

# Characterization of South African Coal for Metals, Inorganic and Organic Sulfur Compounds

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## ABSTRACT

This work characterized South African coal for metals, organic and inorganic sulfur compounds. Microwave assisted extraction (MAE) followed by Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES) were used for extraction, identification and quantification of inorganic, organic, total sulfur forms as well as selected metals related to the presence of sulfur in coal. The total sulfur content was also determined in coal by direct elemental analysis for carbon, hydrogen, nitrogen and sulfur. Thiophene organic sulfur compounds in coal were extracted with ultrasonication system followed by identification and quantification using gas chromatography and flame ionization detector. The ultrasonication extraction system was optimized for the extraction organic solvent, the extraction time and influence of sample concentration. Microwave assisted extraction followed by ICP-OES gave an average of 8758, 4500, 3600 and 600 mg kg<sup>-1</sup> for total sulfur, pyrite sulfur, organic sulfur and sulfate sulfur, respectively. Pyrite and organic sulfur forms were found to compete for the largest amounts in coal samples. The total sulfur content in South African coal was found to be less than 20 000 mg kg<sup>-1</sup> which suggests that the coal may be of low sulfur content compared to others in the world. The mean percentages of carbon, hydrogen, nitrogen and sulfur in coal samples was 66.20, 2.98, 1.15 and 1.11 confirming that it is of bituminous rank. The concentration levels of selected metals were found in this decreasing order; Na>Ca>Fe>Mg>K>Ba>Mn>Cr>Pb>Zn>Cu>As>Co>Sb>Hg. Thiophene organic sulfur compounds were best extracted with dichloromethane with five sequential extractions of 15 min each. Recovery of extraction from spiked concentration ranged from 40 % to 70 % depending on the individual compound. More volatile organic sulfur compounds showed lowest recovery especially at low spiked concentrations. 2-methyl thiophene was the only compound identified in all coal samples. The concentration of thiophene sulfur compounds ranged from about 4–16 mg kg<sup>-1</sup>. Dibenzothiophene was found with the highest concentration (15.5 mg kg<sup>-1</sup>) while 2-ethyl thiophene was found with the lowest concentration.

## KEYWORDS

Coal, sulfur, metals, microwave assisted extraction, and ultrasound assisted extraction, inductively coupled plasma optical emission spectrometry, gas chromatography.

## 1. Introduction

The major use of coal is mainly as a source of energy for domestic and industrial use. The energy demand especially in new emerging markets such as South Africa, India and China has increased the use of coal for energy production. Despite this major benefit, coal has negative effects like environmental pollution from by-products that are released from mining, processing and use of coal. Solid waste as a by-product of mining and processing of coal contain a lot of heavy metals<sup>1–4</sup> that are toxic to fauna and flora. Further, some sulfur forms in solid coal waste when exposed to water and air is a source of acid mine drainage (AMD).<sup>5–7</sup> Tar, a by product of coal is a complex mixture of organic compounds with different chemical classes such as aromatic and sulfur heterocyclic compounds.<sup>8</sup> Some of these organic compounds are harmful to the environment. Various sulfur gases like sulfur dioxide and hydrogen sulfide released during processing and use of coal are a source of air pollution.<sup>9,10</sup> These gaseous compounds originate from sulfur compounds that are found in coal especially organic sulfur ones.<sup>5,9,11–13</sup>

Many studies have thus been reported dealing with characterization of coal for both its inorganic<sup>1,3,4,14</sup> and organic sulfur

compounds.<sup>5,11,12,15</sup> Others have studied the generation of AMD from coal mines.<sup>6,7</sup> Inorganic chemicals in coal samples have been determined using various techniques such as Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES) after microwave digestion of coal samples.<sup>4,14</sup> Direct methods such as X-Ray Diffraction (XRD) and X-Ray Photoelectron Spectroscopy (XPS) have also been used for inorganic sulfur determination in coal.<sup>4,14</sup> Various sulfur forms have been determined by direct methods such as using XPS<sup>12</sup> and X-ray absorption near edge structure (XANES).<sup>13</sup> Others have used microwave assisted extraction followed by separation techniques for identification and quantification to determine the various forms of sulfur in coal.<sup>16</sup> Ultrasonic bath assisted extraction has also been used to extract organic sulfur forms from coal.<sup>17,18</sup> Organic sulfur compounds are generally grouped into thiophenes, mercaptans and sulfides but their abundances differ from one coal sample to another. Thiophenic forms are almost well known than other forms.<sup>19–21</sup>

A number of studies have been done on the chemical characterization of South African coal which has been summarized by Wagner and Hlatswayo.<sup>4</sup> However, very few studies have investigated organic sulfur compounds in South African coal.

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The present study is one of the few that has attempted to study the presence of heavy metals, inorganic and organic sulfur compounds in South African coal. Further, the percentage of moisture, ash and organic carbon was also determined in addition to the percentage of carbon, hydrogen, nitrogen and sulfur in South African coal.

## 2. Research Methodology

### 2.1. Coal Samples

Coal samples were provided from six South African power stations: Camden (CRC), Duvha (DRC), Kriel (KRC), Thuthuka (TRC) and Majuba (MRC) in Mpumalanga and Letabo (LRC) in Free State. These samples were each prepared for analysis in the laboratory.

### 2.2. Chemicals

The following solvents were used: dichloromethane, methanol, tetrahydrofuran, toluene, hexane, pyridine and acetone (Sigma-Aldrich, Johannesburg, South Africa). All sulfur standards were purchased from Sigma-Aldrich (Johannesburg, South Africa). These are dibenzothiophene, 2-ethyl thiophene, 2-methyl thiophene and 3-methyl thiophene. Sulfuric acid, nitric acid, boric acid, hydrogen peroxide, hydrofluoric acid, hydrochloric acid, potassium dichromate, orthophosphoric acid, ferrous sulfate and BRIJ-35 were also bought from Sigma-Aldrich. Certified multi-element standards (DeBruyn Spectroscopic solutions, Johannesburg, South Africa) were used for calibration of ICP-OES. All chemicals and solvents used were of analytical grade. Deionized water was prepared from Millipore instrument (Millipore, Massachusetts, USA).

### 2.3. Equipment

Ultrasonic bath extractor ElmaTranssonic 460 (Elma, Singen, Germany) was used for ultrasonic extraction of target organic sulfur compounds from coal samples. Microwave assisted extraction (MAE) Anton Paar Multiwave 3000 Solv (SwissLab, Johannesburg, South Africa) was used for the extraction of sulfate, pyrite, organic and total sulfur forms from coal samples. A LECO-932 CHNS analyser (LECO Corporation, Michigan, USA) was used to determine the concentration of carbon, hydrogen, nitrogen and sulfur in various coal samples. The analysis of organic sulfur compounds in various coal samples was done on an Agilent 7890A Gas chromatograph (Agilent technologies, California, USA). The instrument was equipped with Supelco SPB™-1 Sulfur, fused silica capillary column, 30 m × 0.32 mm × 4.0 μm film thickness (SUPELCO, Pennsylvania, USA) connected to FID detector. Inductively coupled plasma-optical emission spectrometer (ICP-OES) supplied by Spectro Analytical Instruments (Johannesburg, South Africa) was used to determine sulfur and selected metals in coal samples.

### 2.4. Preparation of Solutions

#### 2.4.1. Solutions for Organic Carbon Determination

Potassium dichromate and ferrous sulfate solutions were respectively prepared at concentration of 0.16 M and 0.5 M in 1 L volumetric flasks. The indicator solution was prepared by dissolving 250 mg of diphenylamine-sulfonate in deionized water in 100 mL volumetric flask. The solution was made up to the mark with deionized water.

#### 2.4.2. Solutions for MAE

One litre solutions of hydrochloric acid and nitric acid were

respectively prepared at concentrations of 5 M and 2 M. 100 mL solutions of boric acid and BRIJ-35 were prepared at 5 % and 1 %, respectively.

#### 2.4.3. ICP-OES Solutions and Standards for GC-FID

The stock solutions of standards used for various elements analysed were initially prepared at 1000 mg L<sup>-1</sup>. Working standards were prepared from 0.1 to 1 mg L<sup>-1</sup> from stock solutions. Standard solutions for GC analysis were made by preparing stock solutions of 1000 mg L<sup>-1</sup> from pure organic sulfur compounds in appropriate solvent. Working standards were then prepared in the range of 100 to 1000 mg L<sup>-1</sup> from stock solutions.

### 2.5. Experimental

#### 2.5.1. Sampling, Sample Storage and Grinding

The collection of coal samples from each power station was done by taking samples from various piles. Collected samples were then mixed to make the gross sample which was then stored at 4 °C. The samples were manually crushed to a size of less than 240 μm in diameter by means of mortar and pestle. Three sets of samples were collected.

#### 2.5.2. Sample Extraction Procedures

*MAE for various forms of sulfur.* The MAE instrument used has digestion rotor that can accommodate eight 120 mL Teflon lined vessel assemblies. The extraction method used was developed by Laban and Atkin.<sup>16</sup> Important considerations here are the type of acid, proper rinsing in between stages to make sure previous acid is not carried over to the next stage and microwave power. Trial extractions were done with coal samples by varying the power programme. High power (more than 800 w) could remove appreciable amount of sulfur as pyrite when extracting sulfate, but other forms like organic sulfur were also extracted. 500 w power was settled as optimum and used in all microwave assisted extractions.

*Total sulfur.* 0.250 g of pulverized and dried coal sample was weighed in the vessel liner. From the fume hood, 10 mL of 5 M HCl was added in the vessel. The vessel was then closed with its cap before being taken out of the fume hood. The vessel was placed in the jacket and set in the rotor. The set up was then placed in the digestion system with the power programmed as in Table 1. The vessels were allowed to cool down and taken out. They were opened while in fumehood and 2 mL of concentrated hydrofluoric acid and 1 mL of hydrogen chloride were added. Vessels were closed and heated again as before. Finally, the digested sample was filtered. The filtrate was diluted to 30 mL with boric acid (12 mL) and de-ionized water and then analysed on ICP-OES.

The total sulfur content was also determined as the sum of sulfate, pyrite and organic sulfur forms in the samples. The different sulfur forms were determined as stated below. The following selected metal ions were also determined in the extract used for total sulfur: iron, copper, mercury, cobalt, lead, arsenic, chromium, antimony, manganese, magnesium and zinc. These elements were chosen because of pollution concerns once they are released in the environment and their affinity for sulfur.

**Table 1** MAE power programme.

	Power/w	Ramp/min	Hold/min
Phase 1	500	15	15
Phase 2	400	5	15
Phase 3	0	0	10

*Stage 1: Sulfate sulfur form.* 0.250 g of the coal sample was accurately weighed into a digestion vessel and 10 mL of 5 M HCl was added. The sample was digested in a MAE system as in Table 1. 20 mL of 2 M HCl was used to quantitatively transfer the digested solution and residue from the vessel into a 50 mL polypropylene centrifuge tube. The sample was initially centrifuged for 5 min at 3300 rpm. To assist particulate settling, 0.5 mL of 1 % BRIJ-35 surfactant solution was then added to the sample which was then centrifuged for a further 7 min. The clear solution (8 mL) was collected in a volumetric flask then transferred into a vial for the determination of the sulfate sulfur concentration by ICP-OES.

*Stage 2: Pyritic sulfur form.* About 50 mL of deionized water was added to the residue from stage 1 and centrifuged for 5 min at 3300 rpm. To this, 0.5 mL of 1 % BRIJ-35 was added. The sample was centrifuged further for 7 min and the clear solution was discarded. The residue was transferred into the digestion vessel using 10 mL of 2 M HNO<sub>3</sub>. The sample was microwave digested using the same programme in Table 1. The filtrate (8 mL) was collected for analysis of sulfur on ICP-OES after separation using the centrifuge.

*Stage 3: Organic sulfur form.* The residue from pyrite extraction was mixed with same strong acid solvents as for total sulfur determination and extracted on MAE system according to the method in Table 1. The concentration of sulfur in collected filtrate (8 mL) was determined by ICP-OES.

*Ultrasonication extraction. Optimization experiments.* Hexane, toluene, dichloromethane and pyridine were used to optimize the type of extraction solvent for organic sulfur compounds. Optimization was done by extracting 3 g of coal sample with appropriate solvent (50 mL) for 75 min. Six simultaneously extractions could be performed. The best extraction solvent was one that extracted as many compounds as possible including the target ones. The extraction time was then studied at 15, 45 and 75 min with 50 mL of dichloromethane as solvent. The replacement of water used for ultrasonic bath was also crucial after each extraction sequence (15 min) to avoid loss of target compounds during evaporation. For quality assurance each experiment was repeated at least three times.

*Spiking extractions for recovery calculations.* 3 g of dried coal sample was weighed and placed in a beaker. Five, 25 and 50 mg of standard organic sulfur compounds were respectively mixed thoroughly with weighed coal samples. The final concentrations of spiked amounts were 1700, 8300 and 17 000 mg kg<sup>-1</sup> of standard organic sulfur compounds in coal samples. 50 mL dichloromethane was added to the spiked samples for extraction of organic sulfur compounds. The beaker was placed in a steel basket of ultrasonic bath and the solution was ultrasonicated in 5 sequences taking each 15 min. Water for ultrasonic bath was replaced at each sequence to prevent the boiling of sample solution in the beaker. The solution was filtered and 30 mL of filtrate was collected and analysed on GC-FID. Each experiment was repeated at least three times and simultaneous extraction was performed.

### 2.5.3. Sample Analysis

*CHNS analysis.* Prepared samples were dried at 35 °C for a day. About 200 µg of coal sample was weighed into silver crucibles on a microbalance. The determination of carbon, hydrogen, nitrogen and sulfur was performed on LECO-932 CHNS analyzer after calibration with sulfamethazine as standard. The data processing was simply performed by the software incorporated in the instrument and the results are given in percentage of carbon, hydrogen, nitrogen and sulfur in the sample. The analysis was

done in replicate and the average values were taken into consideration.

*ICP-OES.* Sample solutions prepared after each digestion were analysed on ICP-OES for sulfur and selected metals after calibration with certified multi-element standards. Typically for sulfur determination, sulfur emission line was set at 182.037 nm. The sample solutions with much higher concentrations were diluted until the concentration was within the calibration range. The concentration obtained from ICP-OES was converted in actual concentration of the total digested solution according to the dilution factor. The mass of the each investigated element was then calculated and compared to the initial mass of sample digested as percentage and in mg kg<sup>-1</sup>. The sulfur and selected metals calibration curves were linear with correlation coefficients close to 1.

*GC-FID.* The determination of organic sulfur compounds from ultrasonic bath extracts was made on GC-FID with SPB<sup>TM</sup>-1 Sulfur, fused silica capillary column. 10 µL of solutions was injected in the column through the inlet using a manual syringe. Standard organic sulfur compounds were analysed for calibration of the instrument and their correlation coefficients were high or closer to the unit value. This was followed by analysis of all samples. The temperature programme used was as follows: The temperature of the inlet was set at 250 °C and the injection mode was splitless; FID temperature was at 300 °C; the initial oven temperature was 40 °C for 4 min; the temperature was increased to 260 °C at 10 °C min<sup>-1</sup> and held for 15 min; it was finally increased to 300 °C at 20 °C min<sup>-1</sup> and held for 20 min. The organic sulfur calibration curves were also linear with correlation coefficients close to 1.

### 2.5.4. Quality Assurance

Several factors were taken into account to ensure the quality of the results. For organic carbon and organic sulfur determination on GC, glassware was thoroughly cleaned with soap and deionized water and dried. They were then rinsed twice with dichloromethane or the organic solvent used for the GC analysis. For MAE, glassware was respectively cleaned with soap, rinsed with tap water and deionized water. The glassware used for sulfate form determination was soaked in 10 % HCl whilst the ones used for pyrite form was soaked in 10 % HNO<sub>3</sub> solution.

Samples and reagents were weighed on analytical balance and the mass was read at three decimal places. High precision micro-pipettes were used for preparation and dilution of solutions. In case of small volumes of lower concentration, higher concentrations (stock solutions) were first prepared.

These were used to make working stock solutions. All prepared standard solutions were kept at 4 °C in the fridge and were stable for a week.

Spiking of samples was done to determine the extraction efficiency in the analysis. Standard organic sulfur compounds were spiked in coal samples and thoroughly mixed to ensure a good homogeneity. Blank samples were used to check for any possible contamination. Extractions were done in replicates and each extract was also analysed in replicates. Standards for GC-FID analysis were injected starting with lower concentration. Linear external calibration curves were used for each analysis. The correlation coefficients were used to check how good the calibration curves were.

## 3. Results and Discussion

### 3.1. Proximate Analysis

The determination of moisture, ash and organic carbon of various coal samples were done and the mean results are

**Table 2** Proximate analysis.

Sample	% Moisture	% Ash	% Organic carbon
Mean ( $\pm$ S.D.)	4.0 (1.9)	31.6 (5.1)	43.6 (5.3)
Certified range*	1.2–17.5	14.6–35.5	nd**
Hsieh and Wert <sup>15</sup>	nd	14.2–14.4	nd
Roberts <sup>22</sup>	nd	26.0–30.0	nd
DME <sup>23</sup>	3.9–6.2	20.5–31.2	42.2–50.1

\*Certified data of bituminous coal from South Africa bureau of standards (SABS), South African reference material (SARM), Community bureau of reference (BCR), National institute for standards and technology (NIST) and National bureau of standards (NBS).

\*\* nd: not determined.

presented in Table 2. The organic carbon content was generally higher than ash and moisture content in all coal samples. Moisture content was the least in content as expected. The average amount of organic carbon found in coal samples allows understanding the calorific value. The higher the organic carbon in coal, the more calorific value is expected which is better for energy use. Proximate analysis results were compared to literature and certified reference material values. Results indicate that South African coal has similar range of moisture, ash and organic carbon as compared to other values found in literature on South African coal.<sup>22,23</sup> The proximate results reveal that analysed coal samples falls under bituminous coal which is the rank for most South African coal.

### 3.2. Ultimate Analysis

The determination of major elements (CHNS), as part of organic compounds in coal was done using a CHNS analysis. Table 3 shows the results obtained for ultimate analysis which is compared to certified reference material and literature values. The carbon concentration is far higher than hydrogen, nitrogen and sulfur concentrations in coal samples as expected. Higher concentrations of carbon and nitrogen were found with MRC samples while higher concentrations of hydrogen and sulphur were seen in KRC samples. On the other hand, LRC samples gave low concentration values for carbon, hydrogen and sulfur whilst low nitrogen concentration was observed with TRC samples. Sulfur concentration in coal varied considerably from each sample to others. This proves that sulfur present in coal is affected by several parameters such as its concentration in coal parent plant. However, the concentrations of carbon,

nitrogen and hydrogen were each found within the same range. This is obviously the reason why the relative standard deviations of carbon, hydrogen and nitrogen were lower than that of sulfur. The carbon, hydrogen, nitrogen and sulfur concentrations in coal samples were comparable to the certified values from South African Bureau of Standards. Except for carbon concentration which is slightly higher, hydrogen, nitrogen and sulfur concentrations are also similar to the ones found in literature about South African coal.<sup>22,23</sup>

The sum of carbon, nitrogen, hydrogen and sulfur contents gave an average concentration of  $71.3 \times 10^4 \text{ mg kg}^{-1}$  in coal. This value is below  $100 \times 10^4 \text{ mg kg}^{-1}$  for whole coal constituents. Other components such as oxygen, inorganic elements and moisture may account for this difference.

### 3.3. Determination of Sulfur Forms in Coal Samples

The determination of sulphur forms in coal was assessed using MAE. The obtained results are presented in Fig. 1. Organic and pyrite sulfur forms competed for their concentration in coal samples whilst sulfate form was found in a lower concentration in coal. The sulfur forms and the total sulfur concentrations are not similar from one sample to another. Higher concentrations of sulfate, pyrite and organic sulfur form were, respectively, found with LRC, DRC and KRC samples. On the other hand, a lower concentration of sulfate was observed with KRC sample. Pyrite and organic sulfur forms were found in lowest amount with CRC sample. The concentration of total sulfur was highest in DRC sample whilst the lowest total sulfur amount was found with CRC sample. Despite slight differences observed particularly with some samples, the concentration of total sulfur agreed with the sum of individual amount of sulfur forms determined in coal samples. The mean values are shown in Table 4 which also gives some literature values obtained by various researchers. Considering the concentration of all sulfur forms analysed, one can see that high value of total sulfur does not necessarily imply a highest amount of organic sulfur than pyrite and sulfate or *vice versa*. This means that sulfur forms in coal are influenced by the genesis of coal. The slight difference between the analytical determination of total sulfur and the sum of concentrations of sulfur forms could be due to any of the protocols followed during the determination of each form of sulfur. This could include small loss during filtration, cooling down and opening digestion vessels. However, the difference between the total sulfur determined by the two approaches is not very significant

**Table 3** Ultimate analysis: CHNS analysis.

ID	C $10^4/\text{mg kg}^{-1}$	H $10^4/\text{mg kg}^{-1}$	N $10^4/\text{mg kg}^{-1}$	S $10^4/\text{mg kg}^{-1}$
TRC	65.70	2.92	1.12	0.76
DRC	66.88	2.97	1.13	1.12
KRC	69.64	3.22	1.15	1.26
LRC	51.24	2.69	1.14	0.41
MRC	75.05	3.15	1.20	0.84
CRC	68.68	2.95	1.15	1.11
Mean ( $\pm$ S.D.)	66.20 (8.01)	2.98 (0.19)	1.15 (0.03)	0.92 (0.31)
Certified range*	50.80–78.10	2.20–5.70	0.90–1.70	0.50–4.80
Gryglewicz <i>et al.</i> <sup>24</sup>	79.40	5.40	1.30	1.75
Roberts <sup>22</sup>	40.00–52.00	3.07–3.20	0.78–0.09	1.47–1.56
Marinov <i>et al.</i> <sup>25</sup>	49.00	4.00	0.70	9.58
DME <sup>23</sup>	49.70–58.23	2.60–3.13	0.56–1.44	0.74–1.23
Wagner and Hlatshwayo <sup>4</sup>	nd**	nd	nd	0.40–1.29

\*Certified data from South Africa Bureau of Standards (SABS), South African reference material (SARM), Community Bureau of Reference (BCR), National Institute for Standards and Technology (NIST) and National Bureau of Standards (NBS).

\*\*nd: not determined.

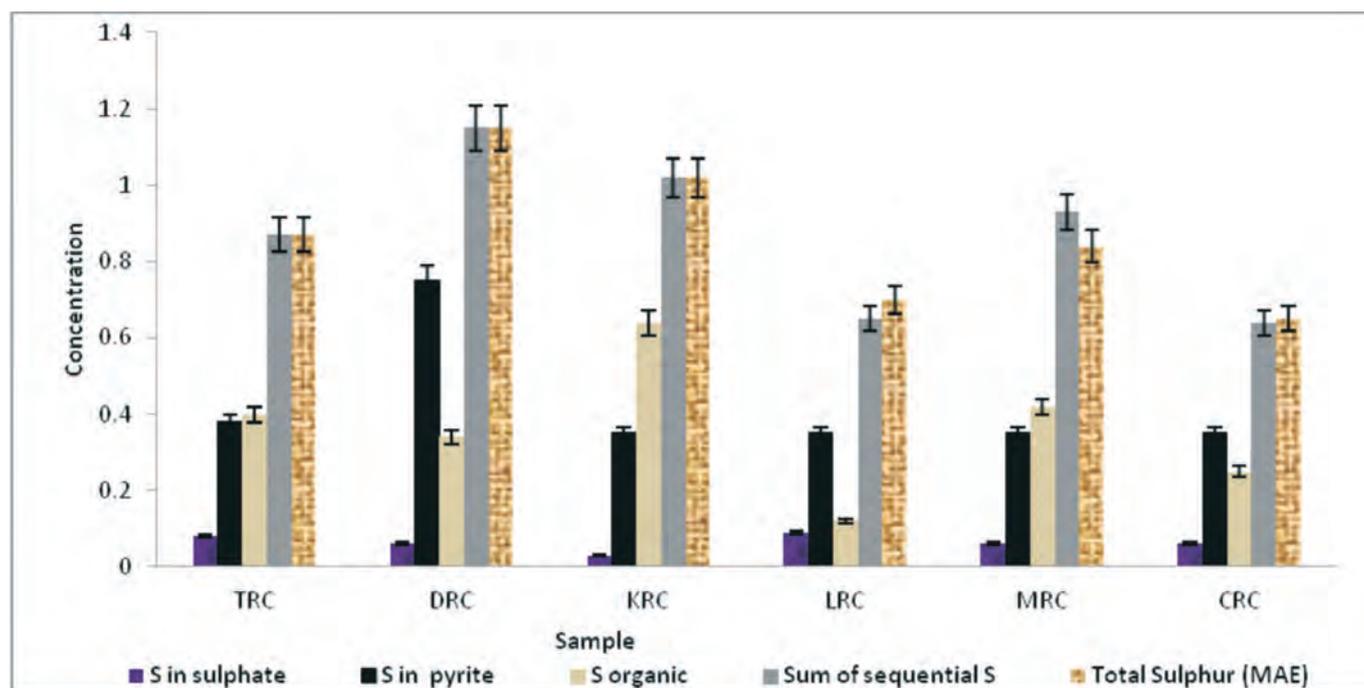


Figure 1 Pattern of sulfur content in coal samples ( $10^4 \text{ mg kg}^{-1}$ ).

since it is within the calculated relative standard deviations (Fig. 1).

The average of total sulfur concentration agrees with the range of values found in the studies on South African coal by DME.<sup>23</sup> The values of various forms of sulfur in coals under study also agree with the certified ranges especially with the South African reference material. Results generally comply with various data ranges of standard material analysed from NIST, BCR, NBS and SARM<sup>16</sup>. Comparing the total sulfur content to other coal samples shown in Table 4, one can see that South African coal can be considered as low sulfur coal. In other coal samples around the world, the total sulfur of  $5.4\text{--}15.1 \times 10^4 \text{ mg kg}^{-1}$ ,<sup>26</sup>  $0.4\text{--}1.3 \times 10^4 \text{ mg kg}^{-1}$ ,<sup>4</sup>  $0.93\text{--}3.35 \times 10^4 \text{ mg kg}^{-1}$ ,<sup>27</sup> and  $19.6 \times 10^4 \text{ mg kg}^{-1}$ ,<sup>25</sup> have been reported.

Although CHNS and MAE followed by ICP-OES results concerning total sulfur content were within the certified range, MAE-OES values slightly differed from the results obtained from CHNS. This might be due to the accuracy of methods. The used analytical methods do not show any similarity since CHNS analysis is a direct method while MAE-OES is an indirect one.

ICP-OES in principle should be more accurate since it is less matrix interfered as the sample is digested first.

#### 3.4. Determination of Selected Metals in Coal

Based on their affinity with sulfur and/or impact on the environment, a number of metals were selected namely arsenic, barium, calcium, cobalt, chromium, copper, iron, mercury, magnesium, manganese, sodium, lead, antimony and zinc. Results obtained after MAE followed by ICP-OES analysis are given in Table 5. Sodium, calcium, iron and magnesium were found in greater amount compared to other metals analysed in coal samples. The highest metal concentration was found with sodium which was at  $25294 \text{ mg kg}^{-1}$  while mercury was the lowest at  $0.21 \text{ mg kg}^{-1}$ . Mercury was the metal with lowest concentration in each sample analysed whilst calcium and sodium competed for the highest concentrations in the analysed samples. The average metal concentrations showed a decreasing trend as follows:  $\text{Na} > \text{Ca} > \text{Fe} > \text{Mg} > \text{K} > \text{Ba} > \text{Mn} > \text{Cr} > \text{Pb} > \text{Zn} > \text{Cu} > \text{As} > \text{Co} > \text{Sb} > \text{Hg}$ . High concentration of iron found in DRC sample explains why the amount of pyrite, as well as ash is

Table 4 Determination of sulfur forms in coals ( $10^4 \text{ mg kg}^{-1}$ ).

Sample	S in sulfate	S in pyrite	S organic	Sum of sequential S	Total sulfur (MAE)
Mean ( $\pm$ S.D.)	0.06 (0.02)	0.45 (0.16)	0.36 (0.18)	0.88 (0.20)	0.87 (0.19)
Certified range*	0.05–1.40	0.84–1.13	0.18–1.07	0.53–4.78	0.53–4.78
Marinov <i>et al.</i> <sup>25</sup>	0.59	0.30	8.69	9.58	9.58
Hsieh and Wert <sup>15</sup>	1.50	3.90	0.46–4.30	0.59–9.45	0.59–9.45
Olivella <i>et al.</i> <sup>26</sup>	0.30–7.60	0.30–3.30	2.70–12.20	5.40–15.10	5.40–15.10
William <sup>27</sup>	0.70–2.17	0.11–1.15	0.12	0.93–3.35	0.93–3.35
Gryglewicz <sup>24</sup>	0.03	0.52	1.18	1.75	1.75
Boudou <i>et al.</i> <sup>28</sup>	0.15	2.95	1.70	4.80	4.80
Wagner and Hlatshwayo <sup>4</sup>	nd	nd	nd	0.40–1.29	0.40–1.29

Note: the standard deviation for each analysis is indicated in brackets.

\*Certified data from SABS, SARM, BCR, NIST and NBS

\*\*nd: not determined.

**Table 5** Analysis of selected metals in coal.

Sample	Concentration/mg kg <sup>-1</sup>						
	As	Ba	Ca	Co	Cr	Cu	Fe
TRC	6.12 (2.63)	309.7 (0.18)	19226 (1.02)	3.67 (4.91)	58.60 (1.47)	8.03 (9.35)	924 (0.23)
DRC	9.75 (9.32)	338.8 (0.08)	10283 (0.32)	3.49 (2.75)	62.26 (1.80)	8.79 (8.62)	13375 (0.45)
KRC	8.26 (4.7)	299.9 (0.17)	20471 (0.17)	2.41 (6.11)	50.71 (6.96)	10.03 (3.18)	3021 (0.60)
LRC	8.18 (10.8)	778.1 (0.65)	12906 0.09	7.05 (8.32)	95.9 (2.15)	8.98 (4.22)	4957 (0.46)
MRC	5.36 (8.14)	396.5 (1.08)	13196 (0.29)	2.09 (10.06)	64.29 (1.62)	7.86 (9.14)	7649 (0.18)
CRC	4.50 (9.28)	158.3 (0.22)	12536 (0.23)	3.05 (4.67)	50.14 (6.11)	8.57 (6.17)	7406 (0.25)
Mean	7.03 (28.63)	380.2 (55.29)	14770 (27.66)	3.63 (49.19)	63.65 (26.46)	8.71 (8.93)	7609 (47.04)
Wagner and Hlatshwayo <sup>4</sup>	0.90–8.20	nd	nd	3.3–14	12–63	4.2–16	nd
Goodarzi <i>et al.</i> <sup>14</sup>	1.30–5.90	11–774	6091–763 158	7.5–14.2	4–15	2–23	2030–113 360
Willis <sup>29</sup>	0.9–8.2	nd	nd	3.3–14	12–63	4.2–16	nd

Note: nd means not determined.  
R.S.D. values are given in brackets.

considerably high in this sample as observed when determining various forms of sulfur in coal. The variation of concentration of studied metals in coal samples was considerably high with arsenic, barium, calcium, cobalt, chromium, iron, magnesium and zinc. These metal concentrations showed high relative standard deviations with their mean values. On the other hand, copper, mercury, manganese, potassium, sodium, lead and antimony were found within a narrow range and therefore yielded lower relative standard deviations.

The high concentration of some of these metals compared to others is indicative of their abundance in coal samples. Although the values of metals in various coal samples were not uniform, their concentrations could partly explain the high values of ash content in coal sample. The values obtained agreed with the range of values found in literature.<sup>4,14,29,30</sup> Details of comparison of the found and literature values are also shown in Table 5.

Most of the determined elements have an affinity to sulfur; these metals are mostly associated with sulfide like pyrite. Others are attached to organic sulfur compounds. For this reason, they affect sulfur removal process from coals besides the potential environmental impact. Temperature is the main parameter that affects the behaviour of metal in sulfur compounds, which has been investigated by Yan *et al.*<sup>31</sup> Mercury is one of the metals that form complexes with organic sulfur forms. This metal forms one of the most toxic species when combined with organic sulfur compounds. This is the case of methyl mercury which is formed by accumulation and reaction of organic sulfur in sediment. Reduced mercury can therefore be activated and combined with this organic form. The product can enter the food chain and be noxious to life.<sup>32</sup>

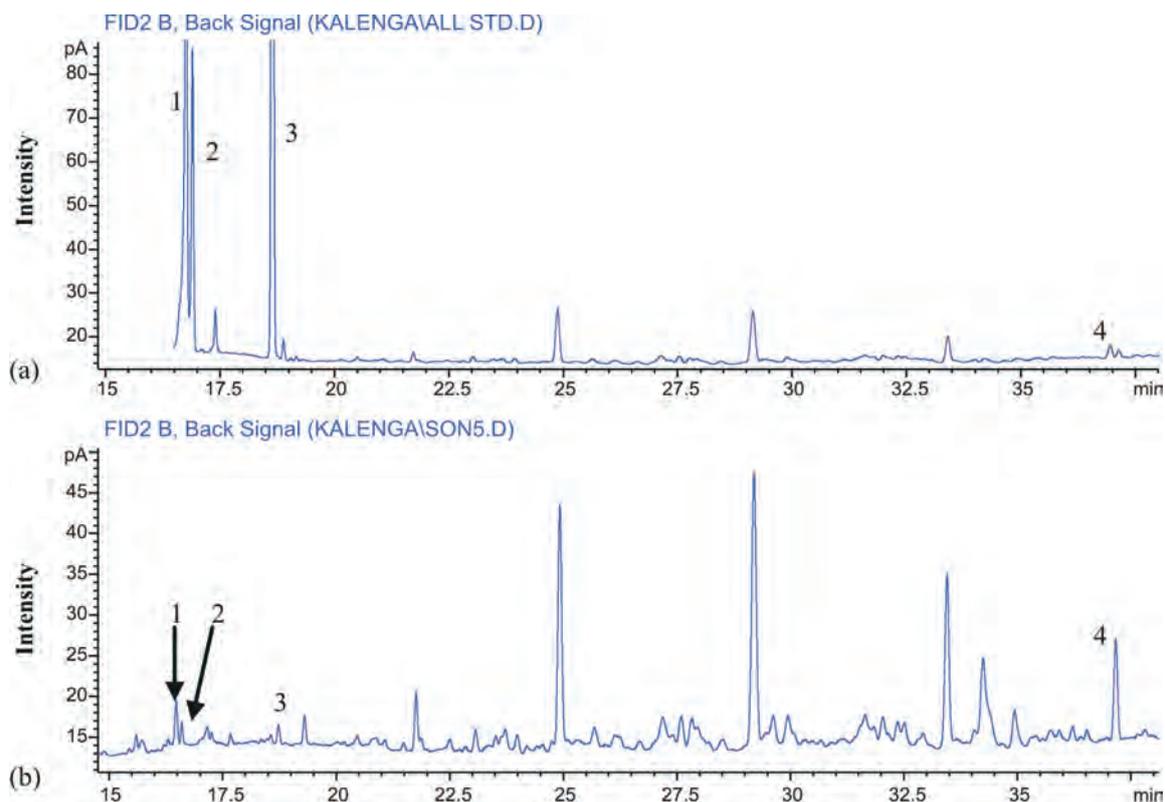
### 3.5. Determination of Organic Sulfur Compounds in Coal

#### 3.5.1. Optimization of Extraction Procedure

The ultrasonic extraction method was optimized for various parameters such as the extraction solvent, extraction time and spiked sample concentration.

A series of solvents were studied to see which one could extract most organic sulfur compounds. This included dichloromethane, hexane, tetrahydrofuran, methanol, pyridine and toluene. Preliminary results helped to focus on toluene, dichloromethane and hexane while pyridine was discarded due to its wide range of noxious effects. Further experimental conditions could not properly control pyridine vapour released during sample extraction. This is because extraction was not performed in a closed vessel. Dichloromethane was selected as good solvent for the present study because of its ability to extract many organic sulfur compounds from coal compared to other solvents investigated. Hexane was the least performing solvent because very few peaks were obtained from its chromatogram. Toluene on the other hand, was not as good as dichloromethane. Dichloromethane was then used to screen various samples for the target organic sulfur compounds. This was done by comparing the chromatograms of standards to those from extracted samples. Target compounds were much found in DRC and KRC samples. Figure 2 shows the chromatogram obtained after analysis of standard of organic sulfur compounds (a) and after ultrasonic extraction of DRC sample (b) with dichloromethane. In DRC samples four organic sulfur compounds were identified based on retention time. The chromatogram presented in Fig. 2b shows that many compounds could be extracted and detected besides the target organic sulfur compounds. The presence of these compounds in DRC samples was fortunately expected from the colour of the extracts.

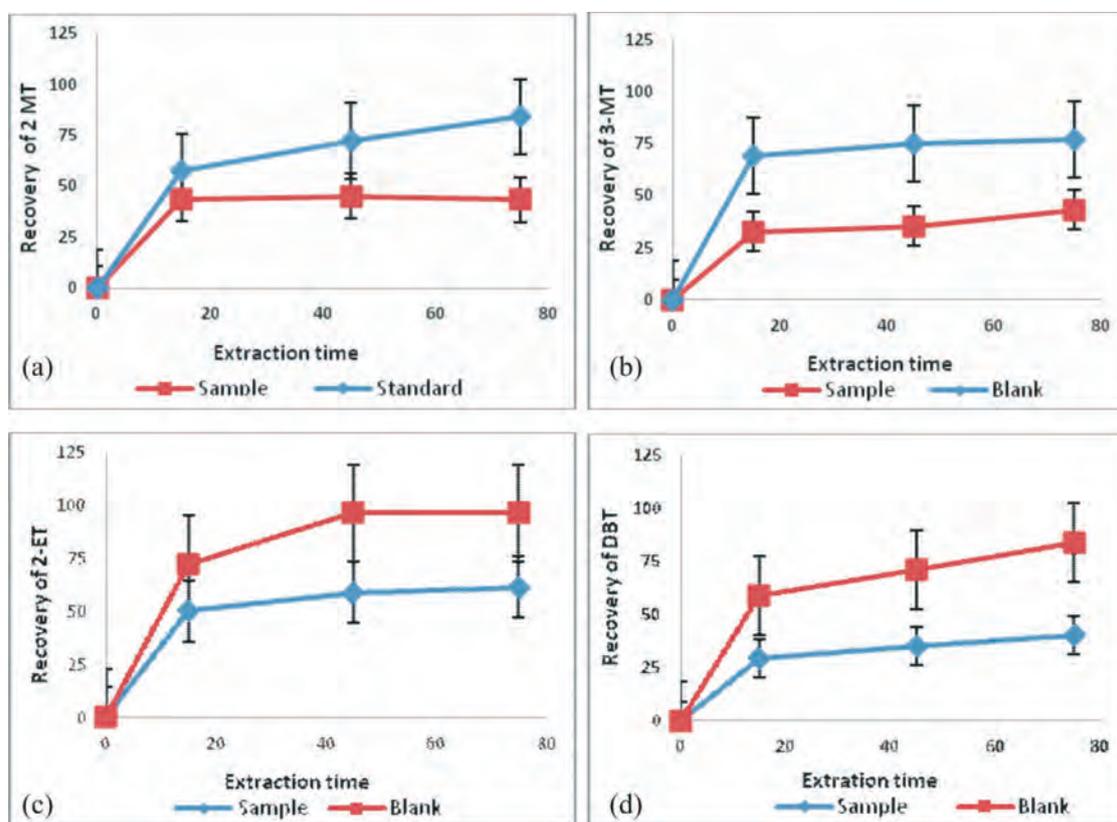
The extraction of organic sulfur compounds from coal samples was further investigated by varying the extraction time. Extraction times of 15, 45 and 75 min were studied and the recovery of the spiked target compounds was determined. Figure 3 gives the recoveries obtained from extraction of each target compound in DRC spiked sample and that from solution of standard organic compounds only. Results showed that the recovery of target compounds was in a range of 32.76–88.07%. The recovery generally increased with extraction time for all compounds studied except for 2-MT and 3-MT in spiked samples. Highest



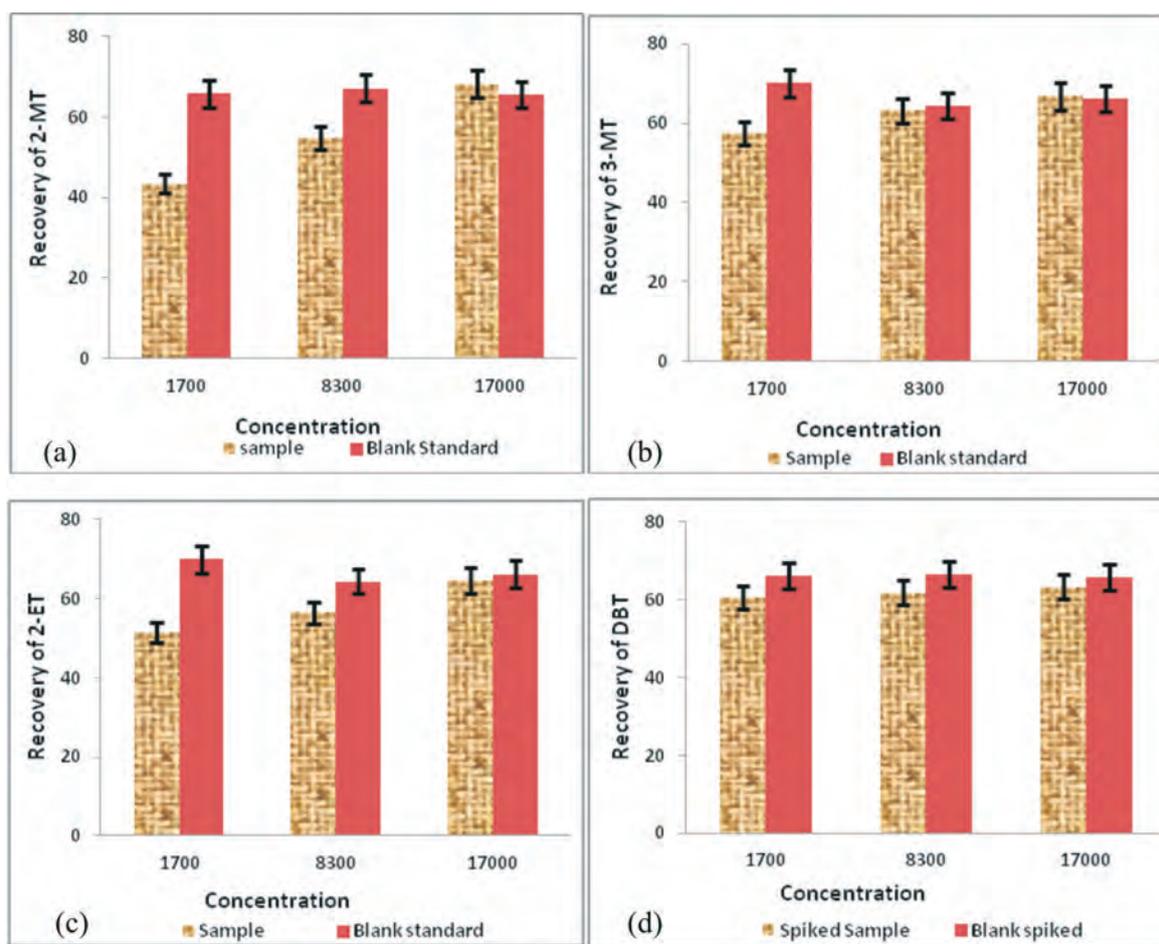
**Figure 2** Chromatogram of standards (a) and DRC sample (b) sonication extract with dichloromethane. 1 = 2MT; 2 = 3MT; 3 = 2ET and 4 = DBT.

recovery was generally found with 75 min of extraction while 15 min of extraction could not allow the total recovery of target organic sulfur compounds. Lower time could not allow all organic sulfur to be extracted whilst exceeding optimal extrac-

tion time could decompose and/or volatilize the analyte. The recoveries from solutions of standard sulfur compounds were higher than in the sample ones at any given extraction time. The lower recovery of organic sulfur compounds from extraction



**Figure 3** Extraction time (min) effect on the percentage recovery of 2-methyl thiophene (a), 3-methyl thiophene (b), 2-ethyl thiophene (c) and dibenzothiophene (d).



**Figure 4** Spiking concentration ( $\text{mg kg}^{-1}$ ) effect on the percentage recovery of 2-methyl thiophene (a), 3-methyl thiophene (b), 2-ethyl thiophene (c) and dibenzothiophene (d).

of samples could be mainly caused by adsorption of standard compounds spiked on sample matrix. This phenomenon means that target compounds have pronounced difficulty to be extracted from samples than their standard solutions. Results further show that for 2-MT and 3-MT, recoveries were lowest compared to that of standards. 2-MT and 3-MT are the most volatile organic sulfur compounds. The results for these compounds suggest they may also have been lost during extraction.

### 3.5.2. Spiking Concentration

The dependency of recovery on the spiked concentration was investigated from 1700 to 17 000  $\text{mg kg}^{-1}$ . TRC, DRC and KRC samples were used for this study as they proved to contain target compounds during preliminary analysis. Results (Fig. 4) showed that the recovery of spiked target organic sulfur compounds in blank samples seemed to be independent on the spiked concentration. This recovery was generally high and in similar range, which was 64.42–70.11 %. However, spiked samples showed a slight variation in recovery. The recovery increased with increase in spiked increase to some extent. Perhaps, a low concentration of spiked standards was strongly adsorbed onto the matrix and the solvent was unable efficiently extract the spiked compounds. Alternatively, the low recovery could be due to some loss from the low concentration of organic sulfur compounds spiked in coal samples during extraction. This was discussed before and seemed to have been pronounced for 2-MT.

From the lowest spiked concentration chromatogram, the detection limit of the method was estimated. Table 6 shows the detection estimated as concentration of target compound that

**Table 6** Detection limits of the method.

Compound	Detection limit/ $\text{mg kg}^{-1}$
2-MT	3.39
3-MT	3.27
2-ET	3.57
DBT	4.20

gives peak area three times to the noise. The detection limit of the method was generally not very low due to the poor sensitivity of FID for the studied compounds. However, the detection limit could be improved by reducing the volume of the extract from 20 mL to 5 mL.

### 3.5.3. Sample Analysis

The external calibration was used for a trial quantification of target compounds. For this purpose, blank and spiked samples were extracted and quantified by mean of the calibration curve. Table 7 gives the results of the quantified compounds.

**Table 7** Quantification of organic sulfur compounds in coal

Sample	Concentration/ $\text{mg kg}^{-1}$			
	2-MT	3-MT	2-ET	DBT
TRC	4.96	nd	nd	nd
DRC	15.00	8.67	3.82	15.50
KRC	8.30	nd	nd	nd

Results showed that 2-methyl thiophene was the only target organic sulfur compound to be quantified in all coal samples studied. This compound had a higher concentration in DRC sample. DRC sample was the only one where all target compounds were quantified. This could mean DRC sample had an appreciable amount of organic sulfur compounds compared to other samples investigated. Other sulfur compounds could have been present in coal samples since other unidentified peaks were observed. This suggests the use of a more specific detector such as mass spectrometer as possible future work. Identification of these organic sulfur compounds is mostly reported qualitatively in literature.<sup>24</sup> This therefore makes it difficult to compare the obtained quantitative results from other studies. Other studies on organic sulfur compounds in coal have confirmed the presence of many such compounds.<sup>24–26</sup> The thiophenic organic sulfur forms are the most dominant organic sulfur in bituminous coal.<sup>27</sup> This may explain why in this study these types of sulfur compounds were the most predominant.

#### 4. Conclusion

The total and various forms of sulfur were identified and quantified in South African coal samples using MAE with acid reagents followed by ICP-OES. Selected metals with an affinity to sulfur were also determined with this method. Ash content was generally high in the coal samples as compared to coal from other parts of the world. The high ash content was attributed to considerable amount of metals and their impact on other components in the samples. The total sulfur concentration investigated with MAE followed by ICP-OES was comparable to that from CHNS analysis. The average amount of total sulfur in coal samples was 8758 mg kg<sup>-1</sup>. This value confirmed that all coal samples analysed are low sulfur content. High concentration of total sulfur was found in Duvha raw coal sample. Kriel, Duvha and Lethabo raw coal samples were respectively found with higher concentration of organic, pyrite and sulfite forms. Coal from Duvha power station showed a large number of target organic compounds. 2-methyl thiophene, 3-methyl thiophene, 2-ethyl thiophene and dibenzothiophene proved to be one of the major thiophene compounds present.

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#### REFERENCES

- 1 G.S. Fernandez, J.G. Vega, A.B. Fuertes, A.B. Garcia and M.R. Tarazona, *Fuel*, 2001, **80**, 255–261.
- 2 C.A. Booth, D.A. Spears, P. Krause and A.G. Cox, *Fuel*, 1999, **78**, 1665–1670.
- 3 H. Inaner and A. Karayigit, *Energy Sources*, 2008, **A 30**, 289–296.
- 4 N.J. Wagner and B. Hlatshwago, *Int. J. Coal Geol.*, 2005, **63**, 228–246.
- 5 W.H. Calkins, *Fuel*, 1994, **73**, 475–484.
- 6 A. Akcil and S. Koldas, *J. Cleaner Production*, 2006, **14**, 1139–1145.
- 7 S. Geldenhuis and F.G. Bell, *Geol.*, 1998, **34**, 234–242.
- 8 M.E. Machado, E.B. Caramao and C.A. Zini, *J. Chrom A*, 2011, **1218**, 3200–3207.
- 9 C.Z. Li, *Fuel*, 2007, **86**, 1663–1683.
- 10 World Bank Group, *Pollution Prevention and Abatement Handbook, Thermal Power: Guidelines for New Plants*, 1998.
- 11 R.M. Davidson, *Fuel*, 1994, **73**, 988–1005.
- 12 S.R. Kelemen, G.N. George and M.L. Gorbaty, *Fuel* 1990, **69**, 939–944.
- 13 G.P. Huffman, N. Sha, F.E. Huggins, L.M. Stock, K. Chatterjee, J.J. Kilbane, M.M. Chou and D.H. Buchanan, *Fuel*, 1995, **74**, 549–555.
- 14 F. Goodarzi, H. Sanei, L.D. Stasiuk, H.B. Sadeghi and J. Reyes, *Int J. Coal Geol.*, 2006, **65**, 35–50.
- 15 K.C. Hsieh and C.A. Wert, *Fuel*, 1985, **64**, 255–262.
- 16 K.L. Laban and B.P. Atkin, *Fuel*, 2000, **79**, I, 173–180.
- 17 T.J. Mason and J.P. Lorimer, *Applied Sonochemistry – The Uses of Power Ultrasound in Chemistry and Processing*, Wiley, VCH, Verlag, Weinheim, Germany, 2002, 1–57, 293.
- 18 K.S. Suslick, Y. Didenko, M. Fang, T. Hyeon, K.J. Kolbeck, W.B. McNamara III, M. Mdleleni and M. Wong, *Roy. Soc. A*, 1999, **357**, 335–353.
- 19 X. Xu, L. M. McDonald, C.W. McGowan and R.J. Glinski, *Fuel*, 1995, **74**, 1499–1504.
- 20 J.H. Harker and J.R. Backhurst, *Fuel and Energy*, Academic Press, London, 1981, 27–42.
- 21 R.A. Meyers, *Coal Structure*, Academic Press, USA, 1982, 132–133; 170–193.
- 22 D.L. Roberts, *Chromium Speciation in Coal Combustion By Products: Case Study at a Dry Disposal Power Station in Mpumalanga Province, South Africa*, Ph.D. thesis, University of Witwatersrand, Johannesburg, 2008, 60–76, 112–127.
- 23 Department of Minerals and Energy South Africa (DME). Mineral Economics Directorate (Minerals Bureau). Operating and Developing coal mines in the Republic of South Africa. Directory D2/2004.
- 24 G. Gryglewicz, P. Rutkowski and J. Yperman, 2002, **77–78**, 167–172.
- 25 S.P. Marinov, M. Stefanova, V. Stamenova, R. Carleer, R. and J. Yperman, *Fuel Processing Technology*, 2005, **86**, 523–534.
- 26 M.A. Olivella, J.M. Palacios, A. Vairavamurthy, J.C. del Río and F.X.C. de las Heras, *Fuel*, 2002, **81**, 405–411.
- 27 H.C. William, *Fuel*, 1994, **73**, 475–484.
- 28 J.P. Boudou, J. Boulqgue, L. Makchaux, M. Nipt, J.W. de Leeuw and J.J. Boon, *Fuel*, 1987, **66**, 1558–1669.
- 29 J.P. Willis, *Geological Society of South Africa*, 1983, **7**, 129–135.
- 30 South African Bureau of Standards, South African Reference Material, SARM 20, certificate of analysis, coal (Sasolburg) certified reference material. SABS, Pretoria, South Africa, 1984, 2.
- 31 R. Yan, D. Gauthier, G. and Flamant, *Fuel*, 2001, **80**, 2217–2226.
- 32 G.W. Van Loon and S. Duffy, *Environmental Chemistry, A Global Perspective*, 2nd edn, Oxford University Press, 2005, 108–123, 227–231, 361–364.