PAPER

Multi-elemental analysis of sulfuric acid by oaTOF-ICP-MS after matrix modification with barium bromide†

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In this work a novel method for the simultaneous multi-elemental 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 and after the precipitation of sulfates, the resulting liquid phase was aspirated with a concentric glass nebulizer for TOF-ICP-MS determination. The 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^+ on the determination of e.g. Ti, Zn, Ge, and 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, and Te) at trace and ultra-trace levels in sulfuric acid were performed under optimum instrumental conditions and by using Rh as an internal standard. Accuracy and precision were assessed by analysing sulfuric acid and by comparison of the results of the proposed method with those obtained by the high resolution ICP-MS method. The results of both methods were in good agreement for Ti, V, Cr, Mn, Ni, Co, Cu, Zn, Ga, Ge, and As. The accuracy for all of the 15 elements was also checked by an analytical recovery study. The reported method has a precision greater than 12.5%.

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 manufacturing.[1] 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 applications.[2] As the quality and purity of sulfuric acid determines its use for different industrial processes, the targeted trace metal content must be frequently monitored.[2–6]

In order to determine trace element purity levels in sulfuric acid, inductively coupled plasma mass spectrometry is an indispensable analytical tool. However, the 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-MS.[6] 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 (w/w) in high purity water,[3–6]

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evaporation of the sample,[3] use of hot-plasma conditions,[2] analysis by standard additions or by the use of an internal standard for elements.[4] However, spectral interferences[7,8] originating from the 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 performed.[2–5] For conventional low-resolution quadrupole ICP-MS the collision/reaction cell ICP-MS is a powerful correction technique to minimize interferences on analytes of interest.[2,3] While for older Q-ICP-MS systems the reduction of the multi-element capabilities can be observed, for modern quadrupole ICP-MS systems this problem has been overcome. Sector-field ICP-MS with its high mass resolution can deal with polyatomic interferences originating from major elements even for samples with a complex matrix.[4,6] While losing sensitivity in the high resolution mode, the multi-element capability is maintained. These methods may be, however, less accessible to routine analytical laboratories owing to the high cost of instrumentation.

ICP time-of-flight mass spectrometers are more accessible to routine analytical laboratories, and can overcome the major limitations associated with the scanning nature of other ICP-MS

instrumentation with the advantages of high speed and simultaneous mass determination without any compromise on the mass range, sensitivity or precision.[10] Enhanced resolution for the oaTOF mass analyzer is another advantage; however, this is not sufficient to completely resolve interference signals from different polyatomic species during the analysis of complex samples. In order to control the spectral effects during the TOF-ICP-MS analysis the mathematical correction equations[11,12] without[11] or with the implementation of microwave digestion[12] or some other approaches employing matrix modification[13] were used for the analysis of urine[11] and food samples previously.[12,13]

Despite the development of methods for the analysis of sulfuric acid by quadrupole ICP-MS which employ collision/reaction cells for interference removal[2,3,5] and high resolution ICP-MS instruments,[4,6] currently no method is available for this purpose when using TOF-ICP-MS. In this work the modification of the sample preparation procedure by the addition of barium bromide to sulfuric acid samples in order to precipitate and separate sulfates prior to TOF-ICP-MS analysis is introduced. The main advantage of this approach is that it serves as a cheap, rapid and simple solution for overcoming the spectral effects from different S-based polyatomic species on the determination of some elements (*e.g.* on Ti, Zn, and Cu) whose determination is difficult when using instruments with a 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. The details of the instrument and the operating conditions are summarized in Table 1. Using typical operating conditions, a sensitivity of 15 000 counts per s per μg per L (mass integrated peak) and resolution (full width at half maximum intensity) of 1800 was achieved for $^{139}La^+$. For $^{238}U^+$, the same parameters were 17 000 counts per s per μg per L 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 as the line source (lamp current 15 mA, wavelength 553.6 nm, and spectral bandpass 0.5 nm). The sample solutions were introduced to the spectrometer through a standard GBC pneumatic nebulizer. The gas flame

Table 1 Instrumental operating conditions for oaTOF-ICP-MS

Instrument	GBC Optimass8000
Sample uptake rate	1.0 mL min^{-1}
Sample introduction	Concentric nebulizer with cyclonic spray chamber (70 mL, 10 °C)
ICP source	
Rf power (27.12 MHz)	1250 W
Plasma gas flow rate	11 L min^{-1}
Auxiliary gas flow rate	0.600 L min^{-1}
Nebuliser gas flow rate	0.980 L min^{-1}
Mass spectrometer	
Ion optics	
Sampler cone	Nickel
Skimmer cone	Nickel-plated copper
Extraction	−1300 V
Z1	−190 V
Y mean	−495 V
Y deflection	−1 V
Z lens mean	−1050 V
Z lens deflection	−35 V
Lens body	−140 V
Pulse shaping	
Fill	−39 V
Fill bias	−0.1 V
Fill grid	−2.0 V
Pushout plate	577 V
Pushout grid	−473 V
Blanker	200 V
Spectral frequency	33 kHz
Reflectron	600 V
Detection	
Multiplier gain	2630 V
Ion threshold	8.4 mV
Integration window	Auto
Measurement mode	Pulse counting/analog
SMARTGATE ion blanking system	
Range m/z	Interfering ions
11.5–44.5	$^{12}C^+$, $^{14}N^+$, $^{16}O^+$, $^{17}OH^+$, $^{18}H_2O^+$, $^{28}N_2^+$, $^{30}NO^+$, $^{32}O_2^+$, $^{32}S^+$, $^{40}Ar^+$, $^{41}ArH^+$, $^{80}Ar^{2+}$
55.5–57.0	$^{56}ArO^+$, $^{56}Fe^+$
66.5–70.0	$^{132-138}Ba^{++}$
77.5–82.5	$^{40}Ar_2^+$, $^{79}Br^+$, $^{81}Br^+$, $^{1}H^{81}Br^+$
94.7–97.5	$^{79,81}Br^{16}O^+$
129.0–140	$^{130-138}Ba^+$, $^{139}BaH^+$
149.8–155.3	$^{154}BaO^+$, $^{155}BaOH^+$, $^{150}BaO_2^+$, $^{152}BaN^+$

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 elsewhere.[14]

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

Table 2 Operating conditions of HR-ICP-MS attached to the CETAC Aridus II™ desolvating nebulizer

Instrument	Element 2 attached to the CETAC Aridus II™ desolvating nebulizer system
Rf power (27.12 MHz)	1200 W
Plasma gas flow rate	16 L min^{-1}
Auxiliary gas flow rate	0.9 L min^{-1}
Nebulizer gas flow rate	0.9 L min^{-1}
Sweep gas flow rate	3.6 L min^{-1}
Sample uptake rate	100 μL min^{-1}
Spray chamber temperature	110 °C
Membrane temperature	160 °C
Sampler cone	Ni 1.1 mm
Skimmer cone	Ni 0.8 mm
Lens settings	Optimized for ^{238}U
Resolution mode	Medium resolution, $R = 4000$ (Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga)
	High resolution, $R = 10\,000$ (Ge, As)
Total acquisition time per replicate	0.6 min^{-1}
Number of replicates	10
Number of measurements per sample	5

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 of 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). A 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

The following sulfuric acid samples were used throughout the study: 95–98% (w/w) H$_2$SO$_4$ of TraceSELECT® Ultra grade for ultratrace analysis (Sigma-Aldrich Co. LLC), 96% (w/w) G.R. H$_2$SO$_4$ of pre-analysis grade and 96% (w/w) H$_2$SO$_4$ of pure quality (both from Lach-Ner Ltd., Czech Republic). The accurate sulfuric acid concentrations were determined by titration with sodium hydroxide and with potentiometric indication.[15] For H$_2$SO$_4$ of TraceSELECT, pre-analysis grade and of pure quality they were as follows: 96.8 ± 0.1, 96.2 ± 0.4 and 98.6 ± 0.3%. The results are expressed as the mean ± 2SD of two independent determinations.

2.4. Sample and calibration standard preparation

The sample preparation for the oaTOF-ICP-MS analysis consisted of the addition of 0.85 mL of 500 g L^{-1} BaBr$_2$ to 1.25 mL of 10% (w/w) H$_2$SO$_4$. The solution was gently mixed and centrifuged for 5 min at 2500 rpm followed by filtration through a 0.45 μm nylon syringe filter (Whatman Autovial). The sample blanks were prepared by the same method using TraceSELECT® Ultra grade purity level acid.

The matrix matched calibration solutions were prepared as follows. To 5 mL of 10% H$_2$SO$_4$ (TraceSELECT® purity level), 3.4 mL of 500 g L^{-1} BaBr$_2$ were added. The solution was mixed, centrifuged and filtered as described above. The filtrate was divided into seven aliquots. The individual aliquots were spiked with the standard so that they contained 0, 5, 10, 20, 30, 40, and 50 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, Sn, Sb, Te, Cs, Hf, Ta, W, Re, Pt, Hg, Tl, Pb, Bi, Th, and U, and 0, 50, 100, 200, 300, 400, and 500 μg L^{-1} of Zn, and Rh at a final concentration of 1 μg L^{-1}.

The sample preparation for analysis by HR-ICP-MS consisted of dilution of the concentrated acids to obtain 10% solutions of the individual samples. The prepared samples were given to an independent laboratory for reference measurements.

2.5. Sample analysis

2.5.1. ICP-MS. Quantification of trace element concentrations by the TOF-ICP-MS method was performed by establishing calibration curves using matrix matched standards prepared using the method described in Section 2.4. Peak area mode, five second data acquisition time and ten replicates were used for the measurement. For the HR-ICP-MS method direct aqueous calibration was used for determinations and prepared from the multi-elemental standard (Epond SA, Switzerland). For both TOF-ICP-MS and HR-ICP-MS methods internal standardization with the implementation of Rh and In, respectively, was used for the compensation of non-spectral effects.

2.5.2. Flame atomic absorption spectrometry (FAAS). In order to determine Ba concentration in the liquid sample after the separation of the sulfate precipitate, the FAAS method was used. For this purpose a calibration graph was constructed from which all calculations were made in one analytical run. Five

aqueous standards within the concentration range of $0–20$ mg L^{-1} Ba were used to obtain the calibration curve. Five replicates of three-second integration time were used. The calibration curve was linear in the investigated concentration range with the correlation coefficient of 0.999.

2.6. Statistical data treatment

The data were processed using the Statistica 12 computer program (StatSoft, Inc., USA) and QC Expert™ 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 ESI† 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 $^{48}Ti^+$, $^{49}Ti^+$, $^{64}Zn^+$, $^{66}Zn^+$, $^{65}Cu^+$ and $^{82}Se^+$. Fig. 1 shows the influence of S (sulfuric acid) concentration within the range of $0–500$ mg L^{-1} on the relative concentration signal of

Fig. 1 Influence of the amount of S (as H_2SO_4) on the relative concentrations of 5 µg L^{-1} of $^{48}Ti^+$, $^{49}Ti^+$ and $^{64}Zn^+$ from the 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} of the standard under conditions without the interfering matrix element) × 100. The bars indicate the range for each determination ($n = 10$, 2 SD).

5 µg L^{-1} of $^{48}Ti^+$, $^{49}Ti^+$, and $^{64}Zn^+$ 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 interferences were observed during the analysis of 10% (w/w) solutions. Other interferences could be observed during the analysis of more concentrated solutions; however, these investigations were not performed in order to protect the nickel sampler and skimmer cones.

3.2. Effect of barium salt on the removal of spectral interference

It has been previously shown that precipitation of the chloride matrix can effectively reduce chloride based interferences[16] and the precipitation of Ca^{2+} as an oxalate may overcome interferences from different calcium containing species on the determination of nickel in serum analysis[17] and on the determination of As, Se, Co and Ni in milk[13] when using conventional quadrupole[17] and TOF-ICP-MS instruments,[13] respectively. However, the technique of precipitating interfering species from the matrix is not a commonly used approach in ICP-MS practice for overcoming the spectral effects. There are many sulfates of low solubility,[18] such as calcium sulfate, strontium sulfate, or lead(II) sulfate. Barium sulfate is highly insoluble, and is commonly used for the gravimetric analysis of sulfate, and hence was chosen for this study.

In this study, barium nitrate was initially employed in order to precipitate and separate sulfate as non-soluble barium sulfate enabling the elimination of the interference. However, the disadvantage of barium nitrate is its lower solubility which limits the concentration of sulfuric acid that can be analyzed. With barium nitrate addition, a sulfuric acid concentration of 2% (w/w) concentration is the maximum that can be used in order to avoid any further dilutions. In addition, significant changes in solubility relating to the temperature are a critical consideration given the cold working environment within the glass spray chamber. Due to this fact $Ba(CH_3COO)_2$, and $BaBr_2$ were considered for use. The use of barium acetate led to an excessive input of C into the spectrometer causing interferences at masses 48 and 52 hampering the determination of $^{48}Ti^+$ and $^{52}Cr^+$ (data not shown here). Finally, $BaBr_2$ was chosen for the optimization purposes even though interferences from Br^+ and $BrOH^+$ were observed at m/z 79, 81, 95–100.

The influence of $BaBr_2$ on the determination of $^{48}Ti^+$, $^{49}Ti^+$, $^{64}Zn^+$ in the presence of $0–500$ mg L^{-1} of S can be seen in Fig. 1, from which it is obvious that the interferences caused by $^{32}S^{16}O^+$, $^{33}S^{16}O^+$, $^{32}S_2^+$ and $^{32}S^{16}O_2^+$ were successfully eliminated. Similarly, the suppression of the interference from different S containing species was observed for other interfered isotopes like $^{82}Se^+$ and $^{65}Cu^+$ (data not shown here).

3.3. Application to the analysis of sulfuric acid

The concentration of sulfuric acid used for precipitation was optimized in order to analyze solutions with the acid content as
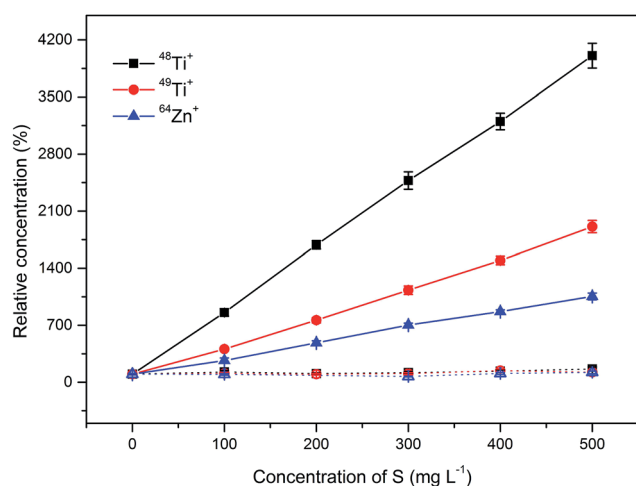
high as possible to avoid further dilutions which would negatively impact the detection limits of the method. The optimization was performed for 40, 30, 20, 10, 5, and 2% solutions of sulfuric acid, which were spiked with 0, 10, and 20 µg L^{-1} of multi-elemental standard described in Section 2.2. Each concentration was prepared in two sets. The first set was spiked with the standards before the precipitation with BaBr$_2$, while the other set was spiked with the standards after the precipitation of BaSO$_4$ and its removal from the solution. This approach helped to both monitor the influence of the sample matrix on the analyte sensitivity and to reflect the influence of co-precipitation and/or inclusion of the analyte in the precipitated matrix. It was found that the determination of elements in sulfuric acid of a concentration higher than 10% led to irreproducible results, which is in contrast to the analysis of lower concentrations of sulfuric acid (10, 5, and 2%). Good agreement between the slopes of the solutions, which were constructed for solutions spiked before or after the precipitation, was obtained for 10, 5, and 2% (w/w) sulfuric acid with differences less than 5% between the slopes and thus 10% solutions were used for the analysis. Fifteen elements (^{9}Be$^+$, ^{48}Ti$^+$, ^{51}V$^+$, ^{52}Cr$^+$, ^{55}Mn$^+$, ^{58}Ni$^+$, ^{59}Co$^+$, ^{63}Cu$^+$, ^{64}Zn$^+$, ^{71}Ga$^+$, ^{72}Ge$^+$, ^{75}As$^+$, ^{118}Sn$^+$, ^{123}Sb$^+$, ^{128}Te$^+$) could be determined using the 10% solution, however, co-precipitation or inclusion of elements such as Cd, Pb, Ag, Li, Rb, Hf, or Hg occurred even for the lowest tested concentration of sulfuric acid. Co-precipitation of elements such as Ag, Pb, Hg, or Tl could be expected as these elements form sparingly soluble bromides. Besides that, for Sr, Pb or Hg, it is also possible that they co-precipitate during the formation of barium sulfate.[18] With the excess of BaSO$_4$, isomorphic substitution where the position replacement of one cation by another of a similar size leading to the incorporation of a variety of cations into solid crystals can take place. This would lead to the formation of rhombic crystals similar to those of BaSO$_4$. As for the other elements, for which we did not obtain reproducible results, the whole problem will be much more complex and was not part of this study.

The comparison of slopes of aqueous calibration and the standard additions method, which is a robust strategy for compensating for matrix effects is shown in Fig. 2. In addition, the slope values of matrix matched calibration are also included in this figure. As can be seen from Fig. 2, the slope values of matrix matched calibration and standard additions technique are in a good agreement with the biggest apparent difference being only 9.2% for ^{59}Co. The approach using matrix matched calibration for quantification is less time consuming than the standard additions method.

3.4. Drawbacks and solutions of the use of barium bromide

There are several drawbacks associated with the employment of barium bromide in ICP-MS analysis to which attention must be paid in order to avoid them. A high concentration of the residual barium salt may both contaminate the spectrometer and be a source (precursor) of other interfering species and/or compounds like Ba^{++}, BaO$^+$, BaH$_2^+$, BaOH$^+$, BaO$_2^+$, or BaN$^+$, interfering the determination of $^{66-68}$Zn$^+$, ^{133}Cs$^+$, ^{152}Sm$^+$, ^{153}Eu$^+$,
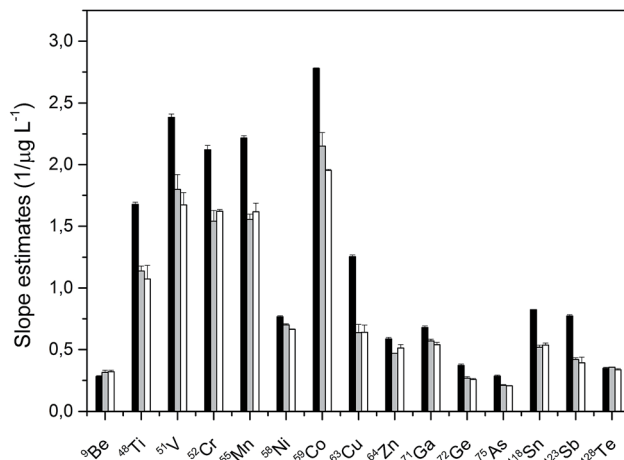

Fig. 2 Comparison of the slopes (1/µg L^{-1}) of aqueous calibration (black bar) and that of matrix matched calibration (grey bar) with standard additions method (white bar) evaluated with the use of Rh as the internal standard. The bars indicate the standard deviation error of the estimate of the slope.

^{155}Gd$^+$. However, Zn, Ga, and Ge could be determined using different isotopes, namely 64, 71, and 72, respectively. In this study, the barium salt was calculated to be added in strictly equimolar amounts to that of sulfuric acid. Using these proportions, the majority of barium was precipitated as barium sulfate and separated from the analyzed solution. Solutions of 10% of H$_2$SO$_4$ were precipitated with an increasing amount of BaBr$_2$ starting at 825 µL of 500 g L^{-1}, which was calculated to be equimolar to 1.25 mL of 10% H$_2$SO$_4$, up to an excess of 25 µL. During this experiment, the decrease in the signal at $m/z = 48$ and increase in the signal at $m/z = 217$ corresponding to ^{138}Ba^{79}Br$^+$ was monitored. This peak was first observed with an excess of 20 µL compared to the calculated amount while the signal at $m/z = 48$ remained constant with further addition of
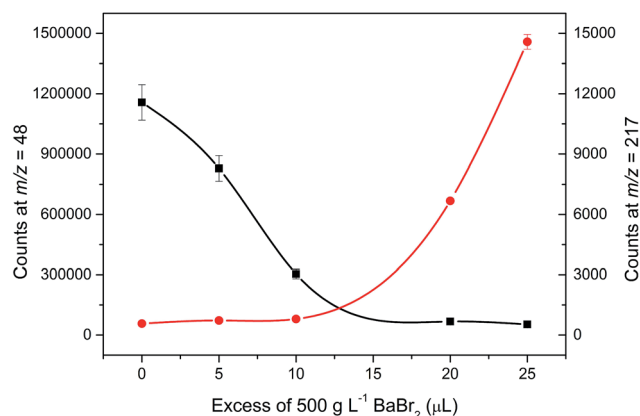

Fig. 3 Optimization of barium bromide (500 g L^{-1}) amount, more exactly of the volume being necessary to be added over those to be calculated as equimolar to 10% (w/w) H$_2$SO$_4$ via the monitoring of the signal at the mass of 48 and 217, corresponding to the decrease of interference at mass 48 (black line) and excess of barium bromide via the ^{138}Ba^{79}Br$^+$ creation (red line), respectively. The bars indicate the range for each determination ($n = 10$, 2 SD).
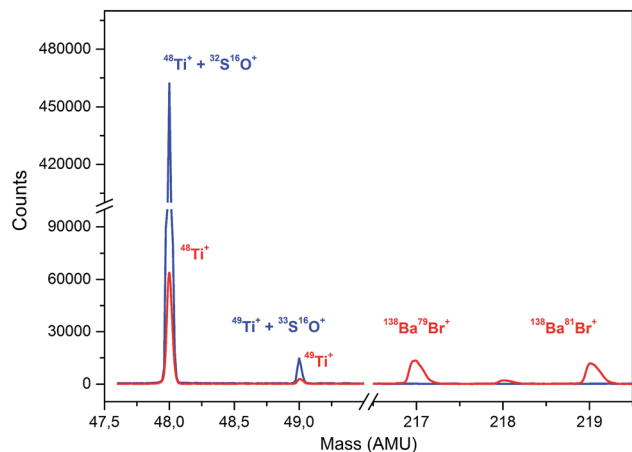
Fig. 4 Mass spectra for the analysis of sulfuric acid without (blue line) and with (red line) the employment of the optimal amount of barium bromide for matrix modification at masses of 48 and 49 for Ti and within the range of 216 and 220 amu reflecting the formation of the BaBr$^+$ species.

$BaBr_2$, which suggests that the interfering sulfur has been removed and the signal corresponds to only $^{48}Ti^+$. The change in the signal for the monitored masses can be seen in Fig. 3. Mass spectra for the analysis of sulfuric acid without and with the employment of an optimal amount of barium bromide for matrix modification at masses of 48 and 49 for Ti and within the range of 216 and 220 amu reflecting the formation of BaBr$^+$ species are shown in Fig. 4. The concentration of the remaining S determined by ICP-OES in the samples prepared using the optimized amount of $BaBr_2$ was for all samples less than 9.5 mg L^{-1}, which suggests that the removal of the interfering S as $BaSO_4$ was efficient. The remaining concentration of Ba^{2+} in filtrates determined by the FL-AAS method did not exceed the value of 4 mg L^{-1}. However, this concentration may still influence the analysis. Due to this fact, specific SMARTGATE ion blanking setting (see Table 1) was used in order to avoid these species reaching the detector and thus prolong its life. At this point, any unwanted ions can be rejected from the flight path by deflection plates in the SMARTGATE, while ions of interest are passed on for detection.

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 the paired sample t-test. In this case the results of the proposed TOF-ICP-MS method were compared with those obtained by the 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 H_2SO_4 of p.a. grade and Ti, V, Cr, Mn, Ni, Co and As in pure H_2SO_4 were not significantly different for a 95% confidence level ($p = 0.28$ and $p = 0.20$ for H_2SO_4 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 H_2SO_4 ($n = 3$) using standard additions 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 the 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 over a period of one month. Every solution was analysed in ten replicates yielding a mean value used for the calculations. The RSD values of intra-day and inter-day studies were typically found to be below 12.1% and 10.3%, respectively, which show that the precision of the method was satisfactory (see Table 3).

3.5.2. Limits of detection.
Limits of detection (LODs) for each isotope, based on three times the standard deviation of the blank response at the given m/z position divided by the slope of the calibration graph are given in Table 3 for 10% (w/w) sulfuric acid samples. The integration time was set to 5 s and standards and blanks were determined with 10 replicates. The blank was prepared from sulfuric acid of TraceSELECT® Ultra purity using the same method as described in Section 2.4. Significantly lower detection limits of HR-ICP-MS are evident from the data presented in Table 3 when compared to the TOF-ICP-MS method. However, it is difficult to compare these methods for several reasons. Firstly, for HR-ICP-MS a desolvating nebulizer system was employed for sample introduction that can enhance the analyte sensitivity up to 10 times in contrast to a more conventionally used concentric nebulizer used also in this study for TOF-ICP-MS.[19] Secondly, a very low random background is observed for high resolution ICP-MS instrumentation even for a high resolution setting.[20] These low noise levels yield a significant improvement in the detection limits for elemental determinations, especially with an increased data acquisition time.[21] Another factor is that a lower dilution factor for the HR-ICP-MS method in contrast to TOF-ICP-MS described in this work was used during the sample preparation as a 10% w/w H_2SO_4 was analysed using the former method, while the concentration of H_2SO_4 after the dilution with barium bromide solution is about 5.4% (w/w). Similarly, previously reported studies employing high resolution instrumentation[4] or quadrupole based instruments with various collision/reaction cell technologies[2,3] also describe the analysis of about 10% (w/w) H_2SO_4. These studies reported favourable limits of detection, which meet SEMI (the Semiconductor Equipment and Materials International

Table 3 Summary of results for the analysis of sulphuric acid using HR-ICP-MS and oaTOF-ICP-MS

	H₂SO₄, p.a.					H₂SO₄, pure					H₂SO₄, TraceSELECT® LOD[bc] µg L⁻¹	
	Concentration[abc] µg L⁻¹		R^{ad} %	RSD[c] (%)		Concentration[abc] µg L⁻¹		R^{ad} %	RSD[c] (%)			
	HR-ICP-MS	TOF-ICP-MS		e	f	HR-ICP-MS	TOF-ICP-MS		e	f	HR-ICP-MS	TOF-ICP-MS
⁹Be⁺	g	<LOD	108	3.5	3.4	g	<LOD	102	0.7	5.5	g	0.19
⁴⁸Ti⁺	0.43 ± 0.05	0.44 ± 0.05	98	5.7	4.5	0.84 ± 0.04	0.97 ± 0.15	102	7.7	9.8	0.012	0.44
⁵¹V⁺	0.72 ± 0.12	0.82 ± 0.04	98	2.5	6.2	0.18 ± 0.03	0.21 ± 0.05	91	11.2	4.7	0.009	0.09
⁵²Cr⁺	0.31 ± 0.08	0.28 ± 0.02	101	3.6	5.9	33.5 ± 1.2	28 ± 6	91	10.7	4.4	0.009	0.21
⁵⁵Mn⁺	0.44 ± 0.04	0.46 ± 0.05	90	5.4	3.5	3.7 ± 0.2	3.7 ± 0.2	106	2.7	5.1	0.006	0.26
⁵⁸Ni⁺	0.63 ± 0.13	<LOD	94	4.5	9.8	20.6 ± 0.7	20.9 ± 1.4	90	3.3	3.2	0.012	0.56
⁵⁹Co⁺	<LOD	<LOD	95	1.9	7.6	0.21 ± 0.02	0.23 ± 0.04	97	8.7	5.3	0.006	0.04
⁶³Cu⁺	0.1 ± 0.06	<LOD	93	2.6	4.7	0.75 ± 0.03	<LOD	101	3.9	4.0	0.012	0.90
⁶⁴Zn⁺	3.4 ± 0.2	3.6 ± 0.4	98	5.6	7.7	0.15 ± 0.05	<LOD	106	2.1	3.3	0.018	0.34
⁷¹Ga⁺	0.35 ± 0.06	0.38 ± 0.04	99	5.3	12.0	<LOD	<LOD	100	4.7	7.0	0.012	0.15
⁷²Ge⁺	<LOD	<LOD	98	0.3	4.6	<LOD	<LOD	101	7.6	8.7	0.012	0.71
⁷⁵As⁺	271 ± 3	270 ± 28	102	5.2	1.2	2.7 ± 0.2	2.7 ± 0.6	93	10.3	10.3	0.027	0.54
¹¹⁸Sn⁺	g	1.07 ± 0.20	97	9.3	2.2	g	0.82 ± 0.20	105	12.1	3.5	g	0.29
¹²³Sb⁺	g	0.86 ± 0.04	96	2.3	5.7	g	1.69 ± 0.28	91	8.3	7.8	g	0.56
¹²⁸Te⁺	g	<LOD	99	3.7	9.1	g	0.82 ± 0.12	96	7.3	9.1	g	0.25

[a] Mean ± 2 SD (n = 3). [b] All values are reported in 10 w/w H₂SO₄. [c] Values for HR-ICP-MS and that of TOF-ICP-MS method were evaluated with the use of In and Rh, respectively, as internal standard elements. [d] Analytical recovery, R (%) evaluated for the TOF-ICP-MS method and the samples spiked with 4 µg L⁻¹ for the listed elements except for Zn, which was spiked with 40 µg L⁻¹. [e] Relative standard deviation (%) expressing the precision of the method in terms of intra-day precision. For the analytes whose determination was below the LOD the results are shown for the samples spiked similarly as described (see[d]). [f] Relative standard deviation (%) expressing the precision of the method in terms of inter-day precision. For the analytes whose determination was below the LOD the results are shown for the samples spiked similarly as described (see[d]). [g] Not determined.

Standards organization) requirements for the highest quality Tier C H_2SO_4 that has guideline impurity limits of 100 pg g^{-1} for 18 of 21 (Al, Sb, As, Ba, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Sn, Ti, Zn) required trace elements[22] and of Tier B H_2SO_4 with a permissible level of 1 ng g^{-1} for all of the above mentioned elements and additionally for Be, Bi, Cd, Co, Ga, Ge, Au, Li, Mo, Nb, Si, Ag, Sr, Ta, Tl, V, Zr. These studies however arise mainly from the product literature.

Also of note is that barium bromide used in this study was not of the highest purity available, which will further significantly impact the LOD values. It is also important to note that direct analysis of 10% (w/w) sulfuric acid is also possible with TOF-ICP-MS ensuring approximately ten times better LOD values for non-interfered elements like Li, Be, Cd, Mo, Sn, Sb, W, or Bi when compared with the values given in Table 3. However we did not use this approach in a higher extent in order to protect the nickel cones as platinum ones were not available. In this case, also determination of elements such as Li, Be, Cd, Mo, Sn, Sb, W, or Bi, whose determination is impacted by the matrix modification method will ensure analytical recoveries within 86–112%. The recoveries were calculated for the samples of 10% H_2SO_4 spiked with 4 µg L^{-1} of the analytes.

The detection capability of the proposed method, however, is adequate to determine the impurities of H_2SO_4 of Grade 1 and 2, as suggested by SEMI. The obtained detection limits are one to two orders of magnitude lower than the maximum permissible content of elements for Grade 2 and Grade 1 purity being in the range of 5 to 300 ppb in concentrated sulfuric acid.

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 an internal standard, took approximately 25 minutes.

4. Conclusions

The proposed method employing barium bromide for the precipitation of sulfates prior to the analysis of sulfuric acid offers a simple and efficient way for the accurate quantification of 15 elements in this difficult matrix by the 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 the matrix matched calibration method can be performed even for elements like Ti, Cu, or Zn, which are more troublesome if ICP-MS instruments with an 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 the Q-ICP-MS or HR-ICP-MS methods. The proposed method using precipitation with the 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 Cd, Pb, Hg, Sr, Bi, or Ag cannot be determined properly with the proposed methodology due to the problems with co-precipitation and/or inclusion in the precipitated matrix. Despite the above mentioned drawbacks, for TOF-ICP-MS instrumentation this procedure is currently the only solution to attenuate the interferences to a manageable level.

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