Accurate determination of high sulfur content in sulfide samples: an optimized ICP-OES method

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Abstract

Determination of high sulfur content in sulfide minerals is crucial for various applications, including geochemistry, mining, and environmental monitoring. While inductively coupled plasma optical emission spectrometry (ICP-OES) is the preferred method for sulfur analysis, conventional sample preparation techniques often fall short when dealing with high sulfur concentrations. This study investigated optimized digestion conditions for accurate sulfur determination in sulfide minerals using ICP-OES. We employed anti-corrosion acid digestion bombs, an aqua regia–hydrofluoric acid system, and a digestion temperature of 180 °C, achieving exceptional results. Certified reference material recoveries ranged from 99.9 to 100.5%, with relative standard deviations between 0.42 and 0.84%. These results demonstrate the high accuracy and precision of the method. The optimized digestion protocol presented in this study provides a robust and reliable approach for accurate sulfur analysis in sulfide minerals, particularly for high concentrations.

Keywords Sulfide, Sulfur content, ICP-OES, Anti-corrosion acid digestion bomb

Introduction

Sulfur (atomic number 16), a member of Group VIA on the periodic table, constitutes 3.79% of the Earth's composition, primarily residing in the mantle with a significantly lower abundance (0.04%) in the crust (Zhao 2016). Due to varying redox conditions, sulfur readily forms sulfide minerals alongside numerous accompanying elements, often existing as sulfates or sulfides (Xue and Li 2013). Examples include pyrite, chalcopyrite, galena, and sphalerite. Sulfur exhibits diverse valence states in nature, including $+6, +4, -1, -2$, and 0 (native sulfur), leading to the formation of a vast array of compounds that constitute valuable mineral resources, thus attracting significant interest from geologists and mineral deposit scientists (Li et al. 2001).

Sulfur analysis is a routine practice in geochemical investigations. Traditional methods, including barium sulfate gravimetric, combustion-volume, titration colorimetric, ion chromatography, X-ray fluorescence (XRF), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS), each have limitations. The barium sulfate gravimetric and combustion-volume methods are time-consuming, reagent-intensive, and pose safety risks (Hu et al. 2017). Titration colorimetric methods offer low pre-treatment efficiency (Tian et al. 2023;

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Chen et al. 2018). While ion chromatography boasts high accuracy, its upper detection limit is restricted to 10–1000 mg/kg (Shimizu et al. 2015, Evans et al. 1981, Bie 1986). XRF methods, employing pressing or melting techniques, exhibit good accuracy but possess a higher detection limit of 51 mg/kg (Zhang et al. 2008; Yuan et al. 1992). ICP-OES, renowned for its high accuracy and low detection limit, is currently the preferred method for major element analysis (Zha et al. 2011, Lukáš et al. 2012, Wang et al. 2018,　Li et al. 2013), albeit requiring appropriate pre-treatment (Li and Xue 2013; Li et al. 2015; Liu 2015; Wen et al. 2011). ICP-MS, utilizing anti-corrosion and high-efficiency sample dissolution tanks, effectively analyzes trace elements in sulfide samples (Yin et al. 2018, 2011). Despite ICP-OES being the optimal technique for sulfur analysis, traditional pre-treatment methods are inadequate for high sulfur content (> 30%).

To address this limitation, this study systematically investigated different digestion conditions, including vessel types, acid systems, and temperatures, employing inductively coupled plasma optical emission spectroscopy (ICP-OES) for analysis. The goal was to develop a pre-treatment method capable of accurately determining high sulfur content in sulfide ores.

Experimental part
Instruments and working conditions

(1) Inductively coupled plasma optical emission spectrometer (ICP-OES): The analysis was conducted using an American Varian Company 720ES ICP-OES system, equipped with a transverse observation configuration, a quartz swirl atomization chamber, a concentric quartz atomizer, and a CCD solid-state detector. The system operates with a carrier gas flow rate of 0.9 L/min, an auxiliary gas flow rate of 1.2 L/min, and a plasma gas flow rate of 15 L/min, at an ICP RF power of 1300 W. The instrument exhibits a sensitivity exceeding 50,000 cps for 1 µg/L Mn and a resolution of 0.08 nm (at 200 nm).

(2) Anti-corrosion electric heating oven (JKHF-140L): This oven features a polytetrafluoroethylene (PTFE)-coated inner cavity, allowing for temperature control from ambient to 200 °C w/n2 with an accuracy of ± 2 °C.

(3) Anti-corrosion electric heating plate (JK-60TH): The heating plate is constructed with stainless steel coated with PTFE, providing a temperature range from ambient to 200 °C with a control accuracy of 2 °C.

(4) Microwave digestion instrument (CIM-MARS X press): This instrument utilizes microwave technology with a maximum installation power of 2500 W and an adjustable output power ranging from 0 to 1600 W, operating at a frequency of 2450 MHz. The furnace chamber is constructed from 316 grade stainless steel with a multi-layer corrosion-resistant fluorine polymer coating. The digestion vessel consists of a 100 mL TFM inner tank and an aerospace fiber outer tank. The temperature control range is 10–300 °C, and the pressure range is 0–1500 psig.

(5) Anti-corrosion acid digestion bombs (JKB-15FC): The digestion bombs feature a PTFE inner tank with a wedge-shaped insertion closure mechanism for efficient sealing. The inner tank incorporates a double inner arc design, facilitating rapid reflux and enhanced sample digestion efficiency. The outer tank, crafted from PTFE-coated aluminum alloy, provides excellent pressure resistance. The three-buckle fastening mechanism ensures secure closure, minimizing labor and resource expenditure. A cross-sectional and physical schematic of the diges-
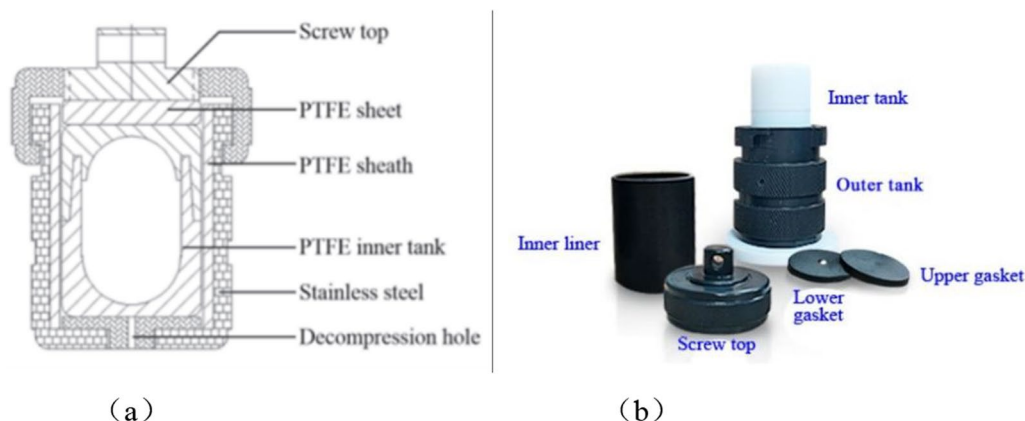

（a）　　　　　　　　　　　　（b）

Fig. 1 Anti-corrosion acid digestion bomb **a** is the profile diagram of digestion bomb and **b** is the actual picture of the bomb

Table 1 Standard values of certified reference materials

Reference materials	GBW07267	GBW07268	GBW07270	WMS-1a
Standard values (%)	52.72 ± 0.21	34.69 ± 0.19	32.33 ± 0.17	28.17 ± 0.27

Table 2 Digestion acid combination

	2 mL HNO₃	1.5 mL HNO₃ + 0.5 mL HF	2 mL aqua regia + 0.5 mL HF
GBW07267	$N=5$	$N=5$	N = 5
GBW07268	–	–	N = 5
GBW07270	$N=5$	$N=5$	N = 5
WMS-1a	$N=5$	$N=5$	N = 5

tion bomb is presented in Fig. 1 (Patent number: ZL201220612911.6).

(6) Pure water machine: Millipore's Milli-Q Academic pure water machine was utilized to provide purified water.

Reagents and reference materials

(1) Experimental water: Ultrapure water with a resistivity of 18.2 MΩ·cm was employed throughout the experiments.

(2) Acids: Nitric acid (HNO_3), hydrochloric acid (HCl), and hydrofluoric acid (HF) were all of electronic-grade purity (MOS), with metal element concentrations below 1 µg/L.

(3) Standard solution: A single-element sulfur (S) standard solution (1000 mg/L) was sourced from Inorganic Ventures.

(4) Certified reference materials: The following certified reference materials (CRMs) were utilized:

National reference materials (China): GBW07267 (Pyrite), GBW07268 (Chalcopyrite), and GBW07270 (sphalerite).

National Research Council of Canada (NRC): WMS-1a (massive sulfide).

A detailed summary of the standard values and uncertainties for all CRMs is presented in Table 1.

Sample preparation

(1) Digestion vessel: Five portions of 40 mg standard samples were accurately weighed and transferred to either a crucible, microwave digestion tank, or anti-corrosion acid digestion bomb. Each sample was treated with 2 mL of aqua regia and 0.5 mL of hydrofluoric acid (HF). The vessels were sealed and subjected to digestion at 180 °C for 12 h. After cooling to room temperature, the digests were diluted to 40 mL with ultrapure water and analyzed using the ICP-OES instrument.

(2) Digestion acid combination: Three groups of standard samples, each consisting of five 40 mg portions, were prepared in polytetrafluoroethylene contain-

ers. The following Table 2 acid combinations were employed for each group:

Each group was placed in an aluminum alloy outer tank and digested in a 180 °C anti-corrosion electric heating oven for 12 h. After cooling to room temperature, the inner containers were removed, and the digests were subjected to acid evaporation on a 150 °C electric heating plate for 2 h. Subsequently, 4 mL of ultrapure water was added, and the samples were re-dissolved in a 180 °C anti-corrosion electric heating oven for 12 h. Following cooling, the solutions were diluted to 40 mL with ultrapure water for ICP-OES analysis.

(3) Digestion temperature: Based on the results obtained from the digestion acid combination experiments, an appropriate combination was selected for further temperature optimization. Digestion experiments were conducted using GBW07267, GBW07268, GBW07270, and WMS-1a at four temperature gradients: 120 °C, 150 °C, 180 °C, and 200 °C. All procedures followed the previously established protocol. The experimental setup is depicted in Fig. 2.

Results and discussion
Optimize the digestion vessels
The selection of an appropriate digestion vessel is paramount in achieving accurate and complete sample dissolution. To assess the digestion efficiency of various vessels for sulfide minerals, three different vessels were employed: a crucible, a microwave digestion instrument, and an anti-corrosion acid digestion bomb.

The experimental results, depicted in Fig. 3, highlight the efficacy of each vessel. Analysis of the experimental data reveals that the recovery rates of sulfide samples digested using crucibles consistently fall below 90%. This may be attributed to the loss of digestion solution during the digestion process. The recovery rate of samples digested using a microwave digestion instrument, while approaching 90%, suggests incomplete digestion.
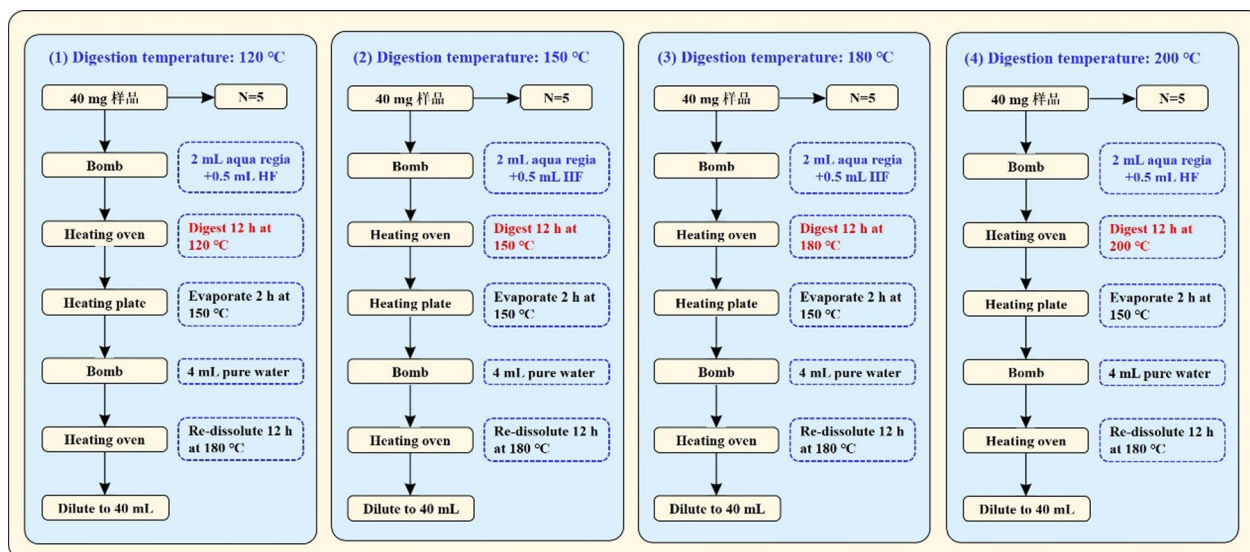
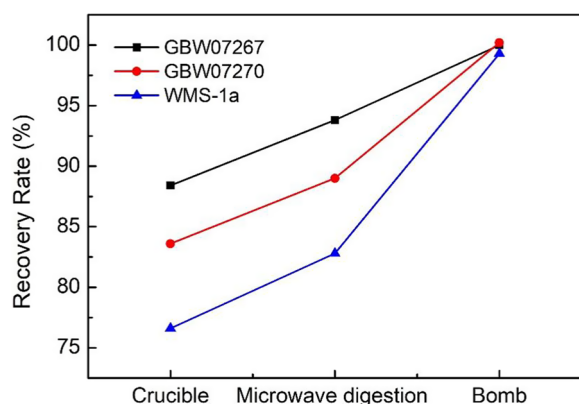**Fig. 2** Flowchart of digestion temperature experiment

Fig. 3 Recovery rates of certified reference materials obtained from experiments with different digestion acid vessels
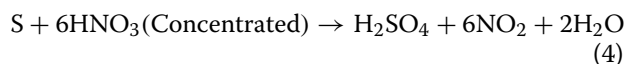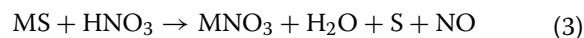
Conversely, samples digested using an anti-corrosion acid digestion bomb consistently achieve a recovery rate of approximately 100%, indicating complete digestion. Based on these findings, the anti-corrosion acid digestion bomb is recommended as the optimal vessel for sample digestion.

Optimization of digestion acid system

Sulfide minerals are primarily composed of sulfur-containing compounds, elemental sulfur, and a minor proportion of silicates. Hydrofluoric acid (HF) effectively reacts with silicates in sulfides, forming hexafluorosilicate anions (SiF_6^{2-}) and volatile silicon tetrafluoride (SiF_4) at low temperatures and standard atmospheric conditions. The reactions are represented by the following equations:

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \tag{1}$$

$$H_2SiF_6 \rightarrow SiF_4 \uparrow + 2HF \tag{2}$$
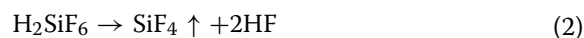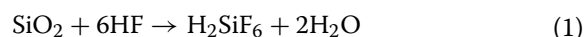
Concentrated nitric acid (HNO_3) reacts with sulfides to oxidize sulfide ions (S^{2-}) to elemental sulfur (S) and sulfate ions (SO_4^{2-}), with the majority being converted to SO_4^{2-}. The reactions are represented by:

$$MS + HNO_3 \rightarrow MNO_3 + H_2O + S + NO \tag{3}$$

$$S + 6HNO_3(\text{Concentrated}) \rightarrow H_2SO_4 + 6NO_2 + 2H_2O \tag{4}$$

Elemental sulfur, being insoluble and chemically stable, can hinder accurate sulfur content determination if not completely reacted. Aqua regia, possessing stronger oxidizing properties than HNO_3, effectively reacts with sulfides under high temperature and pressure conditions. This process completely oxidizes sulfide ions (S^{2-}) to elemental sulfur and subsequently to sulfate ions (SO_4^{2-}), providing the foundation for accurate sulfur content determination.

To investigate the recovery rates of certified reference materials (CRMs) under various acid digestion systems, anti-corrosion acid digestion bombs were employed to dissolve sulfide CRMs. Subsequent elemental analysis was performed using inductively coupled plasma optical emission spectrometry (ICP-OES). The results are presented in Fig. 4. Under nitric acid (HNO_3) single acid digestion, sulfur recoveries in the three CRMs ranged from 91.1 to 95.2%. While GBW07270 exhibited no visible precipitation, complete digestion was not achieved
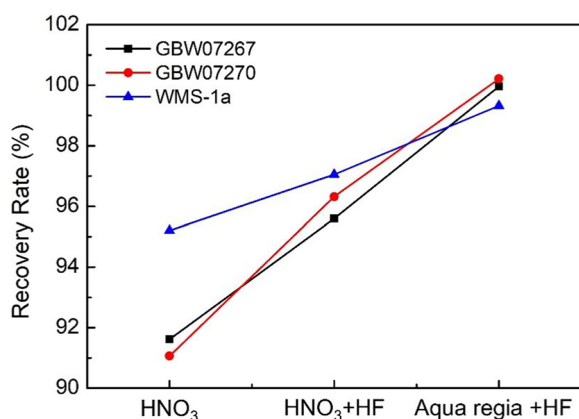
Fig. 4 Recovery of reference materials under different digestion acid systems
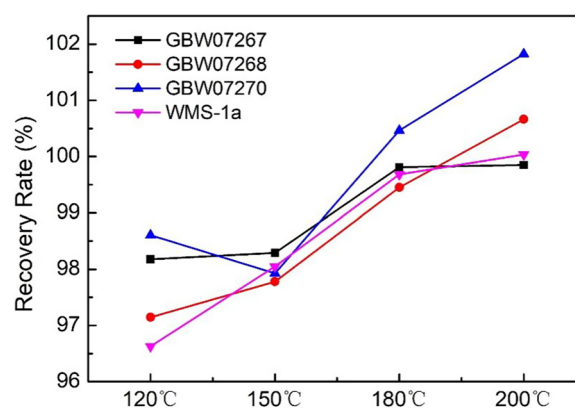

Fig. 5 Recovery rates of certified reference materials at different temperatures

for GBW07267 and WMS-1a. GBW07267 displayed a light yellow insoluble substance, presumed to be elemental sulfur, while WMS-1a exhibited a reddish–brown insoluble substance, likely iron oxide. These undigested residues negatively impacted sulfur recovery rates. The HNO_3 and hydrofluoric acid (HF) system yielded no visible residue in the digestion solution; however, slight turbidity persisted, suggesting the presence of microparticle sulfur components. Sulfur recoveries in this system ranged from 95.6 to 97.1%.

Utilizing aqua regia and HF as a digestion system resulted in complete dissolution of all CRMs, producing a clear and transparent digestion solution devoid of residue. The sulfur recoveries for the three CRMs ranged from 99.4 to 100.2%, demonstrating accurate and reliable data acquisition. These findings indicate that the aqua regia and HF digestion system effectively dissolves sulfide minerals, providing the most reliable method for analyzing sulfur content in these materials.

Influence of digestion temperature

To assess the influence of digestion temperature on the recovery rate of certified reference materials (CRMs), a standardized aqua regia + HF digestion system was employed. Four sulfide CRMs were subjected to digestion using anti-corrosion acid digestion bombs at four temperature gradients: 120, 150, 180, and 200 °C. Subsequent elemental analysis was performed using ICP-OES, and the results are presented in Fig. 5.

The data demonstrate that within the aqua regia + HF digestion system, temperature exerts minimal influence on the state of the digestion solution. At all temperature gradients (120, 150, 180, and 200 °C), complete digestion of the samples was observed, resulting in clear and

transparent solutions without residue. The recovery rates exhibited a consistently high range of 96.6–101.8%, indicating a reliable and accurate determination of sulfur content.

A slight variation in recovery rates was observed across the different temperature gradients. At 120 and 150 °C, recovery rates ranged from 96.6 to 98.6%, slightly lower than the standard values. At 180 °C, recovery rates fell between 99.5 and 100.5%, demonstrating conformity with standard values. However, at 200 °C, while recovery rates were generally high (99.8%–101.8%), the sulfur content results for GBW07267 and WMS-1a partially deviated from the standard values.

This analysis suggests that temperature exerts a minimal impact on the recovery rate of CRMs within the established temperature range. Therefore, 180 °C is deemed the optimal digestion temperature for sulfide minerals, ensuring both complete digestion and accurate sulfur content determination.

Summary

This study employed an aqua regia + HF acid digestion system to dissolve two groups (five parallel samples per group) of sulfur compounds (GBW07267, GBW07268, GBW07270, and WMS-1a) using anti-corrosion acid digestion bombs. The comprehensive data analysis is summarized in Table 3.

At a digestion temperature of 180 °C, the sulfur within the sulfides was efficiently converted into SO_4^{2-}, forming a sulfate solution. The overall recovery rates ranged from 99.9 to 100.5%, with a relative standard deviation of less than 1%. Notably, the sulfur content data for all certified reference materials fell within the standard values and uncertainty ranges. These results demonstrate that this

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Table 3 Summary of data results

	GBW07267	GBW07268	GBW07270	WMS-1a
Test value	52.9	34.4	32.5	28.1
Test value	53.0	34.6	32.4	27.8
Test value	52.4	34.8	32.7	28.0
Test value	52.8	34.1	32.0	28.1
Test value	52.4	35.1	32.4	27.9
Test value	52.6	34.6	32.8	28.1
Test value	52.4	34.3	32.6	28.3
Test value	52.9	34.3	32.5	28.2
Test value	52.7	34.7	32.2	27.8
Test value	52.5	34.6	33.0	28.0
Average (%)	52.7	34.6	32.5	28.0
RSD (%)	0.42	0.79	0.84	0.55
Accuracy (%)	99.9	99.6	100.5	99.6
Standard value(%)	52.72 ± 0.21	34.69 ± 0.19	32.33 ± 0.17	28.17 ± 0.27

method enables the accurate determination of high sulfur content in sulfide materials.

Conclusions

In this article, anti-corrosion acid digestion bombs were selected as the digestion vessels, and the combination system of dissolved acid and the experimental temperature were explored, and eventually the ideal test data were obtained, realizing the accurate determination of high sulfur content in sulfide minerals.

This study establishes a robust protocol for accurately determining high sulfur content in sulfide minerals using anti-corrosion acid digestion bombs. By systematically exploring digestion parameters, we identified optimal conditions: aqua regia + HF digestion system, 180 ℃ temperature, and a double inner arc liner design in the digestion bombs. This protocol yielded accurate results, with sulfur content data falling within standard values and uncertainty ranges, and a relative deviation of 0.42–0.84%. These findings contribute valuable insights to the field of sulfide analysis.

Author contributions
Xuebo Yin provided method ideas and test guidance, Lin Zhang and Min Yang wrote the main manuscript text, Kaixin Yu, Zhuoyun Chen, and Xue Bing completed the experiment part and provided the test data, and Dong Wang and Yiqing Bao finished the data analysis. All authors reviewed the manuscript.

Availability of data and materials
All data included in this study are available upon request by contact with the corresponding author.

Declarations

Competing interests
No potential conflict of interest was reported by the authors.

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