

Accurate Determination of Sulphur Content in Sediments by Double Focusing Inductively Coupled Plasma Mass Spectrometry Combined with Microwave Digestion and Studies on Related Matrix Effect



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Abstract: A robust method for measuring sulphur content in sediments was established using double focusing inductively coupled plasma mass spectrometry at medium resolution combined with microwave digestion technique. The capability of Standard curve method (SCM) and Standard addition method (SAM) using Rh as internal standard was compared in correction of the matrix effect. The results showed that the matrix effect was not suppressed by SCM, but was effectively eliminated by SAM with drawback of low sample throughput. Therefore, the Standard addition calibration method (SACM) was creatively proposed in this study, which could simply and easily correct the matrix effect as the matrix content of sample and standard solution was matched within $\pm 50\%$. The detection limit and liner range of this method were proved to be 0.5 mg kg^{-1} and $3.0\text{--}1000 \text{ }\mu\text{g L}^{-1}$, respectively, with spiked recovery of 95.8%–99.2%. Four sediment standard reference materials GBW07306, GBW07309, GBW07313 and SRM1646a were measured repetitively with the obtained sulphur contents of $(853 \pm 14) \text{ }\mu\text{g g}^{-1}$ ($2\sigma, n = 12$), $(181 \pm 7) \text{ }\mu\text{g g}^{-1}$ ($2\sigma, n = 9$), $(3131 \pm 52) \text{ }\mu\text{g g}^{-1}$ ($2\sigma, n = 12$) and $(3543 \pm 70) \text{ }\mu\text{g g}^{-1}$ ($2\sigma, n = 9$), respectively. The relative error of the four reference materials was +8.8%, +13.3%, +1.0% and +0.7%, respectively, with precision (RSD) less than 2%. This method was applied to measure the sulphur content in the sediment cores collected in the Yangtze Estuary and Hangzhou Bay. This proposed method was demonstrated as an accurate and rapid way of determining sulphur content in great batch of sediment samples, and has a broad application range including soil samples.

Key Words: Microwave digestion; Inductively coupled plasma mass spectrometry; Sediment; Sulphur; Matrix interference; Standard addition calibration method

1 Introduction

Sediment, as the accumulation library of matter migration and transformation, is worthy and used as the sample to study environmental geochemistry. The biogeochemical recycle of sulphur (S) in sediments is complex and uncertain, which would provide important technical information for global iron and carbon cycle^[1,2], paleo-climate change^[3,4], and early diagenetic

processes^[5]. A simple and fast method with effective sample pretreatment and accurate determination is required.

Hot plate^[6] and microwave digestion^[7,8] are two commonly used techniques for sediment or soil samples pretreatment. Microwave digestion is most adopted with less digestion time, less reagent consumption, higher digestion efficiency and lower contamination as it is operated in closed systems with high temperature and pressure. Inductively coupled

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plasma-mass spectrometry (ICP-MS) has been widely adopted in environmental and geological samples due to its rapid accurate measurement with high sensitivity and low detection limit^[9–11]. So far most published research about S determination aboard were studying mining and oil samples^[12,13] and very few on sediment and soil of which the matrix effect was much harder to eliminate. In this study, an innovative Standard addition calibration method (SACM) was proposed, and the matrix effect was effectively corrected. Therefore, a complete method by double focusing ICP-MS for accurately measuring S content in sediments was established. The results of analyzing sediment standard reference materials were within the scope of the certified value, the accuracy and precision were better than previous study^[14,15]. This method was quite feasible to measure the sulphur content in soil samples.

2 Experimental

2.1 Instruments, reagents and standards

Double focusing inductively coupled plasma-mass spectrometer (Element 2, Thermo Fisher Scientific, USA). Thermostatic heating apparatus (BHW-09A, Broadcom Company, Chinese). Microwave digestion system (Multiwave PRO, Anton Paar company, Austria) equipped with 16HF100 high pressure rotor (100 mL PTFE-TEM reaction tube and ceramic pressure casing). PTFE-TEM reaction tubes were cleaned in microwave cleaning progress with 10 mL of concentrated HNO₃. The PMP volumetric flask (Brand, German), LDPE bottle (Nalgene, USA) and some other vessels were cleaned before use by the following procedure: soaked in 3.0 M HCl (AR) at room temperature more than two weeks and then in 2% (V/V) of high purity HNO₃ at least one week, washed with ultrapure water (Milli-Q) at least five times and dried in 100 Class clean work bench.

High-purity concentrated HNO₃ (distilled by sub-boiling), HF (AR), HClO₄ (GR), H₂O₂ (GR) (Sinopharm Chemical Reagent Company, China) were used for the microwave digestion. S and Rh standard solution were prepared from 1000 mg L⁻¹ S standard solution (Fluka, Swiss) and 10.00 mg L⁻¹ Rh standard solution (Merck, Germany) by diluting with 0.25 M HNO₃, respectively. The stream sediment certified reference materials GBW07306, GBW07309 and seabed sediment reference material GBW07313 from China Institute of Geophysical Geochemistry Exploration, and estuarine sediment certified reference material SRM1646a from National Institute of Standards and Technology of American were used in this study. All standards and aqueous solutions were prepared with ultrapure water (Milli-Q gradient purity system equipped with an Elix pure water system, Millipore, USA).

2.2 Sample preparation procedure

Accurately weighed sediment samples (0.1 g, accurate to 0.2 mg) were put into 100-mL PTFE-TEM digestion vessels, and soaked in 6.0 mL HNO₃ and 1.5 mL HF. Then the vessels were put into the 16 high-pressure rotors with ceramic pressure jacket tubes after mixing and caps tightened. The digestion program is listed in Table 1. After cooling, the solutions were evaporated at 180 °C to dryness using thermostatic heating apparatus within about 2 h. Subsequently, the residue was dissolved in about 2.1 mL HNO₃ (6.0 M) at 80 °C within 10 min. After cooling, the solutions were transferred into PMP volumetric flasks and diluted to 50.0 mL with ultrapure water. The S content was detected by ICP-MS. In this case, matrix concentration of the sample solution was about 2.0 g L⁻¹. In addition, parallel and blank experiments were conducted.

2.3 Standard addition calibration method (SACM)

By accurately taking 5.00 mL (stream sediments) or 0.50 mL (seabed/estuarine sediments) solution from the above treated samples to six 15 mL LDPE bottles, adding 0.00, 0.10, 0.30, 0.50, 0.70 and 1.00 mL 10.00 mg L⁻¹ S and 0.60 mL 100.0 µg L⁻¹ Rh, respectively, diluting to 10.00 mL by 0.25 M HNO₃, the standard sample solution series with matrix concentration about 1.0 g L⁻¹ (stream sediments) or 0.10 g L⁻¹ (seabed/estuarine sediment), and S addition concentrations of 0, 100, 300, 500, 700 and 1000 µg L⁻¹, respectively, with 6.00 µg L⁻¹ internal standard Rh were obtained. The addition standard concentration was used as the X-axis, and S/Rh correction intensity ratio as the Y-axis under the optimized working conditions (Table 2) of Element 2, respectively to draw SACM curve or obtain regression equation calculated by the least squares method.

2.4 Sample determination

Appropriate volume of the sample solutions prepared in Section 2.2 ((5.00 ± 2.50) mL for stream sediments, (0.50 ± 0.25) mL for seabed/estuarine sediments, depending on S content in sediments) were taken accurately to 15-mL LDPE bottles, added with 0.60 mL 100.0 µg L⁻¹ Rh solution, and then diluted to 10.00 mL by 0.25 M HNO₃. S and Rh intensity of sample solutions were measured under the same instrument conditions to SACM calibration curve. S content in sediments were calculated by SACM calibration curve or regression equation.

Table 1 Microwave digestion program

Step	Power (W)	Ramp time (min)	Remaining time (min)	Fan (Level)	Working temp (°C)
1	700	5	5	1	~80
2	1000	5	5	1	~120
3	1500	5	30	1	~200
4	0	0	60	3	~55

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