Fast Determination of Trace Elemental Sulfur Residue in Rare Earth Sulfide Samples by Inductively Coupled Plasma Optical Emission Spectrometry

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ABSTRACT: A new method for the fast determination of elemental sulfur (ES) in rare earth sulfide samples was developed, using ultrasonic wave-assisted solvent extraction and oxygen flask combustion (OFC), followed by analysis with inductively coupled plasma optical emission spectrometry (ICP-OES). Toluene was used as the solvent to separate ES from the rare earth sulfide matrix by ultrasonic wave-assisted solvent extraction. All factors that played key roles in both the extraction and OFC methods were systematically investigated. It was found that after ultrasonic extraction with 10 mL toluene for 2 min, the complete extraction of ES in 15 g could be realized, while for the OFC method, 100 μ L of the extraction solvent solution combusted in a 500 mL flask with 10 mL of the mixed solution (9.6 mL H₂O + 0.2 mL H₂O₂ + 0.2 mL HNO₃) as the absorbent was enough for the complete transformation of ES under atmospheric pressure. After method optimization, the sample treatment time was less than 40 min, and the LOD of 1.00 μ g g⁻¹ and the RSD (n=6) of 4.55% were achieved. To verify accuracy, the method was evaluated by a spike test and conducted in four real samples, the recoveries rate ranged from 96% to 100%, which proved that the method was accurate and reliable.

INTRODUCTION

Rare earth sulfides, environmentally friendly pigments and thermoelectric materials, have been extensively studied and are potentially widely used in coatings and luminescent materials industries.¹⁻⁴ According to a reported elemental sulfur (ES) based synthetic strategy,^{1,3} the residual ES undoubtedly becomes one of the major impurities that not only influences the chemical or physical properties of the sulfide products, but also contributes to a major environmental toxicity during practical applications, since ES is harmful to the human body and likely volatilizes upon heating.^{5,6} Therefore, it is of utmost importance to develop accurate methods for the determination of ES residue in rare earth sulfide materials.

However, there is difficulty in the direct determination of trace ES in the presence of inorganic sulfides because a highly efficient separation of the two kinds of S species (S⁰ and S⁻²) must be conducted to ensure no interference from the matrix. It is well known that ES is much more prone to be dissolved in non-polar organic solvents, such as toluene and carbon tetrachloride, than in inorganic sulfides; thus, solvent extraction was mostly adopted for the separation purpose.⁷⁻¹⁰ Soxhlet extraction, using toluene as the solvent, was recommended and is reported as the Chinese national standard method (GT/B 2382-2015). The major drawbacks of this method are the use of large amounts of solvent (100-150 mL), a very time-consuming analysis (9-10 h) and low sample throughput. Fortunately, with the development of technology, more advanced solvent

extraction methods, such as microwave^{11–13} or ultrasonic wave-assisted solvent extraction,^{14–17} became available offering higher separation efficiency and requiring greatly reduced solvent consumption and time.

For the direct quantification of ES in organic solvents, organic chromatographic techniques coupled with molecular detectors, such as high performance liquid chromatography (HPLC)^{7–10} and gas chromatography mass spectrometry (GC-MS),¹⁸ were adopted. Then, the atomic spectroscopic techniques with element specific detectors, such as inductively coupled plasma optical emission spectrometry (ICP-OES)^{19–23} and X-ray fluorescence (XRF),^{24,25} were reported as good choices. Especially ICP-OES, which has the advantages of high sensitivity, high sample throughput, and accuracy, became the most popular technique for the detection of inorganic elements.^{26–28} However, because a special organic sample introduction system is required, the direct analysis of organic solvent samples with high volatility was a challenge for most laboratories. An additional sample preparation was needed to transform the organic solutions to aqueous solutions. Considering the volatile property of both the organic solvent and ES, conventional wet digestion strategies^{29–32} for organic samples, employing mineral acids, such as HNO₃ and/or H₂O₂ at elevated temperature in open vessels or in closed systems, were not good choices due to the loss of the analyte or the explosion risk. To solve this problem, combustion in a closed system with the aid of oxygen, usually named the oxygen flask combustion (OFC) technique, was a promising solution. The OFC technique was frequently used for the analysis of volatile elements, such as halides in organic samples, by ion chromatography^{33–35} and was developed as a versatile sample treatment method for both volatile and non-volatile elemental analysis by atomic spectrometry.^{36–39} By comparison, the outstanding merits of this technique were its clean, fast and highly efficient decomposition ability, easy operation and low cost.^{40,41}

The aim of the present work was to develop a new method for the fast and highly sensitive determination of trace ES residue in rare earth sulfide samples. The combination of ultrasonic wave-assisted solvent extraction and OFC technique for sample treatment with ICP-OES for S determination was successfully adopted.

EXPERIMENTAL

Instrumentation and reagents. An iCAP 6300 ICP-OES, (Thermo Fisher, USA) was used for S detection. The operating conditions were summarized in Table 1. Argon (99.99%) was used for plasma generation and auxiliary and nebulizer gas for the ICP-OES. A highly precise balance with 0.001 mg accuracy (MX5, Mettler Toledo, Switzerland) was used for weighing ES

Table 1. Instrumental Parameters of ICP-OES

Parameter	Values
RF power (W)	1400
Plasma gas flow rate (L min ⁻¹)	15
Auxiliary gas flow rate (L min ⁻¹)	0.90
Nebulizer gas flow rate (L min ⁻¹)	0.75
Spray chamber	Cyclonic
Observation view	Axial
Calibration range (μg mL ⁻¹)	0~100 (R ² =0.99995)
Wavelength for S detection (nm)	180.7

in the spike test. An ultrasonic wave device (KH3200DE, 40 KHz, 150 W, Hechuang Ultrasonic Corporation, Jiangsu, P.R. China) and a centrifuge (TDL-40B, Shanghai Anting Scientific Instrument Factory, Shanghai, P. R. China) were used for the extraction separation. HNO₃ of electronic purity was purchased from Sungkok-Dong Ansan-city (Kyungkido, Korea). Toluene and other chemicals of analytical grade quality were procured from Beijing Chemical Works (Beijing, P.R. China). Ultra-pure water (resistivity > 18.2 MΩ•cm), used for the preparation of all blanks, standards, and samples, was obtained with an ELGA water purification system (ELGA, England). ES (99.9%) was purchased from Linyi Haiquan Chemical Co., Ltd (Shandong, P.R. China). The calibration solutions for S in the range of 0~100 μg mL⁻¹ were prepared by sequential dilution of a 1000 μg mL⁻¹ stock solution, purchased from the National Center for Analysis and Testing of Steel Materials (Beijing, P.R. China). The oxygen flask of 500 mL volume and all other containers used were soaked in 30% HNO₃ (v/v) for at least 12 h, then rinsed with ultra-pure water prior to use.

Analytical procedure. For the proposed method, the rare earth sulfide powder sample (passing through 200 mesh sieves) of about 15 g was subjected to ultrasonic wave-assisted solvent extraction with 10 mL toluene in a conical glass flask, then centrifugation was conducted at 4000 rpm for 2 min, and the supernatant organic phase was collected. Subsequently, 100 μL of the obtained organic phase was dropped onto a piece of ashless filter paper, which was then folded and fixed with a platinum wire onto the quartz stick connected to the flask plug, ignited, and inserted immediately into the flask, which was charged with oxygen and filled, in advance of inserting filter paper, with 10 mL of the absorbent (9.6 mL H₂O, 0.2 mL H₂O₂ and 0.2 mL HNO₃). After the combustion was finished, the flask (kept tightly closed to ensure complete absorption of the volatile combustion product) was shaken for about 2 min and allowed to stand for about 30 min. Finally, the absorption solution was directly analyzed by ICP-OES for ES determination.

RESULTS AND DISCUSSION

Ultrasonic wave-assisted solvent extraction separation. For

Fig. 1 Effect of solvent volumes (A), sample mass (B), and extraction time (C) on the ES extraction separation efficiencies (ultrasonic power of 150 W for 5 min).

Fig. 2 Photograph of sediments of different sample masses after centrifugation.

liquid/solid extraction, the property of the solvent, the ratio of the solvent volume to the sample mass, and the extraction time and strength are all important for the extraction efficiency. For the proposed method, an ultrasonic wave device with the power of 150 W was used, and the power was set at the highest throughout to provide the highest energy as possible. For selecting the solvent of choice, toluene, benzene, chloroform and carbon disulfide were studied. All had good solubility for ES; however, considering toxicity, viscosity, density and the combustion products, toluene was the best solvent. The following steps included the optimization of other key factors.

First, using Ce_2S_3 as the studying objective and fixing the sample mass at 2 g, the effect of solvent volumes (10, 20, 30, 40 and 50 mL) on the extraction efficiencies was studied, and the ES contents after extraction in the solvent were determined according to the *analytical procedure* listed above to observe the difference. The results in Fig. 1A revealed that an increased solvent volume does not lead to a significant improvement in extraction efficiency; however, an increased solvent volume would result in a larger dilution factor and a larger consumption of the solvent. Since the former was harmful to the sensitivity

of the method, while the latter was not desirable due to lack of environmental friendliness and cost-efficiency, the volume of the solvent for extraction was set as 10 mL.

Secondly, using 10 mL toluene as the extraction solvent, different amounts of Ce_2S_3 ranging from 1 g to 18 g were tested. The results shown in Fig. 1B revealed that up to 15 g of sample, the ES extraction efficiencies remained similar, while a further increase in the sample mass resulted in a sharp decrease of extraction efficiency. The reason might be co-precipitation during phase separation by centrifugation, as indicated by Fig. 2, where there was apparent ES deposition on the surface of the Ce_2S_3 sediments for samples with a mass above 16 g. Thus, 15 g was set as the optimal sample treatment amount.

As mentioned above, the ratio of solvent volume to sample mass reached 2/3, which questioned if the phase separation would be sufficient by subsequent centrifugation at 4000 rpm. Since the sulfide matrix could also combust in oxygen in the following OFC step and produced the same products of SO_2 or SO_3 as ES, the least residue of the sulfide matrix in the supernatant organic phase due to insufficient separation would

cause severe influence on the accurate quantification of trace ES. Thus, an additional experiment was carried out, where the Ce content in the solvent was also determined along with S; see report in a previous work.⁴² Fortunately, no Ce was found, which meant that the S in the solvent only came from the ES rather than from the rare earth sulfide matrix, which also proved that the whole separation strategy was successful.

Finally, the extraction time was optimized, while keeping the other factors unchanged. Different extraction times, ranging from 0.5 min to 8 min, were separately adopted to observe their effects on the extraction efficiency, and the results are shown in Fig. 1C. It was found that extraction duration of less than 2 min was inadequate; while too long a time spent in the extraction process would inevitably lead to a reduced sample throughput. Thus, 2 min was chosen as the optimal extraction time.

Therefore, after optimization, 10 mL of toluene achieved nearly 100% extraction and separation of ES from 15 g of the rare earth sulfide matrix with the assistance of ultrasonic wave energy.

Oxygen flask combustion. For a fixed volume of 500 mL in the flask, 100 mg of ashless filter paper was used as the carrier to load the obtained solvent solution, and different volumes of the solvent aliquots were dropped on the filter paper to observe the combustion effect. It was found that more than 100 μL of the solvent exceeded the adsorption capacity of the filter paper and resulted in sample loss, while volumes of less than 100 μL were desirable for safe combustion but would reduce the sensitivity of the method. Of course, considering the high volatility of toluene, the sample treatment amount could be greatly improved by repeatedly dropping the solvent onto the filter paper and waiting for drying, but this operation increased the length of time for and the complexity of the procedure. Thus, one drop of 100 μL of the solvent solution was drawn for the OFC treatment.

In addition, for the subsequent ICP-OES determination and since the standard curve solutions were prepared from the stable SO_4^{2-} stock solution, it required the complete conversion of the ES to SO_4^{2-} during combustion and absorption. Otherwise, the existence of SO_3^{2-} would lead to a signal enhancement during ICP-OES determination, since the high volatile SO_2 produced in the acidic solution had higher transportation efficiency than the SO_4^{2-} aerosol in the sample introduction system of the ICP-OES. Fortunately, according to references,^{43–46} when the absorption solution is composed of alkaline solution (such as NaOH and K_2CO_3) and H_2O_2 , for different S species, a complete conversion to SO_4^{2-} can be fully guaranteed, which was also very important for ion chromatography detection. However, the introduction of high concentrations of metal ions in the sample solution is not appropriate with ICP-OES. Therefore, an adjustment of the

Table 2. Spiking Recovery of ES (n=6)

^a Added, $\mu\text{g mL}^{-1}$	^a Found, $\mu\text{g mL}^{-1}$	^b Recovery, %
0	10.1	--
0.54	10.6	98.1 ± 1.39
1.01	11.1	99.8 ± 3.46
5.02	15.1	99.8 ± 2.54
9.63	19.6	99.1 ± 1.37
21.4	30.7	96.3 ± 0.20

^a The concentrations in the absorption solutions.

^b The mean $\pm$ SD.

Table 3. Results of ES in Real Samples (n=6)

Samples	^a Measured value, $\mu\text{g g}^{-1}$
La_2S_3	20.4 ± 0.58
Pr_2S_3	59.2 ± 2.63
Nd_2S_3	69.9 ± 2.94
Ce_2S_3	9636 ± 95.8

^a The mean $\pm$ SD.

adsorption solution was carried out by replacing the alkaline solution with a dilute HNO_3 solution and by comparing the analytical results to observe the difference. It was found that when the adsorption solution consisted of 9.6 mL H_2O + 0.2 mL H_2O_2 + 0.2 mL HNO_3 , no difference was observed between the acidic and alkaline solutions as the adsorbent. Finally, referring to previous literature,^{10,28,47} the absorption time was set at 30 min to achieve a complete adsorption in this experiment.

Spike test. To verify the accuracy of the method, a spike test was carried out. Different amounts of high purity solid ES powder were precisely weighed and mixed with the Ce_2S_3 sample, and then the mixture was subjected to the analytical procedure. The recoveries were calculated according to the obtained ES concentration in the adsorption solution. The results listed in Table 2 show that the method is accurate and reliable.

Method evaluation and real sample analysis. The method was linear with a coefficient of 0.99995 (R^2) between the concentration range of 0–100 $\mu\text{g mL}^{-1}$. Based on IUPAC definition, the limit of detection (LOD, 3s) of the method was 1.00 $\mu\text{g g}^{-1}$, and the relative standard deviation (RSD, n=6) for parallel analysis was 4.55%, which indicated that the method was of high sensitivity and precision. In addition, compared with GB/T 2382-2015, the proposed method greatly reduced the experimental time from 9–10 h to 40 min, and the total organic solvent reagent consumption decreased by one order of magnitude.

Finally, four rare earth sulfide pigments in different colors were analyzed by employing the proposed method. The results are listed in Table 3.

CONCLUSIONS

A fast, concise, high sensitivity and cost-effective new method was developed for the determination of elemental sulfur in rare earth sulfide samples by inductively coupled plasma optical emission spectrometry. With the combination of ultrasonic wave-assisted solvent extraction and oxygen flask combustion in sample treatment, the proposed method greatly simplified the experimental procedure, reduced the total amount of reagent consumption and the time from 9~10 h to 40 min.

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Notes

The authors declare no competing financial interest.

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