Chapter 5

Sampling and analysis for monitoring arsenic in drinking water

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5.1 INTRODUCTION

Monitoring of water supplies for arsenic and associated parameters may be required for the purposes of (i) checking compliance with relevant regulations; (ii) designing locally-relevant treatment systems; (iii) checking the efficacy of treatment systems; and (iv) for better understanding of the natural and man-made controls on arsenic concentrations in a water supply. The data requirements for each of these purposes may be very different and therefore so may the nature of the associated sampling and analytical protocols that are required to be put in place to enable the monitoring data requirements to be met. Determining the most appropriate sampling and analysis protocols therefore requires an awareness of the data requirements. These protocols collectively involve (i) sampling strategy; (ii) sampling and preservation protocol; (iii) selection of analytical instrumentation; (iv) analytical and data reduction protocols; (v) total quality management protocols, including for chain-of-custody, documentation and, where appropriate, training. This chapter considers each of these in turn. See also Polya *et al*. (2017) for a relevant case-study.

There is an extensive literature available on methods for the sampling and analysis of water for a wide range of analytes, including arsenic. These include: BS1427:2009 (BSI, 2008) and APHA/AWWA/WEF (1999) amongst others. In this chapter, we focus on the principles of sampling and analytical protocols with a view to informing the professional: (i) in their choice, if there is one, of which protocols to follow, or – (ii) if the protocol selected is a matter not of choice but instead is determined by local or national regulation

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or guidelines and/or by resource or logistical constraints, then information to aid the assessment of the accuracy and precision of analysis and of the representativeness of the samples being obtained.

5.2 DATA REQUIREMENTS

5.2.1 Overall aims of monitoring

Project data requirements are informed by the types of questions required to be answered (Table 5.1). For example, assessing the seasonal controls on arsenic concentration in drinking water or the long-term effectiveness of arsenic removal treatment technologies requires sampling over a period of time, whilst assessing the homogeneity with respect to arsenic of a groundwater drinking source may require sampling of wells screened at various depths and spread over a particular area. The sampling density, both in temporal and spatial dimensions, depends in part on the variability of the water being sampling and on the pre-determined levels of confidence required for any decision made on the basis of the data obtained. Since often such variability is not known in advance of sampling and analysis, sampling design may need to rely on expert judgement, conditional design protocols or be iteratively updated.

Table 5.1 Typical questions informing data requirements for arsenic-in-water sampling and monitoring.

Does the arsenic concentration in the drinking water exceed a regulatory value?
Is the arsenic concentration significantly higher than background values?
Is the arsenic concentration likely to lead to an unacceptable health risk?
Is arsenic concentration too high for recommended operational limits of a treatment technology?
Has the arsenic concentration changed significantly (i) since last year? (ii) since last week? (iii) since a new treatment technology was put in place?
Is the effectiveness of arsenic by a water treatment technology degrading with time?
Does the arsenic concentration change on a cyclic (e.g. seasonal, diurnal) basis?
Are arsenic concentrations consistent with a particular biogeochemical hypothesis?

5.2.2 Representativeness

Sampling and monitoring protocols need to ensure that a sample is sufficiently representative of the water supply being investigated. In particular, the protocols should be designed to ensure that all of the following are considered if required: (i) differences between dissolved aqueous species, colloidal species, arsenic associated with suspended particulates; (ii) unrepresentative first-taken samples e.g. waters lying in pipes or boreholes; (iii) preservation/contamination during sampling; (iv) preservation/contamination during storage prior to analysis; (v) seasonal, diurnal, other cyclic changes and secular and other non-cyclic changes in composition on various timescales.

5.2.2.1 Speciation

In drinking waters, arsenic may occur (i) as various dissolved species; (ii) in colloids; (iii) or associated with suspended particulates. The most common dissolved forms are inorganic arsenic species; as As(III) these forms are typically charge-neutral at acidic, neutral and slightly alkaline pHs; as As(V) these forms are typically negatively charged for all but extremely acidic waters (Figure 5.1). Arsenic may also occur, in waters with high nutrient loadings and hence high levels of biological activity, or in waters contaminated

by pesticides or herbicides, as various methylated forms (Bednar *et al.* 2002; Wallschlager & London, 2008). Even where the concentrations of methylated forms are low, determination of these species may be important to inform understanding of biogeochemical processes in which they act as intermediary species (Maguffin *et al.* 2015). In alkaline waters where there is sufficiently high dissolved sulphide, arsenic may also occur predominately as thioarsenates or thioarsenites – recognition of these species may be important because they are often not preserved well by commonly used sampling and preservation protocols, notably acidification, and this may lead to underestimation of total arsenic in such waters (Planer-Friedrich *et al.* 2007; Suess *et al.* 2011). Colloidal arsenic concentrations are generally low except in waters that are high in organics and/or iron – peat-land derived waters are a notable example (Rothwell *et al.* 2007). A significant fraction of arsenic may also be associated with suspended particulates, especially when the loading of such particulates is high – environments where this may be significant include areas of high physical weathering, resulting from climate and/or anthropogenic activities, such as mining (Schafer & Blanc, 2007) – in most waters, however, the difference between total arsenic and total dissolved arsenic is relatively small.

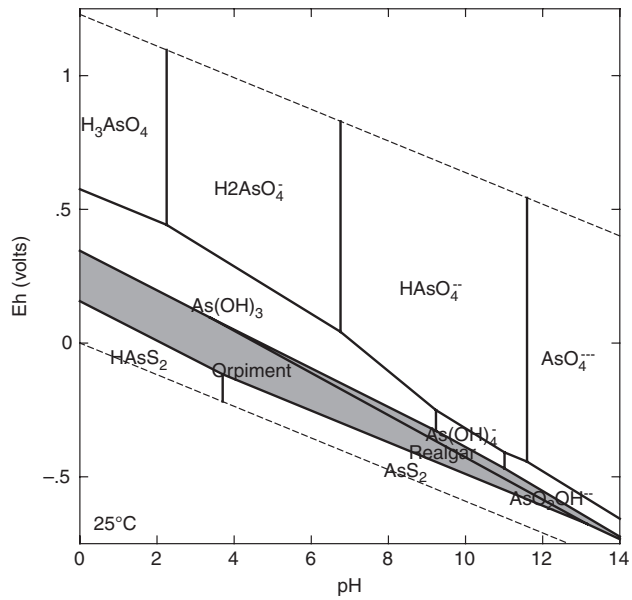

Figure 5.1 Eh vs pH arsenic species predominance diagram at 25°C/1 bar showing the predominance fields of As(V) and As(III) species and the stability fields for the arsenic sulphide minerals, orpiment and realgar. $\sum As = 10^{-6}$ molal; $\sum S = 10^{-4}$ molal. Calculated using Geochemists Workbench® Professional Version 11.0.2.

5.2.2.2 Spatial and temporal variations

The first water samples taken from taps, pipes or boreholes may not be representative of the bulk water supplied for a variety of reasons including: (i) in boreholes, particularly those with iron-based casings, the water standing in the borehole itself may be considerably different from that in the aquifer, especially with regard to components and chemical species whose concentrations depend upon the state of oxygenation of the water; (ii) in piped systems that have not recently been used, turning on a tap may result in flakes of deposits built up on the interior of the pipe to be flushed out upon initial sampling.

Similarly, in surface waters, the bulk composition of the river, pond or lake, may be significantly different from that at the boundaries of the water body – notably the surface layer, the bottom or even near the sides of the water body.

Irrespective of these issues, representative samples need to be collected recognising possible or likely cyclic, irregular or secular changes in arsenic concentration as well as spatial variations in concentration. Seasonal variations in arsenic concentrations in lakes and rivers (McLaren & Kim, 1995; Masson *et al.* 2006) are well known, and have also been observed in shallow groundwater systems (Polizzotto *et al.* 2008). Diurnal cycles of arsenic concentrations have been noted in geothermal waters (Farnfield *et al.* 2012; Ullrich *et al.* 2013), upland catchments in the UK (Rowland *et al.* 2011) and rivers draining mining areas (Barringer *et al.* 2008). In eutrophic lakes, seasonally dependent redox processes can also lead to abrupt discontinuities in the spatial distribution of arsenic concentrations (e.g. Kuhn & Sigg, 1993).

5.2.2.3 Contamination during sampling

Contamination of surface water samples may arise from the process of sampling itself – for example by an operator who has entered a water body upstream of the sampling point or who has disturbed fine-grained sediments or deposits at the bottom of a shallow river or pond. Contamination may also arise from inadequately washed or chosen sampling equipment, *in situ* measuring equipment or other equipment.

5.2.2.4 Preservation

Any removal of water samples from their ambient environment may create the potential for homogeneous reactions changing solute speciation, including that of arsenic, and heterogeneous reactions, such as degassing of CO_2 (g) or precipitation of Fe-O-H or Fe-S phases, all of which may result – if adequate steps are not taken – in subsequent analyses under-representing arsenic solute concentrations. Preservation steps required may vary from water-type to water-type – for example, high bicarbonate groundwaters may typically require larger amounts of added acid to achieve a target pH of less than 2, and where high bicarbonate concentrations are anticipated (or even if they are not) prudent practice would be to test, on representative disposal samples, whether or not the target pH for preservation is achieved by the protocol utilised and to amend the protocol accordingly.

5.2.3 Data & data quality objectives (DQOs)

Data and data quality objectives (DQOs) include field site related parameters, a list of analytes (including arsenic) to be determined and chemical measurement performance characteristics. These should be informed by the relevant project aims.

5.2.3.1 Field site related parameters

A site conceptual model may be helpful in determining relevant field site related parameters (Yeskis & Zavala, 2002). For example, the nature and connectivity of surface and sub-surface water bodies, land use and its distribution, distribution of anthropogenic and other inputs, climatic and other geographic controls, including river stage, rainfall, humidity and temperature – may all be relevant parameters to a useful site specific conceptual model.

5.2.3.2 Analytes

In addition to arsenic, other analytes may be required to be determined for a project. Over and above those that might be required, for example, by regulatory or contractual drivers, some of the example analytes

below may be of utility in better understanding sources and controls on arsenic concentrations in source waters, for quality assurance or for assessing risk:

(i) Arsenic speciation, notably of inorganic As(III) and As(V), and – where contamination of a water supply is suspected, of methylated arsenicals, monomethylarsenic(III) and monomethylarsonic(V) acids, dimethylarsenic(III) and dimethylarsenonic ~ (V) acids, TMAO; and in reduced high sulphur waters, thioarsenites and thioarsenates
(ii) Fe, Mn, Al, PO_4, DOC, HCO_3, CO_3, pH, Eh, dissolved oxygen, turbidity, suspended solids – are all parameters that may influence the mobility/solubility of arsenic in water or the efficacy of preservation methods or the suitability of various remediation technologies aimed at removing arsenic to below regulatory or other standards
(iii) Na, K, Ca, Mg, HCO_3, Cl, SO_4 – are parameters that collectively typically account for most of the ions in natural waters and accordingly analysis of which can be collectively used to obtain a charge balance, which may in turn be used for quality assurance purposes; additionally measurement of electrical conductivity may be helpful in this regard
(iv) Thermally tolerant coliforms, E. coli or other microbiological parameters – particularly where the purpose of a project is to calculate overall water supply associated health risks

5.2.3.3 DQOs – required chemical measurement performance characteristics

It is important to have an awareness of the specifications required of a meaningful chemical analysis – this is irrespective of whether the analysis is carried out in-house or by an external sub-contractor. Awareness of these Data Quality Objectives (DQOs), both the parameters and their target values, for the relevant project can be of critical value in informing the selection of appropriate analytical instrumentation and methods, and may also contribute to more cost-effective analyses being procured. Table 5.2 lists commonly used chemical measurement performance characteristics and typical values that might be required in a routine monitoring of drinking water supplies. It is worth emphasising, however, that the actual values required for a given monitoring project should depend upon the project aims and consequent data requirements.

The values of precision (Table 5.2) are commonly achieved in routine analysis of arsenic in drinking water, although it is worth noting that the analytical precision is generally dependent upon concentration, particularly for low concentrations below or just above the method detection limit. The difference in typical values for repeatability and reproducibility reflects that replicate analysis of the samples on the same day, by the same operator by the same method generally reveals a better (i.e. numerically smaller) precision than replicate analysis involving different methods and laboratories and so may, on its own, give an overestimation of the quality of a chemical analysis.

Use of long-term LODs can help to provide a more robust approach in addition to long-term QC charts to define instrumental trends in performance characteristics. Laboratory proficiency testing schemes (e.g. Aquacheck) provide another level of defining analytical precision and accuracy for a variety of matrices (e.g. clean, waste water) through scoring against a true ‘spike’ value and in a blind comparison with other peer laboratories. Proficiency schemes can provide an additional layer of confidence in the precision and accuracy of analyses.

The typical values for maximum total dissolved solids (TDS) in a sample are based on the lower limit of unacceptable tasting drinking water (WHO, 1996), although under some circumstances analysis at higher concentrations might be required.

Table 5.2 List of commonly used chemical measurement performance characteristics and typical values that might be required for routine monitoring of a drinking water supply. See glossary for definitions.

Parameter	Explanation	Typical Values
Detection limit (DL)	The minimum concentration at which the presence of an analyte can be determined to a specified degree of confidence	0.05 μg/L (99%)
Limit of quantification (LOQ)	The minimum concentration at which the concentration of an analyte can be quantified to a specified degree of confidence	0.10 μg/L (99.5%)
Precision – repeatability	The dispersion of repeat measurements of an analyte in a sample by the same method and by the same operator on the same day.	±1% @ 10 μg/L
Precision – reproducibility	The dispersion of repeat measurements of an analyte in a sample by different methods and different laboratories/operators.	±2% @ 10 μg/L
Accuracy/Bias	The difference between a measured concentration of an analyte and the true concentration	<5%
Concentration range	The range between the expected minimum and maximum concentrations of the analyte in a set of samples	0.1–1000 μg/L
Matrix & impacts on sensitivity & selectivity	The matrix refers to chemicals present in a sample other than the analyte – these may include H_2O as the solvent, major ions such as HCO_3^-, CO_3^-, Cl^-, SO_4^-, Ca^{++}, Mg^{++}, Na^+ and K^+ or other chemical moieties.	1200 μg/L
	Sensitivity refers to instrumental response for a given concentration of an analyte	<10%
	Selectivity refers to a uniqueness of an instrumental response to a particular analyte.	<10%

5.3 SAMPLING STRATEGIES/DESIGN

In many, indeed in perhaps most applications, the purpose of analysing drinking water samples for arsenic requires that the samples obtained are representative of some suitably defined water body – whether that be groundwater, surface water, water in specific stage of a treatment plant, water in a supply pipe or water at the point of use. Although its importance is often overlooked, good sampling is often critical to obtaining meaningful chemical analyses – conversely poor, unrepresentative sampling can, under some circumstances, render even the most accurate and precise analyses next to useless or potentially highly misleading.

"Good" sampling is defined by Gy (1995) as sampling that results in unbiased samples representative of a batch of material that cannot "be submitted to analysis in totality" and further requires that such sampling is "probabilistic", meaning that "all the constitutive elements of a batch [of, say, a water body, for example] [have] a [known] non-zero probability of being selected to make up a sample". In contrast "poor" sampling, often the result of a strategy to obtain samples from the most accessible points in the cheapest manner possible, is non-probabilistic and consequently non-representative and associated with (sometimes

high) sampling errors with non-zero means. Gy (1995) further describes sampling as "the most dangerous quality destroyer" – its importance should not be underestimated. USGS (2006) states "field personnel must take steps to ensure that … samples collected will be representative of the aqueous system being investigated. [Representative samples are] delineated by the objectives and scope of the study."

Geostatistics may be of utility in identifying deficiencies in sampling regimes as well as indicating the scale of spatial hetereogeneity (de Gruiter, 2006; Webster & Lark, 2013). Temporal heterogeneities should also be addressed, as appropriate, in designing a sampling strategy. Good sample design will accordingly take into account possible regular diurnal, weekly or seasonal variations and more irregular variations due to precipitation events and anthropogenic events, such as discharges of effluent (Gault *et al.* 2003).

5.4 SAMPLING/PRESERVATION PROTOCOLS

Suitable sampling and preservation of water samples are required to ensure that samples are neither unacceptably contaminated nor unacceptably altered prior to analysis.

Guidance on suitable sampling protocols are provided by, amongst others, USGS (2006) and Johnson (2008), and should include consideration of contamination of water samples by (i) operators; (ii) sampling media or reagents; (iii) non-target waters; (iv) the atmosphere. Operator contamination may be reduced by clean handling techniques and ensuring that the operator and/or associated measuring devices are downstream of the sample being collected. Washing out pre-cleaned sampling media with the water to be sampled is a widely used protocol, whilst the use of field blanks is essential to check whether or not sampling devices and or storage vessels contribute to sample contamination. For surface water sampling, samples should not be taken close to effluent discharge, transport infrastructure, water surface or turbid basal flow zones (unless that is the target sample to be taken). The use of flow cells are extremely useful in (i) ensuring that measuring devices do not contaminate the collected sample; (ii) permitting parameters such as pH, Eh, electrical conductivity and/or D.O. to be monitored to aid the collection of uncontaminated samples; and (iii) where oxygen poor waters are being sampled, aiding the preservation of redox sensitive analytes, including arsenic, during sample storage.

Preservation issues include: (i) precipitation of (hydrated) oxides or iron and other transition metals; (ii) microbiological activity; (iii) abiotic oxidation of As(III); and (iv) UV-induced photo-oxidation (Polya *et al.* 2003). Effective preservation protocols are designed to address these issues and notably variably include: (i) filtering through 0.45 μm (or smaller pore diameter, e.g. 0.10 μm) cellulose nitrate filters, if appropriate after the use of a 1 or 2 μm pre-filter; (ii) acidification to a target pH of around 2 with AnalaR or equivalent grade hydrochloric acid; (iii) storage in a refrigerator (but not a freezer under some circumstances); and (iv) storage in the dark. Addition of a bacteriocide (Scudlark & Johnson, 1982) or additions of complexing agent such as EDTA (Gallagher *et al.* 2000) have also been used to preserve arsenic or arsenic speciation. Ultimately, these techniques may not be 100% effective in preserving analytes, so an important further protocol to maximise sample preservation is to analyse collected samples as promptly as possible. Further discussion of preservation techniques may be found in APHA/AWWA/WEF (1999), Polya *et al.* (2003), Gault *et al.* (2005), USGS (2006) and Johnson *et al.* (2008) amongst others.

5.5 ANALYTICAL METHODS

Total arsenic and arsenic speciation (Francesconi & Keunhelt, 2004) are routinely measured by a variety of methods, involving a variety of analytical techniques involving ICP-MS, ICP-AES, HG-AAS or field based separations and techniques, and a variety of data reduction protocols.

The criteria for selecting the most appropriate methods include both logistical and technical criteria. Logistical criteria include convenience, availability, turnaround time, cost and documentation/reporting

standards. Technical criteria include precision, accuracy, detection limits, limits of quantification, sensitivity, selectivity and traceability. The relative weighting given to each of these criteria will depend upon project constraints and the purpose of the analyses.

Notwithstanding the relative technical merits of various methods, analyses undertaken as part of project to test/demonstrate regulatory compliance (WHO, 2011a; WHO, 2011b) or as otherwise contractually required may be required to be performed by certain approved methods (cf. APHE/AWWA/WEF, 1999) or under methods validated under an appropriate national accreditation body.

5.5.1 Analytical instrumentation

5.5.1.1 Total arsenic

Total arsenic may be determined in waters using a wide variety of instruments, with ICP-MS, ICP-AES, HG-AAS amongst the most widely used. The main consideration for the selection of the methodology besides available resources, must consider the sensitivity and ability to measure arsenic at concentrations below guideline concentrations and ability to provide accurate analyses despite the presence of matrix components that may inhibit analytical performance. An alternative approach was reported by Dominguez-Gonzalez *et al.* (2014) who was able to achieve a detection limit of 2.5 µg/L for visible spectrometry using functionalised gold nanoparticles. Field kits widely used for total arsenic determinations include the Merckoquant®, HACH®, Wagtech® Digital Arsenator test kits (UNICEF, 2010). The use of such field kits is particularly indicated where rapid on-site measurements are required and where the precision requirements are not tight and where there are logistical difficulties, including ensuring appropriate preservation, in transporting samples to fixed laboratories and returning data to the field. The reliability of such kits has been evaluated by van Geen *et al.* (2005) amongst others whilst Mukherjee *et al.* (2005) comments on human factors that may impact this.

5.5.1.2 Arsenic speciation

With nearly 1000 original articles on arsenic speciation analysis (Tyson, 2013), hyphenated techniques are established as the preferred methods for arsenic speciation due to their reproducibility of results, short analysis times and development of advanced instrumentation, capable of measuring more than 20 arsenic compounds (Akter *et al.* 2005; Ronkart *et al.* 2007). However, not all laboratories have the necessary infrastructure, such as a stable power supply, abundant supply of argon or resources to support consumables and associated reagents. Field kits for arsenic speciation facilitate measurements that can be robust, inexpensive and can in some cases provide real-time analyses for a fast response to remediation (Gupta *et al.* 2012). Some field methods can reduce the need for preservation reagents in the field to prevent oxidation of As(III) to As(V), as required for return of samples to laboratory based hyphenated techniques (Meng *et al.* 2001; Kumar & Riyazuddin, 2010; O'Reilly *et al.* 2010; Sugar *et al.* 2013). Field kits can be used on-site by field workers who do not have extensive training and therefore present an affordable approach for arsenic speciation. Significant efforts have been reported in the scientific literature in recent years to improve the robustness, sensitivity and prevent transformation of As(III) and As(V). A range of technologies, including: colorimetry, ion-exchange solid phase exchange (SPE) cartridges, voltammetry (Dozortsev, 2017; this volume) and biosensors (Siegfried, 2017; this volume) have been employed.

5.5.1.2.1 Colorimetry and UV-Visible spectrophotometry

Hu *et al.* (2012) employed a colorimetric method for field arsenic speciation in groundwater using $KMnO_4$ and CH_4N_2S as effective As(III) oxidant and As(V) reductant, respectively, in the formation of a

molybdenum blue complexes enabling the differentiation of As(III) and As(V), with a detection limit of 8 µg/L. A cloud point extraction method provided a limit of detection of 1.14 µg/L with a preconcentration of 65 following complexation of As(V) with acridine orange as a fluorescence cationic dye and subsequent analyses using UV-Visible spectrophotometry (Gurkan *et al.* 2015).

5.5.1.2.2 Ion exchange – solid phase extraction (SPE)

One of the earlier field-based methods for separating As(V) and As(III) using ion exchange cartridges was developed by Ficklin (1983) but suffered from the lack of separation of organo-arsenicals from As(V). An improved system, involving a resin based cation exchange cartridge and anion exchange cartridge connected in series, was developed by Le *et al.* (2000) and enabled the separation of As(III), As(V), MA and DMA from water samples. Ion exchange resins offer the advantage of being low cost, portable, easy to use, without the need for reagents in the field. Considerations for the employment of SPEs in the field should include the influence of competitor ions and extreme pH, such as found in acid mine drainage waters Impelleteri (2004). Watts *et al.* (2010) reported the impact on MA recoveries in slightly saline water samples or in the presence of elevated phosphate or sulphate. However, cation and anion exchange SPE cartridges were employed successfully for ground and surface waters from Argentina for the four arsenic species (O'Reilly *et al.* 2010) and in Hungarian well waters for inorganic arsenic species (Sugar *et al.* 2013). These methods provide the advantage of a pre-concentration enabling the measurement of lower concentrations (sub-µg/L) of arsenic species (Issa *et al.* 2010; Issa *et al.* 2011), but also a limited need for reagents to modify the water samples, simply requiring a preconditioning of the ion exchange cartridges and elution with weak acids. Many reported techniques described in reviews by Clough *et al.* (2012) and Chen *et al.* (2014) used a different approach. For example, Rahman *et al.* (2011) used SPE's and differences in pH to affect quantitative separation of As(III), As(V), MA and DMA, firstly buffering the sample to pH 5, then passing it through a TE-01 column retaining As(V) and MA, effluent adjusted to pH 9 and loaded onto an AS-01 column which retained As(III) and eluted DMA. As(V) and MA were eluted together, pH adjusted into two portions at pH 5 and 8 and washed separately into separate AN-01 columns and selectively eluted, whilst As(III) was eluted with weak nitric acid. Overall, this approach provides arsenic speciation where expensive laboratory methods are not available, but does need careful logistical considerations for use in the field. Ideally no reagents should be required in the field, with a minimum of effort to precondition the SPE cartridges, preferably in advance with stability of SPEs sufficient over a number of weeks to enable return of the cartridges to the laboratory for simple elution of the arsenic species. Strong Based anion exchange (SBAE) and hydrate iron oxide particles integrated HY resin possess high adsorption capacities toward arsenic species in elevated concentrations i.e. more than 370 µg g^{-1} for As(V) in SBAE resin, more than 4150 µg g^{-1} of As(III) and 3500 µg g^{-1} of As(V) for the HY resin (Issa *et al.* 2010). Doker *et al.* (2013) employed a relatively straightforward technique using PHEMA microbeads in a micro-pipette tip to selectively adsorb As(III) in snow samples, with As(V) calculated by the difference between total As and As(III).

5.5.1.2.3 Biosensors

Biosensors (e.g. Pfeiffer *et al.* 2015; Siegfried, 2017) are devices that use a biological recognition element to detect a specific analyte, which then converts this response into a quantitative output signal in the form of luminescence, fluorescence or an electrical current or potential. Molecular recognition features: enzymes that recognise substrates, receptors their ligands or nucleic acids their complimentary strands. This process is highly specific and sensitive, but can be fragile, which is a critical design feature for a biosensor robustness

(French *et al.* 2012). Merulla *et al.* (2013) reviewed bioreporter and biosensor assays capable of determining As(III) at 10–50 µg/L and below. Arsenite sensitive electrochemical biochips using bacterial (E. coli) resistance to As(III), providing detection limits of 0.8 µg/L in tap water. Ezeh *et al.* (2013) employed As(III) specific chemodosimeters, which incorporate a coumarin fluorescent reporter coupled with an As-reactive benzothiazoline functional group, to yield a highly fluorescent coumarin-6 dye with detection limits of 0.23 µg/L. Male *et al.* (2007) reported the development of a bionsensor for arsenite using arsenite oxidase and multiwalled carbon nanotube-modified electrodes. This approach is specific for As(III) with a detection limit of 1 µg/L. Solid phase biosensors using a GFP-tagged ArsR protein and fluorescence detection have been developed for the measurement of As(III) in tap and mineral water with detection limits of 5 µg/L for field use, but with analysis times of 15 to 30 minutes (Siddiki *et al.* 2011). There is a disadvantage to these methods as they do not measure As(V), so cannot be used across a complete pH/Eh range, leaving large swathes of water supplies across the world that cannot provide reliable As data, unless additional total As measurements are undertaken to calculate As(V) concentrations by subtraction. A number of biosensors have been developed based on whole cell or cell-free (DNA, protein) based biosensors. Optimisation of detection limits, specificity and response times are required. The advent of aptamer-targeted technology provides the potential for target specific biosensors (Chen & Rosen, 2014; Kaur *et al.* 2015).

5.5.2 Analytical & data reduction protocols

5.5.2.1 Control samples & standards

Control samples and standards are necessary to assure the quality of analysis and sample preparation. Although often determined by a laboratory carrying out the analyses, the nature and number of these may also form part of the analytical criteria specified to a laboratory (see Table 5.3). Reporting the outcomes of the analysis of control samples and standards may be critical to better enable a reader to judge data quality.

5.5.2.2 Order of Analysis – randomisation

Randomisation of presentation of samples for analysis is recommended to minimise systematic biases arising, for example, from any drift in sensitivity over the course of an analytical session or of carry-over effects.

5.5.2.3 Data reduction – calibration models

Reduction of instrumental responses to analyses is typically done through the use of model calibration curves (Table 5.4). Such curves are most commonly first order linear, but other models are used from time to time – these include first order linear forced through zero (generally not recommended, but worth being aware of as a bias-introducing model), and second and higher order linear and error weighted (generally recommended) (Table 5.5) models. Several commonly used models may give rise analytical bias particularly for samples in concentration ranges that either lie outside the concentration ranges of the calibration standards or at very low concentrations. The appropriateness of calibration models should be checked by (i) inspecting residuals as a function of concentration – any significant association found indicates that the calibration model is biased, the extent to which this requires consideration of a different calibration models depends upon project requirements; (ii) determining the association between analytical precision and concentration – a heteroscedastic distribution of such precisions indicates that a weighted calibration model should be considered; and (iii) comparing sample concentrations with the range of concentrations for the calibration standards – the reliability of calibration models much above the highest calibration standard concentration is suspect, particularly for polynomial calibration models.

Table 5.3 List of commonly used control samples and standards. Numbers required for each type will depend upon project including, where appropriate, regulatory or contractual, requirements.

Sample/Standard Type	Purpose	Typical Number
Replicate samples	Estimate sampling error	One set of replicates per 10 to 30 samples.
Sample repeats	Estimate repeatability of measurement	One set of replicates per 10 to 30 samples.
Blank	Facilitate calculation of detection limit and limit of quantification.	One per 10 to 20 samples. Minimum 3 per set of samples.
Procedural blank	Estimate contamination arising from sample processing.	Minimum 3 per set of samples.
Calibration Standards	To determine the instrumental response to analyte.	Minimum 5 to 7 different standards, analysed at least 3 times each.
		Concentrations should range from 0 to somewhat above the highest expected sample concentration.
		Mean concentration of the calibration standards should be in a concentration range where the highest analytical precision is required.
Internal standard	To correct for irregular instrumental responses	Typically μg/L concentrations of Ge (or other trace if Ge is of analytical interest) added to all samples and standards. The concentration is typically determined after an assessment of instrument sensitivity.
Spiked (with a range of amounts of arsenic) samples	To determine and correct for matrix effects	Indicated where matrix of calibration standards and samples differ significantly and where matrix effects are suspected; recommended 5 different additions per selected sample; numbers of samples selected for spiking strongly dependent upon project requirements and budget.
Certified Reference Materials (CRMs)	To ensure accuracy of analyses and traceability	At least one CRM analysed in triplicate per sample set; further CRMs as required depending upon range of arsenic concentrations and matrix compositions.

Table 5.4 Commonly used calibration curve models, together with the equations to calculate concentrations from signals for samples, using the calibration curve models.

Model	Equation of Calibration Curve	Equation to Calculate Concentration from Signal	Comments
First order linear; forced through zero	$y = bx$	$x = y/b$	Simple; may result in bias, if the best calibration curve is not 1st order linear or if the signal errors are not homoscedactic
First order linear;	$y = bx + a$	$x = (y - a)/b$	Simple; may result in bias, if the best calibration curve is not 1st order linear or signal errors are not homoscedactic
Second order linear (quadratic); forced through zero	$y = cx^2 + bx$	$x = \{-b +/- \text{sqrt}(b^2 + 4cy)\}/2c$	May result in bias at low concentrations or at higher concentrations beyond the calibration range
Second order linear (quadratic);	$y = cx^2 + bx + a$	$x = \{-b +/- \text{sqrt}(b^2 - 4c(a - y))\}/2c$	May result in bias at low concentrations or at higher concentrations beyond the calibration range
Logarithmic	$y = b \ln(x) + a$	$x = \exp((y - a)/b)$	Useful where there is a logarithmic relationship between concentration and signal
Logarithmic with offset	$y = b \ln(x + \psi) + a$	$x = \exp((y - a)/b) - \psi$	Useful where there is a logarithmic relationship between concentration and signal and there is also non-zero signal at very low concentrations

Table 5.5 Commonly used error weighting models.

Weighting Model	Equation to Calculate Weighting Factor	Comments
Uniform weighting	$W_i = 1$	Simple; may result in very high relative biases at low concentrations in the common case where absolute signal errors are heteroscedastic and higher at higher concentrations
Weight by inverse of error	$W_i = 1/E_i$	Theoretically difficult to justify in many cases
Weight by inverse of square of error	$W_i = 1/E_i^2$	Preferred weighting model provided that the added computational complexity is justified by project requirements

Table 5.6 Equations for calculation of calibration model and estimation of concentration from the calibration model for first order linear calibration without weighting.

Parameter	First Order Linear Model with No Weighting
Calibration model	$y = bx + a$
Weighting	$w_i = 1$
Mean concentration of *n* calibration standards	$\bar{x} = \frac{\sum_i x_i}{n}$
Mean signal of n calibration standards	$\bar{y} = \frac{\sum_i y_i}{n}$
Unbiased estimate of slope, *b*, of calibration curve	$b = \frac{\sum_i [(x_i - \bar{x})(y_i - \bar{y})]}{\sum_i (x_i - \bar{x})^2}$
Unbiased estimate of intercept, *a*, of calibration curve	$a = \bar{y} - b\bar{x}$
Unbiased estimate of the concentration of an unknown sample with signal response, y_0	$x_0 = \frac{(y_0 - a)}{b}$
Standard deviation of the slope	$s_b = \frac{s_{y/x}}{\left[\sum_i (x_i - \bar{x})^2\right]^{1/2}}$
Standard deviation of the intercept	$s_a = s_{y/x}\left[\frac{n\sum_i x_i^2}{n\sum_i (x_i - \bar{x})^2}\right]^{1/2}$
$S_{y/x}$	$s_{y/x} = \left[\frac{\sum_i (y_i - \hat{y}_i)^2}{n-2}\right]^{1/2}$
Standard deviation of the estimated concentration of the unknown sample, given that *g* (see below) is less than 0.05	$s_{x_0} = \frac{s_{y/x}}{b}\left[1 + \frac{1}{n} + \frac{(y_0 - \bar{y}_i)^2}{b^2\sum_i (x_i - \bar{x})^2}\right]^{1/2}$
g	$g = \frac{t^2}{b^2}\left[\frac{(s_{y/x})^2}{\sum_i (x_i - \bar{x})^2}\right]$
Standard deviation of the estimated concentration of the unknown sample from m replicate measurements, given that *g* (see below) is less than 0.05	$s_{x_0} = \frac{s_{y/x}}{b}\left[\frac{1}{m} + \frac{1}{n} + \frac{(y_0 - \bar{y}_i)^2}{b^2\sum_i (x_i - \bar{x})^2}\right]^{1/2}$

Source: After Miller, 1991.

5.6 TOTAL QUALITY MANAGEMENT (TQM), QA & QC

5.6.1 Total quality management

General requirements for the competence of testing and calibration laboratories are set out by the International Standard Organisation, specifically in EN ISO IEC 17025:2005. Accreditation to this standard is monitored through national bodies such as the United Kingdom Accreditation Service (UKAS) in the UK, who monitor; firstly the attainment of accredited status or secondly the maintenance of accredited status. This is achieved through annual visits to laboratories by using independent experts. Laboratories are tested as to whether they are maintaining standard operating procedures which form the basis of a management system and against which they attained accreditation. The laboratory's management system policy relating to quality, including a quality policy statement shall be defined in a quality manual, which states overall objectives and is reviewed periodically.

"Laboratory facilities for testing and/or calibration, including but not limited to energy sources and environmental conditions [are required to enable appropriate performance and] ensure that "environmental conditions do not invalidate results or adversely affect the quality of" data (ISO/IEC 17025, 2005). Management systems can also consider the laboratories environmental management systems, with guidance provided in ISO 14001:2004. This standard involves the management of waste, control and records of chemical use, storage and disposal, and, in addition, operational activities that may have an environmental impact, such as maintenance of equipment to ensure efficient operation and power consumption.

To ensure the quality of results, laboratories should have "quality control procedures for monitoring the validity of tests and calibrations" (ISO/IEC 17025). This may include "the use of certified reference materials or internal quality control using secondary reference materials, participation in" [inter-laboratory] comparison or proficiency testing programmes or replicate tests" (ISO/IEC 17025, 2005). These data must be "monitored and reviewed and where found to be outside [of] pre-defined criteria, action [should] be taken to correct the problem and to prevent incorrect results from being reported" (ISO/IEC 17025, 2005).

The control of documents should include the maintenance of procedures, instrument and service logs, quality control charts, and training records detailing the competency of a laboratory to undertake specific tests or calibrations. Laboratories should have a procedure to implement when any aspect of testing or calibration work does not conform to its own procedures, with responsibilities assigned for corrective action to be taken. "Records for each test or calibration [should] contain sufficient information to [enable the] identification of factors affecting uncertainty and [allow for] the test to be repeated under conditions as close as possible to the original. [Such] records [should] include the identity of personnel responsible for [each stage] of [a] test" (ISO/IEC 17025, 2005) and include details of the sample from the registration of a sample into a laboratory management system through to the analyses and reporting of data to the client. A clear audit trail could then be established, including details regarding the correct storage and location of samples to demonstrate chain-of-custody or to enable repeat analyses if required and the return of samples to the client.

Laboratories should periodically conduct internal audits by trained and qualified staff, where possible independent of the specific activity "to verify that its operations continue to comply with the requirements of the management system and [the] international standard [against which accreditation is gained]" (ISO/IEC 17025, 2005). Management reviews are necessary to review procedures, the outcome of internal audits, non-conforming tests, customer feedback, sufficient staff training and resources.

5.7 CONCLUSION

Sampling and analysis of waters for arsenic, arsenic speciation and associated parameters ideally requires (i) understanding of the sampling and analytical requirements, including representativeness, accuracy,

precision and limits of detection , in the context of project aims; (ii) consideration of sampling, preservation and analytical protocols to achieve the required aims; and (iii) consideration of total quality management requirements including sample and data chains of custody, operator training, use of appropriate control charts and project- and laboratory- specific documentation control.

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