

## DETERMINATION OF ARSENIC IN HIGH-SALINE MINERAL WATERS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Determination of As by ICP-MS is aggravated by the presence of  $\text{Cl}^-$  ions, forming in the plasma the  $^{40}\text{Ar}^{35}\text{Cl}^+$  ion from which the  $^{75}\text{As}^+$  ion cannot be discriminated. The presence of  $1\,000\text{ mg l}^{-1}\text{ Cl}^-$  gives rise to a signal corresponding approximately to  $3\text{ }\mu\text{g l}^{-1}\text{ As}$ . Interferences can be reduced by about 70% by the addition of 4 vol.% methanol, the remaining fraction has to be corrected mathematically. A treatment based on the measured intensities of the  $^{40}\text{Ar}^{37}\text{Cl}^+$  or  $^{35}\text{Cl}^{16}\text{O}^+$  ions can result in overcorrection; the signal of the  $^{35}\text{Cl}^+$  ion was found more suitable for the purpose. The  $^{35}\text{Cl}^+ / ^{40}\text{Ar}^{35}\text{Cl}^+$  signal ratio is constant in the concentration range of  $400\text{--}1\,000\text{ mg l}^{-1}\text{ Cl}^-$  at least. The detection limit ( $3\sigma$ ) found by measuring solutions which contained various amounts of  $\text{Cl}^-$  ions was  $0.03\text{ }\mu\text{g l}^{-1}\text{ As}$ . This two-step correction for interferences was applied to the analysis of a mineral water with a chloride concentration of  $1\,400\text{ mg l}^{-1}$ . The results obtained by the calibration graph method and by the standard addition method were in a good agreement ( $1.50\text{ }\mu\text{g l}^{-1}$  vs  $1.44\text{ }\mu\text{g l}^{-1}$  As, respectively), whereas a high overestimation ( $4.2\text{ }\mu\text{g l}^{-1}\text{ As}$ ) resulted if the correction was omitted. Relative standard deviation of the determination was 3.2%.

**Key words:** Arsenic; Mineral water; Inductively-coupled plasma mass spectrometry.

The advantages of inductively-coupled plasma mass spectrometry (ICP-MS) in the quantification of elements include, in particular, a high sensitivity of determination and a wide dynamic range of the method. In some cases such as the determination of arsenic, however, the matrix effect, particularly that of accompanying salts, is a limitation.

The total salt content of solutions analyzed by ICP-MS is a limiting factor. Apart from a possibility of blockage of the interface cones, easily ionizable elements, frequently present in mineral water (Na, K, Mg, Ca), appreciably affect the ionization equilibrium in the plasma and ultimately reduce the signals of the remaining ions. This effect can be eliminated by using a suitable internal standard. For arsenic, yttrium can serve the purpose well<sup>1</sup>.

The isobaric overlap is another kind of interferences. Natural arsenic contains a single stable isotope  $^{75}\text{As}$ , the mass of which is virtually identical with that of the polyatomic ion of  $^{40}\text{Ar}^{35}\text{Cl}^+$ , which is formed in the argon plasma by reaction with chloride ions present in the sample matrix. There are several ways to eliminate or, at least, reduce the effect of chloride on the quantification of arsenic. The separation of

the two elements is most radical. This can be achieved by separating arsenic in the form of the hydride,  $\text{AsH}_3$  (see, *e.g.*, ref.<sup>2</sup>), or by separating chloride by liquid chromatographic treatment<sup>3,4</sup>. The second way to suppress interferences consists in a modification of the plasma and finding a plasma composition limiting the formation of the interfering  $\text{ArCl}^+$  ion. This can be achieved by feeding nitrogen<sup>5,6</sup> or methane<sup>7</sup> into the plasma. Similarly, the  $\text{ArCl}^+$  signal can be substantially reduced by adding organic compounds to the solution analyzed. The mechanism of this effect has been sought in reduced ionization in the plasma and/or establishment of different conditions, suppressing the formation of  $\text{ArCl}^+$  ions in favour of the competitive  $\text{CCl}^+$  ion<sup>8</sup>. The organics to be added are usually ethanol<sup>9</sup> or methanol<sup>10</sup> at a concentration of 3–4 vol.%. As a drawback of this approach, the interferences are not eliminated completely, the  $\text{ArCl}^+$  ion still exerting some effect. The last approach to elimination of interferences consists in a mathematical correction treatment. The correction based on the calculation

$$I(\text{As}) = I(75) - \frac{X(^{35}\text{Cl})}{X(^{37}\text{Cl})} \left( I(77) - \frac{X(^{77}\text{Se})}{X(^{82}\text{Se})} I(82) \right), \quad (1)$$

where  $I(m/z)$  is the signal intensity measured on proper  $m/z$ ,  $I(\text{As})$  is the corrected signal intensity and  $X$  means the isotope abundance, is frequently used. This correction is convenient in that being based on the isotope composition of the elements involved, the constants are independent of the conditions of measurement. Drawbacks include the fact that the signals at  $3m/z$  have to be measured, whereby the error of measurement increases. Moreover, this correction is not final either. In fact, the  $I(82)$  signal may not be solely due to  $^{82}\text{Se}$  ions; the  $^{34}\text{S}^{16}\text{O}_3^+$  or  $^1\text{H}^{81}\text{Br}^+$  ions also contribute. As pointed out in ref.<sup>11</sup>, application of Eq. (1) can result in overcorrection of the signal, leading to a bias and thus correction based on measurement of the signal of the  $^{35}\text{Cl}^{16}\text{O}^+$  ion was used:

$$I(\text{As}) = I(75) - k_1 I(51). \quad (2)$$

The factor  $k_1$  is determined before or during the analysis by analyzing a solution containing  $\text{NH}_4\text{Cl}$  or  $\text{NaCl}$  and calculating the factor as the  $^{40}\text{Ar}^{35}\text{Cl}^+ / ^{35}\text{Cl}^{16}\text{O}^+$  signal ratio. The presence of vanadium in the analyzed solution, consisting mainly of the  $^{51}\text{V}$  isotope, can also bring about a wrong correction. Here, the weak signal of the molecular ion ( $^{35}\text{Cl}^{16}\text{O}^+$ ) can be distorted by a strong signal of the atomic ion ( $^{51}\text{V}^+$ ). Direct measurement of the signal of the  $^{35}\text{Cl}^+$  ion is assumed to be better for making the correction. In fact, the signal may be distorted by the presence of the  $^{34}\text{S}^1\text{H}^+$  ion but this effect can be neglected: first, the signal of  $^{35}\text{Cl}^+$  is approximately 2 000 times more intense than that of the molecular ion  $^{35}\text{Cl}^{16}\text{O}^+$ , and second, the interfering  $^{34}\text{S}$  isotope is of rather

low abundance (4.21%). Thus the strong atomic ion ( $^{35}\text{Cl}^+$ ) can be distorted only by weak molecular ion ( $^{34}\text{S}^1\text{H}^+$ ). The correction is based on the relation

$$I(\text{As}) = I(75) - k_2 I(35) . \quad (3)$$

The factor  $k_2$  is determined by measuring one or more solutions containing NaCl and calculating the corresponding  $I(75)/I(35)$  ratio. Possible inaccuracy of the mathematical correction can be minimized by methanol addition. In the combined procedure, mathematical correction is applied to the residual interferences only, owing to which the correction error, if any, is smaller.

## EXPERIMENTAL

### Reagents

For both elements used (As and Y), stock solutions of chemicals (Analytica, Prague, Czech Republic) were prepared at concentrations of 1 000 mg l<sup>-1</sup>, working solutions being obtained by dilution with redistilled water. Both NaCl and HNO<sub>3</sub> (Merck, Darmstadt, Germany) as well as methanol employed to mask interferences (Lachema, Brno, Czech Republic) were of reagent grade purity.

### Apparatus

The measurements were performed on a Perkin–Elmer SCIEX Elan 6000 mass spectrometer (Perkin–Elmer SCIEX, Norwalk, CT, U.S.A.) equipped with a cross-flow nebulizer and a Scott-type spray chamber. The major operating conditions are given in Table I. When optimizing the Ar nebulizer flow rate and the radio-frequency (r.f.) power, the plasma was allowed to stabilize for a minimum of 30 s prior to each measurement under modified conditions.

### Determination of Arsenic in Mineral Waters

The analytical procedure was as follows. To 50 ml volumetric flasks, 25 ml aliquots of water sample and 1 ml portions of concentrated HNO<sub>3</sub> were added. Carbon dioxide was removed from the sample by heating, the solution allowed to cool down, and 1 ml of a solution of 5 mg l<sup>-1</sup> Y and 2 ml of methanol were added. The flasks were made up to the volume.

## RESULTS AND DISCUSSION

### *Quantification of Interferences*

To quantify the effect of interferent on the determination of analyte, Vanhoe *et al.*<sup>12</sup> introduced the interference factor  $i_f$ :

$$i_f = \frac{\text{apparent concentration of analyte}}{\text{concentration of interferent}} \cdot 10^6 . \quad (4)$$

The authors determined this interference factor to be approximately 16 for the interfering effect of chloride in the determination of arsenic. As it will be shown later, the value of interference factor is not constant. In fact, it depends particularly on the Ar nebulizer flow rate and on the r.f. generator power. The design and condition of the plasma torch play a role as well and so the degree of interference should be determined and optimized in each individual case.

### *Effect of Addition of Methanol on Spectral Interferences*

The effect of addition of methanol to suppress interferences arising from the chloride ion was examined on solutions containing 1 000 mg l<sup>-1</sup> Cl<sup>-</sup> (prepared from NaCl), yttrium as an internal standard at a concentration of 100 µg l<sup>-1</sup>, and HNO<sub>3</sub> as an acidifying agent at a final concentration of 2 vol.%. Methanol was present at concentrations of 0, 2, 4, 6, 8, and 10 vol.%. The signal intensity for the <sup>40</sup>Ar<sup>35</sup>Cl<sup>+</sup> ion was measured applying an Ar nebulizer flow rate of 0.75 l min<sup>-1</sup> and r.f. power of 1 000 W using the calibration solution containing 10 µg l<sup>-1</sup> As. It was found that increasing the methanol concentration above 4 vol.% has no marked effect; moreover, concentrations in excess of 10 vol.% can bring about plasma instability. The attained reduction of interference stemming from <sup>40</sup>Ar<sup>35</sup>Cl<sup>+</sup> was about 70%. All subsequent measurements were performed using solutions containing 4 vol.% methanol.

### *Effect of Ar Nebulizer Flow Rate and Radio-frequency Generator Power on Spectral Interferences*

The effect of the Ar nebulizer flow rate on the <sup>40</sup>Ar<sup>35</sup>Cl<sup>+</sup> and <sup>75</sup>As<sup>+</sup> signals and on their ratio has been studied, for instance, in refs<sup>8,9</sup>. The two studies, however, were carried out using a rather high r.f. power (1 350 and 1 320 W, respectively), which may not be very suitable, as it will be demonstrated later. Moreover, when analyzing solutions which contain methanol, such a high power requires platinum cones because nickel

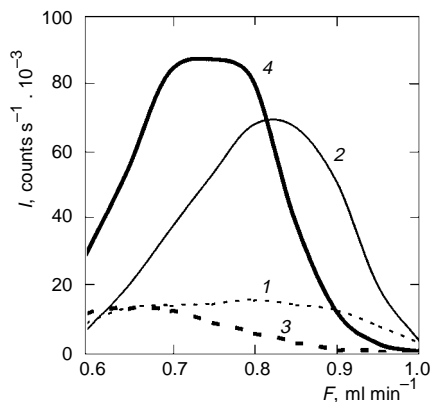


FIG. 1  
Dependence of signal intensity,  $I$ , of the <sup>40</sup>Ar<sup>35</sup>Cl<sup>+</sup> (1, 3) and <sup>75</sup>As<sup>+</sup> (2, 4) ions on the Ar nebulizer flow rate,  $F$ , with (3, 4) and without (1, 2) 4 vol.% of methanol added

cones can be damaged<sup>8</sup>. The dependence of the  $^{40}\text{Ar}^{35}\text{Cl}^+$  and  $^{75}\text{As}^+$  signals (at 1 000 mg l<sup>-1</sup> Cl<sup>-</sup>, 10 µg l<sup>-1</sup> As) on the Ar nebulizer flow rate for an r.f. power of 1 000 W is shown in Fig. 1 (2 vol.% HNO<sub>3</sub> or 2 vol.% HNO<sub>3</sub> + 4 vol.% methanol). The figure demonstrates a slight increase in the  $^{75}\text{As}^+$  signal (from 67 400 to 82 900 counts s<sup>-1</sup>) and a shift of the  $^{40}\text{Ar}^{35}\text{Cl}^+$  intensity maximum towards lower Ar nebulizer flow rates (from 0.80 to 0.65 l min<sup>-1</sup>) accompanied by a slight decrease in the value of this maximum (from 15 500 to 13 000 counts s<sup>-1</sup>). The combined effect of these factors appears in the signal offset from the background expressed through the interference factor. Its dependences on the Ar nebulizer flow rate pass through a minimum (lying at 0.8 ml min<sup>-1</sup> without methanol or at 0.90 ml min<sup>-1</sup> if the methanol was present); however, as it will be demonstrated later, the region of maximum sensitivity is more convenient for the analysis than the region of minimum interferences.

The behaviour of the two ions examined,  $^{40}\text{Ar}^{35}\text{Cl}^+$  and  $^{75}\text{As}^+$ , is also affected by the r.f. power, as shown in Fig. 2 for a solution containing 10 µg l<sup>-1</sup> As, 1 000 µg l<sup>-1</sup> Cl<sup>-</sup> and 4 vol.% methanol. The Ar nebulizer flow rate was 0.775 l min<sup>-1</sup>. The increase in the r.f. power was accompanied by an increased sensitivity (the As signal increased from approximately 80 000 counts s<sup>-1</sup> at 1 000 W to approximately 115 000 counts s<sup>-1</sup> at 1 200 W) but, at the same time, the interference factor increased unfavourably as well. The value of 1 000 W, recommended by the manufacturer, seems to be a reasonable compromise and hence it was used in subsequent measurements.

### *Mathematical Correction for Residual Interferences After Addition of Methanol*

By adding 4 vol.% methanol, the interference from chloride ions was reduced to about 30%. This residual interference has to be eliminated by mathematical treatment. Before the correction based on Eq. (3) can be used, the independence of the multiplication factor  $k_2$  ( $I(75)/I(35)$  intensity ratio) from the Cl<sup>-</sup> concentration has to be proved. This was verified by analyzing solutions containing chloride concentrations of 200, 400,

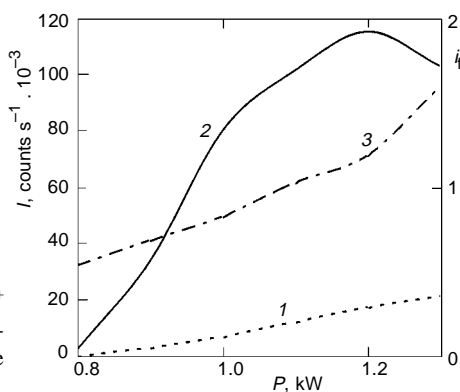


FIG. 2

Dependence of signal intensity,  $I$ , of the  $^{40}\text{Ar}^{35}\text{Cl}^+$  (1) and  $^{75}\text{As}^+$  (2) ions and of the interference factor,  $i_f$  (3), on the r.f. generator power,  $P$ , in the presence of 4 vol.% methanol

600, 800, and 1 000 mg l<sup>-1</sup> (2 vol.% HNO<sub>3</sub>, 4 vol.% methanol, 100 µg l<sup>-1</sup> Y as an internal standard, Ar nebulizer flow rate 0.75 l min<sup>-1</sup>, r.f. power 1 000 W). Figure 3 demonstrates that the ratio was independent on the concentration of chloride, ρ, in the range from 400 to 1 000 mg l<sup>-1</sup> Cl<sup>-</sup> at least. Minor deviations can be explained in terms of the experimental error.

The detection limit for this two-step interference correction procedure was determined as follows. Eight solutions containing 400 to 1 000 mg l<sup>-1</sup> Cl<sup>-</sup> were analyzed. Along with them, a calibration solution containing 10 µg l<sup>-1</sup> As and a blank solution containing no chloride were also analyzed. All solutions contained 2 vol.% HNO<sub>3</sub>, 4 vol.% methanol, and 100 µg l<sup>-1</sup> Y as an internal standard. Based on the measurements, the average value of the factor  $k_2$  in Eq. (3) and the corrected signal intensity  $I(\text{As})$  calculated by this equation were evaluated, the detection limit being obtained as the concentration of As corresponding to the three-fold standard deviation of the eight  $I(\text{As})$  values. The measurements were performed applying Ar nebulizer flow rates of 0.70, 0.75, and 0.80 l min<sup>-1</sup> (lying around the As<sup>+</sup> intensity maximum) and of 0.90 l min<sup>-1</sup> (corresponding to the minimum value of the interference factor). The calculated limits of detection along with the sensitivities of determination (in counts s<sup>-1</sup> per µg l<sup>-1</sup> As) are given in Table II, demonstrating that it is more suitable to work in the maximum sensitivity range than in the maximum signal background offset range.

#### *Determination of Arsenic in Mineral Waters*

Verification of the proposed procedure of two-step correction for interferences in the determination of arsenic met the obstacle of unavailability of a suitable certified reference material (CRM). The entire ISO-REMCO COMAR database, which in its latest version involves 9 700 CRMs, does not contain a CRM with a certified As concentration and with such an excess of chloride as the level examined in this work. There were only two CRMs of sea water available: CASS-3 with 1.09 ng l<sup>-1</sup> As and NASS-4 with

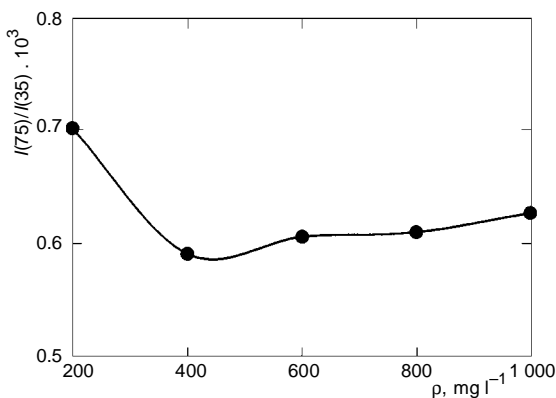


FIG. 3  
Dependence of the  $I(75)/I(35)$  ratio on the concentration of chloride ions,  $\rho$

1.26 ng l<sup>-1</sup> As (both National Research Council, Ottawa, Canada), which are out of use since their As content after appropriate sample dilution falls close to the detection limit of the method described. Therefore, the procedure was applied to a mineral water with a high concentration of NaCl and the evaluation based on sample spiking with known amounts of As. The approximate composition of the "Vincentka" mineral water (Ondrasov, Czech Republic) is given in Table III. The mineral water was analyzed by the procedure described in the experimental section. In addition, some of the samples were spiked with 0.25, 0.50, and 1.00 ml of a solution of 100 µg l<sup>-1</sup> As, which corresponded to As concentration increase by 0.5, 1, or 2 µg l<sup>-1</sup>. All samples together with a reagent blank and calibration solution containing 5 µg l<sup>-1</sup> As were measured applying the optimum conditions established – Ar nebulizer flow rate 0.75 l min<sup>-1</sup> and r.f. power 1 000 W. The recovery was 100–106% and the As content of the mineral water was

TABLE I  
Operating conditions for the Perkin-Elmer Elan 6000 instrument

Radio-frequency power	800–1 300 W (typically 1 000 W)
Dwell time	50 ms
Sweeps/replicate	20
No. of replicates	6
Total acquisition time per a.m.u.	6 s
Acquisition mode	peak hopping
Ar nebulizer flow	0.6–1.00 l min <sup>-1</sup> (typically 0.75 l min <sup>-1</sup> )
Ar plasma flow	17 l min <sup>-1</sup>
Ar auxiliary flow	1.2 l min <sup>-1</sup>
Lens voltage	autolens mode, optimized before each measurement
Sample uptake rate	1 ml min <sup>-1</sup>

TABLE II  
Detection limit and sensitivity of determination for the two-step background correction

Ar nebulizer flow, l min <sup>-1</sup>	LOD, µg l <sup>-1</sup> As	Sensitivity, counts s <sup>-1</sup> per µg l <sup>-1</sup> As
0.70	0.06	8 300
0.75	0.03	8 700
0.80	0.03	8 100
0.90	0.25	1 200

determined to be  $1.50 \mu\text{g l}^{-1}$ . The value obtained by the method of standard additions was  $1.44 \mu\text{g l}^{-1}$  As. When the mathematical correction was omitted and only the addition of methanol applied, As concentration was found to be  $2.75 \mu\text{g l}^{-1}$ . The resulting value without any background correction was  $4.2 \mu\text{g l}^{-1}$  As. Hence, making no correction or applying the one-step correction only resulted in a substantial overestimation of the As content of the mineral water analyzed. Relative standard deviation of determinations using the procedure suggested was found to be 3.2% ( $n = 6$ ).

A comparison between two-step correction method and matrix-free method ICP-MS with hydride generation (HG-ICP-MS) was performed using another batch of mineral water. HG-ICP-MS analyses were made by an independent laboratory (Analytika Prague Ltd, equipped by Varian UltraMass). Three samples were analyzed: one sample of original mineral water and two spiked samples, the results of analyses being shown in Table IV. Apparently, HG-ICP-MS gave somewhat lower both results and recovery

TABLE III  
Concentration of components of the "Vincentka" mineral water ( $\text{mg l}^{-1}$ )

Cations		Anions		Molecules	
$\text{Li}^+$	8.5	$\text{F}^-$	3.5	free $\text{CO}_2$	2 200
$\text{Na}^+$	2 200	$\text{Cl}^-$	1 438	$\text{H}_2\text{SiO}_3$	16.0
$\text{K}^+$	125	$\text{Br}^-$	4.6	$\text{H}_3\text{BO}_3$	420
$\text{Ca}^{2+}$	238	$\text{I}^-$	7.2		
$\text{Mg}^{2+}$	17.0	$\text{NO}_3^-$	0.0		
$\text{Sr}^{2+}$	3.8	$\text{NO}_2^-$	0.8		
$\text{Ba}^{2+}$	10.4	$\text{HCO}_3^-$	4 430		
$\text{Mn}^{2+}$	0.5	$\text{HPO}_4^{2-}$	0.03		
$\text{Al}^{3+}$	0.3	$\text{SO}_4^{2-}$	0.4		

TABLE IV  
Comparison of results of HG-ICP-MS and of the proposed method

Solution	HG-ICP-MS, $\mu\text{g l}^{-1}$ As	Proposed method, $\mu\text{g l}^{-1}$ As
Sample	0.53	1.22
Sample + $1.4 \mu\text{g l}^{-1}$ As	1.66	2.77
Sample + $2.8 \mu\text{g l}^{-1}$ As	2.49	4.39



(approximately 74%) than the presented method. The agreement between both methods seems to be reasonable with respect to the arsenic level.

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