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 $^{75}As^+$ in the presence of 5 w w^{-1} sulfuric acid) 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 ion 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.

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 for 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 monoelemental 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 together 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.

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

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,

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