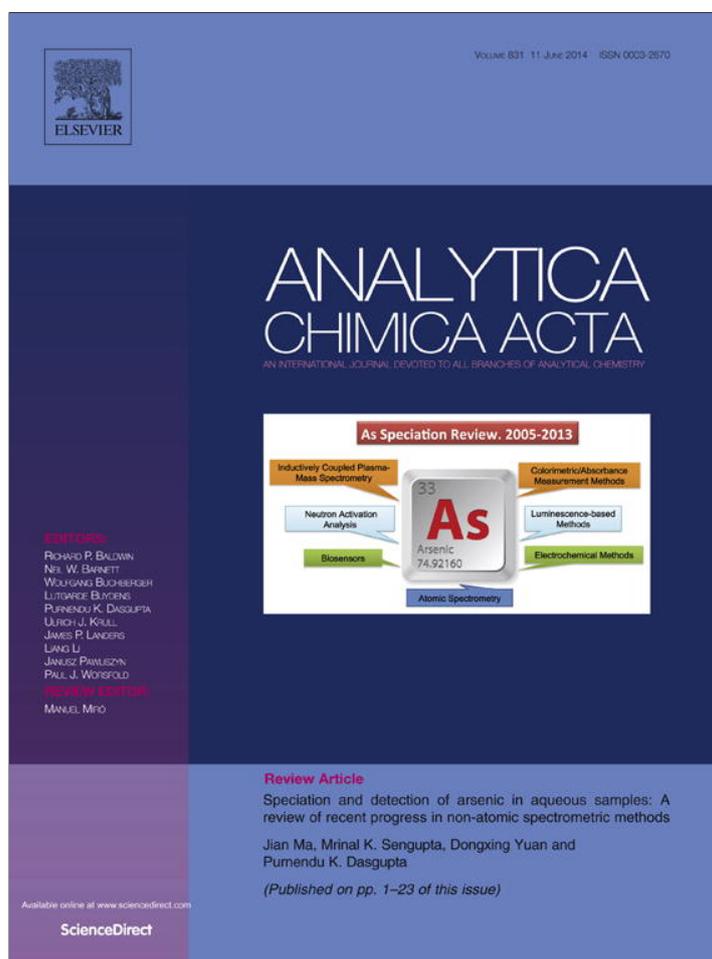


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Review

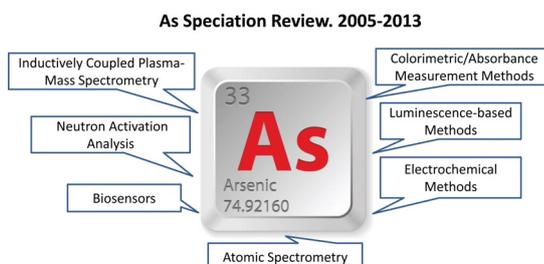
Speciation and detection of arsenic in aqueous samples: A review of recent progress in non-atomic spectrometric methods

Jian Ma^{a,b}, Mrinal K. Sengupta^{b,c}, Dongxing Yuan^a, Purnendu K. Dasgupta^{b,*}^a State Key Laboratory of Marine Environmental Science, College of the Environment and Ecology, Xiamen University, Xiamen 361102, China^b Department of Chemistry and Biochemistry, University of Texas, 700 Planetarium Place, Arlington, TX 76019, United States^c Thermo Fisher Scientific, Dionex Products, 445 Lakeside Drive, Sunnyvale, CA, 94085, United States

HIGHLIGHTS

- Compilation of principal official documents and major review articles, including the toxicology and chemistry of As.
- Review of non-atomic spectrometric methods for speciation and detection of arsenic in aqueous samples (2005–2013) of the performance of field-usable methods.

GRAPHICAL ABSTRACT



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ABSTRACT

Inorganic arsenic (As) displays extreme toxicity and is a class A human carcinogen. It is of interest to both analytical chemists and environmental scientists. Facile and sensitive determination of As and knowledge of the speciation of forms of As in aqueous samples are vitally important. Nearly every nation has relevant official regulations on permissible limits of drinking water As content. The size of the literature on As is therefore formidable. The heart of this review consists of two tables: one is a compilation of principal official documents and major review articles, including the toxicology and chemistry of As. This includes comprehensive official compendia on As speciation, sample treatment, recommended procedures for the determination of As in specific sample matrices with specific analytical instrument(s), procedures for multi-element (including As) speciation and analysis, and

Abbreviations: AAPTS, *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane; AES, atomic emission spectrometry; APDC, ammonium pyrrolidine dithiocarbamate; ASV, anodic stripping voltammetry; ATR-FTIR, attenuated total reflectance Fourier transform infrared spectroscopy; AuNP, gold nanoparticle; BGE, background electrolyte; CCD, charge-coupled device; CE, capillary electrophoresis; CME, capillary microextraction; CNFs, carbon nanofibers; CRM, certified reference material; CSV, cathodic stripping voltammetry; CTAB, cetyltrimethylammonium bromide; DGT, diffusive gradients in thin films; DMA, dimethylarsinic acid; DS, diffusion scrubber; DIT, dithiothreitol; ETV, electrothermal vaporization; FI, flow injection; GCE, glassy carbon electrode; GFAAS, graphite furnace atomic absorption; GPCL, Gas phase chemiluminescence; GSH, glutathione; HG, hydride generation; HGAAS, hydride generation atomic absorption spectrometry; HGAFS, hydride generation atomic fluorescence spectrometry; HPLC, high performance liquid chromatography; IC, ion chromatography; ICP-MS, inductively coupled plasma-mass spectrometry; LIBS, laser-induced breakdown spectroscopy; LLME, liquid-liquid microextraction; LOD, limit of detection; LPCL, liquid phase chemiluminescence; LSV, linear sweep voltammetry; MA, mercaptoacetic acid; MB, molybdenum blue; MCL, maximum contaminant level; MDL, method detection limit; MMA, monomethylarsonic acid; MPPTS, mercaptopropyltrimethoxysilane; NAA, neutron activation analysis; NaDBC, sodium dibenzylidithiocarbamate; PMT, photomultiplier tube; PTFE, polytetrafluoroethylene; QDs, quantum dots; RTIL, room temperature ionic liquid; SAM, self-assembled monolayer; SBSE, solvent bar microextraction; SERS, surface-enhanced Raman spectroscopy; SPE, solid phase extraction; SPME, solid phase microextraction; SPR, surface plasmon resonance; SWASV, square wave anodic stripping voltammetry; SWNTs, single-wall carbon nanotubes; TMAO, trimethylarsine oxide; TXRF, total reflection X-ray fluorescence spectrometry; USEPA, United States Environmental Protection Agency; UV, ultra violet; VMOAs-HPA, vanadomolybdoarsenic heteropoly acid; WHO, World Health Organization.

* Corresponding author. Tel.: +1 817 272 3171; fax: +1 817 272 3808.

E-mail address: Dasgupta@uta.edu (P.K. Dasgupta).<http://dx.doi.org/10.1016/j.aca.2014.04.029>

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prior comprehensive reviews on arsenic analysis. The second table focuses on the recent literature (2005–2013, the coverage for 2013 is incomplete) on As measurement in aqueous matrices. Recent As speciation and analysis methods based on spectrometric and electrochemical methods, inductively coupled plasma-mass spectrometry, neutron activation analysis and biosensors are summarized. We have deliberately excluded atomic optical spectrometric techniques (atomic absorption, atomic fluorescence, inductively coupled plasma-optical emission spectrometry) not because they are not important (in fact the majority of arsenic determinations are possibly carried out by one of these techniques) but because these methods are sufficiently mature and little meaningful innovation has been made beyond what is in the officially prescribed compendia (which are included) and recent reviews are available.

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Jian Ma is an associate professor in the state key laboratory of marine environmental science, college of the environment and ecology, Xiamen University, China. He got Ph. D. in Xiamen University, 2008 and has postdoctoral experience (2009–2012) in University of Texas at Arlington and University of South Florida, USA. His research interests include in field trace nutrient and metal analysis, flow analysis and automatic instrumentation. As the first/corresponding author, he has published 12 papers in international journals such as *Anal. Chem.*, *Environ. Sci. Technol.*, *Anal. Chim. Acta*, etc.



Mrinal K. Sengupta earned his Ph.D. degree from SOES, Jadavpur University, India. He did his Post-doctoral research work in Analytical and Bioanalytical Chemistry from University of Texas at Arlington. Currently, he is working as a Senior Chemist at Thermo Fisher Scientific at Sunnyvale, California. He has published over 40 scientific articles in peer reviewed journals and co-authored in several book chapters.



Dongxing Yuan is a Professor at the State Key laboratory of Marine Environmental Science at Xiamen University since 1994. She earned her Ph. D. from the University of Iowa in 1988 and was a Visiting Scholar at PerkinElmer (Uberlingen, Germany), Hong Kong University of Science and Technology and Texas A&M University. Her broad research interests are in environmental analytical chemistry, and specifically in metals and nutrients in seawater.



Purnendu K. (Sandy) Dasgupta is Jenkins Garrett professor of chemistry and biochemistry at the University of Texas at Arlington, USA. His interest in arsenic was sparked by a visit to Bangladesh in 1998 when he first encountered the plight of the arsenic afflicted first hand. He is a big proponent of the gas phase chemiluminescence method for measuring arsenic. He is the author of 400+ publications and has been one of the editors of *Analytica Chimica Acta* since 2004.

1. Introduction

Arsenic (As) is the 20th most abundant element in the terrestrial crust [1]. Arsenic has become increasingly important because of its effects on human health [2–9], its ecotoxicological [10] and ecological [11] consequences, and geochemistry [12–16] and environmental science [17] in general. Arsenic occurs in the environment in several oxidation states (–3, 0, +3 and +5) but in natural waters it is mostly found as inorganic oxyanions as trivalent arsenite (As(III)) or pentavalent arsenate (As(V)). Organic As compounds, such as methylarsonic acid (also called monomethylarsonic acid, MMA), dimethylarsinic acid (DMA) and trimethylarsine oxide (TMAO) may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important [18]. Long-term exposure to arsenic through drinking As contaminated water results in chronic poisoning that leads to changes in skin pigmentation and thickening and various types of cancers of skin, lungs, bladder, kidney, etc. [18]. Based on the increased cancer risks, the International Agency for Research on Cancer [19] has classified arsenic as a group I human carcinogen. The World Health Organization (WHO) estimated in 2001 that about 130 million people worldwide are exposed to arsenic concentrations above $50 \mu\text{g L}^{-1}$, and the principal affected major countries include Bangladesh, India, China and the United States [18]. In Bangladesh, where perhaps the problem is best characterized, problems with arsenic pollution have not been resolved [20]. On a global scale, the probability of occurrence of excessive concentrations of arsenic in groundwater has been summarized by the International Groundwater Resources Assessment Centre [21].

The maximum permissible levels of arsenic in drinking water have been reduced in many countries after the severity of the effects of groundwater arsenic contamination in Bangladesh has become widely known. Since January, 2006, the United States Environmental Protection Agency (USEPA) [22] has reduced the maximum contaminant level (MCL) in drinking water from 50 to $10 \mu\text{g L}^{-1}$, the same as the guidelines of the WHO [23], the European Union [24] and China [25], to name a few. Some have adopted even stricter guidelines: Australia has a drinking water MCL for arsenic of $7 \mu\text{g L}^{-1}$ [26]; New Jersey has a state regulation of $5 \mu\text{g L}^{-1}$ [27] and the American Natural Resources Defense Council has recommended that the drinking water standard be set at $3 \mu\text{g L}^{-1}$ [28]. One recent paper [29] states that it is technically feasible for large scale water treatment to reduce As content to less than $1 \mu\text{g L}^{-1}$ and this is the level that public water supply companies should aim for. While public health will definitely benefit from reducing the arsenic MCL, it would be a challenge towards routine monitoring of compliance and carry out either the removal or the monitoring in an affordable fashion.

The USEPA has reviewed the science and technologies for monitoring arsenic in the environment [30]. The approved methods include inductively coupled plasma-mass spectrometry

(ICP-MS), ICP-atomic emission spectrometry (ICP-AES), graphite furnace atomic absorption (GFAAS) and gaseous hydride generation atomic absorption spectrometry (HGAAS), which have method detection limits (MDL) ranging from 0.5 to $50 \mu\text{g L}^{-1}$ [31]. Relatively recent reviews on hydride generation and electrothermal atomic spectrometric methods of measurement of As are available [32,33]. While these techniques meet most legislated requirements, the instruments used are bulky, expensive, with high consumable costs and for ICP-based methods require large amounts of pure Argon. Special journal issues devoted to the topic [34] highlight the importance of arsenic measurement. Table 1 is a comprehensive list of the many review papers that cover different aspects of environmental arsenic. There are several reviews focusing primarily on the sampling aspects of water [35,36], algae, aquatic plants [37] and terrestrial plants [38]. Other reviews center on the detection and speciation of arsenic in ocean water [39], gaseous and particulate arsenic in air [40], soil and sediment [41], speciation and surface structure in solid phases [42], biological tissues [43] and rice [44]. Analytical methods for arsenic-containing carbohydrates (arsenosugars) are the focus of another review [45]. Very recently, Chen et al. reviewed new sample treatment techniques for arsenic speciation [46]. Several reviews center on the specific techniques of arsenic measurement, e.g., atomic spectrometry [32,33] including ICP-MS [47] and hydride generation atomic fluorescence spectrometry (HGAFS) [48], high performance liquid chromatography (HPLC)-ICP-MS [49], HGAAS and GFAAS [50,51], voltammetry and stripping analysis [52–54], HPLC coupled to various detection methods and other hyphenated techniques [55–57], bacteria-based bioassays [58], and ion chromatography (IC) [59]. One recent review covers chromatographic speciation along with HGAAS and voltammetric detection [60].

Arsenic analysis is an integral part of several review papers that generically cover elemental speciation [61–74]; however, the coverage on arsenic is too diffuse to be of much value to those solely interested in arsenic. There are several comprehensive reviews on the measurement of arsenic in water [75–83], the most recent dates from 2006 [84] but covers literature only through 2004. A 2007 review [85] claims to cover all technologies capable of measuring environmental As, but actually focuses on electro-analytical methods only. There are more recent comprehensive reviews [86,87] but in Chinese and thus of limited value to most.

We limit this review to papers published since 2005 on techniques other than atomic spectrometry for the measurement of arsenic in water. We have deliberately excluded atomic optical spectrometric techniques as recent reviews are available. Also, field-usable methods are much needed, and atomic spectrometry, despite its many virtues, does not fit that bill. Table 2, the heart of this review, summarizes these papers (2005–2013); solution phase concentrations are cited throughout in $\mu\text{g L}^{-1}$. Some pre-2005 citations illustrate a specific point but the omission of others does not connote that they are of less importance.

Table 1
Summary of published reviews about the chemistry, toxicology, speciation and detection of arsenic.

Year	Title	Contents and comments	References
1989	Chemistry and toxicology Arsenic speciation in the environment	Very comprehensive description of As speciation, including interaction of microorganism with As compounds without As-carbon bond formation, microbiological methylation of As, As compounds in marine environment, in terrestrial environment, in atmosphere, in aquatic system, in soils, sediments and fossil fuels, prediction of environmental arsenic speciation.	[17]
1997	Ecotoxicology of arsenic in the marine environment	Biogeochemistry of As in seawater and sediment, the speciation, bioaccumulation and biotransformation of As and toxicity of As to marine organisms.	[10]
2000	Arsenic: occurrence, toxicity and speciation techniques	General description of the occurrence of As in the environment, its toxicity, health hazards, and measurement techniques for speciation analysis.	[5]
2001	Genetic toxicology of paradoxical human carcinogen, arsenic: a review	Evaluation the mutagenic and genotoxic effects of As and its compounds based on the published experiments data about mutagenicity assays, DNA damage assays and cytogenetic assays.	[2]
2002	Arsenic round the world: a review	Detailed description of the environmental origin, occurrence, episodes, and impact on human health of As. Naturally and industrially As contaminated areas were summarized. As can cause dermal changes (pigmentation, hyperkeratosis, and ulceration), respiratory, pulmonary, cardiovascular, gastrointestinal, hematological, hepatic, renal, neurological, developmental, reproductive, immunologic, genotoxic, mutagenic, and carcinogenic effects.	[12]
2002	A review of the source, behavior and distribution of arsenic in natural waters	The abundance, distribution and speciation of As in water bodies; sources of As in minerals, rocks, sediments, soils and atmosphere; mineral water interaction of As; groundwater environments with high As concentration.	[13]
2003	The ecology of arsenic	Arsenic-metabolizing bacteria and their impact on speciation and mobilization of As in nature.	[11]
2004	Arsenic in groundwater: probability of occurrence of excessive concentration on global scale	Abundance of As in hard rocks, unconsolidated sediments, soils and groundwater; groundwater As distribution on global scale.	[21]
2005	Arsenic in coal: a review	Historical introduction, analytical comments, peculiarities of the As geochemistry in environment, estimation of coal Clarke value of As, coals enriched in As, mode of As occurrence in coal, factors influencing the As distribution in coal matter and coal bed, genetic topics, environmental impact of As by the coal combustion.	[15]
2006	Arsenic contamination in Bangladesh: an overview	Overview of the latest findings and statistical data on the As issue especially on soil, water and food cycle in Bangladesh, where high levels of As in groundwater are causing widespread poisoning.	[20]
2007	Seafood arsenic: implications for human risk assessment	Nature and quantities of the various arsenical compounds found in dietary seafood; discussion about the metabolic processing and fate of seafood As.	[3]
2008	Ecotoxicology of arsenic in the hydrosphere: implications for the public health	Bioaccumulation and metabolism of As in the hydrosphere, biogeochemistry of As, toxicology of As.	[4]
2008	Arsenic in food and water: a brief history	Development of the human understanding about chronic arsenic poisoning with Bangladesh as a particular example.	[6]
2009	Arsenic contamination in groundwater in the Southeast Asia region	103 references. The adverse impact of groundwater contaminated with arsenic (As) on humans has been reported worldwide, particularly in Asian countries. Also mentions several ongoing arsenic research studies in South East Asia viz., about the prevalence and impact of As, notably in its epidemiology, temporal variations, social factors, patient identification, treatment, etc. Also suggests urgent need to coordinate these various studies to useful ensure better delivery of the research outcome. Further research is recommended to improve field testing and monitoring of drinking water sources, and to develop new treatments for chronic As toxicity and new sources of safe drinking water.	[8]
2009	Human arsenic exposure and risk assessment at the landscape level: a review	120 papers cited. The review discusses about the groundwater contaminated with arsenic, due to extensive used for irrigation causing potentially long term detrimental effects to the landscape, and exposing a large populations at risk. The focus of more recent studies has been to perform risk assessment at the landscape level involving the use of biomarkers to identify and quantify appropriate health problems and large surveys of human dietary patterns, supported by analytical testing of food, to quantify exposure. The review highlights the benefit of GIS technology and its likely use in risk assessment studies at the landscape level to predict the future trends of human As exposure.	[9]

Table 1 (Continued)

Year	Title	Contents and comments	References
2009	Aquatic arsenic: toxicity, speciation, transformations, and remediation	The toxicity, speciation and biogeochemistry of arsenic in aquatic environmental systems are reviewed. The effect of pH, Eh, adsorbing surfaces, biological mediation, organic matter, and key inorganic substances on the unique assemblages of arsenic species that influence the toxicity of arsenic are discussed. Arsenic removal from water using adsorbents, chemical oxidation, photolysis and photocatalytic oxidation techniques is also reviewed.	[16]
2010	The chemistry and behavior of antimony in the soil environment with comparisons to arsenic: a critical review	Characteristics of inorganic antimony (Sb) in soil systems, including speciation, sorption and phase association. Comparison is made with As, which is shown to behave differently.	[14]
2001	Comprehensive official reports about arsenic United Nations Synthesis Report on Arsenic in drinking-water	390 pages expert synthesis report on arsenic in drinking-water as an UN system-wide initiative by the World Health Organization. Eight chapters including source and behavior of As in natural waters, environmental health and human exposure assessment, exposure and health effects, diagnosis and treatment of chronic As poisoning, drinking water guidelines and standards, safe water technology, communication for development and strategies to mitigate As contamination of water supply.	[18]
2007	Toxicological profile for arsenic	559 pages toxicological profile for As by Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services; ten chapters including public health statement, relevance for public health, health effects, chemical and physical information, production, import/export, use and disposal, potential for human exposure, analytical methods, regulations and advisories, references and glossary.	[7]
Sample treatment			
2004	Preservation of water samples for arsenic(III/V) determinations: an evaluation of the literature and new analytical results	Evaluation of published reports on As redox preservation and explanation of the discrepancies in the literature; synthetic laboratory preservation experiments and time experiments for natural waters from several field sites; filtration, adding reagents preventing Fe and Mn oxidation and precipitation, and isolation of sample from solar radiation can preserve As (III/V) ratio.	[35]
2010	Preservation of inorganic arsenic species in environmental water samples for reliable speciation	Field filtration, refrigeration and storage in the dark are prerequisites for stabilization of As(III)/As(V). Filtration removes suspended matter and most microbes, refrigeration suppresses most biotic and abiotic reactions, and storage in the dark avoids photochemical reactions of Fe(III) and As(III). There are reagents that inhibit the oxidation of Fe(II), but the efficiency of preservation depends on the sample matrix and its response to these methods of preservation.	[36]
2010	Sample pre-treatment and extraction methods that are crucial to arsenic speciation in algae and aquatic plants	Detailed summarization and discussion of sample handling, drying and powdering of fresh samples and the later extraction of As species based on the references from 2000 to 2010.	[37]
2013	Sample preparation for arsenic speciation in terrestrial plants: a review	The review critically discussed the published papers dealing with extraction procedures, analytical methods, and studies of species conservation in plants cultivated in terrestrial environment. Analytical procedures based on extractions using water or diluted acid solutions associated with HPLC-ICP-MS are considered as good alternatives owing to their versatility and sensitivity. Other less expensive strategies are shown as feasible choices.	[38]
Analysis in specific sample matrix			
1996	The analytical chemist at sea: measurements of iodine and arsenic in marine waters	Brief introduction about the shipboard measurement of iodine and arsenic (inorganic and organic form), no extraordinary precautions on sampling and preservation because of the immediate analysis on the ship laboratory.	[39]
2003	The speciation of arsenic in biological tissues and the certification of reference materials for quality control	Discussion of the accepted techniques for the speciation of As in biological issues, focusing on the use of CRM; discussion of a certification process of a candidate oyster-tissue reference material for different chemical species of elements (including As species).	[43]
2004	Extraction and analysis of arsenic in soils and sediments	Overview of methods for extraction and analysis of As in soils and sediments and strong recommendation of adoption of universal standard techniques and CRM, especially for sequential extraction schemes.	[41]
2005	Sampling technologies and air pollution control device for gaseous and particulate arsenic: a review	Evaluation of full field-scale and laboratory scale techniques for capturing particulate and gaseous emissions of As from	[40]

Table 1 (Continued)

Year	Title	Contents and comments	References
		the thermochemical treatment of different sources of As; summary of trace As concentration in ambient air, national standard sampling methods and As analysis methods; combination of particle control and vapor control device for complete capture of As species.	
2008	Speciation and surface structure of inorganic arsenic in solid phases: a review	Recent advancement in As speciation in solid phase including sample treatment (selective sequential extraction), analytical method (X-ray techniques and vibrational spectroscopy) and modeling aspects.	[42]
2010	Analytical methods for the determination of arsenosugars: a review of recent trends and developments	Overview of achievements and trends in the field of instrumental analysis of arsenic-containing carbohydrates (arsenosugars); discussion of typical experimental approaches for sample pretreatment, extraction, separation and detection; current possibilities and limitations of modern instrumental techniques.	[45]
2011	Does the determination of inorganic arsenic in rice depend on the method?	Evaluation of the state of the art of analytical capability for the determination of total and inorganic As in rice; total As result from 98 laboratories and inorganic As result from 32 laboratories all over the world; conclusion that inorganic As determined in rice does not depend on analytical method and that introduction of a maximum permissible level for inorganic As in rice should not be postponed because of analytical concerns.	[44]
Specific instrumental methods			
1999	Speciation of arsenic and selenium compounds by HPLC hyphenated to specific detectors: a review of the main separation techniques	Liquid phase separation of major arsenic and selenium species followed by element specific detection; publications since 1980 dealing with environmental matrices; comparison of methods performances on the basis of efficiency, rapidity, absolute and concentration detection limits and applicability to real world environmental samples.	[55]
2003	Analysis and speciation of traces of arsenic in environmental, food and industrial samples by voltammetry: a Review	Literature from 1970 to 2002; special attention to stripping modes and the choice of working material and supporting electrolyte; management of real samples and aspects of sample preparation; extensive compilation organized by real sample type with essential experimental conditions; compares voltammetric detection after preconcentration with FIA, chromatography, CE and ICP techniques.	[52]
2004	Ion-exchange column chromatography: an attempt to speciate arsenic	Covers literature spanning the 30 years up to 2004; different strategies for separation and pre-concentration of As species based on classical ion-exchange column chromatography with strong cation or anion-exchange resins. Atomic spectrometry is the measurement technique. Highlights sample pre-treatment including preservation and extraction of As species.	[51]
2004	Arsenic and its speciation analysis using high-performance liquid chromatography and inductively coupled plasma mass spectrometry	Description of essential background and toxicity of arsenic in the environment, currently used chromatographic applications, sample handling procedures and HPLC-ICP-MS applications for As speciation of environmental and biological samples.	[49]
2005	Analysis and speciation of arsenic by stripping potentiometry: a review	Literature spanning 1980–2003; illustration of the applications of stripping potentiometry for the determination and speciation of arsenic in different samples; comparison of the main advantages of stripping potentiometry with other electrochemical methods.	[54]
2005	Arsenic speciation analysis in water samples: a review of the hyphenated techniques	Information about occurrence of the dominant arsenic forms in various water environments; description of the main factors governing arsenic speciation in water; description of hyphenated methods used in As speciation analysis; highlights improvement and modifications of existing techniques with insufficient selectivity and sensitivity.	[54]
2007	Environmental applications of arsenic speciation using atomic spectrometry detection	Discussion of environmental chemistry and toxicity of As, reviews of As speciation, instrumentation including chromatography systems and atomic spectrometric detectors, accessories/techniques for sample preparation.	[23]
2009	Development of bacteria-based bioassays for arsenic detection in natural waters	Focus of bacteria-based assays as an emerging method that is both robust and inexpensive for the detection of As in groundwater both in the field and in the laboratory.	[56]
2009	Voltammetric methods for determination and speciation of inorganic arsenic in the environment: a review	Overview of voltammetric techniques from 2001 to 2009; more than 50 papers cited; new approaches for voltammetry including development of novel measurement protocols through media variation, development and use of new boron doped diamond electrodes modified with metals, nano Au-modified electrodes on carbon or carbon nano-tubes, novel rotating disc and vibrating electrodes to enhance mass transfer, and modified Hg(I) and thin film Bi on carbon for cathodic stripping voltammetry.	[53]

Table 1 (Continued)

Year	Title	Contents and comments	References
2011	Arsenic speciation analysis by ion chromatography: a critical review of principles and applications	Critical discussion of IC based methods; recommendations for robust and reliable As-speciation methods.	[59]
2011	Multicommutation flow techniques in the hydride generation-atomic fluorescence determination of arsenic	Evaluation of methods exploiting multicommutation flow techniques coupled to HG-AFS; focus on-line pre-concentration procedure as integral to automated methods.	[48]
2011	Arsenic and its speciation in water samples by high performance liquid chromatography inductively coupled plasma mass spectrometry: last decade review	Description of As speciation by HPLC-ICP-MS based on literature spanning 2000–2011; review of arsenic chemistry, occurrence in different kind of water, total arsenic determination with interferences elimination and its validation and analytical performance.	[57]
2012	Review: the application for estimation of limit of detection for ICP-MS trace analysis of arsenic	The paper focuses on the LOD of ICP-MS measurements employed for the determination of arsenic. The current approaches for the calculation of LOD are summarized and critically discussed.	[47]
2012	Analysis of arsenic species in environmental samples	Compares the hydride generation atomic spectrometry, voltammetry and chromatography (HPLC and GC), their advantages and disadvantages, argues that HPLC is the most powerful tool for (speciated) As analysis.	[60]
2012	Arsenic speciation in environmental samples by hydride generation and electrothermal atomic absorption spectrometry	Overview of analytical methods, preconcentration and separation techniques using HG-AAS and ET-AAS for determination of inorganic As and organoarsenic species in environmental samples; highlight of specific advantages, disadvantages, selectivity, sensitivity, efficiency, speed, detection limit, and aspects of recent improvements and modifications for different analytical and separation techniques.	[50]
1997	Multielement speciation and analysis including arsenic Speciation of methylarsenic, methyl- and butyltin, and methylmercury compounds and their inorganic analogues by hydride formation	Description of hydride derivatization (by sodium borohydride) of selected organometallic compounds and their inorganic analogues in complex environmental media.	[61]
2000	Speciation and analysis of mercury, arsenic, and selenium by atomic fluorescence spectrometry	As related content relies on only 2 references.	[62]
2004	Hydride generation: recent advances in atomic emission spectrometry	Advances in the HG technique hyphenated with different sources used in AES, including ICP, microwave-induced plasma, direct-current plasma and glow discharge; discussion of various aspects of vapor-phase introduction, including instrumentation for performing the reaction, the influence of the chemical interference effects, approaches to eliminating or decreasing the interferences, application to real samples; latest trends, e.g., expansion to transition and noble metals and the use of micellar media for sensitivity enhancement.	[68]
2007	Non-chromatographic hydride generation atomic spectrometric techniques for the speciation analysis of arsenic, antimony, selenium, and tellurium in water samples: a review	Review of non-chromatographic separation techniques including careful control of experimental conditions, offline/online sample pretreatment methods employing batch, continuous and FI techniques, cryogenic trapping of hydrides, solvent extraction, ion exchange and selective retention by microorganisms; for As, speciation using pH dependence of HG with NaBH ₄ is discussed.	[66]
2009	A review of non-chromatographic methods for speciation analysis	Very detailed account of the literature on non-chromatographic trace elements speciation; 332 references; discussion of advantages and drawbacks of the published state-of-the-art of fast and inexpensive methodologies applied to environmental, clinical and food samples; ~100 of the references relate to As, majority using atomic spectrometric detection.	[74]
2009	25 years' experience of vapor generation techniques for quantifying trace levels of mercury, arsenic, selenium and antimony in a range of environmental samples	Primary focus is mercury, As related material is scant.	[71]
2010	High performance liquid chromatography coupled to atomic fluorescence spectrometry for the speciation of the hydride and chemical vapour-forming elements As, Se, Sb and Hg: a critical review	Most recent applications of HPLC-HG/CVG-AFS for determination and speciation of the selected hydride-forming elements As, Se and Sb and chemical vapor-forming metal Hg; sample preparation, post-column treatments and application to various liquid and solid samples; limitations of HPLC-HG/CVG-AFS (necessity of post-column manipulations including the oxidation of organometallic species and pre-reduction to a suitable valence state). For As, ~90 papers cited.	[63]
2010	Chemical interferences in hydride-generation atomic spectrometry	Discussion of the mechanisms of liquid-phase and gas-phase interferences in the light of recent studies reporting on HG-AAS and HG-ICP-AES; source of interferences including concomitant mutual hydride forming transition elements; choice of acids (e.g., HNO ₃ and HF) used for sample digestion.	[67]
2010	Environmental application of elemental speciation analysis based on liquid or gas chromatography hyphenated to inductively coupled plasma mass spectrometry: a review	Summarization of developments of isotope dilution and isotopically labeled species-specific standards. Highlights recent trends in environmental application of ICP-MS	[70]

Table 1 (Continued)

Year	Title	Contents and comments	References
2010	Determination of As, Cd, Cu, Hg and Pb in biological samples by modern electrothermal atomic absorption spectrometry	coupled to GC and HPLC. For As, HPLC-ICP-MS is more popular. Spans literature from 2000 to 2010; overview of advances and applications of ETAAS for the determination of the named metals in biological samples; sample pretreatment; use of FIA and chromatography systems. For As, highlights modifiers, chemical vapor generation, temperature programs, and spectrometer improvements.	[72]
2011	Recent developments in solid phase extraction in elemental speciation of environmental samples with special reference to aqueous solutions	Highlights SPE for its effectiveness, robustness, speed and its “greenness”; illustration of the combination of SPE with highly sensitive detection methods for accurate measurement and speciation.	[64]
2011	Dynamic reaction cell ICP-MS for determination of total As, Cr, Se and V in complex matrices: still a challenge? A review	Review of analytical challenges for a reliable assay of As, Cr, Se and V by DRC-ICP-MS; illustration of different approaches and mechanisms involved in the analysis of polymers, biological fluids (serum, urine and whole blood), rock, soil and particulate matter; for As, the main interferences including $^{40}\text{Ar}^{35}\text{Cl}^+$, $^{59}\text{Co}^{16}\text{O}$; Sm^{2+} and Nd^{2+} are discussed.	[65]
2011	Review: the role of atomic spectrometry in plant science	310 papers cited; summary of sample pretreatment, extraction and multi-dimensional separation for characterization of important metallo-biomolecules in plants; emphasis of studies of covalently bound Se and As species	[73]
2011	Recent achievements in chemical hydride generation inductively coupled and microwave induced plasmas with optical emission spectrometry detection	Literature survey on progress in HG for ICP- and MIP-OES detection; description and discussion of different aspects of this technique, including design of HG reaction and separation systems, chemical reaction conditions, accompanying chemical interferences, means of their reduction, procedures of sample treatment for determinations of total concentrations and speciation forms of hydride and non-hydride forming elements in relevant samples, performance metrics attainable with ICP and MIP.	[69]
Comprehensive reviews on arsenic analysis			
1992	Determination of arsenic species in environmental and biological samples	164 references; HG, HPLC-AAS; ICP-AES; ICP-MS; thin layer chromatography/GC coupled with AAS; sample preparation. Presents the main source of problems including matrix interference, incomplete recovery and analyte instability.	[78]
1997	Analytical methodology for speciation of arsenic in environmental and biological samples	157 references; one table for analytical details of As speciation in different samples; highlights HG following separation procedures (e.g. ion-exchange or HPLC) coupled to AAS or AES.	[77]
1998	Determination of arsenic species in environmental samples: use of the alga <i>Chlorella vulgaris</i> for arsenic(III) retention	48 references; one table summarizes instrumental techniques for As speciation. Use of micro-organisms for As speciation, alga, esp. <i>Chlorella vulgaris</i> as an example.	[79]
2002	Arsenic speciation analysis	179 references; separation and speciation of As species using ion-pair chromatography are summarized in two tables; detailed illustration of techniques of separation, detection and sample handling; highlight of methods based on HPLC separation with IC-MS, HG-atomic spectrometry and electrospray MS detection.	[76]
2003	Arsenic speciation in environmental samples	76 references- described as “mini review”; description of analytical progress in extraction and identification of different arsenic species in various environmental materials, i.e., sediments, soils as well as foods including vegetables, fruits and marine biological samples; description of separation, detection and extraction; highlights of ion exchange and ion-pair chromatography in combination with element specific detection.	[75]
2004	Determination of arsenic species: A critical review of methods and applications, 2000–2003	451 references; one table summarizes previous reviews; description of the relevant terms and arsenic compounds; compilation of relevant methods in particular areas such as sample preparation, separation and detection; very detailed summary of different methods based on sample types including natural waters, marine organisms, terrestrial and fresh water organisms, soil/sediment/minerals and mineral wastes, sewage/wastewater, drinking water, food and related items, reference materials, human urine, blood, cells and tissues, biotransformation/conversion studies.	[80]
2004	Analytical methods for inorganic arsenic in water: a review	165 references; one table for performance parameters of various techniques for As(III) and As(V) in water samples; covers 1994–2004.	[81]
2006	Toxic arsenic compounds in environmental samples: speciation and validation	64 references; focuses on only As species considered toxic, including As-containing warfare agents and arsenobetaine (AB).	[84]
2007	Analytical tools for monitoring arsenic in the environment	72 references; focus on electrochemical methods of As detection in drinking water; discussion with respect to	[85]

Table 1 (Continued)

Year	Title	Contents and comments	References
2008	Recent development of speciation analysis for trace arsenic	sensitivity, ability to detect the chemical states of As, reliability, potential interferences, and ease of operation. 52 references; UV–vis spectrometry, AAS, HG-AFS, ICP-AES, X-ray fluorescence, characteristics of chromatography-atomic spectrometry; in Chinese, most citations are in Chinese.	[86]
2009	Arsenic speciation analysis	65 references; discussion of the benefits and defects of various speciation techniques as applied to studies of environmental and toxicological chemistry of As; highlights HPLC-ICP-MS or ESI/MS/MS; in Chinese.	[87]

2. Colorimetric/absorbance measurement methods

2.1. Kits

Arsenic field test kits are mostly based on the Gutzeit reaction; this involves the reaction of HgBr_2 with AsH_3 . In principle, field kits provide a semi-quantitative cost-effective approach for the field measurement of arsenic-contaminated drinking water. Typically tens of milliliters of the water sample are needed. The sample is strongly acidified and a powerful reducing agent, e.g., an As-free metal that would liberate H_2 or NaBH_4 is added. The liberated gas is passed through a filter soaked with $\text{Pb}(\text{OAc})_2$ to remove any H_2S that may be present. AsH_3 passes through this filter to an HgBr_2 impregnated filter, and the color of which changes from yellow to brown depending on the level of As present. While the technique is relatively inexpensive and convenient, the sensitivity is barely adequate at the regulation limit, highly toxic AsH_3 can leak from the test container if not carefully sealed and toxic Pb- and Hg-containing waste is generated. There are several brands of commercial arsenic test kits (Arsenic Quick [88], Arsenator [89], PurTest Arsenic [90], EZ Arsenic [91], Merckoquant Arsenic [92]). The kits rely on color strip comparison or LED based photometers that read the strip to provide a digital readout. Independent evaluation reports for some of the kits are in the literature [93–95].

Salman et al. [96] generated arsine in a specially designed cell with the gas passing through an HgBr_2 -impregnated filter paper that is then scanned by a color scanner. Custom software then provides a quantitative measure of the color intensity. The repeatability is better than “naked eye” detection but given that LED-photodiode based detectors (as used for example in the Arsenator) are even simpler, the merit of using a scanner is not clear.

There are also recent reports of new field usable kits. Baghel et al. [97] used magnesium turnings and oxalic acid to generate AsH_3 which was reacted with an HAuCl_4 impregnated filter. Exposure to AsH_3 produces elemental gold that appears as a pink-violet color. It takes ~ 10 min to detect $10 \mu\text{g L}^{-1}$ of As concentrations higher than $50 \mu\text{g L}^{-1}$ can be detected in less than 1 min. The great virtue of this method is that there is no need for toxic mercury compounds. However no validation has been conducted with real samples. Yusof and Rashid [98] reported a galloyanine immobilized chitosan membrane that changes color when dipped in a solution containing As(III). Even with a bench top spectrophotometer to read the exposed membrane only mg L^{-1} level As(III) could be detected. The authors propose implausibly that the color change is due to the formation of an ion associate with the protonated form of galloyanine; if so a variety of anions will likely interfere.

2.2. Absorbance/reflectance measurement

2.2.1. Molybdenum blue (MB) method

In acid medium, molybdate undergoes the well-known reaction with phosphate, arsenate, and silicate to form the corresponding

yellow heteropolyacid; the latter can be reduced to intensely absorbing molybdenum blue, which can be sensitively measured. The MB chemistry has been widely applied for all three analytes. Although chemical strategies exist to determine phosphate and arsenate in the presence of silicate, phosphate and arsenate are isoelectronic and the corresponding heteropolyacids are isomorphous, they cannot be distinguished from each other. In freshwater and drinking water, silicate levels are low in any case and phosphate is the main interference towards measuring arsenic. The most common strategy [99] is to oxidize all the As in one sample aliquot to As(V) and in another to reduce it all to As(III), which does not react with molybdate. Carrying out the MB reaction with the first aliquot thus yields the sum of P(V) and As(V) while only P(V) responds in the second aliquot. The difference then gives the As content with the shortcoming common to all difference-based procedures: an accurate estimation of As is difficult in the presence of large amounts of P(V). One interesting strategy [100] passes the sample through an anion exchange resin minicolumn held in the loop of an injector valve; when the valve is switched to the inject position and the 2% CH_3COOH carrier solution passes through it, weak arsenious acid (HAsO_2) held in the column interstitial space is easily eluted while P(V) and As(V) are retained. Downstream, the eluted As(III) is oxidized with KBrO_3 to As(V) and the MB reaction is then carried out. This approach has no interference from P(V) and silicate is converted to fluorosilicate by the prior addition of fluoride; the fluorosilicate is also retained by the anion exchanger. Total As is determined by inline pre-reduction to As(III) by acidic cysteine in an automated system. While the approach has the advantage that As is not determined by difference, with an LOD of $\sim < 8 \mu\text{g L}^{-1}$, the utility at low As levels is marginal. There are a large number of oxidants that rapidly and completely oxidize As(III) to As(V) but the reduction is much more difficult. More recently dithionite has been proposed as the reductant of choice [101], the reduction is complete in < 10 min at 80°C ; these authors also report an optimized composition of the MB reagent. The utility of the completely manual procedure described will doubtless benefit from an automated adaptation. Thiourea and KMnO_4 were respectively used as reductant and oxidant in another recent paper [102]; the stated LOD of $8 \mu\text{g L}^{-1}$ is again of marginal utility in As determinations in drinking water.

Several automated approaches to As determination via MB chemistry were reported. Toda et al. [103] reported a speciation-capable field instrument for measurement of As(III) and As(V) in water. Arsenic was reduced to AsH_3 by NaBH_4 and the liberated AsH_3 was reactively preconcentrated as As(V) in an alkaline KMnO_4 receiver contained in a porous hydrophobic membrane based diffusion scrubber (DS). The As(V) was then determined via the MB reaction. The oxidation state of the As could be differentiated based on the reduction pH; at low pH (~ 1), all the inorganic As is reduced to AsH_3 while at pH 7, only As(III) was reduced. An LED/photodiode-based absorbance detector was used. The limit of detection (LOD) could be as low as 70 ng L^{-1} with 80 mL sample.

Table 2
Analytical performance of the recently published non atomic spectrometric methods for arsenic detection (2005–2013).

Method	Sample type	LOD, $\mu\text{g L}^{-1}$	Range, $\mu\text{g L}^{-1}$	r^2	RSD, %	Recovery, %	Analysis time, min	Interferences/comments	References
Color scanner	Well and canal water	1, As(III)	2–20	0.992	0.13–2.85, $n=5$	–	–	10 fold of Na^+ , K^+ , SO_4^{2-} and Cl^- no interference; lead acetate trap eliminates serious S^{2-} interference.	[96]
Visual kit	–	10, total As	–	–	–	–	<10	No interference study; no real sample tested.	[97]
Visual kit	Mineral and tap water	40, As(III)	10,000–30,000	0.9607	0.87, $n=10$	89, 97	5	1 fold of Pb^{2+} and Ni^{2+} interference.	[98]
UV-vis-MB	–	0.7, As(V)	0–375	–	–	–	>45	Elimination of phosphate interference by sodium dithionite; no real sample tested.	[101]
UV-vis-MB	Groundwater	8, total As	10–10,000	0.9979	–	85–127	–	0.3 M SO_4^{2-} , 10 mg L^{-1} humic acid and common ions in groundwater have no interference.	[102]
UV-vis-MB	River, well and lake water	0.07, As(III); 0.09, total As	0–50	0.9981, 0.9995, 0.9982	–	100 \pm 3	<10	Detailed interference data; most ions no interference; 20 fold Fe^{2+} and Cu^{2+} interference on As(V).	[103]
UV-vis-MB	Wastewater	–	0–250	–	–	96–101	~15	No interference from Fe^{3+} and phosphate	[104]
UV-vis-MB	Ultra pure water	59, As(III); 74, As(V)	75–3750	0.9904–0.9998	0.8–9.5, $n=3$	95–101	–	No interference study	[105]
UV-vis Molybdoarsenate-ethyl violet ion associate	Tap, ground, river and mine water	4, As(V)	0–300	–	3.5, $n=5$	96–103	–	Most ions no interference; masking silicate with NaF and eliminate phosphate with anion exchange resin(1)	[106]
UV-vis Hollow fiber extrxn MB	–	27, As(V)	200–2000	0.9969	3, $n=6$	–	–	30-fold enrichment; no real sample tested	[107]
UV-vis-AuNPs	Well, tap and bottled water	0.003, total As	0.001–50	0.9216	–	–	<10	1 fold of Hg^{2+} , Na^+ , Pb^{2+} , Cu^{2+} , Zn^{2+} , Ca^{2+} , Li^{2+} , K^{2+} , Zn^{2+} , Fe^{2+} , Cd^{2+} , Ni^{2+} , and Sb^{3+} ; large dilution for most samples	[108]
UV-vis AuNPs	Not specified, but more likely artificial water	0.6, As(III)	0–100	0.989	2.0–8.2	94.6–124	–	Common ions and metals have insignificant	[109]
UV-vis Hexamethylene ammonium hexamethylenedithiocarbamate	Tap water	60, total As	200–1000	–	1.9–2.7, $n=3$	99–105	–	50,000 fold of Cl^- , 10,000 fold of K^+ and Na^+ , 1000 fold of Mg^{2+} and Ca^{2+} , 500 fold of Mn^{2+} , Fe^{3+} and Cr^{3+} , and 50 fold of Cu^{2+} , Co^{2+} , Cd^{2+} and Sn^{2+} no interference; LOD too high for drinking water	[110]
UV-vis AuNPs, ss-DNA	–	2, As(III)	5–2000	0.9937	–	–	–	Pb^{2+} , Fe^{2+} , Ca^{2+} , Cr^{3+} , Mg^{2+} , CO_3^{2-} , Br^- , NO_2^- , NO_3^- , PO_4^{3-} and SO_4^{2-} no interference; Hg^{2+} significant interference; no real sample tested	[111]
HPLC-UV	Water from contaminated area	29, As(III) 52, As(V) 56, MMA 30, DMA 20–70	50/100/200–10,000	–	–	–	~10	No interference study	[112]
MEKC-indirect UV (PDCA)	–	–	–	–	8.1–12.9	–	~10	No interference study; no real sample tested	[113]
CE-in situ arsenomolybdate-UV	Pore water	5, As(III) 5, As(V) 20, MMA 16, DMA	20–200 or 200–2000	–	0.03–0.25, $n=12$	87–106	~20	Sodium perchlorate masks silicate; 30,000 fold of sulfate on interference	[114]
CE-SDME-UV	Spiked tap water	15, As(III) 15, As(V) 7.5, MMA 52, DMA	375–1500/ 37.5–150	0.9889, 0.9946, 0.9954, 0.9830	1–2, 7–15, $n=4$	80–134	>33	No interference study; LODs too high even with 390–1500 fold enrichment	[115]
Vis-iodine liberation from iodate	Ground and polluted water	25, As(III)	90–900	0.998	0.08, 0.05, $n=10$	99.5, 100	>10	Common ions no interference; EDTA masks 100 fold of Fe^{2+} , Fe^{3+} , Sn^{2+} , Cr^{6+} and Ce^{6+} .	[116]
Vis-iodine liberation	–	308, 250, As(III)	–	–	0.25–3.57	98–100.5	>5	–	[117]

	Ground, tap, industrial and river water		1200–10,500, 400–11,500	0.9996, 0.9998				Common ions and urea, uric acid, glucose, citrate and tartarate no interference	
Vis HG reduce KMnO_4	Tap and artificial sea water	34, As(III)	300–3000	0.998	1.3, n = 5	92–101	>12	Chelex 100 resin removes transition metal interference	[118]
Color Scanner As(III) reduces Sulfanilic acid	Tap water	18, As(III)	1000–10,000, 25,000–10,000	0.9997, 0.9995	5.18–12.92	92, 96	>30	Sulfamic acid eliminates nitrite interference; contrary unit shown in interference study ($\mu\text{g L}^{-1}$ vs. $\mu\text{g mL}^{-1}$)	[119]
Vis HG pervaporation, reduce KMnO_4	River water	22, As(III) 51, As(V)	50–1000, As(III) 100–2000, total As	0.999, As(III) and total As	3.0, As(III); 2.6, As(V), n = 10	98–104	19.4	2000 fold of Cl^- , CO_3^{2-} , NO_3^- , PO_4^{3-} , SO_4^{2-} and one fold of Se^{4+} , Sn^{2+} , Sb^{3+} , Hg^{2+} no interference	[120]
QDs-FL quenching	Tap and river water	1.5, As(III)	225–11,250	0.999	1.2–1.9, n = 5	97–106	–	1 fold of Na^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , Ni^{2+} , Cr^{3+} , Mn^{2+} , Zn^{2+} , Cu^{2+} and Fe^{3+} no interference	[121]
HG-Gas Diffusion-QDs-FL quenching	Ground water	70, As(III)	6000–240,000	0.9919, 0.9972	1.4, n = 8	93–95	~ 4	1000 fold of SO_4^{2-} , NO_3^- , CO_3^{2-} , PO_4^{3-} , Cl^- , Br^- and I^- ; 10 fold of Ni^{2+} , Cu^{2+} , Cd^{2+} , Fe^{3+} and Pb^{2+} , and 1 fold of Hg^{2+} no interference; LOD too high for drinking water	[122]
Ion exch. preconcn. QDs-FL quenching	Spring, river and tap water	0.75, As(V)	1.5–75	0.9984	2.8, n = 7	94–106	–	10000 fold of Ca^{2+} , Mg^{2+} , N^+ , K^+ , NH_4^+ , Cl^- , NO_3^- ; 1000 fold of SO_4^{2-} , HCO_3^- , AsO_2^- , Co^{2+} , Ni^{2+} , Cu^{2+} , Mn^{2+} , Fe^{2+} , Zn^{2+} ; 200 fold of Pb^{2+} , Cd^{2+} , Hg^{2+} , I^- , PO_4^{3-} , Ag^+ , Cr^{3+} , Fe^{3+} no interference	[123]
VMOAs-heteropolyacid-luminol FI-LPCL	Fresh water	0.15	0.15–7	0.9989	0.8–2.5	–	0.5	Metals, eliminated by iminodiacetate chelating column; phosphate, eliminated by reduction to As(III) then precipitation	[124]
VMOAs-HPA preconcn. Luminol LPCL	Mineral, tap drinking water	6.7	7.5–37,500	0.9943	5.9	90–110	–	Chromate and phosphate, eliminated by anion exchange resin	[125]
HG- O_3 -GPCL	Groundwater, tap water	0.05 (total As) 0.09 (As(III))	–	0.9975			6	No interference found with drinking water	[129]
HG-gas diffusion- O_3 -GPCL	Drinking water	0.6	0.6–25,000	0.9998	–	–	0.13–0.2	10 fold Ni(II) and Cu(II)	[130]
Electrochem HG- O_3 -GPCL	Tap water and spiked water	Total As 0.36		0.9999			8	No interference study	[134]
Electrochem HG- O_3 -GPCL	Ground water, tap water	0.09 (total As) 0.76 (As(III))		0.9975		+95% (As(III))		No interference study	[135]
Manual HG- O_3 -GPCL	Ground water, tap water	Total As 1.0 (height based)		0.9988 (As(III)) 0.9977 (As(V))		95.2–101	3	No interference study	[136]
LC-HG- O_3 -GPCL	Irrigation water	0.27, 0.44 As(III), As(V) (area based) As(III) 0.35 As(V) 0.16 MMA 0.49 DMA 0.28					20–22	No interference study	[137]
LC-HG- O_3 -GPCL	Human urine	As(III) 3.7 As(V) 10.3 MMA 10.2 DMA 10		As(III) 0.9932 As(V) 0.9964 MMA 0.9802 DMA 0.9879 0.9998		As(III) 93 As(V) 92.1 MMA 90.5 DMA 87.8	10	No interference study	[138]
LIBS	Wastewater	Total As low g/L level	2–8 g/L	0.9638, 0.9622	–	–	–	No interference study	[139]
SERS on Ag nanofilm	–	10	10–500	0.9638, 0.9622	–	–	–	100 mg L^{-1} CO_3^{2-} , NO_3^- , SO_4^{2-} , K^+ , Na^+ has no interference; 50 mg L^{-1} Cl^- , 1 mg L^{-1} Ca^{2+} , 10 mg L^{-1} Mg^{2+} interfere	[140]
SERS on polyhedral Ag nanocrystals	Ground water	1	1–180	–	–	–	–	100 $\mu\text{g L}^{-1}$ As(V); no real sample tested	[141]
Prereduction dithiocarbamate chelation SPE preconcn TXRF	Seawater	0.01	1.2–16	–	5	95.2–104.6	–	No interference study	[142]
TXRF, mine tailings, drainage	Surface water	20	–	–	–	–	–	No interference study	[144]

Table 2 (Continued)

Method	Sample type	LOD, $\mu\text{g L}^{-1}$	Range, $\mu\text{g L}^{-1}$	r^2	RSD, %	Recovery, %	Analysis time, min	Interferences/comments	References
Preconcn on Al_2O_3 TXRF	DI water	0.7	2–200	–	–	95, 98	–	No interference study	[145]
ATR-IR on iron sol-gel	–	120	120–1875	0.94	–	–	–	No interference study; no real sample tested	[146]
SPR on thiol bearing surfaces	Ground water	0.0015 in DI H_2O but 4 could not be detected in real samples	–	–	>55	–	–	No interference study	[147]
HG-gas diffusion-amperometry	Wastewater	5	100–10,000	0.9996	1.96	98–99	1	No interference study	[148]
HG-pervaporation-Amperometry	Industrial water	1	50–60,000	0.9998	3.2	98.7–100	5	50-fold Sn(II), Sb(III), Se(IV)	[149]
Oxidative amperometry of As(III) on Pt nanotube arrays	River water	0.1	75–15,000	0.9989	3.5	99 \pm 5	–	No interference study	[150]
Oxidative amperometry of As(III) on HSC ₂ H ₄ NH ₂ modified Au, neutral soln.	Lake water	0.02	0.2–300	0.999	1.39, n=6	101.4	–	100-fold of Al ³⁺ , Mg ²⁺ , Ca ²⁺ , 20-fold of Fe ³⁺ , Fe ²⁺ , Hg ²⁺ and 5-fold of Bi ³⁺ , Zn ²⁺ , Cd ²⁺ and Pb ²⁺ have no significant interference on 10 $\mu\text{g L}^{-1}$ As	[151]
DPASV on vibrating Au microwire	River water	0.07 As(V)	0.07–3.0	0.998	9	–	–	1000 fold Al, 300 fold Mn, 10 fold Fe, 1 fold Ni and Cr, Zn has severe interference. Samples were also measured with ICP-MS	[152]
2-amino-1-cyclopentene-1-dithiocarboxylate ASV of As(III) on Hg film after Cr(III) preaccum	Tap, lake and NIST natural water	0.3, As(III)	0.5–440	0.998	2.5, n=6	98.4–104	–	1000 fold F ⁻ , HCO ₃ ⁻ , PO ₄ ³⁻ , Co ²⁺ , Cr ³⁺ , Zn ²⁺ , Fe ²⁺ , Mn ²⁺ , Cd ²⁺ , 700 fold Ni ²⁺ , 300 fold Hg ²⁺ and SCN ⁻ no interference; 30 fold Sb ³⁺ , Sn ²⁺ , Se ⁴⁺ and 5 fold Bi ³⁺ interference	[153]
DPASV, Sqr Wave ASV on Au lateral surface	Drinking water	0.06	1–15	0.9534–0.9997	1, n=3	82	–	1 fold Bi ³⁺ , Cd ²⁺ , Cr ³⁺ , Cu ²⁺ , Fe ³⁺ , Hg ²⁺ , Mn ²⁺ , Mo ²⁺ , Ni ²⁺ , Sn ²⁺ , Zn ²⁺ interference	[154]
CSV of As(III), ASV of total As on vibrating Au microwire	Raw borehole sample, groundwater, mineral, river, lake and tap water	0.035, As(III)	0.07–7500	–	5, n=8	–	–	2 fold I ⁻ , 20 fold Br ⁻ , 2000 fold F ⁻ and As(V), 20,000 fold SO ₄ ²⁻ , 20 fold Zn, 10 fold Bi, 4 fold Sb ³⁺ , 200 fold MMA and DMA, 5000 fold Triton have no interference; HS ⁻ , Al, Mn, Fe, HA interference	[155]
ASV on Mn-coated vibrating Au microwire	Seawater	0.015, As(V)	–	–	4, n=20	–	–	Detailed experiment about interferences for As(III), other metals, MMA, DMA and organic matter.	[157]
Au/Pd NPs on GCE, ASV	–	0.25, As(III)	1–25	0.989	–	–	–	Cu ²⁺ and Hg ²⁺ interfered, no interference from Pb ²⁺ , Cd ²⁺ , Mn ²⁺ and Zn ²⁺ ; no real sample tested	[158]
CSV on Hg electrode, long accumulation times	River, lake, rain and tap water	0.2, As(III)	0.75–750	0.999	2.2–3.8, n=5	95–105	–	Surfactants were pre-removed with Amberlite XAD-7 resin	[159]
CV on poly(taurine)-Nano Au film on GCE	River, spring and tap water	35 As(III)	450–2100	–	–	–	–	No interference study; LOD too high for drinking water	[160]
Pt/Fe(III) mps-MWCNT on GCE,ASV	–	0.75 As(III)	0.75–22.5	0.9992	–	–	–	200 fold Cu ²⁺ no interference; no real sample tested	[161]
CN/Amino acid modified Pt, CV	Wastewater	25	0.075–37.5	–	7.3	95–116	–	No metal interference at pH 4.0 acetate buffer; LOD too high for drinking water	[162]
Glutathione, dithiothreitol and N-acetyl-L-cysteine SAMs on Au, ASV/LSV	Tap, bottled, mineral, river and seawater	0.5	3–100	0.996	3.6–5.1, n=5	83.5–98.5	–	1000 fold Ca ²⁺ , K ⁺ , Na ⁺ , Mg ²⁺ , Cl ⁻ , NO ₃ ⁻ and SO ₄ ²⁻ , 100 fold Pb ²⁺ and Cd ²⁺ , 10 fold Cu ²⁺ and Hg ²⁺ no interference	[163]
Fe ₃ O ₄ -RTIL composite modified screen-printed carbon disposable electrode, SWASV	Ground water	0.0008, As(III)	1–10	0.997	–	–	–	Cu ²⁺ interferes; linear range starts from more than three orders of magnitudes higher than LOD	[164]
AuNPs internal electrolysis deposited on GCE, ASLSV	Tap, spring and river water	0.07, As(III)	1.5–225	–	–	98–101	–	Cu ²⁺ no interference	[165]
Modified Au electrode, CV	Drinking, tap, river and ground water	0.018, As(III)	0.1–1800	0.9996	3.0, n=50	–	–	One fold of Cu ²⁺ , Zn ²⁺ , Cd ²⁺ , Pb ²⁺ , Ni ²⁺ , Hg ²⁺ , Co ²⁺ , Ca ²⁺ , K ⁺ , Na ⁺ , NO ₃ ⁻ , SO ₄ ²⁻ , PO ₄ ³⁻ , CH ₃ COO ⁻ and OH ⁻ no interference	[166]

Modified Au electrode, CV	Lake and drinking water	0.047, As(III)	0.1–120	0.999	1.2, n = 8	100–102	–	100 fold of Cu ²⁺ , Hg ²⁺ , Pb ²⁺ , Fe ³⁺ , Co ²⁺ , Ni ²⁺ , Zn ²⁺ , Sn ²⁺ , Vi ³⁺ , Cd ²⁺ ; no interference	[167]
Polyacrylonitrile-silica gel ISE Potentiometry	Drinking water	75, As(V)	75–7,500,000	0.9878	–	89.9–95.06	–	Useful pH range of 5.0–10.0	[169]
CE-C ⁴ D 90° reflecting ion optics ICP-MS	Ground water	11.25	37.5–7,500	0.9998	1.3–2.3	88–120	10	No interference study	[170]
Carbon nanofiber SPE-ICP-MS	Ground, waste, estuarine, sea water	0.2, total As	0.5–275	0.992	1–6, n = 7	89.2–108.5	–	Dilution and optical design of the instrument eliminate Cl ⁻ interference	[173]
SWCNT SPE-ICP-MS	Ground, lake water	0.0045 As(III); 0.24 As(V)	–	–	2.6 As(III); 1.9 As(V), n = 9	92–106	–	5000 fold of Na ⁺ and K ⁺ ; 4000 fold of Cl ⁻ ; 2000 fold of PO ₄ ³⁻ , SiO ₃ ²⁻ and SO ₄ ²⁻ ; 1000 fold of Ca ²⁺ , Mg ²⁺ , Cu ²⁺ , Mn ²⁺ and Zn ²⁺ ; 500 fold of SeO ₃ ²⁻ and 200 fold of Fe ³⁺ and Al ³⁺ have no interference on 5.0 μg L ⁻¹ As(III)	[177]
Strong base resin-hydrated Fe oxide composite for As Speciation-ICP-MS	Tap, lake and well water	0.0039 As(III); 0.23 As(V)	–	–	3.1 As(III); .5 As(V), n = 9	92.7–103	–	5000 fold of Na ⁺ and K ⁺ and Cl ⁻ ; 2000 fold of PO ₄ ³⁻ , SiO ₃ ²⁻ and SO ₄ ²⁻ ; 1000 fold of Ca ²⁺ , Mg ²⁺ , and 200 fold of Fe ³⁺ and Al ³⁺ have no interference on 5.0 μg L ⁻¹ As(III)	[178]
Above sorbent, now including AgCl-ICP-MS –SH and –NH ₂ functionalized silica gel for speciation-ICP-MS	Tap, lake and well and wastewater	0.03, As(III), As(V), MMA and DMA	0.03–20	–	1.26–1.84, n = 7	88.4–102.4	–	10–100 mg L ⁻¹ Cl ⁻ and SO ₄ ²⁻ ; no interference on 100 μg L ⁻¹ sample	[180]
CME-ICP-MS	Ultrapure and drinking water	0.041	–	0.9991	–	87–104	–	No interference study	[181]
Capillary microextraction-ICP-MS	Mineral, tap and lake water	0.0034 for As(III); 0.0007 for As(V)	–	–	3.1, 4.0, n = 7	94–105	7.5	10,000 fold of Na ⁺ and K ⁺ ; 5000 fold of Ca ²⁺ and Mg ²⁺ ; 3000 fold of Cl ⁻ ; 2000 fold of PO ₄ ³⁻ , SiO ₃ ²⁻ and SO ₄ ²⁻ ; and 100 fold of Fe ³⁺ have no interference on 20.0 μg L ⁻¹ As(III) and As(V)	[182]
SBSE-ICP-MS	Purified, tap rain, lake and river water	0.0109 for As(III); 0.0062 for As(V)	0.05–16	0.9983, 0.9927	4.3, 5.8, n = 7	88–108	7.5	10,000 fold of Na ⁺ and K ⁺ ; 5000 fold of Ca ²⁺ and Mg ²⁺ ; 3000 fold of Cl ⁻ ; 2000 fold of PO ₄ ³⁻ , SiO ₃ ²⁻ and SO ₄ ²⁻ , and 100 fold of Fe ³⁺ have no interference on 20.0 μg L ⁻¹ As(III) and As(V)	[183]
Polyaniline on PTFE for speciation HG-ICP-MS	Synthetic, lake and tap water	0.00032 As(III)	0.01–30	0.9920	8.8, n = 9	96.2–107	Extraction time, 15	20,000 fold of Na ⁺ and NO ₃ ⁻ ; 10,000 fold of K ⁺ ; 4000 fold of Ca ²⁺ and Mg ²⁺ ; 250 fold of Cl ⁻ ; 0.5 fold of SeO ₃ ²⁻ and 0.2 fold of Fe ³⁺ , Zn ²⁺ , Hg ²⁺ and Co ²⁺ have no interference on 0.1 μg L ⁻¹ As(III); very low LOD with 220-fold enrichment	[184]
Automated HG-ICP-MS	Ground water	0.05, As(III); 0.09, As(V)	0.5–50	>0.997	2.0, 2.5, n = 5	95–105	3	200,000 fold of Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺ , Cl ⁻ , NO ₃ ⁻ and SO ₄ ²⁻ ; 50 fold of Fe ³⁺ , Cu ²⁺ , Zn ²⁺ , Mn ²⁺ , Al ³⁺ and PO ₄ ³⁻ have no interference on 5 μg L ⁻¹ As(III) and As(V)	[185]
FI-HG-ICP-MS	Groundwater rice extracts	0.0301, AsB 0.0022, DMA 0.0021, As(III) 0.0021, MMA 0.00208, As(V)	–	AsB 0.9982 DMA 0.9995 As(III) 0.9999 MMA 0.9997 As(V) 0.9997	–	99.2 ± 0.6	4	No interference study	[186]
FI-HG-ICP-MS	Groundwater rice extract	0.0192, AsB 0.0145, DMA 0.0177, As(III) 0.0192, MMA 0.0321, As(V)	–	AsB 0.9985 DMA 0.9999 As(III) 0.9999 MMA	–	100.2 ± 0.8	–	No interference study	[186]

Table 2 (Continued)

Method	Sample type	LOD, $\mu\text{g L}^{-1}$	Range, $\mu\text{g L}^{-1}$	r^2	RSD, %	Recovery, %	Analysis time, min	Interferences/comments	References
Ferrihydrite gel DGT-ICP-MS	Stream water, in situ As(V) collection	5 ng/DGT	-	0.9999 As(V)	-	93.7 ± 1.4	-	No interference study	[189]
TiO ₂ gel DGT-ICP-MS	Stream and coastal lagoon water	0.01	-	>0.998	<8	-	-	No interference study	[190]
TiO ₂ gel DGT-ICP-MS	Seawater	0.03	-	>0.998	<9	-	-	No interference study	[191]
TiO ₂ gel DGT-ICP-MS	Porewater	0.02	-	-	-	-	-	No interference study	[192]
LLME-ICP-MS	Pond, river, tap and bottled water	0.0031	0.0084–0.0800	0.999	<4, n=6	95–108	-	No interference study	[193]
CE-ICP-MS	Ground water	0.9–3	20–250	0.9949–0.9994	0.8–5.7, n=5	89–107	35	No interference study; absolute LOD 19–65 fg As	[194]
NAA	Tube-well water, vegetation, soil	<20	-	-	1.1–5	-	-	No interference study	[195]
Add Pb(II), co-precipitate w APDC, NAA	Hot spring and river water	<5	100–10000	-	-	82–119	-	No interference study	[196]
Buffer-conditioned Anex column for speciation-NAA	Drinking water	0.9–16	-	-	-	97.5	-	No interference study	[197]
Acid phosphatase + polyphenol oxidase entrapped in double layer hydroxide	-	0.15 follows phenyl phosphate hydrolysis, As(V) inhibits acid phosphatase	0.7–6	0.9846	6.7	-	20	Phosphate no effect; no real sample tested	[199]
Arsenite Oxidase on MWCNT modified GCeR	River water	1	0–500	0.996	2–5	101	0.17	Cu no effect	[200]

The results of some real samples compared well with an HPLC–ICP–MS method. The instrument was used for field analysis for sub- $\mu\text{g L}^{-1}$ level As samples. Later the same group used the same principles to build an automated batch mode analyzer centered around a multiport programmable syringe pump [104]. Hanrahan et al. [105] described an automated flow injection (FI) instrument for the determination of As(III) and As(V) in natural waters based on MB chemistry using KI/KIO₃ for oxidation of As(III) to As(V). The instrument utilized solenoid micropumps and valves with a charge-coupled device (CCD) spectrometer; detection limits were high and no real samples were tested.

In another publication ethyl violet was used as the cationic dye to form micro particulate ion associates with anionic molybdoarsenate; the procedure is laborious and time-consuming, and is not particularly sensitive [106]. A conventional hollow fiber membrane was used for continuous, on-line extraction and enrichment of arsenic prior to carrying out MB chemistry, but despite a 30-fold enrichment factor, the LOD was only 27 $\mu\text{g L}^{-1}$; no real application was reported [107].

2.2.2. New reagents

Reports of new colorimetric reagent for As are relatively limited. Kalluri et al. [108] reported an extremely sensitive gold nanoparticle (AuNP) based assay that relies on aggregation of the particles which can be observed visually, or more sensitively by dynamic light scattering. As(III) crosslinks AuNPs functionalized with glutathione, dithiothreitol (DTT) or cysteine. The resulting aggregation causes changes in color or light scattering properties. Wu et al. [109] reported another AuNP based assay that can be followed visually, colorimetrically or by light scattering, with LODs of 40, 0.6 and 0.8 $\mu\text{g L}^{-1}$ by the three respective observation techniques. The principle is based on the aggregation of AuNPs caused by a cationic surfactant, cetyltrimethylammonium bromide (CTAB). The method uses an aptamer that selectively binds As(III). The aptamer can also react with CTAB to form a supramolecule that is unreactive towards AuNPs. The procedure involves adding the sample and the aptamer reagent together, followed by a small aliquot of CTAB. Finally the AuNP reagent is added. If As(III) is present it binds to the aptamer which can no longer bind to CTAB. The free CTAB causes AuNPs to aggregate to form a blue color. If As(III) is not present, the aptamer forms supramolecules with CTAB, which is thus rendered unavailable.

Karayünlü and Ay [110] were able to determine total As spectrophotometrically using hexamethylene ammonium-hexamethylenedithiocarbamate as a reagent in a Triton X-100 micellar medium. Liang et al. [111] propose a label-free naked eye or spectrometric method to detect As(III) based on the different adsorption properties on Au nanoparticles between random coil G-/T-rich ssDNA and folded DNA bound to As(III).

2.2.3. Ultra violet (UV) detection after chromatographic separation

Jedynak et al. [112] used UV detection at 191 nm for speciation of As(III), As(V), MMA and DMA after HPLC separation on an anion exchanger. Several parameters were studied to optimize separation and detection; the method was applied to determine As species in highly contaminated water samples and compared with ICP-MS measurements. Given that nearly all substances absorb in the deep UV, the possibility of interference from unknown species co-eluting with one or more of these anions is high.

Jaafar et al. [113] successfully separated As(III), As(V), MMA and DMA by electrokinetic chromatography using a 3-layer sandwich coating of polybrene, dextran sulfate and polybrene, and indirect UV detection with 2,6-pyridinedicarboxylic acid as the visualizing agent. Even with electrokinetic injection resulting in 200–1500 fold enrichment, the LOD ranged from 20 to 70 $\mu\text{g L}^{-1}$; no real sample was analyzed.

Koshcheeva et al. [114] also used UV detection at 250 nm after *in situ* formation of the heteropolymolybdate from As(V), MMA and DMA, using a slightly acidic molybdate solution as the background electrolyte (BGE) in a capillary electrophoresis (CE) system. The authors advance some remarkably new chemistry: after repeated attempts when they failed to detect any signal from arsenite, they speculated that this must be because As(III) was unstable. They also incorporated perchlorate in the BGE ostensibly because perchlorate is a “well known masking agent for silicate”. The paper cited to document this remarkable statement utilizes the well-known chemistry that silicomolybdate does not form in strongly acid medium and recommends using HClO₄ as the acid of choice for this purpose; hence perchlorate is a masking agent for silicate!

Cheng et al. [115] developed a technique for As compounds based on single drop microextraction coupled in-line with CE. The extraction efficiency was improved by employing the scheme of carrier-mediated counter-transport using Aliquat 336 as carrier in organic layer as it enhances the transport of As compounds across the organic layer by forming hydrophobic complexes.

2.2.4. Harnessing properties of As species as a reductant

When As(III) is added to iodate in acidic solution, iodate is reduced to iodide, which reacts with excess iodate to form iodine. The iodine is measured, e.g., by the oxidation of leuco-malachite green to malachite green [116] or by bleaching dyes such as toluidine blue or safranin O [117] or reduce KMnO₄ to measure decreased absorbance [118].

Sharma et al. [119] report that arsenite reduces sulfanilic acid which then couples with *N*-(1-naphthyl) ethylenediamine dihydrochloride to form a purple color. The reaction is carried out with the two reagents sequentially spotted on paper and 18 μ L of the sample then applied. Quantitation is carried out by a color scanner, with the results interpreted by custom MATLAB software.

In methods that depend on As(III) acting as a reducing agent, it is not clear how attempts to measure As(V) by prereduction to As(III) will fare, as such procedures invariably utilize an excess of the reducing agent.

Boonjob et al. [120] reported a concept of novel pervaporation sequential injection analysis method for automatic non-chromatographic speciation analysis of inorganic arsenic in complex aqueous samples. The method is based on HG of arsine followed by its on-line pervaporation-based membrane separation and CCD spectrophotometric detection of bleaching of KMnO₄. The speciation of As(V) and As(III) was based on the HG of As species at different pH. The method was successfully applied to As speciation in river water samples with elevated content of dissolved organic carbon and suspended particulate matter with no prior sample pretreatment and the recoveries ranged from 98 to 104%.

3. Luminescence-based methods

3.1. Fluorescence

Reports of fluorometric As measurements are scant. Three reported approaches all use surface derivatized quantum dots (QDs). Wang et al. [121] examined the reaction of As(III) with mercaptoacetic acid (MA)-capped CdTe, MA-capped CdTe/ZnS and glutathione (GSH)-capped CdTe QDs. As(III) has affinity for the thiol groups and in particular reacts with -GSH to form As(SG)₃. The emission of the GSH-capped CdTe QDs was quenched upon adding As(III); the Stern–Volmer relationship was followed at least up to a concentration of 1900 μ g L⁻¹.

A very similar chemistry, MA-capped CdS QDs was used by Butwong et al. [122] except they first generated AsH₃, which was then reacted with the QDs. Hosseini and Nazemi [123] describe a method for As speciation by combination of preconcentration of As

(V) and spectrofluorometric determination. The As extracted with a column containing Amberlite IRA-410 anion exchange resin was treated with L-cysteine capped QDs and the fluorescence quenching of the QDs due to reduction of As(V) by L-cysteine was considered as signal relevant to As(V) concentration. As(III) was also determined after oxidation of As(III) to As(V) with H₂O₂ and measurement of total As content. The LOD was 0.75 μ g L⁻¹ and different water samples were analyzed successfully.

3.2. Liquid phase chemiluminescence (LPCL)

Chemiluminescence (CL) based methods are generally highly sensitive. Two separate LPCL methods reported As(V) detection based on luminol CL upon reaction with vanadomolybdoarsenic heteropoly acid (VMOAs-HPA), formed by As(V) and molybdate in the presence of vanadate in an acidic solution. Phosphate must first be removed, however. Rehman et al. [124] accomplished this by using the magnesium induced coprecipitation process that has been widely used to measure dissolved phosphate in seawater. A proper adaptation of this process requires that all As is first reduced to As(III) so it does not precipitate with phosphate. After the phosphate is removed, the As(III) must be oxidized back to As(V) so it can form VMOAs-HPA when vanadate and molybdate are added. A FIA configuration was used to measure the As(V); the LOD was as low as 0.15 μ g L⁻¹ but the upper limit of the linear dynamic range was only 7.5 μ g L⁻¹.

Som-aum et al. used the same formation of VMOAs-HPA but formed an ion associate by pairing this anion with the cetyltrimethylammonium cation and adsorbing the ion associate on polystyrene beads inside a well in a microfluidic device [125]. Subsequently, as alkaline luminol was flowed into the device, it reacted directly with the sorbed material in the well – the resulting CL signal was read by a photomultiplier tube (PMT) placed directly atop the transparent cover of the well. Interference from heavy metals was eliminated by adding EDTA. The LOD was 6.7 μ g L⁻¹. The authors claim that they removed phosphate selectively by passing through a small column of a weak base anion exchanger (Amberlite IRA-35, no longer commercially available). In the senior author's experience, no commercially available anion exchange resin can selectively remove phosphate and pass arsenate unaffected. Indeed, this separation is not trivial on a high efficiency chromatographic column.

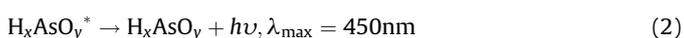
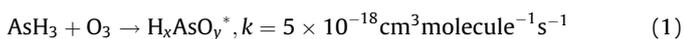
3.3. Gas phase chemiluminescence (GPCL)

Initial work on GPCL from the reaction of arsine and ozone was reported by Fujiwara et al. [126], Fraser et al. [127] independently with a followup by and Galban et al. [128]. However, these did not provide a practical field deployable analyzer; Idowu et al. were the first to report a simple fully automated inexpensive instrument for measuring aqueous inorganic As down to sub-ppb levels [129]. As(III) and As(V) could be differentiated based on different pH for AsH₃ generation. The apparatus consisted of a batch reactor with all fluid handling carried out by a syringe pump equipped with a multiport valve. The sample was either maintained at pH 4 with a citrate buffer (inorganic As(III) only measured) or made strongly acid (total inorganic As measured) with H₂SO₄ before adding NaBH₄. After a brief reaction period the evolved arsine was released from the reactor (which was further purged with air to remove it completely) to a reflective reaction chamber built directly on a PMT window and allowed to react with ozone generated by a miniature ozone generator with air feed. The LODs were 0.05 μ g L⁻¹ As at pH ~1 and 0.09 μ g L⁻¹ As(III) at pH 4–5 for a 3-mL sample requiring 4 min per assay. The authors also demonstrated a sequential approach where As(III) is first determined at pH 4.5 and then the solution was strongly acidified before

the further addition of NaBH_4 to determine the remaining As, requiring 6 min in total. There were no significant practical interferences.

Lomonte et al. [130] independently proposed the same principles of As measurement shortly after the Idowu et al. publication. Their proposed arrangement used a FI configuration, where 250 μL sample was injected into a acid stream that then merged with a NaBH_4 stream with a total liquid flow rate of 7.7 mL min^{-1} . The LOD was 0.6 $\mu\text{g L}^{-1}$. One outstanding feature of this system was the short analysis time; at the 25 $\mu\text{g L}^{-1}$ level, it required only 8 s per analysis.

The basic reaction in the $\text{AsH}_3\text{—O}_3\text{CL}$ reaction proceeds as follows:



While AsH_3 has generally been generated from aqueous As with NaBH_4 prior to the CL reaction [131–133] including a demonstration of direct As measurement in soil/dust samples [131], it is also possible to do this electrochemically [134,135].

Based on the study of 22 different cathode materials (this choice greatly affects arsine generation efficiency), a graphite cathode was chosen for electrochemical arsine generation [134]. Because AsH_3 generation efficiency distinctly differed for As(III) vs. As(V), all As was oxidized into to As(V) by NaOCl in a batch reactor prior to electrochemical reduction to AsH_3 and GPCL. The system used the anodically generated O_2 as ozone feed to increase the generated O_3 concentration enhancing the sensitivity; the LOD was 0.36 $\mu\text{g L}^{-1}$. Comparison of total As measurements in native and spiked water samples using this technique vs. ICP-MS and other GPCL techniques was further documented and showed a high correlation ($r^2 = 0.9999$) and near unity slopes.

The same authors subsequently reported a continuous flow electrochemical system where As(III) and As(V) could be differentiated – As(V) was only reduced at high current densities [135]. The cylindrical anode compartment of the electrochemical reactor was isolated from the outer concentric cathode compartment by a Nafion tube in which a hole was deliberately made and the entire anode compartment was inside the cylindrical cavity of a small volume ($\sim 115 \mu\text{L}$) cathode chamber. The evolved arsine is then quantitated by GPCL reaction with ozone; the latter again was generated from oxygen formed during electrolysis. Inorganic As (III) could be selectively determined at a current of 0.1 A while total inorganic As (both As(III) and As(V)) responded equally at an applied current at 0.85 A, without any sample treatment. For a 1 mL sample, the system provided an LOD of 0.09 $\mu\text{g L}^{-1}$ for total As ($i = 0.85 \text{ A}$) and an LOD of 0.76 $\mu\text{g L}^{-1}$ for As(III) ($i = 0.10 \text{ A}$); As(V) is obtained by difference. The basic electrochemical arsine generation technique and current-differentiated oxidation state speciation can obviously be applicable as the front end to many other arsenic measurements techniques, including atomic spectrometry.

Manual fluid dispensing was implemented to substitute the syringe pump to simplify the basic chemical reduction GPCL system to reduce its cost and weight [136]. This instrument could be incorporated in a briefcase, weighed less than 3 kg, consumed $< 25 \text{ W}$ in power with USD \$1000 in parts cost. Such an instrument is meaningful in developing counties which need such an analyzer the most. The work of Assegid et al. [133] also aimed at reducing the cost of the basic chemical reduction GPCL instrument.

The HG-GPCL technique is far less sensitive for organic As species. Nevertheless, Idowu and Dasgupta showed how the GPCL method could be used as a post column reaction detection technique [137]. They separated arsenite, arsenate, DMA, and MMA by anion exchange chromatography using carbonate-bicarbonate and NaOH eluents in a step-gradient elution mode by valve

switching eluents supplied to the input of an isocratic pump. The separated species were passed through a UV photo oxidation reactor which decomposed the organic species and converted them to inorganic As(V). Segmentation with N_2 was used to reduce dispersion. Subsequent on-line AsH_3 generation with acid and NaBH_4 and gas-liquid separation in a simple gravity based separator was used prior to GPCL detection. For a 100 μL injection volume, the LODs for all the species of interest were at the sub- $\mu\text{g L}^{-1}$ levels.

Subsequently, Xue et. al [138] claimed an improvement in the general performance of the above approach by using a much higher efficiency higher power UV photoreactor which required a lot less residence time for complete photo-oxidation of various As species to As(V). Some other parts of the system, however, must not have been as well designed, as the LODs were uniformly about an order of magnitude greater than those reported by the previous authors.

4. Other spectroscopic methods

4.1. Laser-induced breakdown spectroscopy (LIBS)

Laser-induced breakdown spectroscopy has been applied for the determination of arsenic in wastewater by Lin et al. [139]. While an analysis can be completed in seconds, the LOD is at the g L^{-1} level. The authors suggest applicability for the qualitative identification of the presence of arsenic.

4.2. Surface-enhanced Raman spectroscopy (SERS)

SERS is increasingly becoming popular for detecting a wide variety of substances adsorbed on certain surfaces that show surface plasmon activity. Nanostructures of gold, silver and copper are the most common substrates. While Raman spectroscopy itself is not especially sensitive; in favorable cases, SERS can detect a single molecule. Xu et al. [140] developed a modified mirror reaction to prepare a sensitive and reproducible Ag nanofilm substrate for the SERS measurement of arsenate and arsenite. The effect of eight common ions present in natural waters on the SERS determination of inorganic As species was studied. The possible reasons for interferences from Cl^- , Mg^{2+} and Ca^{2+} were discussed. Mulvihill et al. [141] reported that Langmuir-Blodgett assemblies of polyhedral Ag nanocrystals were highly active SERS substrates for arsenate and arsenite sensing in aqueous media with an LOD of 1 $\mu\text{g L}^{-1}$ of As. Good agreement with results from AFS for low level arsenic bearing groundwater was demonstrated.

4.3. Total reflection X-ray fluorescence spectrometry (TXRF)

TXRF has the advantages as low sample requirement, relatively low LOD and negligible matrix effect in case of diluted samples. In some laboratories, heavy metals in seawater are measured by TXRF after carrying out the Prange et al. procedure [142] that involves removing of the salt matrix by complexing trace metals with sodium dibenzylidithiocarbamate (NaDBC) followed by automated solid phase extraction (SPE) of the complexes. This complexing agent reacts only with As(III), however, so Staniszewski and Freimann [143] pre-reduced As(V) to As(III) with L-cysteine prior to carrying out the Prange et al. procedure and TXRF measurement. They validated the procedure using a near-shore certified reference seawater sample for trace metals prior to applying the method to samples from the North Sea.

TXRF was also applied for the determination of As and other trace metals at substantially higher levels than in seawater in the tailings from a gold-copper mine, after leaching the tailings with *aqua regia*. Similar measurements were made in acid mine drainage water [144]. Barros et al. [145] utilized alumina for

selective sorption of arsenic from water. While the pre-concentration factor could be 100 (attaining an LOD of $0.7 \mu\text{g L}^{-1}$), the overall procedure is very slow.

4.4. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)

McAuley and Cabaniss [146] developed an ATR-FTIR technique utilizing an oxide coated internal reflection element to measure arsenate, sulfate and selenite. IR spectroscopy is not especially sensitive; even though relative to an uncoated reflector, an iron sol-gel coating improved the LOD by nearly $\sim 500\times$ for arsenate, it was still not sufficiently sensitive LOD ($\sim 120 \mu\text{g L}^{-1}$) for water analysis.

4.5. Surface plasmon resonance (SPR) sensor

Forzani et al. [147] reported a SPR sensor to detection As in ground water with somewhat contradictory results. Using several thiol-containing organic compounds as the sensor coating, the LOD was reportedly as low as 1.5 ng L^{-1} . On the other hand in comparing results of groundwater analyses with those from GFAAS, the method showed poor precision RSD $\sim 55\%$ and the results were in poor agreement (30–40% different). Moreover despite the claimed LOD, even $4 \mu\text{g L}^{-1}$ As in a real sample could not be detected.

5. Electrochemical methods

Compared with the benchmark methods (atomic spectroscopy, ICP-MS), which all need expensive instruments, operator skill and are not particularly fieldable, electrochemical measurements (polarography, cathodic stripping voltammetry (CSV) and anodic stripping voltammetry (ASV)) [85] have no such drawbacks and can be sufficiently sensitive. Recently, Mays and Hussam [53] reviewed voltammetric methods for the determination and speciation of inorganic arsenic. The new approaches include novel media for measurement to affect speciation, development and use of boron doped diamond electrodes modified with metals, nanogold-modified electrode on carbon or carbon nanotubes, novel rotating disc and vibrating electrodes to enhance mass transfer, and modified Hg and Bi film electrodes on carbon for CSV. Below we address some developments that were not covered in the above reviews.

Lolic et al. [148] and Rupasinghe et al. [149] described similar FI systems with amperometric detection of As(III). As is reduced by NaBH_4 to AsH_3 that diffuses across a membrane in a gas diffusion cell [148] or a pervaporation cell [149] into the acceptor flow stream, KI_3 that converts the AsH_3 to As(III) [148] or dilute H_2SO_4 [149]. Interestingly Lolic et al. stated that the use of dilute H_2SO_4 as an acceptor result in no signal but note that very different potentials, 0.10 V [148] and 0.90 V [149], both vs. Ag/AgCl , were applied on the Pt working electrode. For total As measurement, Rupasinghe et al. incorporated L-Cysteine in the carrier stream while Lolic et al. reduced As(V) first offline with KI. As has already been discussed, As(III) and total As can be differentiated in a simpler fashion by varying the acidity of the HG conditions.

Xu et al. [150] investigated highly ordered platinum-nanotube array electrodes for the novel method for the oxidative determination of trace As(III). These electrodes have a highly organized structure that is fabricated by electrochemical deposition of platinum in a 3-aminopropyltrimethoxysilane-modified porous anodic alumina template. Electrochemical experiments proved that they exhibited much better performance for As(III) determination compared to glassy carbon electrodes coated with Pt nanoparticles or Pt foil electrodes. They provided better reproducibility (RSD 3.5%, $n = 50$) and lower LOD ($0.1 \mu\text{g L}^{-1}$) than the stated comparison electrodes.

Li et al. [151] used a mercaptoethylamine modified gold electrode to measure As(III) in neutral media. They reported a wide linear range of $0.2\text{--}300 \mu\text{g L}^{-1}$ and an impressive LOD of $0.02 \mu\text{g L}^{-1}$. This approach has the obvious advantage that it not only can detect the As(III) in natural water samples at original pH without having to add acid it also shows little or no interference from Cu(II).

Alves et al. [152] described a differential pulse ASV (DPASV) method for the simultaneous determination of As, Cu, Hg and Pb on a vibrating gold microwire ($25 \mu\text{m } \phi$) electrode in a medium containing 0.1 M HCl and 0.5 M NaCl , the LOD of As was $0.07 \mu\text{g L}^{-1}$ with 30 s deposition time Al, Cd, Cr, Fe, Mn, Ni, Sb and Zn did not cause any significant interference.

Ensafi et al. [153] reported using ammonium 2-amino-1-cyclopentene-1-dithiocarboxylate in ASV determination of As(III) (total As determined after prior reduction with NaHSO_3), on a Hg film electrode after first accumulating Cr(III) on the surface.

Giacomino et al. [154] evaluated the efficiency of a lateral gold electrode for the determination of As(III) with ASV. Potential waveforms (differential pulse and square wave), potential scan parameters, deposition time, deposition potential and surface cleaning procedures were examined for their effects on arsenic peak intensity and shape.

Gibbon-Walsh et al. [155] use CSV at a vibrating, gold microwire electrode to determine “reactive” As(III) after adsorptive deposition of “ $\text{As}(\text{OH})_3$ ”, followed by a potential scan to measure the reduction current from As(III) to As(0). This method worked over a wide pH (7–12) and concentration ($0.07\text{--}7500 \mu\text{g L}^{-1}$) range. As (III) could be measured first at the original pH with CSV and then total As measured after acidification to pH 1 with ASV on the same electrode. Total dissolved As was determined with ASV after UV-digestion at pH 1. Samples with high levels of Fe and Mn could be measured accurately after EDTA addition [156]. The method was field-tested in West Bengal (India) on a series of groundwater samples and results were compared with ICP-MS and HPLC. Most of the arsenic ($78 \pm 0.02\%$) was found to be inorganic As(III) in the freshly collected waters. EDTA was also found to be effective in stabilizing arsenic oxidation states for long term sample storage at room temperature. Without sample preservation, As(III) was found to oxidize rapidly to As(V) especially in air and sunlight and Fe(II) was oxidized to Fe(III), removing the As(V) by adsorption on precipitated Fe(III)-hydroxides within a few hours.

Direct electrochemical determination of As(V) at neutral pH has thus far been considered impossible, As(V) is not electroactive at this pH. Gibbon-Walsh et al. [157] demonstrated that elemental Mn on an electrode surface mediates the reduction of As(V) to As(III) in a novel two electron reduction step; the Mn is oxidized to Mn(II). Based on this finding, they first reported the electrochemical determination of As(V) in natural waters of neutral pH (including seawater) by ASV using a manganese-coated gold micro wire electrode. Total inorganic As was quantified after oxidation of As(III) to As(V) using hypochlorite.

Lan et al. [158] modified a glassy carbon electrode by casting gold-palladium (Au-Pd) nanoparticles onto its surface and then used it for the ASV determination of As(III). The LOD of $0.25 \mu\text{g L}^{-1}$ was sensitive enough for most applications but an upper linear dynamic limit of $25 \mu\text{g L}^{-1}$ may be a serious disadvantage.

Grabarczyk [159] utilized Amberlite XAD-7 resin for prior removal of surface actives substances and CSV determination of As(III). Applicability in the presence of large surfactant concentrations (1, 2 and 2 mg L^{-1}) anionic, cationic and nonionic surfactants) was demonstrated.

Rajkumar et al. [160] made a poly(taurine) nano gold film on a glassy carbon electrode (GCE) and indium tin oxide for measuring As(III) Shin and Hong [161] fabricate a platinum-iron(III) nanoparticles modified multiwalled carbon nanotube coating on a

GCE; the new electrode was examined with CV, SEM and ASV. Yusof et al. [162] prepare carbon nanotubes/amino acid modified platinum electrodes for As(III) measurement; however, performance parameters reported in this paper makes little sense.

Chen et al. [163] utilized the synergy of glutathione, dithiothreitol and *N*-acetyl-L-cysteine to make mixed self-assembled monolayers (SAMs) to enhance the specificity and sensitivity of As(III) detection in water samples. The LOD improved as a result of the immobilization of a large number of As(III) species on the gold electrode surface via As—O and As—S linkages. After accumulating As(III), ASV and linear sweep voltammetry (LSV) were used for measurement. A variety of commonly occurring ions in water samples were tested and showed no obvious interference on the As(III) determination; the method was applied for several types of water samples.

Gao et al. [164] reported a disposable platform completely free from the noble metals for electrochemical detection of As(III) in drinking water under nearly neutral condition by square wave ASV (SWASV). By combining the high adsorptivity of Fe₃O₄ microspheres toward As(III) and the advantages of room temperature ionic liquid (RTIL), the Fe₃O₄-RTIL composite modified screen-printed carbon electrode showed better electrochemical performance than commonly used noble metals.

Gu et al. [165] applied a glassy carbon electrode (GCE) modified with internal-electrolysis deposited gold nanoparticles (AuNPs_{ied}) to detect As(III) with anodic stripping linear sweep voltammetry. The AuNPs_{ied}/GCE was prepared based on the redox replacement reaction between supporting-electrolyte-free aqueous H₂AuCl₄ and a copper sheet in saturated KCl separated by a salt bridge. An appropriate high-scan-rate for ASLSV can enhance both the sensitivity and signal-to-noise ratio. Accounts of two other Au modified electrode has been published and the sub- $\mu\text{g L}^{-1}$ LOD were obtained [166,167].

Although many papers were published on the electrochemical analysis for arsenic, most are only applicable for As(III). At least in our hands, electrodes are finicky and field analysis with electrochemical analyzers without standard addition is rarely robust for real samples [168].

5.1. Potentiometry and conductometry

Khan and Baig [169] prepared and characterized a polyacrylonitrile-silica gel composite anion-exchange membrane and applied it as ion-selective membrane electrode for the determination of As(V) in spiked water samples. However, the LOD of 75 $\mu\text{g L}^{-1}$ is high and the potential interference of phosphate was simply not studied.

Although conductometry is not really an electrochemical technique (no chemistry occurs) and is nonspecific, we consider here contactless conductometric measurement of As(III) and As(V), individually, after capillary electrophoretic separation from other ions. Nguyen et al. [170] used a background electrolyte consisting of 50 mM CAPS/2 mM L-arginine (Arg) at pH 9.0 for As(III) and 45 mM acetic acid (pH \sim 3.2) for As(V). Large-volume injection was used to maximize the sensitivity. The analysis of contaminated well water samples from Vietnam was demonstrated.

6. Inductively coupled plasma-mass spectrometry (ICP-MS)

Mass spectrometry is well known for its ability to provide unambiguous qualitative identification and superb sensitivity. ICP-MS has been routinely used in many diverse research fields such as earth, environmental, life and forensic sciences and in food, material, chemical, semiconductor and nuclear industries [171]. In the case of arsenic, ICP-MS is often been hyphenated with other sample pretreatment or separation techniques for the

measurement of As. Unless introduced as the hydride, direct analysis with ICP-MS can be subject to matrix interference due to variations in ionization, as in most mass spectrometric techniques. A complicating factor for As is that it is a monoisotopic element; isotope dilution mass spectrometry is not possible. A second problem is the interference from isobaric ArCl⁺, especially in samples of high and variable chloride content (see the next subsection for more details). This is not a problem, however, if a collision cell is used to dissociate ArCl⁺. Perhaps for these reasons, in the past several years, very few studies [172,173] have been published where a liquid sample is directly introduced into an ICP-MS for As measurement. Serapinas et al. [172] utilized a procedure of standard addition of selenium as internal standard. They also developed a mathematical model of this concept. They report that if the internal standard is properly selected (ionization potential of Se and As are very close: 9.75 vs. 9.81 eV), results as good as that with standard isotope dilution methods can be obtained. Interestingly, as Se occurs commonly in various samples and its amount can vary, it cannot normally be used as a single point internal standard. As a generic concept, standard addition of the internal standard permits using elements already present in the sample as an internal standard. However, it may be important to note that the authors used a double focusing (electric and magnetic sector) instrument and comment that at least “medium mass resolution” is needed for the internal standard element for reliable integration of the peaks and low frequency noise can be a problem – averaging of the final results provided more reliable values.

Vázquez et al. [173] developed a method that they state should permit the routine determination of As and Se in fresh water and waste water using a commercially available high sensitivity instrument (Varian 810 MS) that uses a 90° reflecting ion optics system. If chloride is present in large amounts the sample must be diluted so that total dissolved solids will go below 0.2% (as judged by specific conductance). Although ArCl⁺ and As⁺ are nominally isobaric they are not exactly the same mass and this instrument has enough mass resolution to separate the two as long as the chloride concentration is not excessive.

6.1. Interference in ICP-MS

For a reliable assay of trace elements using ICP-MS, mass interferences from (poly) atomic species having the same mass/charge ratio as the analyte can be a severe problem. For arsenic, a monoisotopic element ($m/z=75$), the interference is from the overlapping of polyatomic species ⁴⁰Ar³⁵Cl⁺ (75.47%), oxide ⁵⁹Co¹⁶O (99.76%) and doubly charged ions Sm²⁺ (7.47%) and Nd²⁺ (5.63%), the parenthetical values represent the isotopic abundance of that particular species [65]. The mass resolution to separate these ions from As⁺ is 7773, 11,498, 2023, and 1929, respectively. The interference from chloride (i.e., ArCl⁺) is of the greatest concern because chloride is ubiquitous and can occur in very high concentrations in some samples. ICP-MS instruments equipped with a collision or reaction cell are available with a number of manufacturers. After the initial ion is selected, it is made to undergo collisions with small molecule weight gases (He, H₂, CH₄ and O₂ are most commonly used to deal with ArCl⁺) whence the poly atomic species breaks apart. A second quadrupole then selects the m/z corresponding to As⁺ again [65,174,175]. The reflecting ion optics system to obtain improved resolution is also effective [173].

6.2. SPE-ICP-MS

SPE techniques are particularly attractive for sample treatment (e.g. speciation) because of their simplicity, the wide variety of available sorbents, and low/no consumption of organic solvents.

Mondal et al. [176] packed a short column with a strong base form anion exchanger AG1 X8 resin in chloride form. The sample, adjusted to pH ~3 renders the very weak acid HAsO_2 (As(III)) neutral while As (V) remains ionized and hence is captured by the resin bed. The same scheme was used by Dasgupta et al. earlier [92]. Mondal et al. [176] also studied the effect of the presence of Fe(II) and/or Mn(II) in the sample; while +97% of the As(III) passed through the column and As (V) was fully retained, the total As in the effluent was greater in the presence of Fe(II) and less in the absence of Mn(II). No other performance parameters, however, were reported.

Chen et al. [177] developed a novel SPE sorbent based on carbon nanofibers (CNFs) for speciated preconcentration and separation of As(III) before ICP-MS measurement. As(III) was selectively sorbed on a CNF microcolumn when the sample was adjusted to a pH of 1–3, mixed with ammonium pyrrolidine dithiocarbamate (APDC) and passed through the column. As(V) was not retained under the same conditions. These authors also evaluated single-wall carbon nanotubes (SWNTs) as SPE sorbent instead of CNFs: the enrichment factor increased from 33 to 50 and the LOD decreased to 3.9 ng L^{-1} As(III) [178].

Issa et al. [179] combined a strong base anion exchange resin and hydrated iron oxide particles to make a hybrid resin for As speciation. At pH values ≤ 8.00 , strong base anion exchange resin retains As(V) while allowing As(III) to pass through. Between pH 5.00 and 11.00, the hydrated iron oxide retain both inorganic As(III) and As(V). These authors then incorporated another sorbent, AgCl, in their hybrid composite [180] to perform speciation of both inorganic and organic arsenic (MMA and DMA) speciation. At pH < 8.0, As(III) again passes through the composite bed; the iron oxide retains all arsenic species except for DMA, which made possible direct measurements of this species. AgCl in contrast retains inorganic As(III) and As(V), this allows organic As (notably MMA and DMA) to be measured in the effluent. Boyaci et al. [181] prepared a bifunctional silica sorbent containing both amine and thiol functionalities by modification of silica gel with 3-(triethoxysilyl) propylamine and (2-mercaptopropyl) trimethoxysilane. If functionalized with —SH alone, the sorbent only sorbed As(III) but did so quantitatively through a large pH range of 1.0–9.0 (albeit, strangely, not at pH 2.0). In contrast, NH_2 -silica selectively sorbed As(V) at pH 3.0. The bifunctional material sorbed both forms of As efficiently at pH 3.

6.3. Capillary microextraction (CME)-ICP-MS

While solid phase microextraction (SPME) utilizes a solid metal or silica fiber/rod on which a sorbent is coated/bonded, in CME the extraction device is a capillary tube with the active sorbent as a layer on its inner wall or present as a relatively porous monolith. The aqueous sample bearing the analyte is made to flow through the device; it is thus extracted and preconcentrated [182,183]. Hu et al. [182] prepare ordered mesoporous Al_2O_3 for use in CME; As (V) could be extracted with an enrichment factor of 5. LOD of As(V) and As(III) were 0.7 and 3.4 ng L^{-1} , respectively, with a throughput of 8 h^{-1} [182]. Similar to bifunctional silica discussed above, this group also prepared CME columns composed of monolithic silica gel modified by 3-mercaptopropyltrimethoxysilane (MPTS) or *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AAPT). Under pH 3, As(III) could be absorbed by MPTS modified column and As(V) in the effluent could be retained on AAPT modified column. With the aid of valve-switching, the retained As species were sequentially desorbed by $100 \mu\text{L}$ of appropriate eluents for subsequent on-line ICP-MS determination [183]. However, the reported enrichment factors and LODs in these two papers are not concordant: the first reported a LOD of 0.7 ng L^{-1} As(V) with an enrichment factor of 5 [182] while the second reported a LOD of 6.2 ng L^{-1} As(V) with an enrichment factor of 34.3 [183].

6.4. Solvent bar microextraction (SBSE)-ICP-MS

In SBSE, the extractant solvent is confined within a short length of a hollow fiber membrane (sealed at both ends) that is placed in a stirred aqueous sample solution. Tumbling of the extraction device within the sample solution facilitates extraction. Pu et al. [184] combined SBSE with electrothermal vaporization (ETV) ICP-MS for arsenic speciation. The method was based on the chelation of As (III) and ammonium pyrrolidine dithiocarbamate (APDC); the resulting As(III)-APDC complex is solvent-extractable. The extract was directly injected into ETV-ICP-MS with iridium as a chemical modifier. Any As(V) was pre-reduced to As(III) by l-cysteine and then subjected to SBSE prior to total As determination. SBSE typically provides a higher enrichment factor and makes for faster extraction kinetics compared with hollow fiber liquid phase microextraction.

6.5. HG-ICP-MS

Chandrasekaran et al. [185] used a microcolumn containing polyaniline on PTFE for on-line separation of As(III) from As(V) followed by FI-HG-ICP-MS. Polyaniline is well known for both its ion-exchange and conducting properties. At neutral pH, As(III) is in the form of H_3AsO_3 , which was not retained on polyaniline while As(V) was retained as H_2AsO_4^- and then eluted with nitric acid for measurement.

Sengupta and Dasgupta [186] reported an automated hydride generation (AHG) interface to ICP-MS as well as FI-HG-ICPMS for measuring total As in environmental samples. Using AHG-ICPMS, total arsenic was measured directly from complex environmental samples without pretreatment. The technique provided statistically indistinguishable response slopes (within about 3%) for HG-ICP-MS analysis of all major As species, As(III), DMA, MMA and inorganic As(V); thereby eliminating the sensitivity difference between the different organic and inorganic As species while measuring total As in composite samples. The FI-HG-ICP-MS technique was used for measuring both total arsenic and individual chemical species of arsenic. For speciation analysis, the flow injection mode was interfaced with a chromatographic column and a post-column photoreactor. Rice extracts were analyzed: while DMA was present, inorganic As(V) was the dominant species (75–90%). This HG-ICP-MS technique provides high analyte transport efficiency, no memory/dispersion effects, no matrix interference and improved detection limits below 100 pg As for all four major As species.

6.6. Diffusive gradients in thin films (DGT)-ICP-MS

DGT is an in situ technique incorporating diffusive and binding gels to sample and preconcentrate species from different environmental matrices. The DGT technique is convenient for obtaining time-weighted average concentrations of the analyte and generally preserves sample speciation during sampling, and can permit high preconcentration factors, which allows, e.g., HG-AAS to be used for arsenic speciation [187,188]. Österlund et al. [189] applied a previously reported ferrihydrite-backed gel for arsenate, molybdate, antimonite, vanadate and tungstate determination. Arsenate was included in the characterization to allow comparison with literature data; the LOD was 5 ng for a week-long exposure. Bennett et al. [190–192] utilized a TiO_2 -based sorbent (Metsorb) for total inorganic As determination and 3-mercaptopropyl-functionalized silica gel for As(III) determination. These methods showed good linear mass uptake over time ($r^2 > 0.998$) and have been applied for in situ deployment in streams.

6.7. HPLC/IC-ICP-MS

As different arsenic species vary considerably in their toxicity, it is often desirable to completely speciate the different forms of As present in a sample. HPLC/IC separation with ICP-MS detection represents the most popular approach to such measurements. However, the high capital and running costs and the need for experienced operators might limit the use of such instrumentation in developing countries where such analysis is most needed. Komorowicz and Barańkiewicz [57], Popp et al. [70] and Amman [59] have recently reviewed arsenic speciation in water samples with HPLC-ICP-MS and IC-ICP-MS.

6.8. Liquid–liquid microextraction (LLME)-ICP-MS

Elçi et al. [193] developed a method for inorganic As speciation with a microsample injection system coupled with ICP-MS following a validated dispersive LLME procedure. Under the optimized conditions, the analyte from only 5.0 mL water sample was concentrated by a factor of 48 with LOD reaching $0.0031 \mu\text{g L}^{-1}$ for As. While the method is sensitive, it has a rather narrow linear range ($0.0084\text{--}0.0800 \mu\text{g L}^{-1}$).

6.9. CE-ICP-MS

A CE coupled with ICP-MS was developed by Liu et al. [194] for the simultaneous determination of ten arsenic compounds including As(III), As(V), MMA, DMA, arsenobetaine, arsenocholine, 3-nitro-4-hydroxyphenylarsonic acid, o-Arsanilic acid, p-ureido-phenylarsonic acid, and 4-nitrophenylarsonic acid. The CE-ICP-MS system was hyphenated by a novel highly efficient interface which was directly used as the nebulizer. The method was successfully applied to determine various arsenicals in two certified reference materials and environmental samples.

7. Neutron activation analysis (NAA)

In NAA, target nuclides in the sample undergo bombardment by neutrons to form radioactive nuclides, which typically decay via β and/or γ emission with unique half-lives and unique energy signatures. The γ rays produced are typically detected by a multichannel γ -ray spectrometer [81]. NAA has been used for quantifying arsenic in water, herbal and soil samples collected from Bangladesh [195]. Sano et al. [196] preconcentrated As(III) by adding Pb(II) and coprecipitating with APDC; the precipitate was then analyzed with NAA. The technique was applied to the determination of arsenic in natural hot spring and river waters in Japan and was applicable from $\mu\text{g L}^{-1}$ to mg L^{-1} levels. Sanchez et al. [197] proposed an interesting speciation method that is potentially applicable in the field. A strong base type anion exchanger is conditioned by a succinic acid buffer at pH 6.5. The sample is also adjusted to the same pH using the same buffer. As(V) and DMA are captured on the column as the anions while As(III) passes through. DMA is too weakly held to be captured by a succinate form anion exchanger. The effluent containing DMA and As(III) is then passed through a strong acid type cation exchanger, also conditioned by the same buffer. DMA is captured by the column in its protonated form but As(III) passes through. Bismuth (III) is added to the effluent containing As(III) and the latter is coprecipitated as sulfide in a strongly acid medium. MMA and As(V) are sequentially eluted from the anion exchange column with an acetate buffer at pH 3.4 and 1 M HNO_3 , respectively. DMA is eluted from the cation exchanger also using 1 M HNO_3 . These solutions as well as the Bi_2S_3 containing AsS are all analyzed with NAA; with LODs of 0.9, 1.7, 1.6, 3.8, and $16 \mu\text{g L}^{-1}$ for As(III), As(V), MMA, DMA and total As, respectively, with a neutron

flux of $2.5 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ using anticoincidence counting γ -spectrometry.

Miura et al. [198] chose gold as internal standard in NAA to compensate for the difference of the neutron exposure in different irradiation capsules and thus improved the sample-to-sample repeatability. They used this approach to the determination of As in a certified reference material (CRM) containing arsenobetaine.

8. Biosensor and concentration on biomaterials

A biosensor combines a biological component with a physico-chemical detector component. Recently, Diesel et al. [58] reviewed the bacteria-based bioassays for arsenic detection in natural waters. Below we discuss three typical publications in this area.

Cosnier et al. [199] developed an amperometric biosensor based on the simultaneous entrapment of acid phosphatase and polyphenol oxidase into anionic clays (layered double hydroxides) for specific detection of As(V). The functioning principle of the bienzyme electrode consisted of the successive hydrolysis of phenyl phosphate into phenol by acid phosphatase, followed by the oxidation of phenol into o-quinone by polyphenol oxidase. The phenyl phosphate concentration was monitored at -0.2 V vs. Ag/AgCl to amperometrically measure the generated quinone. As(V) inhibits acid phosphatase activity toward the hydrolysis of phenyl phosphate into phenol and the presence of As(V) thus reduces the quinone reduction signal proportionately. The As(V) can be specifically determined in a pH 6.0 acetate buffer without any interference from As(III) or phosphate.

Male et al. [200] develop a biosensor for As(III) using arsenite oxidase, a molybdenum containing enzyme prepared from the chemolithoautotroph NT-26 that oxidizes arsenite to arsenate. The enzyme was galvanostatically deposited for 10 min at $10 \mu\text{A}$ onto the active surface of a multiwalled carbon nanotube modified glassy carbonate electrode. The resulting biosensor enabled direct electron transfer, i.e., effecting reduction and then re-oxidation of the enzyme without an artificial electron-transfer mediator. Copper, which is common in trace levels in groundwater and normally interferes in electrochemical As measurement, did not interfere. The biosensor was used for repeated analysis of spiked arsenite in tap water, river water, and a commercial mineral water.

Yang et al. [201] studied *Bacillus subtilis*, a spore forming bacterium, for preconcentrating As, both with and without pretreatment with Fe(III). *B. subtilis* takes up both inorganic As(III) and As(V). Incubating the bacteria with Fe(III) causes iron uptake (up to $\sim 0.5\%$ w/w), and some of the iron attaches to the cell membrane as hydrous ferric oxide with additional hydrous ferric oxide as a separate phase. Remarkably, 30% of the *B. subtilis* cells remain viable after treatment with 8 mM Fe(III). At pH 3, upon metalation, As(III) binding capacity becomes ~ 0 , while that for As(V) increases more than three times, offering an unusual high selectivity for As(V) against As(III). At pH 10 both arsenic forms are sorbed, the As(V) sorption capacity of the ferrated *B. subtilis* is at least 11 times higher than that of the native bacteria. At pH 8 (close to the pH of most natural waters), the arsenic binding capacity of the ferrated bacteria per mole iron is greater than that reported for any iron containing sorbent. A sensitive arsenic speciation approach is thus developed based on the binding of inorganic arsenic species by the ferrated bacteria and its unusual high selectivity toward As(V) at low pH.

9. Conclusions and future outlook

This review summarizes available review papers on arsenic and the recent literature (2005–2013) on arsenic analysis and speciation in aqueous samples. Several papers have compared available methods for arsenic speciation [82,202,203]. HPLC

separation is followed by either ICP-MS or HG-AFS. While ICP-MS is most commonly used and this is expected to continue to grow as the required instrumentation becomes more widely available. It provides reliable quantitative data for arsenic species at environmentally relevant levels in diverse matrices. HG-AFS has a sensitivity for arsenic rivaling that of ICP-MS. It has the added advantage of much lower capital and operating costs, and can be an attractive alternative to ICP-MS [80]. The latter, however, has true multi element capabilities and few buy an instrument for a single purpose only.

Since chemical speciation analysis aims to determine the nature and concentration of an element in its original state in the sample, preservation of arsenic speciation between sampling and analysis represents a major challenge. Different approaches, such as sample acidification, addition of complexing agents and oxidation inhibitors, low temperature storage, and on-site separation, have all been applied [197]. Field filtration, refrigeration and dark storage are prerequisites for stabilization of As(III)/As(V) speciation [36]. However, low concentration samples may still suffer from long time storage or long distance transportation under tropical conditions; in situ analysis might be the best choice. Accurate, low cost, fast measurement of arsenic in the field remains a technical challenge. GPCL potentially can meet these criteria.

A GPCL analyzer is simple, highly sensitive, relatively inexpensive and portable. Arsenic is converted to arsine (electro)chemically and detected via GPCL reaction with ozone. In one form, the analyzer uses anodically generated oxygen as a feed to the ozone source thus enhancing sensitivity and recycles the waste it produces. The analyzer requires only water, air, electricity (potentially provided by a rechargeable battery) and a small amount of recycled sulfuric acid that is used for maintaining an acidic pH for its operation and can detect arsenic down to sub-part per billion levels, reliably and efficiently. The philosophical value of such a concept where a chemistry based analyzer makes its own chemicals and recycles them may be pedagogically as important as the actual utility of the device.

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References

- Ahmed M F, C&EN, Periodic Table. <http://pubs.acs.org/cen/80th/arsenic.html>. (accessed 01.04.14).
- A. Basu, J. Mahata, S. Gupta, A.K. Giri, *Mutation Research* 488 (2001) 171–194.
- J. Borak, H.D. Hosgood, *Regulatory Toxicology and Pharmacology* 47 (2007) 204–212.
- B.C. Gbaruko, G.R.E.E. Ana, K.K. Nwachukwu, *African Journal of Biotechnology* 7 (2008) 4737–4742.
- C.K. Jain, I. Ali, *Water Research* 34 (2000) 4304–4312.
- S. Sambu, R. Wilson, *Toxicology and Industrial Health* 24 (2008) 217–226.
- Agency for Toxic Substances and Disease Registry, *Toxicological Profile for Arsenic*, (2007) <http://www.atsdr.cdc.gov/ToxProfiles/tp2.pdf>, (accessed 01.04.14).
- M.M. Rahman, R. Naidu, P. Bhattacharya, *Environmental Geochemistry and Health* 31 (2009) 9–21.
- N.I. Khan, G. Owens, D. Bruce, R. Naidu, *Environmental Geochemistry and Health* 31 (2009) 143–166.
- J.M. Neff, *Environmental Toxicology and Chemistry* 16 (1997) 917–927.
- R.S. Oremland, J.F. Stolz, *Science* 300 (2003) 939–944.
- B.K. Mandal, K.T. Suzuki, *Talanta* 58 (2002) 201–235.
- P.L. Smedley, D.G. Kinniburgh, *Applied Geochemistry* 17 (2002) 517–568.
- S.C. Wilson, P.V. Lockwood, P.M. Ashley, M. Tighe, *Environmental Pollution* 158 (2010) 1169–1181.
- Y.E. Yudovich, M.P. Ketris, *International Journal of Coal Geology* 61 (2005) 141–196.
- V.K. Sharma, M. Sohn, *Environment International* 35 (2009) 743–759.
- W.R. Cullen, K.J. Reimer, *Chemical Reviews* 89 (1989) 713–764.
- World Health Organization, *United Nations Synthesis Report on Arsenic in Drinking Water*, World Health Organization, Geneva, 2001 Separated chapter link at http://www.who.int/water_sanitation_health/dwq/arsenic3/en/ and full pdf filelink at <http://www.bvsde.paho.org/bvsacd/who/arsin.pdf>. (accessed 01.04.14).
- International Agency for Research on Cancer, *Some drinking-water disinfectants and contaminants, including arsenic*, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans 84 (2004) <http://monographs.iarc.fr/ENG/Monographs/vol84/volume84.pdf> (accessed 01.04.14).
- M.F. Hossain, *Agriculture, Ecosystems & Environment* 113 (2006) 1–16.
- International Groundwater Resources Assessment Center, *Arsenic in Groundwater: Probability of Occurrence of Excessive Concentrations of on Global Scale*, International Groundwater Resources Assessment Center, Utrecht, 2004 http://www.igrac.net/dynamics/modules/SF10100/view.php?fil_id=124 (accessed 01.04.14).
- United States Environmental Protection Agency (U.S. EPA), *National primary drinking water regulations*, United States Environmental Protection Agency, 2009 <http://www.epa.gov/ogwdw000/consumer/pdf/mcl.pdf>. (accessed 01.04.14).
- World Health Organization, *Guidelines for Drinking-Water Quality*, third ed., World Health Organization, Geneva, 2008 pp.188, http://www.who.int/water_sanitation_health/dwq/fulltext.pdf. (accessed 01.04.14).
- Official Journal of the European Union, *Commission Directive 1998/83/EC*, 1998. <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:1998:330:0032:0054:EN:PDF> (accessed 01.04.14).
- Ministry of Health of the People's Republic of China, *Standards for drinking water quality*. GB 5749–2006. <http://www.moh.gov.cn/public-files/business/cmsresources/zwqkzt/wsbz/new/20070628143525.pdf> (accessed 01.04.14).
- National Health and Medical Research Council. *Australian drinking water guidelines 6*, 2004. http://www.nhmrc.gov.au/_files_nhmrc/file/publications/synopses/adwg_11_06.pdf. (accessed 01.04.14).
- New Jersey Department of Environmental Protection. *Safe drinking water act regulations* (N.J.A.C. 7:10), 2004. www.state.nj.us/dep/watersupply/sdwarule.pdf. (accessed 01.04.14).
- Natural Resources Defense Council. *Arsenic and Old Laws. A scientific and public health analysis of arsenic occurrence in drinking water, its health effects, and EPA's outdated arsenic tap water standard*. <http://www.nrdc.org/water/drinking/arsenic/aoilnx.asp>. (accessed 01.04.14).
- A.A. Meharg, A. Raab, *Environmental Science & Technology* 44 (2010) 4395–4399.
- United States Environmental Protection Agency (U.S. EPA), *Monitoring arsenic in the environment: a review of science and technologies for field measurements and sensors*. http://www.epa.gov/tio/download/char/arsenic_paper.pdf. (accessed 01.04.14).
- United States Environmental Protection Agency (U.S. EPA), *Analytical methods support document for arsenic in drinkingwater*. <http://www.epa.gov/safewater/arsenic/pdfs/methods.pdf>. (accessed 01.04.14).
- H.M. Anawar, *Talanta* 88 (2012) 30–42.
- D.J. Butcher, *Applied Spectroscopy Reviews* 42 (2007) 1–22.
- P.K. Dasgupta, *Talanta* 58 (2002) 1–2.
- R.B. McCleskey, D.K. Nordstrom, A.S. Maest, *Applied Geochemistry* 19 (2004) 995–1009.
- A.R. Kumar, P. Riyazuddin, *Trends in Analytical Chemistry* 29 (2010) 1212–1223.
- R. Rubio, M.J. Ruiz-Chancho, J.F. López-Sánchez, *Trends in Analytical Chemistry* 29 (2010) 53–69.
- C.D.B. Amaral, J.A. Nóbrega, A.R.A. Nogueira, *Talanta* 115 (2013) 291–299.
- E.C.V. Butler, *Trends in Analytical Chemistry* 15 (1996) 45–52.
- L. Helsen, *Environmental Pollution* 137 (2005) 305–315.
- K.A. Hudson-Edwards, S.L. Houghton, A. Osborn, *Trends in Analytical Chemistry* 23 (2004) 745–752.
- S. Wang, C.N. Mulligan, *Environment International* 34 (2008) 867–878.
- S. McSheehy, J. Szpunar, R. Morabito, P. Quevauviller, *Trends in Analytical Chemistry* 22 (2003) 191–209.
- M.B. de la Calle, H. Emteborg, T.P.J. Linsinger, R. Montoro, J.J. Sloth, R. Rubio, M.J. Baxter, J. Feldmann, P. Vermaercke, G. Raber, *Trends in Analytical Chemistry* 30 (2011) 641–651.
- C. Niegel, F.-M. Matysik, *Analytica Chimica Acta* 657 (2010) 83–99.
- M.-L. Chen, L.-Y. Ma, X.-W. Chen, *Talanta* 125 (2014) 78–86.
- L.V. Rajaković, D.D. Marković, V.N. Rajaković-Ognjanović, D.Z. Antanasijević, *Talanta* 102 (2012) 79–87.
- L.O. Leal, L. Ferrer, R. Forteza, V. Cerdà, *Trends in Analytical Chemistry* 30 (2011) 761–770.
- C. B'Hymer, J.A. Caruso, *Journal of Chromatography A* 1045 (2004) 1–13.
- H.M. Anwar, *Talanta* 88 (2012) 30–42.
- P. Pohl, *Trends in Analytical Chemistry* 23 (2004) 87–101.
- A. Cavicchioli, M.A. La-Scalea, I.G.R. Gutz, *Electroanalysis* 16 (2004) 697–711.
- D.E. Mays, A. Hussam, *Analytica Chimica Acta* 646 (2009) 6–16.
- E. Muñoz, S. Palmero, *Talanta* 65 (2005) 613–620.
- T. Guerin, A. Astruc, M. Astruc, *Talanta* 50 (1999) 1–24.
- E. Terlecka, *Environmental Monitoring and Assessment* 107 (2005) 259–284.
- L. Komorowicz, D. Barańkiewicz, *Talanta* 84 (2011) 247–261.
- E. Diesel, M. Schreiber, J.R. van der Meer, *Analytical and Bioanalytical Chemistry* 394 (2009) 687–693.

- [59] A.A. Ammann, *American Journal of Analytical Chemistry* 2 (2011) 27–45.
- [60] B. Radke, L. Jewell, J. Namieśnik, *Critical Reviews in Analytical Chemistry* 42 (2012) 162–183.
- [61] J.H. Weber, *Trends in Analytical Chemistry* 16 (1997) 73–78.
- [62] Y. Cai, *Trends in Analytical Chemistry* 19 (2000) 62–66.
- [63] Y.-W. Chen, N. Belzile, *Analytica Chimica Acta* 671 (2010) 9–26.
- [64] D. Das, U. Gupta, A.K. Das, *Trends in Analytical Chemistry* 38 (2011) 163–171.
- [65] S. D'Illo, N. Violante, C. Majorani, F. Petrucci, *Analytica Chimica Acta* 698 (2011) 6–13.
- [66] A.R. Kumar, P. Riyazuddin, *International Journal of Environmental Analytical Chemistry* 87 (2007) 469–500.
- [67] A.R. Kumar, P. Riyazuddin, *Trends in Analytical Chemistry* 29 (2010) 166–176.
- [68] P. Pohl, B. Prusisz, *Trends in Analytical Chemistry* 23 (2004) 63–69.
- [69] P. Pohl, P. Jamroz, *Journal of Analytical Atomic Spectrometry* 26 (2011) 1317–1337.
- [70] M. Popp, S. Hann, G. Koellensperger, *Analytica Chimica Acta* 668 (2010) 114–129.
- [71] P.B. Stockwell, W.T. Corns, J. Allen, *Journal of Analytical Atomic Spectrometry* 24 (2009) 1026–1033.
- [72] J. Sardans, F. Montes, J. Peñuelas, *Spectrochimica Acta Part B* 65 (2010) 97–112.
- [73] S. Husted, D.P. Person, K.H. Laursen, T.H. Hansen, P. Pedas, M. Schiller, J.N. Hegelund, J.K. Schjoerring, *Journal of Analytical Atomic Spectrometry* 26 (2011) 52–79.
- [74] A. Gonzalez, M.L. Cervera, S. Armenta, M. de la Guardia, *Analytica Chimica Acta* 636 (2009) 129–157.
- [75] S. Karthikeyan, S. Hirata, *Analytical Letters* 36 (2003) 2355–2366.
- [76] Z. Gong, X. Lu, M. Ma, G. Watt, X.C. Le, *Talanta* 58 (2002) 77–96.
- [77] M. Burguera, J.L. Burguera, *Talanta* 44 (1997) 1581–1604.
- [78] M. Morita, J.S. Edmonds, *Pure and Applied Chemistry* 64 (1992) 575–590.
- [79] A. Taboada-de la Calzada, M.C. Villa-Lojo, E. Beceiro-González, E. Alonso-Rodríguez, D. Prada-Rodríguez, *Trends in Analytical Chemistry* 17 (1998) 167–175.
- [80] K.A. Francesconi, D. Kuehnelt, *Analyst* 129 (2004) 373–395.
- [81] D.Q. Hung, O. Nekrassova, R.G. Compton, *Talanta* 64 (2004) 269–277.
- [82] D.K. Kinniburgh, W. Kosmus, *Talanta* 58 (2002) 165–180.
- [83] D. Melamed, *Analytica Chimica Acta* 532 (2005) 1–13.
- [84] M. Leermakers, W. Baeyens, M. De Gieter, B. Smedts, C. Meert, H.C. De Bisschop, R. Morabito, P. Quevauviller, *Trends in Analytical Chemistry* 25 (2006) 1–10.
- [85] J.H.T. Luong, E. Majid, K.B. Male, *The Open Analytical Chemistry Journal* 1 (2007) 7–14.
- [86] Z.-L. Zhu, Q. Qin, *Spectroscopy and Spectral Analysis* 28 (2008) 1176–1180.
- [87] C. Yuan, X.C. Le, *Progress in Chemistry* 21 (2009) 467–473.
- [88] www.sensafe.com, (accessed 01.04.14).
- [89] www.wagtech.co.uk, (accessed 01.04.14).
- [90] <http://www.vitasalus.net/purtest-arsenic-water-test-kit-1-test-kit>, (accessed 01.04.14).
- [91] <http://www.hach.com/arsenic-low-range-test-kit/product?id=7640217303>, (accessed 01.04.14).
- [92] http://www.merckmillipore.com/food-analytics/rapid-arsenic-tests/c_Hzib.s10prlAAAEbFfcXP9oy, (accessed 01.04.14).
- [93] J.M. Spear, Y. Zhou, C.A. Cole, Y.F. Xie, *Journal American Water Works Association* 98 (2006) 97–105.
- [94] C.M. Steinmaus, C.M. George, D.A. Kalman, A.H. Smith, *Environmental Science & Technology* 40 (2006) 3362–3366.
- [95] M.M. Rahman, D. Mukherjee, M.K. Sengupta, U.K. Chowdhury, D. Lodh, B.K. Biswas, C.R. Chanda, S. Roy, M. Selim, Q. Quamruzzaman, A.H. Milton, S.M. Shahidullah, M.T. Rahman, D. Chakraborti, *Environmental Science & Technology* 36 (2002) 5385–5394.
- [96] M. Salman, M. Athar, W.U. Zaman, U. Shafique, J. Anwar, R. Rehman, S. Ameer, M. Azeem, *Analytical Methods* 4 (2012) 242–246.
- [97] A. Baghel, B. Singh, P. Pandey, K. Sekhar, *Analytical Sciences* 23 (2007) 135–137.
- [98] N.A. Yusof, K. Rashid, *Asian Journal of Chemistry* 21 (2009) 1747–1753.
- [99] D.L. Johnson, M.E.Q. Pilson, *Analytica Chimica Acta* 58 (1972) 289–299.
- [100] P.K. Dasgupta, H. Huang, G. Zhang, G. Cobb, *Talanta* 58 (2002) 153–164.
- [101] S. Tsang, F. Phu, M.M. Baum, G.A. Poskrebyshev, *Talanta* 71 (2007) 1560–1568.
- [102] S. Hu, J. Lu, C. Jing, *Journal of Environmental Sciences* 24 (2012) 1341–1346.
- [103] K. Toda, T. Ohba, M. Takaki, S. Karthikeyan, S. Hirata, P.K. Dasgupta, *Analytical Chemistry* 77 (2005) 4765–4773.
- [104] K. Toda, M. Takaki, M.A. Hashem, *Chemosphere* 72 (2008) 1517–1523.
- [105] G. Hanrahan, T.K. Fan, M. Kantor, K. Clark, S. Cardenas, D.W. Guillaume, C.S. Khachikian, *Review of Scientific Instruments* 80 (2009) 104101.
- [106] K. Morita, E. Kaneko, *Analytical Sciences* 22 (2006) 1085–1089.
- [107] K. Hylton, S. Mitra, *Analytica Chimica Acta* 607 (2008) 45–49.
- [108] J.R. Kalluri, T. Arbneshi, S.A. Khan, A. Neely, P. Candice, B. Varisli, M. Wahington, S. McAfee, B. Robinson, S. Banerjee, A.K. Singh, D. Senapati, P.C. Ray, *Angewandte Chemie International Edition* 48 (2009) 9668–9671.
- [109] Y. Wu, L. Liu, S. Zhan, F. Wang, P. Zhou, *Analyst* 137 (2012) 4171–4178.
- [110] S. Karayünlü, Ü. Ay, *Journal of Analytical Chemistry* 65 (2010) 244–249.
- [111] R.-P. Liang, Z.-X. Wang, L. Zhang, J.-D. Qiu, *Chemistry: A European Journal* 19 (2013) 5029–5033.
- [112] L. Jedynak, P. Kieroński, J. Kowalska, J. Golimowski, *Chemia Analityczna (Warsaw)* 53 (2008) 557–568.
- [113] J. Jaafar, K. Konishi, S. Terabe, T. Ikegami, N. Tanaka, *Chromatographia* 69 (2009) 1437–1441.
- [114] O.S. Koshcheeva, O.V. Shuvaeva, L.I. Kuznetzova, *Electrophoresis* 30 (2009) 1088–1093.
- [115] K. Cheng, K. Choi, J. Kim, I.H. Sung, D.S. Chung, *Microchemical Journal* 106 (2013) 220–225.
- [116] H.D. Revanasiddappa, B.P. Dayananda, T.N.K. Kumar, *Environmental Chemistry Letters* 5 (2007) 151–155.
- [117] C. Pasha, B. Narayana, *Bulletin of Environmental Contamination and Toxicology* 81 (2008) 47–51.
- [118] M. Hashemi, P. Modasser, *Talanta* 73 (2007) 166–171.
- [119] R.D. Sharma, S. Joshi, S. Amlathe, *Analytical Methods* 3 (2011) 452–456.
- [120] W. Boonjob, M. Miró, S.D. Kolev, *Talanta* 117 (2013) 8–13.
- [121] W. Wang, Y. Lv, X. Hou, *Talanta* 84 (2011) 382–386.
- [122] N. Butwong, T. Noipa, R. Burakhan, S. Srijaranai, W. Ngeontae, *Talanta* 85 (2011) 1063–1069.
- [123] M.S. Hosseini, S. Nazemi, *Analyst* 138 (2013) 5769–5776.
- [124] A.U. Rehman, M. Yaqoob, A. Waseem, A. Nabi, *International Journal of Environmental Analytical Chemistry* 88 (2008) 603–612.
- [125] W. Som-aum, H. Li, J. Liu, J.-M. Lin, *Analyst* 133 (2008) 1169–1175.
- [126] K. Fujiwara, Y. Watanabe, K. Fuwa, J.D. Winefordner, *Analytical Chemistry* 54 (1982) 125–128.
- [127] M.E. Fraser, D.H. Stedman, M.J. Henderson, *Analytical Chemistry* 54 (1982) 1200–1201.
- [128] J. Galban, J. Vela, M.T. Martinez Soria, M. Aured, J.R. Castillo, *Applied Spectroscopy* 49 (1995) 785–790.
- [129] A.D. Idowu, P.K. Dasgupta, G. Zhang, K. Toda, J.R. Garbarino, *Analytical Chemistry* (2014) 78.
- [130] C. Lomonte, M. Currell, R.J.S. Morrison, I.D. McKelvie, S.D. Kolev, *Analytica Chimica Acta* 583 (2007) 72–77.
- [131] M.F. Sawalha, M.K. Sengupta, S. Ohira, A.D. Idowu, T.E. Gill, L. Rojo, M. Barnes, P.K. Dasgupta, *Talanta* 77 (2008) 372–379.
- [132] M.A. Hashem, T. Jodal, S.I. Ohira, K. Wakuda, K. Toda, *Analytical Sciences* 27 (2011) 733–738.
- [133] K. Assegid, F. Ahmed, S. Ahamed, A. Hussam, *Analytical Methods* 3 (2011) 2921–2928.
- [134] M.K. Sengupta, M.F. Sawalha, S.I. Ohira, A.D. Idowu, P.K. Dasgupta, *Analytical Chemistry* 82 (2010) 3467–3473.
- [135] M.K. Sengupta, P.K. Dasgupta, *Analytical Chemistry* 83 (2011) 9378–9383.
- [136] M.K. Sengupta, Z.A. Hossain, S.-I. Ohira, P.K. Dasgupta, *Environmental Pollution* 158 (2010) 252–257.
- [137] A.D. Idowu, P.K. Dasgupta, *Analytical Chemistry* 79 (2007) 9197–9204.
- [138] J. Xue, Z. Zhu, S. Zhang, X. Zhang, *Luminescence* 24 (2009) 290–294.
- [139] Z.-X. Lin, L. Chang, J. Li, L.-M. Liu, *Spectroscopy and Spectral Analysis* 29 (2009) 1675–1677.
- [140] Z. Xu, J. Hao, F. Li, X. Meng, *Journal of Colloid and Interface Science* 347 (2010) 90–95.
- [141] M. Mulvihill, A. Tao, K. Benjauthrit, J. Arnold, P. Yang, *Angewandte Chemie International Edition* 47 (2008) 6456–6460.
- [142] A. Prange, A. Knöchel, W. Michelis, *Analytica Chimica Acta* 172 (1985) 79–100.
- [143] B. Staniszewski, P. Freimann, *Spectrochimica Acta Part B* 63 (2008) 1333–1337.
- [144] R. Juvonen, A. Parviainen, K. Loukola-Ruskeeniemi, *Geochemistry: Exploration, Environment, Analysis* 9 (2009) 173–178.
- [145] H. Barros, L.-M.M. Parra, L. Bennun, E.D. Greaves, *Spectrochimica Acta Part B* 65 (2010) 489–492.
- [146] B. McAuley, S.E. Cabaniss, *Analytica Chimica Acta* 581 (2007) 309–317.
- [147] E.S. Forzani, K. Foley, P. Westerhoff, N. Tao, *Sensors and Actuators B* 123 (2007) 82–88.
- [148] A. Lolic, S. Nikolic, J. Mutic, *Analytical Sciences* 24 (2008) 877–880.
- [149] T.W.T. Rupasinghe, T.C. Cardwell, R.W. Cattral, S.D. Kolev, *Analytica Chimica Acta* 652 (2009) 266–271.
- [150] H. Xu, L. Zeng, S. Xing, G. Shi, J. Chen, Y. Xian, L. Jin, *Electrochemistry Communications* 10 (2008) 1893–1896.
- [151] D. Li, J. Li, X. Jia, Y. Han, E. Wang, *Analytica Chimica Acta* 733 (2012) 23–27.
- [152] G.M.S. Alves, J.M.C.S. Magalhães, P. Salaün, C.M.G. van den Berg, H.M.V.M. Soares, *Analytica Chimica Acta* 703 (2011) 1–7.
- [153] A.A. Ensafi, A.C. Ring, I. Fritsch, *Electroanalysis* 22 (2010) 1175–1185.
- [154] A. Giacomino, O. Abollino, M. Lazzara, M. Malandrino, E. Mentasti, *Talanta* 83 (2011) 1428–1435.
- [155] K. Gibbon-Walsh, P. Salaün, C.M.G. van den Berg, *Analytica Chimica Acta* 662 (2010) 1–8.
- [156] K. Gibbon-Walsh, P. Salaün, M.K. Uroic, J. Feldmann, J.M. McArthur, C.M.G. van den Berg, *Talanta* 85 (2011) 1404–1411.
- [157] K. Gibbon-Walsh, P. Salaün, C.M.G. van den Berg, *Analytica Chimica Acta* 710 (2012) 50–57.
- [158] Y. Lan, H. Luo, X. Ren, Y. Wang, Y. Liu, *Microchimica Acta* 178 (2012) 153–161.
- [159] M. Grabarczyk, *Electroanalysis* 22 (2010) 2017–2023.
- [160] M. Rajkumar, S.-C. Chiou, S.-M. Chen, S. Thiagarajan, *International Journal of Electrochemical Science* 6 (2011) 3789–3800.
- [161] S.-H. Shin, H.-G. Hong, *Bulletin: Korean Chemical Society* 31 (2010) 3077–3083.
- [162] N.A. Yusof, N. Daud, T.W. Tee, A.H. Abdullah, *International Journal of Electrochemical Science* 6 (2011) 2385–2397.
- [163] L. Chen, N. Zhou, J. Li, Z. Chen, C. Liao, J. Chen, *Analyst* 136 (2011) 4526–4532.

- [164] C. Gao, Y.-Y. Yu, S.-Q. Xiong, J.-H. Liu, X.-J. Huang, *Analytical Chemistry* 85 (2013) 2673–2680.
- [165] T. Gu, L. Bu, Z. Huang, Y. Liu, Z. Tang, Y. Liu, S. Huang, Q. Xie, S. Yao, X. Tu, X. Luo, S. Luo, *Electrochemistry Communications* 33 (2013) 43–46.
- [166] S.S. Hassan, Sirajuddin, A.R. Solangi, T.G. Kazi, M.S. Kalhor, Y. Junejo, Z.A. Tagar, N.H. Kalwar, *Journal of Electroanalytical Chemistry* 682 (2012) 77–82.
- [167] J.-F. Huang, H.-H. Chen, *Talanta* 116 (2013) 852–859.
- [168] H. Huang, P.K. Dasgupta, *Analytica Chimica Acta* 380 (1999) 27–37.
- [169] A.A. Khan, U. Baig, *Desalination* 289 (2012) 21–26.
- [170] H.T.A. Nguyen, P. Kubán, V.H. Pham, P.C. Hauser, *Electrophoresis* 28 (2007) 3500–3506.
- [171] A.A. Ammann, *Journal of Mass Spectrometry* 42 (2007) 419–427.
- [172] P. Serapinas, G. Labarraque, P. Charlet, Ž. Ežerinskis, V. Juzikienė, *Journal of Analytical Atomic Spectrometry* 25 (2010) 624–630.
- [173] E. Á. Vázquez, R.B. Deaño, M.T. Rodríguez, A.J.F. Espinosa, *International Journal of Environmental Analytical Chemistry* 91 (2011) 462–472.
- [174] M. Colon, M. Hidalgo, M. Iglesias, *Journal of Analytical Atomic Spectrometry* 24 (2009) 518–521.
- [175] M. Colon, M. Hidalgo, M. Iglesias, *Talanta* 85 (2011) 1941–1947.
- [176] P. Mondal, C. Balomajumder, B. Mohanty, *Clean* 35 (2007) 255–260.
- [177] S. Chen, X. Zhan, D. Lu, C. Liu, L. Zhu, *Analytica Chimica Acta* 634 (2009) 192–196.
- [178] L. Zhu, S. Chen, D. Lu, X. Cheng, *Atomic Spectrometry* 30 (2009) 218–222.
- [179] N.B. Issa, V.N. Rajaković-Ognjanović, B.M. Jovanović, L.V. Rajaković, *Analytica Chimica Acta* 673 (2010) 185–193.
- [180] N.B. Issa, V.N. Rajaković-Ognjanović, A.D. Marinković, L.V. Rajaković, *Analytica Chimica Acta* 706 (2011) 191–198.
- [181] E. Boyacı, A. Çağır, T. Shahwan, A.E. Eroğlu, *Talanta* 85 (2011) 1517–1525.
- [182] W. Hu, F. Zheng, B. Hu, *Journal of Hazardous Materials* 151 (2008) 58–64.
- [183] F. Zheng, B. Hu, *Journal of Analytical Atomic Spectrometry* 24 (2009) 1051–1061.
- [184] X. Pu, B. Chen, B. Hu, *Spectrochimica Acta Part B* 64 (2009) 679–684.
- [185] K. Chandrasekaran, M.V. BalaramaKrishna, D. Karunasagar, *Journal of Analytical Atomic Spectrometry* 25 (2010) 1348–1353.
- [186] M.K. Sengupta, P.K. Dasgupta, *Analytical Chemistry* 81 (2009) 9737–9743.
- [187] J.G. Panther, K.P. Stillwell, K.J. Powell, A.J. Downard, *Analytica Chimica Acta* 622 (2008) 133–142.
- [188] J.G. Panther, K.P. Stillwell, K.J. Powell, A.J. Downard, *Analytical Chemistry* 80 (2008) 9806–9811.
- [189] H. Österlund, S. Chlot, M. Faarinen, A. Widerlund, I. Rodushkin, J. Ingri, D.C. Baxter, *Analytica Chimica Acta* 682 (2010) 59–65.
- [190] W.W. Bennett, P.R. Teasdale, J.G. Panther, D.T. Welsh, D.F. Jolley, *Analytical Chemistry* 82 (2010) 7401–7407.
- [191] W.W. Bennett, P.R. Teasdale, J.G. Panther, D.T. Welsh, D.F. Jolley, *Analytical Chemistry* 83 (2011) 8293–8299.
- [192] W.W. Bennett, P.R. Teasdale, D.T. Welsh, J.G. Panther, R.R. Stewart, H.L. Price, D.F. Jolley, *Environmental Chemistry* 9 (2012) 31–40.
- [193] L. Elçi, A. Elçi, T.A. Berg, J.F. Tyson, *International Journal of Environmental Analytical Chemistry* 93 (2013) 1065–1073.
- [194] L. Liu, B. He, Z. Yun, J. Sun, G. Jiang, *Journal of Chromatography A* 1304 (2013) 227–233.
- [195] M.T. Islam, S.A. Islam, S.A. Latif, *Bulletin of Environmental Contamination and Toxicology* 79 (2007) 327–330.
- [196] J. Sano, Y. Kikawada, T. Oi, *Journal of Radioanalytical and Nuclear Chemistry* 278 (2008) 111–116.
- [197] W.M. Sanchez, B. Zwicker, A. Chatt, *Journal of Radioanalytical and Nuclear Chemistry* 282 (2009) 133–138.
- [198] T. Miura, K. Chiba, T. Kuroiwa, T. Narukawa, A. Hioki, H. Matsue, *Talanta* 82 (2010) 1143–1148.
- [199] S. Cosnier, C. Mousty, X. Cui, X. Yang, S. Dong, *Analytical Chemistry* 78 (2006) 4985–4989.
- [200] K.B. Male, S. Hrapovic, J.M. Santini, J.H.T. Luong, *Analytical Chemistry* 79 (2007) 7831–7837.
- [201] T. Yang, M.-L. Chen, L.-H. Liu, J.-H. Wang, P.K. Dasgupta, *Environmental Science and Technology* 46 (2012) 2251–2256.
- [202] K.F. Akter, Z.Z. Chen, L. Smith, D. Davey, R. Naidu, *Talanta* 68 (2005) 406–415.
- [203] B. Planer-Friedrich, D. Wallschläger, *Environmental Science and Technology* 43 (2009) 5007–5013.