Trace Element Determination in Sulfur Samples Using a Novel Digestion Bomb Prior to ICP-MS Analysis

Xuebo Yin^{a,c}, Xiaoyuan Wang^{a,b,c}, Shuai Chen^{a,c}, Yao Ma^{a,c}, Guo Kun^{a,d}, and Zhigang Zeng^{a,b,c}

^a Key Laboratory of Marine Geology and Environment,
Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, P.R. China

^b Laboratory for Marine Mineral Resources,
Qingdao National Laboratory for Marine Science and Technology, Qingdao 266071, P.R. China

^c Center for Ocean-Mega Science, Chinese Academy of Sciences, Qingdao 266071, P.R. China

^d College of Earth Science and Engineering, Shandong University of Science and Technology,
Qingdao 266590, P.R. China

INTRODUCTION

Trace elements play an important role in investigating the origin of sulfur in many geological systems such as hydrocarbon-bearing basins, near active or dormant volcanoes, or in seafloor hydrothermal settings (1-12), and provide micro-scale information on the metal transport via sulfur-rich volcanic degassing (13-16). In addition, the concentration of trace elements is significant to establish the quality of sulfur which is widely used in agriculture, medicine, synthetic rubber, building materials, powders, and the manufacture of petroleum and coal products, etc. (6). Researchers have made great progress towards the accurate determination of trace elements in sulfur samples (15-18). Inductively coupled plasma mass spectrometry (ICP-MS) has become one of the most powerful techniques due to its high sensitivity, large dynamic linear range, and multi-element capabilities (19-30). The interference encountered in ICP-MS is reduced by using hydride generation, aerosol dilution after iron hydroxide co-precipitation, Ar-CH₄ or CH₄ plasma, and analysis by dynamic reaction cell (DRCTM) (19, 23, 24, 26-28). The analysis of trace elements in sulfur is challenging due to the difficulties in digestion and the high sulfur matrix in the final solution for ICP-MS analysis.

ABSTRACT

A method has been developed for the ICP-MS determination of trace elements in sulfur samples using a novel closed digestion bomb with a double inner arc seal design. The method is simple, precise, and accurate, completely digests the sulfur sample, and allows for the determination of the trace elements Ba, Ce, Cd, Co, Cr, Cs, Dy, Er, Eu, Ga, Gd, Ho, La, Li, Lu, Nd, Pb, Pr, Rb, Sm, Sr, Tb, Tm, U, V, Y, and Yb. Upon the addition of trace element standards to a high purity sulfur chemical reagent, the recoveries were 91.5% for La to 109.7% for U. The detection limits of this method were 1.49 ng g⁻¹ for Sr to 0.009 ng g⁻¹ for Tm and Lu.

Burning and sublimation methods for the determination of trace elements in sulfur samples using ICP-MS has been proposed (13, 16-18). Examples of such procedures require 1 g sulfur sample, heating to above 236 °C (sulfur burning temperature) in a muffle furnace to eliminate sulfur as SO₂ or heating the sample at 200 °C in a beaker on an electrothermal plate to vaporize the sulfur. The ashes or residues are then dissolved using HNO₃, HF, and HClO₄. However, these methods can cause contamination and loss of volatile elements, particularly for sulfur samples with a very low abundance of trace elements. For geological samples, a high-pressure digestion technique (31-33) has been generally applied. Neverthe-

less, acid leakage often occurs during the digestion process which may leave undissolved residues.

In this study, the traditional high pressure digestion technique has been improved by using a corrosive-resistant digestion bomb with a double inner arc seal design. The bomb has a tight seal and offers effective circulation of the acid during the digestion process. The sulfur sample can be digested directly at high temperature and pressure which speeds up the digestion process, improves the dissolution effect, and is a practical and simple sample digestion method for the analysis of sulfur samples by ICP-MS.

EXPERIMENTAL

Instrumentation

An ELAN[®] DRCII ICP-MS (PerkinElmer, Inc., Shelton, CT, USA) was used for the sample analysis at the Institute of Oceanology, Chinese Academy of Sciences. The instrumental parameters used for the trace element determinations are listed in Table I. The detection isotopes were as follows: ⁷Li, ⁵¹V, ⁵²Cr, ⁵⁹Co, ⁷¹Ga, ⁸⁵Rb, ⁸⁶Sr, ⁸⁹Y, ¹¹⁴Cd, ¹³³Cs, ¹³⁵Ba, ²⁰⁸Pb, ²³⁸U and ³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁶⁰Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, and ¹⁷⁵Lu. ¹⁸⁷Re was used as an internal standard. The background counts for the 2% HNO₃ solutions were normally <2 cps.

Reagents and Standards

A 10-mg L⁻¹ multi-element mixed standard solution and a 10-mg L⁻¹

*Corresponding author.
E-mail: wangxiaoyuan@qdio.ac.cn
Fax: +86-532-82898526

REE standard solution (PerkinElmer, Inc., Shelton, CT, USA) were used and diluted with 2% HNO₃ to 1 ng mL⁻¹, 5 ng mL⁻¹, and 10 ng mL⁻¹. A 1000-mg L⁻¹ Re standard solution (Environmental Express, USA) was diluted to 10 µg L⁻¹ with 2% HNO₃. A 1000 mg L⁻¹ S standard solution (Environmental Express) was diluted to 100 mg L⁻¹ with 2% HNO₃. The reagents applied were ultrapure HNO₃ (J. T. Baker, USA), electronic industry-grade HF and chemical reagent-grade sulfur (sulfur content >99.5%). Distilled water (18.2 MΩ·cm grade) was obtained with an ULTRA IONIC ultrapure water system (ELGA, UK).

Laboratory Ware

A screw-top, PTFE-lined, corro-

sive-resistant digestion bomb (Figure 1) was used for this study with a volume of ~15 mL. The upper part of the inner tube plugs into the top of the lower part and the axial cross of the inner tube is oval. The inner tube was pre-cleaned with 10% HNO₃ and heated to boiling for about 12 hours at 120 °C on an electrothermal plate, then rinsed with DI water.

Sample Preparation

The sulfur samples were first milled to 200 mesh with an agate mortar. Next, 0.0400 g of the sample powder was digested using 0.5 mL HNO₃, 0.1 mL HF, and 4 mL DI water, then heated at 180 °C for 12 hours. After cooling, the PTFE inner tank was placed on an electrothermal plate and heated to dryness at 150 °C, then 0.2 mL of HNO₃ was added, and heated to dryness again. To this residue, 1.5 mL of 2% HNO₃ was added, the high pressure bomb was sealed, and the contents were dissolved again at 150 °C for 12 hours. Finally, the solutions were diluted 50 times using 2% HNO₃ and analyzed by ICP-MS.

RESULTS AND DISCUSSION

Calibration Curves and Limits of Detection

Before determination, the ICP-MS instrument was optimized using a tuning solution containing 1 ng mL⁻¹ of Be, Co, In, Mg, Ce, Pb, and U, and 10 ng mL⁻¹ of Ba, then calibrated using three synthetic trace element standard solutions of 1 ng mL⁻¹, 5 ng mL⁻¹, and 10 ng mL⁻¹ in 2% HNO₃. A Re internal standard (10 ng mL⁻¹) was added on-line using a polypropylene T-connector. The detection limit was calculated as three times the standard deviation of 10 individual procedural reagent blanks, divided by the sample mass. The limits of detection (3σ) ranged from 1.49 ng g⁻¹ for Sr to 0.009 ng g⁻¹ for Tm and Lu for a

sample of 0.0400 g prepared into a 2-mL analytical solution, i.e., a dilution factor of 50 (Table II).

Interference and Correction

Combining the methods of sulfur oxidation into stable sulfate using a mixed acid (34, 35) and the previously described high pressure digestion technique (31-33), the sulfur samples were dissolved with the mixed acid at high pressure in a custom-designed digestion bomb (built in this laboratory) into a clear liquid. The sulfur content in the solutions before ICP-MS determination was 873 – 883 mg L⁻¹ as analyzed using ICP-OES (Thermo IRIS Intrepid II XSP) and thus, interference from sulfur has to be considered. Sulfur has four stable isotopes at nominal masses of 32, 33, 34, and 36, with a representative isotopic composition of 94.99, 0.75, 4.25, and 0.01%, respectively (36). Most spectral interferences arise from the sulfur, oxygen, and argon polyatomics. The mass spectra for the 100 mg L⁻¹ sulfur standard solution indicates significant interferences for ⁴⁸Ti (interference by ³²S¹⁶O), ⁶⁴Zn (interference by ³²S₂, ³²S¹⁶O₂), ⁶⁵Cu (interference by ³²S³³S and ³³S¹⁶O₂), ⁶⁶Zn (interference by ³²S¹⁶O¹⁸O, ³²S³⁴S and ³³S₂), and ⁷²Ge (interference by ³⁶S₂ and ³²S⁴⁰Ar) (Figure 2). The interference coefficient correction method does not reduce or eliminate the interferences, therefore, the concentration of Ti, Zn, Cu, and Ge in the sulfur sample cannot be determined accurately using the proposed method. During the analysis of the sulfur sample, the interference of the Ba-oxides on the REEs was significant, i.e., of ¹³⁶Ba¹⁶O on ¹⁵²Sm, ¹³⁵Ba¹⁶O on ¹⁵¹Eu, and ¹³⁷Ba¹⁶O on ¹⁵³Eu. ¹⁴⁷Sm was selected to be analyzed, thus avoiding the interference of ¹³⁶Ba¹⁶O. The BaO⁺/Ba⁺ ratio (1.936%) obtained by the determination of a 10-mg L⁻¹ Ba standard solution and the correction formula (¹⁵¹Eu_{true} = ¹⁵¹Eu_{analyzed} - 0.001936 × ¹³⁵Ba) were

TABLE I
Instrumental Operating
Parameters for ICP-MS Analysis

Parameters	Values
RF power	1250 W
Plasma gas	15 L min ⁻¹
Aux gas	1.20 L min ⁻¹
Nebulizer gas	0.80 L min ⁻¹
Sweeps	10
Readings	1
Replicates	3
Scan mode	Peak hopping
Channel dwell time per sweep	100 ms
Sampling cone (Pt)	1.10 mm
Skimmer cone (Pt)	0.90 mm

Fig. 1. Diagram showing the design of the anticorrosive efficient digestion bomb.

TABLE II
Blank Level (ng g⁻¹) and Method's Limit of Detection (ng g⁻¹)

Elements	Blank-1	Blank-2	Blank-3	Blank-4	Average	DL (3σ)
Li	0.75	0.74	0.87	0.80	0.79	0.18
V	2.06	2.06	1.66	2.14	1.98	0.66
Cr	1.34	1.54	1.28	1.13	1.32	0.51
Co	0.41	0.33	0.48	0.32	0.38	0.22
Ga	0.29	0.26	0.34	0.22	0.28	0.15
Rb	0.33	0.13	0.14	0.21	0.20	0.28
Sr	3.31	2.41	2.24	2.33	2.57	1.49
Cd	0.045	0.044	0.036	0.047	0.043	0.015
Cs	0.023	0.017	0.015	0.011	0.016	0.014
Ba	2.42	2.62	2.45	2.20	2.42	0.64
Pb	2.40	2.49	2.14	2.45	2.37	0.47
U	0.81	0.78	0.73	0.80	0.78	0.11
La	0.32	0.26	0.28	0.30	0.29	0.080
Ce	0.53	0.60	0.51	0.58	0.55	0.13
Pr	0.066	0.053	0.05	0.056	0.056	0.021
Nd	0.23	0.21	0.28	0.17	0.22	0.14
Sm	0.048	0.019	0.048	0.035	0.038	0.042
Eu	0.029	0.018	0.023	0.015	0.021	0.019
Gd	0.050	0.035	0.032	0.038	0.039	0.024
Tb	0.010	0.007	0.016	0.005	0.010	0.015
Dy	0.035	0.017	0.060	0.016	0.032	0.062
Ho	0.010	0.005	0.013	0.005	0.008	0.011
Er	0.023	0.012	0.030	0.013	0.020	0.026
Tm	0.012	0.007	0.012	0.007	0.010	0.009
Yb	0.029	0.017	0.047	0.010	0.026	0.048
Lu	0.015	0.012	0.016	0.009	0.013	0.009
Y	0.18	0.12	0.17	0.11	0.15	0.10

used to correct the interference of the Ba-oxides on Eu. In addition, ⁷¹Ga was selected to be analyzed, thus avoiding the interference of ¹³⁸Ba⁺⁺.

Method Efficiency

The advantages of the corrosive-resistant digestion bomb (Figure 1) are its double inner arc seal design which allows the evaporating acid to return from the top of the inner tank to the bottom without clinging on the tank wall, thus providing an effective circulation. The upper and lower parts of the inner tank couple tightly and the double inner arc seal design ensures a tight seal as the pressure increases. This prevents any leaking of the acid and avoids incomplete digestion. In comparison to previously reported methods that pretreat the native sulfur samples and require 4 – 6 days (13, 16, 17, 18), the present method requires 24 hours with no contamination problems, consumes a small amount of sample (40 mg) and acid (0.7 mL of HNO₃ and 0.1 mL of HF), and has good precision and accuracy. In addition, 27 elements can be measured at the same time with high accuracy (Table III).

Procedural Recovery and Precision

Lacking a native sulfur reference material, the recovery was used to

Fig. 2. The mass spectra recorded for a 100-mg L⁻¹ sulfur standard solution using ICP-MS.

validate the accuracy of this method. In order to evaluate analyte recovery, 50 ng g⁻¹ trace element standards and 2.5 ng g⁻¹ REE standards were added to 40 mg of the unknown samples, and the samples were prepared as described above and analyzed. The samples were digested completely, and the digestion solution was clear without any undissolved substances. The added concentrations were obtained by subtracting the concentrations of the sample with free trace element standards from the corresponding sample with the addition of trace element standards. The recovery varied from 91.5% (La) to 109.7% (U) for the sulfur sample (Table III). The recovery of this method was found to be much better than for the burning and sublimation methods (Table III). The data obtained in the present study show reasonable precision, better than 6.2% for trace elements and 5% for the REEs and is, therefore, suitable for the analysis of sulfur samples.

CONCLUSION

The proposed method for the analysis of sulfur samples is novel and has some important advantages when compared to previously reported analytical techniques. An anti-corrosive, lab-made efficient digestion bomb was used which required a dilution factor of only 50 for the preparation of the analytical solutions. The method is reliable, simple, has no contamination problems, is fast (24 hours in comparison to 4 to 6 days with other methods), with a precision 0.5% for Ba to 6.2% for Ga, and is suitable for the routine determination of most trace elements found in sulfur samples.

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Element	Sulfur (n=5)	RSD (%)	Sulfur Sample With Added Standard Solution (n=5)	Recovery (%)	Recovery (%) Sublimation Method ^b	Recovery (%) Burning Method
Li	7.34	3.1	57.3	100.0	-	-
V	37.1	1.5	87.6	101.0	89.0	-
Cr	94.7	5.8	144	99.5	-	-
Co	5.30	3.7	58.7	106.9	88.4	78.3
Ga	3.15	6.2	51.0	95.7	107.1	86.5
Rb	5.19	6.0	51.9	93.5	84.9	-
Sr	55.9	3.0	106	105.9	-	-
Cd	3.06	1.4	54.0	101.9	-	-
Cs	0.31	0.9	54.3	107.9	118.6	76.2
Ba	336	0.5	386	100.0	-	-
Pb	603	2.1	657	107.2	-	-
U	4.40	2.4	59.2	109.7	97.1	90.2
La	5.74	2.9	8.02	91.5	91.4	-
Ce	11.5	2.1	13.9	97.3	-	-
Pr	1.39	2.1	4.05	106.5	92.2	-
Nd	5.54	4.7	7.93	95.9	90.3	-
Sm	1.20	4.9	3.57	94.9	129.2	91.5
Eu	0.24	4.4	2.84	104.0	101.7	96.1
Gd	0.84	3.5	3.45	104.4	97.4	-
Tb	0.14	3.2	2.61	98.6	104.8	86.5
Dy	0.76	2.5	3.41	106.0	110.7	91.2
Ho	0.15	1.9	2.71	102.5	101.5	95.1
Er	0.42	3.3	2.98	102.2	108.1	98.0
Tm	0.07	3.8	2.65	103.1	98.6	92.7
Yb	0.40	3.3	3.01	104.1	97.2	92.6
Lu	0.07	4.3	2.62	102.2	98.5	92.1
Y	2.81	4.3	5.37	102.7	115.0	92.4

^a Data in ng g⁻¹.

^b Data from References 17 and 18.

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