ARSENIC SPECIATION ANALYSIS METHODS USING NEUTRON ACTIVATION: FIT FOR THE PURPOSE

Amares Chatt

Trace Analysis Research Centre, Department of Chemistry, Dalhousie University,
6274 Coburg Road, Room 212, PO BOX 15000, Halifax, Nova Scotia, B3H 4R2, Canada.
chatt@dal.ca

We have developed several methods for the separation of single as well as multiple species of arsenic and other elements using Chelex-100, Chitosan, coprecipitation, cloud point extraction, liquid-liquid extraction, solid-phase extraction, and reversed-phase and high performance liquid chromatography in conjunction with neutron activation analysis. At the end, we ask ourselves which of these methods we use and when. Our answer to the above questions is to use the method fit for the purpose. We will discuss various scenarios regarding the suitability of a given method to solve a given problem.

I. INTRODUCTION

It is well known that the toxicity of arsenic largely depends on its physico-chemical form otherwise known as species. Arsenate has been reported to be the main species in natural waters. Arsenite, dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA) have also been found as minor components in surface water. However, in marine organisms, the main forms of arsenic are arsenobetaine (AsB) and arsenosugars. By far the most toxic as well as labile species of arsenic are As(III) and As(V). However, almost all foods and drinks do not provide levels of arsenic species in them. One of the reasons for it is said to be the lack of appropriate methods for the speciation analysis of arsenic.

Most speciation analysis methods consist of two steps. In the first step the species of interest is separated from the sample by a chemical method followed by its detection and measurement in the second step. Several techniques including hydride generation, thermal decomposition, microwave-assisted oxidation, liquid-liquid extraction, solid-phase extraction, coprecipitation, biopolymer, and many types of chromatography are used for the separation of various arsenic species. The elemental detection techniques generally employed include atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), atomic emission spectrometry (AES), and inductively-coupled plasma spectrometry (ICP)-AES as well as -mass spectrometry (ICP-MS). ICP-MS is perhaps the most widely used technique today.

Neutron activation analysis (NAA) is also a very effective and sensitive element determination technique. Unlike some of the commonly used techniques noted above, NAA has several unique features which can be advantageously applied to speciation analysis. NAA has been characterized as a 3-dimensional spectroscopic technique because (i) signal strength can be measured as functions of both energy and time; (ii) it allows separation of elements with same gamma-ray energies but different half-lives; and (iii) verification of half-life provides check on radiochemical purity. NAA offers multielement specificity, excellent sensitivity, simultaneous speciation of elements which are not chemically similar, and analysis of elements which are rather difficult to determine by many other techniques. CCQM has recognized NAA as a primary ratio method. NAA has some unique quality assurance capabilities such as built-in analytical redundancy which can lead to excellent precision and accuracy because (i) multiple radionuclides with different half-lives are often available, (ii) multiple photopeaks of the same radionuclide can be assayed simultaneously, (iii) multiple counts can be performed for each sample, and (iv) alternate radionuclides can sometimes be produced by epithermal and fast neutrons. These and other features of NAA can be conveniently used in arsenic speciation analysis.

II. METHODOLOGIES

We have developed a number of chemical separation methods over the years to determine arsenic species using NAA. First we have used Chelex-100 resins in 1970’s to separate anionic and cationic arsenic species in rain and tap water. However, it could not be used to identify individual arsenic species. Then we have used Chitosan to do speciation analysis for arsenic in seawater and drinking water. Here we have been able to separate As(III) from As(V) but could not identify
the other arsenic species. We then developed a reversed-phase extraction chromatographic method using TAN and have been able to quantitatively measure As(III) in drinking water. We also developed a coprecipitation method with APDC and Bi to measure low levels of As(III) in drinking water. We have developed a green chemistry cloud point extraction method to speciate As(III) and As(V) in drinking water and seaweeds. We have also been able to separate water soluble As(III) and As(V) compounds in freshwater fish/shellfish and plant samples by solvent extraction using APDC/MIBK. It is evident that all these methods have been successful for the measurement of low levels of As(III) and in some cases also As(V) in drinking water and fish samples. However, we could not reliably measure the levels of other arsenic species.

We then developed the first reported HPLC-NAA method for the determination of low levels of five arsenic species, namely As(III), As(V), MMA, DMA, and AsB in water samples. We also determined organically bound arsenic (OBAs) and total arsenic in these samples. The detection limits of the method have been found to be 0.005 ng mL\(^{-1}\) for OBAs, 0.02 ng mL\(^{-1}\) for AsB, DMA, MMA, As(III), and As(V) and 0.12 ng mL\(^{-1}\) for total arsenic. In the past, several authors postulated the existence of about 25% of "hidden" arsenic species in certified reference materials and natural waters using hydride generation (HG). We found no evidence of it by our HPLC-NAA method. We concluded that although the HG technique is sensitive enough for the determination of low levels of arsenic species, it is incapable of detecting the non-hydride forming species. Our HPLC-NAA method is also good for studying interactions that occur among various arsenic species. However, it could not be used to investigate interaction of arsenic species with species of other elements such as Sb and Se.

We then combined solid phase extraction (SPE), coprecipitation, and NAA to develop a speciation analysis method based on green chemistry for the major arsenic species in drinking water. In this method As(V), MMA, and DMA are separated and preconcentrated by strongly anion and cation exchange columns in tandem while As(III) remained in the effluent. These species are then selectively eluted and As(III) coprecipitated with bismuth sulphide. This simple method has been applied to the analysis of water reference materials with good results. The detection limits are 0.9, 1.7, 1.6, 3.8 and 16 ng mL\(^{-1}\) for As(III), As(V), MMA, DMA and total arsenic, respectively, using a neutron flux of 2.5x10\(^{11}\) cm\(^{-2}\) s\(^{-1}\) at the Dalhousie University SLOWPOKE-2 reactor (DUSR) facility and anti-coincidence gamma-ray spectrometry. We then extended the method to include the determination of Sb(III), Sb(V), Se(IV) and Se(VI). We have been able to study inter-element as well as intra-element species interactions using this SPE-NAA method.

**III. CONCLUSIONS**

At the end, we ask ourselves what we do with all these methods. Today we are faced with many questions like what kind of species we are looking for and why. Just because we have analytical techniques available should we then measure all species on the earth? Should we measure a single species of an element in a given matrix and be happy that we got something or should we investigate interactions that may exist among this and other species leading to synergistic or antagonistic effects? We also want to measure the species as is. So when do we do the experiments? Are the species changing during the experimentation? Can we measure them on-site to avoid some of these problems? What type of analytical techniques should we use?

Our answer to the above questions is to use the method fit for the purpose. If a monitoring body is looking for a simple method to measure the most toxic arsenic species, namely As(III), then perhaps a simple SPE, solvent extraction or coprecipitation method will do provided there is no interference from other species. Of course, the availability of laboratory facilities with expertise would play a big part. Other factors, such as distance of the sampling site from the laboratory and other considerations necessitating on-site separation, can greatly influence the choice of a separation method and determination technique. These factors will be discussed in detail with practical examples and performance of the arsenic speciation analysis methods described above.