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A MATHEMATICAL CORRECTION METHOD FOR SPECTRAL INTERFERENCES ON SELENIUM IN INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Summary—Despite the fact that Se has six isotopes, its determination in biological samples by inductively coupled plasma mass spectrometry is seriously hampered by spectral interferences. The resolution of quadrupole mass analyzers is insufficient to resolve Se^+ from molecular species having the same nominal mass.

A mathematical correction method based on signal ratio measurement of $^{78}Se^+/^{76}Se^+$ and $^{78}Ar_2^+/^{76}Ar_2^+$ is described. It allows us to correct for the argon dimer interference at m/z 78 and thus to determine Se down to the 1 μg/l level. The method was applied to the determination of Se in human serum. Good agreement with the certified value was obtained.

Inductively coupled plasma mass spectrometry (ICP–MS) has a potential for Se determination but the accuracy obtained often is degraded by spectral interferences. The nominal mass of polyatomic species, *i.e.* $ArCl^+$, $ArAr^+$ and SO_3^+ coincides with one or more Se isotopes[1] and, due to the limited resolution of quadrupole mass analyzers, spectral overlap occurs. As can be seen from Table 1, no unobstructed isotopes are available for Se determination in matrices that contain important amounts of Cl and S. In some instances, this problem can be circumvented by introducing Se as a hydride into the ICP[2–6] or by the use of a separation procedure prior to analysis.[7–8] The effect of N_2 addition to the argon plasma or nebulizer gas to alleviate some polyatomic interferences was reported on by several authors[9–14] but was barely applied to the determination of Se in real samples. Recently the combination of CH_4 addition[15] to the arbon nebulizer gas or EtOH addition[16] to the sample solutions with the adjustment of some instrumental parameters was successfully applied to Se determinations in samples of biological and clinical origin.

In the present paper a mathematical correction method based on signal ratio measurements of $^{78}Se^+/^{76}Se^+$ and $^{78}Ar_2^+/^{76}Ar_2^+$ is described. The detection limit obtained by hydride generation is superior but the method proposed combines the convenience of solution nebulization from the perspectives of sample throughput and ease of calibration with the possibility of multi-element analysis, one of the most powerful features of ICP–MS. Although the correction procedure can be applied to all kinds of matrices, it was developed in view of Se determinations in human serum. ICP–MS has indeed demonstrated its usefulness for the rapid analysis of this material as up to 20 elements can quasi-simultaneously be determined in 5–10-fold diluted serum.[17] However, the quantitation of a number of elements, one of which Se, is impossible due to the occurrence of spectral overlap, rather than to the insufficiency of the intrinsic sensitivity of the ICP–MS instrument.[17]

The procedure described allows accurate correction for Ar_2^+ interferences at m/z 78 without requiring any further pretreatment of the human serum and leads to a substantial improvement in the detection limit for Se in multi-element analysis.

EXPERIMENTAL

Instrumentation

The instrument used is a VG PlasmaQuad ICP-mass spectrometer (VG Elemental, Winsford, U.K.) equipped with a Fassel torch, a

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Table 1. Spectral interferences on Se[1]

Se isotope (abundance (%))	Main interfering molecular species (respective abundances (%))
^{74}Se (0.9)	^{37}Cl^{37}Cl (24.2, 24.2)
	^{40}Ar^{34}S (99.6, 4.2)
^{76}Se (9.0)	^{40}Ar^{36}Ar (99.6, 0.34)
^{77}Se (7.5)	^{40}Ar^{37}Cl (99.6, 24.2)
^{78}Se (23.6)	^{40}Ar^{38}Ar (99.6, 0.07)
^{80}Se (50.0)	^{40}Ar^{40}Ar (99.6, 99.6)
	^{32}S^{16}O$_3$ (95.0, 99.8)
^{82}Se (9.0)	^{34}S^{16}O$_3$ (4.2, 99.8)

Gilson Minipuls-2 peristaltic pump (maintaining a 1.0 ml/min sample uptake rate), a Meinhard type Tr-30-A3 concentric glass nebulizer and a double pass Scott-type spray chamber with surrounding liquid jacket, the temperature of which is controlled at 10°C with a recirculating refrigeration–heating system. Operation conditions are summarized in Table 2.

Reagents and solutions

A 1 g/l standard solution was prepared by dissolving Se metal (purity > 99.99%) in a limited amount of concentrated nitric acid, followed by dilution to volume with 0.14 mol/l HNO_3. A 1 g/l Ga standard solution was purchased from Johnson–Matthey. Throughout all experiments, HNO_3 (14 mol/l), prepared by sub-boiling distillation and de-ionized water obtained with a Milli-Q system (Millipore-waters, Milford, MA, U.S.A.) were used. Dilution of standard solutions was carried out with 0.14 mol/l HNO_3.

Sample preparation

Approximately 1.4 g of freeze-dried human serum reference material[18] (1.0 g of freeze-dried material is equivalent to 11.0 ml of liquid serum) was reconstituted with water and was further diluted to 25 ml with 0.14 mol/l HNO_3. By pipetting twice 10 ml in a 50 ml glass volumetric flask, the sample solution was divided into two subsamples one of which was spiked with a known amount of Se standard (500 μg/l) for calibration by standard addition. All solutions were brought to volume with 0.14 mol/l HNO_3 after addition of Ga (200 μg/l) as an internal standard. Concentrations in parentheses refer to the final solutions analyzed. The whole procedure thus implied a *ca* 8-fold sample dilution in order to minimize matrix effects.

Analysis procedure

Before each experiment the settings of the electrostatic lenses and the gas flow rates were optimized in order to obtain maximum signal intensity for $^{71}Ga^+$. In Fig. 1 the signal intensities of $^{77}Se^+$ and $^{78}Ar_2^+$ are plotted as a function of the nebulizer gas flow rate. Assuming that $^{78}Se^+$ behaves identically to $^{77}Se^+$, it can be seen that the nebulizer gas flow rate applied strongly influences the relative contribution of $^{78}Ar_2^+$ and $^{78}Se^+$ to the total signal at m/z 78. However, it is difficult to optimize the nebulizer gas flow rate to a maximum Se^+/Ar_2^+ signal intensity ratio as the shape and location of these plots strongly depend on the sample matrix composition and the instrumental parameters.[16] Typical count rates (integrated over a 0.8 u mass region) thus obtained are: 15 cps noise (m/z 77) and 2000 cps Ar_2^+ background (m/z 78) for a 0.14 mol/l HNO_3 blank solution and 2500 cps (m/z 77) for a 100 μg/l Se standard solution.

The mass scanning data acquisition mode was used for all serum samples (acquisition parameters are listed in Table 2). Standard addition (single addition) was applied as a calibration method and the solutions were analyzed in order of increasing concentration (*i.e.* blanks, unspiked sample solutions, spiked samples solutions) to avoid memory effects. Each solution was measured five times and the Se^+ signals were normalized to the $^{71}Ga^+$ signal.

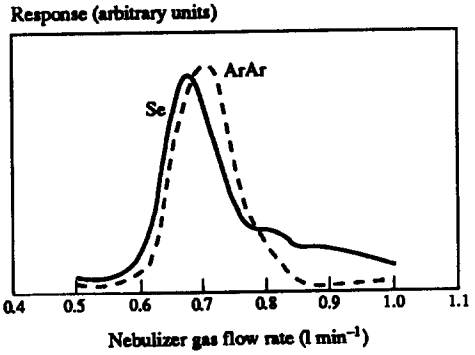

Fig. 1. Signal intensities of $^{77}Se^+$ (100 μg/l) and $^{78}Ar_2^+$ as a function of the nebulizer gas flow rate in a 0.14 mol/l HNO_3 matrix.

Table 2. VG PlasmaQuad operating conditions and acquisition parameters

Operating conditions		
Plasma	r.f. power	forward: 1350 W reflected: <5 W
	Gas flows	plasma: 13.5 l/min nebulizer: 0.725 l/min auxiliary: 0.9 l/min
Ion sampling	Sampling cone	nickel, 1.0 mm orifice
	Skimmer cone	nickel, 0.75 mm orifice
Vacuum	Expansion stage	2.3 mbar
	Intermediate stage	2.0×10^{-4} mbar
	Analyser stage	4.6×10^{-6} mbar
Sample uptake rate		1.0 ml/min
Acquisition parameters		
Mass range	69–79 u	
Number of channels	512	
Dwell time	160 μsec	
Number of sweeps	500	
Total acquisition time	40.9 sec	

Correction formula

For the derivation of the correction formula (from equations (1) to (4)), it is assumed that calibration is carried out by single standard addition. In the equations described below, I represents the total net signal intensity for the solution (s = sample solution, m = spiked sample solution) and the m/z-value specified. Each total signal consists of several "subsignals" (i), produced by the species given in parentheses. Subscripts denote uncontrollable (x) or controllable contributions (st). The sensitivity factors a (m/z 78) and b (m/z 76) represent the correlation between the molar concentration of a species (denoted by brackets) and the corresponding signal intensity (i) and hence correct for mass discrimination effects.

$$\begin{cases} {}^{78}I_s = {}^{78}i(\mathrm{Se})_x + {}^{78}i(\mathrm{Ar_2})_x & (1a) \\ {}^{78}I_s = a \cdot [{}^{78}\mathrm{Se}]_x + {}^{78}i(\mathrm{Ar_2})_x & (1b) \end{cases}$$

$$\begin{cases} {}^{78}I_m = {}^{78}i(\mathrm{Se})_x + {}^{78}i(\mathrm{Se})_{st} + {}^{78}i(\mathrm{Ar_2})_x & (2a) \\ {}^{78}I_m = a \cdot [{}^{78}\mathrm{Se}]_x + a \cdot [{}^{78}\mathrm{Se}]_{st} + {}^{78}i(\mathrm{Ar_2})_x & (2b) \end{cases}$$

$$\begin{cases} {}^{76}I_s = {}^{76}i(\mathrm{Se})_x + {}^{76}i(\mathrm{Ar_2})_x & (3a) \\ {}^{76}I_s = b \cdot [{}^{76}\mathrm{Se}]_x + {}^{76}i(\mathrm{Ar_2})_x & (3b) \end{cases}$$

$$\begin{cases} {}^{76}I_m = {}^{76}i(\mathrm{Se})_x + {}^{76}i(\mathrm{Se})_{st} + {}^{76}i(\mathrm{Ar_2})_x & (4a) \\ {}^{76}I_m = b \cdot [{}^{76}\mathrm{Se}]_x + b \cdot [{}^{76}\mathrm{Se}]_{st} + {}^{76}i(\mathrm{Ar_2})_x & (4b) \end{cases}$$

These equations express that the signal intensity observed at m/z 76 and 78 equals the sum of the subsignals by Ar_2 and Se. In spiked samples, the latter contribution is proportional to the sum of $[\mathrm{Se}]_x$, the unknown concentration of Se originally present in the sample and $[\mathrm{Se}]_{st}$, the concentration of Se added. The deduction is based on equation (1b) from which $[{}^{78}\mathrm{Se}]_x$ is calculated. The ArAr contribution to the total signal at m/z 78 (equation (1b)) is strongly matrix dependent and therefore cannot be determined directly. It will be further expressed as the ratio to the ArAr signal at m/z 76 with use of equation (3b). Subtraction of equation (1b) from equation (2b) and subtraction of (3b) from (4b), respectively provides an expression for the sensitivity factors:

$$a = \frac{{}^{78}I_m - {}^{78}I_s}{[{}^{78}\mathrm{Se}]_{st}} \quad (5)$$

$$b = \frac{{}^{76}I_m - {}^{76}I_s}{[{}^{76}\mathrm{Se}]_{st}} \quad (6)$$

The ratio of the signal intensity at m/z 78 to m/z 76 for Se and Ar_2 can be defined as follows:

$${}^{78/76}R_{Se} = \frac{{}^{78}i(\mathrm{Se})_x}{{}^{76}i(\mathrm{Se})_x} = \frac{a}{b} \cdot \frac{\theta({}^{78}\mathrm{Se})}{\theta({}^{76}\mathrm{Se})} = \frac{a}{b} \cdot \frac{[{}^{78}\mathrm{Se}]}{[{}^{76}\mathrm{Se}]} \quad (7)$$

$${}^{78/76}R_{Ar_2} = \frac{{}^{78}\mathrm{i}(\mathrm{Ar_2})_x}{{}^{76}\mathrm{i}(\mathrm{Ar_2})_x} \quad (8)$$

where Θ represents the relative abundance of the isotope specified. Taking into account that $[{}^{76}\mathrm{Se}] = [{}^{78}\mathrm{Se}] \cdot \Theta({}^{76}\mathrm{Se})/\Theta({}^{78}\mathrm{Se})$, (3b) can be rewritten as follows:

$${}^{76}i(\mathrm{Ar_2})_x = {}^{76}I_s - b \cdot [{}^{78}\mathrm{Se}]_x \cdot \frac{\theta({}^{76}\mathrm{Se})}{\theta({}^{78}\mathrm{Se})} \quad (9)$$

Combination of equations (8) and (9) and rearrangement results in:

$$^{78}i(Ar_2)_x = \left(^{76}I_s - b \cdot [^{78}Se]_x \cdot \frac{\theta(^{76}Se)}{\theta(^{78}Se)} \right) \cdot {}^{78/76}R_{Ar_2} \quad (10)$$

Substitution of equation (10) in (1b) and solving for $[^{78}Se]_x$ leads to:

$$[^{78}Se]_x = \frac{^{78}I_s - {}^{78/76}R_{Ar_2} \cdot {}^{76}I_s}{a - {}^{78/76}R_{Ar_2} \cdot b \cdot \frac{\theta(^{76}Se)}{\theta(^{78}Se)}} \quad (11)$$

Substitution of a and b with use of equation (5) and (6) results in:

$$[^{78}Se]_x = \frac{^{78}I_s - {}^{78/76}R_{Ar_2} \cdot {}^{76}I_s}{\frac{^{78}I_m - {}^{78}I_s}{[^{78}Se]_{st}} - {}^{78/76}R_{Ar_2} \cdot \frac{^{76}I_m - {}^{76}I_s}{[^{76}Se]_{st}} \cdot \frac{\theta(^{76}Se)}{\theta(^{78}Se)}} \quad (12)$$

Taking into account that $[^{76}Se] \cdot \Theta(^{78}Se)/\Theta(^{76}Se) = [^{78}Se]$ and the fact that the isotopic composition of Se in the sample and the standard solution is equal, (12) can be rewritten as follows:

$$[Se]_x = \frac{^{78}I_s - {}^{78/76}R_{Ar_2} \cdot {}^{76}I_s}{(^{78}I_m - {}^{78}I_s) - {}^{78/76}R_{Ar_2} \cdot (^{76}I_m - {}^{76}I_s)} \cdot [Se]_{st} \quad (13)$$

With use of (5), (6) and (7), this can be rewritten as:

$$[Se]_x = \frac{^{78}I_s - {}^{78/76}R_{Ar_2} \cdot {}^{76}I_s}{(^{78}I_m - {}^{78}I_s) \cdot \left(1 - \frac{^{78/76}R_{Ar_2}}{^{78/76}R_{Se}}\right)} \cdot [Se]_{st} \quad (14)$$

If we finally assume that $^{78/76}R_{Se} = \Theta(^{78}Se)/\Theta(^{76}Se) = 2.63$[19] (we will re-evaluate this assumption later):

$$[Se]_x = \frac{^{78}I_s - {}^{78/76}R_{Ar_2} \cdot {}^{76}I_s}{(^{76}I_m - {}^{78}I_s) \cdot (1 - 0.380 \cdot {}^{78/76}R_{Ar_2})} \cdot [Se]_{st} \quad (15)$$

Determination of $^{78/76}R_{Ar_2}$

The Ar_2^+ signal ratio was determined by analyzing a 0.14 mol/l HNO_3 solution. The photon background at m/z 77 (or at any other "free" m/z-value) was subtracted from the count rate at m/z 76 and 78 and $^{78/76}R_{Ar_2}$ was calculated by dividing the net signal intensity at m/z 78 by the net signal intensity at m/z 76.

RESULTS AND DISCUSSION

It appears from (15) that the unknown Se concentration $[Se]_x$ can be calculated from the net signal intensities at m/z 76 and m/z 78 in the sample solution ($^{76}I_s$ and $^{78}I_s$) and the signal intensity at m/z 78 in the spiked sample solution ($^{78}I_m$). The symbol I stands for the net signal intensity which means that the photon background of the instrument (typically $< 1\%$ of the total signals at m/z 76 and 78) should be subtracted. In practice, all net signals are normalized to the $^{71}Ga^+$ signal which does not affect the validity of (15).

It can be shown that a similar correction is possible when applying external calibration instead of standard addition. However, experience learned that in biological samples internal standardization alone sometimes is insufficient for accurate correction for matrix effects. This is particularly true for As and Se determinations[16] as the presence of large amounts of carbon containing species such as in human serum affects the slope of the calibration graphs (illustrated for Se in Fig. 2). The extent of this effect is unpredictable and typical only for some elements[20] (including Se). Hence standard addition was preferred. The concentration of the Se spike added to the samples for calibration is relatively high (500 μg/l). As a result $^{78}I_m \gg {}^{78}I_s$ and therefore the accuracy of the calibration is not affected by possible fluctuations on the Ar_2^+ background.

It can be noted here that Se determination by monitoring m/z 78 and correction for $^{78}Ar_2^+$ interference by blank subtraction is dubious. The extent to which Ar_2^+ is formed strongly depends on matrix conditions and hence the contribution to the total signal at m/z 78 in a real sample cannot be determined. Therefore detection limits obtained by analysis of blanks and standard solutions do not always reflect the real capabilities of Se determination in real

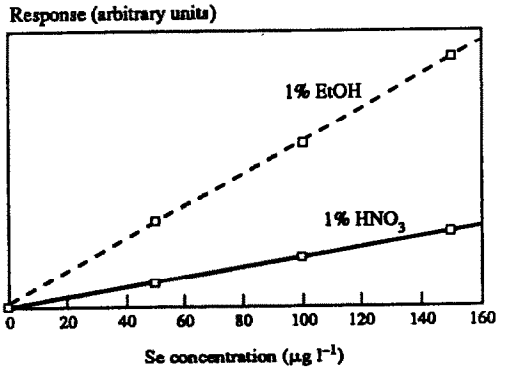

Fig. 2. Se calibration graph both in the presence and in the absence of carbon.

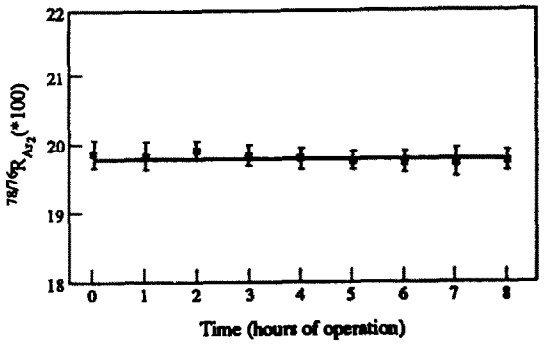

Fig. 3. Stability of $^{78/76}R_{Ar_2}$ during a day of operation. The error bars represent the standard deviation on five consecutive measurements.

samples. However, whereas the $^{78}Ar_2^+$ signal intensity varies as a function of the sample matrix composition, the $^{78}Ar_2^+/^{76}Ar_2^+$ signal ratio ($^{78/76}R_{Ar_2}$) does not. The value of this ratio only depends on the Ar abundances and mass discrimination effects. It could indeed be calculated from the results of the analysis of 8-fold diluted serum reference material that switching from a 0.14 mol/l HNO_3 blank solution to a serum sample resulted in a substantial increase of the Ar_2^+ signals (*ca* 50%) while, on the contrary, the $^{71}Ga^+$ signal slightly decreased (*ca* 10%). However, the relative signal enhancements of $^{78}Ar_2^+$ and $^{76}Ar_2^+$ were identical.

The only condition for the application of the correction formula is that the interference at m/z 76 and m/z 78 is only caused by molecular species consisting of Ar. Germanium can interfere at m/z 76 but generally is not present in significant concentrations in biological samples (*e.g.* human serum) and therefore the contribution of $^{76}Ge^+$ to the $^{76}Ar_2^+$ signal can be neglected. However, the absence of Ge should always be checked at m/z 72, 73 or 74. Theoretically, contributions by $^{39}K^{39}K$ and $^{23}Na_2^{16}O_2$ to the signal at m/z 78 are also possible but were found not to be significant at the level of Na and K present in the (diluted) human serum samples.

Mass discrimination effects

Measured isotope ratios deviate from theoretical values (calculated from isotopic abundances) as a function of the difference in mass between the two nuclides involved. This effect is recognized to be dependent, to some extent, on operation conditions of the instrument and is variously referred to as bias, fractionation and discrimination.[21–24] Since isotope ratio measurements are involved in the application of the correction formula, it was desirable to have an idea of the importance of this effect. Therefore, we compared experimentally determined $^{82}Se/^{77}Se$ isotope ratios to the theoretical one during a period of several months. Assuming that, within a narrow mass range, the instrumental bias is a linear function of the difference in mass,[22] the fractionation per mass unit (f.m.u.) can be calculated as follows:

$$\text{f.m.u.} = \frac{1}{5} \times \frac{\left(\frac{^{82}Se}{^{77}Se}\right)_{Exp} - \left(\frac{^{82}Se}{^{77}Se}\right)_{Theor}}{\left(\frac{^{82}Se}{^{77}Se}\right)_{Theor}} \times 100\% \qquad (16)$$

Values thus obtained varied from day to day but never exceeded 3% and generally were <2% and positive. The latter is in accordance with the fact that mass discrimination effects generally produce an enhanced sensitivity for the high mass isotope.

Accuracy and precision of $^{78/76}R_{Se}$ *and* $^{78/76}R_{Ar_2}$

It can be calculated from (14) that for values of $^{78/76}R_{Ar_2}$ and $^{78/76}R_{Se}$ close to the theoretical ones (approximately 0.20 and 2.6, respectively) the accuracy of $^{78/76}R_{Se}$ is of minor importance to the accuracy of the final result (*i.e.* $[Se]_x$). A systematic error of 4% in the determination of $^{78/76}R_{Se}$ will effect the accuracy of $[Se]_x$ by only 0.35%. If therefore in (14), we replace the experimentally determined ratio $^{78/76}R_{Se}$ by the theoretical value of 2.63,[19] a systematic error on $[Se]_x \leqslant 0.4\%$ would be made, by neglecting the fractionation effect over two mass units (typically $\leqslant 4\%$). This error, however, is completely outweighed by the possible difference in isotopic composition between the sample and standard solution. Indeed, the relative variation in the abundance of a given Se isotope over different materials can amount to several percents.[19] Of course, this is a general problem in the quantitation of Se by mass spectrometry and is not related to the application of the correction formula only. For the analysis of the serum samples, the value of $^{78/76}R_{Se}$ was stipulated to be 2.63 and thus (15) was applied for correction.

The impact of $^{78/76}R_{Ar_2}$ on the accuracy of the final result depends on the relative importance of the contributions of $^{78}Se^+$ and $^{78}Ar_2^+$ to the total signal at m/z 78 and is at any rate more important than in the instance of $^{78/76}R_{Se}$. As an example, it can be calculated that in the instance where the contribution of $^{78}Se^+$ and $^{78}Ar_2^+$ is

Table 3. Determination of Se in human serum

Experiment	$^{78/76}R_{Ar_2}$	Ar_2^+ background (μg/l Se)†	Number of replicates	Mean value (μg/l Se)	Certified value (μg/l Se)
1	0.196	38	3	99.0 ± 5.1*	
2	0.196	32	3	94.5 ± 1.7	95.5 ± 4.6
3	0.197	47	2	93.2 ± 2.6	

*Uncertainties are expressed as standard errors on the mean.
†Ar_2^+ background (m/z = 78) obtained from a 1% HNO_3 blank solution and expressed as an "apparent" Se concentration.

equal, a systematic error of 1% on the value of $^{78/76}R_{Ar_2}$ will result in a 1% error on the determination of $[Se]_x$. Therefore, the numeric value of $^{78/76}R_{Ar_2}$ was experimentally determined before each analysis by five consecutive measurements of a blank solution. Standard deviations $\leqslant 2\%$ could be obtained routinely. The variation of $^{78/76}R_{Ar_2}$ during a single day of operation is presented in Fig. 3. It can be seen that the ratio remains constant within 1%.

Detection limit

The detection limit of the method is related to the precision of $^{78/76}R_{Se}$ and $^{78/76}R_{Ar_2}$ and to the signal ($^{78}Se^+$) to background ($^{78}Ar_2^+$) ratio in general. The latter in turn depends on matrix composition[13] and operation conditions such as RF power[13] and nebulizer gas flow rate (cf. Fig. 2). At the operation conditions specified, an Ar_2^+ background at m/z 78 equivalent to *ca* 40 μg/l Se is observed when analyzing a 0.14 mol/l HNO_3 blank solution. Under these conditions (and of course in the absence of other spectral interferences) a detection limit (3 s criterion) of 1 μg/l could be achieved. This value was obtained by applying the correction method to blank solutions ($n = 5$) and calculating the standard deviation on the results obtained.

Determination of Se in human serum

A lyophilized human serum reference material prepared by Versieck and coworkers was analyzed. At 8-fold dilution, all Se isotopes are interfered by a factor $\geqslant 3$.[16] Serum samples were analyzed on three different days during which the value for $^{78/76}R_{Ar_2}$ was established to be consistently 0.196 ± 0.01. For each analysis, at least two blank solutions (0.14 mol/l HNO_3) were analyzed. When determining Se in the blanks with use of the same procedure the concentrations obtained ranged from -0.5 μg/l to $+0.5$ μg/l. Of course, when analyzing a Cl-free blank solution (such as 0.14 mol/l HNO_3), there is no use in application of the correction formula as the Se content can be determined directly by monitoring the ^{77}Se isotope. The signal at m/z 77 from the blank solutions did not differ significantly from the background count rate and therefore no further blank corrections were carried out. All results are listed in Table 3. The actual Se concentration in the measured sample solutions ranged between 11 and 13 μg/l ($n = 8$). Taking into account the exact sample masses and the 8-fold dilution of the solutions, a mean value of 95.9 ± 1.4 μg/l is obtained which is in very good agreement with the certified value (95.5 ± 4.6 μg/l).

Other applications

The method described can be used for Se determination in solutions of other materials on the condition that, apart from Ar_2^+, no supplemental interferences on m/z 76 and 78 are present.

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