



Sulfur determination in coal using molecular absorption in graphite filter vaporizer

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ARTICLE INFO

Article history:

Received 3 November 2010

Received in revised form

23 November 2010

Accepted 26 November 2010

Available online 3 December 2010

Keywords:

Sulfur determination

Coal slurry

Molecular absorption

Filter furnace

ABSTRACT

The vaporization of sulfur containing samples in graphite vaporizers for atomic absorption spectrometry is accompanied by modification of sulfur by carbon and, respectively, appearance at high temperature of structured molecular absorption in 200–210 nm wavelength range. It has been proposed to employ the spectrum for direct determination of sulfur in coal; soundness of the suggestion is evaluated by analysis of coal slurry using low resolution CCD spectrometer with continuum light source coupled to platform or filter furnace vaporizers. For coal in platform furnace losses of the analyte at low temperature and strong spectral background from the coal matrix hinder the determination. Both negative effects are significantly reduced in filter furnace, in which sample vapor efficiently interacts with carbon when transferred through the heated graphite filter. The method is verified by analysis of coals with sulfur content within 0.13–1.5% (m/m) range. The use of coal certified reference material for sulfur analyte addition to coal slurry permitted determination with random error 5–12%. Absolute and relative detection limits for sulfur in coal are 0.16 μg and 0.02 mass%, respectively.

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1. Introduction

Sulfur is one of the relevant elements in coals. Due to the different compositions of coals, sulfur content can range from 0.1 up to 6% m/m. Furthermore, sulfur compounds in coals can be listed in three distinct groups:

- Organic sulfur, i.e. sulfur bound in carbon structures. These species show a limited thermal stability.
- Inorganic sulfur, i.e. sulfur bound in inorganic compounds (sulfides, sulfates, etc.). These species show a thermal stability related to the specific compound.
- Pyritic sulfur, i.e. sulfur as FeS_2 . This species show relative chemical stability but limited thermal stability.

Sulfur content is usually determined to evaluate the emissions of SO_2 in the atmosphere after coal combustion. Sulfur is also determined in coal ash as a by-product in coal combustion.

Various test methods have been developed by standardization bodies. In particular, ASTM International (American Standards for Testing and Materials) developed the test method D 4239, first published in 1983 and reapproved in 2002 [1]. In this method, the coal sample is burned in a high temperature furnace (minimum operat-

ing temperature 1350 °C). Sulfur oxides formed during combustion are collected and then determined via acid–base titration or via measurement of infrared absorption. The latter determination is commonly employed in automated instruments. The reproducibility of infrared method is about 0.13% (m/m) at 1.5% (m/m) sulfur content. Both methods are capable to overcome the problems associated with the different sulfur species in coal, as all sulfur species are oxidized and detected. However, the precision of both test methods becomes less satisfactory when the sulfur content in the samples is lower than 0.5–1.0%.

An alternative test method should provide better precision but at the same time should overcome the problems related to the different thermal stabilities of sulfur species. Furthermore, a new method should guarantee correct sample introduction for a variety of coals with different compositions of organic and inorganic constituents, short analysis time and simple calibration. Hence, it is reasonable to evaluate other spectroscopic techniques for sulfur determination in coal. The simplest approach could be coal slurry analysis using the technique of electrothermal atomic absorption spectrometry (ET AAS). Several problems can be envisaged on this approach.

One problem is related to the detection of sulfur. Direct determination of atomic sulfur using atomic lines in far-ultraviolet region (180.7, 182.0 and 182.6 nm) would require special vacuum or inert gas purged instrumentation [2]. Alternatively, CS bands could be used for detection of sulfur. This idea was applied, first, by Tittarelli and Lavorato in the determination of sulfur in oil [3]:

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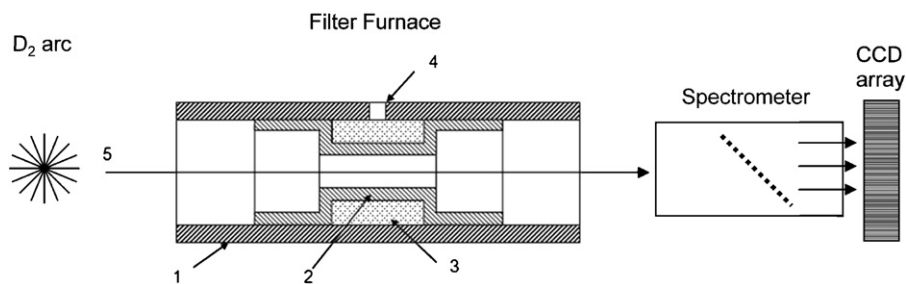


Fig. 1. Experimental setup. 1: pyrocoated graphite tube, 2: graphite filter, 3: ring cavity (empty for the slurries or filled with carbon fiber for liquid samples), 4: sampling port, and 5: light beam.

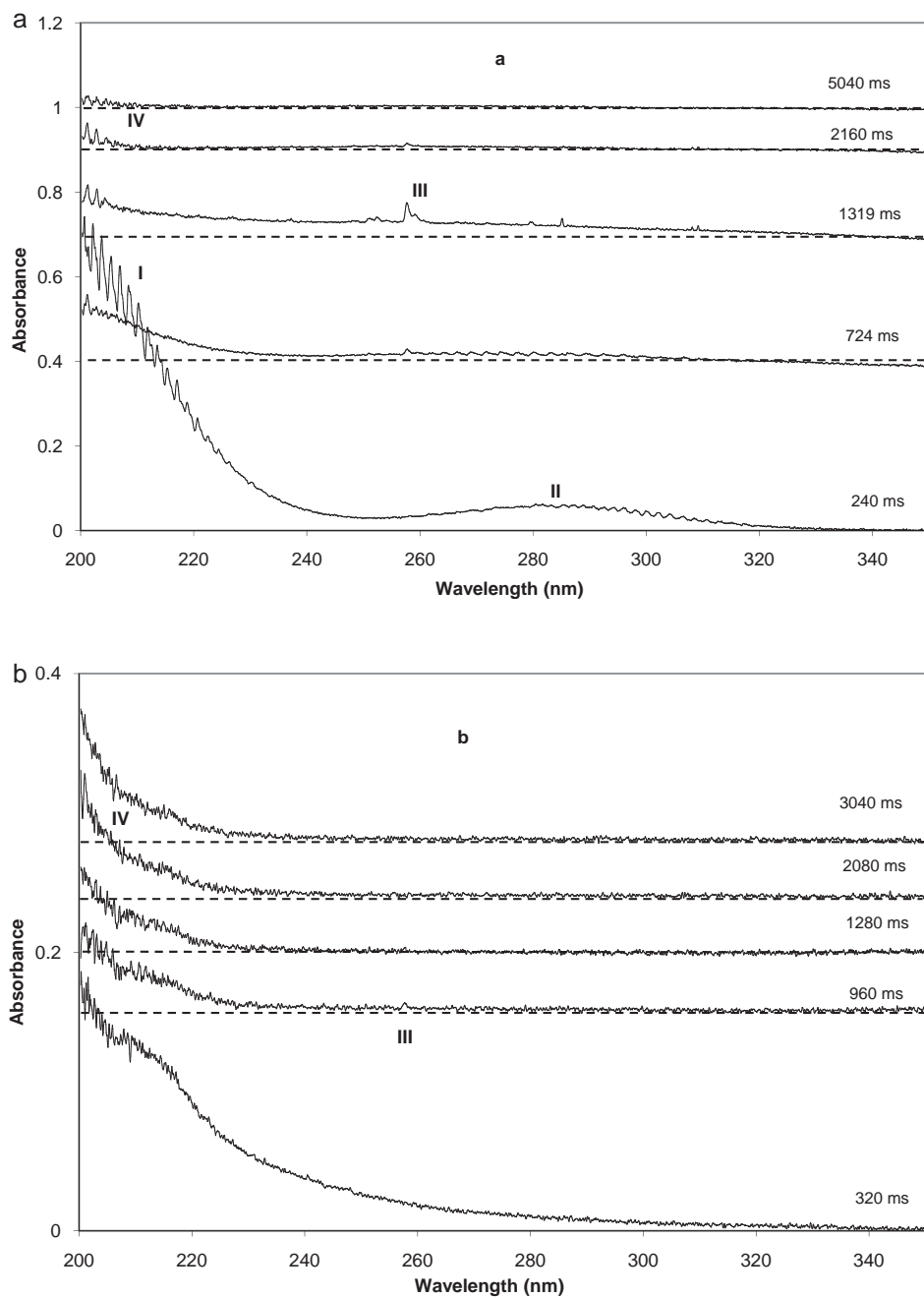


Fig. 2. Absorption spectra acquired during the vaporization of 20 μg sulfur injected in platform furnace as solutions in water (a) and hexane (b). Dashed lines indicate zero absorbance for respective spectrum.

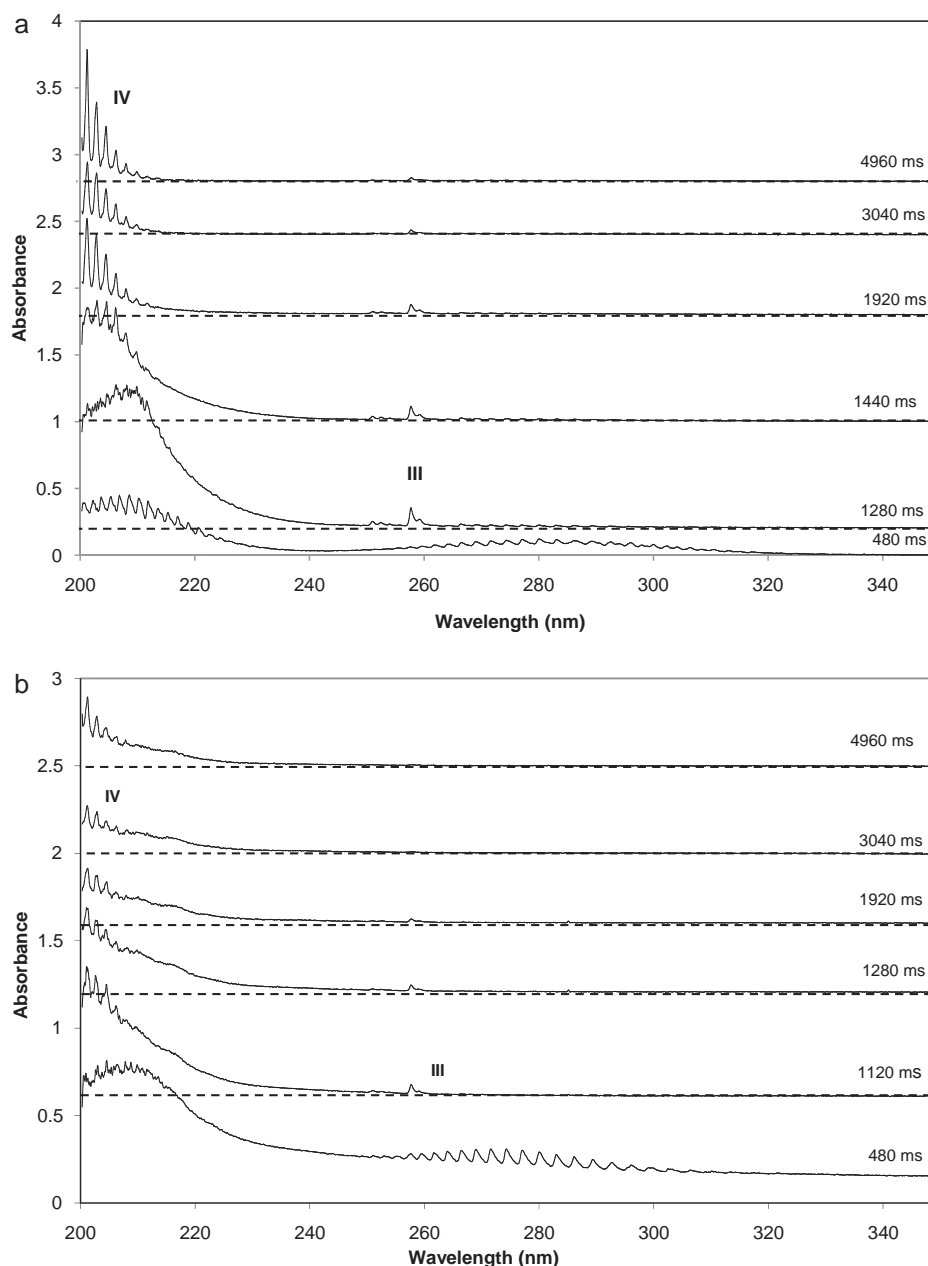


Fig. 3. Absorption spectra acquired during the vaporization of 20 $\mu\text{g S}$ injected in filter furnace as solutions in water (a) and hexane (b).

They employed a platform furnace (PF) atomizer, deuterium lamp as a continuum spectrum light source and diode array for detection of absorption of CS band at 257.6 nm. Structure of CS absorption bands in 257–258 nm wavelength area was investigated in details by Huang et al. [4] using high resolution continuum source AA spectrometer (HR CS AAS) [5] and flame atomizer. The authors used CS band head at 258.056 nm for quantification of sulfur content in water solutions in the presence of various metals.

Another problem is related to accuracy of the measurements. The investigation of vapor spectra in 200–350 nm wavelength region and thermal behavior of inorganic sulfur compounds in graphite tube atomizer using low resolution CCD (charge coupled device) spectrometer showed presence of multiple discrete and diffuse molecular bands, partially temporarily resolved and overlapped to absorption continuum [6,7]. The experiments with sulfur, sulfates and sulfides showed that a variety of sulfur species is evolved from each compound during the vaporization cycle,

depending on the nature of compound, and its (or its constituents) reactivity towards graphite. For various compounds containing similar amounts of sulfur, the ratio of intensities of S_2 , CS, or other bands was different and could not be predicted. Thus, for coals an extremely complicated pattern of sulfur species evolution can be expected that is confirmed by experiments on atmospheric pressure-temperature-programmed reduction (AP-TPR) of different rank coals [8].

Intense spectral interferences due to organic and inorganic constituents of coal can also be expected. A modification of vapor absorption spectra from various sulfur containing species occurs if filter furnace (FF) atomizer is used instead of graphite tube or PF [9]. Analytical practice with the FF confirms efficient reduction of spectral background for direct element determination in the organic and inorganic matrices, and suppression of chemical interferences. In the FF, vapor absorption spectra of sulfur containing samples are much simpler than those recorded in the tube vaporizer [7].

The broad bands appearing during decomposition of sulfates in the tube furnace and attributed to SO/SO₂ species disappear almost completely in the FF. In fact, only group of bands belonging to S₂ (260–300 nm), to CS (around 258 nm) and to not identified species (around 200–210 nm) appear sequentially with rise of temperature together with respective atomic lines.

These considerations provide prerequisites to the possible use of molecular spectra in filter furnace for the measurement of sulfur content in coal samples. The outcome of this investigation is presented and discussed in this work.

2. Experimental

2.1. Instrumentation

The diagram of the experimental setup is shown in Fig. 1. It included continuum light source, FF vaporizer and Ocean Optics HR4000 spectrometer with charge coupled device (CCD) detector connected to PC. A grating of 1200 grooves/mm and spectral slit of 25 μm provided full width at half maximum (FWHM) of the transmittance profile of the spectrometer of about 0.3 nm in spectral area 200–420 nm; the instrument was equipped with Toshiba 3680 pixels CCD. Radiation from the deuterium continuum spectrum lamp (Mikropack D2000) was transferred through optical cable (QP450-0.25-XSR) and focused in the centre of the absorption volume of the FF by collimating lens (74-UV). Second lens focused radiation on the entrance slit of the spectrometer.

The software (Ocean Optics SpectraSuite) provided monitoring of the spectra with a frequency controlled by data collection time. Low light output at short wavelength area did not allow the use of data collection time less than 15 ms.

Standard Perkin Elmer platform furnace (B30001264) and in-house built filter furnace were employed in comparative experiments using Perkin Elmer HGA-500 power supply and atomization unit. In the FF, pyrocoated tube Perkin Elmer (BO 091 504) 6 mm in internal diameter, was employed for accommodation of graphite filter (spool shaped insert made of graphite rod (AGKSP grade, Alfa Aesar, Massachusetts, USA)). Central part of the insert formed absorption volume 10 and 2 mm in length and diameter, respectively; external surface of the filter together with internal surface of the pyrocoated tube formed a ring cavity in which the sample was to be injected. In the FF for analysis of liquids, the cavity was loosely filled with carbon fiber (Alfa Aesar) collector. Presence of collector helped to keep liquid sample within the cavity thus preventing its penetration in the filter at the drying stage. Normally, when the FF was employed for elements determination, presence of collector helped to improve atomization efficiency providing a delay in vaporization of the analyte [9]. It was recently shown that for analysis of coal slurry the FF without collector could also be employed [10]. In this work various amounts of carbon fiber collector were accommodated in the FF depending on the task of particular experiment.

The settings of argon flow from the ends of the tube towards the injection hole through the filter were applied as indicated in Table 1.

2.2. Samples and reference materials

Sulfur (ASC, Christville, SA) was introduced in the platform and filter furnaces as 10–20 μL of 1 g L⁻¹ sulfur reference material (RM) in water (Spectrascan, Technolab, Norway) or as solution of similar concentration in hexane (SMM Chemicals, Germany).

Table 1

Temperature program used in the experiments.

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Gas flow (mL min ⁻¹)
Drying	50 ^a –100	1	30	50
Pyrolysis	200 ^a –700	1	20–100	300
Vaporization	2200/2600	0	10	0–30
Cleaning	2200/2600	1	2	300

^a Lowest temperatures used in the experiments with platform furnace and sulfur solution in hexane.

Table 2

Molecular bands observed at high temperature during vaporization of micrograms of sulfur containing substances in graphite vaporizers.

	Absorption band	
	Wavelength (nm)	Relative intensity ^a
1	201.25	1.0
2	202.87	0.7
3	204.56	0.41
4	206.31	0.28

^a Difference between respective maximum and average of the adjacent minimums.

Coal Standard Reference Material SARM 18 (Coal (Witbank), South Africa Bureau of Standards) with sulfur content 0.56% (m/m) was employed in the optimization of analytical procedure and as added analyte for quantification of sulfur content in other coals. The list of those included coal samples SARM 19 (Orange Free State) and SARM 20 (SASOLBURG) with sulfur content 1.49 and 0.51%, respectively, four coals, provided by Stazione Sperimentale per i Combustibili (SSC), Italy, with sulfur content 0.94, 0.42, 0.16, and 0.13% (m/m) determined using the ASTM method, and the sample of Witbank coal earlier analyzed using ICP-OES slurry nebulization method [11]. The SARM reference materials were supplied with the coal particle size below 100 μm. Other samples were further ground to make particle size similar to that in reference material.

To prepare slurry samples, coal portions were weighted in 10 mL volumetric flasks and deionized water was added to the mark. For each type of coal to be analyzed and its mixtures with SARM 18 three samples were prepared with total masses of coal between 0.08 and 0.4 g. Twenty (in some experiments, 40) μL aliquots were used for slurry sampling immediately after intense shaking of the flasks that made delivery of coal in the vaporizer about 0.2–0.8 mg.

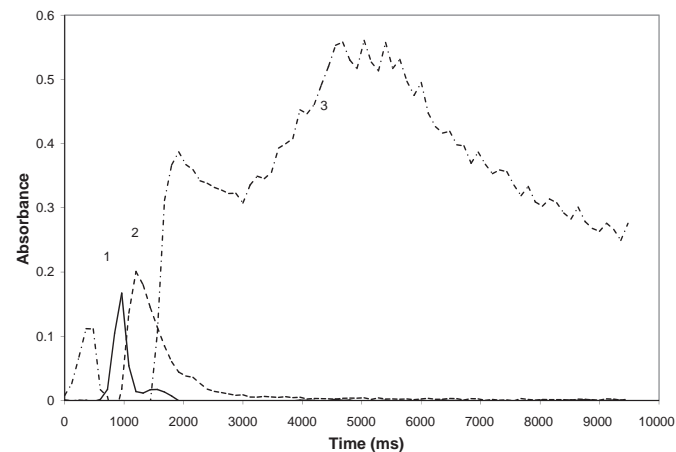


Fig. 4. Temporal evolutions of the bands shown in Fig. 3a. Curves 1, 2, and 3 correspond to the maximums of bands II (S₂), III (CS) and IV (not identified specie), respectively.

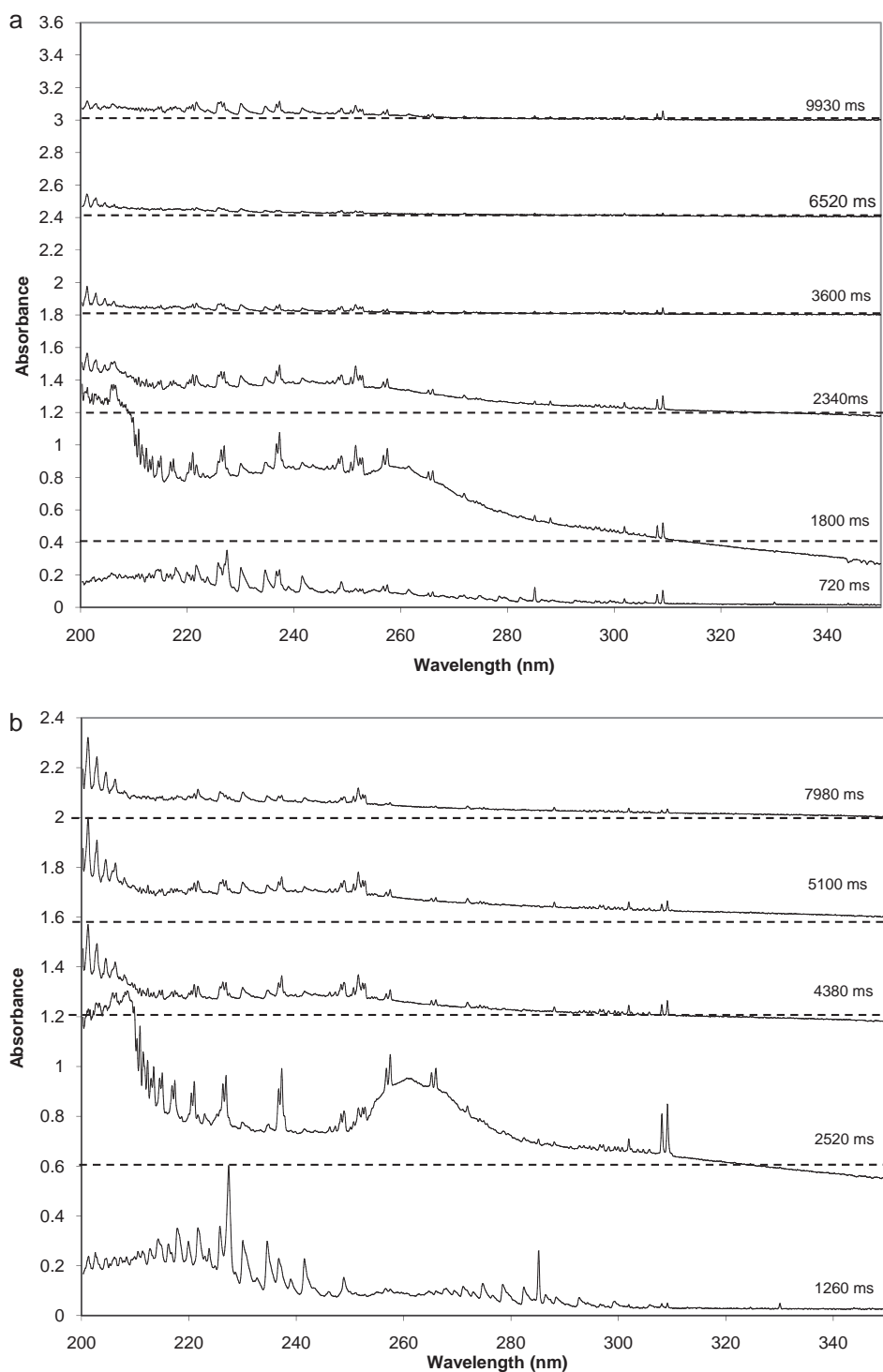


Fig. 5. Absorption spectra observed in the platform (a) and filter (b) furnaces during the vaporization of 0.8 mg of SARM 18 coal sampled as 20 μL of 0.04 g mL^{-1} slurry.

2.3. Procedure

The solutions and slurries were injected in the furnaces manually with micropipette. The samples were treated in accordance with the heating program in Table 1, where the drying and pyrolysis temperatures varied according to the sample type. During the vaporization stage, temperature of the external tube reached stabilization level within 2–3 s. Temperature of platform and filter lagged behind that of the tube. In case of the FF, effective temperature established in the absorption volume was by 100–200 °C

higher than the respective program settings, depending on amount of graphite fiber wound around the filter [12]. Various gas flows were applied during different stages of temperature program (Table 1).

Radiation continuum was repeatedly monitored within 200–400 nm range during the vaporization stage, and respective data from 80 spectra acquisitions transferred to the computer. After running the sample, the heating program was repeated as blank measurement. From the sample and blank measurements, the absorbance was calculated using Excel software. The

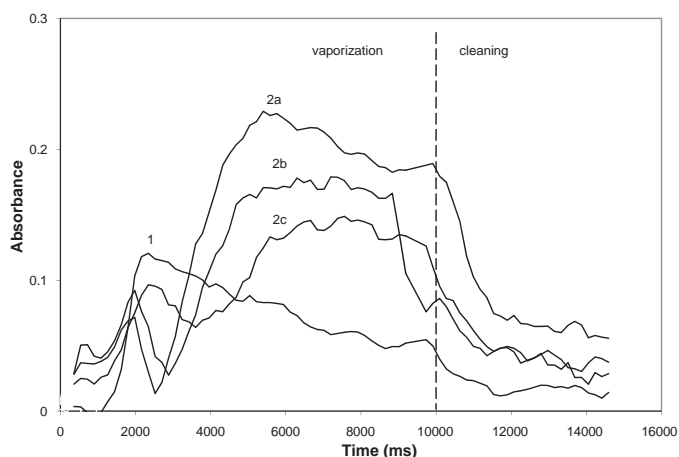


Fig. 6. Sulfur vapor release from 0.8 mg of coal SARM 18 in platform (1) and filter furnace (2a–2c) without (2a) and with (2b and 2c) 10 and 20 mg carbon fiber, respectively; pyrolysis and atomization temperatures 500 and 2200 °C.

required data were extracted from the respective data matrix and calculations performed using specially developed Macro routine.

3. Results and discussion

3.1. Modification of sulfur vapor spectra in filter furnace

Vaporization of microgram sulfur samples in the graphite ET vaporizers is accompanied by evolution of various absorption spectra. The spectra observed in a platform furnace for dry residues of the inorganic and organic solutions are shown in Fig. 2a and b, respectively. Each spectrum in the figures corresponds to the moments when specific bands are highlighted. For inorganic sulfur (Fig. 2a) the group of structured bands (I) between 200 and 220 nm (average distance between the maxima is 371 cm^{-1}) appears simultaneously with group (II) within 260–300 nm wavelength range at the very beginning of the vaporization stage. The most intense bands of the latter group can be attributed to S_2 molecule [13]. At higher temperature CS band (III) appears simultaneously with not identified group of bands between 200 and 210 nm (IV), however, the latter persists much longer that shows difference in their origin. The CS band (III) had been used for sulfur determination in oil [3]; the bands (200–210 nm) were not noticed by the authors [3],

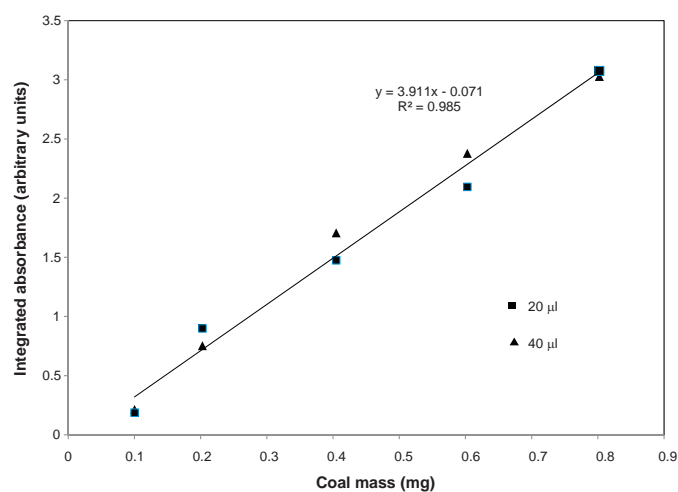


Fig. 8. Calibration curve integrated absorbance at 201.25 nm vs. mass of coal SARM 18 injected in the filter furnace without collector as 20 and 40 µL slurries.

probably, because of their superposition with intense background originated from the oil matrix.

For sulfur introduced in the atomizer as solution in hexane (Fig. 2b), in fact, only absorption continuum highlighted at the beginning of the vaporization stage is observed. In some replicate experiments very weak absorption at 200–210 and 257–258 nm followed the continuum. The randomness of the effect can be, probably, associated with not controllable distribution of the analyte on the surface of graphite platform. Difference in the absorption at 257–258 nm in this experiment and in [3] can be, most probably, attributed to variety of sulfur compounds in oil matrix.

Temporal behavior of the 200–210 nm bands in Fig. 2a permits suggestion that they originate from sulfur–carbon interaction. In that case, the interaction should be facilitated in FF due to large surface provided by carbon fiber and porous structure of graphite filter. Thus, modification of the released species by carbon can be expected that should reduce difference between spectra of organic and inorganic sulfur. The suggestion is confirmed by comparing the spectra in Fig. 3a and b for organic and inorganic sulfur, respectively, obtained in the FF furnished with 20 mg carbon fiber collector: For organic sulfur the structured bands appear instead of absorption continuum; at high temperature the spectra originated from both solutions become similar; for inorganic solution the bands become much more highlighted than in platform furnace.

The bands observed at high temperature between 200 and 210 nm are listed in Table 2; the wavelengths of the maxima are reported according to the CCD pixel readings. Average distance between adjacent maxima for this group is 416 cm^{-1} , that differs substantially from the structured spectrum (I) in Fig. 2a also located in the same spectral area. Attribution of the bands in Table 2 is not clear yet, however it can be suggested that the absorbing species include C and S atoms. For example, these species can be CCS or CCS^- [14,15]. At lower temperature they can exist in equilibrium with CS, at higher temperature the equilibrium could be shifted towards formation of these species due to increased concentration of carbon in gas phase. Otherwise, these bands can arise from the excited vibrational levels of the ground electronic states of CS or CS_2 molecules.

The evolution of most characteristic bands in Fig. 3a, calculated as difference between adjacent maxima and minima, is reported in Fig. 4. It is seen from comparison of the curves that peak area attributed to the absorption band at 201.25 nm (curve 3) is much higher than that of CS (curve 2) or S_2 (curve 1) band. Slow release of the species responsible for the bands 200–210 nm points out

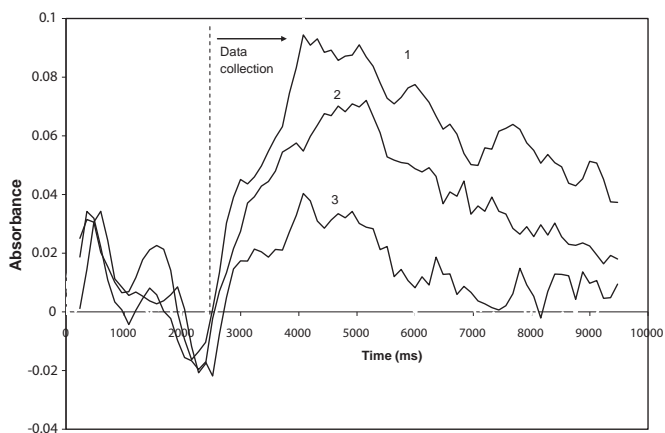


Fig. 7. Effect of Ar flow through the filter furnace on absorbance at 201.25 nm during the vaporization of 0.8 mg of SARM 18 coal. Pyrolysis and vaporization temperatures are 500 and 2200 °C, respectively, FF without carbon fiber collector; curves 1, 2 and 3 correspond to gas flows 10, 20 and 30 mL min^{-1} , respectively.

Table 3
Determination of sulfur in coals SARM 19 and SARM 20 using coal SARM 18 for the analyte addition.

Sample, known sulfur content (%)	Mass of coal in 10 mL slurry (g)		Integrated absorbance ^a (arbitrary units)			Sulfur (mg)		Sulfur content determined (%)	
	Sample	Added SARM 18	For the mixed slurry	For the sample slurry	For the addition	Added ^b	Found in the sample	In the replicate	Average
SARM 19, 1.49 ± 0.07	0.1	0.161	1.62	0.99	0.63	0.9	1.41	1.41	1.52 ± 0.11
			1.51	0.95	0.56		1.53	1.53	
			1.66	1.06	0.6		1.51	1.51	
	0.074	0.201	3.45	1.74	1.71	1.12	1.13	1.53	
			3.14	1.51	1.63		1.04	1.40	
			3.38	1.68	1.7		1.1	1.49	
	0.18	0.212	2.48	1.78	0.7	1.19	3.03	1.68	
			2.22	1.60	0.62		3.07	1.7	
			2.38	1.62	0.76		2.53	1.41	
SARM 20, 0.51 ± 0.03	0.2	0.161	1.47	0.86	0.61	0.9	1.27	0.63	0.53 ± 0.05
			1.28	0.73	0.55		1.19	0.59	
			1.24	0.66	0.58		1.02	0.51	
	0.1	0.1	7.11	3.53	3.58	0.56	0.58	0.58	
			3.92	1.78	2.14		0.46	0.46	
			3.06	1.45	1.61		0.5	0.50	
	0.17	0.22	1.78	0.72	1.06	1.23	0.83	0.49	
			1.86	0.76	1.10		0.85	0.5	
			1.78	0.77	1.01		0.93	0.54	

^a20 µL injected.

^bTaking into account 0.56% (m/m) sulfur content in the coal SARM 18.

to deep penetration and bounding of sulfur in the tube wall, carbon fiber or graphite filter. Formation of intercalations of sulfur in graphite lattice [16] can be suggested to explain the effect.

3.2. Coal absorption spectra and optimization of experimental conditions

Taking into account sulfur content in coals, it was expected that vaporization of milligram masses of coal in filter furnace should provide measurable absorbance at the wavelengths indicated in Table 2. To verify the suggestion, 0.8 mg of coal SARM 18 was introduced as slurry in the platform and filter furnaces and vaporization spectra collected. The most characteristic spectra obtained are shown in Fig. 5a and b for the respective vaporizers.

In general, the spectra in both figures look similar, although specific patterns appear in substantially different moments. In both spectra Al, Mg and Fe atomic lines dominate together with Al₂O absorption band and Al ionization continuum [5,13,17]. The CS 257–258 nm bands are disguised by Al lines at 257.54, 257.51 nm that prevents their use for sulfur determination in coal. The bands at 200–210 nm are highlighted in the FF that leads to the presumption that absorbance of these bands integrated during the vaporization time could be employed for sulfur determination after optimization of experimental conditions.

It can be suggested that optimal condition for sulfur determination in coal slurry are to provide as complete as possible

modification of various sulfur species, maximum intensity of the absorption bands and full vapor release during the data collection time. The variables to be optimized include amount of carbon fiber collector, sampling volume and mass of carbon slurry, pyrolysis and atomization temperature and gas flow.

In the experiments performed, the most difficult requirement to satisfy turned out to be full release of sulfur compounds responsible for the bands during reasonable registration time. Although FF provided much higher absorption than PF due to modification efficiency and narrower absorption volume, vapor release from the FF was substantially slower (Fig. 6, curves 2 vs. curve 1) that reduced the advantage. Highest absorption peaks and vapor release rate with gas-stop mode was obtained for the FF without collector (Fig. 6, curve 2a). Although presence of collector could be considered as positive factor for modification efficiency, in practice it hardly helped: In the presence of 10 or 20 mg of carbon fiber the absorption peaks were reduced on account of slower vapor release (curves 2b and 2c). Increase of vaporization temperature above 2200 °C also caused reduction of absorption peaks but did not provide tangible reduction of the signal tailings.

At the cleaning stage gas flow through the FF (from the tube ends through the filter) provided effective removal of sulfur vapor, especially for the tube without fiber (Fig. 6, curves 2a). Accordingly, it was considered expedient to apply gas flow also at the vaporization stage to facilitate vapor release through the sampling hole. Although this method caused reduction of detection sensitivity, as

Table 4
Determination of sulfur in coals.

Coal sample	Sulfur content (%)		
	Certified	Determined using	
		ASTM method	ICP-OES coal slurry nebulization
SARM 19	1.49 ± 0.07		1.52 ± 0.11
SARM 20			0.53 ± 0.05
1 (SSC)		0.94	0.96 ± 0.08
2 (SSC)		0.16	0.16 ± 0.02
3 (SSC)		0.42	0.43 ± 0.02
4 (SSC)		0.13	0.13 ± 0.01
Witbank [11]			1.05 ± 0.17
			1.0 ± 0.1

it is shown in Fig. 7 for various gas flows, it could not influence efficiency of vapor modification by carbon. Apparently, the modification process occurred mostly during the pyrolysis stage: Lower pyrolysis temperature within 500–700 °C range provided higher intensity of the absorption bands; temperature could not be set below 500 ° because of increasing background absorption during the vaporization stage.

To find out optimal slurry concentration and sampling volume the spectra were collected for various masses of coal SARM 18 injected as 20 and 40 μL slurry. The sum of absorbance data at 201.25 nm from the appearance of the band (as shown in Fig. 7) till the end of vaporization stage was calculated for each sample in three replicates. The function integrated absorbance vs. sampled mass was found to be close to linear regression with correlation coefficient 0.98 (Fig. 8) within the mass range below 0.8 mg of injected coal. Above this limit the correlation was lost.

3.3. Calibration measurements and determination of sulfur in various coal samples

It was earlier discovered in the work on simultaneous determination of metals in coals that storage of 5 mg of carbon in the FF without collector did not affect release rate for the analyte metals [10]. Under consideration of similar effect for sulfur determination in coal, sets of 10–12 measurement or more, depending on coal content in the slurry, could be performed. However, between the sets, the FF should be taken from the atomization unit, dismantled, filter and tube brushed, and FF again assembled and installed back.

Consequently, resistance of electric contacts of the vaporizer or permeability of filter could slightly change after each set of measurements that should affect the measured signals. Those changes, as well as possible deviations of modification efficiency for various types of coal prevented direct data calibration according to the regression in Fig. 8 for the coal with certified content of sulfur. The analyte addition method was expected to be less prone to systematic errors.

The detailed presentation of the verification measurements with analyte addition is given in Table 3. Sulfur content 0.56% (m/m) in coal SARM 18 was taken for granted; the content in the examined samples (SARM 19 and SARM 20) was considered unknown. For each coal to be analyzed a set of slurries was prepared, made up of three slurries containing mixtures of the sample with SARM 18 coal at various ratios; single component slurries of the sample were also prepared. The measurements were performed in three replicates for each slurry and final results determined from the three sets of independent measurements that provided enough data for estimation of random determination error. Similar procedure was repeated for other coal samples. Final determination results are presented in Table 4 together with the certified data and results of independent determination.

It can be concluded from the data in Table 4 that sulfur content in various coals differs by more than ten times from 1.5 to 0.13%. Random error varies between 5 and 12% independent of sulfur content within the identified range. The determination results are close to the respective data obtained independently within the range of

random deviation. Absolute limit of detection for sulfur can be evaluated from the results for SARM 20 (Table 3): 10 mL of coal slurry contains 0.56 ± 0.0265 mg of sulfur. Thus, average mass of sulfur corresponding to limit of detection (3 RSD of measured quantity) in the injected volume 20 μL is 0.16 μg. Considering 0.8 mg as maximum for the injected coal mass (Fig. 7), relative limit of detection for sulfur in coal can be estimated as 0.02% (m/m).

4. Conclusion

It was verified that interaction of coal sample vapor with the heated graphite provides modification of various sulfur containing species and evolution of molecular vapor with structured absorption spectra in 200–210 nm region wavelength area. This phenomenon was successfully employed for quantitative determination of sulfur in coal using low resolution CCD spectrometer with continuum light source and filter furnace vaporizer. Coal slurry preparation and sampling substantially improve speed of analysis in comparison with traditional analytical procedure. The measurements of sulfur content can be combined with simultaneous determination of other major inorganic components in the coals [10].

Acknowledgement

The authors express their gratitude to National Research Foundation of South Africa for financial support of this project

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