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# A practical method for the determination of sulphur in coal samples by high-resolution continuum source flame atomic absorption spectrometry

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ABSTRACT

Sulphur in coal was determined using a high-resolution continuum source flame atomic absorption spectrophotometer (HR-CS-FAAS) with actylene/air flame. The C–S absorption band at 258.056 nm was found the most suitable analytical line with respect to sensitivity and spectral interferences. The instrumental parameters were optimized. The coal samples were dried and dissolved using microwave-assisted digestion technique. The validity of the method was tested using standard reference material and certified values were found in the limits of 95% confidence level. Since the concentrations of matrix elements of coal other than carbon are low enough not to cause any spectral interferences, the linear calibration method was applied in all quantifications without any problem. The calibration standards were prepared in sulphuric acid. The method was accurate, fast, simple and sensitive. The limit of detection (LOD, 3$\delta$, $N = 10$) and the limit of quantification (LOQ, 10$\delta$, $N = 10$) were found to be 0.01 and 0.03% (w/w), respectively. The sulphur concentrations of various kinds of the coal samples received around Turkey were determined. The sulphur contents of the coal samples were ranged from $\leq$LOQ to 1.2%.

## 1. Introduction

Without doubt, sulphur is a vital essential element for human, animals and plants to be involved in the structure of many proteins and enzymes through amino acids. Sulphur with a content of about 0.048% is the 15th most abundant element of earth's crust. It can also be found in fossil fuels such as coal, crude oil, and natural gas. Upon their combustion, $SO_2$ is produced, which is highly toxic for human. When it is released into the atmosphere, it can cause acid rains, which have negative impact on livings and cause corrosion on non-living things. Sulphur is found everywhere in earth crust in different forms and are used in many fields of science and technology. Therefore, determination of sulphur and sulphur compounds is a great interest in many fields such as medicine, environment, and agriculture, fossil fuel, iron-steel, and food industries.

Sulphur has been determined by different methods such as Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) [1], Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) [2,3] Ultraviolet–Visible Spectroscopy (UV–VIS) Spectrometry [4–9], X-Ray Fluorescence (XRF) [10] and chromatography [11]. Every method has its own advantages and disadvantages such as high cost, time consumption, poor precision, and selectivity. Among these techniques, none of them was free of interferences.

Atomic absorption resonance line of sulphur (180.7 nm) is in the vacuum ultraviolet region. Therefore, it cannot be practically determined by conventional AAS at atomic absorption line using a sulphur hollow cathode lamp. Sulphur can be determined by ETAAS only in vacuum using a special instrumental design, which is very complicated and practically not suitable to be used in routine analysis [12]. On the other hand, it has been determined by the Molecular Absorption Spectrum (MAS) of sulphur-containing diatomic species (CS, GeS, AlS, InS and SnS) and using conventional flame and electrothermal atomic absorption spectrophotometers with deuterium or hollow cathode lamps as the emission sources [13–15].

The determination of sulphur from molecular absorption of AlS, InS and SnS in electrothermal atomizer was investigated by Parvinen and Lajunen [15]. In another study, MAS of AlS, SnS and InS were used for the determination of sulphur and $D_2$ lamp was used for background correction. However, the use of conventional AAS instruments caused spectral interferences due to insufficient resolution of the monochromator to separate very close adjacent lines of hyperfine MAS. In addition, the wavelength of the source isolated may not match exactly with the very narrow rotational absorption line of the analyte-containing diatomic molecule selected for utilization.

Recently, as alternative to Inductively Coupled Plasma – Optical Emission Spectrophotometers (ICP-OES),

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High Resolution – Continuum Source Atomic Absorption Spectrophotometers (HR-CS-AAS) have been developed and these instruments are now commercially available [16–19]. HR-CS-AAS includes a high intensity xenon short-arc lamp used as continuous radiation source over the entire spectral range from 190 to 900 nm; a ultra high-resolution monochromator and a charge-coupled device (CCD) array detector, which provides a resolution of 140,000 in a 0.3–1 nm, corresponding to a bandwidth of about 1.6 pm per pixel at 200 nm. The spectral environment of the analytical 'line' becomes visible within an interval of 0.3–1.0 nm. HR-CS-AAS has been proven to be a reliable and accurate technique [16,20–22].

The main advantages of HR-CS-AAS are (i) improved signal and baseline stability resulting in much lower LOD, (ii) effective correction of complex, high and extremely fast changing, continuous and discontinuous spectral interferences and (iii) determination of low levels of nonmetals, such as Cl, F, P, Br and S due to the extremely high resolution power of the double monochromator to provide intense and very narrow emission lines at any wavelength. Therefore, it is possible to select extremely narrow wavelength (a few picometer) overlapping exactly with molecular hyperfine structured (rotational) absorption line of the analyte-containing molecule and to eliminate spectral interferences [23,24].

As a result of above-mentioned properties, the HR-CS-AAS is suitable technique not only for atomic absorption, but also for molecular absorption. However, the number of studies especially on the determination of non-metals by HR-CS-AAS is quite limited. Huang et al. [25,26] determined sulphur in wine samples by HR-CS-AAS with fuel-rich air–acetylene flame using a rotational line of CS molecular absorption at 258.056 nm formed in the flame. The results found by HR-CS-AAS and ICP-MS have a good correlation. They did not find any spectral and non-spectral interferences from diverse ions and various matrices.

Welz et al. [24] reviewed determination of phosphorus, sulphur and the halogens using line source conventional flame and electrothermal AAS and HR-CS-AAS. Finally, Jim et al. [27] reported the determination of sulphur in coal slurry using low resolution CCD spectrometer with continuum light source coupled to platform or filter furnace vaporizers and investigated the behaviour of sulphur in the furnace.

The aim of this study is to investigate the determination of sulphur in coal by HR-CS-AAS by means of molecular absorption lines of CS formed in acetylene–air flame. The experimental parameters were optimized and validity of the method was tested using certified reference materials. Sulphur is determined from the molecular lines of CS generated both in flame and graphite furnace. However, the concentration of S in coal is mostly high enough to be detected in flame. In addition, since the major content of coal is carbon, CS could be easily generated in flame.

## 2. Materials and methods

### 2.1. Instrumentation

An Analytik Jena ContrAA 700 High Resolution Continuum Source Atomic Absorption Spectrometer (Analytik Jena, Berlin, Germany) equipped with a 300W xenon short-arc lamp (XBO 301, GLE, Berlin, Germany) as a continuum radiation source was used throughout the work. This new equipment presents a compact high-resolution double echelle monochromator and a charge-coupled device (CCD) array detector with a resolution of about 5 pm per pixel. The measurements were carried out at 258.056 nm wavelength. The number of pixels of the array detector used for detection of CS line was 5 (central pixel ±2). All measurements were carried out in triplicates. A Topwave microwave-assisted digestion system decomposition system (Analytik Jena, Berlin, Germany) equipped with pressure decomposition teflon vessels of 50-mL capacity each was employed for the coal decomposition. All glassware and polyethylene flasks used for solution preparations were previously immersed overnight in a 10% (v/v) $HNO_3$ bath and then rinsed with abundant ultra pure water to avoid contamination.

**Table 1**
The microwave-assisted digestion programme for the digestion of coal samples.

| Temperature (°C) | Pressure (bar) | Ramp | Time (min) | Power (%) |
|---|---|---|---|---|
| 150 | 50 | 10 | 10 | 90 |
| 190 | 50 | 5 | 30 | 90 |
| 250 | 50 | 5 | 30 | 90 |
| 50 | 0 | 1 | 1 | 0 |
| 50 | 0 | 1 | 1 | 0 |

### 2.2. Reagents and analytical solutions

High-purity water (resistivity 18.2 MΩ cm) obtained by a TKA reverse osmosis and a TKA deionizer system (TKA Wasseraufbereitungsysteme GmbH, Niederelbert Germany) was used throughout the work. Inorganic acids and reagents were of analytical grade ($HNO_3$ 65% (v/v), HCl 37% (v/v), $H_2SO_4$, $NH_2SO_4$, $Na_2SO_4$, $Na_2SO_3$, Merck, Darmstad, Germany). For comparison, the sulphur standards prepared from sulphuric acid, sodium sulfite, sodium thiosulphate, and ammonium sulphate (Merck, Darmstadt, Germany) were also used. The standard reference material Trace Element in Coal (SRM 1632b) was provided by the National Institute of Standards and Technology (Gaithersburg, MD, USA). Twelve different coal samples with different origins and types were obtained from market arbitrarily in Istanbul, Turkey.

### 2.3. Sample preparation

The samples and CRM were stored in polyethylene bags and kept in room temperature. Prior to analysis, the samples were dried at 50 °C in an air-ventilated oven for 12 h. The samples were allowed to cool over silica gel and stored in tightly closed folding polyethylene cups. All samples were ground manually in an agate mortar. Approximately a 0.2 g of each coal sample was weighed precisely and dissolved by microwave-assisted digestion using 10 mL of concentrated $HNO_3$. The microwave-assisted digestion programme was shown in Table 1. The results were given as the average of at least 3 repetitive determinations for each sample which means three independent sample treatments of the each sample.

## 3. Results and discussion

### 3.1. Choice of wavelength

The most well known primary CS lines, 257.593, 257.959 and 258.056 nm, have been well documented in the literature with respect to sensitivity and isolation from their neighboring hyperfine lines (refs). Due to the very high resolution power of HR-CS-AAS, it is indeed even very close lines can be separated enough to measure the absorbance without spectral interference. Therefore, sensitivity is more important than separation of analytic line from its neighboring complicated lines. The above mentioned CS lines as well as some others given as in the literature were investigated for the determination of S (refs). After a set of experiments with different CS lines, it was found that 258.056 nm gave the maximum sensitivity and well separated from its neighboring hyperfine lines. Thus, it was selected as the most appropriate line for the determination of sulphur in acetylene/air flame.

**Table 2**
Recoveries of sulphur in SRM 1632b coal sample using HR-CS FAAS (number of repetition: 3, λ: 258.056 nm; fuel rate: 80 L h$^{-1}$; burner height: 10 mm).

| Sample | Certified value[a] (%) | Added (%) | Found[a] (%) | Recovery (%) |
|---|---|---|---|---|
| SRM 1632b (Trace Elements in Coal) | 1.89 ± 0.06 | – | 1.85 ± 0.18 | 98 |
| | | 0.5 | 2.36 ± 0.14 | 100 |
| | | 1.0 | 2.83 ± 0.08 | 99 |

[a] Mean ± 2 standard deviation.

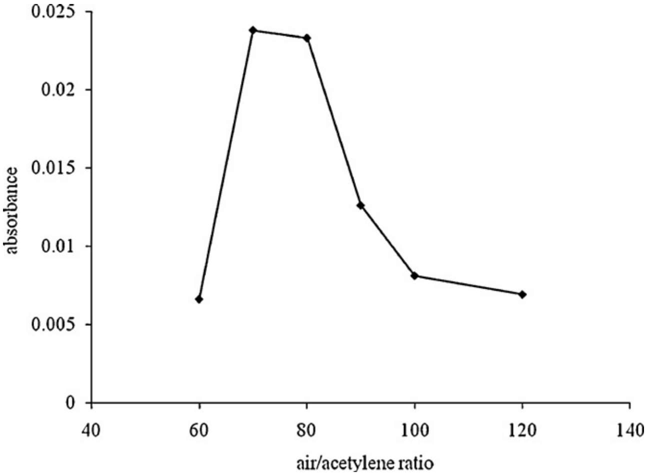

**Fig. 1.** Fuel rate (air/acetylene ratio) for the determination of S in coal samples by HR-CS-FAAS.

### 3.2. Optimization of flame conditions

First, the fuel rate (acetylene ratio/air) and burner height, which are the most important parameters for the determination of sulphur by HR-CS FAAS, were optimized. For this purpose, 1% $H_2SO_4$ was used for all optimization experiments. The fuel rates between 60 and 120 L h$^{-1}$ were tested to find the optimum condition and as shown in Fig. 1, the maximum absorbance was gained at 70–80 L h$^{-1}$ fuel rate.

Another important instrumental parameter is burner height for the HR-CS FAAS. As shown in Fig. 2, for a burner height of 10 mm, the maximum absorbances were obtained for CS at 258.056 nm.

Another critical parameter is the type of flame. In the literature, both acetylene/air and nitrous oxide/acetylene flames were used. In this study, acetylene/air was preferred due to the satisfactory results and the ease of use. The air flow rate of nebulizer was constant (by the manufacturer) whereas the fuel was adjusted to the maximum value of 80 mL h$^{-1}$.

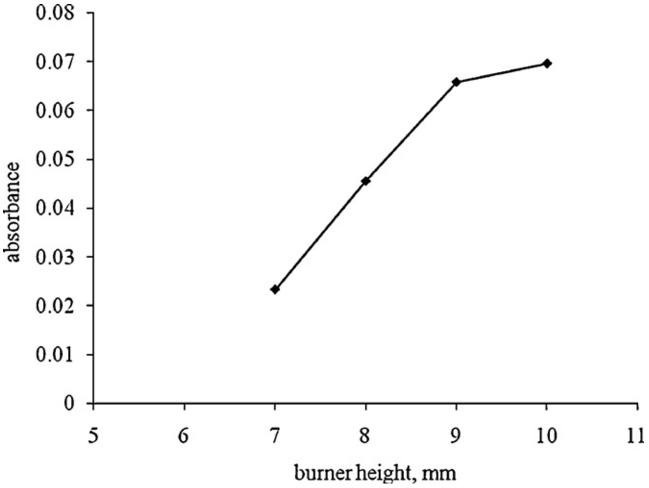

**Fig. 2.** Burner height for the determination of S in coal samples by HR-CS-FAAS.

### 3.3. Choice of calibrant and sample digestion method

After the optimization of the instrumental conditions, several sulphur compounds such as sulphuric acid, sodium sulphide, sodium thiosulphate, and ammonium sulphate were used as the possible calibrants and the results were compared with respect to accuracy, precision, linear range. Under optimum experimental conditions, the most appropriate calibrant was sulphuric acid. The calibration curves with $H_2SO_4$ were perfectly linear between 0.005 and 20% of S with correlation coefficients ≥0.999 for the determination of sulphur at 258.056 nm line. The LOD ($3\delta$, $N = 10$) and LOQ ($10\delta$, $N = 10$) for sulphur calculated according to $3\delta$ and $10\delta$ of 10 replicates of blank were 0.01 and 0.03% (w/w), respectively.

In addition to microwave-assisted digestion described in experimental section, various open system digestions were performed. For this purpose, 0.2 g of coal samples were treated with 10 mL of 3 mol L$^{-1}$, 5 mol L$^{-1}$ and the concentrated $HNO_3$ at room temperature and 100 °C on a magnetic stirrer for 1 h. For all open system digestion procedures, the accuracies for S were worse than that obtained after microwave-assisted digestion. Obviously, the use of other open digestion procedures caused analyte losses (lower recoveries), which was not the case for microwave assisted digestion. Therefore, for all determinations, the microwave-assisted digestion procedure described in experimental section was applied.

### 3.4. Validation

After optimization of experimental parameters, the validity of the method was tested by the determination of sulphur in a certified (or standard) reference material, namely, Trace Elements in Coal (SRM 1632b), containing a sulphur concentration of 1.89% (±0.06%). The quantification was performed by linear calibration technique using aqueous standards prepared from sulphuric acid. As shown in Table 2, there was no significant difference between mean value of the sulphur found as the average of three replicate determinations and its certified value. The accuracy was 98%. In addition,

**Table 3**
Determination of sulphur in coal samples using HR-CS FAAS (number of repetition: 3, λ: 258.056 nm; fuel rate: 80 L h$^{-1}$; burner height: 10 mm).

| Sample no. | S content (%)[a] |
|---|---|
| 1[b] | 1.18 ± 0.08 |
| 2[b] | 0.08 ± 0.11 |
| 3[b] | 0.89 ± 0.05 |
| 4[b] | 0.04 ± 0.10 |
| 5[b] | <LOQ |
| 6[b] | <LOQ |
| 7[b] | <LOQ |
| 8[b] | 1.08 ± 0.07 |
| 9[b] | 0.04 ± 0.05 |
| 10[c] | <LOQ |
| 11[c] | <LOQ |
| 12[c] | <LOQ |

[a] Average (%) ± RSD.
[b] These coal samples are lignite coals.
[c] These coal samples are charcoal.

the sulphur concentrations spiked to the same CRM were accurately (94%) determined. Since accurate results were obtained by calibration against only aqueous standards, which means no interference occurred during the determination of sulphur in all steps of the analysis, the standard addition method was not applied. It can be concluded that after optimization of experimental conditions, the sulphur concentrations in coal could be easily and successfully determined by HR-CS-FAAS.

Finally, the method was applied to the direct determination of sulphur in 12 different coal samples obtained from various sources in Turkey. The concentrations found by HR-CS-FAAS are given in Table 3.

## 4. Conclusion

The present work proves that the HR-CS-FAAS technique can be employed for the direct determination of sulphur in coal by measuring an appropriate molecular absorption line of CS generated in an air–acetylene flame. The method is faster and simpler than alternative sulphur determination techniques and reliable as much as conventional sulphur specific techniques.

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