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# Internal standardization using a dual mode sample introduction system in the determination of As by HG-ICP-MS

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Internal standardization was studied by introducing internal standards simultaneously by liquid nebulization (Y, Pd) and hydride generation (Ge, Bi) with a dual mode sample introduction system in the determination of arsenic by HG-ICP-MS. The effects of the gas flow rates and ICP-MS parameters were examined for all the elements. Sample introduction for Ge and Bi is similar to arsenic and therefore they could correct the signal variations originating from the hydride generation sample introduction system. The results indicated, that in addition to hydride forming internal standards, the signal variations caused by the changes in the main plasma conditions can be corrected by using aqueous internal standards introduced by solution nebulization. The accuracy of the measurements were studied by analyzing two different certified reference materials (ERM-CA615 and NIST 1573a) and the results were in good agreement with the certified values. However, it was found out, that the Bi was not suitable hydride forming internal standard for the real samples because it can occur in the samples in small concentrations and the formed hydride is instable.

## 1. Introduction

Hydride generation (HG) coupled with inductively coupled plasma mass spectrometry (HG-ICP-MS) is a powerful method for the determination of trace and ultratrace concentrations of arsenic [1–3]. The determination of arsenic may suffer from reduced sensitivity when ordinary solution nebulization is used. This is due to poor sample introduction efficiency and the fact that arsenic has a high ionization potential. Therefore hydride generation is widely used to enhance sensitivity, by reducing arsenic to volatile hydride, usually with sodium borohydride ($NaBH_4$). Hydride generation improves the transport efficiency of the analyte to nearly 100% and also some matrix effects are less severe as the analyte is separated from the sample constituents [4].

ICP-MS technique is prone to instrumental signal variations due to various reasons including matrix effects and variations in plasma conditions, ion optics and sample introduction system [5]. Internal standardization is used to correct the signal instabilities among the other methods like isotope dilution or calibrating the instrument more frequently. Internal standardization is routinely used in ICP-MS measurements but with HG-ICP-MS it is rarely used. Matrix effects in plasma are reduced significantly when hydride generation method is used since the analytes and matrix constituents are separated from each other. However, instrumental drift is present due to other reasons like sample transportation and variations in plasma conditions. Internal standards should be carefully selected. It should not be an element that is present in the sample and it should have a mass number close to that of the analyte and preferably similar ionization potential [6,7].

It is possible to use internal standardization also in HG mode but then the internal standard should be a hydride forming element. The amount of possible elements is restricted, but a few candidates can be found. Stroh et al. [8] examined Bi as an internal standard when measuring As, Sb and Hg in chloride containing water samples with FI (flow injection) HG-ICP-MS. They found that internal standardization led to a better precision and accuracy. Bismuth can be present at low concentrations for example in biological samples and due to the high sensitivity of hydride generation method even very low Bi concentrations may produce variation to the signal. Dos Santos et al. [9] investigated Bi and Ge as internal standards with CVG-ICP-OES (chemical vapor generation inductively coupled plasma optical emission spectrometry). They determined simultaneously As, Hg, Sb, Se and Sn in sediment slurries and corrected As and Se signals with Ge and Bi. The use of Ge improved the accuracy of the results for the certified reference materials significantly but with Bi the recoveries were even lower than without correction. Chen et al. [10] determined trace levels of lead in biological and geological samples by HG-ICP-MS and found that the use of bismuth as an internal standard improved especially long-term stability. Anderson et al. [11] used indium in sequential HG/pneumatic nebulization (PN) ICP-MS system. Indium was used as an internal standard both in PN and HG modes. However, no signal for In was obtained in HG mode although Indium can form volatile hydrides.

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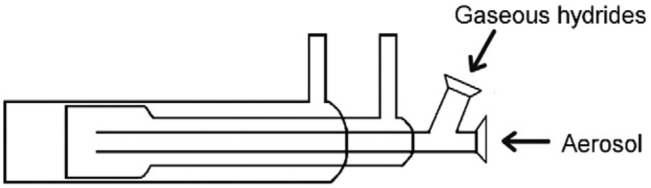

**Fig. 1.** XSERIES dual mode ICP-MS sample introduction system.

It is also possible to combine vapor generation and liquid nebulization with ICP-OES and ICP-MS techniques using a commercial or house-made multi-mode sample introduction systems (MSIS) [12–17]. Our research group [18] reported on the usage of this kind of system for internal standardization in the determination of mercury in natural waters with cold vapor (CV) ICP-MS. Pt, Pd, Tl and Bi were used to correct the variation in mercury signals. Rayman et al. [19] connected a hydride generation system and a spray chamber to the torch with an Y-piece and fed indium internal standard solution through the nebulizer while determining selenium in blood serum samples with HG-ICP-MS.

The purpose of this study was to compare the suitability of several internal standards (Ge, Bi, Y and Pd) to correct signal variations in the determination of arsenic by HG-ICP-MS. With the use of a dual sample introduction system it was possible to introduce internal standards both as hydrides (Ge, Bi) and with normal liquid nebulization (Y, Pd). The hypothesis was that the drift could be caused by the signal fluctuations in plasma and in addition due to the changes in hydride generation sample introduction.

## 2. Experimental

### 2.1. Reagents and standards

Standard solutions were prepared by diluting a commercial stock solution containing 1000 mg L$^{-1}$ $As_2O_5$ (Titrisol, Merck, Germany). Internal standard solution for hydride generation containing Bi and Ge was prepared by diluting commercial 100 mg L$^{-1}$ Bi (Accutrace, Accustandard, USA) and in-house 1000 mg L$^{-1}$ Ge (Merck, Germany) solutions. The concentrations in final sample solutions were 0.1 μg L$^{-1}$ Bi and 2.0 μg L$^{-1}$ Ge. Internal standard solution containing 50 μg L$^{-1}$ Pd and 10 μg L$^{-1}$ Y for liquid nebulization was prepared by appropriate dilutions of 1000 mg L$^{-1}$ Pd (Merck, Germany) and in-house 1000 mg L$^{-1}$ Y (Reak. Khim., Russia). The concentrations of internal standard solutions were chosen to produce signal intensities of the same order of magnitude. $NaBH_4$ solution (0.5% *w*/*v*) was prepared daily by dissolving $NaBH_4$ (Sigma Aldrich, USA, p.a.) in 0.05 M NaOH, which was prepared by dissolving NaOH pellets (Merck, Germany, p.a.) in water. Nitric acid (Romil, UK, 67–69%, sp.) was used to acidify the samples before hydride generation and in sample digestion. Hydrogen peroxide (Merck, Germany, 30%, p.a.) was used in sample digestion. Ultrapure water (Millipore Gradient, Millipore Corp., Billerica, MA, USA) was used in all dilutions.

**Table 1**
Measured isotopes and ionization potentials.

| Element | Isotope (Abundance) | Ionization potential (eV) |
|---|---|---|
| Ge | 72 (27.43%) | 7.9 |
| As | 75 (100.00%) | 9.79 |
| Y | 89 (100.00%) | 6.38 |
| Pd | 105 (22.60%) | 8.34 |
| Bi | 209 (100.00%) | 7.29 |

A certified reference materials ERM-CA615 (groundwater) and NIST 1573a (tomato leaves) were used as control samples. The reference materials were digested with CEM MARS 5 X microwave oven (CEM, Matthews, USA) using XP-1500 Teflon vessels (CEM). The vessels were cleaned with nitric acid (pa, Merck, USA). The method used for groundwater was the EPA 3015A [20]. Tomato leaves were digested with 5 mL $HNO_3$ + 3 mL $H_2O_2$ using a two stage program: At first the vessels were heated to 180 °C at 10 min and after that held at 180 °C for 10 min. The final dilution was made to 100 mL and all the samples contained approximately 5% (*v*/v) nitric acid. Hydrochloric acid was avoided in sample pretreatment and measurements because of ArCl molecular ion interference. After sample digestion arsenic is at the oxidation state V and can be directly measured against As (V) standard solutions. Better sensitivity with hydride generation method can be reached by measuring arsenic as As (III) but it requires more sample pretreatment since a pre-reduction step is needed, e.g. with *L*-cysteine [21,22]. Mihaltan et al. [23] have also measured samples as As (V) without pre-reduction after oxidizing sample pretreatment.

### 2.2. Instrumentation

A Thermo Elemental X 7 ICP-MS (Thermo Elemental, Windsford, England) equipped with an XSERIES dual mode sample introduction system (Thermo Elemental, Windsford, England) was used to introduce simultaneously liquid and gaseous samples to the plasma. The dual mode system (Fig. 1) has been developed for LA-ICP-MS and GC-ICP-MS coupling but in this study it was used for simultaneous coupling of a hydride generation system (HGX-200, Cetac Technologies) and a conventional sample introduction system consisting of a concentric glass nebulizer with a Peltier cooled (+3 °C) conical spray chamber.

Only some elements form covalent volatile hydrides and in this study germanium and bismuth were chosen as internal standards for the hydride generation method. $^{72}$Ge has a mass that is very close to the $^{75}$As and $^{209}$Bi is another hydride forming element that has been used in internal standardization with hydride generation method. Yttrium and palladium were used as internal standards with conventional nebulization. $^{89}$Y was chosen since its mass is close to $^{75}$As and $^{105}$Pd was chosen because it has a high ionization potential like arsenic (8.34 eV and 9.79 eV respectively). The used isotopes and ionization potentials of arsenic and the internal standards are listed in Table 1.

The samples containing Ge, As and Bi were reduced with sodium borohydride ($NaBH_4$) to gaseous hydrides which were introduced to the dual mode system with argon gas flow. The HGX-200 system has two gas flows, the first before the gas liquid separator and the second after it above the membrane. In this study the argon gas flow was divided in ratio of 1:1 to these two inlets. An autosampler (CETAC

**Table 2**
Operating conditions for HG-ICP-MS.

| Parameter | Value/setting |
|---|---|
| $NaBH_4$ concentration | 0.5% (*w*/*v*) in 0.05 M NaOH |
| Acid concentration | 5% (*v*/v) $HNO_3$ |
| Reagent and sample uptake | 1 mL min$^{-1}$ |
| Nebulizer gas flow | 0.36 L min$^{-1}$ |
| HG gas flow | 0.50 L min$^{-1}$ |
| Cooling gas flow | 13.5 L min$^{-1}$ |
| Auxiliary gas flow | 0.8 L min$^{-1}$ |
| RF power | 1300 W |
| Sampling depth | 50 |
| Sample uptake time | 60 s |
| Signal stabilizing time | 40 s |
| Washout time | 60 s |
| Dwell time / isotope | 30 ms for $^{75}$As<br>10 ms for $^{72}$Ge, $^{89}$Y, $^{105}$Pd, $^{209}$Bi, $^{140}$Ce, $^{156}$CeO |
| Number of repetitions per sample | 5 |