



Analytical note

Determination of sulfur in coal and ash slurry by high-resolution continuum source electrothermal molecular absorption spectrometry



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ABSTRACT

We propose a procedure for the determination of sulfur in coal slurries by high resolution continuum source electrothermal molecular absorption spectrometry. The slurry, whose concentration is 1 mg mL^{-1} , was prepared by mixing 50 mg of the sample with 5% v/v nitric acid and 0.04% m/v Triton X-100 and was homogenized manually. It sustained good stability. The determination was performed via CS molecular absorption at 257.592 nm, and the optimized vaporization temperature was 2500 °C. The accuracy of the method was ensured by analysis of certified reference materials SRM 1632b (trace elements in coal) and SRM 1633b (coal fly ash) from the National Institute of Standards and Technology, using external calibration with aqueous standards prepared in the same medium and used as slurry. We achieved good agreement with the certified reference materials within 95% confidence interval, LOD of 0.01% w/w, and RSD of 6%, which confirms the potential of the proposed method.

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1. Introduction

The sulfur content in the earth's crust is about 0.05%, making it the 15th most abundant element in the planet. It is essential for plants and animals because it is part of various amino acids, co-enzymes, and vitamins. However, its gaseous compounds H_2S and SO_2 are highly toxic. The latter gas is emitted in large quantities during combustion of fossil fuel and mineral coal, and it has significantly contributed to acid rains. Reduction of the sulfur content in diesel fuel is currently one of the greatest international projects aiming at improved air quality, and this should diminish the environmental impact of SO_2 [1].

The method D4239 proposed by the ASTM (American Society for Testing and Materials) details a standard procedure to determine sulfur in coal. This method subjects coal to high temperature (minimum operating temperature 1350 °C), generating sulfur oxides that can be determined by acid-base titration or infrared absorption spectroscopy [2].

Although the method D4239 can overcome problems such as the influence of different sulfur species, it is not precise for sulfur concentrations lower than 1% w/w. Another issue is to quantitatively transfer the SO_x produced by coal combustion and determine their concentration. Therefore, some works have proposed different techniques for sulfur determination, such as X-ray fluorescence [3], electrothermal vaporization and inductively coupled plasma optical emission [4],

and mass spectrometry (ICP-MS) [5–7]. However, the latter technique involves a critical, difficult, and time-consuming dissolution step.

Miller-Ihli [8,9] established the analysis of coal slurries by electrothermal atomic absorption spectrometry (ET AAS) with satisfactory results. This method uses small amounts of sample (about 50 mg), and sample preparation is easy and fast. Maia and co-workers [10,11] developed a method involving slurry electrothermal vaporization and inductively coupled plasma mass spectrometry (ETV-ICP-MS) to quantify some elements, since this method consists of a faster and simpler way to achieve the same goal. Although this technique also allows to determine sulfur, it generates acid species, which can damage the equipment.

Sulfur cannot be directly determined by atomic absorption spectroscopy (AAS) because its main resonance line at 180.671 nm and the two other lines at 181.974 nm and 182.565 nm lies in the range of vacuum-UV, which is not accessible with conventional instrumentation [12].

High-resolution continuum source molecular absorption spectrometry (HR-CS MAS) detects the rotational and vibrational bands of the diatomic molecules and allows one to visualize the entire spectral environment of several tenths of a nanometer in the vicinity, providing a new level of information [13]. Therefore, this method enables one to indirectly determine non-metals like sulfur, fluorine, bromine, and chlorine.

Huang et al. determined sulfur by HR-CS MAS using flame (F AAS) [14]. This method generates carbon monosulfide absorption spectra in an air-acetylene flame using a high-resolution echelle spectrometer. Heitmann et al. [15] investigated electrothermal vaporization and CS molecular absorption, using Ca as modifier. Baumbach et al. [16]

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reported a new strategy to determine sulfur by HR-CS MAS using the molecule SnS which absorbs at 271.578 nm. Some authors combined HR-CS AAS and F AAS for direct analysis of wine and plants [17–19]. Baysal and Akman [20] also determined sulfur in coal using HR-CS flame absorption spectrometry. The coal samples were dissolved using microwave-assisted digestion and the calibration standards were prepared in sulfuric acid.

Resano and Flórez [21] evaluated Pd, in the form of nanoparticles, as chemical modifier for the direct determination of sulfur in different types of solid samples using HR-CS MAS, circumventing the traditional drawbacks associated with sample digestion. Mior et al. [22] reported the determination of sulfur in coal by solid sampling HR-CS MAS using L-cysteine aqueous solution as standard.

Jim et al. [23] determined sulfur in coal slurry using a low resolution absorption spectrometer with charge-coupled device detection and a continuum light source (deuterium lamp) coupled to platform or filter furnace vaporizers. The authors achieved a good limit of detection as compared with the ASTM D4239 method.

The goal of this work was to develop a simple and reliable method to determine sulfur in coal and ash slurries using MAS and a high-resolution continuum source atomic absorption spectrometer with electrothermal atomization, to generate the target molecule.

2. Experimental

2.1. Instrumentation and furnace conditions

All the measurements were performed with a high-resolution continuum source atomic absorption spectrometer ContraAA 700 (Analytik Jena AG, Jena, Germany) equipped with a transversely heated graphite tube atomizer. Sample injection was conducted with an MPE-60 furnace autosampler (Analytik Jena). The CS absorption at 257.592 nm was employed. The spectral bandwidth per pixel was approximately 1.5 pm, and assessment of all the 200 pixels of the detector corresponded to the evaluation of a spectral region of approximately 0.29 nm, with the analytical wavelength located in the center. The absorbance values were measured over three pixels (central pixel ± 1). The experiment was carried out using pyrolytically coated graphite tubes with an integrated PIN platform (Analytik Jena Part No. 407-A81.025). Table 1 shows the temperature program used. Argon (99.999%, White Martins, São Paulo, Brazil) was used as purge and protective gas.

2.2. Standards, reagents, and samples

Two NIST (National Institute of Standards and Technology) certified reference materials, NIST 1632b (trace elements in coal) and NIST 1633b (coal fly ash), were used to assess the feasibility of this method. A stock standard sulfur solution with a concentration of 1000 mg L⁻¹ was prepared using ammonium sulfate (Sigma-Aldrich, Munich, Germany). Water with a resistivity of 18.2 M Ω cm was purified in a Milli-Q system (Millipore, Bedford, MA, USA); nitric acid (Carlo Erba, Milan, Italy) was purified by double sub-boiling distillation in a quartz still (Marconi, Piracicaba, Brazil). Triton X-100 (Merck, Darmstadt, Germany) was employed to stabilize the slurry and to improve the CS molecule generation.

Table 1
Temperature program used for the determination of sulfur in coal and ash slurries by HR-CS ET MAS without chemical modifier.

Step	Temperature, °C	Ramp, °C s ⁻¹	Hold, s	Ar flow rate, L min ⁻¹
Drying	90	3	20	2.0
Drying	110	5	10	2.0
Pyrolysis	300	300	10	2.0
Gas adaption	300	0	5	0
Vaporization	2500	3000	10	0
Cleaning	2700	500	4	2.0

2.3. Procedures

The slurries were prepared with a sample concentration of approximately 1 mg mL⁻¹. The samples were weighed, and a 5% v/v nitric acid solution (previously prepared) was used to fill the slurry to a known volume. Triton X-100 was then added to a final concentration of 0.04% w/v in solution. The slurry was stable for about 4 min, which accounted for the diminished accuracy of the last replicate in relation to the former. This slurry was immediately submitted to the furnace temperature program (as shown in Table 1). Before each replicate, the sample was mixed by bubbling air with a pipette placed inside the cup to avoid precipitation of the coal. The calibration curve ranged from 5 to 30 mg L⁻¹.

3. Results and discussion

3.1. CS molecular absorption spectra

Sulfur exhibits a relatively strong molecular absorption spectrum, attributed to CS [14]. In Fig. 1, the most intense band of the spectrum appeared around 257.59 nm and therefore this wavelength was used to determine sulfur. The spectrometer software (Aspect CS) automatically fitted the base line during the absorption measurement, as represented by the dotted line in Fig. 1. Because the central peak did not fit the base line correctly, we applied a manual background correction; we used pixels 95 (257.577 nm) and 113 (257.602 nm) for this procedure, as shown by the straight line in Fig. 1. We employed this background correction in all the determinations, including the standard solution.

Time-resolved absorbance signals for the CS molecule appear at 257.59 nm, and the highest absorbance peak occurs around 0.75 s. We decided to evaluate the signal by peak height and not by integrated absorbance, because the former gave lower standard deviation (2.5 vs 4.3%).

3.2. Optimization of the pyrolysis and vaporization temperature

We conducted optimization of the pyrolysis and vaporization temperature with an ammonium sulfate standard solution (Appendix A, Fig. S1). As expected, a high pyrolysis temperature cannot be used in the absence of a chemical modifier, because sulfur loss may occur. Thus, we fixed pyrolysis at 300 °C, the lowest temperature

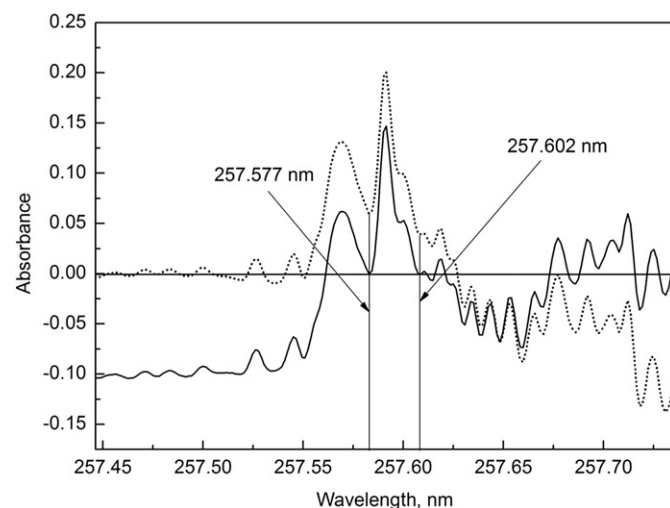


Fig. 1. CS molecular spectra obtained with a 30 mg L⁻¹ of S standard solution with automatic background correction of pixel (dotted) and manual background correction (solid). Wavelengths 257.577 and 257.602 nm are the pixels 95 and 113 respectively used for manual background correction.

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