

Analytical Methods

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3 **Multi-element analysis of sulfuric acid by oaTOF-ICP-MS after matrix**
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6 **modification with barium bromide**
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11 Lenka Husáková*, Iva Urbanová, Tereza Šídová, Tomáš Mikysek

12 *Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice,*

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14 *Pardubice, Studentska 573 HB/D, CZ-532 10, Czech Republic*
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21 * Corresponding author: Tel. +420 466 037 029 fax: +420 466 037 068
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23 E-mail address: Lenka.Husakova@upce.cz
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Abstract

In this work a novel method for simultaneous multi-element analysis of sulfuric acid by inductively coupled plasma orthogonal acceleration time-of-flight mass spectrometry (oaTOF-ICP-MS) after matrix modification with barium bromide was introduced. For this purpose sample aliquots consisting of 10% (w/w) sulfuric acid were mixed with barium bromide, after the precipitation of sulfates the resulting liquid phase was aspirated with a concentric glass nebulizer for TOF-ICP-MS determination. Separation of sulfur as a precipitated non-soluble barium sulfate enables the elimination of spectral interferences originating from different sulfur containing species like SN^+ , SNH^+ , SO^+ , SOH^+ , SOH_2 , SCO^+ , SNOH^+ , SO_2^+ , S_2^+ , SO_2H^+ , or S_2H^+ onto the determination of e.g. Ti, Zn, Ge, Cu,. After that, direct, reliable, and simultaneous determination of 15 elements (Be, Ti, V, Cr, Mn, Ni, Co, Cu, Zn, Ga, Ge, As, Sn, Sb, Te) at trace and ultra-trace levels in sulfuric acid can be performed under optimum instrumental conditions and by using Rh as an internal standard. Accuracy and precision was assessed by analysing sulfuric acid and by comparison of the results of the proposed method with those found by high resolution ICP-MS method. Results of both methods were in a good agreement for Ti, V, Cr, Mn, Ni, Co, Cu, Zn, Ga, Ge, and As. The accuracy was for all of the 15 elements also checked by analytical recovery study. The reported method has a precision better than 12.5%.

Keywords: oaTOF-ICP-MS; Trace elements; Sulfuric acid; Interferences in inductively coupled plasma mass spectrometry; Precipitation; Barium bromide; Matrix modification

1. Introduction

Large quantities of sulfuric acid are used in many applications in a wide range of industries including the manufacture of fertilizers, lubricants, drugs-pharmaceuticals, rayon, metal processing, batteries, food, dyes and pigments, or chemical manufacturing¹. Due to its aggressive dissolution properties sulfuric acid is prone to acquire metals from other sources and may represent a significant source of contamination in the above applications². As the sulfuric acid quality and purity determines its use for different industrial processes, the targeted trace metal content must be frequently monitored²⁻⁶.

In order to determine trace element purity levels in sulfuric acid, inductively coupled plasma mass spectrometry is an indispensable analytical tool. However, direct analysis of even diluted sulfuric acid is not easy as it can produce rapid corrosion of nickel cones which are commonly used in ICP-MS⁶. In addition matrix-based interferences make the determination difficult^{3,4}. Some non-spectroscopic effects can be compensated by dilution of the sample 1:10 m/m in high purity water³⁻⁶, evaporation of the sample³, use of hot-plasma conditions², analysis by standard addition or the use of internal standard elements⁴. However, spectral interferences^{7,8} originating from S-based species produced from matrix components in the plasma can be difficult to overcome^{2-6,9}, especially with conventional low-resolution quadrupole mass spectrometers^{2,3,5}. While cool-plasma ICP-MS can be used successfully to remove Ar, ArH⁺, ArO⁺ interfering species on Ca, K, and Fe respectively^{3,4}, S-based interferences are still important with the elements such as Ti, Cr, Co, Ni, Cu, Zn, As, when direct analysis is performed²⁻⁵. For conventional low-resolution quadrupole ICP-MS the collision/reaction cell ICP-MS is a powerful correction technique to minimize interferences on analyte of interest^{2,3}. While for older Q-ICP-

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3 MS systems the reduction of the multi-element capabilities can be observed, for modern
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5 quadrupole ICP-MS systems this problem has been overcome. Sector-field ICP-MS with its high
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7 mass resolution can deal with polyatomic interferences originating from major elements even for
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9 samples with a complex matrix.^{4,6} While losing sensitivity in the high resolution mode, the
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11 multi-element capability is maintained. These methods may be, however, less accessible to
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13 routine analytical laboratories owing to the high cost of the instrumentation.
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17 ICP time-of-flight mass spectrometers are more accessible to routine analytical
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19 laboratories, and can overcome the major limitations associated with the scanning nature of other
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21 ICP-MS instrumentation with the advantages of high speed and simultaneous mass determination
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23 without any compromise in mass range, sensitivity or precision¹⁰. Enhanced resolution for the
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25 oaTOF mass analyzer is another advantage; however this is not sufficient to completely resolve
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27 interference signals from different polyatomic species during the analysis of complex samples. In
28
29 order to control the spectral effects during the TOF-ICP-MS analysis the mathematical correction
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31 equations^{11,12} without¹¹ or with the implementation of microwave digestion¹² or some another
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33 approaches employing matrix modification¹³ were used for the analysis of urine¹¹ and food
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35 samples previously^{12,13}.
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41 Despite the development of methods for the analysis of sulfuric acid by quadrupole ICP-
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43 MS which employ collision/reaction cells for interference removal^{2,3,5} and high resolution ICP-
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45 MS instruments^{4,6}, currently no method is available for this purpose when using TOF-ICP-MS.
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47 In this work modification of the sample preparation procedure by the addition of barium bromide
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49 to sulfuric acid samples in order to precipitate and separate sulfates prior to TOF-ICP-MS
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51 analysis is introduced. The main advantage of this approach is that it serves as a cheap, rapid and
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53 simple solution for overcoming the spectral effects from different S-based polyatomic species on
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55 the determination of some elements (e.g. on Ti, Zn, and Cu) whose determination is difficult
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when using instruments with low resolving power. Finally, the developed method was found to be accurate and precise for a multi-element determination of 15 trace elements in sulfuric acid.

2. Material and methods

2.1 Instrumentation

The Optimass8000 oaTOF-ICP-MS instrument (GBC Scientific Equipment Pty. Ltd., Australia) of which a detailed description is given in ref.¹⁰ was used throughout this study. Details of the instrument and the operating conditions are summarized in Table 1. Using typical operating conditions sensitivity of 15000 counts s⁻¹ per µg L⁻¹ (mass integrated peak) and resolution (full width at half maximum intensity) of 1800 was achieved for ¹³⁹La⁺. For ²³⁸U⁺, the same parameters were 17000 counts s⁻¹ per µg L⁻¹ and 2100, respectively.

Comparative measurements were performed using a high performance, double focusing magnetic sector field Thermo Scientific™ ELEMENT 2™ ICP-MS (Thermo Scientific, Bremen) attached to a CETAC Aridus II™ Desolvating Nebulizer system (CETAC Technologies Inc., USA). The Aridus II™ couples an Aspire™ low-flow PFA nebulizer and a heated PFA spray chamber with a PTFE membrane desolvator unit. Instrument settings and measurement parameters for the ELEMENT2 are shown in Table 2.

The determination of Ba was carried out with an Avanta P double beam atomic absorption spectrometer (GBC Scientific Equipment Pty. Ltd., Australia). A hollow cathode lamp (Photron Pty. Ltd., Australia) was used the line source (lamp current 15 mA, wavelength 553.6 nm, spectral bandpass 0.5 nm). Sample solutions were introduced to the spectrometer through a standard GBC pneumatic nebulizer. The gas flame mixture was formed with 10.0 L min⁻¹ nitrous

oxide (99.5%, from Linde Gas, Inc., Czech Republic) and 4.5 L min⁻¹ acetylene (99.5%, from Linde Gas, Inc.).

The determination of S was done on an inductively coupled plasma optical emission spectrometer (ICP-OES) Integra XL 2 (GBC Scientific Equipment Pty. Ltd., Australia) by an independent laboratory. The parameters of the instrument setup as well as the wavelength used in these measurements are given elsewhere¹⁴.

Centrifugation of the samples was performed using a NF 400 bench top centrifuge (NÜVE INC., Turkey).

2.2 Reagents and standards

All solutions were prepared using deionised water purified by means of the UltraClear (SG, Germany) pure water system to 0.05 µS cm⁻¹.

Sub-boiled nitric acid was prepared from nitric acid (65%, w/w) of Selectipur quality (Lach-Ner, Neratovice, Czech Republic). Barium nitrate and barium acetate used for interference studies were TraceSelect quality and obtained from Fluka (Fluka, Buchs, Switzerland). Barium bromide 99.999% was purchased from Hi-Chem Ltd. (Czech Republic). Rhodium internal standard solution was prepared from 1 g L⁻¹ Rh solution obtained from SCP Science (Canada). Multi-element stock solution containing 10 mg L⁻¹ of Li, B, Be, Ti, V, Cr, Mn, Ni, Co, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Zr, Mo, Ru, Pd, Ag, Cd, Sn, Sb, Te, Cs, Hf, Ta, W, Re, Pt, Hg, Tl, Pb, Bi, Th, and U, being routinely used in our laboratory was prepared from single element standards of 1 g L⁻¹ obtained from Analytika Ltd. (Prague, Czech Republic) or SCP Science. The stock solution of Ba (1 g L⁻¹) was obtained from Analytika Ltd. (Prague, the Czech Republic).

2.3 Samples

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3 The following sulfuric acid samples were used throughout the study: 95–98% H₂SO₄ of
4 TraceSELECT[®] Ultra grade for ultratrace analysis (Sigma-Aldrich Co. LLC), 96% (w/w) G.R.
5 H₂SO₄ of pre-analysis grade and 96% (w/w) H₂SO₄ of pure quality (both from Lach-Ner Ltd.,
6 Czech Republic). The accurate sulfuric acid concentrations were determined by titration with
7 sodium hydroxide and with potentiometric indication¹⁵. For H₂SO₄ of TraceSELECT, pre-
8 analysis grade and of pure quality they were as follows: 96.8 ± 0.1, 96.2 ± 0.4 and 98.6 ± 0.3%.
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10 The results are expressed as the mean ± 2SD of two independent determinations.
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23 2.4 Sample and calibration standards preparation

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25 The sample preparation for oaTOF-ICP-MS analysis consisted of the addition of 0.85 mL
26 of 500 g L⁻¹ BaBr₂ to 1.25 mL of 10% (w/w) H₂SO₄. The solution was gently mixed and
27 centrifuged for 5 min at 2500 rpm followed by filtration through a 0.45 µm nylon syringe filter
28 (Whatman Autovial). Sample blanks were prepared by the same method using TraceSELECT[®]
29 Ultra grade purity level acid.
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37 Matrix matched calibration solutions were prepared as follows. To 5 mL of 10% H₂SO₄
38 (TraceSELECT[®] purity level) 3.4 mL of 500 g L⁻¹ BaBr₂ were added. The solution was mixed,
39 centrifuged and filtered as described above. The filtrate was divided into seven aliquots. The
40 individual aliquots were spiked with the standard so they contained 0, 5, 10, 20, 30, 40, and 50
41 µg L⁻¹ of Li, B, Be, Ti, V, Cr, Mn, Ni, Co, Cu, Ga, Ge, As, Se, Rb, Sr, Zr, Mo, Ru, Pd, Ag, Cd,
42 Sn, Sb, Te, Cs, Hf, Ta, W, Re, Pt, Hg, Tl, Pb, Bi, Th, and U, , and 0, 50, 100, 200, 300, 400, and
43 500 µg L⁻¹ of Zn, and Rh at final concentration 1 µg L⁻¹.
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3 The sample preparation for analysis by HR-ICP-MS consisted of dilution of the
4 concentrated acids to obtain 10% solutions of individual samples. The prepared samples were
5 given to an independent laboratory for reference measurements.
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10 11 12 13 14 **2.5 Sample analysis**

15 16 17 **2.5.1 ICP-MS**

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19 Quantification of trace element concentrations by TOF-ICP-MS method was performed
20 by establishing calibration curves using matrix matched standards prepared using the method
21 described in section 2.4. Peak area mode and five second data acquisition time and ten replicates
22 were used for the measurement. For HR-ICP-MS method direct aqueous calibration was used for
23 determinations and prepared from multi-element standard (Epond SA, Switzerland). For both
24 TOF-ICP-MS and HR-ICP-MS method internal standardization with the implementation of Rh
25 and In, respectively was used for compensation of non-spectral effects.
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38 39 **2.5.2 Flame atomic absorption spectrometry (FAAS)**

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41 In order to determine Ba concentration in the liquid sample after the separation of sulfate
42 precipitate, FAAS method was used. For this purpose a calibration graph was constructed from
43 which all calculations were made in one analytical run. Five aqueous standards within the
44 concentration range of 0–20 mg L⁻¹ Ba were used to obtain the calibration curve. Five replicates
45 of three-second integration time were used. Calibration curve was linear in the investigated
46 concentration range with the correlation coefficient 0.999.
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2.6 Statistical data treatment

The data were processed using the Statistica 12 computer program (StatSoft, Inc., USA) and QC ExpertTM 2.5, TriloByte Statistical Software, (Pardubice, Czech Republic).

3. Results and discussion

3.1 Evaluation of spectral interference

In the direct analysis of sulfuric acid, polyatomic species such as SN^+ , SNH^+ , SO^+ , SOH^+ , SOH_2^+ , SCO^+ , SNOH^+ , SO_2^+ , S_2^+ , SO_2H^+ or S_2H^+ interfere with important elements such as Ti, Cr, Co, Ni, Cu, Zn or Ga^3 . Table S1 from the Supplementary Material summarizes potential interferences, which might be encountered during an oaTOF-ICP-MS analysis. For the problematic elements which are listed above, a resolving power higher than 4000 ($m/\Delta m$) is needed for successful interference removal as can be seen from the data presented in Table 2 and from the data available in the literature^{6,8}. Quantitative data of apparent elemental concentration in the presence of sulfuric acid as measured on the Optimass 8000 within the range of 0–500 mg L^{-1} of S were evaluated. Interferences from different sulfur containing species were observed for $^{48}\text{Ti}^+$, $^{49}\text{Ti}^+$, $^{64}\text{Zn}^+$, $^{66}\text{Zn}^+$, $^{65}\text{Cu}^+$ and $^{82}\text{Se}^+$. Figure 1 shows the influence of S (sulfuric acid) concentration within the range of 0–500 mg L^{-1} on the relative concentration signal of 5 $\mu\text{g L}^{-1}$ of $^{48}\text{Ti}^+$, $^{49}\text{Ti}^+$, and $^{64}\text{Zn}^+$ as the most interfered isotopes from the multi-elemental standard. In contrast to the literature^{5,6} no significant interference was observed on the determination of V, Ge, As or Ga. However, the highest investigated concentration in the solutions was 500 mg L^{-1} , which corresponds to 0.3% (w/w) solution of H_2SO_4 , while the cited interference were observed during the analysis of 10% (w/w) solutions. Other interferences could be observed during the

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3 analysis of more concentrated solutions; however these investigations were not performed in
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5 order to protect nickel sampler and skimmer cones.
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10 11 **3.2 Effect of barium salt on the removal of spectral interference**

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13 It has been previously shown that precipitation of chloride matrix can effectively reduce
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15 chloride based interferences¹⁶ and the precipitation of Ca^{2+} as an oxalate may overcome
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17 interferences from different calcium containing species on the determination of nickel in serum
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19 analysis¹⁷ and onto the determination of As, Se, Co and Ni in milk¹³ when using conventional
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21 quadrupole¹⁷ and TOF-ICP-MS instruments¹³, respectively. However, the technique of
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23 precipitating interfering species from the matrix is not a commonly used approach in ICP-MS
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25 practice for overcoming the spectral effects. There are many sulfates of low solubility¹⁸, such as
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27 like calcium sulfate, strontium sulfate, or lead(II) sulfate. Barium sulfate is highly insoluble, and
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29 is commonly used for gravimetric analysis of sulfate, and hence was chosen for this study.
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35 In this study, barium nitrate was initially employed in order to precipitate and separate
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37 sulfate as non-soluble barium sulfate enabling the elimination of the interference. However, the
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39 disadvantage of barium nitrate is its lower solubility which limits the concentration of sulfuric
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41 acid that can be analyzed. With barium nitrate addition, a sulfuric acid concentration of 2% (w/w)
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43 concentration is the maximum that can be used in order to avoid any further dilutions. In
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45 addition, significant changes in solubility relating to the temperature are a critical consideration
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47 given the cold working environment within the glass spray chamber. Due to this fact
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49 $\text{Ba}(\text{CH}_3\text{COO})_2$, and BaBr_2 were considered for use. The use of barium acetate led to an excessive
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51 input of C into the spectrometer causing interferences at masses 48 and 52 hampering the
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53 determination of $^{48}\text{Ti}^+$ and $^{52}\text{Cr}^+$ (data not shown here). Finally, BaBr_2 was chosen for the
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3 optimization purposes even though interferences from Br^+ and BrOH^+ were observed at m/z 79,
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6 81, 95–100.

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8 The influence of the BaBr_2 onto the determination of $^{48}\text{Ti}^+$, $^{49}\text{Ti}^+$, $^{64}\text{Zn}^+$ in the presence of
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10 0–500 mg L^{-1} of S can be seen in Figure 1, from which it is obvious that the interferences caused
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12 by $^{32}\text{S}^{16}\text{O}^+$, $^{33}\text{S}^{16}\text{O}^+$ a $^{32}\text{S}_2^+$ a $^{32}\text{S}^{16}\text{O}_2^+$ were successfully eliminated. Similarly, the suppression of
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14 the interference from different S containing species was observed for other interfered isotopes
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16 like $^{82}\text{Se}^+$ and $^{65}\text{Cu}^+$ (data not shown here).

23 3.3 Application to the analysis of sulfuric acid

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25 The concentration of sulfuric acid used for precipitation was optimized in order to analyze
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27 solutions with as high as possible acid content to avoid further dilutions which would negatively
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29 impact the detection limits of the method. The optimization was performed for 40, 30, 20, 10, 5,
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31 and 2% solutions of sulfuric acid, which were spiked with 0, 10, and 20 $\mu\text{g L}^{-1}$ of multi-elemental
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33 standard described in section 2.2.. Each concentration was prepared in two sets. The first set was
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35 spiked with the standards before the precipitation with BaBr_2 , while the other set was spiked with
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37 the standards after the precipitation of BaSO_4 and its removal from the solution. This approach
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39 helped to both monitor the influence of sample matrix on the analyte sensitivity and to reflect the
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41 influence of co-precipitation and/or inclusion of the analyte in the precipitated matrix. It was
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43 found that the determination of elements in sulfuric acid of concentration higher than 10 % led to
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45 irreproducible results, which is in contrast with the analysis of lower concentrations of sulfuric
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47 acid (10, 5, and 2%). Good agreement between the slopes of the solutions, which were
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49 constructed for solutions spiked before or after the precipitation, was obtained for 10, 5, and 2%
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51 (w/w) sulfuric acid with differences less than 5% between the slopes and thus 10% solutions
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3 were used for the analysis. Fifteen elements (${}^9\text{Be}^+$, ${}^{48}\text{Ti}^+$, ${}^{51}\text{V}^+$, ${}^{52}\text{Cr}^+$, ${}^{55}\text{Mn}^+$, ${}^{58}\text{Ni}^+$, ${}^{59}\text{Co}^+$, ${}^{63}\text{Cu}^+$,
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5 ${}^{64}\text{Zn}^+$, ${}^{71}\text{Ga}^+$, ${}^{72}\text{Ge}^+$, ${}^{75}\text{As}^+$, ${}^{118}\text{Sn}^+$, ${}^{123}\text{Sb}^+$, ${}^{128}\text{Te}^+$) could be determined using the 10% solution,
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7 however, co-precipitation or inclusion of elements such as Cd, Pb, Ag, Li, Rb, Hf, or Hg
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9 occurred even for the lowest tested concentration of sulfuric acid. Co-precipitation of elements
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11 such as Ag, Pb, Hg, or Tl could be expected as these element form sparingly soluble bromides.
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13 Besides that, for Sr, Pb or Hg, it is also possible that they co-precipitate during the formation of
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15 barium sulfate.¹⁸ In the excess of BaSO_4 , isomorphic substitution where position replacement of
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17 one cation by another of similar size leads to incorporation of a variety of cations into solid
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19 crystals can take place. This would lead to formation of rhombic crystals similar to those of
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21 BaSO_4 . As for the other elements, for which we did not obtain reproducible results, the whole
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23 problematics will be much more complex and was not part of this study.
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29 The comparison of slopes of aqueous calibration and the standard additions method,
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31 which is a robust strategy for compensating for matrix effects is shown in Figure 2. In addition,
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33 the slope values of matrix matched calibration are also included in this figure. As can be seen
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35 from Figure 2, the slope values of matrix matched calibration and standard additions technique
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37 are in a good agreement with the biggest apparent difference being only 9.2% for ${}^{59}\text{Co}$. The
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39 approach using matrix matched calibration for quantification is less time consuming than the
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41 standard additions method.
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49 **3.4 Drawbacks and solutions of the use of barium bromide**

50 There are several drawbacks associated with the employment of barium bromide in ICP-MS
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52 analysis to which attention must be paid in order to avoid them. A high concentration of residual
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54 barium salt may both contaminate the spectrometer and be a source (precursor) of other
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3 interfering species and/or compounds like Ba^{++} , BaO^+ , BaH_2^+ , BaOH^+ , BaO_2^+ , or BaN^+ .
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5 interfering the determination of $^{66,67,68}\text{Zn}^+$, $^{133}\text{Cs}^+$, $^{152}\text{Sm}^+$, $^{153}\text{Eu}^+$, $^{155}\text{Gd}^+$. However, Zn, Ga, and
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8 Ge could be determined using different isotopes, namely 64, 71, and 72, respectively. In this
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10 study, barium salt was calculated to be added in strictly equimolar amounts to that of sulfuric
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12 acid. Using these proportions, the majority of barium was precipitated as barium sulfate and
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14 separated from the analyzed solution. Solutions of 10% of H_2SO_4 were precipitated with
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16 increasing amount of BaBr_2 starting at 825 μL of 500 g L^{-1} , which was calculated to be equimolar
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18 to 1.25 mL of 10% H_2SO_4 , up to an excess of 25 μL . During this experiment, the decrease in the
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20 signal at $m/z = 48$ and increase in the signal at $m/z = 217$ corresponding to $^{138}\text{Ba}^{79}\text{Br}^+$ was
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22 monitored. This peak was first observed with an excess of 20 μL compared to the calculated
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24 amount while the signal at $m/z = 48$ remained constant with further addition of BaBr_2 , which
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26 suggests that the interfering sulfur has been removed and the signal corresponds to only $^{48}\text{Ti}^+$.
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28 The change in the signal for the monitored masses can be seen in Figure 3. Mass spectra for the
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30 analysis of sulfuric acid without and with the employment of optimal amount of barium bromide
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32 for matrix modification at mass of 48 and 49 for Ti and within the range of 216 and 220 amu
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34 reflecting the formation of BaBr^+ species are shown in Fig. 4. The concentration of remaining S
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36 determined by ICP-OES in the samples prepared using the optimized amount of BaBr_2 was for all
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38 samples less than 9.5 mg L^{-1} , which suggests that the removal of the interfering S as BaSO_4 was
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40 efficient. The remaining concentration of Ba^{2+} in filtrates determined by FL-AAS method did not
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42 exceed the value of 4 mg L^{-1} . However, this concentration may still influence the analysis. Due to
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44 this fact, specific SMARTGATE ion blanking setting (see Table 1) was used in order to avoid
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46 these species reaching the detector and thus prolong its life. At this point, any unwanted ions can
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48 be rejected from the flight path by deflection plates in the SMARTGATE, while ions of interest
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50 are passed on for detection.
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3.5 Analytical figures of merit

3.5.1 Accuracy of measurements

Accuracy was evaluated in terms of trueness and precision (see Table 3) and different approaches were used in this study to assess the trueness. The first approach utilized a method as implemented using paired sample *t*-test. In this case the results of the proposed TOF-ICP-MS method were compared with those obtained by reference HR-ICP-MS method which was selected for comparative purposes as no certified reference material is available for the validation of trace element concentration in sulfuric acid. The analysis by HR-ICP-MS Element 2 (Thermo Fisher Scientific, Bremen, Germany) was performed at the Laboratory of Geological Processes at the Institute of Geology AS CR, v.v.i.. The results obtained using both procedures for the determination of Ti, V, Cr, Mn, Zn, Ga and As in H₂SO₄ of p.a. grade and Ti, V, Cr, Mn, Ni, Co and As in pure H₂SO₄ were not significantly different for a 95% confidence level ($p = 0.28$ and $p = 0.20$ for H₂SO₄ of p.a., and pure quality, respectively) and thus both methods are comparable.

A second approach for the accuracy assessment involved the computation of analytical recoveries determined in samples of p.a. and pure H₂SO₄ (n=3) using standard addition at concentrations as indicated in Table 3. The concentration of the standard additions was chosen as a compromise to be at the same concentration level as the analytes and to cover the whole range of the elements present in the analyzed samples. The recoveries obtained were in all cases between 90 and 108 % for all elements, indicating that the method is accurate to within 10%.

The precision of the method was evaluated in terms of intra-day and inter-day comparison. Intra-day precision was determined as relative standard deviation (RSD) of analyses of the sample prepared independently three times during the same day, while inter-day precision (as RSD) was evaluated based on the results of analyses of the samples on three different days

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3 over a period of one month. Every solution was analysed in ten replicates yielding a mean value
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5 used for the calculations. The RSD values of intra-day and inter-day studies were typically found
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7 to be below 12.1 % and 10.3 %, respectively, which show that the precision of the method was
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9 satisfactory (see Table 3).
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12 13 14 15 3.5.2 Limits of detection

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17 Limits of detection (LODs) for each isotope, based on three times the standard deviation
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19 of the blank response at the given m/z position divided by the slope of the calibration graph are
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21 given in Table 3 for 10% (w/w) sulfuric acid samples. The integration time was set to 5 s and
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23 standards and blanks were determined with 10 replicates. The blank was prepared from sulfuric
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25 acid of TraceSELECT[®] Ultra purity using the same method as described in Section 2.4.
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29 Significantly lower detection limits of HR-ICP-MS are evident from the data presented in Table 3
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31 when compared to TOF-ICP-MS method. However, it is difficult to compare these methods for
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33 several reasons. Firstly, for HR-ICP-MS a desolvating nebulizer system was employed for
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35 sample introduction that can enhance analyte sensitivity up to 10 times in contrast to more
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37 conventionally used concentric nebulizer used also in this study for TOF-ICP-MS¹⁹. Secondly,
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39 very low random background is observed for high resolution ICP-MS instrumentation even for a
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41 high resolution setting²⁰. These low noise levels yield a significant improvements in the detection
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43 limits for element determinations, especially with an increased data acquisition time²¹. Another
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45 factor is that lower dilution factor for HR-ICP-MS method in contrast to TOF-ICP-MS described
46
47 in this work was used during the sample preparation as 10% w/w H₂SO₄ was analysed using the
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49 former method, while the concentration of H₂SO₄ after the dilution with barium bromide solution
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51 is about 5.4% (w/w). Similarly, previously reported works employing high resolution
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53 instrumentation⁴ or quadrupole based instruments with various collision/reaction cell
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3 technologies^{2,3} also describe the analysis of about 10% (w/w) H₂SO₄. These works reported
4
5 favourable limits of detection, which meet SEMI (The Semiconductor Equipment and Materials
6
7 International Standards organization) requirements for the highest quality Tier C H₂SO₄ that has
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9 guideline impurity limits of 100 pg g⁻¹ for 18 of 21 (Al, Sb, As, Ba, B, Ca, Cr, Cu, Fe, Pb, Mg,
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11 Mn, Ni, K, Na, Sn, Ti, Zn) required trace elements²² and of Tier B H₂SO₄ with permissible level
12
13 of 1 ng g⁻¹ for all of the above mentioned elements and additionally for Be, Bi, Cd, Co, Ga, Ge,
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15 Au, Li, Mo, Nb, Si, Ag, Sr, Ta, Tl, V, Zr. These studies however arise mainly from product
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17 literature.
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22 Also of note is that barium bromide used in this study was not of the highest purity
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24 available, which will further significantly impact LODs values. It is also important to note, that
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26 direct analysis of 10% (w/w) sulfuric acid is also possible with TOF-ICP-MS ensuring
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28 approximately ten times better LODs values for non-interfered elements like Li, Be, Cd, Mo, Sn,
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30 Sb, W, or Bi when compared with the values given in Table 3,. However we did not use this
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32 approach in a higher extent in order to protect the nickel cones as platinum ones were not
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34 available. In this case, also determination of elements such as Li, Be, Cd, Mo, Sn, Sb, W, or Bi,
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36 whose determination is impacted by the matrix modification method will ensure analytical
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38 recoveries within 86–112%. The recoveries were calculated for samples of 10% H₂SO₄ spiked
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40 with 4 μg L⁻¹ of the analytes.
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47 Detection capability of the proposed method, however is adequate to determine impurities
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49 of H₂SO₄ of Grade 1 and 2, as suggested by SEMI. The obtained detection limits are one to two
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51 orders of magnitude lower than maximum permissible content of elements for Grade 2 and Grade
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53 1 purity being in the range of 5 to 300 ppb in the concentrated sulfuric acid.
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3.5.3 Sample throughput

Simultaneous analysis of all elements took for each sample (including sample introduction, ten-replicate measurements and rinsing) approximately three minutes under the conditions described in Table 1, i.e. ca 20 samples could be measured within an hour. The preparation of eight samples, whose number was limited due to the space arrangement of the centrifuge, included pipetting of the acid and of the bromide, precipitation, centrifugation and filtration, and spiking of the filtrate with internal standard, took approximately 25 minutes.

4. Conclusions

The proposed method employing barium bromide for precipitation of sulfates prior to the analysis of sulfuric acid offers a simple and efficient way for accurate quantification of 15 elements in this difficult matrix by TOF-ICP-MS method. One advantage is that using this approach the interference of the matrix is decreased significantly and accurate analysis with the use of matrix matched calibration method can be performed even for elements like Ti, Cu, or Zn, which are more troublesome if ICP-MS instruments with insufficient resolving power are used. Another benefit of this procedure is its simplicity, speed and low price of the analysis. Moreover, all the elements are determined simultaneously without the need of specific setting for individual analytes which may be another benefit over Q-ICP-MS or HR-ICP-MS methods. The proposed method using precipitation with barium salt is expected to be applied for TOF- as well as for Q-ICP-MS as the purpose of this procedure is to get rid of spectral interferences caused by sulfur-based polyatomic species, which is beneficial for both of these instrumentations. However, the detection limits are limited by the quality of barium bromide and additionally some elements like

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3 Cd, Pb, Hg, Sr, Bi, or Ag cannot be determined properly with the proposed methodology due to
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5 the problems with co-precipitation and/or inclusion in the precipitated matrix. Despite of the
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7 above mentioned drawbacks, for TOF-ICP-MS instrumentation this procedure is currently the
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9 only solution to attenuate the interferences to a manageable level.
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12 13 14 15 16 17 **Acknowledgements**

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Figure captions

Fig. 1 Influence of the amount of S (as H₂SO₄) on the relative concentrations of 5 μg L⁻¹ of ⁴⁸Ti⁺, ⁴⁹Ti⁺ and ⁶⁴Zn⁺ from multi-elemental standard in the absence (closed symbols, straight line) and in the presence of barium bromide (open symbols, dotted line). Relative concentration (%) = (concentration evaluated for 5 μg L⁻¹ multi-elemental standard in the presence of barium bromide and sulphur within the investigated range/concentration evaluated for 5 μg L⁻¹ standard at conditions without the interfering matrix element) x 100. Bars indicate the range for each determination (n = 10, 2 SD).

Fig. 2 Comparison of the slopes (1/ μg L⁻¹) of aqueous calibration (black bar) and that of matrix matched calibration (grey bar) with standard additions method (white bar) evaluated with the use of Rh as internal standard. Bars indicate the standard deviation error of the estimate of the slope.

Fig. 3 Optimization of barium bromide (500 g L⁻¹) amount, more exactly of the volume being necessary to be added over those to be calculated as equimolar to 10% (w/w) H₂SO₄ via the monitoring of the signal at the mass of 48 and 217, corresponding to the decreasing of interference at the mass 48 (black line) and excess of barium bromide via the ¹³⁸Ba⁷⁹Br⁺ creation (red line), respectively. Bars indicate the range for each determination (n = 10, 2 SD).

Fig. 4 Mass spectra for the analysis of sulfuric acid without (blue line) and with (red line) the employment of optimal amount of barium bromide for matrix modification at mass of 48 and 49 for Ti and within the range of 216 and 220 amu reflecting the formation of BaBr⁺ species.