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Non-spectral interferences due to the presence of sulfuric acid in Inductively Coupled Plasma Mass Spectrometry

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Abstract

Results of a systematic study concerning non-spectral interferences from sulfuric acid containing matrices on a large number of elements in inductively coupled plasma - mass spectrometry (ICP-MS) are presented in this work. The signals obtained with sulfuric acid solutions of different concentrations (up to 5% w w^{-1}) have been compared with the corresponding signals for a 1% w w^{-1-} nitric acid solution at different experimental conditions (i.e., sample uptake rates, nebulizer gas flows and r.f. powers). The signals observed for $^{128}Te^+$, $^{78}Se^+$ and $^{75}As^+$ were significantly higher when using sulfuric acid matrices (up to 2.2-fold for $^{128}Te^+$ and $^{78}Se^+$ and 1.8-fold for $^{75}As^+$) for the whole range of experimental conditions tested. This is in agreement with previously reported observations. The signal for $^{31}P^+$ is also higher (1.1-fold) in the presence of sulfuric acid. The signal enhancements for $^{128}Te^+$, $^{78}Se^+$, $^{75}As^+$ and $^{31}P^+$ are explained in relation to an increase in the analyte ion population as a result of charge transfer reactions involving S^+ species in the plasma. Theoretical data suggest that Os, Sb, Pt, Ir, Zn and Hg could also be involved in sulfur-based charge transfer reactions, but no experimental evidence has been found. The presence of sulfuric acid gives rise to lower ionic signals (about 10-20% lower) for the other nuclides tested, thus indicating the negative matrix effect caused by changes in the amount of analyte loading of the plasma.

The elemental composition of a certified low-density polyethylene sample (ERM-EC681K) was determined by ICP-MS after two different sample digestion procedures, one of them including sulfuric acid. Element concentrations were in agreement with the certified values, irrespective of the acids used for the digestion. These results demonstrate that the use of matrix-matched standards allows the accurate determination of the tested elements in a sulfuric acid matrix.

Keywords: sulfuric acid; signal enhancement; charge transfer; ICP-MS; polyethylene

1. Introduction

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) is a powerful technique for the determination of trace and ultra-trace elements in a great variety of matrices due to its multi-element capabilities and low limits of detection (LoDs). The main limitation of this technique is the occurrence of spectral (isobaric or polyatomic) and non-spectral interferences originating from the sample matrix constituents.

Inorganic acids, mainly nitric acid, are common matrices involved in ICP-MS analysis since they are often used in different sample pretreatment procedures (e.g., solid sample digestion, sample storage and analyte stabilization, etc.). The use of sulfuric acid is suggested for sample dissolution purposes in the elemental analysis of food-packaging materials [1], petroleum products [2,3], fish tissues [4] or minerals [5] among others [6,7]. Nevertheless, sulfuric acid is preferably avoided by ICP-MS users since it is a source of spectral and non-spectral interferences [8-10]. From several studies, it seems to be clear that the effect of sulfuric acid in ICP-MS depends, for given experimental conditions, on the acid concentration and sample introduction system used, but also on the element determined [10]. Thus, Mora et al., [11] operating with low concentration acid solutions (i.e., 0.2% w w^{-1} nitric acid and 0.3% w w^{-1} sulfuric acid) did not observe any difference in the LoD of selected nuclides (i.e., $^{51}V^+$, $^{52}Cr^+$, $^{75}As^+$, $^{103}Rh^+$, $^{140}Ce^+$ and $^{208}Pb^+$) for nitric acid and sulfuric acid solutions when operating with a pneumatic concentric nebulizer coupled to a double-pass Scott-type spray chamber. Björn and Frech [12] compared the signals of eight elements with ionization potential ranging from 5.39 to 10.43 eV in 4.8% w w^{-1} sulfuric and 4% w w^{-1} nitric acid solutions using three different sample introduction systems (i.e., a direct injection high efficiency nebulizer, a large-bore direct injection high efficiency nebulizer and a microconcentric nebulizer attached to a cyclonic spray chamber). They concluded that, irrespective of the system used, lower ion signals were measured in sulfuric than in nitric acid. Non-spectral interferences were attributed to changes in the aerosol generation and transport processes and in the plasma ionization conditions. Similar conclusions were obtained by Vanhaecke et al. [13] when registering the ion signals of twelve elements in 2.7% w w^{-1} sulfuric acid and comparing the results with those obtained in a 0.6% w w^{-1} nitric acid solution. However, Vanhaecke et al. [13] also reported significantly higher ion intensities for Te, Se and As due to the presence of sulfuric acid in the plasma. The enhanced signals were found when using high resolution as well as quadrupole-based ICP-MS instruments. The authors concluded that the observed signal enhancements could not be rationalized. They pointed out the need of further systematic investigations to obtain a more profound insight into the origin of these effects, which “probably result from an interaction of different mechanisms.

It is interesting to note that Machat et al. [14] found an enhancement of the Se emission intensity in ICP-Atomic Emission Spectrometry (ICP-AES) when operating with sulfuric acid matrices or when sulfur dioxide was introduced into the plasma.

Signal enhancement for Te, Se and As has also been observed by several authors when operating with carbon-containing matrices in ICP-MS [13,15-19]. Recently, Grindlay et al. [20] studied the influence of carbon on the signals of a large number of easy and hard-to-ionize elements in ICP-MS and reported that Sb, Te, Au, Se, As, Hg, I and P sensitivities were always higher for carbon-containing solutions than those obtained without carbon. This behavior was related to an increase in analyte ion population as a result of charge transfer reactions involving carbon-containing charged species in the plasma.

In the present work, the origin of sulfuric acid-induced signal enhancement in ICP-MS has been studied and the feasibility of charge transfer reactions between sulfur and several hard-to-ionize elements has been investigated. To this end, the influence of sulfuric acid concentration and experimental conditions (*i.e.* sample uptake rate, nebulizer gas flow rate and r.f. power) on the ion signals of a large number of elements covering a wide range of ionization energies (5.21-10.49 eV) and m/z ratios (7-238 u) has been measured and the atomization-ionization mechanism has been discussed. To evaluate the practical implications of the presence of a sulfuric acid matrix in ICP-MS, the multi-element analysis of a certified low-density polyethylene sample was performed after sulfuric acid digestion.

2. Experimental

2.1. Reagents

Sulfur-containing solutions were prepared from sulfuric acid (Suprapur, Merck, Darmstadt, Germany). High-purity water (i.e., with a resistivity > 18 MΩ cm) was obtained from a Milli-Q water system (Millipore Inc., France). Ba, Li, Ce, Sr, In, Al, U, Sc, Cr, Pb, Ag, Mn, Ni, W, Cu, Co, Au, Pd, Os, Sb, Pt, Ir, Cd, Te, Au, Be, Zn, Se, As, Hg and P mono-elemental solutions (Merck, Germany) were employed to prepare multi-element test solutions. A 1% w w^{-1} nitric acid (Suprapur, Merck, Darmstadt, Germany) solution containing all the above mentioned elements was prepared as reference solution.

All glassware and polypropylene flasks were soaked in 6.5% w w^{-1} HNO_3 overnight and rinsed with Milli-Q water prior to use. Test solutions were freshly prepared daily.

2.2. ICP-MS instrumentation

A 7700X ICP-MS instrument (Agilent, Santa Clara, CA, USA) was operated under the conditions listed in Table 1.

Nuclides monitored, their ionization potential and ionization degree (estimated via Saha equation) [21] are listed in Table 2. In order to evaluate the plasma ionization conditions and the matrix load of the plasma, the $^{138}Ba^{2+}/^{138}Ba^{+}$ and $^{156}CeO^{+}/^{140}Ce^{+}$ signal ratios were also registered.

2.3. Aerosol drop size distribution measurements

Drop size distributions (DSD) of the aerosols generated by the nebulizer (i.e. primary aerosols) and at the exit of the spray chamber (i.e., tertiary aerosols) using different acid matrices were measured by means of a laser Fraunhofer diffraction system (Model 2600c, Malvern Instruments Ltd., Malvern, UK). Description of the instrument setup and experimental details can be found elsewhere [22].

2.4. Solvent and analyte transport measurements

Solvent transport measurements were performed using a direct method in which the aerosol was adsorbed in a U-tube filled with silica gel during 10 minutes. Solvent transport rate was calculated by weighing the tube before and after the aerosol exposure.

Analyte transport rate measurements were performed by nebulizing a solution of 500 µg Mn mL^{-1} during a given period of time (15 minutes) and trapping the aerosol at the exit of the spray chamber with a glass fiber filter (type A/E, 47 mm diameter, 0.3 µm pore size, Gelman Sciences, Ann Arbor, MI, USA). The filter was then washed out into a volumetric flask with 1% w w^{-1} nitric acid and the manganese concentration measured by flame atomic absorption spectrometry. A set of three replicates was performed in each case, being the RSD of these measurements always lower than 4 %.

2.5. Sample

The elemental composition of a certified low-density polyethylene sample (ERM-EC681K, Institute for Reference Materials and Measurements, Geel, Belgium) was determined by ICP-MS. To this end, 0.25 g of the sample was digested using a CEM Mars 5 microwave system (Matthews, NC, USA) according to the programs described in Table 3. Two different sample digestion procedures using nitric acid (as recommended by the manufacturer for this type of sample) and a mixture of nitric and sulfuric acids [23] were used for comparison. Digested samples were made up to 200 g using high-purity water before introduction in the ICP-MS.

Standards and sample solutions were spiked with gold (100 µg kg^{-1}) in order to allow the accurate determination of mercury [24].

External calibration using matrix-matched standard solutions was employed to determine the element concentration.

3. Results and discussion

3.1. Sulfuric acid matrix effects

Fig. 1 shows the ratio of the net signal intensities obtained using a sulfuric acid 2% w w^{-1} solution to the corresponding net signal intensities in the reference matrix (i.e., 1% w w^{-1} nitric acid solution), I_{rel}, as a function of the ionization potential of the elements tested. Signal repeatability for the different nuclides tested was about 2% RSD (10 replicates). Therefore, it can be considered that I_{rel} values exceeding the 0.96-1.04 range (corresponding with ± 4% error) indicate matrix effects (see dashed lines in Fig. 1). The results in Fig. 1 show that the presence of sulfuric acid in the matrix gives rise to a reduction in the ion signals (i.e., I_{rel} values lower than 0.96) for almost all the nuclides tested, thus indicating a negative matrix effect (of about 20% on average). A completely different behavior was observed for $^{128}Te^+$, $^{78}Se^+$, $^{75}As^+$ and $^{31}P^+$. For these nuclides, signals were higher when sulfuric acid was present in the matrix (I_{rel} values are 2.1, 2.0, 1.5 and 1.1 for $^{128}Te^+$, $^{78}Se^+$, $^{75}As^+$ and $^{31}P^+$, respectively). It should be noted that similar signal enhancements for Te, Se and As due to the presence of 2.7% w w^{-1} sulfuric acid have been previously reported [13].

Fig. 2 shows the influence of sulfuric acid concentrations up to 5% w w^{-1} on the I_{rel} values obtained for $^{128}Te^+$, $^{78}Se^+$, $^{75}As^+$ and $^{31}P^+$. The averaged I_{rel} value for the other nuclides is also included. It can be observed that matrix effects (positive or negative) increase when increasing the sulfuric acid concentration. Thus, the mean I_{rel} value of the nuclides showing reduced ion signals (indicated by 'other nuclides' in Fig. 2) decreases from 0.9 to 0.8 when the sulfuric acid concentration is increased from 0.1% w w^{-1} to 5% w w^{-1}. The same change in sulfuric acid concentration affords an enhancement in the I_{rel} values from 1.4 to

2.2 for $^{128}Te^+$, $^{78}Se^+$ and from 1.2 to 1.8 for $^{75}As^+$. For $^{31}P^+$, I_{rel} remains almost constant irrespective of the sulfuric acid concentration.

3.2. Origin of the matrix effects

Matrix effects in ICP-MS can originate from changes in: (i) aerosol generation and transport to the plasma; (ii) plasma ionization conditions; (iii) ion distribution; and/or, (iv) atomization-ionization mechanism. In the next sections, the possible causes of the reported sulfuric acid matrix effects will be discussed.

3.2.1. Aerosol generation and transport to the plasma.

Drop size distributions of the aerosols generated by the nebulizer (primary aerosols) have been measured when operating with different acid matrices. Results indicate no significant differences between the characteristics of the aerosols generated, irrespective of the acid nature (i.e., nitric or sulfuric acid) and sulfuric acid concentration (i.e., 0.5 and 2% w w^{-1}). The accumulated aerosol drop size distribution curves are presented in Fig. S1 (Appendix). These results are as expected, taking into account that there are no noticeable differences in the main physical properties that affect the DSD of aerosols generated pneumatically (i.e., surface tension and viscosity) between the different solutions tested (at least, up to the maximum sulfuric acid concentration used, i.e., 5% w w^{-1}) [25].

Results of the drop size distributions of the aerosols emerging the spray chamber reveals finer tertiary aerosols with sulfuric acid than with nitric acid. Thus, at the experimental conditions used in Fig. 1, the median of the volume drop size distribution (D_{50}) is 3.6 µm and 2.1 µm for nitric acid 1% w w^{-1} and sulfuric acid 2% w w^{-1}, respectively. These results are in agreement with those previously reported [10,26,27].

Results of the solvent transport measurements are also similar for all the solutions tested. Thus, the solvent transport rates were 0.0283 ± 0.0004 and 0.0281 ± 0.0005 mg min^{-1} for nitric acid 1% w w^{-1} and sulfuric acid 2% w w^{-1} solutions, respectively. In agreement with these data, also the $^{156}CeO^+/^{140}Ce^+$ ratio remains almost constant (ranging between 1.3% and 1.1%) irrespective of the solution introduced into the ICP-MS.

As regards the analyte transport, the results indicate that when operating with 2% w w^{-1} sulfuric acid solution, the analyte transport rate decreases about 14% (on average) with respect to that with 1% w w^{-1} nitric acid solution. The apparent contradiction between the behaviors of solvent and analyte transport rates have been previously reported and attributed to the existence of the so-called aerosol ionic redistribution phenomenon [27].

The results discussed in this paragraph would satisfactorily explain the signal suppression observed for most of the elements as shown in Fig. 1. Nonetheless, the signal enhancement observed for Te, Se, As and P cannot be explained on this basis [13].

3.2.2. Plasma ionization conditions.

The influence of the matrix on the plasma characteristics has been evaluated by monitoring the $^{138}Ba^{2+}/^{138}Ba^+$ signal ratio. The double charged ion ratio for the reference nitric acid solution was 1.6%. For sulfuric acid the $^{138}Ba^{2+}/^{138}Ba^+$ signal ratio varied from 1.5% to 1.0% when the acid concentration was increased from 0.1 w w^{-1} to 5% w w^{-1}. In agreement with the findings previously reported [10,12,26], these results would indicate that the presence of sulfuric acid could have a negative impact on the plasma ionization characteristics and then, on the ion signal.. Obviously, results obtained for $^{128}Te^+$, $^{78}Se^+$, $^{75}As^+$ and $^{31}P^+$ cannot be explained in terms of deterioration of the plasma ionization conditions. In fact, taking into account the high ionization potential of these four elements (as well as others such B, Pt, Be, Zn, etc., see Table 2), their signals would rather be expected to be more suppressed than those for elements with lower ionization potential such as Ba, Li, Sr, etc. Opposite to the results previously reported [12] we have not observed any influence of the ionization potential on the detrimental effect due to the presence of sulfuric acid solutions. These results seems to indicate that the changes in plasma conditions are not the main responsible of the matrix effects observed in Fig. 1.

3.2.3. Signal profiles

Some authors have indicated that the magnitude of the acid matrix effects strongly depends on the experimental conditions employed [10,28]. Taking into account this fact, the influence of the experimental variables (i.e., nebulizer gas flow rate, Q_g, sample uptake rate, Q_l, and r.f. power) on the ion signal intensities has been studied. Figs. 3 and 4 show the influence of Q_g on $^{111}Cd^+$ and $^{75}As^+$ signals measured in 1% w w^{-1} nitric acid and 1% w w^{-1} sulfuric acid solutions at different r.f. powers and Q_l, respectively. These elements were selected to represent elements affording signal reduction and signal enhancement in the presence of sulfuric acid, respectively. Thus, $^{75}As^+$ illustrates the behavior of $^{128}Te^+$, $^{78}Se^+$ and $^{31}P^+$ whereas $^{111}Cd^+$ was selected to represent the remaining nuclides tested. As it can be derived from Figs. 3 and 4, the optimum Q_g does not depend on the matrix. These results seem to corroborate the hypothesis that changes in the plasma conditions are not the main cause of sulfuric acid-induced matrix effects. However, as shown in Fig. 3 and in agreement with previous findings [29], the optimum Q_g value increases with about 0.05 L min^{-1} (i.e., from 0.90 to 0.95 L min^{-1} for $^{111}Cd^+$ and $^{75}As^+$) when increasing the r.f. power from 1100 to 1400 W. Fig. 4 shows that the optimum gas flow rate is somewhat higher when the sample uptake rate is reduced from 0.75 to 0.25 mL min^{-1}.

From the signal profiles shown in Figs. 3 and 4 it can be concluded that the magnitude of the matrix effects, and hence I_{rel} values, in the presence of sulfuric acid in the sample strongly depend on the spatial distribution of ions in the plasma. Nevertheless, it is clear that, irrespective of the experimental conditions employed, for the group of nuclides represented by $^{111}Cd^+$, the use of 1% w w^{-1} sulfuric acid solutions affords lower signals than those obtained with 1% w w^{-1} nitric acid. In contrast, net signal intensities for $^{75}As^+$ (and also for $^{128}Te^+$, $^{78}Se^+$ and $^{31}P^+$) in sulfuric acid were always higher than those in the reference nitric acid solution.

3.2.4. Atomization-ionization mechanism.

In order to explain the results obtained for $^{128}Te^+$, $^{78}Se^+$, $^{75}As^+$ and $^{31}P^+$, the influence of sulfuric acid on their atomization and ionization has been evaluated. In a previous study, we have demonstrated that the presence of carbon-containing charged species in the plasma causes an increase in the ion population of some hard-to-ionize elements (Te, Se, As and P, among others) as a result of charge transfer reactions [20]. Machat et al., [14] suggested a similar mechanism to explain the behavior of Se in ICP-MS when operating with sulfur-containing matrices. Taking into account these findings, it seems reasonable to think that the presence of sulfur-charged species in the plasma could affect the ion population of Te, Se, As and P, affording higher signals in sulfuric acid compared to nitric acid solution. Two requirements must be fulfilled for appreciable charge transfer [20]: (i) total electron spin conservation; and, (ii) minimum energy defect (ΔE). These requirements have been evaluated for S^+ and the studied elements (M) in order to estimate the probability to form an excited element ion ($M^{+}*$):

$$S^+ + M \rightarrow S + M^{+}*$$

Table 4 presents the spectroscopic states and energy defects for the above reaction between S^+ and the closest ion electronic states of Te, Se, As and P. In addition, the total electron spin number of the reactants (S_r) and the products (S_p) involved in the reaction is included. All data were obtained from the NIST database [30]. Similar to our previous study of charge transfer reactions involving carbon-containing charged species we assume that the reaction probability is high when – 1.0 eV < ΔE < 0.50 eV [20]. Using this criterion, data in Table 4 reveal that charge transfer reactions between S^+ and Te, Se, As and P can indeed be expected to occur. As a consequence, the plasma ion population would increase for these elements, affording higher signal intensities in ICP-MS when operating with sulfuric acid-containing matrices.

It is interesting to note that according to the above criteria, some other hard-to-ionize elements (Os, Sb, Pt, Ir, Zn and Hg) could also be involved in a charge transfer reaction with S^+ (see Table S1, Appendix). Nevertheless, no experimental evidence has been found (i.e., these elements do not show signal enhancement in the presence of sulfuric acid), at least under the experimental conditions used in the present work. A similar contradiction between experimental and theoretical data has been reported by Grindlay et al., [20] for the influence of carbon on the signals of B, Os, Pt, Ir, Cd, Be and S in ICP-MS and by Chan et al., [31] who studied Ar^+-based charge transfer reactions with Sr in ICP-AES.

3.3. Analysis of certified polyethylene sample

To evaluate the practical implications of the presence of a sulfuric acid matrix in ICP-MS, the elemental analysis of a certified low-density polyethylene sample was performed. Two different sample digestion procedures using nitric acid and a mixture of nitric acid and sulfuric acid (Table 3) were employed for comparison. It is interesting to note that the use of sulfuric acid in the digestion mixture shows some advantages over nitric acid: (i) a reduction in the polyethylene digestion time (from 60 to 25 min, see Table 3); and, (ii) no solid residues are obtained after digestion. In spite of the sample carbon content (up to 1.0 g L^{-1} in the analyzed solution), no evidences of carbon-based non-spectral matrix effects have been observed [20]. Indeed, no significant signal differences were caused by addition of 1.0 g carbon L^{-1} (as glycerol) to a 2% w w^{-1} sulfuric acid solution.

Table 5 shows the results of the determination of eight elements in a certified low-density polyethylene sample (ERM-EC681K) by ICP-MS using matrix-matched standard solutions. The results demonstrate that there is no influence of the matrix composition on the analyte concentrations found in the sample. In all cases, the element concentrations are in agreement with the certified values, thus demonstrating that the use of matrix-matched standards allows the accurate determination of the tested elements in a sulfuric acid matrix with a confidence level of 95% (3 replicates).

4. Conclusions

The presence of sulfuric acid affords signal suppression in ICP-MS for almost all the elements tested mainly because of a decrease in the amount of analyte reaching the plasma. Nevertheless, a signal enhancement is observed for Te, Se, As and P, irrespective of the experimental conditions used. The signal enhancement factor increases when increasing the sulfuric acid concentration (at least up to 5% w w^{-1}). The behavior of the Te, Se, As and P signals is related to an increased analyte ion population caused by charge transfer reactions involving S^+ species in the plasma. Theoretical data suggest that Os, Sb, Pt, Ir, Zn and Hg could also be involved in sulfur-based charge transfer reactions, but no experimental evidence has been found.

Accurate multi-element analysis of polyethylene by ICP-MS after sulfuric acid based digestion can be achieved by using external calibration and matrix-matched standards.

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Highlights

Sulfuric acid containing matrices enhance the signals of Te, Se, As and P in ICP-MS.

Sulfur-based charge transfer reactions have been thoroughly studied

Signal enhancements are related with the presence of S^+ in the plasma

Table 1. ICP-MS operating conditions

Plasma forward power (W)	1100 - 1400
Argon flow rate (L min^{-1})	
Plasma	15
Auxiliary	0.9
Nebulizer	0.80 - 1.05
Sample introduction system	
Nebulizer	Micromist
Spray chamber	Double-pass
Sample uptake rate (mL min^{-1})	0.25 - 0.75
Dwell time (ms)	10
Sweeps	100
Replicates	5

Table 2. Nuclides, ionization energies and degree of ionization (estimated via the Saha equation) of the elements studied in this work [21].

Nuclide	Ionization energy (eV)	Ionization degree (%)
$^{137}Ba^{+}$	5.212	91
$^{7}Li^{+}$	5.392	100
$^{140}Ce^{+}$	5.539	98
$^{88}Sr^{+}$	5.695	96
$^{115}In^{+}$	5.786	99
$^{27}Al^{+}$	5.986	98
$^{238}U^{+}$	6.194	100
$^{45}Sc^{+}$	6.561	100
$^{52}Cr^{+}$	6.766	98
$^{208}Pb^{+}$	7.417	97
$^{107}Ag^{+}$	7.576	93
$^{55}Mn^{+}$	7.434	95
$^{60}Ni^{+}$	7.635	91
$^{182}W^{+}$	7.864	94
$^{63}Cu^{+}$	7.726	90
$^{59}Co^{+}$	7.881	93
$^{11}B^{+}$	8.298	58
$^{105}Pd^{+}$	8.337	93
$^{189}Os^{+}$	8.438	78
$^{121}Sb^{+}$	8.608	78
$^{195}Pt^{+}$	8.959	62
$^{191}Ir^{+}$	8.967	-
$^{111}Cd^{+}$	8.994	85
$^{128}Te^{+}$	9.010	66
$^{197}Au^{+}$	9.226	51
$^{9}Be^{+}$	9.323	75
$^{66}Zn^{+}$	9.394	75
$^{78}Se^{+}$	9.752	33
$^{75}As^{+}$	9.789	52
$^{202}Hg^{+}$	10.438	38
$^{31}P^{+}$	10.487	33

Table 3. Digestion procedures used with the certified low-density polyethylene sample

Digestion procedure	A	B	
Acid	HNO_3	HNO_3	H_2SO_4
Acid concentration (% w w^{-1})	65	65	98
Acid volume (mL)	10	7	3
Sample mass (g)	0.25		
Microwave power (W)	1600		
Ramp time (min)	5		
Pressure (psi)	100		
Temperature (ºC)	130		
Hold time (min)	60	25	

Table 4. States and energy defects (ΔE) for charge transfer reaction between S^+ and P, As, Se and Te. Sulfur ionization energy: 10.36 eV; S ground state: ^3P; S^+ ground state: ^4S

Analyte	Atom ground state term	Ion electronic state energy level closest to the IE of S		ΔE (eV)	Spin		Charge transfer probability
		Term	Energy (eV)		S_I	S_P	
Te	^3P	^2D	10.26	-0.1	5/2,3/2,1/2	3/2,1/2	High
Se	^3P	^4S	9.72	-0.64	5/2,3/2,1/2	5/2,3/2,1/2	High
As	^4S	^3P	10.12	-0.24	3,2,1,0	2,1,0	High
P	^4S	^3P	10.48	0.12	3,2,1,0	2,1,0	High

Table 5. Results of the elemental analysis of a certified low-density polyethylene sample (ERM-EC681K) by ICP-MS after two different sample digestion procedures. Precision is presented as $(t * s/\sqrt{n})$ confidence interval, in which *t* is the Student's t (95% confidence level); *s* is the standard deviation and *n* the number of replicates (3). Q_g 0.95 L min^{-1}; Q_l 0.25 mL min^{-1}; r.f. power 1400 W.

Analyte	Concentration (mg kg^{-1})		
	Procedure A[#]	Procedure B[@]	Certified
As	31 ± 4	29 ± 3	29.1 ± 1.8
Cd	142 ± 5	137 ± 3	137 ± 4
Sb	111 ± 13	99 ± 5	99 ± 6
Pb	104 ± 6	94 ± 3	98 ± 6
Zn	1320 ± 50	1280 ± 10	1250 ± 70*
Sn	81 ± 9	78 ± 7	86 ± 6*
Hg	24.9 ± 1.9	23.8 ± 1.3	23.7 ± 0.8

[#] Matrix: HNO_3 3.3 % w w^{-1}

[@] Matrix: H_2SO_4 1.4 % w w^{-1} + HNO_3 2.3 % w w^{-1}

* Indicative value

Figure captions

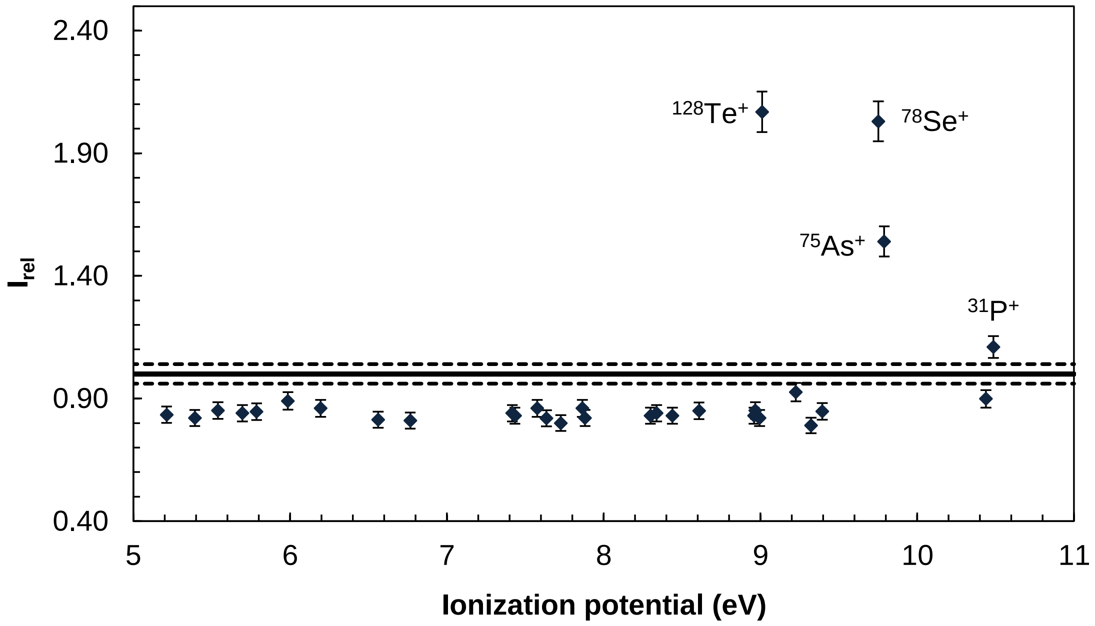
Figure 1. Relative signal intensities, I_{rel}, obtained for a 2% w w^{-1} sulfuric acid solution in comparison to those with 1% w w^{-1} nitric acid as a function of the ionization energy. Error bands indicate the I_{rel} standard deviation of 10 replicates. I_{rel} values between dashed lines (i.e., a range of 4% error) indicate no matrix effect. Q_g 0.95 L min^{-1}; Q_l 0.5 mL min^{-1}; r.f. power 1300 W.

Figure 2. Influence of the sulfuric acid concentration on the I_{rel} value obtained for (X) $^{128}Te^+$; (●) $^{78}Se^+$; (▲) $^{75}As^+$; (■) $^{31}P^+$; and (◆) average I_{rel} value for the remaining nuclides tested in this study. Error bands indicate the I_{rel} standard deviation of 10 replicates. I_{rel} values between dashed lines (i.e., a range of 4% error) indicate no matrix effect. Q_g 0.95 L min^{-1}; Q_l 0.5 mL min^{-1}; r.f. power 1300 W.

Figure 3. Influence of the nebulizer gas flow rate on the net signals for $^{111}Cd^+$ and $^{75}As^+$ with (◆) 1% w w^{-1} nitric acid and (■) 1% w w^{-1} sulfuric acid solutions when operating at different r.f. powers: 1100 W (dashed lines) and 1400 W (solid lines). Q_l 0.5 mL min^{-1}.

Figure 4. Influence of the nebulizer gas flow rate on the net signals for $^{111}Cd^+$ and $^{75}As^+$ with (◆) 1% w w^{-1} nitric acid and (■) 1% w w^{-1} sulfuric acid solutions when operating at different Q_l values: 0.25 mL min^{-1} (dashed lines) and 0.75 mL min^{-1} (solid lines). R.f. power 1300 W.

Figure 1



2.40
1.90
1.40
0.90
0.40
I_rel
128Te+
78Se+
75As+
31P+
5
6
7
8
9
10
11
Ionization potential (eV)

Figure 2

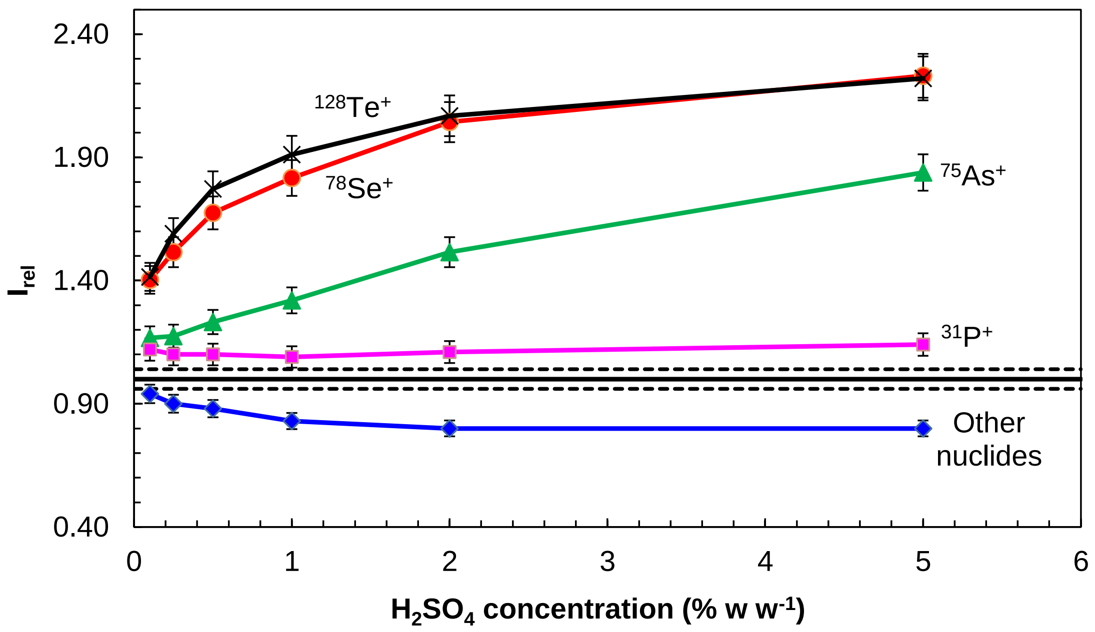
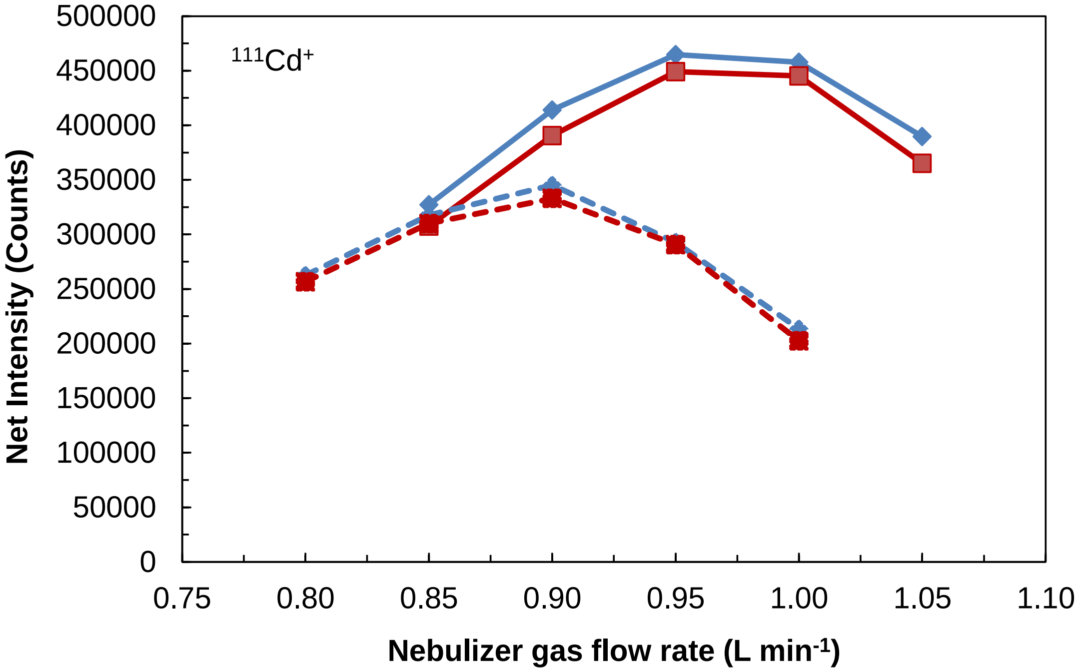

2.40
1.90
1.40
0.90
0.40
I_{rel}
0
1
2
3
4
5
6
H_2SO_4 concentration (% w w^{-1})
$^{128}Te^+$
$^{78}Se^+$
$^{75}As^+$
$^{31}P^+$
Other nuclides

Figure 3


^{111}Cd$^+$
Net Intensity (Counts)
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
0.75
0.80
0.85
0.90
0.95
1.00
1.05
1.10
Nebulizer gas flow rate (L min^{-1})

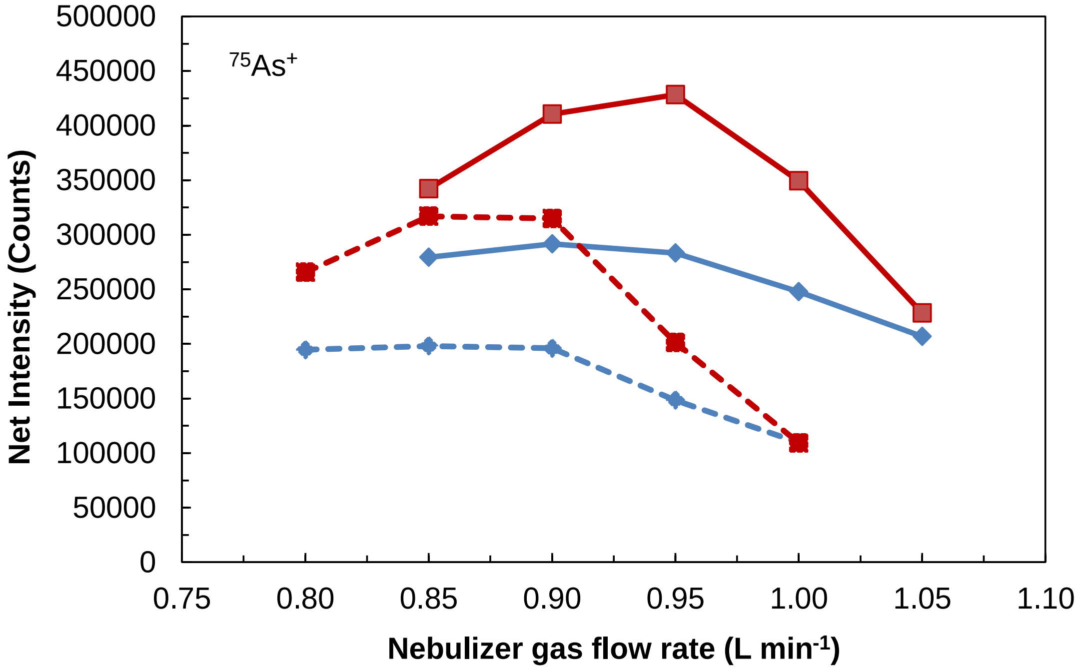
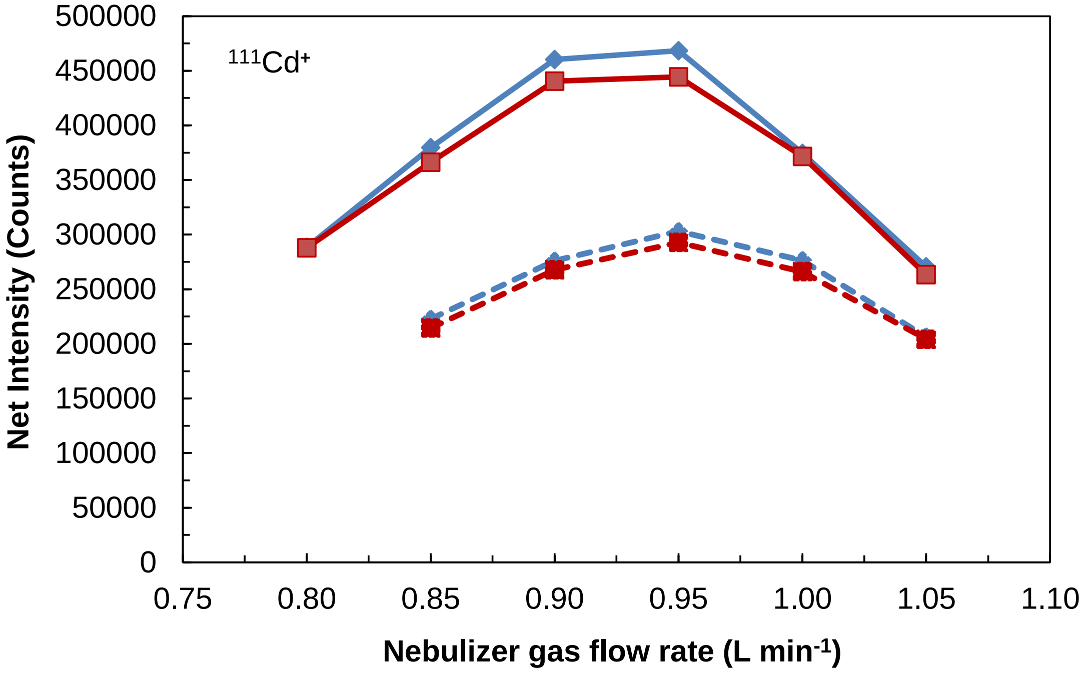
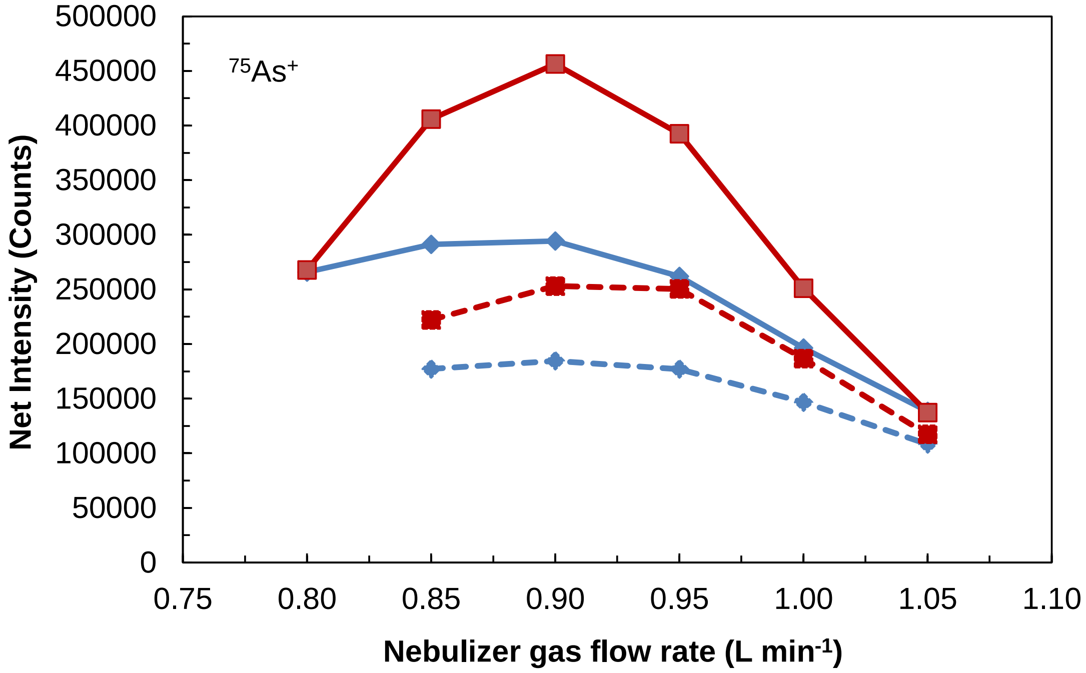

^{75}As$^+$
Net Intensity (Counts)
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
0.75
0.80
0.85
0.90
0.95
1.00
1.05
1.10
Nebulizer gas flow rate (L min^{-1})

Figure 4



$^{111}Cd^{+}$
Net Intensity (Counts)
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
0.75
0.80
0.85
0.90
0.95
1.00
1.05
1.10
Nebulizer gas flow rate (L min^{-1})



$^{75}As^{+}$
Net Intensity (Counts)
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
0.75
0.80
0.85
0.90
0.95
1.00
1.05
1.10
Nebulizer gas flow rate (L min^{-1})

Novelty statement

Results of a systematic study concerning non-spectral interferences from sulfuric acid containing matrices on a large number of elements in inductively coupled plasma - mass spectrometry are presented in this work. The presence of sulfuric acid affords signal suppression in ICP-MS for almost all the elements tested thus indicating the negative matrix effect caused by changes in the amount of analyte loading of the plasma. Nevertheless, a signal enhancement is observed for Te, Se, As and P, irrespective of the experimental conditions used. The signal enhancement factor increases when increasing the sulfuric acid concentration (at least up to 5% w w^{-1}). The behavior of the Te, Se, As and P signals is related to an increased analyte ion population caused by charge transfer reactions involving S^+ species in the plasma. Theoretical data suggest that Os, Sb, Pt, Ir, Zn and Hg could also be involved in sulfur-based charge transfer reactions, but no experimental evidence has been found.