduction, Coelho *et al.* [52] used 1  $\text{mol L}^{-1}$  of HCl with 0.1% THB for selective As(III) determination and 3% THB for total As determination. This avoids the prerelution step reported by many authors [148–153]. The use of a low

THB concentration, i.e. 0.035% with  $2 \text{ mol L}^{-1}$  HCl for As(III) and total As after KI reduction, was reported by Sigrist and Beldomenico [49].

Online pre-concentration of As(III) on activated alumina and total As after prereduction with L-cysteine was also reported [161]. Simultaneous online pre-concentration using an anion-exchange column was reported by Narcise *et al.* [45], in which, the column is selective to As(V) at neutral pH and total As at  $\text{pH} > 12$ . Interference from methylated species was removed by cation exchange before selective adsorption. Anthemidis *et al.* [46] reported a sequential injection system, in which, 0.5% THB with  $1.5 \text{ mol L}^{-1}$  HCl, and 3% THB with  $9 \text{ mol L}^{-1}$  HCl was utilized for As(III) and total As, respectively. The system utilized an integrated reactor and gas-liquid separator, allowing improved sensitivity and interference free determination.

Selective retention of As(V) by an anion-exchange resin and total As after  $\text{KMnO}_4$  oxidation was also proposed [47]. Sequential combination of two different columns, in which, the first selectively retains As(III)-pyrrolidinedithiocarbamate (PDC) complex, while the second retains As(V), was reported for ICP-AES without HG [162]. Simultaneous determination of As(III) and As(V), based on the reduction kinetics using a co-centric HG, was also reported [163].

#### 4.5 HG-GFAAS techniques

An alternative approach to the use of a heated quartz tube atomizer is the deposition and collection of the volatile hydrides inside a preheated graphite furnace. The first report on the use of GF atomizer for the atomization of hydrides was by Knudson and Christian [164] in 1974. Since then, HG coupled with GF atomization technique has been carried out by several workers, and it has been reviewed [165]. Kalahne *et al.* [166] reported a comparative study of the performances of HG coupled to GFAAS, QFAAS, and ICP-AES. HG-GFAAS showed the lowest LOD ( $3 \text{ ng L}^{-1}$ ); however, HG-GFAAS suffered severe interference from other hydride-forming elements than the other two detectors. There are two approaches to using graphite furnace atomization; online atomization and *in situ* trapping of hydrides in the furnace. The *in situ* trapping technique has been shown to enhance the sensitivity significantly and eliminate efficiently the oxidation-state influence on the signal [167]. A comparison of both the techniques was reported [168].

A comprehensive review on FI techniques coupled to GFAAS was presented by Fang and Tao [169]. Various approaches of elemental speciation using GFAAS were also reviewed [170].

The first report on speciation analysis using HG-GFAAS was by Shaikh and Tallman [171]. They determined As(III), As(V), MMA, and DMA utilizing a U trap coupled to GFAAS. Other reported methods on arsenic speciation analysis were based on selective HG, solvent extraction and/or sequential volatilization utilizing the cold trap. Selective HG from As(III) species and total As after reduction was reported by several authors [120–122, 124, 172]. SPE using APDC [173] and 2,3-dimercaptopropane-1-sulfonate on  $\text{C}_{18}$  cartridge was reported [174]. Co-precipitation of As(III) with Cu-PDC and total arsenic after L-cysteine reduction was reported with a  $\text{ng L}^{-1}$  LOD [175]. Russeva *et al.* [176] separated As(V) selectively on a column packed with organotin material. Barrera *et al.* [177] reported a selective HG method to determine the four arsenic species. Wille [178] reported a method to distinguish between hydride active



and inactive species, i.e. first-order speciation, based on online UV oxidation/microwave digestion in alkaline  $K_2S_2O_8$  media. This showed that a significant fraction of As in seawater contains non-hydride active species. Sturgeon *et al.* [179] determined inorganic, methylated, and organoarsenicals such as arsenobetaine (AB) and arsenocholine (AC) based on selective reaction media and ion exchange with a UV irradiation procedure in river-water reference materials. They reported [179] that 22% of total arsenic was present in the non-hydride active form. Cabon and Cabon [54] reported an FI-HG procedure based on selective reaction media and online UV treatment in alkaline  $K_2S_2O_8$  media to determine hydride active and inactive fractions in seawater. About 15% of total arsenic was in the non-hydride active form. An LOD of  $1.5 \text{ ng L}^{-1}$  was reported, with a pre-concentration factor of 1000. Hermelo *et al.* [180] reported the selective online formation of As(III)-PDC complex in a knotted reactor and GFAAS detection with an LOD of  $8 \text{ ng L}^{-1}$ .

The role of modifiers to improve the performance of GF was investigated by various authors. The sensitivity of various As species were reported to differ according to the volatility of hydrides, i.e. less volatile hydrides gave a more intense signal than that of highly volatile hydrides. The addition of Ni was reported to eliminate this effect [181]. Slaveykova *et al.* [182] investigated the atomization behaviour of arsenic species in pyro-coated and tungsten-coated graphite tubes with Pd modifiers and reported that it improved the sensitivity of various As species. Barrera *et al.* [177] investigated the hydride-trapping efficiency with Ir-, W-, and Zr-coated graphite tubes, and reported that Zr-coated tubes gave a better performance. A comparative study of matrix modifiers in GFAAS was reported by Niedzielski *et al.* [183].

#### 4.6 HG-AFS techniques

Tsuji and Kugu [184, 185] first reported HG coupled with AFS. Mester and Foder [186] studied the characteristics of AF signals of As species and emphasized the need for independent calibration for each As species. D'Ulivo *et al.* [187] discussed the methods to improve the performance of HG-AFS techniques using additives and optical fibres. AFS detectors are very sensitive and selective for hydride-forming elements than AAS and AES. An overview of the speciation analysis of As by AFS was reported by Cai [17].

El-Hadri *et al.* [55] determined As(III) with 3% THB, and  $2 \text{ mol L}^{-1}$  of HCl and total As after prereluction with KI and species concentrations were calculated from the slope of the calibration curves. Lee *et al.* [188] described a method based on cation-anion-exchange columns connected in series. Lopez and Castro [189] utilized FI coupled with pervaporation prior to HG for dirty water samples containing highly suspended matter. van Elteren *et al.* [53] reported a procedure based on the co-precipitation of As(III) dibenzylidithiocarbamate. Yan *et al.* [50] reported a FI-HGAFS technique, in which, As(III) was selectively complexed with APDC online, and total As was determined following L-cysteine prereluction. Castro *et al.* [190] reported a method to estimate total hydride active As species and total As including 'hidden As' after UV irradiation. AB was mineralized only in alkaline  $\text{pH} > 11$  with an irradiation time of 60 min. Gong *et al.* [44] reported an SPE method for As(V) selective extraction. Featherstone *et al.* [191] reported a HG-CT-AFS method for the determination of four As species with a  $\text{ng L}^{-1}$  level LODs. Leal *et al.* [192] proposed a new technique based on multisyringe

flow injection (MSFI), in which As(III) and total arsenic were determined simultaneously after KI–ascorbic acid reduction.

#### 4.7 Electrochemical hydride generation (EchG) techniques

Electrochemical hydride generation, as a sample-introduction system to atomic spectrometry, is an alternative to wet chemical HG. Several advantages have been reported over wet chemical methods and the topic being reviewed [193, 194]. It has widely been used for total element determination, but for speciation analysis little information is available. The efficiency of EchG depends mainly upon the cathode material, electrolytic current, dimensions of the flow-through cell, and gas–liquid separator. Cathode materials like Pt, Au, Ag, and glassy carbon generate hydride only from the lower valency state of the hydride-forming elements, whereas Cd, Hg–As, and Pb generate hydrides from a higher valency as well, with different efficiencies [194].

Ding and Sturgeon [195] reported that the efficiency of arsine formation varied according to the nature of the cathode material and reaction matrix. Thus, As(V) could be reduced to AsH<sub>3</sub> using lead as cathode in HCl + H<sub>2</sub>SO<sub>4</sub> media without prereluction. Further, the addition of a high concentration of hydroxylamine hydrochloride completely suppressed the signal of As(V), but MMA and DMA were reported to interfere. Schaumloff and Neidhart [196] selectively determined As(III) using a fibrous carbon cathode and total As after online reduction with L-cysteine. Pyell *et al.* [197] reported the use of fibrous carbon and lead as cathode materials to determine As(III) and total arsenic, and employed a cold trap to remove the interference due to methylated species. Li *et al.* [198] reported a procedure for inorganic As speciation analysis, based on the HG efficiency at 0.6 and 1.0 A electrolytic currents using a glassy carbon cathode. The concentrations of species were calculated from the slope of the calibration curves.

#### 4.8 Speciation analysis using microorganisms

The ability of microorganisms to incorporate elemental species (biosorption) became a useful technique in speciation analysis. The literature on biological substrate for metal preconcentration was reviewed by Madrid and Camara [199] and Zylkiewicz [200].

Calzada *et al.* [25] reported that As(V) was biosorbed by the alga *Chlorella vulgaris*, whereas other species were unadsorbed. Smichowski *et al.* [201] successfully utilized *Saccharomyces cerevisiae* (baker's yeast) for the selective retention of As(III) in a batch system and quantified by HG–ICP–AES. Contrary to this, Koh *et al.* [202] reported that As(V) was retained better than As(III) in an immobilized column. They reported that in an immobilized column, the metal-binding (–SH) groups were blocked, and so As(III) was not adsorbed.

### 5. Selenium speciation analysis

Selenium as an essential trace element has attracted increasing attention in recent years, as evidence for its involvement in human health has become apparent. Selenium exists

in the environment in several oxidation states as well as a variety of inorganic and organic compounds. Dissolved inorganic selenium can be found in natural waters as selenide (–II), as colloidal elemental Se(0), as selenite ion Se(IV), and as selenate anion Se(VI). Organic forms of Se that may be found in the aqueous environment are volatile (methyl selenides) or non-volatile (trimethyl selenonium ion, seleno-amino acids, and their derivatives) [203].

As only Se(IV) is reduced to SeH<sub>2</sub> with THB, the other species should be converted into Se(IV) in order to generate SeH<sub>2</sub>, by performing an analysis using three separate aliquots, i.e. (a) with no further treatment—direct determination of Se(IV), (b) after reduction of Se(VI) to Se(IV) with HCl or HBr/KBr–Br<sub>2</sub>—the sum of Se(IV) and Se(VI), Se(VI) thus being determined by difference, (c) mineralization of organic matrix by UV-irradiation or wet digestion followed by reduction to Se(IV)—determination of total Se. The difference between the total Se and the sum of Se(IV) and Se(VI) is attributed to organic selenium compounds. However, it has been reported recently that the presence of dimethylselenium (DMeSe) and dimethyldiselenium (DMeDSe) compounds also contributes to the Se signal in HG methods [204].

### 5.1 HG–AAS and ICP–AES techniques

Many workers have determined inorganic selenium species, i.e. Se(IV) and Se(VI), utilizing the formation of SeH<sub>2</sub> only from the +IV state. Se(VI) is reduced to the +IV state by heating/boiling with 4–6 mol L<sup>–1</sup> of HCl [205–209] or with bromide ions [210, 211].

Cutter [79, 212] introduced a ‘U’ cold trap at liquid-nitrogen temperature to concentrate the evolved SeH<sub>2</sub> before atomization and achieved ng L<sup>–1</sup>-level LODs. Yu *et al.* [85] proposed selective retention of Se(IV) on thiol cotton, and Se(VI) was determined after reduction with HCl and TiCl<sub>3</sub>. Flores *et al.* [213] determined Se(IV) using a simple microbatch venturi type system, which was reported to consume less of the reagents. Maleki *et al.* [214] proposed a procedure in which the sample was injected into the reactor containing solid THB and tartaric acid. Se(VI) was determined after prereduction with L-cysteine. This method utilizes only solid reagents, thus obviating reagent preparation, and has an extended linear working range (up to 1200 µg L<sup>–1</sup>). Brunori *et al.* [78] reported a microwave prereduction method for Se(VI) coupled with CF–HGAAS. Selenocysteine and selenomethionine were partially reduced to Se(IV); hence their removal by cation exchange resin was recommended for Se speciation analysis.

Narasaki and Mayumi [70] extracted Se(IV) selectively with 4-nitro-*o*-phenylenediamine into toluene as 4-nitropiazselenol. The extract was mineralized with HNO<sub>3</sub>–HClO<sub>4</sub> and subjected to HG–ICP–AES detection. Total Se was determined after HCl reduction. Stripeikis *et al.* [215] reported a method to remove Fe and Cu interferences by retention on Dowex IX-8 resin as their chloro complexes, whereas Se species were not retained. The eluted Se species were passed through a heated PTFE coil for online reduction and determined by HG–ICP–AES. Schermer *et al.* [216] selectively determined Se(IV) by careful optimization of sample flow rate and electrolysis current in EchHG with microwave-induced plasma AES detection. In addition, the selective determination by complexation and solvent extraction has also been reported. Morabito [10] reviewed extraction procedures applied to speciation analysis.

Reaction of aromatic *o*-diamines with Se(IV) to form the corresponding selenodiazoles (piaszelenols) is one of the most commonly used derivatization procedures. As only Se(IV) forms the piaszelenol derivative, Se(VI) could be determined as the difference between total Se and Se(IV) similar to HG techniques. Tamari and Ogura [217] determined Se(IV) selectively by HGAAS, after extracting the complex Se(IV)-DAN (2,3 diaminonaphthalene) into cyclohexane, decomposing the organic phase by HNO<sub>3</sub>-HCCO<sub>4</sub> acids, and then reducing all Se to Se(IV) with HCL. Se(IV) with DAN (2,3-diaminonaphthalene), extracted the complex with cyclohexane and determined by HGAAS, after destructing the organic phase with HNO<sub>3</sub>-HClO<sub>4</sub>. Total Se was determined after HCl prereduction. This procedure allowed an LOD at ppt levels. Reddy *et al.* [77] reported a method for the selective co-precipitation of Se(IV) on CuO at pH 5.5 and desorbed at pH 12.5. Total Se was determined after HCl prereduction.

## 5.2 FI-HGAAS techniques

The introduction of FI systems offers efficient online sample prereduction methods, utilizing chemical, microwave, and photochemical methods. This avoids drawbacks such as analyte loss due to volatilization, reduction to elemental state, etc. associated with conventional offline methods. A detailed discussion of microwave digestion procedures for environmental samples has been published [218].

Fernandez *et al.* [73] determined Se(IV) using 0.5% THB and 4 mol L<sup>-1</sup> HCl, and total Se was determined using 6 mol L<sup>-1</sup> HCl and heating the sample to 140°C to convert all Se(VI) to Se(IV) online. Online preconcentration of Se(IV) by co-precipitation with La(OH)<sub>3</sub> was reported with an LOD of 1 ng L<sup>-1</sup> [219]. Rubio *et al.* [220] described an online UV-irradiation technique for reduction of Se(VI). Online reduction of Se(VI) utilizing the microwave-irradiation technique has been reported by several authors [221–224]. Brunori *et al.* [78] reported a microwave-reduction method for Se(VI) coupled with CF-HGAAS. Seleocysteine and selenomethionine were partially reduced to Se(IV); hence their removal using a cation-exchange resin was recommended prior to HG. Burguera *et al.* [225] utilized a time-based injector for injecting 4 mol L<sup>-1</sup> HCl for Se(IV) and microwave irradiation in 12 mol L<sup>-1</sup> HCl for total Se determination. They reported that it avoids the problems associated with conventional microwave irradiation. LaFuente *et al.* [226] reported an online focused microwave digestion method for the determination of Se(IV), Se(VI), and organic Se. Organic Se was decomposed first by HBr/KBrO<sub>3</sub> reagent with microwave irradiation for total Se determination. Gallignani *et al.* [227] reported an online sequential MW irradiation method in which a 10% v/v mixture of HCl and HBr medium was used. Mendez *et al.* [228] reported a time-based UV and ultrasound (US) irradiation procedure for the reduction of Se(VI) and organic Se using KNO<sub>3</sub> as a photoinhibitor. In spite of the claimed advantages, low recoveries of Se were reported from samples contain high organic matter [229]. Stripeikis *et al.* [230] used a conventional water bath for online reduction of Se(VI) using 6.8 mol L<sup>-1</sup> HCl and reported that it was advantageous over microwave heating.

Selective retention of inorganic Se species prior to the HG step has also been reported. Pyrzynska [231] selectively preconcentrated Se(IV) and Se(VI) on cellex-T anion-exchange resin. Se(IV) was selectively eluted with 0.01 mol L<sup>-1</sup> HNO<sub>3</sub>, whereas Se(VI) was eluted with 4 mol L<sup>-1</sup> HNO<sub>3</sub>. Selective retention on activated alumina

and successive elution with  $1 \text{ mol L}^{-1} \text{ NH}_3$  and  $4 \text{ mol L}^{-1} \text{ NH}_3$  was also reported [232]. Carrero and Tyson [233] immobilized THB and Se(IV) selectively on an anion-exchange resin,  $\text{SeH}_2$  was generated by injecting HCl with QFAAS detection. The immobilization of THB improved the  $\text{SeH}_2$  generation efficiency and reduced the blank signal. An LOD of  $0.12 \mu\text{g L}^{-1}$  was achieved with a preconcentration time of 3 min. Itoh *et al.* [74] reported selective retention of Se(IV) on an anion-exchange resin loaded with bismuthiol-II. Larraya *et al.* [76] reported an online selective retention of Se(IV) on an alumina-filled microcolumn and total Se after reduction with HCl online. Se(IV) was eluted with  $2 \text{ mol L}^{-1} \text{ NH}_3$ . The reported LOD was  $6 \text{ ng L}^{-1}$ . Ornemark and Olin [75] reported a preconcentration procedure using Dowex IX8, in which both Se(IV) and Se(VI) were retained. Se(IV) was retained when the sample pH was  $> 8$ , and Se(VI) was retained at a pH between 1 and 10 with 1 and  $5 \text{ mol L}^{-1} \text{ HCl}$  used for elution. Selective retention of Se species on XAD-8 column was also reported [234]. Gomez-Ariza *et al.* [235] reported the simultaneous retention of Se(IV), Se(VI) and Se(-II) on an XAX anion-exchange resin and eluted with  $1 \text{ mol L}^{-1}$  of  $\text{HCOOH}$ ,  $\text{HCl}$ , and  $\text{CS}_2$ , respectively. Sahin *et al.* [236] reported the selective retention of Se(IV) on mercaptosilica and eluted with 0.2%  $\text{KIO}_3$  and  $1 \text{ mol L}^{-1} \text{ HCl}$ .

### 5.3 HG-ETAAS techniques

Rodden and Tallman [237] reported Se speciation analysis using HG-CT-GFAAS detection, in which the sample was passed through an XAD-8 anion exchange resin at pH 1.6–1.8 for organic-matter removal. Total Se was determined after HCl reduction. Cabon and Erler [71] utilized UV irradiation in basic medium and HCl to reduce Se(-II) and Se(VI) to Se(IV), and attained LODs of 10, 21, and  $13 \text{ ng L}^{-1}$  for Se(IV), Se(VI), and Se(-II), respectively, with a preconcentration factor of 1000. Li and Deng [238] reported a procedure based on the selective adsorption of Se species on  $\text{TiO}_2$ , and subsequent determination by GFAAS. Saygi *et al.* [239] determined Se(IV) after the selective separation of the Se(IV)-PDC complex on Diaion HP-2MG and total selenium after HCl reduction. Chung *et al.* [120] reported the selective extraction of Se(IV) with APDC in  $\text{CCl}_4\text{-CHCl}_3$  and Se(VI) after  $\text{TiCl}_3\text{-HCl}$  reduction. Selective extraction of Se(IV) using APDC-MIBK was also reported [124].

Stripeikis *et al.* [72] reported an online separation and preconcentration procedure, in which Se species were preconcentrated on Dowex IX8 anionic resin, which, on elution with 0.1 and 4 M HCl, separated Se(IV) and Se(VI) species. Interference due to chloride ions during atomization was reduced using iridium-coated graphite tubes. An LOD of  $10 \text{ ng L}^{-1}$  was reported. Niedzielski *et al.* [84, 240] reported the determination of Se(IV) directly and total selenium after HCl reduction with palladium modifier. Sahin *et al.* [241] studied the effect of Ni and Pd + Mg modifiers in Se speciation analysis and proposed that the presence of  $\text{HNO}_3$  is necessary to obtain equal sensitivities from Se(IV), Se(VI), selenocysteine, and selenomethionine. Fragueiro *et al.* [242] reported a novel extraction method based on single-drop microextraction (SDME) of  $\text{SeH}_2$  generated in a headspace, which has subsequently been injected into graphite furnace AAS. Total Se was determined after

UV irradiation. Tuzen *et al.* [243] reported a method based on the selective co-precipitation of Se(IV) on Mg(OH)<sub>2</sub>.

#### 5.4 HG-AFS techniques

As AFS techniques are very sensitive, they can be directly used without a preconcentration procedure. HG-AFS techniques reported for Se speciation analysis are also based on the formation of SeH<sub>2</sub> only from the +IV state, and Se(VI) is calculated as the difference from total Se. He *et al.* [244] reported a direct determination procedure by CF in which higher flow rates (22 mL min<sup>-1</sup>) of sample were used to increase the sensitivity. Se(IV) was determined with 1.5 mol L<sup>-1</sup> HCl and 1.5% of THB, whereas the total Se was determined after reduction with 4% KBr and 1.5 mol L<sup>-1</sup>. An LOD of 0.96–1.3 ng L<sup>-1</sup> was reported. Eva Moreno *et al.* [67] determined Se(IV) directly and total Se after HCl reduction by FI-HGAFS. Lu *et al.* [245] reported a preconcentration procedure in which the Se(IV)-PDC complex is formed online and adsorbed on a polytetrafluoroethylene (PTFE) fibre-packed micro-column. THB is used as eluent, and its subsequent reaction with HCl generates SeH<sub>2</sub>. An LOD of 4 ng L<sup>-1</sup> was reported. Bryce *et al.* [222] reported an online focused microwave reduction method to determine Se(VI), whereas Se(IV) was determined directly. These authors reported another method based on SPE, in which both Se(IV) and Se(VI) were retained and sequentially eluted with formic acid and HCl.

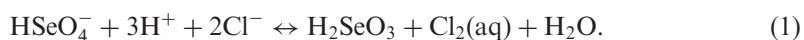
Chen *et al.* [246] investigated the photochemical behaviour of Se(IV), Se(VI), and organic selenium compounds by UV irradiation. Se(IV) was determined with 3 mol L<sup>-1</sup> HCl, and organic Se was determined in the matrix of 1% HNO<sub>3</sub> and 2% HCl with 2.5 h of UV irradiation at 300 nm. Total Se was determined after refluxing the sample from UV irradiation. Mendez *et al.* [228] reported a time-based combination of UV and ultrasound irradiation techniques for Se(VI), selenocysteine, and selenomethionine. KNO<sub>3</sub> was used as photoinhibitor. Tang *et al.* [69] reported the preconcentration of Se(IV) using co-precipitation with La(OH)<sub>3</sub>. Se(IV) is redissolved with HCl, and total Se was determined after HCl reduction. An LOD of 3 ng L<sup>-1</sup> was reported.

#### 5.5 Speciation analysis using microorganisms

The use of common yeast cells (*Saccharomyces cerevisiae*) for selective retention of Se(IV) was reported by Perez-Corona *et al.* [247], whereas Se(VI) was not biosorbed. Robles *et al.* [248] utilized living bacteria (*Pseudomonas putida* and *Escherichia coli*) for the separation of Se(IV) and Se(VI) species.

#### 5.6 Studies on the prerelution of Se(VI) to Se(IV)

Determination of inorganic Se species by HG methods requires the analyte to be present in the +IV state; hence Se(VI) could be determined differentially if total Se is determined after prerelution. It is generally accomplished by heating the analyte in the presence of HCl usually at an acid strength of 4–6 mol L<sup>-1</sup>. The reaction is as follows:



However, there are very conflicting statements in the literature as to the appropriate conditions for the reduction of Se(VI) with HCl. The controversies concern the optimal acid concentration, reaction time, and temperature. Pivonka *et al.* [249] presented a table which clearly demonstrated the differences in the recommended conditions. There are probably several reasons for the controversies. The most likely reason is that the sample solutions have contained other reagents possessing redox properties and that the presence of these will alter the redox potential of the HCl solution, demanding different concentrations of HCl, heating periods, and temperatures.

Cutter [79, 212] recommended that the reduction be carried out in boiling  $4 \text{ mol L}^{-1}$  HCl for 15 min and warned that prolonged boiling could lead to a reduction to an elemental state. However, the conclusion was challenged on thermodynamic grounds by Bye [250], who suggested that the loss of Se from samples, which were boiled for too long, might be due to the formation of volatile Se(IV) compounds such as  $\text{SeCl}_4$  or  $\text{SeOCl}_2$ . But, Krivan *et al.* [251], in a study using radiotracers, showed that the loss of Se was due to the back-oxidation by  $\text{Cl}_2$ , which in turn had formed from the reaction of HCl with strong oxidizing agents like  $\text{H}_2\text{O}_2$ . Bye [250] also concluded that the important component of the reducing solution was the  $\text{Cl}^-$  ion and that the reduction could be carried out quantitatively in con. HCl solution. Brimmer *et al.* [252] investigated the optimal reduction conditions using HCl and concluded that heating at  $91^\circ\text{C}$  in  $6 \text{ mol L}^{-1}$  HCl for 30 min resulted 99.9% reduction of Se(VI). The authors showed that the reaction is first-order ( $k = 5.8 \times 10^{-4}$  and  $3.9 \times 10^{-3} \text{ s}^{-1}$  for 4 and  $6 \text{ mol L}^{-1}$  HCl) with respect to Se(VI), and the reaction rate increased sharply with HCl concentration. No loss of Se was observed when closed vessels were used, which supports the possible formation of volatile chloride species. Contrarily, Hill *et al.* [253] reported that reduction should preferably be carried out in open vessels, to facilitate the escape of  $\text{Cl}_2$  generated, which otherwise may result in back-oxidation. Bye and Lund [254] reported that complete reduction of Se(VI) was achieved in  $10 \text{ mol L}^{-1}$  HCl heated to  $60^\circ\text{C}$  for 15 min, and so boiling is not necessary. According to Bye and Lund [254], the activation energy,  $E_A$ , was  $83 \text{ kJ mol}^{-1}$ , and the pseudo-first-order rate constant of the reaction was  $6.2 \times 10^{-5}$  and  $3.3 \times 10^{-4} \text{ s}^{-1}$  for 60 and  $80^\circ\text{C}$  using  $4 \text{ mol L}^{-1}$ . This is in good agreement with the values reported by Brimmer *et al.* [252]. The standard enthalpy change ( $\Delta H_f^\circ$ ) was found to be  $116 \text{ kJ mol}^{-1}$ , thus indicating an endothermic reaction, and so when the temperature is increased, the equilibrium constant will also be increased, leading to more efficient reduction.

Petterson and Olin [255] reported that a 99.9% reduction in 30 min required heating to 105, 85, and  $65^\circ\text{C}$  for 4, 5, and  $6 \text{ mol L}^{-1}$  HCl. Kinetic calculations showed that  $E_A$  was  $126 \pm 10 \text{ kJ mol}^{-1}$ , about  $40 \text{ kJ mol}^{-1}$  higher than that of Bye and Lund [254]. Furthermore, the authors pointed out that the reaction order was almost 5 at a constant chloride concentration (4–5 M) and a constant ionic strength of 5 M, and is greater than the stoichiometric coefficient for  $\text{H}^+$  in reaction (1). According to Petterson and Olin [255], the high dependence of the reaction rate on acidity indicates that some kind of selenate-proton cluster might be formed before the selenium atom is attacked by chloride. Hill *et al.* [253] reported that the activation energy  $E_A$  was  $90.4 \text{ kJ mol}^{-1}$ , and complete reduction of Se(VI) to Se(IV) could be achieved by heating to  $70^\circ\text{C}$  for 6 min using  $6 \text{ mol L}^{-1}$  HCl.

The prereduction has also been accomplished by heating with bromide ions, and it has been reported to offer several advantages over chloride ions. It prevents vigorous reactions, but shows better interference control [256] and improvement in flow

characteristics in a CF system, resulting in a better stability and reproducibility of AFS signals [244]. It also has an improved sensitivity in CF-HGAAS, as reported recently [257]. He *et al.* [244] reported that solid NaBr could be added to the samples, and so dilution caused by HCl could be avoided.

The equilibrium constant of reaction (1), when  $\text{Br}^-$  is used instead of  $\text{Cl}^-$ , is  $1.1 \text{ kg}^4 \text{ mol}^{-4}$ , whereas with  $\text{Cl}^-$ , it is  $7.1 \times 10^{-11} \text{ kg}^4 \text{ mol}^{-4}$  [258]. This suggests that the prerelution reaction with HBr is more favourable than with HCl, and, the back-oxidation caused by  $\text{Cl}_2$  could be avoided. For example, D'Ulivo *et al.* [256, 259] reported that organic selenium compounds when digested with HBr/ $\text{Br}_2$  converted all Se to Se(IV) only. Despite these advantages, reports on the prerelution using  $\text{Br}^-$  are fragmentary. Brindle and Lugowska [258] reported that bromide ions are found to be 19 times more efficient than chloride ions. They pointed out the particular reduction power of halide ions toward Se(IV), overcoming the kinetic inhibition of the prerelution of Se(VI), may be connected with the mechanism of reaction (1):



Se(IV) halides may be hydrolysed in aqueous solutions to  $\text{H}_2\text{SeO}_3$ .

In all these studies reported so far, the role of halide ions was assumed to be that of a reducing agent. Kenduzler *et al.* [260], in a recent kinetic study, proposed that the initial step of the conversion of Se(IV) to Se(VI) in the presence of  $\text{Br}^-$  is a nucleophilic substitution of the protonated  $-\text{OH}$  group of selenic acid in an acid-catalysed reaction. According to the authors, such a nucleophilic substitution reaction would explain the smaller reactivity of  $\text{Cl}^-$  ions compared with  $\text{Br}^-$  ions.

## 6. Antimony speciation analysis

Antimony is a cumulative toxic element that has been detected in natural waters at ultra-trace levels [261]. In natural waters, it may exist as Sb(III) or Sb(V), and a variety of methylated forms. In seawater at pH 8, both oxidation states are strongly hydrolysed, leading to the formation of  $\text{Sb}(\text{OH})_3$  and  $\text{Sb}(\text{OH})_6^-$ . These two inorganic forms exhibit pronounced differences in their analytical behaviour, toxicity, and mobility [34]. Trivalent species are reported to be more toxic than pentavalent forms. In seawater, methylated species represent about 10% of the total dissolved Sb, with the monomethyl species being predominant [34].

The determination of antimony species in environmental water samples often requires a preconcentration step, because of its presence at  $\text{ng L}^{-1}$  levels. Hence, various preconcentration methods utilizing liquid-liquid extraction (LLE), solid-phase extraction (SPE), and coprecipitation methods precede atomic spectrometric detectors. Smichowski *et al.* [33] published a review on the techniques of antimony speciation in 1998, and Nash *et al.* [34] presented an extensive review on the methodologies for antimony determination in environmental samples in 2000. Both the reviews include various preconcentration methods combined with atomic spectrometric detectors for speciation analysis. Hence, we review the procedures reported after the year 2000.



### 6.1 Speciation analysis based on selective HG

Methods based on selective hydride formation are attractive, as there are no additional steps involved. This method relies on the pH dependency of stibine formation from Sb(III) and Sb(V) species. Sb(III) forms  $\text{SbH}_3$  over a wide range of pHs, i.e. 2–8, and total Sb is determined under strongly acidic conditions ( $\approx 4 \text{ mol L}^{-1}$  HCl) or with prereduction. Nakashima *et al.* [262] utilized this procedure first and reported the selective determination of Sb(III) in  $0.35 \text{ mol L}^{-1}$  HCl and  $4 \text{ mg mL}^{-1}$  of Zr(IV), with  $\text{ng L}^{-1}$  LODs. This pH-dependent reduction of THB has been utilized by many authors [86, 101, 103, 111, 263] to selectively determine Sb(III) and total Sb after prereduction. Apte and Howard [264] utilized the cryogenic-trap method to concentrate the hydrides and attained 1 and  $10 \text{ ng L}^{-1}$  LODs for Sb(III) and total Sb. Andreae *et al.* [265] reported a trap method for methylated species which differ in their boiling points. Various buffers and acids were reported to the selective determination of Sb(III), e.g. citric acid (pH 2) [101, 103], acetate buffer [266], and phosphoric acid (pH 1.81) [267].

Nakahara and Kikui [268] reported a sequential determination of Sb(III) and total Sb in maleic and tartaric acid with an LOD of  $0.19 \mu\text{g L}^{-1}$ . Selective determination of Sb(III) in  $0.1 \text{ mol L}^{-1}$  (pH 5.5) or 6% citric acid and total Sb after KI reduction was also reported [269, 270]. Garcia *et al.* [271] reported a continuous tandem online separation of Sb(III) as its PDC complex and extraction into methylisobutyl ketone (MIBK) phase and aspiration into ICP. Sb(V) was determined after KI reduction of the aqueous phase. However, the reported LOD of  $3 \mu\text{g L}^{-1}$  was not sufficient for real samples without preconcentration. Feng *et al.* [272] reported a method to determine Sb species based on the reduction kinetics with L-cysteine. Ulrich *et al.* [273] determined Sb(III), Sb(V) and trimethylstiboxide (TMeSbO) using fluoride as matrix modifier with LOD of 1.1, 1.2, and  $1.4 \mu\text{g L}^{-1}$ , respectively.

Selective extraction of Sb(III) species using APDC–MIBK [121, 124, 274] and lactic acid–Malachite green [270, 275] have been reported. Similarly, SPE using a variety of adsorbents has been reported. Yu *et al.* [85] reported the selective retention of Sb(III) on thiol cotton, with HGAAS detection. Sb(V) was reduced with KI–ascorbic acid, and an LOD of  $5 \text{ ng L}^{-1}$  was reported. Thionalide loaded on a silica-gel column for selective retention of Sb(III) was also reported [276].

### 6.2 FI–HGAAS techniques

FIHG techniques utilizing online preconcentration and/or selective reduction procedures have been applied to Sb speciation analysis. Guntinas *et al.* [270, 277] used 6% citric acid for Sb(III) and  $4 \text{ mol L}^{-1}$  HCl media to determine total Sb and reported an LOD of  $7 \text{ ng L}^{-1}$ . Garbos *et al.* [82] reported the use of  $0.02 \text{ mol L}^{-1}$  HCl for Sb(III). Cabon and Medac [81] used a ‘U’ trap filled with chromatographic phase for concentration and used Tris-HCl buffer (pH 7.2) for Sb(III) determination with LOD of  $20 \text{ ng L}^{-1}$ . Selective sorption of Sb(III) on Duolite GT-73 with –SH functional groups coupled to segmented FI–HGAAS was reported by Erdem and Eroglu [278] with an LOD of  $60 \text{ ng L}^{-1}$ . Zheng *et al.* [279] used a nanometer-sized  $\text{TiO}_2$  to preconcentrate Sb(III) and Sb(V) and attained an LOD of  $50 \text{ ng L}^{-1}$ .

### 6.3 HG–GFAAS and AFS techniques

HG *in situ* preconcentration on graphite tubes offers another efficient tool for antimony speciation analysis. A comprehensive review of this subject was reported [165]. Smichowski *et al.* [280] reported a method for the simultaneous preconcentration of Sb(III) and Sb(V) based on the selective retention on an alumina microcolumn under controlled pH conditions using phosphoric acid. Garbos *et al.* [82] reported a pH-based selective adsorption procedure for Sb(III) and total Sb using polyorgs 31 with amidoxime and amino functional groups, with an LOD of  $30 \text{ ng L}^{-1}$ . Selective stibine generation from  $\text{Sb}^{3+}$  and *in situ* trapping on graphite tubes were reported by several authors [84, 86, 172] with  $\text{ng L}^{-1}$  LODs. Garbos *et al.* [82] reported a selective preconcentration of Sb(III) as PDC complex, sorbed over  $\text{C}_{16}$  bonded silica gel, with an LOD of  $7 \text{ ng L}^{-1}$ . Chung *et al.* [120] reported the selective extraction of Sb(III) as its PDC complex in  $\text{CCl}_4\text{--CHCl}_3$  and Sb(V) with  $\text{TiCl}_3\text{--HCl}$  reduction. Cabon and Madec [81] utilized the selective determination of Sb(III) using  $0.2 \text{ mol L}^{-1}$  Tris-HCl buffer and total Sb after online UV oxidation, and reported that oxidation led to a better recovery than reduction.

AFS has been demonstrated as a sensitive technique for hydride-forming elements having its resonance lines below 250 nm [186]. Determination of Sb by HGAFS has been described in detail by D'Ulivo *et al.* [281]. Tsujii [282] reported the selective determination of Sb(III) using HF as a masking agent for Sb(V). Selective determination of Sb(III) with acetate buffer (pH 5) was reported by Suo and Huang [283]. Deng *et al.* [83] used 8-hydroxyl quinoline as a masking agent for Sb(V) in the determination of Sb(III). Sb(V) was determined after KI prerelution, and total Sb was determined after microwave digestion and KI prerelution. The difference between total Sb and Sb(III) and Sb(V) was attributed to organic Sb. El-Hadri *et al.* [55] reported a method to determine Sb(III) and Sb(V) based on the efficiency of hydride generation with and without KI reduction.

## 7. Tellurium speciation analysis

Tellurium is regarded as a rare, toxic, non-essential element. In environmental water samples, it occurs normally at  $\text{ng L}^{-1}$  levels. Tellurium can exist as Te(IV), Te(VI), and, very rarely, dimethyl telluride and dimethyl ditelluride [39]. Studies on its speciation in natural waters are scarce. Only inorganic speciation in some seawater samples has been reported. A detailed review on its determination in environmental samples has been reported [39].

As tellurium occurs at  $\text{ng L}^{-1}$  levels, its determination invariably requires a preconcentration step. APDC, sodium diethyldithiocarbamate, and dithiozone are the ligands usually employed in LLE prior to detection [284]. The solvent extraction of Te(IV) has been reviewed [285].

Andreae [286] reported a method in which both Te(IV) and Te(VI) were coprecipitated with  $\text{Mg}(\text{OH})_2$ , which was then redissolved in HCl and determined by HG–GFAAS. Total Te was determined after reduction with HCl. Lee and Edmond [287] used alkaline co-precipitation for preconcentration of Te(IV) and determined by HG–GFAAS with *in situ* trapping. Yu *et al.* [85] reported the selective sorption of

Te(IV) on thiol cotton with HGAAS detection. Chung *et al.* [120] reported the selective extraction of Te(IV) as PDC complex into  $\text{CHCl}_3\text{-CCl}_4$  with GFAAS detection. Te(VI) was reduced with  $\text{TiCl}_3\text{-HCl}$  and determined as Te(IV). Yoon *et al.* [288] determined Te species by *in situ* trapping of  $\text{TeH}_2$  in graphite tubes. Total Te was determined after HCl reduction. Korez *et al.* [289] reported the selective retention of Te(IV) on mercaptosilica and total Te determination after HCl reduction.

## 8. Trends and future prospects

Hydride generation is the oldest method used for vaporization of trace elements. HG combined with atomic spectrometric detection has become the established method for As, Sb, Se, Te, etc. The technique comprises several distinct stages, notably generation of the volatile analyte, its collection (optional) and transfer to the atomizer, and atomization. During the last three decades, significant developments have taken place, which have improved the overall efficiency of the technique. Thus, ppb/sub-ppb levels of elements such as As and Se could be determined without the use of preconcentration (pre- or post-HG) techniques. However, a preconcentration step is necessary for elements such as Sb and Te, as their levels in the environment are normally at ppt levels. Hence, various preconcentration techniques coupled with HG remain an active area of research. Furthermore, an enhancement of the signal-to-noise ratio can be secured by collecting the species in a cryogenic trap prior to its introduction to the detector, thereby minimizing any dilution effects induced from the presence of co-evolved gases and other gases used to achieve phase separation and transport. One of the main advantages of cryogenic trapping technique is that the species do not come into contact with any liquid or solid sorbent materials, thus significantly reducing the possibility of their alteration/decomposition, but its bulkiness and the need to handle cryogenic liquid pose major drawbacks. HG coupled with *in situ* trapping in GF atomizer offers exceptional detection power (ppt levels), and the role of modifiers in atomization is the scope for further studies. EchG offers many advantages, particularly lower costs, freedom from interference, and lower LODs. Despite these, analytical applications reported so far are scarce. The main drawback lies in the production of the reproducible solid cathode surface. Other novel methods of HG include photo-induced generation [290], which is yet to be explored fully.

Elemental speciation based on selective reaction medium continues to be investigated, even though this approach seems to be matured. On the other hand, offline/online SPME techniques and selective HG using a novel reaction medium is a subject of further study, e.g. the use of solid reagents [214]. FI techniques incorporating efficient online preconcentration, matrix modification, and oxidation/reduction for elemental speciation analysis continue to be reported. New approaches to analyte preconcentration techniques such as SPME and SDME have been explored [242]. The use of microorganisms for selective retention of elemental species is an emerging area; however, its applicability to routine analytical applications is scarce.

Sample-pretreatment techniques such as microwave digestion, UV, and US irradiation techniques avoid the use of chemicals and drastic reaction conditions, and allow the determination of non-hydride reactive species (occurring mainly in marine

environments) as well. The photochemical behaviour of organometalloid species offers an alternative route to conventional digestion/prereduction methods.

The field of HG remains a dynamic field of study, as its ability to distinguish between various oxidation states of elements with the use of simple procedures continues to be reported. There is a scope for further improvement if the mechanisms of hydride formation and its atomization in the quartz-tube atomizer are better understood. Recent advances in our understanding of the hydrolysis of THB reagent [291], and discarding of the concept of 'nascent hydrogen' as the mechanism of analyte reduction, may serve to illuminate new approaches to HG, explain the effects of various additives in signal enhancement, and provide a unified approach to optimize the generation of volatile species. The fundamental role played by numerous hydroboran intermediates formed during the derivatization process appears to be vital in these interpretations [292]. The field of HG for elemental speciation analysis is broad and continues to evolve with the development of new methods of generation, e.g. photo-induced HG [290] and preconcentration techniques. Several of the more classical techniques have become stagnant and are used very little for analytical purposes, whereas others are experiencing a resurgence of interest. With the continued improvement in species separation and preconcentration approaches, the HG technique continues to serve as a simple yet powerful tool for the ultra-trace-level determination of elemental species.

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