Talanta 85 (2011) 1941–1947

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Arsenic determination by ICP-QMS with octopole collision/reaction cell. Overcome of matrix effects under vented and pressurized cell conditions

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A R T I C L E I N F O

Article history:
Received 23 December 2010
Received in revised form 28 June 2011
Accepted 7 July 2011
Available online 18 July 2011

Keywords:
Inductively coupled plasma mass spectrometry
Octopole collision/reaction cell
Arsenic
Matrix effect

A B S T R A C T

The determination of arsenic by inductively coupled plasma mass spectrometry (ICP-MS) in natural waters with high sodium and chloride content has been investigated. The instrument used is equipped with an octopole collision/reaction cell to overcome spectroscopic interferences. Thus, the optimization of collision/reaction gas flow rates is required when using a pressurized cell. A mixture of 2.9 mL min^{-1} of H_2 and 0.5 mL min^{-1} of He has been found to be suitable for the removal of $^{40}Ar^{35}Cl^+$ interference.

The effect of the introduction of small amounts of alcohol has also been studied in this work under both vented and pressurized cell conditions. It has been observed that the presence of 4% (v/v) of ethanol or methanol results in an increase in arsenic sensitivity. Moreover, under vented cell conditions the addition of alcohol also decreases the formation of polyatomic interference. However, this decrease is not observed under pressurized cell conditions.

Different elements have been studied as possible internal standards for arsenic determination in presence of high amounts of sodium. Good results have been obtained for rhodium and yttrium under both vented and pressurized cell conditions. Although the presence of alcohol in the sample matrix also affects their behaviour, rhodium and yttrium are still the most suitable elements to correct for these matrix effects.

Different experimental conditions have been compared for arsenic determination in spiked, certified and natural waters with high sodium and chloride content. The best results have been obtained under pressurized cell conditions, in the presence of ethanol and using rhodium as internal standard.

1. Introduction

Arsenic is a naturally occurring element present in the environment in both organic and inorganic forms. Arsenic is found in ground and surface waters as well as in many foods, and it can be combined with more than 150 different elements such as copper, lead or sulphide. Thus, living organisms are continuously exposed to the toxic arsenic species. It has been reported for many years that exposure to arsenic can cause a variety of adverse health effects, including skin and internal cancers or cardiovascular and neurological effects depending, principally, on its chemical form. Inorganic forms are considered to be the more toxic arsenic species. In general, arsenic is present in the environment due to mineral dissolution, but it can also be present as a result of industrial contamination, insecticides or atmospheric deposition. The World Health Organization (WHO) recommends less than 10 μg L^{-1} of arsenic to be present in drinking water [1,2].

The methods usually employed for the determination of trace arsenic concentrations include spectrometric techniques and electrochemical methods [3,4]. Inductively coupled plasma-mass spectrometry (ICP-MS) is one of the most widely applied analytical techniques for arsenic detection. However, it is well known that ICP-MS suffers from both spectroscopic and non spectroscopic interferences. Possibly, in arsenic determination, the most important drawback of quadrupole ICP-MS equipped with a conventional nebulizer is the formation of $^{40}Ar^{35}Cl^+$ interference obtained when moderate chloride (mg L^{-1}) containing samples are analyzed. As this interference cannot be solved from arsenic signal, results can be inaccurate, especially when low levels of arsenic are determined [3,5]. Spectroscopic interferences can be avoided using equipments with higher resolution, as double-focusing sector field instruments, but this is an expensive technique and is not always available [6,7]. Usually, the choice of non interfered isotopes can solve spectroscopic interferences since most elements have more than one isotope but, this choice is not available when working with monoisotopic elements like arsenic. Another way to overcome such interference is the use of an interference equation which allows the subtraction of polyatomic interferences on the ^{75}As signal. The

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doi:10.1016/j.talanta.2011.07.017

US Environmental Protection Agency (EPA) proposes the following equation:

$$^{75}\mathrm{As} = 1.000(^{75}\mathrm{C}) - (3.127)[(^{77}\mathrm{C}) - 0.815(^{82}\mathrm{C})]$$

where ^{75}C, ^{77}C and ^{82}C are counts measured on m/z 75, 77 and 82, respectively. This equation should provide a correction for chloride interference with adjustment for ^{77}Se [8]. Some authors considered that the contribution of krypton on m/z 82 should be taken into account and presented a modified interference equation [9,10]:

$$^{75}\mathrm{As} = 1.000(^{75}\mathrm{C}) - (3.127)[(^{77}\mathrm{C}) - 0.815(^{82}\mathrm{C}) + 0.883(^{83}\mathrm{C})]$$

However, in a recently published work, mass 82 showed strong spectroscopic interferences related with bromine ($^1H^{82}Br^+$) and/or calcium ($^1H^1H^{40}Ca^{40}Ca^+$) content which makes these equations unsuitable for correction on arsenic measurements [11]. Moreover, our research group has pointed out that the signal at $m/z = 83$ is strongly dependent on matrix composition and it shows an important increase when chloride and sodium are both present in the sample matrix [12].

Cold plasma conditions have also been used to reduce polyatomic interferences. However, these conditions cannot be used with elements that have high ionization potentials like arsenic [13,5]. Other efforts reported to reduce interferences included the use of mixed-gas plasma [14] or the separation of some ions by ion-exchange method before vapour generation [15].

The introduction of ICP-MS equipped with collision/reaction cell technology is another way to overcome problems linked with polyatomic interferences. In collision/reaction cell techniques, various gases such as H_2 or He or a combination of them can be efficiently employed to eliminate argon-based polyatomic ions without affecting the analyte of interest via chemical reactions or interactions [16–19]. In a previous work [12] we proposed a modified interference equation which has shown good results for arsenic determination in complex matrix samples under pressurized cell conditions. This equation can be written as:

$$^{75}\mathrm{As} = 1.000(^{75}\mathrm{C}) - (3.127)[(^{77}\mathrm{C}) - 0.321(^{78}\mathrm{C})]$$

On the other hand, it is well known that matrix effects can be very important in plasma based atomic spectrometric techniques, since moderate amounts of matrix ions can significantly change the analyte signal [20,21]. Several techniques can be used to correct these matrix effects, including standard addition, isotope dilution or internal standard calibration [22–26]. Obviously, as it has only one isotope, arsenic cannot be determined by the isotope dilution technique, although some authors have described an internal standard method that adopted the isotope dilution procedure, assuming ^{77}Se as a pseudo-isotope of arsenic [27]. Internal standardization is a useful method which is also used to correct instrumental drift [22]. However, the selection of proper internal standard isotopes can be challenging. An ideal internal standard must not be present (or in very low abundance) in the samples and its signal must change proportionally to that of the analyte. Some studies have been already carried out but the results are not equivalent in all cases [21]. The majority of authors pointed out that isotopes of similar mass give similar signal responses because the transmission of ions to the mass spectrometer depends on the mass of the ions due to the space charge effect. Although some authors state that the ionization potential should also be taken into account [28–30], some others found that this is a less import parameter [27] or even not related with matrix effects [31].

The effect of carbon-containing compounds on the analyte signal in ICP-MS has also been reported. These studies concluded that the enhancement or suppression of analyte signals depends on the volatility, mass and ionization potential of the analytes as well as the ICP-MS operating conditions. It has also been demonstrated that small amounts of alcohol enhance the element signal while higher amounts reduce it due to the resultant cooling of plasma. To explain this enhancement, three mechanisms were described: (1) the charge transfer reaction from the C^+ species to analyte atoms, (2) the improvement in the nebulization transport of the sample, and (3) the shift of the zone of maximum ion density in the plasma [31–37].

The present work aims to investigate the non spectroscopic interferences produced during arsenic determination in complex matrix aqueous samples containing high amounts of sodium and chloride and the strategies to overcome these interferences. The suitability of applying different internal standards together with approaches to overcome spectroscopic interferences such as pressurized cell conditions has been evaluated. Moreover, the presence of small amounts of alcohol in the samples is evaluated under both vented and pressurized cell conditions to develop a simple procedure to determinate As in complex matrix samples. The novelty of the work is the application of these strategies simultaneously and to study the cross effect over each other.

2. Material and methods

2.1. Instrumentation and reagents

Instrumentation used in this work consisted of an Agilent 7500c ICP-QMS equipped with an octopole collision/reaction cell. The operating parameters are shown in Table 1.

Some other parameters, such as ion lens settings, were adjusted daily to obtain maximum sensitivity and precision using 3 isotopes (^{7}Li, ^{89}Y and ^{205}Tl). The oxide level (CeO/Ce) was observed to be a critical value and was therefore maintained under 1 and 3% under vented and pressurized cell conditions, respectively.

All the chemicals used were of analytical reagent grade, and aqueous solutions were prepared in ultrapure MilliQ water obtained from a Millipore system. Sodium chloride and sodium nitrate were purchased from Panreac; hydrochloric acid with low arsenic content was acquired from Fluka and suprapure nitric acid from Merck. Ethanol was obtained from Panreac and methanol from Carlo Erba Reagents. One milligram per liter of arsenic solution was prepared by diluting the commercial 1000 mg L^{-1} solution from Tecknolab A/S. Internal standard solutions were prepared by diluting the necessary amount of each 1000 mg L^{-1} element standard solution from Romil LTD.

Slew-3 and CASS-4 certified reference materials (CRM) were obtained from the National Research Council of Canada. Slew-3 is estuarine water with a salinity of 15‰ and 1.36 μg L^{-1} of arsenic while CASS-4 is sea water with 30‰ of salinity and 1.11 μg L^{-1} of arsenic. Standard reference material 1643e, obtained from the National Institute of Standards and Technology of USA, is synthetic fresh water with 20,230 μg L^{-1} of sodium and 59.0 μg L^{-1} of arsenic.

Table 1
Operational parameters of ICP-MS.

Plasma power	1500 W
Nebulizer gas flow rate	0.9 L min^{-1}
Octopol potential	−14 V
Quadrupol potential	−13 V
Nebulizer	Babington
Nebulizer spray chamber	Scott type double path
Torch	Fassel (Quarz)
Sampling and skimmer cones	Nickel
Collision/reaction gases	He and H_2

2.2. Procedures

2.2.1. Effect of the collision/reaction gases flow rates

For this purpose different solutions in 2% HNO_3 with increasing concentration of chloride coming from HCl were prepared. A solution containing 2 $\mu g\,L^{-1}$ of arsenic as well as a blank in 2% HNO_3 were also prepared.

Two ramps with hydrogen flow rates from 0 to 3 $mL\,min^{-1}$ were applied for each solution. The first ramp was developed without helium gas in the collision/reaction cell while for the second ramp a 0.5 $mL\,min^{-1}$ He flow rate was set.

2.2.2. Alcohol effect on m/z signal

Two sets of experiments were carried out to evaluate the effect of alcohol on ^{75}As and $^{40}Ar^{35}Cl^+$ signals respectively.

For the first set of experiments solutions containing 10 $\mu g\,L^{-1}$ of arsenic, 5000 $mg\,L^{-1}$ of Na^+ and 2% HNO_3 were prepared with different amounts of methanol or ethanol. Signals at *m/z* 75 were determined in these samples at different nebulizer gas flow rates with and without pressurizing the collision/reaction cell.

The second set of samples consisted of solutions containing 5000 $mg\,L^{-1}$ of Na^+ and 2% HNO_3. HCl was added to each sample to obtain four sets of three samples with 5000, 10,000, 15,000 and 20,000 $mg\,L^{-1}$ of Cl^- each set. In one of the samples of each set 4% of methanol was added, a second sample was spiked with 4% of ethanol and the third sample was not modified. The signal at *m/z* 75 produced by $^{40}Ar^{35}Cl^+$ was determined in these samples with and without pressurizing the collision/reaction cell.

2.2.3. Internal standard studies

Solutions containing increasing concentrations of Na^+ were prepared from $NaNO_3$. The necessary amounts of As, Ga, Ge, Y, Rh, Ir, Pt, Au and Tl standard solutions were added in each solution to obtain 2 $\mu g\,L^{-1}$ of each element. Three sets of solutions were prepared in water, 4% ethanol and 4% methanol. Element intensities were measured with and without pressurizing the collision/reaction cell.

2.2.4. Sample preparation

Four synthetic samples were prepared in HCl and NaCl solutions containing 10,000 $mg\,L^{-1}$ of chloride. For each medium two aliquots were spiked with arsenic to concentrations of 2 and 8 $\mu g\,L^{-1}$ and rhodium as internal standards. Four additional samples were prepared in the same way but adding 10 $\mu g\,L^{-1}$ of selenium. All samples were acidified with HNO_3 to 2% of acid. This set of samples was analyzed twice with vented and pressurized cell conditions. The same set of samples was also prepared in 4% of ethanol and analyzed by ICP-MS twice (with vented and pressurized cell).

Arsenic was determined in three different certified reference materials: CASS-4, Slew-3 and 1643e. For this purpose, 4 mL of each sample (0.5 mL for 1643e) was spiked with rhodium as an internal standard; suprapure HNO_3 was also added until an acidity of 2% was reached. Finally, MilliQ water was added to a final volume of 5 mL. Those samples were analyzed by ICP-MS with and without pressurizing the collision/reaction cell. The same procedure was applied to these samples but 4% of ethanol was added.

Four groundwaters, collected in Pannonian Basin, Romania were diluted or remixed by EAWAG (Swiss Federal Institute of Aquatic Science and Technology) to obtain samples with variable element concentration. Arsenic was determined in those waters in order to participate in the ARS-Interlaboratory programme [38].

3. Results and discussion

3.1. Effect of collision/reaction gas flow rates

It is well known that collision/reaction cell devices can be used to reduce spectroscopic polyatomic interferences such as $^{40}Ar^{35}Cl^+$. In such systems, background and analytical signals are affected by the flow rates of the collision/reaction gases. Thus, the study of those flow rates is required. As He is recommended by manufacturers as a collision gas for arsenic determination, it was introduced in the collision/reaction cell at different flow rates varying from 0 to 2 $mL\,min^{-1}$. However, the signal at *m/z* 75 produced by 5000 and 15,000 $mg\,L^{-1}$ of chloride solution was always higher than the signal produced by 2 $\mu g\,L^{-1}$ of As at the same mass to charge ratio, demonstrating that the use of helium alone in the collision/reaction cell was not enough to eliminate $ArCl^+$ interference. In this sense, studies including H_2 as a collision/reaction gas were carried out. When no He was introduced in the collision/reaction cell and the H_2 flow rate was varied from 0 to 5 $mL\,min^{-1}$, both interference and analyte signals decreased with the increasing gas flow rate but in any case the analyte signal was higher than the interference signal. As can be seen in Fig. 1, when the He flow rate was fixed at 0.5 $mL\,min^{-1}$ and the H_2 flow rate was varied from 0 to 5 $mL\,min^{-1}$, interference and analyte signals showed a similar trend. However, between 2 and 3 $mL\,min^{-1}$ of H_2 the arsenic signal was higher than the interference signal and at 2.9 $mL\,min^{-1}$ the interference signal was near to the background while the analyte signal for 2 $\mu g\,L^{-1}$ of As was ten times higher. Thus, flow rates of 0.5 and 2.9 $mL\,min^{-1}$ for He and H_2, respectively, were found to give the largest difference between interference and analyte signals and were used in subsequent experiments that included the pressurization of the collision/reaction cell. These results are in good agreement with those obtained by Darrouzès et al. [18] In that work similar gas flow rates give maximum SBR value for *m/z* = 75 in a 1 $g\,L^{-1}$ NaCl solution, employing the same instrument (Agilent 7500c). This instrumental systems allows the decrease or even suppression of interferences due to collisions which induce some reactions (i.e. charge transfer, dissociation, etc.) or by kinetic energy discrimination (KED), because polyatomic interferences loss more kinetic energy than analyte in the cell. Due to the little potential difference used between the octapole and the quadrupole (−1 V), this KED can take place.

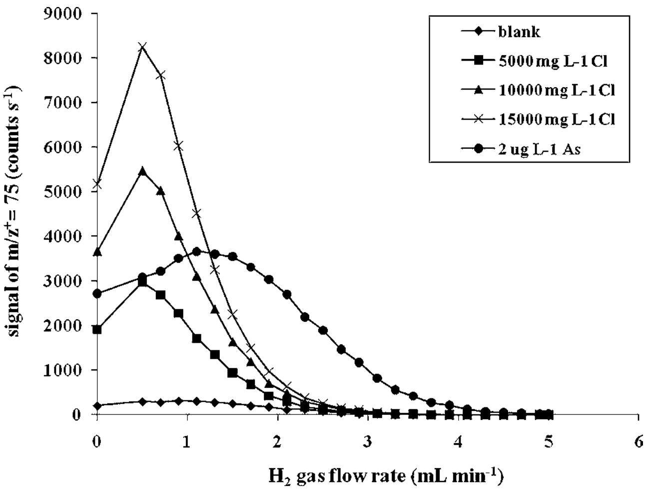

Fig. 1. H_2 gas flow effect on interference and analyte signals.

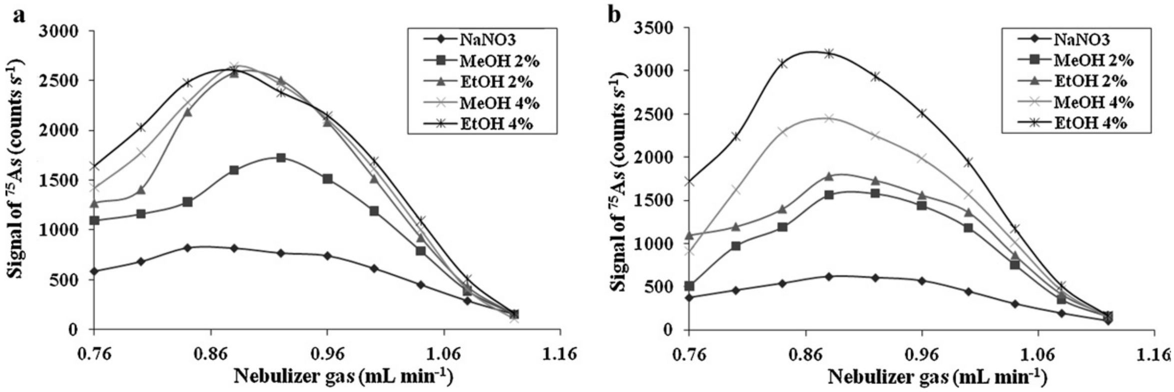

Fig. 2. Signal intensities as a function of nebulizer gas flow rate in different percentages of methanol and ethanol using a vented cell (a) and a pressurized cell (b).

3.2. Effect of addition of alcohol on the m/z signal

Solutions containing 2% of HNO_3, 10 $\mu g\,L^{-1}$ of arsenic, 5000 $mg\,L^{-1}$ of sodium and different percentages of methanol and ethanol were analyzed by using the routine ICP-MS conditions presented in Table 1. In Fig. 2, it can be observed that the signal produced by ^{75}As in those conditions is higher when alcohol is added to the solution and also that this enhancement is more substantial in 4% of alcohol than in 2% for both methanol and ethanol. Some authors have reported that the introduction of small amounts of alcohol (1% of methanol) enhances the analyte signal whereas higher amounts of alcohol produce a local cooling effect in the central channel of the plasma that suppresses some analyte signals. Results obtained in these experiments could indicate that the signal enhancement of ^{75}As is due to a charge transfer reaction between positively charged carbon species and ^{75}As in the central channel of the plasma as some investigators have already observed [34,35]. It is well known that the position of the zone of maximum M^+ density in the central channel of the ICP depends strongly on the nebulizer gas flow rate [35,36]. Thus, an optimization of the nebulizer gas flow rate is required. Fig. 2 illustrates the variation of signal intensity as a function of nebulizer gas flow rate in 2% HNO_3, 2–4% of methanol and 2–4% ethanol. As depicted in that figure, for all solutions and both cases, with and without pressurization of the collision/reaction cell, the maximum signal intensity was obtained around 0.9 $L\,min^{-1}$. Thus, the next experiments were carried out using a fix nebulizer gas flow rate of 0.9 $mL\,min^{-1}$.

When comparing the results under vented and pressurized cell conditions the results show an even greater increase of the signal intensity under pressurized cell conditions. This greater increase, which is between 30 and a 60% higher under pressurized cell conditions and a 4% alcohol addition, has been confirmed on different days, with different initial signal intensities. This behaviour shows that the presence of alcohol promotes another effect, apart from the charge transfer reaction, that leads to a higher transition of ^{75}As ions in the pressurized cell. A possible explanation of this effect would be related with the energy distribution of the ion beam in presence and absence of ethanol. To confirm this fact, the energy distribution of the ion beam has been calculated as explained by Dexter et al. [39]. Surprisingly, the energy distribution of the sampled ion beam peaks at a Quadrupol Bias ≈ -1 V in both cases, with and without ethanol, indicating a similar energy of the ion beam.

It has also been reported that the introduction of small amounts of alcohol to the sample solution reduces the formation of $^{40}Ar^{35}Cl^+$ interference. This suppression is mainly attributed to the competitive formation of carbides with Ar or Cl or both [37]. The effect of 4% of methanol and ethanol on the $^{40}Ar^{35}Cl^+$ signal in solutions containing different amounts of chloride and a fixed amount of sodium is depicted in Fig. 3. As expected, when no gas is introduced in the collision/reaction cell, a decrease of $^{40}Ar^{35}Cl^+$ signal intensity is observed when alcohol is added to the sample solutions. Moreover, it can be seen that this suppression is more important in higher chloride concentrations. In contrast, when He and H_2 are introduced in the collision/reaction cell, the formation of $^{40}Ar^{35}Cl^+$ seems to be similar in presence and in absence of alcohol in the sample solutions. However, the signal under these conditions is very low and cannot be attributed with certainty to $^{40}Ar^{35}Cl^+$.

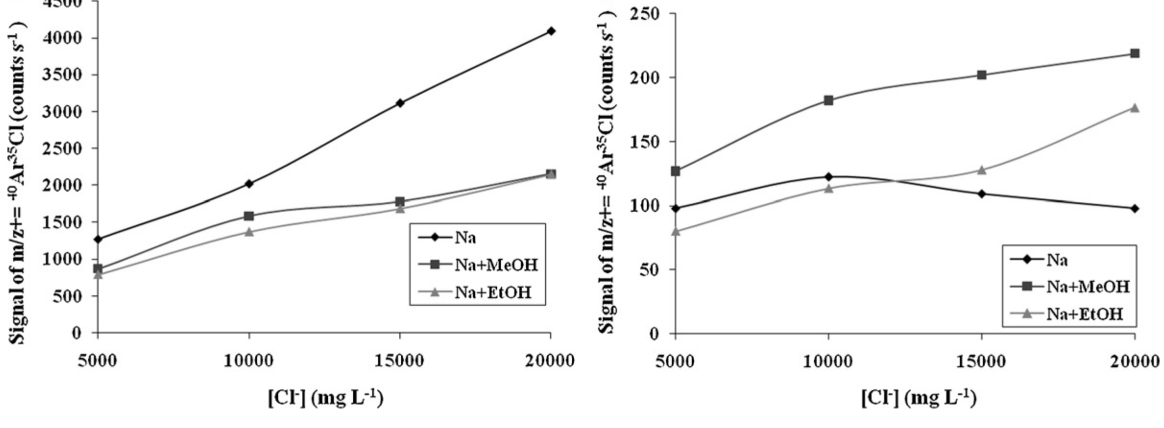

Fig. 3. $^{40}Ar^{35}Cl^+$ interferences as a function of Cl^- concentration coming from HCl in 5000 $mg\,L^{-1}$ of Na^+ solution and 4% of alcohol with a vented cell (a) and a pressurized cell (b).

Table 2
Figures of merit of the calibration curves using rhodium as internal standard ($n = 7$).

	Vented cell		Pressured cell	
	Without ethanol	With ethanol	Without ethanol	With ethanol
Slope	0.0827	0.3266	0.05878	0.2505
r	0.9999	0.9998	0.9988	0.9999
LOD ($\mu g\,L^{-1}$)[a]	0.2	0.3	0.7	0.2

[a] Calculated as three times the standard deviation of the calibration curve.

Calibration curves have been obtained under four experimental conditions using vented and pressurized cell conditions and in each case using standards with and without a 4% ethanol addition. The more important features of these calibration curves have been summarized in Table 2. A clear increase in the sensitivity was observed when ethanol-containing standards were used under both vented and pressurized cell conditions (i.e. 3.9 and 4.3 times respectively). This increase is again more important under pressurized cell conditions, even though internal standard was used, which means that the dependent variable (y) is a signal ratio. Although, the addition of ethanol does not improve the limit of detection when using a vented cell, a substantial improvement can be observed under pressurized cell conditions. This lack of improvement when no gas is added to the cell, can be attributed to the slightly worse linearity obtained in this case, giving an increase of the standard deviation of the calibration curve.

3.3. Internal standards evaluation

The internal standard method has been widely used in ICP-MS to correct for signal drifts and for matrix effects. However, there are some factors that have limited the applicability and accuracy of the internal standard method: the internal standard should not be present in the sample at all or only at a negligible amount and the internal standard signal should behave in the same manner as the analyte signal in different matrix conditions [27].

Eight elements were studied as internal standards for arsenic. The internal standards selected were gallium, germanium, yttrium, rhodium, iridium, platinum, gold and thallium; their elemental mass and ionization potential are described in Table 3. Yttrium and rhodium are two elements commonly used as internal standards in ICP-MS as they both have mid-range masses and ionization potentials. Some authors claim that atomic mass is the most important factor to take into account when choosing an internal standard and this mass should be near to the analyte mass [30]. However, as some investigators stated [28], ionization in the plasma depends directly on the ionization potential, so the ionization potential should be also considered. In this sense, germanium and gallium were studied because they were similar in mass to arsenic while iridium, platinum and gold were chosen because they were similar to arsenic in terms of ionization potential. Thallium was included in the internal standard studies because it has similar ionization potential to yttrium and its mass is similar to iridium, platinum and gold.

Table 3
Mass and ionization potential of different isotopes used as internal standards.

Element	Isotope mass	Ionization potential
Ga	69	5.999
Ge	72	7.620
As	75	9.789
Y	89	6.217
Rh	103	7.459
Ir	192	8.967
Pt	195	8.959
Au	197	9.226
Tl	205	6.108

In Fig. 4, the signal for each element in different concentrations of sodium (from 5000 to 20,000 $mg\,L^{-1}$) has been normalized by the signal of the element in the absence of sodium and divided by the normalized arsenic signal to elucidate which element behaves more similarly to arsenic in the presence of sodium. In this figure, the signal of arsenic at different concentrations of sodium divided by the signal of this element in the absence of sodium has also been included to make clear the effect of sodium on this element. As can be observed, the presence of different amounts of sodium reduces the arsenic signal and in some cases reductions of more than 50% were obtained. This fact demonstrates that the use of internal standard is required. In Fig. 4, light isotopes with low atomic mass (gallium, germanium, yttrium and rhodium) behave more similarly to arsenic than heavy ones in the presence of different amounts of sodium and under pressurized cell conditions. From these results, a more important effect of the sodium matrix is observed for heavy isotopes. When 4% of ethanol is added to all solutions the difference between light and heavy elements is even clearer. Moreover, the ionization potential does not seem to make an effect, as the behaviour of thallium is similar to that of iridium or platinum which has more similar ionization potentials to arsenic. The results could lead to the conclusion that gallium, germanium, yttrium and rhodium would be suitable internal standards for arsenic determination. However, it should be taken into account that while yttrium and rhodium are rare element, gallium and germanium, though in trace concentrations, are usually present in natural samples. Vented cell conditions (data not shown) gives similar results to those observed with the addition of gas in the collision cell.

Based on these results and taking into account the more constant behaviour of rhodium under the different conditions studied (lower S.D. values have been calculated) and the fact that it is usually absent in most matrices, this element was used as internal standard in subsequent experiments.

3.4. Analysis of spiked samples, CRM and real samples

Samples described in Section 2.2.4 were analyzed by ICP-MS twice, with vented cell and pressurized cell. Results for spiked samples are depicted in Fig. 5. When the collision/reaction cell was not pressurized, the interference equation was required as the amount of $^{40}Ar^{35}Cl^{+}$ was considerable. The interference equation used in this work took into account signals given by m/z 77 and m/z 82.

As can be observed in Fig. 5, the results obtained, when 4% of ethanol was added, were usually more accurate than the results obtained without any alcohol. This effect could be related to the fact that in the presence of small amounts of alcohol, the analyte signal is enhanced while the interference formation in the plasma decreases. Moreover, it is also possible that the important matrix effect produced by ethanol, which is corrected thanks to the fact the standards were prepared with the same alcohol content, minimizes other possible matrix effects.

Table 4 displays the determined concentration of arsenic in three CRM (CASS-4, SLEW-3 and 1643e) with associated specific uncertainty. As it can be observed, the results obtained when

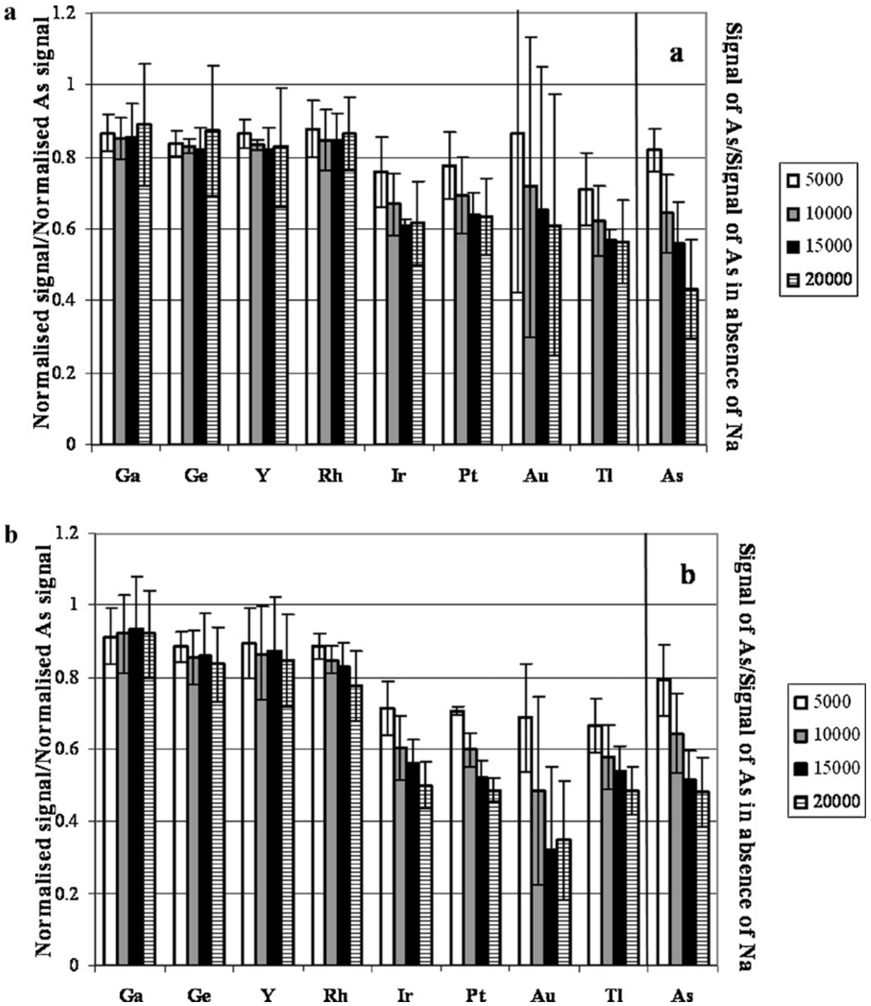

Fig. 4. Effect of sodium concentration on different element signals with pressurized cell conditions. The signal of each element in a sodium concentration is normalized by the signal in absence of sodium and divided by the normalized arsenic signal. Normalized arsenic signal (signal with sodium/signal without sodium) has also been included. Solutions without (a) and with (b) a 4% ethanol addition. Error bars indicate the standard deviation of 3 replicates.

using a vented cell were far more different than the certified value, demonstrating that the interference equation does not usually work properly in real samples where the matrix is quite complex. However, the use of 4% of ethanol resulted in a decrease of interference formation in the plasma, as has been previously demonstrated, and, as a consequence, more accurate results were obtained. On the other hand, when the collision/reaction cell was pressurized, the determined arsenic in the CRM samples was in good agreement with the certified value, with recoveries ranging from 83 to 91% without ethanol. When a 4% ethanol solution is used, the results are very similar and recoveries from 89 to 109% are obtained. This fact confirms the absence of the spectral polyatomic interferences that decrease in the presence of ethanol.

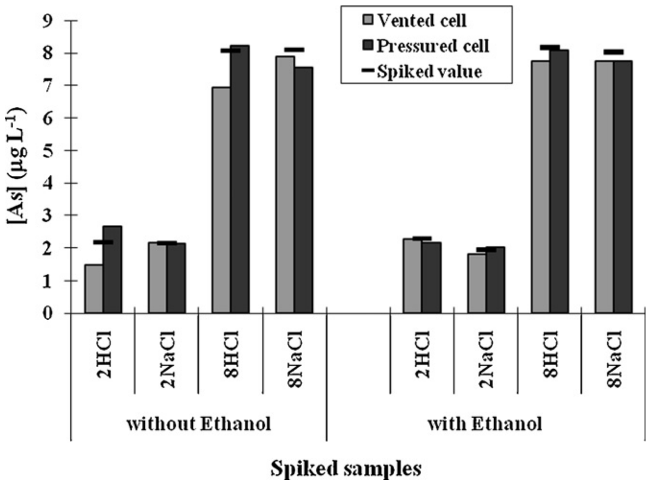

Fig. 5. Arsenic concentration found in spiked samples which contain 10,000 mg L^{-1} of chloride coming from HCl or NaCl when adding 4% of ethanol or not and using rhodium as the internal standard.

It should be mentioned that the interference equation proposed in [12], which used the isotope 78 to correct the signal coming from selenium over the mass 77, has also been tested with those spiked and CRM samples. Using this equation no differences have been observed with the results obtained when ethanol solutions are used. However, when no ethanol was added, determined concentrations slightly differed from certified values.

In addition, four samples were analyzed within an annual intercalibration exercise organized by EAWAG which included arsenic determination [38]. The samples (ARS 29-32) were prepared from natural groundwater collected on 03 April 2009 in the Pannonian Basin, Romania. The results obtained, together with the indicative values, are summarized in Table 5. As can be observed good agreements with the indicative values provided by the organization were obtained.

Table 4
Arsenic concentration ($\mu g\,L^{-1}$) in certified reference materials using rhodium as internal standard.

	Vented cell				Pressured cell				Certified value	
	Without ethanol		With ethanol		Without ethanol		With ethanol			
	[As]	SD	[As]	SD	[As]	SD	[As]	SD	[As]	SD
CASS-4	19.7	0.7	5.1	0.1	1.0	0.1	1.08	0.03	1.1	0.2
SLEW-3	11.5	0.8	3.30	0.03	1.2	0.2	1.48	0.08	1.36	0.09
1643e	52.1	0.8	52.7	0.7	49.0	0.6	52.9	0.1	59.0	0.7

Table 5
Arsenic concentration ($\mu g\,L^{-1}$) determined in ARS using pressurized cell conditions and rhodium as internal standard.

	Without ethanol		With ethanol		Indicative values	
	Average	SD	Average	SD	Average	SD
ARS 29	60.3	0.2	60	1	66	7
ARS 30	24.2	0.3	24.3	0.1	28	3
ARS 31	168	2	169	3	185	15
ARS 32	296.9	0.5	292	3	330	26

4. Conclusions

A study has been conducted for the accurate determination of arsenic by ICP-MS in complex matrix aqueous samples. The effect of using a pressurized collision/reaction cell together with other strategies to overcome matrix effects has been evaluated.

Octopole collision/reaction cell gas flow rates were adjusted to remove $^{40}Ar^{35}Cl^{+}$ interference at flow rates of 2.9 mL min^{-1} of H_2 and 0.5 mL min^{-1} of He.

The presence of different amounts of alcohols enhances the intensity of arsenic at the same time that the formation of polyatomic interferences decreases in the plasma. This enhancement depends on the nebulizer gas flow rate and is more important under pressurized cell conditions. This fact indicates that the presence of alcohol promotes another effect related to the pressurization of the cell but it has been demonstrated that this is not due to the variation of the distribution energy of the ion beam.

It was found that elements with similar atomic mass behave more similarly to arsenic than elements with similar ionization potential, in the presence of different amounts of sodium and under different experimental conditions, such as the use of pressurized collision/reaction cells and the addition of carbon containing compounds. Therefore, elements with similar mass can be used as internal standards if they are not present in the samples.

The results obtained in spiked aqueous samples and certified reference materials show that the alcohol addition slightly improves the accuracy and precision under pressurized collision/reaction cell conditions. Moreover, a comparison of the results obtained with and without alcohol addition can be used to verify the absence of spectral interferences. Good results have been obtained applying this methodology in an intercalibration exercise.

Acknowledgments

The Spanish Ministry of Education and Science supported this work through project CGL2007-66861-C04-02 and grant BES-2005-6962.

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