Determination of sulfur in coal using direct solid sampling and high-resolution continuum source molecular absorption spectrometry of the CS molecule in a graphite furnace

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ABSTRACT

An analytical method has been developed for the determination of sulfur in coal using direct solid sample analysis in a graphite tube furnace and high-resolution continuum source molecular absorption spectrometry (HR-CS GF MAS). The molecular absorbance of the carbon monosulfide molecule (CS), which is formed in the vaporization stage, has been measured using the rotational line at 258.033 nm. Several chemical modifiers were tested and Ru, applied as permanent modifier was chosen, because it exhibited the best performance. The optimum pyrolysis and vaporization temperatures were found to be 500 °C and 2200 °C, respectively. Aqueous standard solutions prepared from l-cysteine were used for calibration, as the linear regression obtained for this standard was not significantly different from that for a certified coal reference material (CRM) according to a Student t-test. The results obtained for sulfur in three coal CRM and six additional samples also showed no significant difference for the two calibration techniques according to the same statistical test. The sulfur concentration in the coal samples was found between 3.5 mg g⁻¹ and 33.7 mg g⁻¹ with a typical repeatability around 10%. The limit of detection for the direct analysis of solid coal samples was better than 0.1 µg S.

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1. Introduction

Coal is, and will remain for at least a few more decades as a major source of energy in many countries of our world. The content of trace and minor elements in coal is clearly relevant to any environmental aspect during mining, beneficiation and usage [1]. Sulfur is one of the most important elements, which can be found in coal at concentrations up to a few percent. Sulfur compounds in coal can be divided in three groups: in the form of organic sulfur (sulfur attached to carbon structures), inorganic sulfur (sulfites, sulfates, etc.) and pyrite sulfur (FeS₂) [2]. The sulfur content is usually determined to evaluate the SO₂ emission into the atmosphere after coal combustion. Coal that is used in thermoelectric power plants is nowadays subject to beneficiation, a rigorous cleaning process, in order to lessen the ash and pyrite concentration, and flue gas desulfurization systems are installed to further reduce the emission of SO₂. Nevertheless, the beneficiation process leaves great amounts of refuse with increased sulfur content, which has to be treated properly. Microorganisms have been shown to play an important role in removing sulfur from coal in open-air deposits with the detrimental side-effect of developing acid mine drainage from storage and refuse piles, which consists mostly of sulfuric acid [3]. Moreover, coal that is used in private households and in the industry does not necessarily undergo a comparable cleaning, resulting in higher emission of SO₂, which is toxic to humans, animals and plants, and is associated with a series of environmental problems, such as acid rain. Oxides of sulfur and nitrogen react with other substances in the air to form acids, which return to earth as rain, fog, snow or dry particles [4].

The determination of sulfur has been reported in the literature using various analytical techniques, including volumetry [5], gas chromatography [6-8], ion chromatography [9], X-ray fluorescence spectrometry (XRF) [10], UV–vis spectrophotometry [11,12], optical emission spectrometry with inductively coupled plasma (ICP OES) [13,14] and mass spectrometry with inductively coupled plasma (ICP-MS) [15,16]. All of these techniques, except for XRF, require extensive sample pretreatment, including complete digestion, which is certainly not trivial in the case of mineral coal.

Atomic absorption spectrometry (AAS) cannot be used for the determination of non-metals, such as sulfur, because the main absorption lines of these elements are below 190 nm, i.e., outside of the range of conventional AAS instrumentation. The determination of non-metals, using the absorption spectra of diatomic molecules in a conventional atomic absorption spectrometer and
a graphite furnace for vaporization, was pioneered by Dittrich and co-workers in the 1970s and 1980s [17]. Using this technique, Parvinen and Launen [18] investigated the determination of sulfur measuring the absorption of tin sulfide (SnS) at 273.5 nm using a tungsten hollow cathode lamp (HCL), and that of indium sulfide (InS) at 243.67 nm using a platinum HCL. Although a few authors were following along this line, the technique never found general acceptance, mostly because of the technical limitations and the insufficient background correction possibilities of line-source AAS. The few examples reported in the literature show that the sulfur determination via molecular absorption requires a more rigorous systematic investigation, with optimization of the parameters involved and use of appropriate analytical instrumentation.

About a decade ago, high-resolution atomic absorption spectrometers with a continuum radiation source (HR-CS AAS) and a linear CCD array detector were introduced commercially [19], and soon after it was recognized that these instruments could be equally used for molecular absorption spectrometry and, hence, the determination of non-metals [20]. This is due to the fact that any wavelength between 190 nm and 900 nm can be accessed at high resolution and selected pixels of the CCD array in “valleys” between the rotational lines may be used for an efficient background correction. Huang et al. [21] described the determination of sulfur using the molecular absorption of carbon monosulfide (CS) in an air-acetylene flame using HR-CS AAS equipment, and soon after the same group reported a sulfur speciation analysis in wine using this technique [22]. Baysal and Akman [23] described a determination of sulfur in coal samples after microwave-assisted digestion using the same technique. Virgilio et al. [24] reported the determination of total sulfur in agricultural samples and Bechlin et al. [25] investigated different analytical lines of sulfur. The determination of sulfur using the molecular absorption of the carbon monosulfide in a graphite furnace was first described by Heitmann et al. [26]. All the above determinations were carried out against aqueous standard solutions, demonstrating the absence of interference using this technique; however, in all cases a previous digestion of the samples was necessary, which is a limitation in the case of refractory samples, such as coal.

Ferreira et al. [27] were the first to report a determination of sulfur in biological materials using direct solid sample analysis with calibration against aqueous standards and palladium as the chemical modifier. Resano and Flórez [28] also investigated the direct determination of sulfur in solid samples using palladium nanoparticles as chemical modifier. They analyzed several certified reference materials and found satisfactory results using aqueous standards for calibration. No interferences were observed in these two publications, and the use of direct analysis of solid samples greatly improved limits of detection and particularly sample throughput.

The objective of this study was to investigate in more detail the determination of sulfur in coal via the CS molecule using molecular absorption spectrometry in a graphite furnace with direct solid sample analysis because of the well-known difficulties to bring coal samples into solution. Special attention was given to the optimization of analytical conditions, including the use of modifiers. An additional important objective of this study was to investigate the feasibility of using aqueous standards for calibration, an approach that was found to be particularly successful in previous work of our group [29].

### 2. Experimental

#### 2.1. Instrumentation

All measurements were carried out using a contrAA 600 or contrAA 700 high-resolution continuum source atomic absorption spectrometer (Analytik Jena AG, Jena, Germany). The difference between the two is that the contrAA 700 has a flame and a transversely heated graphite tube furnace in two separate sample compartments, whereas the contrAA 600 is a graphite furnace-only instrument. Only the graphite tube furnace, which is identical for the two instruments, was used in this work. A 300 W xenon short-arc lamp, operating in a hot-spot mode, is used as the continuous radiation source for the wavelength range from 190 to 900 nm. The spectrometer is equipped with a high-resolution double monochromator, consisting of a prism pre-monochromator and an echelle grating monochromator, providing a spectral bandwidth per pixel of about 1.6 pm at 200 nm, and a linear charge coupled device (CCD) array detector with 588 pixels, 200 of which are used for analytical purposes, displaying the vicinity of the analytical line at high resolution.

Pyrolytically coated solid-sampling graphite tubes without a dosing hole (Analytik Jena Part no. 407-A81.303) were used throughout. 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). A manual solid sampling system SSA 6 (Analytik Jena), 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 manually onto the platform using a micro-pipette. Argon 99.996% (Oxilar, Florianópolis, Brazil) was used as purge and protective gas. The optimized temperature program, used for all determinations with HR-CS GF MAS, is shown in Table 1.

The rotational line at 258.033 nm, which is one of the strongest absorption lines of the CS molecule, was chosen for all measurements, using the sum of the integrated absorbance of three peaks for evaluation (peak volume selected absorbance, PVSA [30]), as this resulted in the best signal-to-noise ratio.

#### 2.2. Reagents and standards

All reagents used in this work were at least of analytical grade. Nitric acid, (Aldrich, St. Louis, MA, USA), was further purified by subboiling distillation in a quartz still (Kürner Analysentechnik, Rosenheim, Germany). The ultrapure water with a resistivity of 18 MQ cm was obtained from a Model Mega ROP (Equisul, Pelotas, Brazil) purification system, and was used for dilution and preparation of the standard solutions. 19.0 mg of l-cysteine (Merck, Darmstadt, Germany), containing 5.0 μg of S, were dissolved in 10 mL of water to prepare the standard solution for calibration.

The following coal certified reference materials (CRM) were used in this study: NIST 1564 (National Institute of Standards and Technology, Gaithersburg, MD, USA), SARM 18 and SARM 19 (South Africa Reference Material, Randburg, South Africa), BCR 040, BCR 180, BCR 181 and BCR 182 (Community Bureau of Reference, Brussels, Belgium); however, only the two CRM from NIST and those from SARM had a certified value for sulfur. In addition, two
real coal samples were investigated in this study ("Mintek" from South Africa and "Camada Bonito" from Brazil).

The following reagents were investigated as chemical modifiers to obtain reliable results: Ru 1000 mg L\(^{-1}\) (Fluka, Buchs, Switzerland), Pd 1000 mg L\(^{-1}\) (Merck), Pd/Mg 0.05% and 0.03%, respectively (Merck) in Triton X-100 (Union Carbide), Zr 1000 mg L\(^{-1}\) (Merck) and W 1000 mg L\(^{-1}\) (Merck).

All lab ware was decontaminated with 10% v/v nitric acid for 24 h and then rinsed with deionized water three times before use.

2.3. Procedure

Ruthenium, tungsten and zirconium were used as permanent chemical modifiers; ten aliquots of 40 μL each of the modifier solution were deposited on the solid sampling platform, which was inserted into the graphite tube and subject to the temperature program in Table 2 after each injection. This way the platform was coated with a mass of 400 μg of the permanent modifier at the end of the procedure. A mass of 100–150 mg of coal was typically weighed directly onto the platform coated with the permanent chemical modifier. The palladium and the Pd/Mg mixed modifiers were applied in solution on top of the coal sample; 0.05% (v/v) of Triton X-100 was added to the modifier solutions in order to improve the wettability of the coal. In one set of experiments, the Pd/Mg mixed modifier was used in addition to the ruthenium permanent modifier.

As it is impossible (and unnecessary) in direct solid sample analysis to weigh always the same sample mass onto the platform for measurement, the added integrated absorbance of 3 pixels (refer to Section 2.1.) was normalized for a mass of 100 mg of coal in each measurement in order to facilitate comparison.

For the calibration with a solid sample, the CRM NIST 1630 was used, weighing between 0.023 mg and 0.234 mg of the CRM directly onto the graphite platform, corresponding to about 0.3 and 3.5 μg S, and plotting the PVS against the calculated sulfur content in the CRM. The calibration with the aqueous l-cysteine standard in 2% (v/v) HNO\(_3\) solution was studied within the linear range from 0.5 to 5.0 μg S.

3. Results and discussion

3.1. The carbon monosulfide molecule and its formation

The carbon monosulfide molecule has a strong absorption band in the spectral range between 257.5 nm and 259 nm, which corresponds to the Δν=0 sequence of the electronic transition X 1Σ\(^+\)→A 1Π [21]. Among the rotational transitions available for measuring the molecular absorption, most authors used the 258.056-nm line [23–25,28], which is one of the strongest ones. Nevertheless, Ferreira et al. [27] preferred the close-by line at 258.033 nm because of a slight spectral interference was observed at the former one due to high Fe concentrations. As coal might contain relatively high concentrations of iron (pyrite), the latter line was chosen for this investigation as well. Unlike molecules such as OH and PO, CS is not a free radical, but a molecule of short lifetime, which is thermodynamically stable, but chemically highly reactive [23].

In contrast to GF AAS, two analytical conditions have to be considered to achieve best results in GF MAS. First of all, the analyte has to be stabilized to high enough pyrolysis temperatures, in order to remove the majority of the matrix without losses of the analyte, which is the same as in the case in GF AAS; the solution usually is choosing an appropriate chemical modifier. Secondly, the formation of the target molecule needs to be promoted in order to obtain maximum sensitivity. This is significantly different from the task to promote analyte atomization, which normally only requires a high enough atomization temperature.

Using a flame, the formation of the CS molecule can be promoted by using an excess of acetylene, which produces a reducing flame with an excess of carbon [23,24]. In a graphite furnace it might be assumed that there is enough carbon around to promote the formation of the CS molecule; however, there is a competitive reaction, which is the formation of carbon disulfide, CS\(_2\) [29]. The reaction between sulfur and coke at elevated temperature is actually used for the technical production of CS\(_2\), which is very volatile and easily lost at low temperatures when it is formed in the graphite furnace. Heitmann et al. [26] tried to avoid this competitive reaction by coating the platform of the graphite tube with Ru as a permanent modifier and by introducing methane as an alternate gas in the pyrolysis stage.

The coating of the graphite platform with ruthenium or another carbide-forming metal has in the meantime become ‘standard’ in the few publications about sulfur determination by HR-CS GF MAS [29–31], and the use of methane as alternate gas was found to be not very useful. The same approach has been used in the present investigation; however, there has been some concern that the coal matrix itself could promote the formation of CS\(_2\), and hence a loss of sulfur at relatively low pyrolysis temperatures. We therefore decided to carry out a very careful investigation of permanent as well as conventional modifiers that were added in solution on top of the solid samples in order to avoid losses of sulfur in the pyrolysis stage. On the other hand, the presence of the high carbon matrix of coal was considered safe to promote the formation of the CS molecule in the vaporization stage, as long as the analyte was not lost before.

3.2. Comparison of modifiers

In order to compare the stabilizing power of the different modifiers investigated, three coal CRM were chosen, NIST 1630, NIST 1635 and SARM 19 to study the thermal behavior of the CS molecule, as is shown in Fig. 1a–c. Although there are differences for the three coal CRM, it is obvious that coating the platform with Ru as the permanent modifier results in the best sensitivity, at least up to a pyrolysis temperature of 500 °C. The big surprise was that other carbide forming modifiers, such as tungsten and zirconium, had very little stabilizing effect, and, at least for two of the investigated coal CRM, the stabilizing power was even inferior compared to the uncoated platform. No explanation can be given up to now for that phenomenon. The use of the palladium or the Pd/Mg mixed modifier increased in some cases the stability of the signal, but the modifier action was not really convincing. The other surprise for us was that the addition of the Pd/Mg modifier together with Ru as the permanent modifier always had a negative effect, i.e., resulting in lower sensitivity and stability. The ruthenium permanent modifier with a pyrolysis temperature of 500 °C was therefore chosen for all future investigations, and the optimum vaporization temperature was set at 2200 °C.

**Table 2**

Temperature program for deposition of ruthenium as the permanent modifier on the solid sampling graphite platform; argon gas flow rate 2.0 L min\(^{-1}\) during all program steps.

<table>
<thead>
<tr>
<th>Step</th>
<th>Temperature (°C)</th>
<th>Ramp (°C s(^{-1}))</th>
<th>Hold (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>130</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>160</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>250</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>1000</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>2000</td>
<td>100</td>
<td>5</td>
</tr>
</tbody>
</table>
3.3. Standard solutions for calibration and figures of merit

The goal of this investigation has been to use direct solid sample analysis for the determination of sulfur in coal, but also to investigate the possibility to use aqueous standard solutions for calibration. First of all, two inorganic standards have been investigated, ammonium sulfate ((NH₄)₂SO₄), which was used by Heitmann et al. [26] and magnesium sulfate (MgSO₄). The former one did not show any significant spectrum of the CS molecule under the conditions used in this investigation, most likely because of the low decomposition temperature of only 280 °C [31] of this compound; Heitmann et al. [26] used calcium as an additional modifier in their work, which probably resulted in the formation of calcium sulfate in the pyrolysis stage, which, with a melting point of 1460 °C [31], is obviously much more stable. The thermal behavior of magnesium sulfate, which has a similarly high melting point of 1127 °C [31] is shown in Fig. 2a. Using this standard, sulfur is thermally stable up to a pyrolysis temperature of 900 °C, which is higher than the 700 °C reported by Heitmann for ammonium sulfate in the presence of the calcium modifier.

We also investigated two organic sulfur compounds as possible standards, thiourea, which was successfully used in the determination of sulfur in biological materials [27] and l-cysteine. One more time, thiourea, the standard recommended in [27] did not give a significant response in the present investigation, most likely because the palladium modifier was used in that work, which has not been found useful in the present investigation. The thermal behavior of l-cysteine, the second alternative, is shown in Fig. 2b.

It is obvious that the thermal behavior of the two standards is significantly different. In contrast to the high thermal stability of the inorganic standard solution (MgSO₄), the organic standard (l-cysteine) exhibits decreasing sensitivity over the entire pyrolysis temperature range investigated, which was, however, more similar to the behavior of the coal samples. Both standards have been

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Fig. 1. Pyrolysis and vaporization curves for the CS molecule at 258.033 nm, with 400 µg of each permanent modifier and 10 µL of the conventional modifiers, respectively, using direct solid sample analysis; the integrated absorbance values are normalized for 100 mg of coal CRM; (a) coal NIST 1630; (b) NIST 1635; (c) SARM 19.

Fig. 2. Pyrolysis and vaporization curves for the CS molecule for aqueous sulfur standards containing 5.0 µg S, using 400 µg Ru as the permanent chemical modifier; (a) magnesium sulfate; (b) l-cysteine.
investigated initially; however, it turned out that the organic standard rendered the much better results for the determination of sulfur in coal. A comparison of the figures of merit obtained with the CRM NIST 1630 as a solid standard and the calibration curve with l-cysteine as an aqueous standard, which is shown in Table 3, reveals that the slopes of the two calibration curves are essentially identical. The limits of detection and quantification were about a factor of three better for the aqueous standard, due to the better precision of solution introduction compared to solid sampling. Calibration against standards made up with l-cysteine and using NIST 1630 as a solid standard were compared in the following investigations.

3.4. Analysis of coal samples

A total of nine coal samples were analyzed: three CRM with a certified value for sulfur, four CRM without a certified value for sulfur and two real samples, one from South Africa and one from Brazil. The results obtained, using both, the solid CRM and the aqueous l-cysteine solution for calibration, are shown in Table 4. The values found for the CRM with certified sulfur content are in accordance with the reported values, based on a Student t-test on a 95% confidence interval, independent on the calibration technique. The values found for the other CRM without a certified value for sulfur and for the two real samples are also in agreement for the two calibration techniques, based on a Student t-test, which means that calibration against aqueous standards prepared from l-cysteine can be used without any problem.

3.5. Vaporization characteristics of sulfur and the CS molecule

It was clear from the very beginning, considering the pyrolysis curves of the three coal CRM and also that for the l-cysteine standard that there might be analyte losses already at relatively low pyrolysis temperatures, even in the presence of the ruthenium permanent modifier. An additional interesting phenomenon that has been observed for essentially all the coal samples investigated, is a pronounced double peak in the vaporization phase, as is shown in Fig. 3 for the CRM NIST 1635. There is always an early, relatively fast appearing signal, followed by a broad spectrum, both of which are clearly due to the CS molecule, suggesting the presence of at least two sulfur species of significantly different volatility. This assumption is also supported by the early drop in the pyrolysis curve, which is followed by a more or less pronounced plateau, depending on the coal sample.

This assumption is even more supported by the time-resolved absorbance signals recorded under different conditions, as shown in Fig. 4. With increasing pyrolysis temperatures above 500 °C (Fig. 4a), the early signal for the CS molecular absorption decreases, and finally disappears at a pyrolysis temperature of 1000 °C (Fig. 4c). The second absorbance signal, in contrast, remains unchanged for all the pyrolysis temperatures, except for a slightly earlier appearance because of the smaller interval between pyrolysis and vaporization temperatures. Another indication is the comparison of different vaporization temperatures: at a vaporization temperature of 1800 °C essentially only the first peak appears (Fig. 4d), whereas much higher vaporization temperatures are necessary to volatilize the second sulfur species (Fig. 4e).

As the thermal behavior of l-cysteine (Fig. 2b) is quite similar to that of the three coal CRM (Fig. 3a–c) at low pyrolysis temperatures it appears to be logic to assume that the first peak in Figs. 3 and 4a–e is due to organically bound sulfur, whereas the second one is due to the much more stable inorganically bound sulfur, such as FeS. This is further supported by the fact that the first absorbance spectrum always appears together with the (perfectly corrected) continuous background signal, which is due to the “smoke” caused by the vaporization of the coal matrix. This background is only missing in Fig. 4c, as the coal matrix has apparently been eliminated during the pyrolysis stage at 1000 °C together with the organically bound sulfur.

We are aware of the fact that the formation of “competitive molecules”, other than the target molecule—in this case CS can cause interference in MAS. The distinct difference not only in thermal stability, but also in sensitivity between the inorganic and the organic standard in Fig. 2 clearly indicates losses of sulfur due to a yet unknown mechanism, but most likely due to the

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**Table 3**

Comparison of the analytical figures of merit obtained with varying masses of NIST 1630 as the solid standard and calibration with aqueous solutions of l-cysteine for the determination of S via the CS molecule using HR-CS GF MAS and 400 μg Ru as permanent chemical modifier.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NIST 1630</th>
<th>l-cysteine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>0.1830 μg⁻¹</td>
<td>0.1832 μg⁻¹</td>
</tr>
<tr>
<td>Correlation coefficient $R$</td>
<td>0.9993</td>
<td>0.9987</td>
</tr>
<tr>
<td>LOD</td>
<td>0.08 μg</td>
<td>0.03 μg</td>
</tr>
<tr>
<td>LOQ</td>
<td>0.1 μg</td>
<td>0.1 μg</td>
</tr>
<tr>
<td>Linear range</td>
<td>0.3–3.5 μg</td>
<td>0.1–5.0 μg</td>
</tr>
</tbody>
</table>

**Table 4**

Results obtained for the determination of sulfur in coal by HR-CS SS-GF MAS; comparison of calibration against NIST 1630 as solid standard and l-cysteine in aqueous solution, respectively; all values in mg g⁻¹.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Certified value</th>
<th>Found value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NIST 1630</td>
<td>l-cysteine</td>
</tr>
<tr>
<td>NIST 1635</td>
<td>3.616 ± 0.017</td>
<td>3.6 ± 0.2</td>
</tr>
<tr>
<td>SARM 18</td>
<td>5.75 ± 0.45</td>
<td>5.8 ± 1.1</td>
</tr>
<tr>
<td>SARM 19</td>
<td>14.62 ± 0.51</td>
<td>14.9 ± 0.5</td>
</tr>
<tr>
<td>BCR 040</td>
<td></td>
<td>10.6 ± 1.1</td>
</tr>
<tr>
<td>BCR 180</td>
<td></td>
<td>30.7 ± 2.0</td>
</tr>
<tr>
<td>BCR 181</td>
<td></td>
<td>12.5 ± 0.3</td>
</tr>
<tr>
<td>BCR 182</td>
<td></td>
<td>4.5 ± 0.5</td>
</tr>
<tr>
<td>Mintek</td>
<td></td>
<td>5.0 ± 0.5</td>
</tr>
<tr>
<td>Camada Bonito</td>
<td></td>
<td>33.7 ± 5.9</td>
</tr>
</tbody>
</table>

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Fig. 3. Time-resolved absorbance spectrum for the CS molecule in the environment of the rotational line at 258.033 nm, using a pyrolysis temperature of 500 °C and a vaporization temperature of 2200 °C obtained for NIST 1635 coal CRM under optimized conditions.
formation of a competitive molecule in the presence of high-carbon matrix. The most important aspect, however, appears to be that using a pyrolysis temperature of only 500 °C, accurate results are obtained for a variety of coal samples using an aqueous solution of l-cysteine for calibration. This facilitates routine analysis significantly, considering the much greater effort in establishing a calibration curve using solid standards, and also the additional uncertainty that enters because of the uncertainty of the certified value of a CRM.

4. Conclusion

A significant difference in the thermal stability and also in the sensitivity has been observed for an inorganic sulfur standard (MgSO₄) and an organic standard (l-cysteine) even in the presence of the sensitivity has been observed for an inorganic sulfur standard.

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