Determination of sulfur in coal by solid sampling graphite furnace high-resolution molecular absorption spectrometry

Gisa Baumbach *, Jürgen W. Einax

Department of Environmental Analysis, Institute of Inorganic and Analytical Chemistry, Friedrich Schiller University of Jena, Lessingstr. 8, 07743 Jena, Germany

ARTICLE INFO

ABSTRACT

An analytical procedure for quantitative analysis of sulfur in coal by direct solid sampling graphite furnace high-resolution continuum source molecular absorption spectrometry (HR-CS GF MAS) is described, which is based on the molecular absorption of tin sulfide. The heating program is optimized, and a series of chemical modifiers (Ir, Mg, Pd, Ru, W, Zr) are tested. All measurements are accomplished with an Ir coated platform and Pd as modifier, because the best results are achieved.

Accurate results are obtained using the central SnS line of the band found at 271.578 nm with precision values between 1 and 6%. A limit of detection of 10 ng S absolute is achieved. Furthermore, the trueness of the procedure is verified by analysis of certified reference materials. Several coal samples with a concentration range from 0.8 to 21.7 mg g^{-1} S and three certified reference materials are analyzed. In all cases, simple calibration with aqueous standards is found to be possible and the sample throughput is 2–3 samples per hour (6 replicates per sample).

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In fossil fuels sulfur can be found up to 10 wt.%. It is one of the most relevant elements in coals [1]. The sulfur compounds in coal are divided into three groups. They first composed of organic sulfur (bound to carbon structures), second inorganic sulfur (sulfides, sulfates, etc.) and third pyritic sulfur [1].

During coal combustion sulfur dioxide is generated and emitted into the atmosphere. This leads to acid rain and decreased air quality. To improve the situation the percentage of sulfur in fuels was reduced. In addition incinerator flue gas desulfurization systems are installed to minimize the emission. Nevertheless acid rain is still a major cause of forest decline all over the world [2].

Sulfur can be determined with different analytical methods. The gravimetric [3], spectrophotometric [4], and volumetric analyses [5] are classical laboratory methods. Other methods, such as UV–vis spectrometry [6,7], inductively coupled plasma mass spectrometry (ICP-MS) [8], X-ray fluorescence spectrometry (XFS) [9,10] and optical emission spectrometry (OES) [9,11,12], are used to achieve an improvement of handling, sensitivity and limit of detection (LOD). All these methods, apart from XFS, require a sample preparation procedure including wet acid digestion, which is not trivial for coal.

The direct determination of sulfur via atomic absorption spectrometry (AAS) is not possible because the resonance line of sulfur is located at 180.7 nm [13], which is in the vacuum ultraviolet wavelength region. Therefore a direct determination is only possible with a special instrumental setup, which is too complex for routine analysis. The indirect atom spectrometric determination via sulfur compounds is the only practical approach.

Dittrich and Vorberg [14] started to investigate the determination of sulfur by sulfide. In routine analysis this procedure is not used, because it has restrictions concerning the resolution of the monochromator, the line selection using different hollow cathode lamps, spectral interferences, and background correction.

The development of the high-resolution continuum source spectrometer [15] brought a new impetus to the non-metal determination [16–18]. Baumbach et al. [19] described a procedure for determination of sulfur in aqueous solutions using HR-CS MAS. Other works determined sulfur in different solid samples using direct solid sampling high-resolution molecular absorption spectrometry in a graphite furnace [20,21]. Sulfur has already been determined in coal with continuum source molecular absorption spectrometry (CS MAS), but only as carbon monosulfide in an air-acetylene flame [22], with graphite furnace atomization [23] or using slurries instead of direct solid sampling [24].

The aim of this investigation was the determination of sulfur in coal by using direct solid sampling graphite furnace high-resolution continuum source molecular absorption spectrometry (HR-CS GF MAS) and to examine the chance to use aqueous standard solutions for calibration. Modifier influences, different coal samples and certified reference materials were investigated.

* Corresponding author. Tel.: +49 3641 948174; fax: +49 3641 948172.
E-mail address: gisa.baumbach@uni-jena.de (G. Baumbach).

2. Material and procedure

2.1. Instrumentation

All measurements have been carried out using contrAA® 700 high-resolution continuum source atomic absorption spectrometer (Analytik Jena AG, Jena, Germany). The xenon short-arc lamp, operating in a 'hot-spot mode', is used as source and generates a continuous spectrum from 185 nm to 900 nm. The spectrometer is equipped with a double monochromator, consisting of a prism and an echelle grating, providing a spectral bandwidth of 1.5 pm at 271 nm. A CCD array detector with high quantum efficiency simultaneously records a spectral range of about 0.3 nm at 271 nm by using 200 pixels for signal registration.

Measurements are accomplished with pyrolytically coated solid-sampling graphite tubes without a dosing hole (Analytik Jena Part No. 407-A81.303).

The solid samples were weighed directly onto solid sampling platforms (Analytik Jena Part No. 407-152.023) using an M2P micro balance (Sartorius, Göttingen, Germany). The samples were weighed in the range of 0.01 mg to 0.5 mg. A solid sampling system SSA 600L (Analytik Jena AG) with automatic metering device, consisting of a rail and a pre-adjusted pair of tweezers was used to introduce the solid sampling platforms into the graphite tube. Aqueous standards and modifier solutions were injected onto the platform using the volumetric metering. The optimized temperature program, used for all determinations with HR-CS GF MAS, is shown in Table 1.

The best sensitivity and signal-to-noise ratio is achieved by using the absorbance of 5 pixels (peak volume selected absorbance, PVSA [25], $A_{\Sigma 5,int}$).

2.2. Reagents and sample preparation

All chemicals are of reagent grade or higher purity. All used solids are of highest purity grade and standard metal stock solutions (1 g L^{-1} or 10 g L^{-1}) were purchased from MERCK KGaA (Darmstadt, Germany). Hydrogen peroxide (3 vol.%), nitric acid (65 vol.%), hydrofluoric acid (40 vol.%) and boric acid (4 vol.%) were also purchased from MERCK KGaA (Darmstadt, Germany).

The sulfur standard is prepared by dissolving thiourea in double-distilled water. In case of tin a standard of 1 g L^{-1} with 6% hydrochloric acid was used (MERCK KGaA). Metal solutions (iridium, magnesium, palladium, ruthenium, tungsten, and zirconium) are prepared by dilution of the corresponding standard stock solutions.

Double-distilled water has been used as the diluent. The coal samples were provided from RAG Deutsche Steinkohle (Ruhrkohle AG, Herne, Germany). The investigated certified reference materials NCS FC 28004h and NCS FC 28011 (China National Analysis Centre for Iron and Steel, Beijing, China) are an anthracite and a bitumite coal type. The certified reference material BCR 331 (Community Bureau of Reference, Belgium) is a steam coal.

Portions of 0.5 g were digested using microwave assisted acid digestion with 3 mL H$_2$O$_2$, 8 mL HNO$_3$ and 1 mL HF, neutralized with 10 mL H$_3$BO$_4$, transferred in a polyethylene flask and filled up to 50 mL with double-distilled water [26]. No preparation was necessary for the coal samples determined by direct solid sampling analysis.

Argon gas of quality 5.0 was purchased from Linde AG (München, Germany).

Throughout all measurements, 10 µL of the tin solution, 5 µL of a 1 g L^{-1} Pd modifier and 10 µL of the sulfur containing solution are injected into the graphite furnace.

2.3. Procedure

Iridium, ruthenium, tungsten and zirconium were tested as permanent chemical modifier. Three aliquots of 20 µL of each modifier solution were pipetted on the solid sampling platform and heated after each injection by the temperature program in Table 2. The palladium modifier solution was pipetted automatically on top of the coal sample.

The initial weight of the sample can be different, because the integrated absorbance was normalized.

NCS FC 28004h was used as solid sample for the calibration. 0.27 mg–2.69 mg standard sample was weighted onto the platform, corresponding to about 2.75 and 27.4 µg S. The concentration values are valid at a minimal mass of 0.3 mg.

The calibration with the aqueous thiourea standard was investigated within the linear range from 2.5 to 30 µg S.

3. Results and discussion

3.1. Standard solution for calibration

Sodium sulfate as inorganic standard has been investigated. The pyrolysis and vaporization curve of sodium sulfate is shown in Fig. 1a. It was stable up to a pyrolysis temperature of 500 °C. The two organic standards thiourea and cysteine were investigated for calibration. The thermal behavior of these sulfur compounds is shown in Fig. 1b. For the moment all standards have been investigated; however, it turned out that the organic standard, thiourea in particular, obtained better results for the determination of sulfur in coal. This was already described by Mior et al. [23]. The example spectrum of SnS from thiourea is shown in Fig. 2. The dissociation energies of SnS and CS are 5.5 eV and 5.6 eV [27]. Dittrich et al. found out that molecules with more than 3–4 eV of dissociation energy are identifiable with MAS [28]. We used SnS for all measurements because it had better robustness at presence of other metals and non-metals than CS and less interferences were observed [19].

3.2. Comparison of modifier

In order to compare the influence of the different permanent modifiers on the investigated absorbance signal, three aqueous standard solutions were chosen. The variation of the absorbance without coating, with zirconium and iridium coated platform is shown in Fig. 3a–c. The solid sampling platform was prepared as described in Section 2.3 and then 10 µL of the sulfur compound, 10 µL of the tin-solution, and then 5 µL Pd solution as temporal modifiers were dropped onto it.

The platform coated with Ir as permanent modifier had the best results in terms of sensitivity for the organic sulfur compounds.

Table 1
Temperature program used for sulfur determination via SnS molecular absorption in the graphite furnace.

Step	Temperature in °C	Heating rate in °C s^{-1}	Hold time in s	Argon flow rate in L min^{-1}
Drying 1	110	5	20	2.0
Drying 2	210	10	10	2.0
Pyrolysis	550	100	15	2.0
Gas adaption	550	0	5	0.0
Vaporization	2100	1500	5	0.0
Cleaning	2450	500	4	2.0