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Internal standardisation for arsenic and its species determination using inductively coupled plasma mass spectrometry

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ABSTRACT

The signal of As measured by inductively coupled plasma mass spectrometry (ICP-MS) suffers from strong non-spectral interferences due to carbon and alkali metals. The accuracy of the determination of total As using ICP-MS and its species using anion-exchange chromatography coupled to ICP-MS was increased by using selenium as an internal standard. For chromatography, selenium was used in the form of a trimethylselenonium cation, which did not interact with the stationary phase and could be added directly to the mobile phase as the selenite was sufficient for total As determination. Selenium is able to correct non-spectral interferences caused by carbon or sodium up to concentrations of 3000 mg L^{-1} C and 35 mg L^{-1} Na, respectively, in the case of total As determination, and up to 3000 mg L^{-1} C and 3450 mg L^{-1} Na in the case of speciation analysis. Selenium as an internal standard was tested for the analysis of arsenobetaine in the DORM-2 standard reference material. The results were in good accordance with certified values regardless of NaCl spikes. Also, the results of total As determination in canned fish using a selenium internal standard were not affected by residual carbon in an imperfectly decomposed sample.

1. Introduction

Quantitative analysis applying internal standardisation is the most popular calibration strategy used in inductively coupled plasma mass spectrometry (ICP-MS). A carefully selected internal standard can compensate for signal drift and noise effects, and reduce matrix effects in ICP-MS [1]. The principle of this calibration method is very simple. An internal standard is added to all calibration standards, blanks and samples at the same amount. The measured signal is then expressed as the ratio of analyte intensity to internal standard intensity. The internal standard should be an element with a similar mass, ionisation potential and physicochemical behaviour, and should not be present in the sample. An internal standard can be added to each solution either by volumetric addition or by mixing the flow of the internal standard and the sample using a T- or Y-piece prior to the nebuliser [2].

The using of an internal standard can also overcome the disadvantages of standard addition methods in speciation analysis. Here, standards for all species are needed, while internal standardisation is also applicable for the determination of unknown species or species for which a standard is not available. Non-spectral interferences can be divided into reversible (e.g. signal enhancement/suppression) and irreversible (e.g. deposition of salts around cones). Their elimination requires a different approach. Errors associated with reversible effects can be corrected only by an appropriate calibration method, while irreversible effects can be eliminated by reducing the amount of matrix present [3].

One of the non-spectral reversible interferences affecting As determination is caused by the presence of carbon in the sample and consequently in the plasma. Carbon in a sample can influence the ionisation conditions in the plasma, leading to As signal enhancement. The mechanism of this effect was revealed by Nakazawa et al. [4]. The process increasing the degree of As ionisation has two steps: the reaction of AsO with a neutral carbon atom produces As and CO and the As is then ionised via a C^+-species to As^+.

The next most important source of non-spectral interferences is alkali metals, which act against the carbon effect, leading to a signal decrease. This effect was demonstrated by Goessler et al. [5] for sodium and potassium during the analysis of arsenobetaine using high performance liquid chromatography (HPLC) coupled to ICP-MS, where the low recovery of arsenobetaine was obtained at high Na and K concentrations (45% at 500 mg L^{-1} Na and 59% at 500 mg L^{-1} K), and quantitative recovery was obtained only up to 5 mg L^{-1} Na or 1 mg L^{-1} K. These interferences, which result in reduced determination accuracy, may occur, especially for samples containing a complex matrix. Such samples are typically seafood, which is often analysed due to the high As content but also contains a large amount of inorganic salts. These

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interferences may affect the determination of total As content when the sample is introduced directly into the ICP-MS, and also the determination of As species using HPLC when the eluent from the column is introduced to ICP-MS. In the case of As, the anion-exchange HPLC (AEC) is the most often used separation technique [6–8].

The internal standard for HPLC can be added in two ways. The first is a post-column addition. Joining the internal standard and effluent behind the chromatographic column is easy and a suitable standard can be selected regardless of the compatibility with chromatographic separation. However, in some cases, the undesired dilution of the eluent accompanied by peak tailing is observed, probably due to a large internal volume of the T-piece that serves to join the flow of the eluent and the internal standard. The problem can be solved by using a small volume T-piece, as described by Chen et al. [9], who mixed the output from the column (anion-exchange PRP-X100) with the internal standard ^{128}Te (20 μg L^{-1}) by means of a zero dead volume T-piece. The method was used for the analysis of As species in diluted urine. The authors proved the accuracy of As species determination in diluted urine, but the effect of Te as an internal standard was not discussed in detail. Other internal standards that were previously used for As speciation were rhodium (measured isotope ^{103}Rh, 10 μg L^{-1}), used for the analysis of sea fish, shellfish, oysters and algae [10] and germanium (^{72}Ge, 5 μg L^{-1}), which was used as an internal standard for As speciation in seafood [11]. An external flow of Rh or Ge was continuously mixed with the chromatographic eluate using a T-junction behind the column and just before the nebuliser. This arrangement eliminates the need for a zero dead volume T-piece. The authors used rhodium and germanium as internal standards for the analysis of much-diluted extracts (0.2 g of sample extracted with 40 mL of solvent and then diluted 10-fold and 100-fold, and 0.25 g of sample extracted with 7.5 mL of solvent, with half of the extract subsequently diluted to 10 mL, respectively), where the effect of matrix is probably negligible and the behaviour of Rh or Ge at high sodium or carbon contents was not tested.

The second and more advantageous possibility is the addition of an internal standard directly to the mobile phase. This does not result in either the dilution of the effluent or in the overlap of peaks due to tailing. Additionally, this system does not require additional accessories for the addition of internal standards and can also eliminate any undesirable effects during chromatographic separation (pressure fluctuation, etc.). However, a suitable chemical form of an element serving as an internal standard must be properly selected to prevent interaction with the stationary phase. This method was previously used for As only by Wahlen [12] who used Rh (100 ng g^{-1}) as an internal standard in the mobile phase of 2.2 mmol L^{-1} NH_4HCO_3-2.5 mmol L^{-1} tartaric acid with 1% methanol (pH = 8.2) on an anion-exchange column PRP-X100 for the analysis of fish tissues extracts. This internal standard was useful only for long-term signal drift monitoring, but not for non-spectral interference correction. Therefore, the fish extracts had to be diluted at least 10-fold.

Despite the more or less successful use of internal standards for the determination of As and its species described in the literature, the direct analysis of undiluted samples remains a real challenge. The aim of this work was to find suitable element for internal standardisation and the chemical form that is compatible with the AEC technique that is commonly used for As speciation. This internal standard should work for total As determination using ICP-MS and for the accurate determination of As species using AEC-ICP-MS in undiluted samples.

2. Materials and methods

2.1. Reagents

A 65% nitric acid (Suprapur, Merck, Germany) solution was used for total As content determination. A standard solution of 1000 ± 2 mg L^{-1} of As (Analytika spol. s.r.o., Prague, Czech Republic) was used for the preparation of calibration solutions in the case of total As content determination. Standard solutions of 1000 ± 2 mg L^{-1} of Se, Ge, Sc, Te, Ga, Rh, and In (Analytika spol. s.r.o., Prague, Czech Republic) were used for the preparation of internal standard solutions for total As determination.

The mobile phase for anion-exchange chromatography consisted of 20 mmol L^{-1} aqueous ammonium dihydrogen phosphate (99.999%, trace element basis, Sigma Aldrich, Steinheim, Germany). The pH of the solution was adjusted to 6.0 by adding aqueous NH_3 (25%, Suprapur®, Merck, Germany). A sodium chloride stock solution (9 g L^{-1}) for interference testing was prepared by the dissolution of solid NaCl (Suprapur®, Merck, Germany) in water. Methanol (HPLC gradient grade LiChrosolv®) for the simulation of organic carbon in the matrix was obtained from Sigma Aldrich, Steinheim, Germany.

The aqueous solutions of As species were prepared from sodium arsenate dibasic heptahydrate (AsV) (≥98%), dimethylarsinic acid (DMA) (approx. 98%) (both from Sigma-Aldrich, St. Louis, USA), disodium methylarsonate (MA) (Supelco, Bellefonte, PA, USA) and arsenobetaine (AB) (purum ≥98%) (Sigma-Aldrich, St. Louis, USA). Trimethylselenonium iodide used as an internal standard was synthesised at the Department of Organic Chemistry, UCT Prague, according to the procedure used earlier [13]. Other selenium species for the testing of co-elution with As species were selenocystine SeCys2, selenate Se(VI) (min. 98%), selenite Se(IV) (min. 99%), selenomethionine SeMet (min. 99%), and Se-methylselenocysteine Se-MetSeCys (min. 95%) (all from Sigma Aldrich, Steinheim, Germany). Demineralized water (Millipore, Bedford, MA, USA) was used for the preparation of all solutions.

The canned fish samples (sprats in rapeseed oil, mackerel in sunflower oil, and mackerel in rapeseed oil) were purchased from the Kaufland supermarket chain in Prague (Czech Republic). After removal of the oil, the meat was carefully dried with cellulose tissue and sliced. Pieces of meat were freeze-dried and consequently milled. The mushroom *Imbleria badia* was picked-up in the forest near the Kostelec nad Orlicí, Czech Republic. The mushroom was also freeze-dried and consequently milled.

Quality control materials consisted of the reference material SRM 2976 “Mussel tissue (trace elements and methylmercury)” (NIST, USA) and DORM-2 “Dogfish muscle” (NRC-CNRC, Canada).

2.2. Instrumentation

Digestions for total As determination in the samples were performed uisng a microwave heated digestion system Speedwave 4 (Berghof, Germany). A PerkinElmer 350D ICP-MS instrument (PerkinElmer, Concord, Canada) was used for the determination of total As and the detection of As species. The dynamic reaction cell mode with ammonium as a reaction gas was used for the elimination of $ArCl^+$ spectral interferences. The speciation analysis was performed using a PerkinElmer Series 200 HPLC system connected to ICP-MS. The parameters of ICP-MS and HPLC measurements are summarised in Table 1. The anionic As compounds were separated by anion-exchange

Table 1
ICP-MS and chromatographic operating conditions.

Parameter	Total As	As speciation
RF power	1400 W	
Measurement mode	Peak hopping	
Measured nuclides	^{75}As, ^{74}Ge, ^{82}Se	^{75}As, ^{82}Se
Acquisition time	500 ms	1000 ms
Cell gas flow	0.3 mL min^{-1} NH_3	
RPq	0.75	
Total acquisition time	–	540 s
Solution uptake	1.3 mL min^{-1}	
Sample injection volume	–	100 μL
Mobile phase flow	–	1.4 mL min^{-1}
Column temperature	–	40 °C