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DETERMINATION AND CHARACTERIZATION OF SULPHUR IN SOUTH AFRICAN COAL

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(367937)

A dissertation submitted to the Faculty of Science, University of the Witwatersrand, in fulfilment of the requirements for the degree of Master of Science

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Johannesburg 2011

DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Science to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

_____

(Signature of Candidate)

_____ Day of _____ 2011

ABSTRACT

Sulphur determination is of priority in coal investigations due to its associated environmental pollution. There are generally various forms of sulphur in coal such as organic and inorganic forms both of which need to be characterized. However, it is the organic sulphur present in coal that is not well understood and studied. In this work, total and various forms of sulphur have been identified in raw coal samples from Camden, Majuba, Lethabo, Kriel, Duvha and Thuthuka power stations in South Africa. Organic sulphur compounds (2-methyl thiophene, 3-methyl thiophene, 2-ethyl thiophene and dibenzothiophene) were characterized from these coal samples in order to determine the quality of South African coal. Organic sulphur compounds were extracted from coal samples by means of ultrasonic bath. The extraction of organic sulphur compounds was first optimised by using various organic solvents such as dichloromethane, toluene and hexane followed by quantification using gas chromatography with a flame ionisation detector. The extraction time was also optimized from 0 to 75 minutes while spiked standard concentrations were varied from 1700 to 17000 mg kg^{-1} to control the process. Ultrasonic extracts were analyzed by GC equipped with SPB-1 Sulphur column and flame ionisation detector. Microwave assisted extraction was used to extract various forms of sulphur in coal. During sequential extraction, sulphate and pyrite sulphur were extracted from coal samples using hydrochloric acid and nitric acid respectively. Total organic or total sulphur and selected metals in coal were extracted by means of a mixture of concentrated hydrofluoric acid, hydrochloric acid and boric acid. Inductively coupled plasma-optical emission spectroscopy allowed the analysis of all total and other inorganic sulphur forms as well as selected metals from

Microwave assisted extraction system after calibration set with standards. Total sulphur compounds and other sulphur forms were also determined using elemental analyzer for carbon, hydrogen, nitrogen and sulphur (CHNS). The standard calibration for CHNS determination was assessed by the use of Sulfamethazine, a certified reference material.

2-methyl thiophene, 3-methyl thiophene, 2-ethyl thiophene and dibenzothiophene were identified in coal samples. The organic sulphur compounds found in most coal samples were methyl thiophenes. Extraction time effect on the recovery of organic sulphur compounds showed that the recovery of organic sulphur investigated was up to 88% with 75 minutes ultrasonic bath extraction. Spiked concentration effect on the recovery of the target compounds was observed at 75 minutes of extraction and the recovery of extraction was generally in the range of 64.42-70.11%. However, an average of 66% recovery of target compounds was obtained from the highest spiked concentration. Duvha raw coal samples were found with more target organic sulphur compounds compared to other samples. Dibenzothiophene was found in highest concentration (15.5 mg kg^{-1}) among the compounds identified.

Products from preliminary pyrolysis of coal samples were identified by coupling pyrolysis furnace with GC-FID. The chromatograms showed four peaks identified in pyrolysis products from blank and spike coal samples. Those compounds proved to be the fragmentation products of target organic sulphur compounds.

CHNS results showed that carbon, hydrogen, nitrogen and sulphur contents in coal had average values of 66.20%, 2.98%, 1.15% and 0.92% respectively. Those values agreed with figures reported by certified coal samples and confirmed the rank of the coal samples which is of the bituminous type.

Microwave assisted extraction followed by Inductively coupled plasma-optical emission spectroscopy results showed that the total sulphur in coal samples had an average value of 8758 mg kg^{-1} and each sample showed that the total sulphur content is less than 20000 mg kg^{-1} (2%). Results also showed that the average value of sulphate content (600 mg kg^{-1}) is lower than pyrite (4500 mg kg^{-1}) and organic (3600 mg kg^{-1}) forms. However organic and pyrite forms competed for their presence in coal samples. Microwave assisted extraction followed by Inductively coupled plasma-optical emission spectroscopy results of the various sulphur forms were in the range of values reported in certified material.

Coal sulphur content is considered low from 0 to 20000 mg kg^{-1} and high when it is beyond 20000 mg kg^{-1}. This means that South African coal generally has low sulphur content as referred to by the results obtained in this work. Sulphur compounds were found in coal samples as sulphate, pyrite and organic forms. Thiophene compounds found within the organic forms, moisture, ash and CHNS contents from this study showed that South African coal is generally bituminous type.

DEDICATION

For you my loving parents

ACKNOWLEDGEMENTS

This project would not have been easily achieved without the support and guidance of particular people. My sincere gratitude is addressed to Prof. Luke Chimuka for the supervision of this project. His encouragement, explanation and patience throughout this work are greatly appreciated. All the best words go to my co-supervisor, Prof. Ewa Maria Cukrowska. Your encouragement and assistance are greatly valued. You always reinforced my knowledge and working spirit. I thank Dr. Hlanganani Tutu for his advices and encouragement which are always considered.

My special thanks also go to the National Research Foundation (NRF) Grant holder Bursary through Prof Luke Chimuka for the financial support during my studies.

My gratitude is also addressed to the following people:

- My parents, for their love and very positive support during all my life;
- My brothers, sisters and everyone for the support and encouragement;
- Mr T. Mabaso for your help in technical assistance throughout my studies;
- My Environmental analytical chemistry group mates for working together amicably. I am proud of you as your presence, help and support through my studies were necessary. I wish to thank particularly J. Lusilao Makiese, E. Bakatula Nsimba, Anel McDowell and Godwin Nhauro for your deep and helpful advices during this project since you could sacrifice your valuable time to help me overcome my issues.

Many thanks to God for keeping me alive. You are always my refuge and shelter. You made me strong and powerful so that I could complete my studies.

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ABBREVIATIONS

2-ET: 2-ethyl thiophene

2-MT: 2-methyl thiophene

3-MT: 3-methyl thiophene

AED: Atomic emission detector

AMD: Acid mine drainage

ARD: Acid Rain Drainage

AP-TPR: The atmospheric pressure temperature - programmed reduction

AP-TPR-MS: The atmospheric pressure temperature - programmed reduction technique coupled with potentiometric detection and mass spectrometry

BCR: Community Bureau of Reference

Btu: British thermal unit

CCT: Clean coal technology

CRC:Camden raw coal

DRC: Duvha raw coal

DBT: Dibenzo-thiophene

DME: Department of mine and energy.

EDX: Energy Dispersive X-ray

EDX-SEM: Energy dispersive X-ray spectroscopy with scanning electron microscopy

EIA: Energy Information Administration

EPA: Environmental protection agency

Eq: Equation

ESCA: Electron Spectroscopy for Chemical Analysis

FGD: Flue Gas Desulphurisation

FID: flame ionization detector

FPD: flame photometric detector

GC: Gas chomatograph

GC-FID: Gas chromatography-flame ionisation detector

GC/MS: Gas Chrmatograph / Mass Spectrometer

I.C.P-A.E.S: Inductively Coupled Plasma - Atomic Emission Spectrometry

ICP-OES: Inductively Coupled Plasma -Optical Emission Spectrometry

i.e.: For example

IGCC: Integrated gasification combined cycle

IUPAC: International Union for Pure and Applied Chemistry

kJg^{-1}: kilojoule per gram

KRC: Kriel raw coal

LRC: Lethabo raw coal

MAE: Microwave assisted extraction

min: minute

MPa: Megapascal

MS: Mass spectrometer

MRC: Majuba raw coal

MWe: Megawatt electric

NBS: National bureau of standards

NEMA: National Environmental Management Act

NEXAFS: Near Edge X-ray Absorption Fine Structure

NIST: National institute for standards and technology

OC: Organic carbon

Py-GC -FID/FPD: pyrolysis-gas chromatography equipped with a flame ionization detector and a flame photometric detector

Rec: recovery

Redox: oxydo – reduction

rpm: rotations per minute

RSD: relative standard deviation

RT: Retention time

S: Sulphur

SABS: South Africa bureau of standards

SARM: South African reference material

SCD: Sulphur chemiluminescence detector

SF: Supercritical fluid

SFE: Supercritical Fluid Extraction

Std: Standard

Spkd: Spiked

TEM: Transmission electron microscope

TOC: Total organic carbon

TRC: Thuthuka raw coal

UHV: Ultra high vacuum

XANES: X-ray absorption near edge structure spectroscopy

XAS: X-ray Absorption Spectroscopy

XPS: X-ray photoelectron spectroscopy

XRD: X-ray diffraction

XRES: X-ray emission spectroscopy

CHAPTER ONE: INTRODUCTION

Coal, which is a fossil fuel, is the largest source of energy worldwide. South Africa is one of the largest coal producers in the world and 90 % of the local electricity is produced through coal combustion (Koper, 2004; Asamoah, 2006). Coal is also considered as an important source of pollution since various toxic chemicals are released as by-products during coal processing. Environmental pollutants such as sulphur dioxide, sulphuric acid and hydrogen sulphide have been linked to the presence of sulphur in coal.

Organic and inorganic forms are both present in coal where they have a very complex structure. However, organic forms are still not well documented despite the fact that they are the most abundant in coal (Larsen 1978; Klaus, 1984; Meyers, 1982). Therefore, the characterization of coal is of importance for a better understanding of its chemical composition and possible reactions during processing.

Different methods are used to characterise the inorganic sulphur compounds in coal. However, it is the determination of organic sulphur forms that is still not well researched (Bartok and Sarofim, 1991; Wilfrid, 1961). The organic compounds consist of heteroatom functionalities that stabilise free radicals in coal, they play an important role determining the needed coal processing mode e.g., whether thermal decomposition, gasification or liquefaction (Harker, 1981; Larsen, 1978; Meyers, 1982).

Calkins, (1994) showed that the organic sulphur structures in coals are mainly components of the macromolecular structures of coal and are not readily separated and analysed without destruction of the macromolecular network.

The composition of coal varies depending on the place where it was formed and the type of soil or rocks accompanying its formation. Knowledge of the complex structure of coal has broadened since the past few decades due to ongoing reserch . This is in order to understand its composition and properties which affect its utilization and environmental impact (Meyers, 1982).

The pollution concerns related to coal mining, processing and use has led to new regulations which tend to decrease its exploitation. However this decrease is mostly observed in some developed countries (EIA, 2009). To date, every country producing coal is being guided by either national or international regulatory bodies with the purpose of reducing pollution (Craig, 1986; Kroschwitz and Grant, 1993; Harker and Backurst, 1981). Research plays a major role in this regard by providing different ways of minimising the impact of coal processing on the environment (Bernard, 1978; Glassman, 1987; Hirinchs and Merlin, 1941; Thompson, 1981).

This project focussed on the characterisation and distribution of sulphur components in South African coal. Results obtained in this work are useful in developing procedures that can minimize the environmental concerns of these compounds during coal mining, processing and use.

1.1 BACKGROUND

Coal is a sedimentary rock resulting from the accumulation of plant material, geodynamic effects and metamorphism processes. The time, temperature and pressure at which the transformation was subjected and the maturity of coal influence the coal chemistry. The underground composition of coal is not homogeneous and depends on the way it was accumulated in its bed during the genesis (Kroschwitz and Grant, 1991; Selsbo, 1996). Coal is composed of macerals, discrete minerals, inorganic elements held molecularly by the

organic matter, water and gases contained in submicroscopic pores. Organically, coal consists primarily of carbon, hydrogen and oxygen, and lesser amounts of sulphur and nitrogen. Inorganically, coal consists of a diverse range of ash -forming compounds distributed throughout the coal. The inorganic constituents can vary in concentrations from several percentage points to parts per billion of coal (Sakaki et *al.*, 1994).

Previous explorations have shown that the type of chemical elements present in coal and the coal chemistry depend on many parameters such as area, coal bed, coalification, rank, parent plant material and procedures used for its characterization. Moreover, other factors such as condensation, rearrangement and concerted reactions can also occur during coalification (Craig, 1986; Kroschwitz and Grant, 1993; Larsen, 1978). Coal as combustible rock contains by weight more than 50 % of carbonaceous matter. Aliphatic compounds are less abundant in high ranks (Kroschwitz and Grant, 1991; Glassman, 1987; Larsen, 1978; Selsbo, 1996).

Volatile matter increases with the rank and the particle size of coal (Clarence, 1978). Different molecules are generally bound or attracted to each other by Van Der Waals forces and/or hydrogen bonding. This explains the presence of pore structures and water molecules in coals (Larsen, 1978). Since almost all the elements are present in coal, its chemistry is complex. Therefore, coal investigations and its utilization are dependent on its variable properties in relation to its chemistry (Selsbo, 1996; Sawyer and Mc Carty, 1978). Coal is transformed by many processes to make different products used all over the world in everyday life. Reactions in coal during processing are complex and some are still not well understood. The heterofunctional groups in coal, for example, are mostly the ones that are released as unwanted by-products causing environmental pollution (Larsen, 1978; Glassman, 1978; Selsbo, 1996). Knowing and characterising coal heterofunctional groups can allow a

good assessment of its environmental concerns such as acid rain and global warming.

1.1.1 Coal Formation

The process of coal formation includes decaying of vegetation, deposition, and burying by sedimentation. It also involves compaction and transformation of the plant remains in the organic rock found nowadays. Coal formation began during the carboniferous period known as the first coal age, 270–350 million years ago. The considerable diversity of coal is due to different climatic and botanical conditions that existed during the main coal-forming periods along with subsequent geophysical actions. Layers of plant debris were deposited in wet or swampy regions under conditions that limited exposure to air and complete decay. The accumulation of debris resulted in the formation of peat which was buried by sediment and was subjected to higher temperatures and pressures resulting in chemical and physical changes that over time formed coal (Kroschwitz and Grant, 1993; Neavel, 1981).

The geochemical process consisting of the alteration of plant debris into coal is called coalification and is structured as follows (Kroschwitz and Grant, 1993):

Peat → Lignite → Sub-bituminous Coal → Bituminous Coal → Anthracite

Geochemically, coalification can be described as consisting of three processes: the microbioloical degradation of the cellulose of the initial plant material; the conversion of plant material lignin into humic substances; and the condensation of these humic substances into larger coal molecules. The kind of decaying vegetation, conditions of decay, depositional environment and

movements of the earth's crust are important factors in determining the nature, quality and relative position of the coal seams (Sakaki *et al.*, 1994).

1.1.2 Importance of coal and associated environmental problems

About eighty percent of world coal production is used to generate power and for other industrial purposes depending on its heat value. Coal is also a raw material used for oil, petrol, tar and other chemicals' manufacturing. It further contributes to the formation of sulphuric acid, amino acids and proteins (Selsbo, 1996; Baird, 1995). Despite the economic value of coal, it has environmental problems associated to its mining process and use. Coal is well known as a precursor of the green house gas and acid rain that contribute to brown haze, global warming besides other environmental concerns (Bartok and Sarofim, 1991; Glassman, 1987; Baird, 1995). The increasing use of coal has to be balanced by the advanced clean coal technology (CCT) so as to avoid global warming and reduce or eliminate its negative effects on the ecosystem (South African Mining and Metallurgy, 2000). Since the Industrial Revolution and the oil crisis, research has been done and has shown how coal causes major damages to the ecosystem through atmospheric pollution, danger to public health, harm to flora and fauna, as well as alteration of nature and manmade structures (Asamoah, 2006; South African Mining and Metallurgy, 2000). Generally, there is no detectable environmental concern with natural coal. It becomes a danger to the ecosystem when it is mined, processed and used for various purposes. Some of the harmful outcomes include air pollution, water pollution, accumulation of solid waste, not to mention the land degradation and human illness. The major pollutants from coal processing are carbon dioxide, nitrogen dioxide, sulphur dioxide, methyl mercaptan, dimethyl sulphide,

dimethyl disulphide, mercury, lead, arsenic, and particulates matter (Baird, 1995; Valkovic, 1983). The exposure of coal or its solid waste to rain can cause environmental concerns such as acid mine drainage (Ohki *et al.*, 2004).

Flue Gas Desulphurisation (FGD) is one of the techniques used for removing sulphur dioxide from exhaust stacks in plants by scrubbing the gaseous compounds resulting from coal processing. Other methods for coal processing require a good knowledge of different organic sulphur compounds present in coal in order to improve the scrubbing gas procedure (Hirinchs and Merlin, 2000; Wilson, 2000).

Volatile organic compounds in coal are more reactive, thus they combine with the atmospheric compounds when released to form new compounds with great consequences on the composition of the atmosphere and the entire ecosystem (Kgaugelo, 2004; Sipone, 2005).

1.1.3 Coal classification

The classification of coal is generally based on the carbon content which is the source of heat value. Table 1 gives the classification of coal according to its main characteristics (Kroschwitz and Grant, 1993; Neavel, 1981). Although the sulphur content in coal differs from one coal bed to another, it is still an important factor to consider in the coal classification. Coal with less than 2 % sulphur content is known as low sulphur coal and above 2 % sulphur content is high sulphur coal. This is independent of the rank since the same rank of coal from different basins can have different sulphur content. A rank represents coal maturity level. It ranges from lignite (representing the less mature coal) to anthracite (most mature coal).

Table 1: Classification of coal

Rank (Coal maturity)	**Carbon content** (%)	Other parameters		
		Moisture (%)	**Heat value** (Btu)[a]	**Vitrinite reflectance** (%)
LIGNITE	25-35	39	8300	$1.7x10^{-3}$- $4.6x10^{-3}$
SUB-BITUMINOUS	35-45	20-30	8300-13000	$4.6x10^{-3}$ - 0.01
BITUMINOUS	45-86	15.9-20	≤15000	0.01 - 0.90
ANTHRACITE	86-98	2.8-16.3	≥15000	0.90 - 2.86

[a]Btu (British thermal unit) is a unit of heat, to convert to kJg^{-1}, divide by 430.2

Generally, as the carbon content increases so does its heat value whereas the moisture content decreases as coal matures. Its heat value tends to decrease in bituminous coal due to the decrease in volatile matter (Sakaki *et al.*, 1994). Another way of ranking coal is to measure its reflectance. Coal reflectance comes from its vitrinite content. Vitrinite is the most abundant part of coal derived from the woody tissues of plants. Vitrinite gives rise to the vitrinite reflectance which is determined by the amount of light reflected from a polished plane surface of a coal particle under specified illumination conditions. It is largely dependent on carbon content in coal and increases with the aromaticity of the coal sample. This reflectance is therefore rank dependant. Precise measurements of reflectance, usually expressed as a percentage, are used as an indication of coal rank (Kroschwitz and Grant, 1993; Neavel, 1981).

Another classification refers to the grade of coal which establishes its economic value for a specific end use. Grade of coal refers to the amount of mineral matter that is present in the coal and is a measure of coal quality. The level of trace elements in coal is also used to grade coal (Sakaki *et al.*, 1994).

1.1.4 Coal structure

The structure of coal depends upon the coal constitution or its formation history and the experimental method of elucidation. Generally, coal structure consists of a mixture of molecules of very broad range and sizes. The organic material is the most dominant and occurs in various petrographic types, called "macerals", which reflect the nature of the precursor plant material (Levine *et al.*, 1982). Extraction of coal compounds is dictated by various parameters due to its complex structure. Fractioning extraction using a mixture of solvents and supercritical fluids is frequently required to get good results. This is also due to the presence of both polar and non polar fractions. Non polar and polar fractions are respectively constituted by heteroatom and hydrocarbon functionalities (Kroschwitz and Grant, 1993; Klaus, 1984; Meyers, 1982). Many models of coal are generally proposed with main building blocks of aromatic, cyclic and heterocyclic units bound to inorganic compounds associated together by a variety of forces and bonds. Aromatic and cyclic clusters are linked through oxygen, methylene, longer aliphatic groups or disulphide bridges. Organic compounds, especially organic sulphur compounds form complex molecules with metals where sulphur is acting as linkage between metal ions in complex compounds. The stability of metal-sulphur

bonding allows mostly the formation of complexes containing sulphur bridges. The overall structure of coal is irregular, open and complex (Craig, 1986; Harker and Backhurst, 1981; Meyers, 1982).

1.1.5 Coal production

The Energy Information Administration (EIA) database has assembled the world production of coal from 1997 to 2006 (Table 2). The United States of America and most of European countries have agreed to new and advanced technologies to monitor coal utilization so that the production does not raise more than environmental concerns due to coal utilization. Coal production in Europe and Northern America has therefore remained fairly constant. However China and Middle East consumption has continued to increase due to rapid industrialisation (Niels, 1998). South Africa covers more than 80 % of African coal production. It is by far the largest producer in Africa and its coal reserve ranks fifth in the world. (Department of Mines and Energy, 2004; Mc Carthy and Rubidge, 2005; EIA, 2009). In 2000, a programme called Coal Technology 2020 was launched to carry out research that aims to assist in the optimal use of South African coal reserves (South African Mining and Metallurgy, 2000).

Table 2: World coal production (EIA, International)

World Coal Production, 1997- 2006 (Million Short Tons)										
REGION AND COUNTRY	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
North, Central, and South America	**1237**	**1266**	**1243**	**1221**	**1281**	**1238**	**1219**	**1269**	**1296**	**1331**
United States	1090	1118	1100	1074	1128	1094	1072	1112	1131	1163
Europe	**941**	**886**	**832**	**832**	**839**	**832**	**825**	**816**	**806**	**799**
Germany	252	233	226	226	227	233	229	235	229	223
Eurasia	**431**	**414**	**421**	**443**	**457**	**440**	**479**	**479**	**502**	**534**
Russia	268	252	270	276	285	273	296	299	321	341
Africa	**251**	**254**	**250**	**256**	**257**	**252**	**270**	**273**	**276**	**276**
South Africa	244	247	243	249	251	246	264	268	270	269
Middle East, Asia and Oceania	**2291**	**2243**	**2210**	**2197**	**2408**	**2507**	**2864**	**3260**	**3609**	**3852**
China	1507	1429	1365	1314	1459	1521	1838	2156	2430	2430
World	**5151**	**5062**	**4955**	**4949**	**5243**	**5268**	**5657**	**6097**	**6490**	**6793**

Note: A short ton = 907.185 kilograms. Only the country which is the most producer of coal for each block of the world is mentioned.

1.1.6 Coal in South Africa

South African coal production is dominated by the following five big suppliers: Anglo coal, Sasol, Exxaro, BHP Billiton (BHPB) and Xstrata. More than 80% of the South African coal market is supplied by these companies. Table 4 below shows the South Africa coal production in 2007. Almost half of South African coal production is used for local energy needs while the third of that raw material is for export (Table 5).

Table 4: South African coal production in 2007

Supplier	**Production** [% of 243Mt]
Anglo Coal	23
Sasol	17
Exxaro	17
BHP Billiton	16
Small Scale Mines	15
Xstrata	8

Source: Department of Minerals and Energy, 2007.

South African coal reserves are projected to last for about two centuries. Table 5 shows South African coal utilization by sector. Local electricity generation by ESKOM is the major coal consumer. About 27 % of coal is exported to other countries.

Beside the pollution occurring during processing, the discarded coal as waste is another challenge. In most cases the properties of this waste is unknown as it is

rarely characterised. The discarded forms of coal are still complex as the original coal although some of the constituents are removed during the processing (http://www.dme.gov.za/energy/coal.stm). Since 1980, South Africa coal demand has been increasing due to its quality and cheaper price compared to other alternative fuels. However the use of this fossil fuel is still a source environmental pollution. More than 1413.5 million tons of coals have been discarded from 1980 until 2007. This quantity is almost 15 % of the annual South African coal production and nowadays the total waste covers more than 5 % of South African coal reserve.

Table 5: South Africa coal utilization in 2007

Sector	**Coal utilization** [% of coal production]
Electricity	45
Synthetic fuels	18
Industries	4
Merchants and domestics	3
Metallurgical process	2.5
Export	27

Source: Energy International Administration, 2007.

1.1.7 Importance of sulphur

Sulphur is needed for the animal growth. It plays a role in the intake of cellulose and synthesis of microbial protein. Sulphur is also used in matches, fireworks, gunpowder, construction, in the vulcanization of natural rubber (a

treatment that gives rubber elasticity and strength). It is converted into a multitude of other useful compounds. Sulphuric acid is by far the most important of all sulphur compounds. Nearly 90 percent of all sulphur produced is converted first into sulphur dioxide and then into sulphuric acid. Sulphuric acid is used in the production of fertilizers, automobile batteries, petroleum products, pigments, iron and steel, and many other products. Most organic sulphur compounds are used in pharmaceutical, chemical industries or directly as fungicide and insecticide. They also play an important role as odorizing agents, preservatives etc. Sulphur is also involved in the formation of amino acids and proteins (Baird, 1995).

1.1.8 Legislation and guidelines for coal utilization

Almost all major industrial processes that are likely to cause air pollution have been listed in the second schedule of the South African Atmospheric Pollution Prevention Act 45 of 1965. This enables the Chief Air Pollution Control Officer to lay down requirements for emission control. To date almost all particulate emissions from industries and major stationary appliances are subject to emission control (Boegamn, 1965). Particulates emission control in South Africa are assessed by means of various devices such as electrostatic precipitators, cyclones and bag filters which generally show more than 80 % efficiency (Fuggle and Rabie,1983). The USEPA has set an emission limit of 516 g/10^6 kJ (490 g/10^6 Btu) of coal burned from any coal activity. To meet this, steam coals have to contain less than 1 % sulphur. Regulations resulting from the clean air act of 1991 (USA) call for reduction of the total amount of sulphur oxide emissions by 8-9 million tons annually. Half of the reduction was required to be met by 1995. Technology is being developed to control SO_x and NO_x through a combination of sorbent injection into the furnace and

scrubbing and/or baghouse treatment to neutralise the acid gases and catalytically convert the NO_x to nitrogen (Kroschwitz and Grant, 1993).

In terms of Section 28 of National Environmental Management Act (NEMA 107 of 1998), every person who causes, has caused or may cause a significant environmental pollution or degradation, must take reasonable measures to prevent it from occurring, continuing or recurring.

The development of a set of environmental requirements for a new thermal power plant in South Africa involves decisions of two distinct kinds. First, there are the specific requirements of the power plant itself. These are the responsibility of the project developer in collaboration with relevant local or other environmental authorities. This document focuses on the issues that should be addressed in arriving at project-specific emissions standards and other requirements. Secondly, there are requirements that are related to the operation of the power system as a whole. These strategic issues must be the concern of national or regional authorities with the responsibility for setting the overall policy framework for the development of the power sector. Examples of such responsibility include measures to promote energy conservation via better demand-side management, to encourage the use of renewable sources of energy rather than fossil fuels, and to meet overall targets for the reduction of emissions of sulphur dioxide, nitrogen oxides, or greenhouse gases (World bank Group, 1998).

Coal pile runoff and leachate may contain significant concentrations of toxic chemicals such as heavy metals. Where leaching of pollutants to groundwater or their transport in surface runoff is a concern, suitable preventive and control measures such as protective liners, collection and treatment of runoff should be put in place. Solid wastes that do not leach toxic substances or other contaminants of concern to the environment, including ash and FGD sludges, may be disposed in landfills or other disposal sites provided that they do not

impact nearby water bodies. Where other contaminants are expected to leach out, they should be treated, for example, by stabilization before disposal. The total sulphur dioxide emissions from the power plant or unit should be less than 0.20 metric tons per day (tpd) per Megawatt electric (MWe) of capacity for the first 500 MWe, plus 0.10 tpd for each additional MWe of capacity over 500 MWe. In addition, the concentration of sulphur dioxide in flue gases should not exceed 2,000 mg/Nm^3, with a maximum emissions level of 500 tpd. Construction of two or more separate plants in the same local area around the plant whose ambient air quality is directly affected by emissions from the plant (airshed) to circumvent this cap is not acceptable (World Bank Group, 1998).

1.2 STATEMENT OF THE PROBLEM

Sulphur compounds which are released from coal during mining, processing and use cause environmental pollution. The characterization of sulphur compounds in coal is the main key to regulate sulphur related environment pollution. Currently, there are limited published studies on the investigation of sulphur compounds, especially organic sulphur compounds, in South African coal (Laban and Atkin, 2000; Wagner and Hlatshwayo, 2005). The cost of technology for coal processing often relies on the knowledge of various constituents of coal especially those linked to environmental pollution and to its heat value.

1.3 GENERAL AND SPECIFIC OBJECTIVES

1.3.1 General objective

The general objective was to investigate various sulphur compounds in South African coal.

1.3.2. Specific objectives

The following were specific objectives:

- To characterise organic sulphur compounds in South African coal by assessing the following compounds: 2-methyl thiophene (2-MT), 3-methyl thiophene (3-MT), 2-ethyl thiophene (2-ET) and dibenzo-thiophene (DBT).
- To compare the quality of South African coal with other coals based on the total sulphur in coal and on the number of individual organic sulphur compounds.
- To compare the quality of South African coal with others based on the amount of inorganic sulphur compounds.
- To determine the total and inorganic sulphur compounds in South African coal.

CHAPTER TWO: LITERATURE REVIEW

This chapter summarizes the coal technology used to reduce pollution, the origin of sulphur in coal, total and various forms of sulphur, behaviour of sulphur compounds in the environment and various analytical methods for its extraction and determination. It also includes sulphur properties and forms as well as its occurrence in coal and its environmental effects. Direct and indirect determination methods for forms of sulphur in coal are also discussed.

2.1 COAL TECHNOLOGY USED TO REDUCE POLLUTION

The technological processes adopted to date in various industries are dependent on coal chemistry. Further investigations on coal could suggest ease and economically profitable ways for coal processing. The pre-combustion desulfurization processes such as coal washing, liquefaction and gasification as well as the post-combustion desulfurization processes such as scrubbing flue gas with various solutions are beyond the present scope of discussion (Batyko *et al.*, 1991; Nelson and Zhang, 1996). Integrated gasification combined cycle (IGCC), Flue gas desulfurization (FGD) and high exhaust stacks (more than 150 metres) are the actual technologies to reduce sulphur emission during coal processing. Many types of FGD systems have been developed. These can be classified in two major groups, wet and dry processes, which include several types depending on the specific chemical reactions taking place and the flow conditions employed. Among them, the wet limestone FGD process is by far the most widely used because of its high desulphurisation performance, reliability and low utility consumption (Kikkawa *et al.*, 2002). In this system SO_2 is removed from the flue gas by absorption into limestone slurry as sulphate which in turn is extracted from the absorber as gypsum slurry and

finally dewatered. The chemical reaction occurring in a wet limestone FGD process (Ayuso *et al.*, 2006) can be summarized as in Eqn 2.1.

$$CaCO_{3\,(s)} + SO_{2\,(g)} + ½\ O_{2\,(g)} + 2\ H_2O_{\,(l)} \rightarrow CaSO_4.2H_2O_{\,(s)} + CO_{2\,(g)} \qquad \text{(Eqn 2.1)}$$

However the above-mentioned strategies prove costly to be used in most plants (Wilfrid, 1961; Hinrich and Merlin, 1941). Whether scrubber systems are eventually installed on many number of coal power plants they might depend on the continued viability of fuel switching (which is in turn sensitive to relative fuel costs). Ongoing concerns about acid deposition, combined with new imperatives to address fine particulate pollution and regional haze, lead to a further tightening of the sulphur dioxide cap (Tatsutani and Amar, 2000).

Researchers always carry out explorations on coal and its products during and after processing. Waste coming from any coal usage should be reprocessed to remove toxic elements or any form of compounds which could contribute to negative consequences on the environment. For that purpose, research on coal is still the main key to facilitate the reuse of its waste, or else the waste generated has to be discarded regardless of any consequence it may yield to the environment. The discarded coal waste is generally one of the major sources of environmental concerns beside other gases and particulate matter occurring during a process. Research should therefore aim to reprocess coal waste with minimal damage to the environment. Figure 1 shows a summarized interdependence between research, coal material, its processing and products.

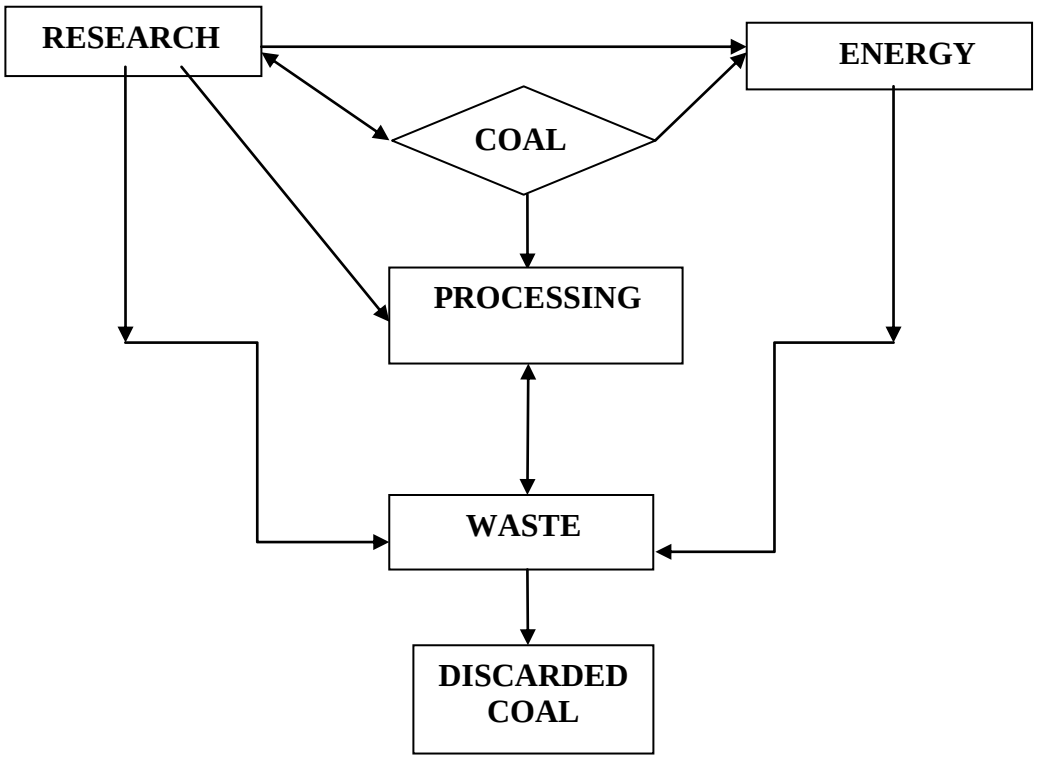


Figure 1: An illustration of interdependence of coal processing, usage and its waste on research.

2.2 ORGANIC CARBON IN COAL

The organic carbon is determined as total organic carbon (TOC) and allows understanding the organic material in coal which originally came from decaying vegetation, bacterial growth, and metabolic activities of living organisms or chemicals. The standard wet chemistry technique for TOC determination extraction involves the rapid dichromate oxidation of organic matter. Perhaps the best known of the rapid dichromate oxidation methods is the Walkley-Black procedure which has been the "reference" method for comparison to other methods in numerous studies (Tiessen and Moir, 1993).

The chemistry of this extraction is based upon the Walkley-Black reaction shown in Equation 2.2 below.

$$2\ Cr_2O_7^{2-} + 3\ C^0 + 16\ H^+ \leftrightarrow 4\ Cr^{3+} + 3\ CO_2 + 8\ H_2O \qquad \text{(Eqn 2.2)}$$

The Walkley-Black procedure is widely used because it is simple, rapid, and has minimal equipment needs (Nelson and Sommers, 1996). The sample and extraction solutions are gently boiled at 150°C for 30 minutes, allowed to cool, and then water is added to halt the reaction. The addition of heat to the system leads to a complete digestion of the organic carbon in the sample; therefore**,** no correction factor is needed (Charles and Simmons, 1986). The characterization of sulphur in coals in relation with its organic content is much recent than the determination of inorganic compounds. However, coal characterisation is still an interesting area as its utilization remains challenging. Enhancing knowledge on coal, its processing and waste could lead to other interesting hints on coal science (e.g. new features, products and technology, etc).

2.3 ORIGIN OF SULPHUR IN COAL

The presence of sulphur in coal is generally originated from parent plant composition. Proteins are the main precursors of sulphur. On the other hand, rocks, inorganic compounds in soil which accompany coal in its formation contribute to sulphur presence in coal. The decomposition of sulphur compounds into others (minerals into mercaptans, into sulphides and thiophenes) plays an interesting role in the diversification of sulphur forms in coal. The sulphur cycle as shown in Figure 2 below explains how sulphur is transformed by weathering, microbial processes and industrial activities into various species.

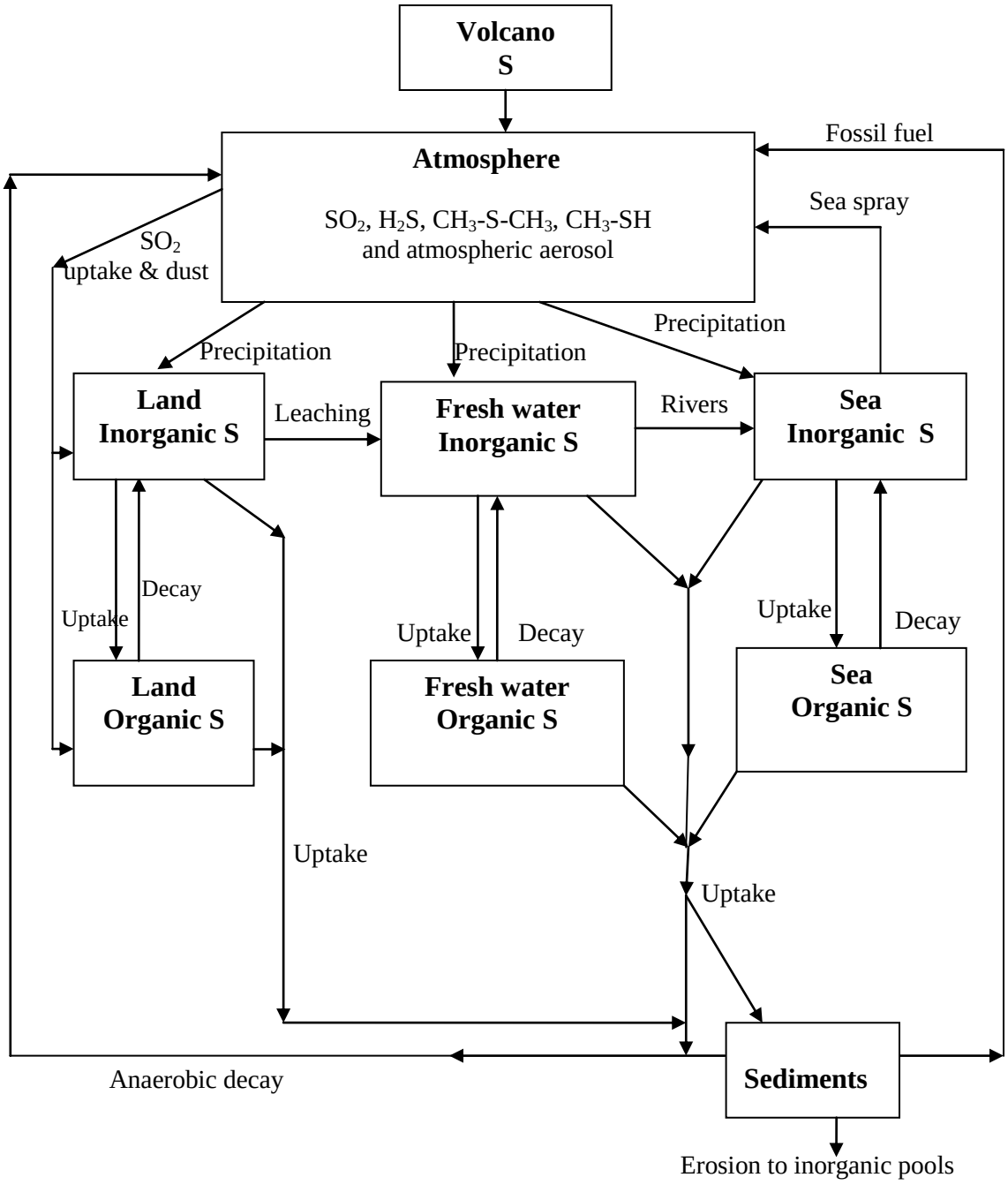


Figure 2: Sulphur cycle in nature

When sulphur dioxide enters the atmosphere it will react with oxygen to produce sulphur trioxide gas (SO_3) or with other chemicals in the atmosphere, to produce sulphur salts. Sulphur dioxide may also react with water to produce sulphuric acid (H_2SO_4). Sulphur acid may also be produced from organic compounds such as dimethyl sulphide, which is emitted to the atmosphere by plankton species. All particles made of sulphur will settle back onto earth or react with rain and fall back onto earth as acid deposition. The particles will then be absorbed by plants again and are released back into the atmosphere, so that the sulphur cycle will start over again.

Sulphur is absorbed by plants via the roots from soil as sulphate ion and reduced to sulphide before it is incorporated into cysteine and other organic sulphur compounds. Sulphur is regarded as a secondary nutrient although plant requirements for sulphur are equal to and sometimes exceed those for phosphorus. However sulphur is recognized as one of the major nutrients essential for growth, root nodule formation of legumes and plants protection mechanisms. Like nitrogen, carbon and phosphorus, sulphur passes through the gaseous, liquid, and solid parts of the planet in a series of continuous reactions known as the sulphur cycle. When plants and animals die, sulphur is returned to the soil where it is converted by microorganisms into hydrogen sulphide. Hydrogen sulphide gas is then emitted to the atmosphere where it is oxidized to sulphuric acid.

2.4 FORMS OF SULPHUR IN COAL

2.4.1 Total sulphur

The total sulphur is the sum of all forms of sulphur encountered in coal. They are influenced by many factors such as parent plant which generated coal, the rocks and minerals involved in coal formation and coal basin. There are several methods for determination of the total sulphur in coal; some have been explained in the next chapter. The determination of the forms of sulphur allows the verification of the total sulphur in all coal samples and provides information on sulphur species. The amount of the total sulphur should be consistent with the sum of sulphur in various forms investigated (Laban and Atkin, 2000). Total sulphur content in coal varies from 0.3 up to 15% by weight according to the rank and the genesis of coal. The average sulphur content of South African coal is generally less than or equal to 1% by weight (Gonenc *et al.*, 1990). Hsieh and Wert (1985) have reported that the total sulphur in coal ranges from 0.59-9.45%. Olivella *et al.* (2002) reported a range of 5.4-15.1 %. South African coals have been reported to contain the total sulphur having a value of 0.40-1.29 % and 1.47% by Wagner and Hlatshwayo (2005) and Roberts (2008) respectively.

2.4.2 Elemental sulphur

Sulphur as an element is more reactive than oxygen. It can react with itself to form -S-S-bonds and it is photosensitive. Elemental sulphur contains a variety of allotropic forms of sulphur as elements. Many allotropic forms can be attributed to sulphur but the most important are rhombic and monoclinic. Natural sources of elemental sulphur are mainly volcanic eruptions,

evaporation from water, bacterial processes and decaying. In coal, elemental sulphur is mainly due to decaying organisms and bacterial process. Gryglewicz and Gryglewicz (2001) are reported to have quantified the elemental sulphur in coal samples after extraction using cyclohexane on Soxhlet apparatus and subsequent quantitative analysis on Gas chromatograph-Mass spectrometer (GC/MS). 0.111 % of elemental sulphur was obtained.

2.4.3 Organic sulphur compounds in coal

Organic sulphur species present in coal depend upon the degree of biochemical change of peat (accumulation of partially decayed vegetation matter), the temperature, pressure and the mineral forms involved in the coal formation (Meyers, 1982; Selsbo, 1996). Organic sulphur compounds are generally grouped into thiophenes, mercaptans and sulphides. Table 3 shows the major organic sulphur compounds encountered in coal. Thiophene forms are almost well known than other forms (Xu *et al*., 1995; Harker and Backhurst, 1981; Meyers, 1982). Some organic sulphur compounds are also formed during condensation, rearranging and concerted reactions during coalification. Others are also formed as a result of biochemical reactions in living systems and the conversion between organic sulphur forms is mainly due to microorganisms (Kroschwitz and Grant, 1991; Gonenc *et al.*, 1990). Beside those occurrences, some complex sulphur compounds are formed at the surface of metals when coal is leached. These sulphur compounds form the layers called self assembled compounds which can be mono or multi-layers (Kroschwitz and Grant, 1993; Wilson *et al.*, 2000). Microbes in coal can degrade some organic sulphur compounds such as dibenzothiophene to sulphate. An example of this is *Thiobacillus, Sulfolobus, Acinobacter* and *Pseudomonas CB1* that can remove about 25 % of both inorganic and organic sulphur compounds (Baird,

1995). These microbes can be used to remediate coal as part of biotechnology now seen as clean environmental technology.

The sulphur compounds in coal are generally transformed from one form to the other during coal processing. Such conversions results in the production of sulphide dioxide responsible for acid rain and global warming. The number and abundance of cyclic organic sulphur compounds increases with the maturity level of coal while the aliphatic sulphide and mercaptan forms decrease (Meyers, 1982). All types of organic sulphur compounds can be identified in coals but their abundance differs from one coal to another. Hsieh and Wert (1985) and Olivella *et al.* (2002) have respectively determined the percentage composition of the organic sulfur in USA from 0.46-4.3 % and 2.7-12.2 %. Literature data showed that South African Reference Materials (SARM 18, SARM 19, SARM 20) have respectively an average organic sulphur content of 4252, 3181 and 1474 mg kg^{-1} (Laban and Atkin, 2000).

Table 3: Organic sulphur forms in coal

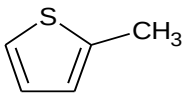
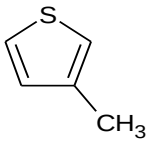
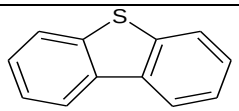
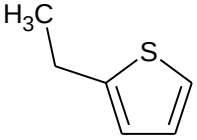
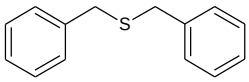
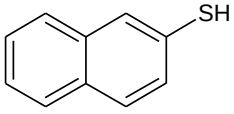
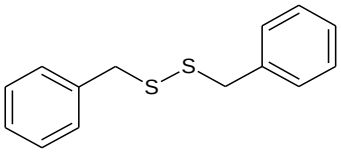
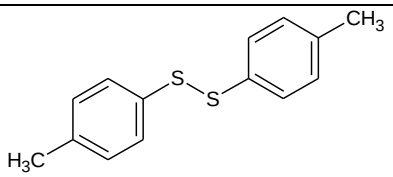
Organic Sulfur form	Sulphur compound	Structure	Physical properties (^{o}C)		Bond dissociation energies (kJmol^{-1})	
			MP	BP	C-S	S-S
Thiophene	2-Methyl thiophene		-63	113		
	3-Methyl thiophene		-69	114		
	Dibenzothiophene		97	332	309	
	2-Ethyl thiophene			133		
Sulfide	Dibenzyl sulfide		49		258.2	
Mercaptan	Methylthiol		-123	5.95		
	2-Naphthalene thiol		80-81	92-94	297.7	

Table 3: Organic sulphur forms in coal (continued)

Organic Sulfur form	Sulphur compound	Structure	Physical properties (^oC)		Bond dissociation energies ($kJmol^{-1}$)	
			MP	BP	C-S	S-S
Disulfide	Dibenzyl disulfide		70	270	266.8	277.9
	p-tolyl disulfide		45	350	311.8	275.8

2.4.4 Inorganic sulphur compounds

Inorganic compounds constitute the major ash content in coal. They are intimately mixed with organic compounds in their matrix. They are also the sources of carbon dioxide and sulphur dioxide emitted during coal processing and usage. Pyritic, sulphate and silicate forms are the main inorganic sulphur forms encountered in coal. They are almost well defined compared to organic forms (Meyers, 1982). In any studies of organic sulphur compounds in coal, inorganic forms are also determined (Laban and Atkin, 2000; Selsbo, 1996). This is because of the inter relationships between various sulphur forms and to set a complete picture. Inorganic sulphur forms are mainly determined in coals as sulphatic and pyritic forms. Sulphate form can be more abundant than pyrite or vice versa according to coal genesis and properties. A study of organic

sulphur compounds in coals by Hsieh and Wert (1985) found 1.5 % of sulphatic sulphur and 3.9 % of pyritic sulphur. SARM 18, SARM 19, SARM 20 which are South African coal reference materials have been reported to contain respectively 481 $mg\ kg^{-1}$, 4267 $mg\ kg^{-1}$ and 1063 $mg\ kg^{-1}$ of sulphate sulphur and 835 $mg\ kg^{-1}$, 7788 $mg\ kg^{-1}$, 2770 $mg\ kg^{-1}$ of pyrite sulphur (Laban and Atkin, 2000).

2.5 ENVIRONMENTAL EFFECTS OF SULPHUR COMPOUNDS IN COAL

Coal burnt by industry and power plants generates sulphur dioxide (SO_2) which reacts with atmospheric water and oxygen to produce sulphuric acid (H_2SO_4). Sulphuric acid is a component of acid rain, which lowers the pH of soil and freshwater bodies, sometimes resulting in substantial damage to the environment and chemical weathering of statues and structures.

The oxidation of pyrite and other reduced-sulphur minerals that occur in coal and metal mines and their wastes can cause the acidification of surface water or groundwater. Therefore metals can be liberated from their ores and be more available. This increases their toxicity which enhances the possibility of metals entering the food chain. Lime addition can allow the control of pH (by neutralization for example) (Akcil and Koldas, 2006). Equations 2.3 to 2.6 show the generation of Acid Mine Drainage (AMD). More protons (H^+) are created and induce the acidification of water enabling the leaching of metals.

The speciation of sulphur in the whole sulphur content system is dependant upon many parameters. To ease the understanding of sulphur species occurrence, the Pourbaix diagram of sulphur species in water is used. This gives boundaries between species according to the environmental conditions.

The Pourbaix diagram (Figure 3) shows the dominating species at equilibrium in different redox potential and acidity. Whereas the pH (x-axis) measures the relative acidity (or hydrogen ion concentration [H^+]) of a solution, the redox potential (E in volt; y-axis) is a measure of the tendency to accept or release electrons. An increase in oxygen pressure means higher oxidizing ability (or higher redox potential) of the system (Stumm 1996). At very reducing conditions or in the absence of oxygen, the elemental sulphur is the most stable sulphur form. It will therefore be the most predominant, but if iron ions are present, they will form pyrite which might coexist with elemental sulphur. At very aerated condition, toward the surface of water, sulphur does exist in its oxidised forms and compounds in which sulphur has its highest oxidation stage. These forms are more stable and therefore likely to occur in that region. On the other hand, the more protonated is the sulphur ion the more acidic is the compound. Thus it is most stable and likely to occur at lower pH. This is justified by the occurrence of H_2S, HS and S^{-2} in various regions on the diagram shown in Figure 3. Organic sulphur compounds might also be stable in some of the conditions above depending on the oxidation state of sulphur they contain. However, their acidity is relatively low because of the weak or absence of H-S bond apart from mercaptans.

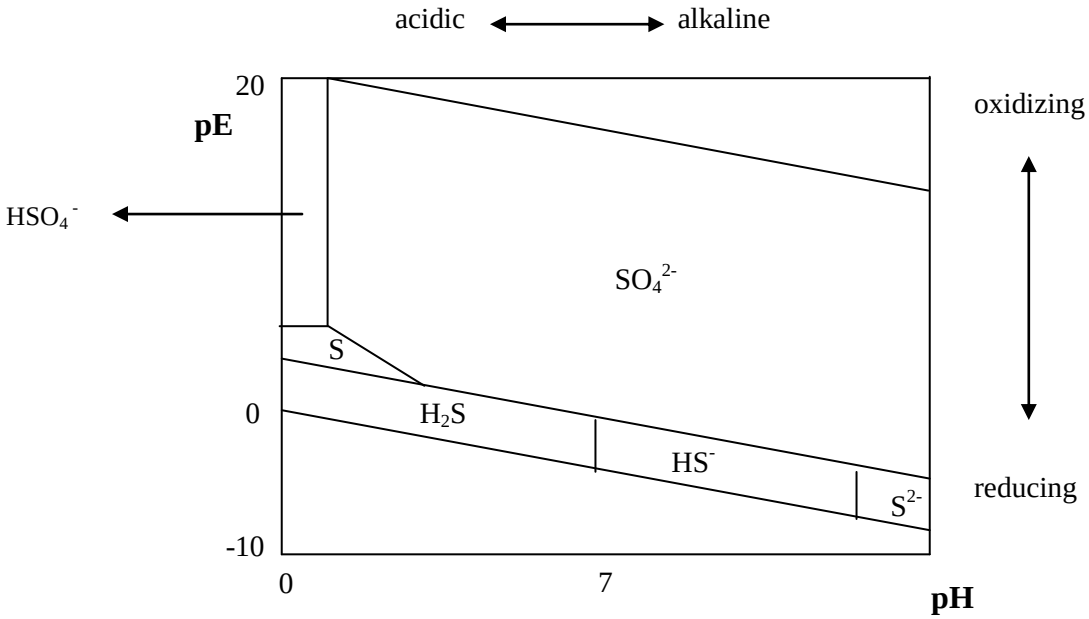


Figure 3: Pourbaix diagram of sulphur species in water

Equations responsible for AMD generation are summarized below.

$2FeS_2+7O_2+2H_2O \longrightarrow 2Fe^{2+} +4SO_4^{2-} +4H^+$ (Eqn 2.3)

$4Fe^{2+} +O_2+4H^+ \longrightarrow 4Fe^{3+} +2H_2O$ (Eqn 2.4)

$4Fe^{3+} +12H_2O \longrightarrow 4Fe(OH)_3 + 12H^+$ (Eqn 2.5)

$FeS_2+14Fe^{3+} +8H_2O \longrightarrow 15Fe^{2+} +2SO_4^{2-} +16H^+$ (Eqn 2.6)

The release of protons in AMD creates massive leaching of metals which will then affect the environment. Sulphuric acid generated due to oxidation of FeS_2 results into Acid Rain Drainage (ARD). The acidic environment results into possible mobilisation of metals. In the stratosphere, photochemical oxidation mostly produces sulphur dioxide as does volcanic activity, and ultimately sulphate anion, which is an important component of the stratospheric aerosol.

Sulphur compounds in the stratosphere take part in other chemical processes having various environmental consequences (VanLoon and Duffy, 2005).

2.6 EXTRACTION TECHNIQUES OF SULPHUR COMPOUNDS IN COAL

2.6.1 Supercritical fluid extraction

Supercritical Fluid Extraction (SFE) is the process of separating one component (the extractant) from another (the matrix) using supercritical fluids as the extracting solvent. Extraction is usually from a solid matrix, but can also be from liquids. Several supercritical fluids can be used as extraction solvents. Carbon dioxide (CO_2) is the most commonly used supercritical fluid, sometimes modified by co-solvents such as ethanol or methanol (McHugh and Krukonis, 1994). SFE is suitable for extraction of organic sulphur in coals. The system must contain a pump for the CO_2, a pressure cell to contain the sample, a means of maintaining pressure in the system and a collecting vessel. The liquid is pumped to a heating zone, where it is heated to supercritical conditions. It then passes into the extraction vessel, where it rapidly diffuses into the solid matrix and dissolves the material to be extracted. The dissolved material is swept from the extraction cell into a separator at lower pressure, and the extracted material settles out. The CO_2 can then be cooled, re-compressed and recycled, or discharged to atmosphere (McHugh and Krukonis, 1994). The schematic of SFE instrument is shown in Figure 4.

SFE is simply performed by pumping the supercritical fluid (SF) through a vessel filled with sample, and further down the line depressurized the SF for collection of extracted components. Hence, a SF instrument consists of one or two high-pressure pumps for delivery of SF and if necessary also a polar

cosolvent such as ethanol, a high-pressure vessel for holding the sample, a restrictor and a collection device such as empty vessel or glass tube containing a collection solvent. The sample vessel is placed in an oven for control of the extraction temperature. The pressure and temperature of SF, the sample matrix, the extraction time, flow rate, the type and amount of solvent to add and the mode of collection are the major parameters taken into account when developing a method for SFE (Turner, 2006).

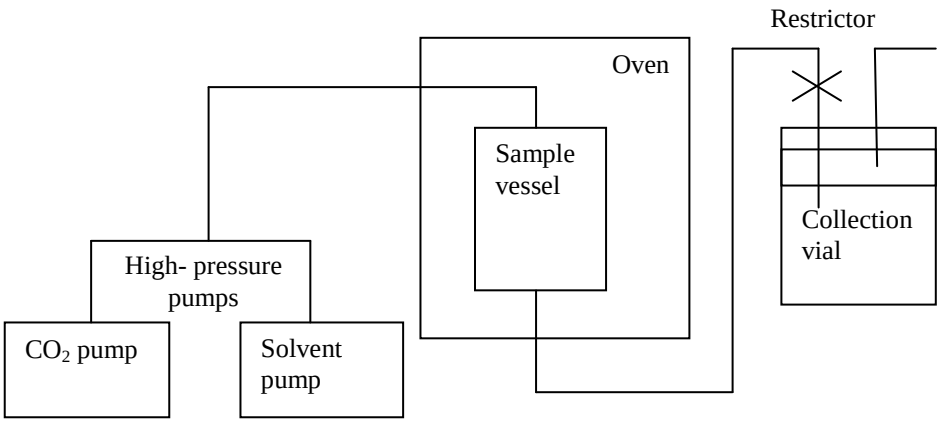


Figure 4: Schematic of a SFE instrument

SFE advantages consist in the fact that the system is an alternative to liquid extraction using solvents such as hexane or dichloromethane. These solvents are later thrown away since only a small volume is analysed. Carbon dioxide is easy to find as it is a by-product of industrial processes or brewing and its use in SFE does not cause any extra emissions (McHugh and Krukonis, 1994). It is easy to remove simply by reducing the pressure, leaving almost no trace. Purchased CO_2 has almost always been reclaimed, which reduces the total carbon foot-print. The properties of a supercritical fluid can be altered by varying the pressure and temperature, allowing selective extraction **(**Tanaka

and Takeshi, 2004**).** Extraction is a diffusion-based process, with the solvent required to diffuse into the matrix, and the extracted material to diffuse out of the matrix into the solvent. Diffusivities are much faster in supercritical fluids than in liquids, and therefore extraction can occur faster. Also, there is no surface tension and viscosities are much lower than in liquids, so the solvent can penetrate into small pores within the matrix inaccessible to liquids. Both the higher diffusivity and lower viscosity significantly increase the speed of the extraction. An extraction using an organic liquid may take several hours, whereas supercritical fluid extraction can be completed in 10 to 60 minutes **(**Skoog *et al.*, 2007).

Despite the above advantages, SFE has few limitations too. The requirement for high pressures increases the cost compared to the advantages of this technique. Carbon dioxide itself is non-polar, and has somewhat limited dissolving power, compared to conventional liquid extraction, particularly for polar solutes. The use of modifiers increases the range of materials which can be extracted (McHugh and Krukonis, 1994).

Supercritical fluid extraction technique was first applied to coal liquefaction by the National Coal Board of England about 20 years ago. The extraction of coals under pyrolysis conditions using supercritical solvents has been studied since then due to its unique characteristics, such as high extraction rate and easy solid-liquid separation, despite its relatively low extract yields (Sakaki et al,1994).

Gryglewicz *et al.*, (2002) is reported to have extracted organic sulphur compounds in coal using SFE. The range of the extraction yield was 11.4 - 39.9 wt. % depending on the type of solvent and coal. Pure toluene, toluene/2-propanol and toluene/tetrahydrofurane mixtures were used as solvents for SFE at 360°C and 10 MPa in an apparatus with continuous flow of solvent. The organic sulphur content in the extract ranged from 2.17 - 3.70 wt. %.

Gryglewicz *et al.*, (2004) used SFE and Pyrolysis-MS to determine organic sulphur functionalities in three Polish coals of different ranks using a mixture of solvents. The atmospheric pressure - temperature programmed reduction technique coupled with potentiometric detection of H_2S (AP-TPR) and mass spectrometry (AP-TPR-MS) were applied to monitor the sulphur-containing compounds which are reduced during pyrolysis to hydrogen sulphide at specific and discrete temperature intervals. The range sulphur recovered was 23 to 65 %. Results showed that thiols, polysulfides, and/or elemental sulphur gave the highest contribution to the detectable sulphur in supercritical extracts by AP-TPR. Thiophenes forms have mostly been detected in highest ranks of coal.

Steven *et al.*, (1992) developed the use of SFE and Pyrolysis/SFE then GC/MS for selective extraction, identification and quantification of organic sulphur forms in coal. The total sulphur was found in the range of 3.27 ─ 3.44 % while sulphate, pyrite and organic forms were respectively 0.07 ─ 0.67, 0.42─1.86 and 0.98 ─ 3.24 %.

2.6.2 Ultrasonic bath extraction

Ultrasonic instruments take standard alternating current frequency and magnify it from 50 or 60 Hz (cycles per second). Standard laboratory ultrasonic instruments run at 20,000 to 23,000 Hz (i.e., 20-23 kHz). The instrument converts incoming electrical current to a high frequency current which is then used to stimulate the piezoelectric crystals. The crystals are attached to either a probe that can be immersed into a liquid or to a pan as with ultrasonic water baths. In either case, the oscillating crystals impart vibrational energy into the

liquid. Ultrasonic probes and baths oscillate up and down at 20,000 cycles per second though the amplitude of the oscillation is very short. A typical oscillation involves a contraction when the electrical current is applied and an expansion when the current is reversed. When the probe contracts, negative pressure causes the liquid to flow up with the probe while the expansion of the crystals pushes the liquid. At a rate of 20 kHz, the liquid turns into a zone of microscopic shockwaves. One consequence of high power output focused in the tip of a probe is that sonication can rapidly generate substantial heat. A few second burst of a sonicator probe can cause water to boil. Consequently, when heat labile samples are processed, they must be kept cold and the sonication must be done in short burst interspersed with cooling periods (OPS Diagnostics, 2007).

It is well known that ultrasonic irradiation can significantly improve the reaction efficiency in chemical synthesis, mainly due to cavitation when mechanical vibrations are produced and transmitted into the liquid as ultrasonic waves. This phenomenon involves the formation, growth and implosive collapse of bubbles in liquids irradiated with high intensity ultrasound, creating shock waves, providing a unique set of conditions to promote chemical reactions and thus increasing the chemical reactivity in such systems (Mason and Lorimer, 2002; Suslick *et al.*, 1999).

Ultrasonic extraction may not be as rigorous a method as other extraction methods for soils/solids. Therefore, it is critical that this method be followed explicitly (including the manufacturer's instructions) to achieve the maximum extraction efficiency (EPA 3550c, 2007). Figure 5 below shows the ultrasonication instrument. The technique is suitable for extraction of organic sulphur compounds in coal. However, because of volatility of some organic sulphur compounds, temperature control is important.



Figure 5: Ultrasonic system closed (a) and opened showing water bath (b)

2.6.3 Microwave assisted extraction

Microwave assisted extraction (MAE) is an extraction technique in which the sample and an appropriate solvent or solvent mixture are put in a vessel, which is then pressurized and heated by microwaves thanks to a temperature programme. After allowing the vessel to cool down, the content is removed and filtered prior to the analysis. Many samples can be processed at the same time and the heating of solvents is very fast and depends upon the microwave energy absorbed in MAE. Properties of solvents affect the absorption of microwave energy. Microwave absorption increases with the increase of polarity of solvents. In order to obtain good heating properties, the mixture of solvents is recommended (Turner, 2006). Figure 6 below gives a schematic of MAE instrument while Figure 7 shows the microwave system.

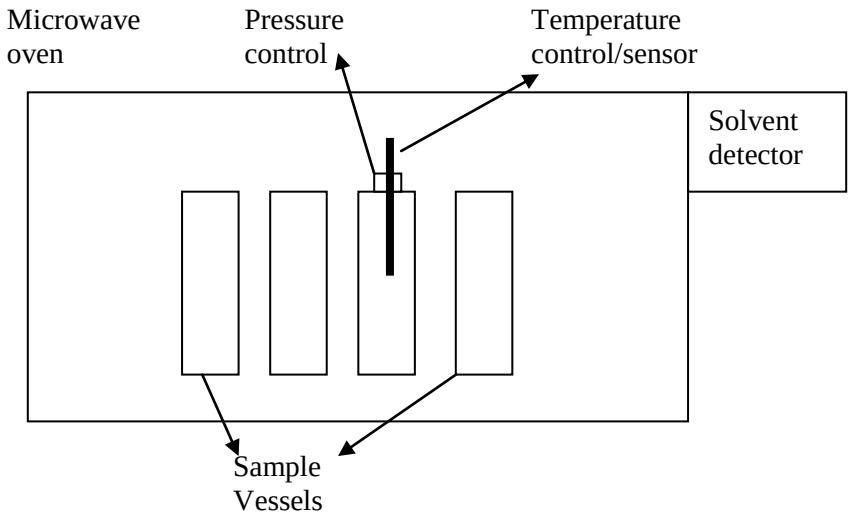


Figure 6: Schematic of MAE instrument



Figure 7: Microwave system (a) closed and (b) opened

MAE can be used for both extractions of organic and inorganic sulphur compounds in coals. This is dependent upon the extraction solvents. For inorganic sulphur extraction, acids are used as extractants while organic solvents are used for organic sulphur extraction. Laban and Atkin, (2000) determined quantitatively the three main forms of sulphur in bituminous and

sub-bituminous coals using different level of acid concentration in microwave oven. The organic sulphur form was determined in the residue obtained after removing sulphate and pyrite sulphur forms from coal. The extract solutions from each stage were rapidly analysed for sulphur using ICP - AES. The sums of the three forms of sulphur have shown consistent agreement with certified total sulphur data for most of the coals studied by Laban and Atkin (2000). Significant time savings are achievable over some of the standard techniques demonstrating the suitability of the method for routine analyses. The sulphate, pyrite, organic and total sulphur concentration in coals obtained by Laban and Atkin (2000) were respectively in the range of 0.05-1.40, 0.08-1.13, 0.15-1.99 and 0.51-4.53% (Values which are 10^4 times mg kg^{-1}).

2.7 PYROLYSIS

Pyrolysis is defined as a thermal degradation of materials in an inert atmosphere. Most coals decompose below temperatures of about 400 ^oC. Heating beyond 900 ^oC results in minor additional weight losses but the solid matter changes its structure. Figure 8 shows a schematic of pyrolysis system. In general, the sulphur pyrolysis products are mostly inorganic than organic. Laboratory scale pyrolysis is used for the chemical characterization of material by qualitative and quantitative analysis of the pyrolysis products. At higher pyrolysis temperatures secondary reactions increase and smaller, less characteristic fragments are formed (Selsbo, 1996; Kroschwitz and Grant, 1993). A well defined and reproducible procedure allows better characterization of products and a predictive decomposition model of a macromolecular network can be built based on the results of analytic measurements.

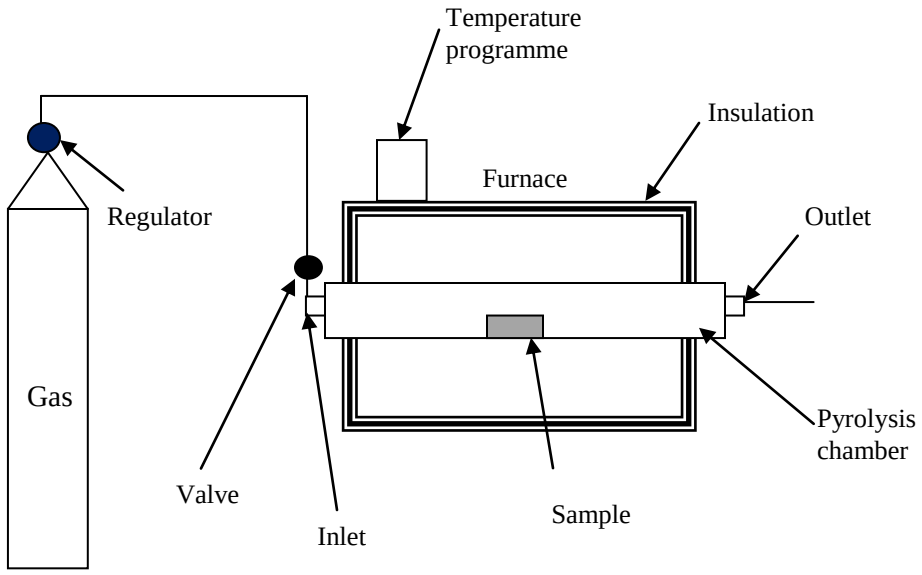


Figure 8: Schematic of pyrolysis system

There are different pyrolysis operation modes (Selsbo, 1996). These are:

- Continuous mode, in which the sample is maintained at the Pyrolysis temperature in a continuously heated furnace (furnace pyrolyzer). This type consumes long time and gives secondary effects;
- The pulse mode pyrolyzers, in which the sample is heated to the pyrolysis temperature on a cold filament.

It has to be noticed that the method assessed in this project was the continuous mode.

Peter *et al.*, (1994) are reported to have used a combination of pyrolysis and SFE for the determination of sulphur compounds in bituminous coals. Coals had total sulphur concentration of 4.3 % which was characterised by Pyrolysis-SFE, at 450°C. CO_2 modified with methanol could remove more organic

sulphur forms while acid pre-treatment enhanced the removal of total sulphur as analysed on LECO titrimetric analyser. 60% of total sulphur was extracted by pyrolysis-SFE with CO_2-methanol while 80% of total sulphur was removed when phosphoric acid was used before Pyrolysis-SFE with CO_2. On-line Pyrolysis-SFE-GC-MS allowed the qualitative analysis of organic sulphur compounds. This demonstrated that the major organic forms of sulphur removed were thiophenic. Selsbo *et al.*, (1996) analysed standard European coal samples using pyrolysis-gas chromatography equipped with a flame ionization detector and a flame photometric detector (Py-GC -FID/FPD). The total amount of sulphur in the pyrolysis products was proportional to the sulphur content of the coals. Predictive models for the content of total sulphur, organic sulphur, the inorganic sulphur as a sum of pyritic sulphur and inorganic sulphur were built from the main volatile sulphur – containing products. Those main volatile compounds were H_2S, COS, SO_2 CH_3SH and CS_2.

Maes *et al.*, (1997) used atmospheric-pressure temperature programmed reduction (AP-TPR) to characterize and quantify organic sulphur functionalities in different rank of coals. Sulphur functionality distribution can vary from coal to coal even at the same rank but larger amount of sulphide were found in low-rank coals whilst the amount of thiophenes generally increased with rank. Xu *et al.*, (1995) applied the extremely selectivity of the newly developed ozone-sulphur chemiluminescence detector (SCD) coupled with controlled-temperature pyrolysis for the qualitative and semiquantitative determination of sulphur forms in coal. Several distinct peaks were observed by the SCD, identified as being due to organic sulphur compounds. Pure organic sulphur compounds were spiked as standards which provided semi-quantitative determination. Three coals were examined and could be quickly

and easily distinguished by their sulphur forms. The results were also compared with those of other pyrolysis methods.

2.8 RECOVERY OF EXTRACTION

The recovery is the fraction or percentage of the total quantity of a substance extracted (usually into the organic solvent phase) under specified conditions (IUPAC, 1997). The recovery gives also information about the loss occurred from extraction to analysis. This is well achieved by using spiked standards which are added to the sample. High recovery value is not absolutely required as long as sensitivity and other requirements such as precision and reproducibility are met (Wu, 2001). Mathematically, the recovery can be expressed as:

$$\%R = \frac{ne\ 100}{ns} \qquad \text{(Eqn 2.7)}$$

Where **ne** is the total amount of analyte extracted; **ns** is the total amount of analyte originally present in the extracted sample.

Once the extraction technique is optimised, the recovery is expected to be constant at those conditions. This optimised recovery is then used to determine the amount of analyte in the original sample. The amount in the original sample is calculated from:

$$ns = \frac{ne\ 100}{\%R} \qquad \text{(Eqn 2.8)}$$

2.9 ANALYTICAL TECHNIQUES FOR COAL DETERMINATION

Various methods allow the determination of different sulphur compounds in coal. These methods can be categorised as direct (non destructive) or indirect (destructive) analytical techniques for qualitative and quantitative analysis of sulphur compounds in coals.

2.9.1 Direct methods for sulphur compounds determination in coal

Direct methods for determination of sulphur in coal are non destructive methods based on a study of model sulphur compounds considered as reference (Davidson, 1994; Hsieh and Wert, 1985; Huffman *et al.*, 1995). As direct methods, X-ray absorption and X-ray photoelectron spectroscopy have been employed extensively. Sulphur K-edge X-ray absorption near edge structure spectroscopy (XANES) has been used to characterize and quantify organic sulphur species (George and Gorbaty, 1989; Huffman *et al.*, 1989, 1991; George *et al.*, 1991).

Direct methods involve expensive instrumentation and since the samples are very small, they have to be analyzed to obtain a representative value of the sulphur content of a coal (Selsbo, 1996). Examples of direct techniques are described in the next pages.

X-ray diffraction (XRD)

Diffraction effects are observed when electromagnetic radiation impinges on periodic structures with geometrical variations on the length scale of the

wavelength of the radiation. The interatomic distances in crystals and molecules amount to 0.15–0.4 nm which correspond to the electromagnetic spectrum with the wavelength of x-rays having photon energies between 3 and 8 keV. Accordingly, phenomena like constructive and destructive interference should become observable when crystalline and molecular structures are exposed to x-rays. The ideal sample is homogeneous and the crystals are randomly distributed. There are three different types of interaction in the relevant energy range. In the first one, electrons may be liberated from their bond atomic states in the process of photoionization. A second kind of inelastic scattering that the incoming x-ray beams may undergo is termed Compton scattering. Also in this last process energy is transferred to an electron, which proceeds, however, without releasing the electron from the atom. Finally, x-rays may be scattered elastically by electrons. This last method is named Thomson scattering. In this latter process, the electron oscillates like a Hertz dipole at the frequency of the incoming beam and becomes a source of dipole radiation. It is the Thomson component in the scattering of x-rays that is made use of in structural investigations by x-ray diffraction (Birkholz, 2006).

Querol *et al.*, (1993) reported to have analyzed pyritic sulphur in subbituminus coals with XRD by oxidizing iron sulphide after ashing coal samples at 750 °C. The values of this form of sulphur in these high sulphur coal samples were found in the range of 0.86-6.75 % in those high sulphur coals.

X-ray photoelectron spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) is a typical surface analysis technique with a sampling volume that extends from the surface to a depth of approximately 50-70 Angstroms and is often applied to quantitative

determination of atomic composition and chemistry of samples. XPS, also known as Electron Spectroscopy for Chemical Analysis (ESCA), can also be utilized for sputter depth profiling for the characterisation of thin films by quantifying matrix-level elements as a function of depth. ESCA process works by focusing monochromatized X-rays on the specimens under ultra high vacuum (UHV) which then produces photoelectrons varying in intensity and kinetic energy. Individual elements within the sample under analysis produces unique characteristic XPS lines corresponding to that particular element. The intensity and position of which determine the concentration and local chemistry or bonding environments of the atom detected (Schweitzer *et al*., 2008). Thus basically ESCA is an elemental analysis technique that is unique in providing chemical state information of the detected elements, for instance, the sulphur 2p line can show as much as 7eV chemical shift between sulphur in a disulfide environment (S^{2-}) and one in a sulphate (SO_4^{2-}) environment (S^{6+}) (Schweitzer, *et al.*, 2008). Therefore this method can distinguish between the oxidised and reduced forms of elements. ESCA is a highly sensitive and a direct method used to confirm the presence of elements identified in other methods like Energy Dispersive X-ray (EDX). It also helps to identify unambiguously even light elements and their bonding environment such as nitrogen, which are not detectable or quantifiable by other methods like EDX (Schweitzer *et al.*, 2008). Hence this method is an exceptional complement to other methods. Therefore ESCA can also distinguish between organic sulphur in bonding environments and those derived from inorganic sedimentary sulphur among other elements (Schweitzer *et al.*, 1999).

Kelemen *et al.*, (1990) are reported to have used XPS to analyse the organically bound form of sulphur. The results showed that organic sulphur

species dominated the XPS sulphur 2p spectrum of fresh Illinois No. 6 coal and that about two-thirds of the surface organic sulphur existed as thiophenes.

X-ray absorption near edge structure (XANES)

X-ray Absorption Near Edge Structure (XANES) is a type of absorption spectroscopy. XANES data indicate the absorption peaks due to the photoabsorption cross section in the X-ray Absorption Spectra (XAS) observed in the energy region, extending over a range of about 100 eV, between the edge region and the Extended X-Ray Absorption Fine Structure (EXAFS) region. XANES is also known as NEXAFS (Near Edge X-ray Absorption Fine Structure) when applied to surface and molecular science. XANES has to be distinguished from edge and EXAFS spectroscopy. The first difference concerns the energy range above the absorption edge. XANES has been extensively used for the investigation of all forms of sulphur. It has been found that the broad so-called "white-line" absorption spectrum, which arises from the sulphur 1s to sulphur 3p electronic transition, can be correlated with major organic functional groups such as sulphide, thiophene, sulphoxide and sulphone. In order to resolve different functional groups in sulphur, Huffman *et al.,* (1995) have used least squares fitting while George *et al.*, (1991) are reported to have employed third derivative analysis methods. Sulphur 2p core level photoelectron spectra have also been used by several groups to identify and quantify organic sulphur forms in coal (Frost *et al.*, 1978; Boudou *et al.*, 1987; Hittle *et al.*, 1993). Kasrai *et al.,* (1996*)* characterized sulphur in coal (with uniform samples) from XANES. Various structures of several inorganic and organic sulphur model compounds were observed in the sulphur from L-edge XANES using available theoretical calculations. Pyrite, elemental sulphur or alkyl disulphide could be resolved visually from alkyl and aryl sulphides.

Sulphides could be distinguished from thiophenic sulphur, and sulphoxide could be distinguished from reduced sulphur forms. The characterization of some organic sulphur in investigated coals could be established (Kasrai *et al.*, 1996). The oxidation of investigated coal in air was investigated from 50 to 200°C. It was found that organic sulphur began to oxidize at 160°C but more rapidly at 200°C. The predominant products were sulphonic acid and sulphate and unlike XPS and the S K-edge XANES, the spectra are not only sensitive to S functional groups but also to slight changes in the substitutions within a functional group. This sensitivity has advantages for chemical fingerprint purposes, but it also has created difficulties in obtaining excellent fits of the coal spectra (Kasrai *et al.*, 1996).

X-ray emission spectroscopy (XRES)

In XRES, the characteristic X-ray photons used for analysis are the ones that arise from transitions between inner electron energy levels in atoms. To generate characteristic emission, the atom must first be ionized the K, L, or M shells. Ionization may be accomplished by any photon or particle whose energy exceeds the binding energy of the electrons in the particular shell. After ionization, the X-ray line emission occurs when the electron vacancy is filled by an electron from one of the outer shells. The energy, *E*, of the characteristic photon is equal to the difference in the binding energies between the two electron levels involved in the transition. Lines are called *K series* lines if the initial ionization is in the K shell, *L series* lines if it is in the L shell and so on **(**Takeshi *et al.*, 1998).

XRES can also be used to determine organic sulphur in coal, usually in an electron microprobe or an SEM. The K_{α} X- ray line of sulphur emitted when

electrons or other charged particles strike a coal specimen is measured using either crystal-dispersive detectors or energy-dispersive detectors. The intensity of the line is proportional to the sulphur content. This is then quantified after the system is calibrated using a standard sample of known sulphur concentration (Valkovic, 1983). Hsieh and Wert (1985) are reported to have studied the organic sulphur content in coals using X-ray emission parameters relatively to the nature of the counting system, operating conditions of the microscope and the geometrical arrangement of the specimen and detector. The range of organic sulphur content in coal samples was 3.3 to 5.2 %.

Energy dispersive X-ray spectroscopy with scanning electron microscopy (EDX-SEM)

Electron microscopy technique is an interdisciplinary technology extensively applied in various disciplines of science. Currently, scanning electron microscopes (SEM) has become the basic measuring and research tool. This is common where the state of the surface and its morphology estimation are needed (Kowalewska and Szwedo, 2009). SEM allows the examination and characterization of both heterogeneous organic and inorganic materials on a nanometer (nm) to micrometer (μm) scale. The popularity of the SEM results from its ability to give 3-dimesional images of a wide range of materials. SEM operates in a similar way to a traditional light microscope.

Light microscopes use wavelength of visible light (400-700 nm) to resolve images whilst a SEM utilizes electron source to resolve images, instead of a source of photons (Goldstein *et al.*, 2003). Hsieh and Wert (1985) used conventional transmission electron microscope (TEM) equipped with an ancillary Si (Li) detector for X-ray spectroscopy to determine the organic

sulphur concentration in various coals. The concentration of organic sulphur form in investigated coals was in the range of 0.46 to 4.3 %. Very small amount of coal has been utilized and the average concentration of organic sulphur was in the range of the one determined by conventional methods which used grams of material. Variation of sulphur forms could also be determined and very low concentration of organic sulphur was measured adequately.

2.9.2 Indirect analytical methods

Indirect analytical methods are essentially based upon chromatographic methods. The most common analytical instrument is a gas chromatograph.

Gas chromatography (GC)

In GC, the liquid or gas prepared samples are injected manually or automatically via the injection port. The injection port is heated to allow the sample evaporation and is introduced into the column using carrier gas (Figure 9). Syringes and autosamplers are respectively used to introduce manually or automatically a known volume (0.1-10 µl for liquid or 0.1-10 ml for gas samples) of a liquid or gas sample through the inlet. The carrier gas allows the sample to be carried from the inlet through the column where each compounds will have to migrate specifically to the detector according to their retention factor. The intensity of peaks detected is processed by incorporated software and the chromatogram is plotted on the screen with all relative measurements such as peak area and/or height. Retention time of the peaks is dependent on

the type of column, carrier gas, flow rate and oven temperature. The peak area obtained is proportional to the concentration of analyte in the sample.

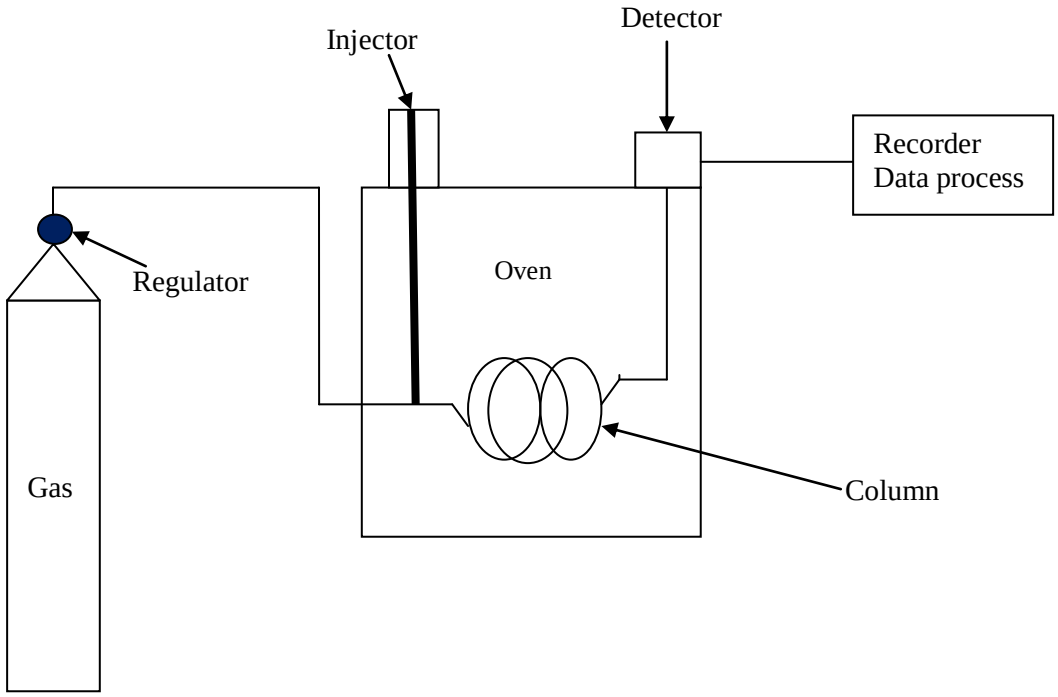


Figure 9: Schematic of GC analysis

Columns are defined as the heart of all chromatographic techniques in which the separation occurs. They can be packed or open tubular (capillary). Capillary columns are 10 to 100 m length and 0.1 to 0.5 mm internal diameter (ID). Development of fused-silica capillary columns has provided more neutral material facilitating trace sulphur analysis (Wardencki, 1998). Due to its very good separation capability especially with capillary columns, GC is most frequently used for determination of volatile and semi-volatile compounds in different matrices like organic sulphur compounds.

Flame ionisation detector (FID) and flame photometric detector (FPD) can be used as detectors to identify sulphur compounds. In literature, FPD atomic

emission detector (AED) and sulphur chemiluminescence detector (SCD) have proven to be the most selective for sulphur analyis. SCD is a two stage detection method in which the sample is reduced in air and hydrogen under vacuum to generate sulphur monoxide. The sulphur monoxide is then carried to a reaction chamber where it reacts with ozone to generate sulphur dioxide and light. The light generated is measured by a photomultiplier tube. The signal generated is linearly proportional to the quantity of sulphur in the sample.

The advantages of SCD are equimolar response to all sulphurs, linearity from ppb to percent concentrations, sulphur specific, no known interferences, not subject to quenching from hydrocarbons, and the use of single component standard for calibration, low hydrogen consumption, and no nuclear / X-ray source (Galvanic applied sciences inc. at http://www.galvanic.com).

Inductively coupled plasma - Optical emission spectrometry

In Inductively coupled plasma - Optical emission spectrometry, Inductively coupled plasma - Optical emission spectrometer (ICP-OES) is used to measure selected major and trace elements in liquid samples and leachates. Ultra high purity gases such as argon are used as carrier gas. The liquid sample is nebulized and fed into the plasma as an aerosol. The high temperature of the plasma (6000-8000 K) evaporates the sample. The molecules contained in the sample dissociate into atoms which are excited and partly ionized. The exited atoms and ions emit an-element specific radiation. A transfer optic feeds this radiation into the optical system. The optical radiation is diffracted into its spectral components in the optical system with an intensity which is measured by semiconductor detectors and processed by incorporated software. Radiation emitted from excited atoms/ions is measured. Each excited radiation

wavelength is specific for a given element. Thus ICP-OES is used to measure the total sulphur in the sample extract analysed. Calibrations for selected elements have to be set prior to measurement. The intensity of the emitted radiation is proportional to the concentration of the element in the sample. Figure 10 below is the schematic of ICP-OES.

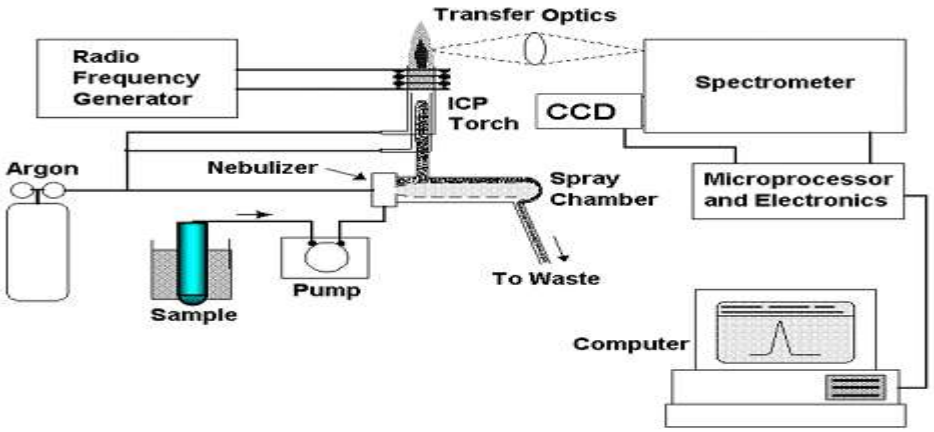


Figure 10: Schematic of ICP- OES (Arcinus, 2000)

CHAPTER THREE: RESEARCH METHODOLOGY

This section of the project presents the methods used from coal sampling to the analysis and identification of target compounds. Coal samples were collected from various power stations and prepared for analysis. Microwave assisted extractor (MAE) was used to extract the various sulphur forms while ultrasonic bath was used to extract organic sulphur forms. Gas chromatograph-flame ionisation detector (GC-FID), carbon, hydrogen, nitrogen and sulphur (CHNS) analyser and inductively coupled plasma-optical emission spectrometer (ICP-OES) were used as analytical instruments. The pyrolysis coupled to GC-FID was also used as a preliminary study to characterise organic sulphur compounds. All results were then processed using Excel 2007.

3.1 STUDY AREA

Samples were provided from six South African power stations in Mpumalanga and Free State (Table 6).

3.2 CHEMICALS

The following solvents were used: dichloromethane, methanol, tetrahydofurane, toluene, hexane, pyridine and acetone (Sigma-Aldrich, Johannesburg, South Africa). All sulphur standards were purchased from Sigma - Aldrich (Johannesburg, South Africa). These are dibenzothiophene, 2-ethyl thiophene, 2-methyl thiophene and 3-methyl thiophene. Sulphuric acid, nitric acid, boric acid, hydrogen peroxide, hydrofluoric acid, hydrochloric acid, potassium dichromate, orthophosphoric acid, ferrous sulphate 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. Deionised water was prepared using from Millipore deioniser instrument (Millipore, Massachusetts, USA).

Table 6: South African Power stations where samples were taken

Power plant	**Province**	**Date commissioned**	**Installed Capacity** [Megawatt]	**Status**
Camden Power Station	Mpumalanga	1967	1,600	Operational
Duvha Power Station	Mpumalanga	1980	3,600	Operational
Kriel Power Station	Mpumalanga	not mentioned	3,000	Operational
Lethabo Power Station	Free State	1985	3,708	Operational
Majuba Power Station	Mpumalanga	1996	4,110	Operational
Tutuka Power Station	Mpumalanga	1985	3,654	Operational

3.3 INSTRUMENTS

3.3.1 Ultrasonic bath extractor

ElmaTranssonic 460 (Elma, Singen, Germany) was used for ultrasonic extraction of target organic sulphur compounds from coal samples. The instrument was also used to dissolve boric acid when preparing its solution.

3.3.2 Microwave assisted extraction (MAE)

Anton Paar Multiwave 3000 Solv (SwissLab, Johannesburg, South Africa) was used for the extraction of sulphate, pyrite, organic and total sulphur forms from coal samples.

3.3.3 Centrifuge and vacuum pump

Residues and extracts were separated using MSE Mistral 1000 Centrifuge (MSE, London, UK) for sulphate and pyrite sulphur sequences from MAE. The instrument could accommodate six samples in centrifuge tubes which are provided with their lids. Various solutions were filtered using Millipore vacuum pump with Millipore filter paper type HVLP 0.45µm (Millipore, Massachusetts, USA).

3.3.4 CHNS analyser

A LECO-932 CHNS analyser (LECO Corporation, Michigan, USA) was used to determine the concentration of carbon, hydrogen, nitrogen and sulphur in various coal samples.

3.3.5 Gas chromatograph

The analysis of organic sulphur compounds in various coal samples was done on an Agilent 7890A Gas chromatograph (Agilent technologies, California, USA). The instrument was equipped with Supelco SPB^{TM}-1 Sulphur, fused silica capillary column, 30 m * 0.32 mm * 4.0 µm film thickness (SUPELCO, Pennsylvania, USA) connected to FID detector. A Supelco 5 µL manual syringe SGE (SUPELCO Analytical, Pennsylvania, USA) was used for injection of 1 µL of sample into the GC. The GC- FID used is presented in Figure 11 below.



Figure 12: Agilent 7890A GC- FID system

3.3.6 Inductively coupled plasma-optical emission spectrometer (ICP-OES)

Spectro Genesis End-on-plasma (Spectro analytical instruments (Pty) Ltd, Johannesburg, South Africa) inductively coupled plasma-optical emission spectrometer (ICP-OES) was used to determine sulphur in coal samples (Figure 12). Selected metals were also analysed using the same instrument.



Figure 12: ICP- OES instrument

3.3.7 Other instruments

The following instruments were also used in this project: Analytical balances Furnace Elite TSH15/50/180-241 (Elite Thermal Systems Ltd, Leicestershire, UK), Metler Toledo PB 303 balance (METLER TOLEDO, Zurich, Switzerland), Precisa 180A balance (Delta Laboratory Services, London,

United Kingdom) and deionised water Millipore system (Direct®-Q3UV) with pump (Millipore, Massachusetts, USA).

3.4 PREPARATION OF SOLUTIONS

3.4.1 Solutions for organic carbon determination

Potassium dichromate (1 N) was prepared by weighing 49.035 g of potassium dichromate and dissolving in one litre volumetric flask with deionised water to the mark. Ferrous sulphate (0.5 N) was prepared by dissolving 140 g of Fe_2SO_4 salt in 14 ml of concentrated sulphuric acid diluted with deionised water to the mark in a 1 l volumetric flask. The indicator solution was prepared by dissolving 250 mg of diphenylamine-sulphonate in deionised water in a 100 ml volumetric flask. The solution was made up to the mark with deionised water.

3.4.2 Solutions for MAE

Boric acid (5%) was prepared by dissolving 5 mg of boric acid (H_3BO_3) with deionised water in 100 ml volumetric flask and diluting to the mark. Hydrochloric acid (5 M) was prepared by diluting 430 ml of concentrated HCl (36%) with deionised water to the mark in a 1 l volumetric flask. Nitric acid (2 M) was prepared by diluting 122 ml of the concentrated acid (69%) with deionised water to the mark in a 1 l volumetric flask. 1% BRIJ-35 was prepared by weighing 1g of polyoxyethylene lauryl ether (ethoxylated dodecyl alcohol) and dissolving it with deionised water to the mark in 100 ml volumetric flask.

3.4.3 ICP –OES solutions

The stock solutions of standards used for various elements analysed were initially prepared at 1000 mg l^{-1}. Calibration curves consisting of standard solutions at concentrations of 0.1, 0.2, 0.5 and 1 mg l^{-1} were prepared by diluting stock solution. In case of higher concentration of analyte in the sample solution (whose concentration was higher than calibration), the extract solution was diluted appropriately.

3.4.4 Standards for GC-FID

Standard solutions were prepared from standard sulphur compounds as follow:

- 1000 mg l^{-1} solutions: a 50 ml beaker and a 50 ml volumetric flask were thoroughly cleaned with soap and deionised water and dried. Afterwards, they were rinsed twice with dichloromethane. 50 (± 0.005) mg of dibenzothiophene (DBT) was weighed in the cleaned 50 ml beaker followed by addition of 20 ml of dichloromethane. The solution was gently stirred manually until complete dissolution of DBT. The dissolved solution was transferred into a clean 50 ml volumetric flask which was then filled to the mark with dichloromethane. 1000 mg l^{-1} of other liquid organic sulphur standards (2- methyl thiophene (2-MT), 3-methyl thiophene (3-MT) or 2-ethyl thiophene (2- ET) solutions were prepared in the fumehood by pipetting 50 µl of pure compounds in a

cleaned 50 ml volumetric flask. Each flask was filled to the mark with dichloromethane.

- A 500 mg l^{-1} standard of organic sulphur compounds was prepared by taking 25 ml of the 1000 mg l^{-1} and transferring into a cleaned 50 ml volumetric flask. The flask was filled to the mark with dichloromethane.

- A 100 mg l^{-1} standard of organic sulphur compounds was prepared from 1000 mg l^{-1} stock solution. 5 ml of the stock solution was transferred into 50 ml volumetric flask with a pipette. This was made up to the mark with dichloromethane.

3.5 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. Table 7 below gives the identity information of all samples used. The samples were manually crushed by means of mortar and pestle then passed through a 240 µm diameter sieve before any process was done. Particles less than 240 µm in diameter were taken for further processing.

3.6 QUALITATIVE DETECTION OF SULPHUR IN A SAMPLE

A gram of coal sample was weighed on a clean glass watch and transferred into a clean beaker. 1 ml fusion solution acidified by acetic acid (2 or 3 drops of dilute lead acetate solution) was then added to the sample. The formation of a black precipitate indicated the presence of sulphur (Pasto *et al.*, 1992).

Table 7: Sample identification

Sample ID	Location
TRC	Thuthuka Power station
DRC	Duvha Power station
KRC	Kriel Power station
LRC	Lethabo Power station
MRC	Majuba Power station
CRC	Camden Power station

3.7 SAMPLE EXTRACTION PROCEDURES

3.7.1 Total organic carbon digestion with ferrous sulphate solution

- Standardization of ferrous sulphate solution

  10 ml of normal potassium dichromate solution was transferred into a 500 ml conical flask using a burette. 20 ml of concentrated sulphuric acid was then added very carefully from a measuring cylinder. The mixture was thoroughly swirled for about 1 minute and allowed to stand on a heat- insulating surface for 30 minutes to allow the oxidation of the organic matter to proceed. During this period, the flasks were protected from draughts. 200 ml of deionised water were added along with 10 ml of orthophosphoric acid and 1 ml of indicator. The mixture was shaken

vigorously. A further 1 ml of indicator was added in case the first was not enough. A 0.5 N ferrous sulphate solution was then added from the second burette in 0.5 ml increments while the content of the flask was swirled until the colour of the solution changed from blue to green. A further 0.5 ml of potassium dichromate solution was then added, changing back the colour to blue. Ferrous solution was then added drop by drop with continued swirling until the colour of the solution changed from blue to green after the addition of a single drop. The total volume of ferrous sulphate solution used (x ml) was noted to the nearest 0.05 ml (1 ml of ferrous sulphate solution is equivalent to 10.5/x ml of potassium dichromate).

- Determination of total organic carbon

5 g of dried and crushed coal sample were placed in a conical flask. 10 ml of 1N potassium dichromate solution was added to the flask. 20 ml of concentrated sulphuric acid was added very carefully from a measuring cylinder. The mixture was thoroughly swirled for about 1 minute and allowed to stand on a heat-insulating surface for 30 min for the oxidation of the organic matter to complete. During this period, the flask was protected from draughts. 200 ml of deionised water was added along with 10 ml of orthophosphoric acid and 1 ml of indicator. The mixture was shaken vigorously. A additional 1 ml of indicator was added. Ferrous sulphate solution was then added from the second burette in 0.5 ml increments while the content of the flask was being swirled until the colour of the solution changed from blue to green. A further 0.5 ml of potassium dichromate was then added, changing back the colour to blue. Ferrous solution was then added dropwise with

continued swirling until the colour of the solution changed from blue to green after the addition of a single drop. The total volume of ferrous sulphate solution used (y ml) was noted to the nearest 0.05 ml. Equation 3.1 below was used to calculate the volume of potassium dichromate used to oxidise carbon in samples. Equation 3.2 was then used for calculation of concentration of organic carbon.

$$V = 10.5 \left(1 - \frac{y}{x} \right) \qquad \text{(Eqn 3.1)}$$

Where **V** is the volume of potassium dichromate required to oxidise carbon in the sample; **y** (ml) is the total volume of ferrous sulphate solution used in the titration of carbon in the sample; **x** (ml) is the volume of ferrous sulphate solution used for standardisation.

The volume of potassium dichromate required to oxidise carbon can allow determining the amount of organic carbon based on stoechiometry in Eqn 2.1 described in the previous chapter. The percentage of organic carbon in coal sample could then be determined using the following expression:

$$OC = \frac{0.6\,V}{S} \qquad \text{(Eqn 3.2)}$$

Where **OC** is the organic carbon content (%); **V** is the volume (ml) of potassium dichromate required to oxidise organic carbon; **S** is the mass of sample in grams.

3.7.2 Microwave extraction for various forms of sulphur

The MAE instrument used had a digestion rotor that could accommodate eight 120 ml Teflon lined vessel assemblies. Each of these comprising a vessel body, safety relief valve, cap and vent. A reproducible torque was applied to the vessels prior to heating homogenising the cap circumference. To enable venting to occur it was important to insert the jackets or safety valves in a correct way on the rotor. The extraction of each sulphur form from coal was based upon their differences in properties. The extraction method used was developed by Laban and Atkin (2000). It was important that the correct type of acid and its concentration are used to extract only the required sulphur forms leaving others behind. The residue from the first stage had to be rinsed to remove any acid that remained so as this could not interfere in the next stage of extraction. However, the rinsing was not necessary for organic sulphur extraction since it is the last sulphur form remaining in the residue to be extracted. Another factor that could affect the extraction of different sulphur forms was the power of the MAE system. Trial extractions were done with coal samples by varying the power programme. High power (more than 800 w) could remove appreciable amount of sulphur as pyrite when extracting sulphate, but other forms like organic sulphur were also extracted. 500 w power was settled as maximum power after optimisation.

Total sulphur

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 in 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 8. The vessels were allowed to cool down and taken out. They were then opened while in fume hood 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 sulphur content was also determined as the sum of sulphate, pyrite and organic sulphur forms in the samples. The different sulphur forms were determined as stated below. The following selected metal ions were also determined in the extract used for total sulphur: 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.

Table 8: 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: Sulphate sulphur 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 8 above. 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 (around 8 ml) was collected in a volumetric flask then transferred into a vial for the determination of the sulphate sulphur concentration by ICP-OES

Stage 2: Pyritic sulphur 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_3. The sample was microwave digested using the same programme in Table 8. The filtrate (around 8 ml) was collected for analysis of sulphur on ICP-OES after separation using the centrifuge.

Stage 3: Organic sulphur form

The residue from pyrite extraction was mixed with same strong acid solvents as for total sulphur determination and extracted on MAE system according to the method in Table 8. The concentration of sulphur in collected filtrate (about 8 ml) was determined on ICP-OES.

3.7.3 Ultrasonication

Optimisation experiments

Hexane, toluene, dichloromethane and pyridine were used to optimise the type of extraction solvent for organic sulphur compounds. Optimisation was done by extracting with an appropriate solvent (50 ml) for 75 min and 3 g of coal sample. Six simultaneous extractions could be performed. Target compounds as well as many other organic compounds present in coal were extracted most with dichloromethane. This was taken as optimum solvent. The extraction time was then studied at 15, 45 and 75 min with 50 ml of dichloromethane as solvent. Literature has shown that there should be optimum time after which promotion of secondary reactions and appreciable loss of compounds occur (EPA 3550c, 2007; Mason and Lorimer, 2002; Suslick *et al.*, 1999). 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. The optimum condition was observed with 75 min extraction. For quality assurance each experiment was repeated at least three times.

Spiking extractions for recovery calculations

2 g of dried coal sample were weighed and placed in a beaker. 5, 25 and 50 mg of standard organic sulphur compounds were respectively mixed thoroughly with weighed coal samples. The final concentrations of spiked compounds were 1700, 8300 and 17000 mg kg^{-1} of standard organic sulphur compounds in coal samples. 50 ml of dichloromethane was added to the spiked samples for extraction of organic sulphur 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 simultaneously.

3.7.4 Pyrolysis

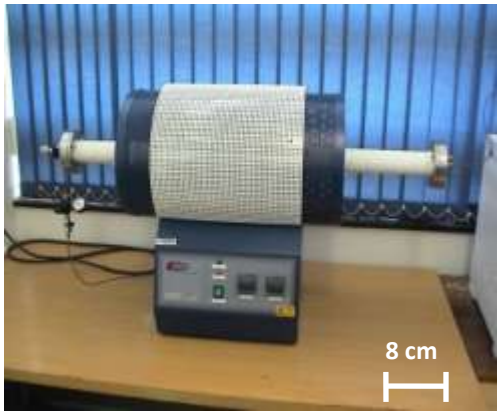
A trial of pyrolysis of coal samples was conducted to identify the organic sulphur in the pyrolysis gas products. The furnace was coupled to the GC and nitrogen was used as carrier gas in the furnace and for the GC. Approximately 10 g of coal sample was weighed in the pyrolysis crucible which was then placed into the pyrolysis tube. Nitrogen was pumped at a flow rate of 0.5 ml sec^{-1} in the tube and allowed to remove oxygen by opening the outlet of the tube (which had a valve) for 10 minutes. The furnace was heated according to the temperature programme presented in Table 9. Pyrolysis products were collected online for GC analysis in two stages as follow: during pyrolysis the inlet gas in the furnace was closed. After pyrolysis, the products were pumped by the gas out to the outlet at a flow rate of 0.5 ml s^{-1}. To make sure that only the plug with highest concentration was injected into the GC, at first the outlet gases were allowed to bubble out in methanol for 5 min. The outlet was then injected into the GC via a syringe at a speed of 0.5 ml for 90 sec. A 10 g coal was then spiked with 1000 mg kg^{-1} of standard organic sulphur compounds. The pyrolysis – GC - FID was then repeated in the same way as the unspiked coal samples. Initial identification was done by comparing the chromatograms of spiked and unspiked samples. Figure 13 shows the furnace used (a), the

coupling of Pyrolysis to GC - FID for this project (b) and the connection link between pyrolysis and GC (c).

Table 9: Furnace temperature programme trial

	Initial [^{o}C]	Final [min]	Ramp [^{o}C min^{-1}]	Hold for [min]
Ramp 1	100	600	15	30
Ramp 2	1200	1200	10	40

(a)



(b)



(c)



Figure 13: Pyrolysis furnace connected with nitrogen gas (a), pyrolysis coupled to GC-FID (b) and pyrolysis outlet syringe connected to GC injector (c).

3.8 SAMPLE ANALYSIS

3.8.1 CHNS analysis

Prepared samples were dried in a vessel 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 sulphur 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 sulphur in the sample. The analysis was done in replicate and the average values were taken into consideration. The calibration results are presented in Table 10.

Table 10: CHNS calibration results with sulfamethazine

	% H	%S	%N	% C
Certified value	5.07	11	20.13	51.78
Calibration	5.06	12.81	20.23	51.66

3.8.2 ICP-OES

Sample solutions prepared after each digestion were analysed on ICP-OES for sulphur and selected metals after calibration with certified multi- element standards. Typically for sulphur determination, sulphur 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^{-1}. The sulphur and selected metals correlation curves which are part of quality assurance are respectively shown in figures 14 and 15. The actual results on calibration and detection limits are shown in Table A3 in the appendix.

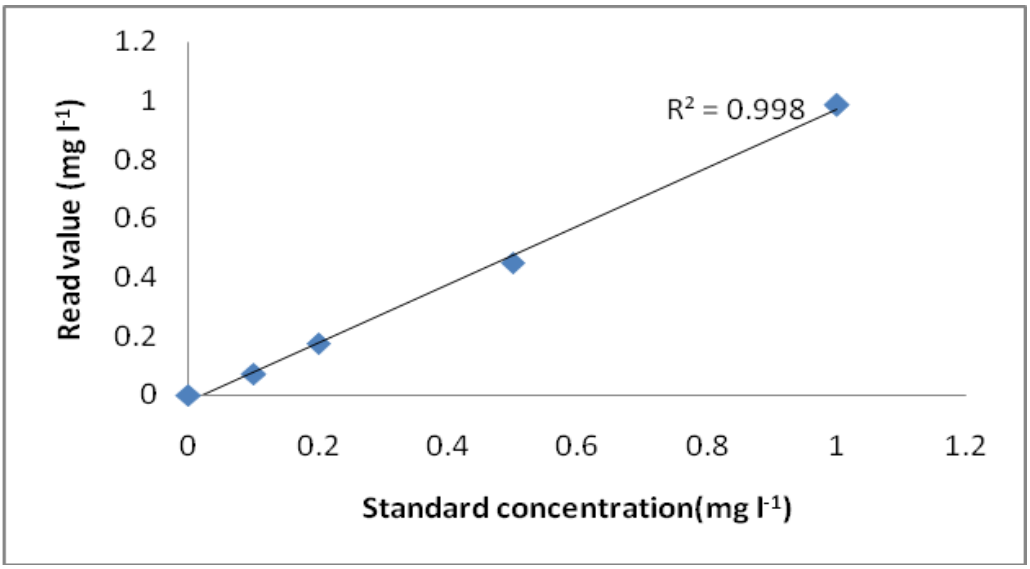


Figure 14: Correlation curve of sulphur for ICP-OES analysis

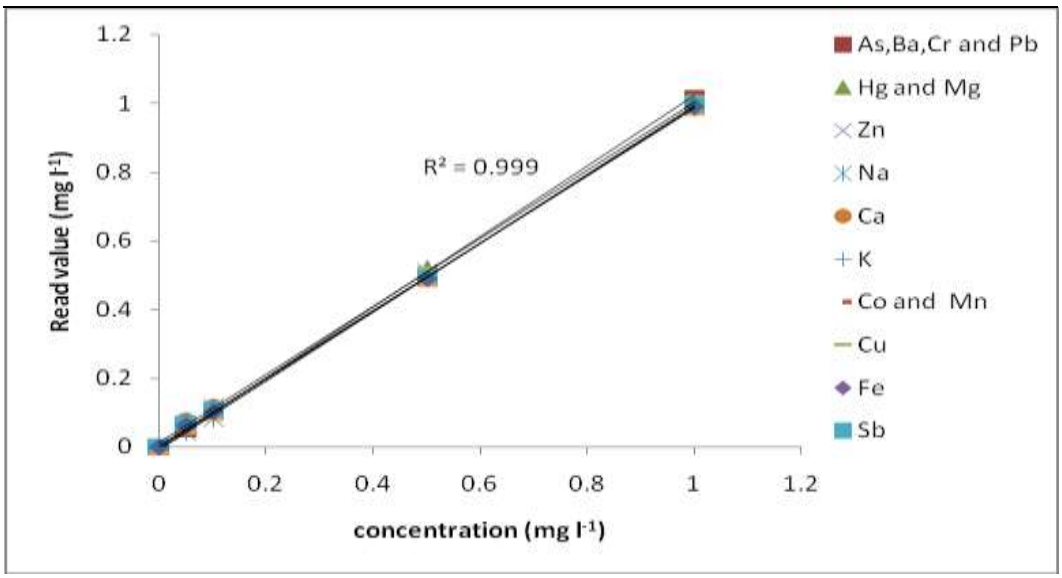


Figure 15: Correlation curves of selected elements for ICP-OES analysis

3.8.3 GC-FID

The determination of organic sulphur compounds from ultrasonic bath extracts was made on GC-FID with SPB^{TM}-1 Sulphur, fused silica capillary column. 10 µl of solutions was injected in the column through the inlet using a manual syringe. Standard organic sulphur compounds were analysed for calibration of the instrument (Figure 16). This was followed by analysis of all samples. The temperature programme used was as follows: The heater of the inlet was set at 250 ^{o}C and the injection mode was splitless; FID temperature was at 300 ^{o}C; the initial oven temperature was 40 ^{o}C for 4 min; the temperature was increased to 260 ^{o}C at 10 ^{o}C min^{-1} and held for 15 min; it was finally increased to 300 ^{o}C at 20 ^{o}C min^{-1} and held for 20 min.

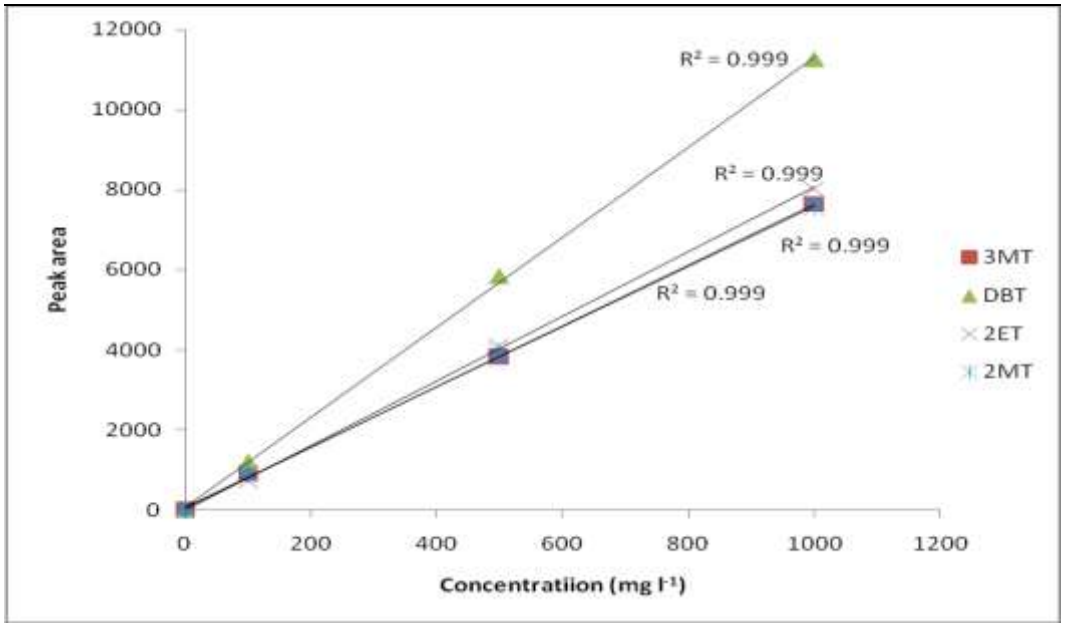


Figure 16: Calibration curves for GC analysis

3.9 QUALITY ASSURANCE

Several factors were taken into account to ensure the quality of the results. For organic carbon and organic sulphur determination on GC, glassware was thoroughly cleaned with soap and deionised 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 deionised water. The glassware used for sulphate form determination was soaked in 10% HCl whilst the ones used for pyrite form was soaked in 10% HNO_3 solution.

Samples and reagents were weighed on analytical balance and the mass was read at 3 decimals 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^oC in the fridge and were stable for a week.

Spiking of samples was done to determine the extraction efficiency in the analysis. Standard organic sulphur 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.

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 PROXIMATE ANALYSIS

The determination of moisture, ash and organic carbon of various coal samples were done and the results are presented in Figure 17. The organic carbon content was generally higher than ash and moisture. MRC sample gave higher concentration of organic carbon whilst the lower concentration was observed with LRC sample. Moisture content was relatively lesser than ash and organic carbon concentrations in all coal samples. Higher concentration of moisture was found in DRC sample whilst CRC gave a lowest value. On the other hand, high ash content was observed in DRC sample while MRC sample showed a lower concentration. The differences in concentration of organic carbon in coal samples are not considerable. The values fall within the range for bituminous coal (Table1). The average amount of organic carbon found in coal samples also allows understanding the calorific value. The higher the calorific value, the better the coal when used. Table 1 shows that bituminous coal is one of the coal types with high calorific value. The mean results are shown in Table 11 where they are compared to literature and certified reference material values. The comparison with other literature values for bituminous coal might show that not all proximate analysis values have similar range. Others like percent of ash could be different (Hsieh *et al.* 1985). Such variations can be expected since coal properties are generally relative to many parameters such as coal basin and parent material of coal. This has been explained in earlier chapters. Proximate analysis also showed 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 (Roberts, 2008; DME, 2004). This is important because it demonstrates that the obtained results are reliable and accurate.

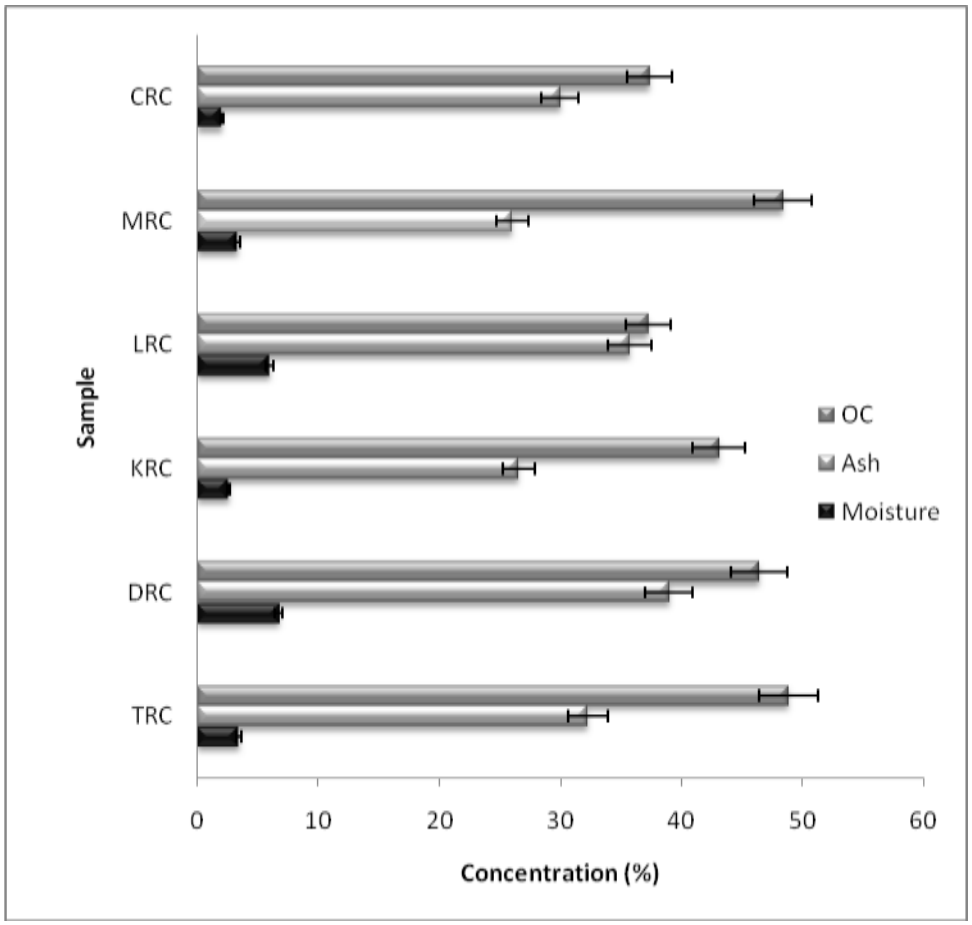


Figure 17: Moisture, ash and organic carbon in coal samples

Table 11: Proximate analysis

Sample	% Moisture	% Ash	% Organic Carbon
Mean (± sd)	**4.0** (1.9)	**31.6** (5.1)	**43.6** (5.3)
Certified range*	1.2- 17.5	4.6-35.5	nd**
Hsieh *et al.* (1985)	nd	14.2-14.4	nd
Roberts (2008)	nd	26.0-30.0	nd
DME, (2004)	3.9-6.2	20.5-31.2	42.2-50.1

* Certified data of bituminous coals 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.

4.2 ULTIMATE ANALYSIS

The determination of major elements (CHNS), as part of organic compounds in coal was done using a CHNS analysis. Table 12 shows the results obtained for ultimate analysis which is compared to certified reference material and literature values. The carbon content was far higher than hydrogen, nitrogen and sulphur 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 sulphur whilst low nitrogen content was observed with TRC samples. Sulphur concentration in coal varied considerably from each sample to others. This might prove that sulphur presence in coal is affected by several parameters such as its content 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 sulphur. The carbon, hydrogen, nitrogen and sulphur contents in coal samples of this project were comparable to the certified values from South African Bureau of Standards. This proves further that the analysed coal samples belong to bituminous coal rank. This is because the certified reference material is for bituminous coal. Except from carbon content which is slightly higher, hydrogen, nitrogen and sulphur values are similar to the ones found in literature about South African coal (Roberts, 2008; DME, 2004).

The sum of carbon, nitrogen, hydrogen and sulphur contents gave an average concentration of 71.3 10^4 mg kg^{-1} in coal. This value is below 100 10^4 mg kg^{-1} for whole coal constituents. Therefore, other components such as oxygen, inorganic elements and moisture had to be taken into account as part of coal.

Table 12: Ultimate analysis: CHNS analysis

ID	C 10^4mg kg^{-1}	H 10^4mg kg^{-1}	N 10^4mg kg^{-1}	S 10^4mg 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 (±sd)	**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**
Francis (1961)	78.80	5.60	1.40	1.12
Gryglewicz et al. (2002)	79.40	5.40	1.30	1.75
Czaplicki and Smolka (1998)	56.70-69.60	4.17-4.72	0.76-1.13	0.43-0.63
Roberts (2008)	40.00-52.00	3.07-3.20	0.78-0.09	1.47-1.56
Marinov *et al.* (2005)	49.00	4.00	0.70	9.58
DME(2004)	49.70-58.23	2.60-3.13	0.56-1.44	0.74-1.23
Wagner and Hlatshwayo (2005)	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.

4.3 DETERMINATION OF SULPHUR FORMS IN COAL SAMPLES

The determination of sulphur forms in coal was assessed using MAE. The obtained results are presented in Figure 18. Organic and pyrite sulphur forms competed for their content in coal samples whilst sulphate form was found in a lower concentration in coal. The sulphur forms and the total sulphur contents are not similar from one sample to another. Higher concentrations of sulphate, pyrite and organic sulphur form were respectively found with LRC, DRC and KRC samples. On the other hand, a lower concentration of sulphate was observed with KRC sample. Pyrite and organic sulphur forms were found in lowest amount with CRC sample. The concentration of total sulphur was highest in DRC sample whilst the lowest total sulphur amount was found with CRC sample. Despite slight differences observed particularly with some samples, the concentration of total sulphur agreed with the sum of individual amount of sulphur forms determined in coal samples. The mean values are shown in Table 13 which also gives some literature values obtained by various researchers. Considering the amount of all sulphur forms analysed, one can see that the high value of total sulphur does not necessarily imply a highest amount of organic sulphur than pyrite and sulphate or vice versa. This means that sulphur forms in coal are influenced by the genesis of coal. The slight difference between the analytical determination of total sulphur and the sum of concentrations of sulphur forms could be due to any of the protocols followed during the determination of each form of sulphur. This could include small loss during filtration, cooling down and opening digestion vessels. However, the difference between the total sulphur determined by the two approaches is not

very significant since it is within the calculated relative standard deviations (Table 13).

The average of total sulphur content agrees with the range of values found in the studies on South African coal by DME (2004). The values of various forms of sulphur in coals under study also agree with the certified ranges especially with the South African reference material. This is not surprising since coal samples investigated were taken from South African areas just as reference material. Results generally comply with various data ranges of standard material analysed from NIST, BCR, NBS and SARM (Laban and Atkin, 2000). Comparing the total sulphur content to other coal samples shown in Table 13, one can see that South African coal can be considered as low sulphur coal. In other coal samples around the world, the total sulphur of 5.4-15.1 10^4 mg kg^{-1} (Olivella *et al.*, 2002), 0.4-1.3 10^4 mg kg^{-1} (Wagner and Hlatshwayo, 2005) 0.93-3.35 10^4 mg kg^{-1} (William, 1994) and 19.6 10^4 mg kg^{-1} (Marinov *et al.*, 2005) has been reported.

Although CHNS and MAE followed by ICP-OES results concerning total sulphur content were within the certified range, MAE - ICP values slightly differed from the results obtained from CHNS. This might be due to the accuracy of methods. These analytical methods used do not show any similarity since CHNS analysis is a direct method while MAE - ICP was an indirect one. ICP-OES in principle should be more accurate since it is less matrix interfered as the sample is digested first.

The analysis of metals having more affinity to sulphur was then done to correlate with the occurrence of the forms of sulphur in coal samples.

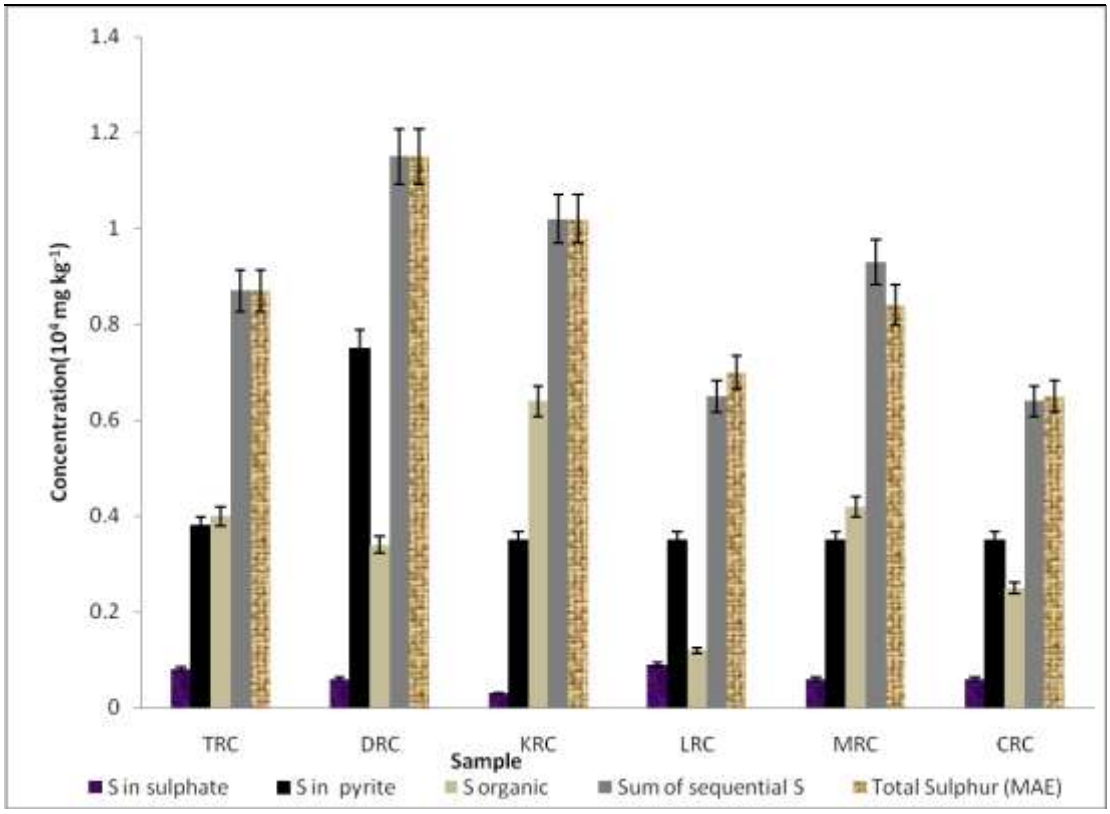


Figure 18: Pattern of sulphur content in coal samples

Table 13: Determination of sulphur forms in coals (10^4 mg kg^{-1})

Sample	S in sulphate	S in pyrite	S organic	Sum of sequential S	Total Sulphur (MAE)
Mean (±sd)	**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 *et al.* (2005)	0.59	0.30	8.69	9.58	
Hsieh and Wert (1985)	1.50	3.90	0.46-4.30	0.59-9.45	
Olivella *et al.*(2002)	0.30-7.60	0.30-3.30	2.70-12.20	5.40-15.10	
William (1994)	0.70-2.17	0.11-1.15	0.12	0.93-3.35	
Gryglewicz (2002)	0.03	0.52	1.18	1.75	
Boudou *et al.* (1987)	0.15	2.95	1.70	4.80	
Wagner and Hlatshwayo (2005)	nd	nd	nd	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.

4.4 DETERMINATION OF SELECTED METALS IN COAL

Based on their affinity with sulphur 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 14 below. 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 mg kg^{-1} whilst the lowest one was attributed to mercury which was at 0.21 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 of those metal concentrations showed a trend which was decreasing as follows: Na> Ca> Fe> Mg> K> Ba> Mn> Cr> Pb> Zn> Cu> As> Co> Sb> Hg. High concentration of iron found in DRC sample explains why the amount of pyrite, as well as ash is considerably high in this sample as observed when determining various forms of sulphur 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 concentrations of some of these metals compared to others means they are the most abundant 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 (Wagner and Hlatshwayo, 2005; Goodarzy *et al.*, 2006; Willis, 1983 and SABS, 1984). Details of comparison of the found and literature values are shown in Table 14.

Table 14: Analysis of selected metals in coal

Sample	**Concentration** (mg kg^{-1})							
	As	**Ba**	**Ca**	**Co**	**Cr**	**Cu**	**Fe**	**Hg**
TRC	**6.12** (2.63)	**309.7** (0.18)	**19226** (1.02)	**3.67** (4.91)	**58.60** (1.47)	**8.03** (9.35)	**9246** (0.23)	**0.25** (4.34)
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)	**0.29** (0.18)
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)	**0.29** (3.38)
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)	**0.25** (3.94)
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)	**0.21** (2.35)
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)	**0.27** (2.5)
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)	**0.26** (11.7)
Wagner and Hlatshwayo (2005)	0.90-8.20	nd	nd	3.3-14	12-63	4.2-16	nd	0.04-0.27
Goodarzy *et al.* (2006)	1.30-5.90	11-774	6091-763158	7.5-14.2	4-15	2-23	2030-113360	0.01-0.07
Willis (1983)	0.9-8.2	nd	nd	3.3-14	12-63	4.2-16	nd	nd

Note: nd means not determined

RSD values are given in brackets

Table 14: Analysis of selected metals in coal (continued)

Sample	Concentration (mg kg^{-1})						
	K	**Mg**	**Mn**	**Na**	**Pb**	**Sb**	**Zn**
TRC	**608** (0.41)	**2458** (0.77)	**80.0** (0.43)	**17743** (0.99)	**19.94** (5.41)	**0.39** (5.87)	**16.90** (1.46)
DRC	**587** (0.22)	**2564** (1.00)	**74.00** (0.47)	**19824** (0.73)	**21.84** (3.76)	**0.41** (6.74)	**12.92** (4.78)
KRC	**707** (0.48)	**2498** (0.53)	**77.60** (0.48)	**18976** (0.25)	**20.58** (7.09)	**0.42** (7.72)	**10.70** (1.77)
LRC	**606** (0.45)	**2476** (0.4)	**92.45** (0.29)	**18704** (0.31)	**19.86** (4.78)	**0.36** (8.01)	**19.63** (0.78)
MRC	**701** (0.35)	**3014** (0.33)	**85.71** (1.44)	**22069** (0.47)	**27.76** (7.45)	**0.39** (10.1)	**14.21** (3.25)
CRC	**658** (0.45)	**1706** (0.07)	**101.4** (0.68)	**25294** (0.10)	**21.72** (3.87)	**0.41** (3.98)	**15.12** (10.03)
Mean	**645** (8.03)	**2453** (17.18)	**85.19** (12.03)	**20435** (13.67)	**21.95** (13.53)	**0.40** (5.45)	**14.91** (20.87)
Wagner and Hlatshwayo (2005)	nd	nd	90.70-107.50	839-5010	nd	nd	8-19
Goodarzy *et al.* (2006)	630-12500	2030-113360	1.2-324	nd	nd	nd	4-32
Willis (1983)	nd	nd	nd	nd	1.9-25	nd	3.20-16
SABS (1984)	580	nd	77-82	960	20-29	nd	14-18

Note: nd means not determined

RSD values are given in brackets

Most of the determined elements have an affinity to sulphur; these metals are mostly associated with sulphide like pyrite. Others are attached to organic sulphur compounds. For this reason, they affect sulphur removal process from coals besides the potential environmental impact. Temperature is the main parameter that affects the behaviour of metal in sulphur compounds, which has been investigated by Yan et al., (2001). Mercury is one of the metals that form complexes with organic sulphur forms. This metal forms one of the most toxic species when combined with organic sulphur compounds. This is the case of methyl mercury which is formed by accumulation and reaction of organic sulphur 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 (VanLoon and Duffy, 2005). General information on the selected metals is presented in section A1 of the appendix.

4.5 DETERMINATION OF ORGANIC SULPHUR COMPOUNDS IN COAL

The analysis of organic sulphur compounds was done after optimisation of extraction solvent, extraction time and spiking concentration. This was confirmed by the use of standard organic sulphur compounds and related results are sequentially presented below.

4.5.1 Optimisation of extraction procedure

Data from literature have already confirmed the presence of all organic forms of sulphur in coal (Marinov *et al.*, 2005; Gryglewicz et al, 2002; Olivella et al.,

2002). However, because of limited project time, attention was made on thiophenic organic sulphur forms as they are the most dominant organic sulphur in bituminous coal (William, 1994). The ultrasonic extraction method used to extract organic sulphur forms requires the investigation of various parameters that affect its performance. These parameters such as the extraction solvent and extraction time were studied. A good set of optimized parameters should allow extraction of all the targeted compounds. Organic sulphur compounds are generally polar because of the free electronic pair on sulphur as revealed by Larsen (1978). Therefore, from theory, a mediun polar organic solvent should be the best extraction solvent. Spiking of samples at various concentrations was also studied to see how this affected the extraction efficiency.

Extraction solvent and screening of samples

A series of solvents were studied to see which one could extract most organic sulphur compounds. This included dichloromethane, hexane, tetrahydrofurane, 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 control properly pyridine vapour released during sample extraction. This is because extraction was not performed in a closed vessel. Figures 19, 20 and 21 below show typical chromatograms from DRC sample extracted from different solvents. Other results are shown in Figure A2 in the appendix. Dichloromethane was selected as good solvent for the present study because of its ability to extract many organic sulphur compounds from coal compared to other solvents investigated. Hexane was the least performing solvent because

very few peaks were obtained from its chromatogram (Figure 19). Toluene on the other hand, was not as good as dichloromethane.

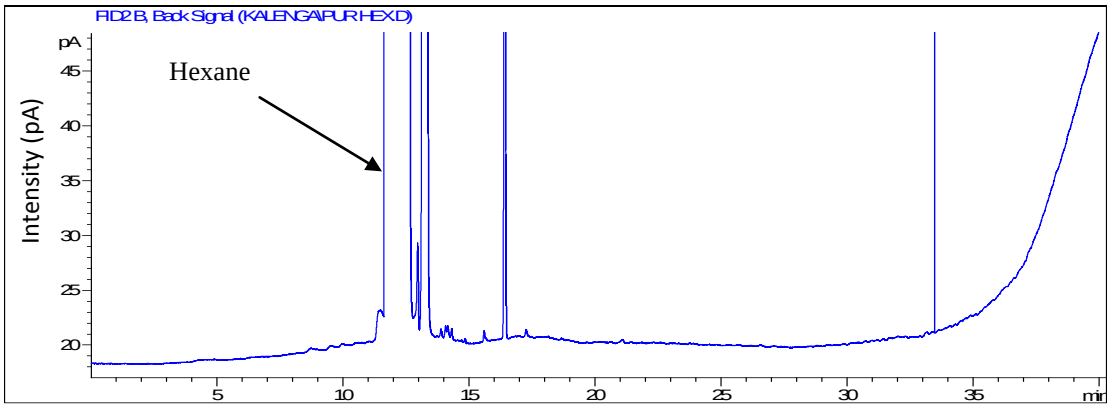


Figure 19: Extraction of organic sulphur compounds from DRC with hexane

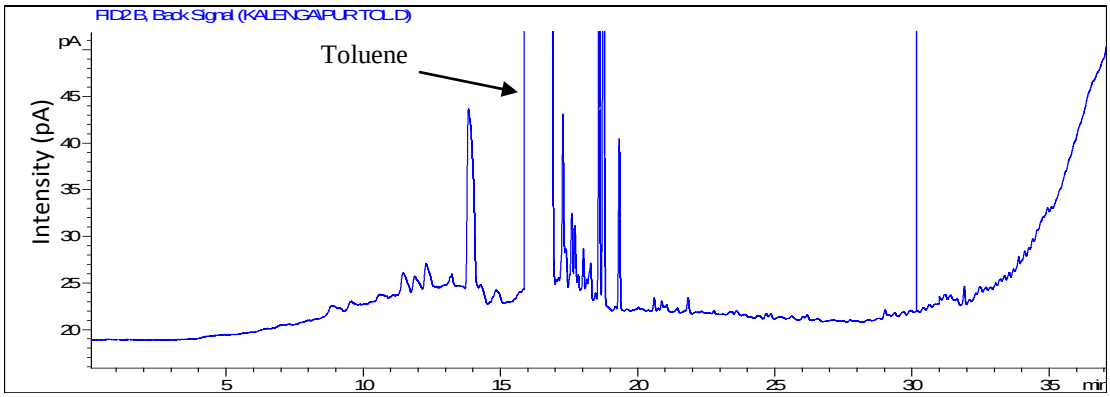


Figure 20: Extraction of organic sulphur compounds from DRC with toluene

Dichloromethane was then used to screen various samples for the target organic sulphur 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 21 shows the chromatogram obtained

after extraction of organic sulphur compounds from DRC samples with dichloromethane.

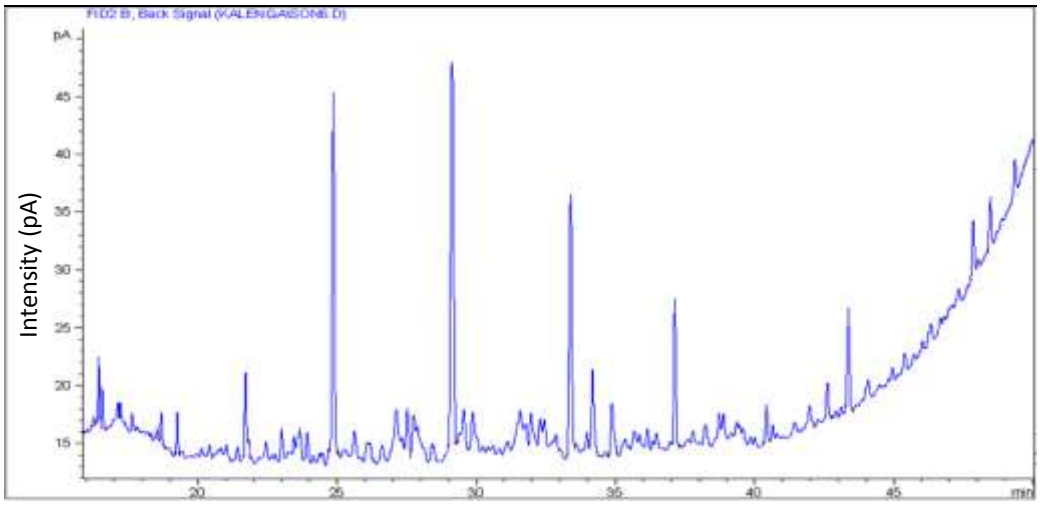


Figure 21: Extraction of organic sulphur compounds from DRC with dichloromethane.

In DRC samples four organic sulphur compounds were identified based on retention time. The chromatogram presented in Figure 22 shows that many compounds could be extracted and detected besides the target organic sulphur compounds. The presence of these compounds in DRC samples was fortunately expected from the macroscopic aspect shown by various colours of extracts. Figure 23 shows that one could expect many compounds in DRC samples which had a darker colour than other ones studied in this project. The mixture of standards gave a clearer solution because of limited number of compounds compared to coal samples.

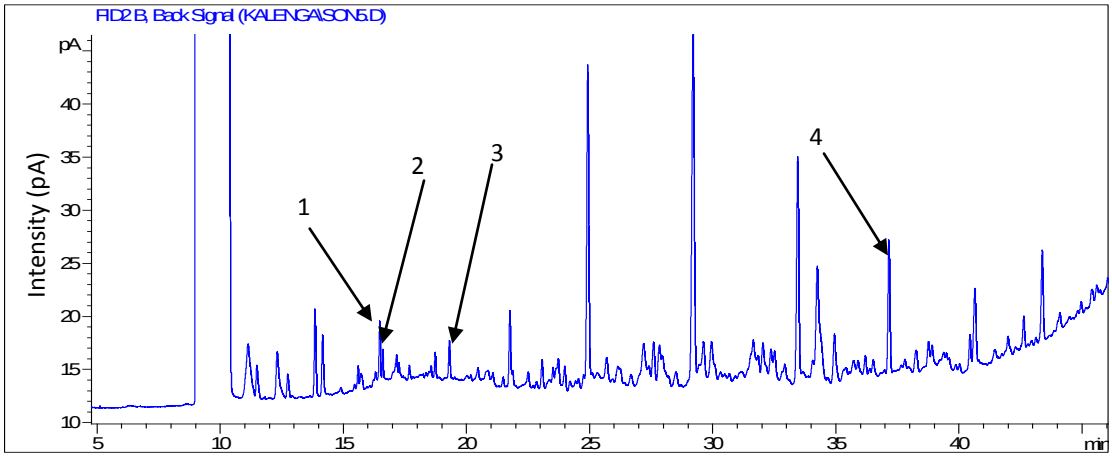


Figure 22: DRC sonication extract with dichloromethane.

1=2MT; 2=3MT; 3=2ET and 4=DBT.

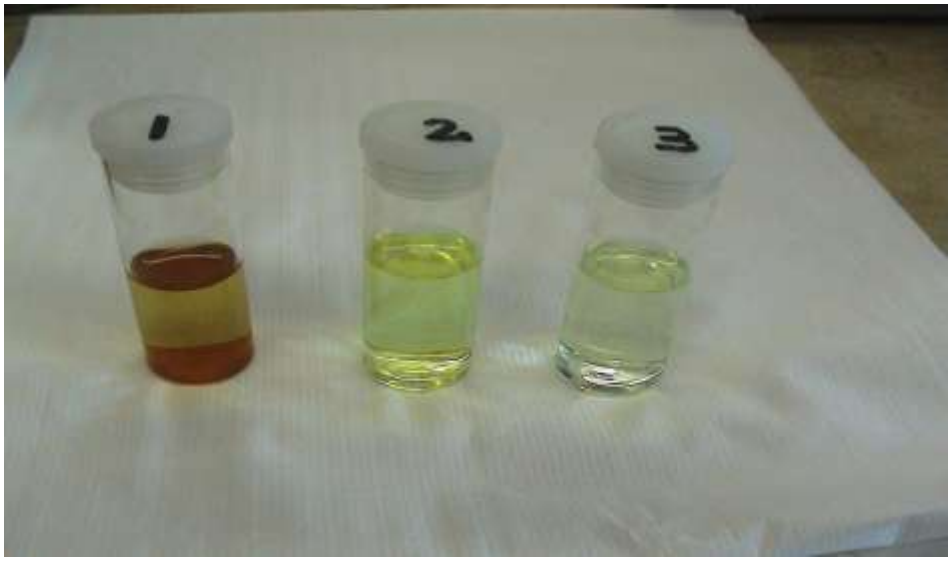


Figure 23: Extracts obtained from ultrasonic bath of DRC (1) and KRC (2) samples and solution of standards (3).

Extraction time

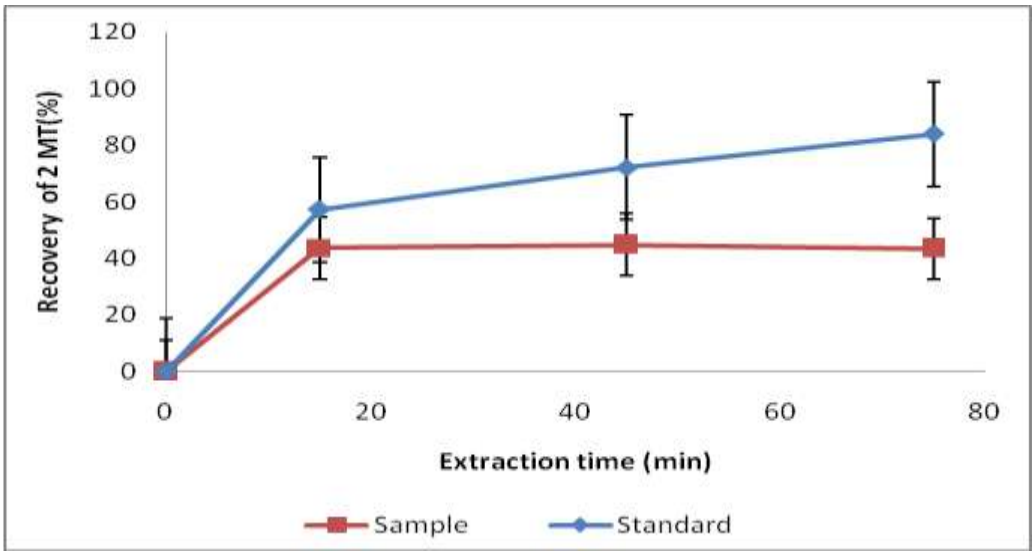
The extraction of organic sulphur compounds from coal samples was further investigated by varying the extraction time. Extraction times of 15, 45 and 75 minutes were studied and the recovery of the spiked target compounds was determined. Table 15 gives the recoveries obtained from the extraction of each target compound in DRC spiked sample and that from solution of standard organic compounds only. A full table ($A2_a$, $A2_b$, $A2_c$ and $A2_d$) showing detailed recoveries is presented in the appendix. Results showed that the recovery of target compounds was in a range of 32.76 – 88.07 %. The recoveries from solutions of standard sulphur compounds were higher than in the sample ones at any given extraction time (Table 15). The lower recovery of organic sulphur compounds from extraction of samples could be mainly caused by adsorption of standard compounds spiked on the sample matrix. This observation means that target compounds have pronounced difficulty to be extracted from samples than their standard solutions. Results in Table 15 show that for 2-MT and 3-MT, recoveries were lowest compared to that of standards, these are the most volatile organic sulphur compounds. The results for these compounds suggest they may also have been lost during extraction.

Highest recovery was generally found with 75 min of extraction while 15 min of extraction could not allow the total recovery of target organic sulphur compounds. The overall behaviour of the compounds with increase in extraction time is shown in Figure 24. The recovery generally increased with extraction time for all compounds studied except for 2-MT and 3-MT in spiked samples.

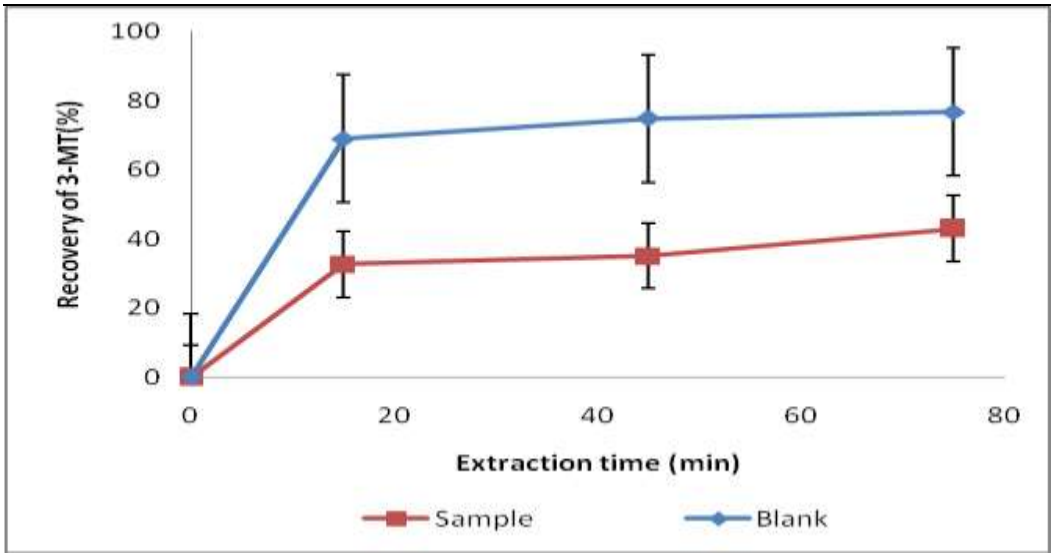
Table 15: Average recovery of organic sulphur compounds at various extraction time

Time	Recovery							
	2-MT		3-MT		2-ET		DBT	
	Sample	Standard	Sample	Standard	Sample	Standard	Sample	Standard
15	43.72	57.20	32.76	68.97	37.63	63.31	39.68	62.86
45	44.83	72.21	35.20	74.83	44.76	82.24	45.54	67.89
75	43.36	83.93	43.06	76.76	51.67	88.07	53.25	80.29

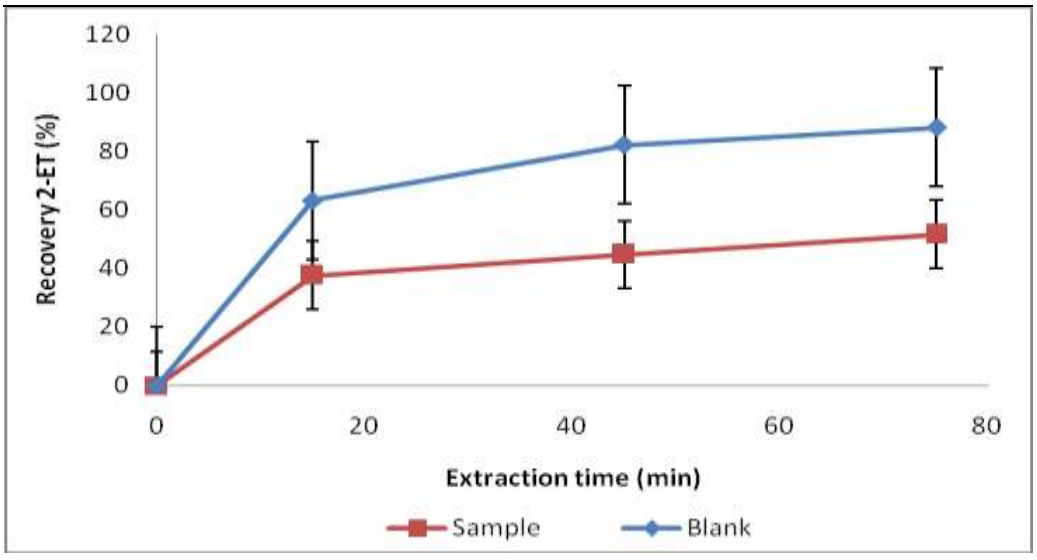
Lower time could not allow all organic sulphur to be extracted whilst exceeding optimal extraction time could decompose and/ or volatilise the analyte.



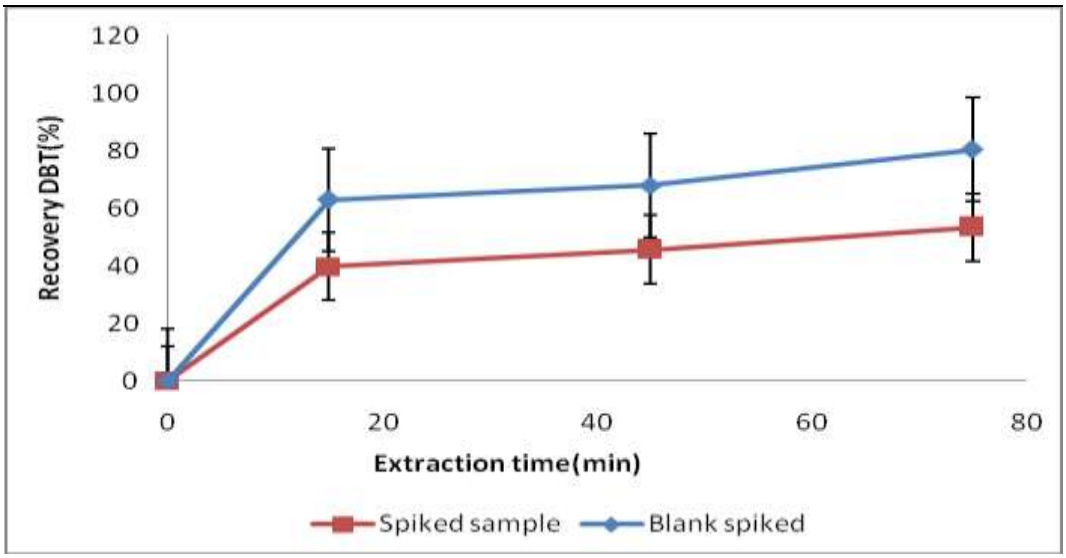
(a)


Recovery of 3-MT(%)
100
80
60
40
20
0
0
20
40
60
80
Extraction time (min)
Sample
Blank

(b)


Recovery 2-ET (%)
120
100
80
60
40
20
0
0
20
40
60
80
Extraction time (min)
Sample
Blank

(c)



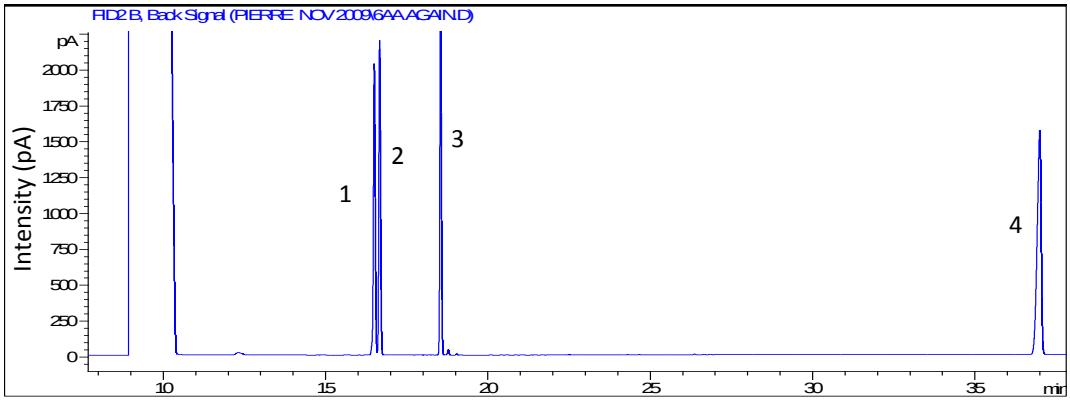
(d)

Figure 24: Extraction time effect on the recovery of 2-methyl thiophene (a), 3-methyl thiophene (b), 2- ethyl thiophene (c) and dibenzo- thiophene (d).

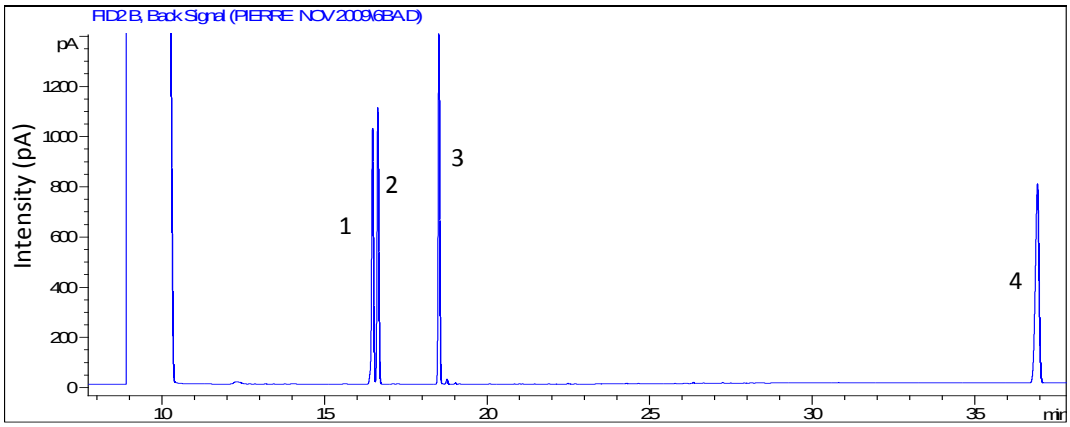
Spiking concentration

The dependency of recovery on the spiked concentration was investigated from 1700 to 17000 mg kg^{-1}. TRC, DRC and KRC samples were used for this study as they proved to contain target compounds during preliminary analysis. Typical chromatograms obtained from spiked organic sulphur compounds in DRC sample are shown in the Figure 25. For other samples, the chromatograms are shown in Figures A7 and A8 in the appendix. These results clearly demonstrate that target compounds could be detected. From the lowest spiked concentration chromatogram, the detection limit of the method was estimated. Table 16 shows the detection estimated as concentration of target

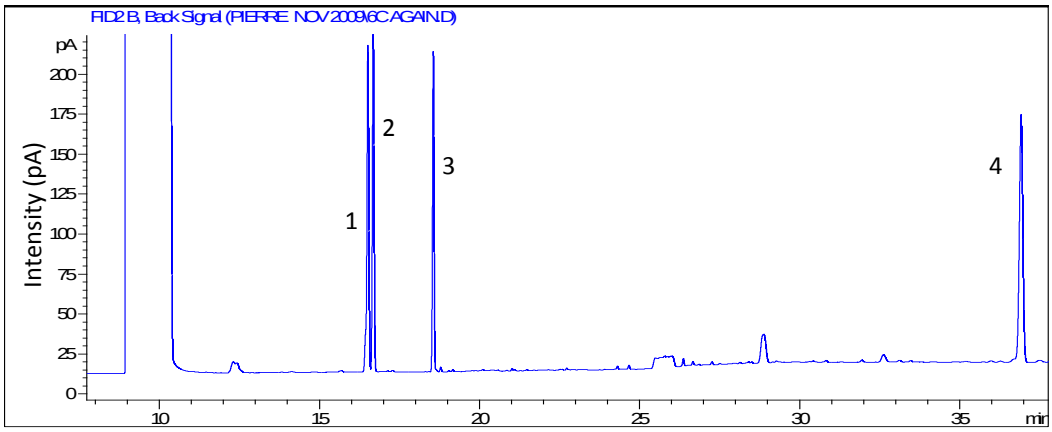
compound that gives peak area three times to the noise. The detection limit of the method was generally not very low due to the poor sensitivity of FID for the studied compounds. However, the detection limit could be improved by reducing the volume of the extract from 20 ml to 5 ml.



(a)



(b)



(c)

Figure 25: Chromatogram of organic sulphur compounds extracted from DRC sample with 17000 mg kg-1 (a), 8300 mg kg-1 (b) and 1700 mg kg-1 (c) spike. 1=2MT; 2=3MT; 3=2ET and 4=DBT.

Table 16: Detection limits of the method

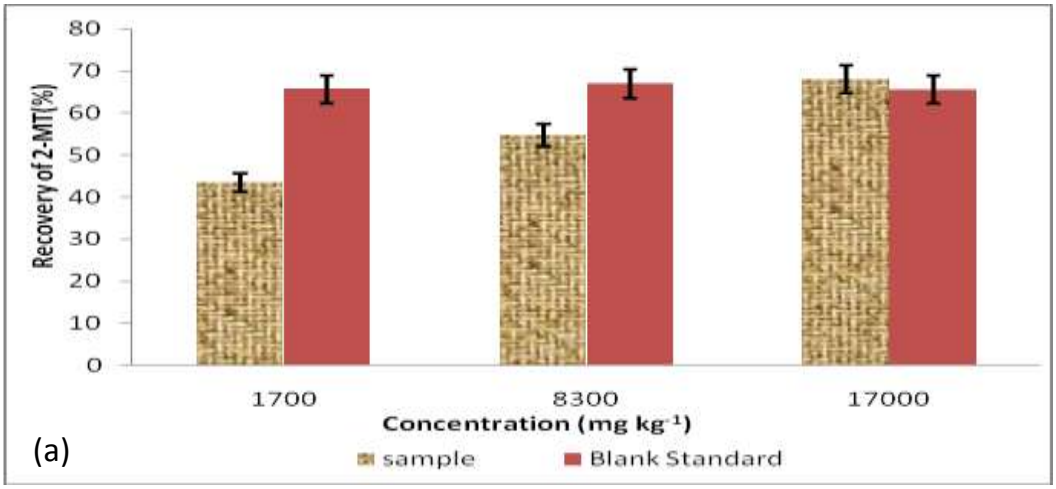
Compound	Detection limit (mg kg^{-1})
2-MT	**3.39**
3-MT	**3.27**
2-ET	**3.57**
DBT	**4.20**

The recovery of organic sulphur compounds from ultrasonic extraction at optimum conditions is presented in Table 17. Detailed data showing all related results are shown in Tables $A2_a$, $A2_b$, $A2_c$ and $A2_d$ in the appendix. The optimum extraction time was 75 minutes but this was done sequentially. This means that the extraction was stopped and water in the ultrasonic bath was replaced after every 15 minutes. This was done in order to control the temperature of the water bath.

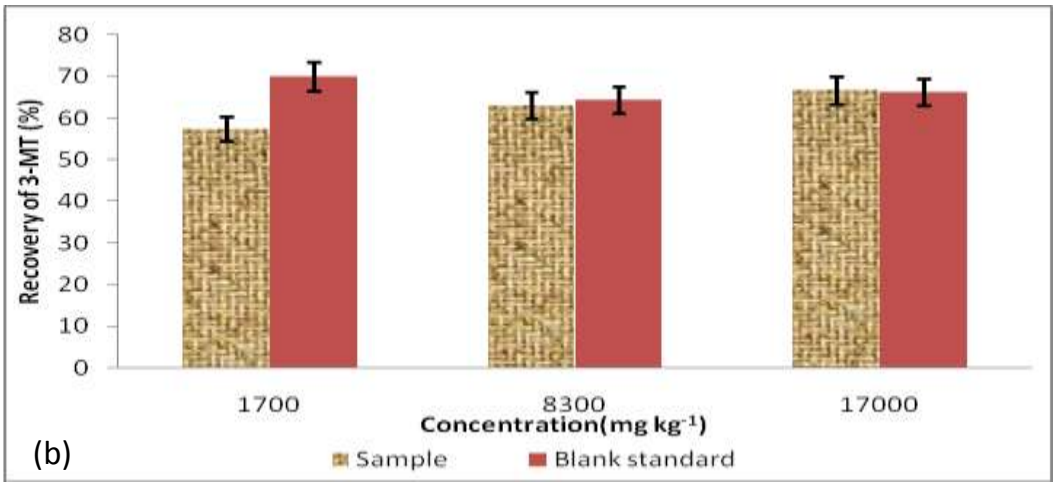
Table 17: Average recovery of organic sulphur compounds at various spiking concentrations

Concentration spiked (mg kg^{-1})	Recovery (%)							
	2-MT		3- MT		2-ET		DBT	
	Sample	Standard	Sample	Standard	Sample	Standard	Sample	Standard
1700	43.71	65.81	57.42	70.11	51.41	70.11	60.71	66.31
8300	54.82	67.13	63.11	64.42	56.43	64.42	61.92	66.63
17000	68.11	65.61	66.81	66.31	64.61	66.31	63.41	65.83

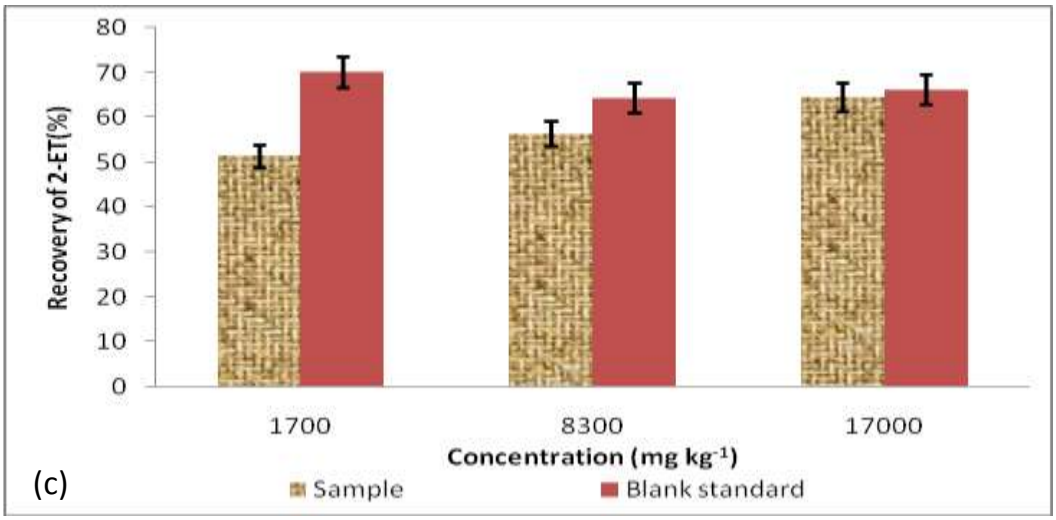
Results showed that the recovery of spiked target organic sulphur compounds in blank samples seemed to be independent upon the spiked concentration. This recovery was generally high and in similar range, which was 64.42 to 70.11 %. However, spiked samples showed a slight variation in recovery. The recovery increased with the increase of spiked concentration 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 sulphur compounds spiked in coal samples during extraction. This was discussed before and seemed to have been pronounced for 2-MT. These results are shown in Figure 26.


Recovery of 2-MT(%)
80
70
60
50
40
30
20
10
0
1700
8300
17000
Concentration (mg kg-1)
sample
Blank Standard

(a)


Recovery of 3-MT (%)
80
70
60
50
40
30
20
10
0
1700
8300
17000
Concentration(mg kg-1)
Sample
Blank standard

(b)


Recovery of 2-ET(%)
80
70
60
50
40
30
20
10
0
1700
8300
17000
Concentration (mg kg-1)
Sample
Blank standard

(c)

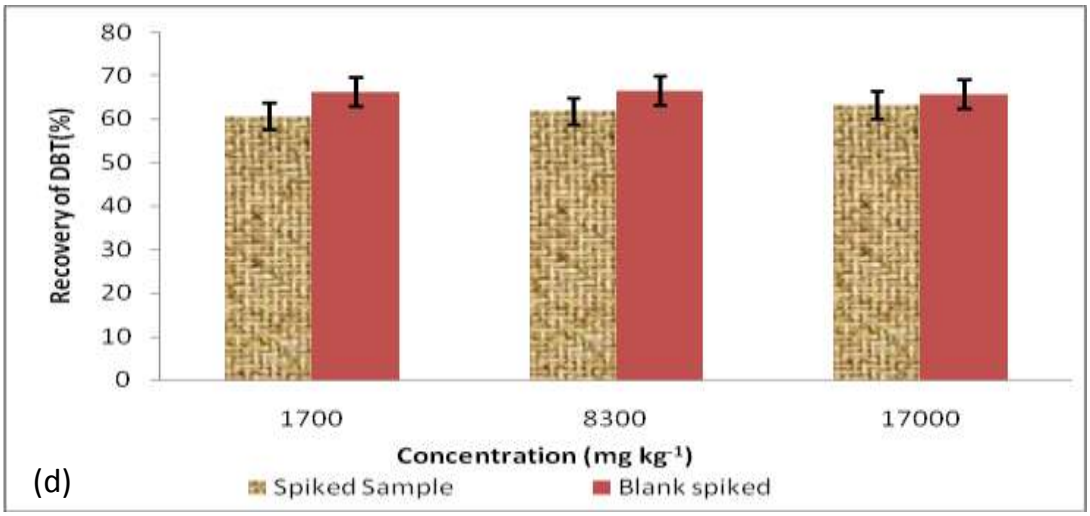


Figure 26: Spiking concentration effect on the recovery of 2-methyl thiophene (a), 3-methyl thiophene (b), 2-ethyl thiophene (c) and dibenzo-thiophene (d).

4.5.2 Sample analysis

The external calibration was used for a trial quantification of target compounds. For this purpose, spiked samples and blank spiked were extracted and quantified by mean of the calibration curve. Table 18 gives the results of the quantified compounds. Detailed results are presented in Tables A1and A2 in the appendix.

Table 18: Preliminary quantification of organic sulphur compounds in coal

Sample	Concentration (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 sulphur compound to be quantified in all coal samples studied. This compound was found in a higher concentration in DRC sample. DRC sample was the only one where all target compounds were quantified. This could mean that DRC sample had an appreciable amount of organic sulphur compounds compared to other samples investigated. Other sulphur 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 sulphur compounds is mostly reported qualitatively in literature (Gryglewicz et al., 2002). This therefore makes it difficult to compare the obtained quantitative results from other studies.

4.6 PYROLYSIS - GC TRIAL

The DRC sample was considered for this preliminary study because of its high organic sulphur content as seen from studies. Pyrolysis study was done by comparing the results of raw coal products to the spiked ones at 600 and1200^{o}C (Figures 27, 28, 29 and 30). Several compounds were detected besides sulphur ones. Organic sulphur compounds were identified alongside standards. However one could presume that the pyrolysis products might be derived from fragmentation of the target organic sulphur compounds.

Although similar products are yielded during pyrolysis, results showed that each single sulphur compound might specifically give a larger amount of a particular product. This behaviour was seen with the four spiked standards used for pyrolysis - GC analysis. These observations agree with studies done

by Selsbo *et al.*, (1996). Peaks on the chromatogram could therefore allow getting probable information on precursor organic sulphur compounds.

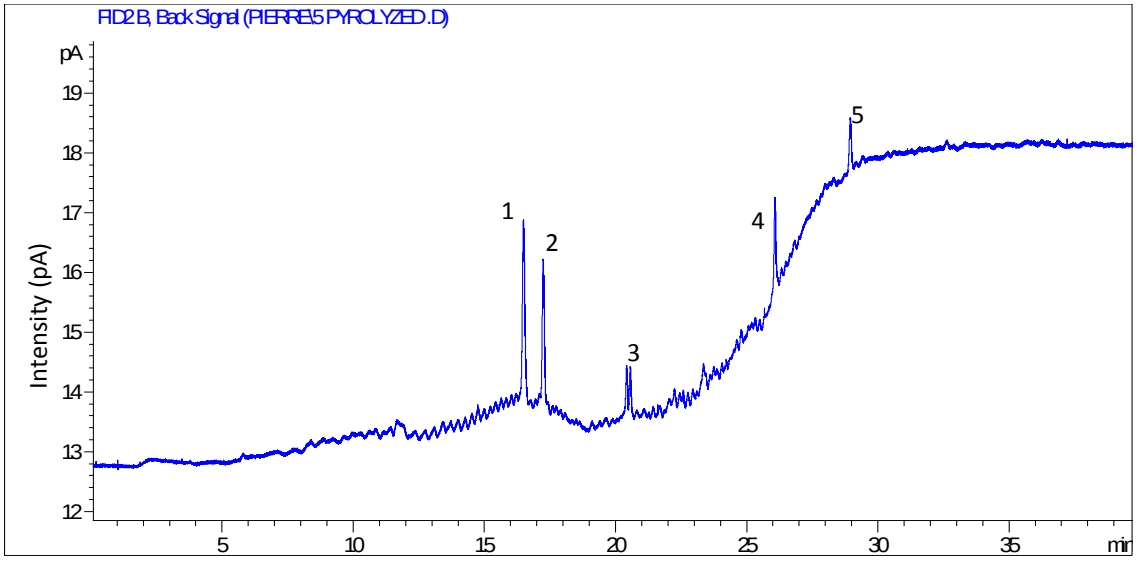


Figure 27: Pyrolysis of DRC at 600°C followed by GC analysis.

The influence of pyrolysis temperature was also investigated both for the blank and spiked samples (Figures 27, 28, 29 and 30). The chromatogram shown in Figure 27 revealed that several compounds were obtained from coal pyrolysis at 600°C. The result indicates that the pyrolysis products can be obtained at relatively low temperature. The pyrolysis of coal was then studied at 1200°C. The gas products were also analysed on GC- FID and the chromatogram obtained is presented in Figure 28 below. The compounds found after 1200°C seemed to be the same as the ones at 600°C pyrolysis. However the peaks seemed to be small. Information regarding the nature of the pyrolysis products and whether where target organic sulphur compounds are assigned could only be assessed after investigation with standard compounds spiked in coal. Figures 29 and 30 showed results of such investigations. The increase of

several peak areas on these chromatograms allowed thinking that the target organic compounds could fragment into several products.

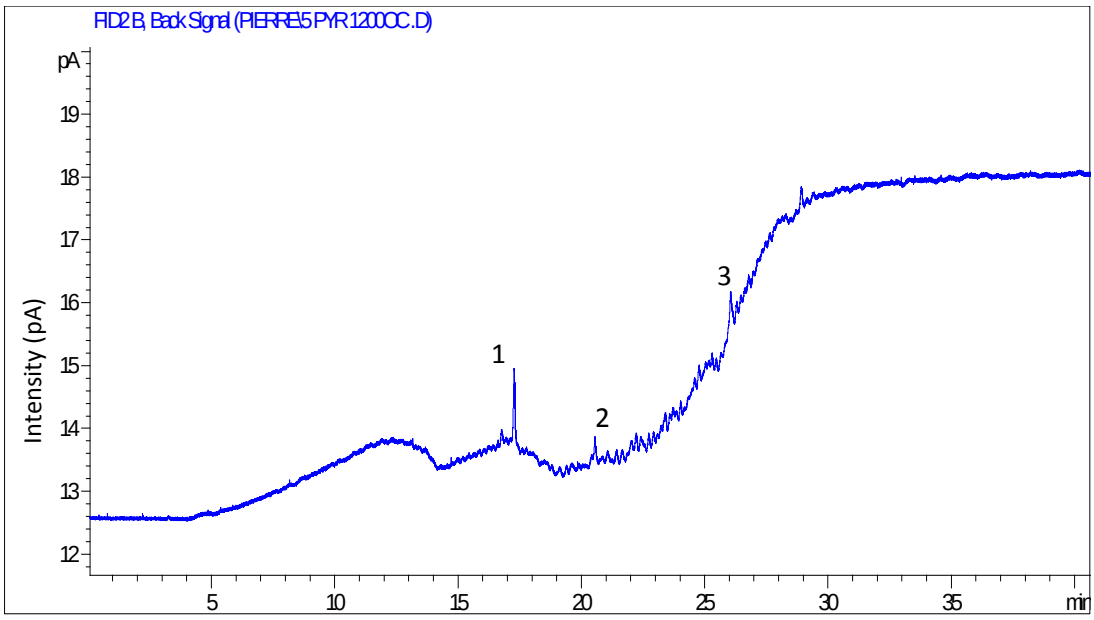


Figure 28: Pyrolysis of DRC at 1200°C followed by GC

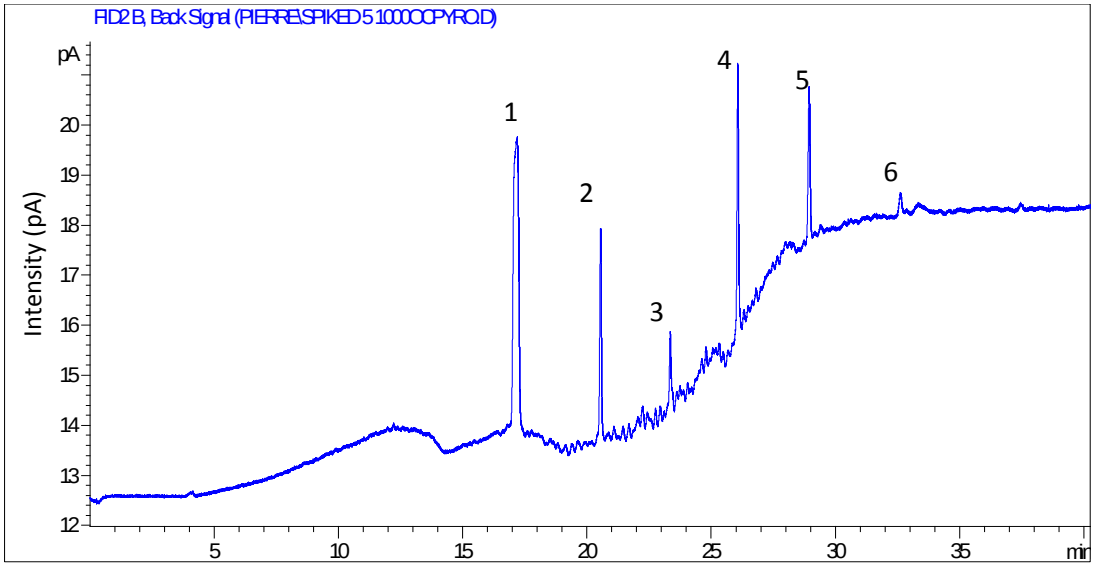


Figure 29: Pyrolysis of spiked DRC at 600°C followed by GC

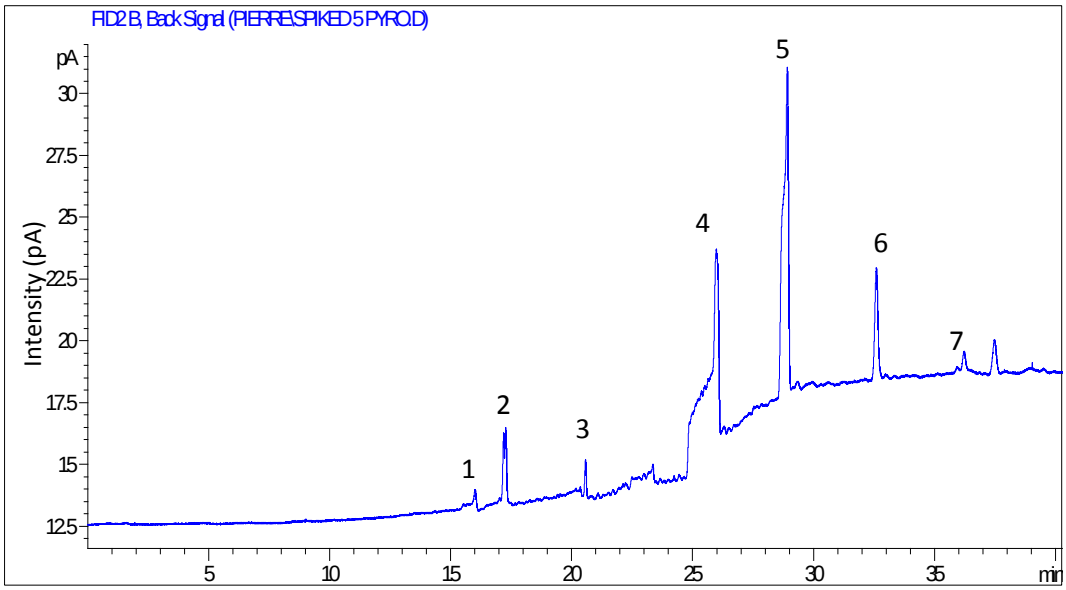


Figure 30: Pyrolysis of spiked DRC sample at 1200°C followed by GC

As all target organic sulphur compounds were thiophenic forms, one could mostly expect a single major product in the pyrolysis yield. The product should be characteristic of these sulphur compounds. This was concluded in the studies done by Selsbo *et al.*, (1996) which showed the dependence of the yield of hydrogen sulphur with thiophenic compounds in coal. As the fragmentation occurred at higher temperature, there might be other possibilities to consider too. Gas compounds that are formed can also secondarily react to produce other compounds which are more stable in the higher pyrolysis temperature media. Secondary products can then make it difficult to explain the obtained pyrolysis products.

Just to have some preliminary identification, retention times and peak areas of the samples product were compared to the spiked samples. Results are shown in Table 19.

Table 19: Comparison of retention time in spiked and unspiked samples

Peak number	Spiked sample		Sample		Standard	
	RT	Peak area	RT	Peak area	RT	Compound
1	17.3	57.7	16.5	30.7	16.5	2-MT
2	20.6	23.9	17.3	21.6	16.8	3-MT
3	23.3	10.9	20.6	4.60	18.7	2-ET
4	26.1	32.6	26.1	15.6	36.9	DBT
5	28.9	23.3	28.9	17.1	-	-
6	32.6	3.3	-	-	-	-
7	36.7	4.3	-	-	-	-

The peak areas of several compounds increased as coal was spiked with the target organic sulphur compounds with same retention time. Several compounds detected in both sample and spiked sample proved the presence of target organic sulphur compounds in coal. Four peaks were identified with similar retention time. However, the retention times of standard organic sulphur studied by direct injection were not similar to the suspected compounds in coal samples and the spiked ones. This suggests that pyrolysis products are from decomposing target organic sulphur compounds giving various fragments as stated previously. To accurately identify these pyrolysis products, a GC-MS system is needed.

CHAPTER FIVE: CONCLUSION AND FUTURE WORK

5.1 CONCLUSION

Proximate and ultimate analysis briefly described the major contents of coal samples, including total sulphur. This analysis showed that all samples belong to bituminous coal rank. 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 and various forms of sulphur were studied in South African coal samples using MAE with acid reagents followed by ICP-OES. Selected metals with an affinity to sulphur were also determined with this method. The total sulphur concentration investigated with MAE followed by ICP-OES was comparable to ultimate (CHNS) analysis. The average amount of total sulphur in coal samples was 8758 mg kg^{-1}. This value allowed confirmed that all these coal samples analysed are low sulphur content. High concentration of total sulphur was found in Duvha raw coal sample. Kriel, Duvha and Lethabo raw coal samples were respectively found with higher concentration of organic, pyrite and sulphate forms. Organic sulphur compounds as well as inorganic forms are mostly related to coal origin and are not equally found in various coal samples studied. Some major and trace elements were also found. These are mostly bound as organic or inorganic sulphur compounds. Pyrite was the most affected by the presence of various metals in coal samples.

The identification of organic sulphur compounds was successfully performed on GC equipped SPB^{TM}-1 Sulphur, fused silica capillary column and using FID as detector. 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. Dichloromethane and 75 minutes were respectively the best solvent and extraction time found in the optimum conditions for extraction of these organic sulphur compounds. The spiking concentration effect on the recovery of organic sulphur compounds was also studied in blank and spiked samples. This recovery was slightly dependent upon the spiked concentration. Higher recovery was generally obtained at higher spiked concentration which was 17000 mg kg^{-1}. A quantification trial of the target organic sulphur compounds was made by comparison of their retention times and peak areas to the standard ones. High concentrations were found with DBT and 2-MT in *Duvha* raw coal samples. Since all coal samples are bituminous type as confirmed from this study, one could expect thiophene groups of organic sulphur forms to be the most predominant.

The thiophenic group studied showed relative influence of sulphur compounds to the products obtained from pyrolysis. In some cases, spiked coal samples gave after pyrolysis, similar peaks but with large area as the samples. However, the retention time of pyrolysis products was not similar to those from direct injection of standards. This suggests that pyrolysis products were degradation of sulphur compounds.

South African coal is one of the most important raw materials for industrial activities. Although it can enhance its activities, the characterization of sulphur content in coal (especially the organic forms) is a major factor to deal with coal environmental issues.

5.2 FUTURE WORK

The following themes are suggested to be addressed in a foreseeable future of this project:

- Pre-concentration of analytes to lower the detection limit as some organic sulphur could not properly be quantified for this. In the current study, the final extract was 20 ml. This could be reduced further to 5 or 1 ml provided no loss of target compounds occur.

- Enlarging the number of target organic sulphur compounds and spiking lower concentrations. Increasing the number of target compounds is justified by other unknown peaks that were seen in the chromatograms. Since the detected organic sulphur compounds were in part per million levels, there is need to spike concentrations close to this.

- Other spectral techniques such as mass spectrometer coupled to the GC to help in identification and quantification of target compounds as this method relies directly on actual mass of compounds analysed.

- Characterization of each form of organic sulphur compounds (thiophenes, sulphides as well as mercaptans) in various coal samples to define the fraction of each of these forms within the total organic sulphur, the total sulphur and the whole coal.

- Detailed optimization of pyrolysis system and the use of GC-MS to identify sulphur compounds from combustion and pyrolysis products

along with the study of fragmentation of sulphur compounds present in coals.

- To further characterize fractions of metal concentrations which are more susceptible to bind with sulphur in coal. This is important in order to draw confirmations on organic as well as inorganic sulphur compounds found in coal.

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APPENDIX

A.1 SELECTED METALS IN COALS AND THEIR EFFECT ON SULPHUR

Arsenic

Arsenic, one of the potentially hazardous trace elements, is usually concentrated in the sulphidic minerals of coal, especially pyrite. There may even be some organically associated arsenic, although this would be a minor component. The arsenic content in coal worldwide is highly variable, with an average value around 5 mg kg^{-1} and extreme high values of up to 35,000 mg kg^{-1} in coals from endemic arsenosis areas in China (Zhou and Ren, 1992; Finkelman, 1994; Valkovic, 1983).

Barium

Barium is not identified as a Hazardous Air Pollutant (HAP) by environmental authorities. It likely occurrences in coal are sulphate, carbonate and phosphate. The most common minerals in coal are barite (BaSO4) and gorceixite ($BaAl_3(PO4)_2(OH)\ 5H_2O$) (Valkovic, 1983).

Cobalt

Cobalt is one of the Hazardous Air Pollutants (HAPs) and its content in coals is of environmental concern in general. In coal, cobalt occurs in the rare mineral linnaeite (Co_3S_4), other sulphides and in clay minerals, and is associated with organic matter (Finkelman, 1994).

Antimony

Antimony is likely to occur in accessory sulphides (e.g., stibnite, Sb_2S_3) associated with the pyrite. The latter compounds are mostly found dispersed throughout the organic matrix in coal (Finkelman, 1994).

Lead

Lead occurs predominantly as sulfides or is associated with sulphide minerals. Galena may be the most common form of lead in coal, but galena can have several significantly different associations. Galena can occur as large, epigenetic crystals in cleat and fractures. It can also occur in minute grains associated with pyrite or as micrometer-sized grains dispersed in the organic matrix (Finkelman, 1985).

Manganese

Most of the manganese in coal, especially bituminous coal, occurs in solid solution in the carbonate minerals siderite and ankerite. In low-ranking coals, lignites and brown coal, a substantial part of the manganese may be organically associated (Finkelman, 1994).

Magnesium

Magnesium mainly occurs in coals as carbonates and silicates. It is also organically bound in coal. Direct interference of magnesium to sulphur determination in coal was reported not be significant. However element

replacement in several compounds could, at the end of the day, affect sulphur analysis (Clarke and Sloss, 1992).

Mercury

Most of the mercury in coal is in solid solution in pyrite. Epigenetic pyrite probably has substantially greater mercury contents than does the early-stage (syngenetic) pyrite like framboidal pyrite. Mercury is the potential hazardous element (Finkelman, 1994; VanLoon, 2005).

Chromium

Chromium appears to be associated with most mineral groups such as clay minerals, carbonates, oxides (hematite,chromite), sulphides(pyrite) (Davidson, 2000; Galbreathe *et al*., 1999; Goodarzi and Riediger, 2000) and also though organic association as Cr^{3+} (Goodarzi and Huggins, 2001).

Calcium

Calcium is mostly encountered in coal as a mineral such as calcite, dolomite and ankerite. However, calcium can also be found in organic compounds that have been leached (Valkovic, 1983).

Iron

Iron can occur in several different forms in coal including sulphides, oxides, sulphates, carbonates and silicates. Pyrite is the most abundant iron mineral in coal (Swaine, 1990).

Copper

Copper mainly occurs as chalcopyrite ($CuFeS_2$) and as finely dispersed mineral in organic matrix in coal. The sulphur form the most likely to be affected by copper presence in coal is pyrite (Swaine, 1990; Valkovic, 1983).

Zinc

The occurrence of zinc in coal is in form of mineral called Sphalerite. Zinc can also be associated with pyrite by replacement of ion and in solid solution. Sulphur content in this mineral might affect sulphate concentration (Finkelman, 1994; Goodarzi *et al.*, 2006).

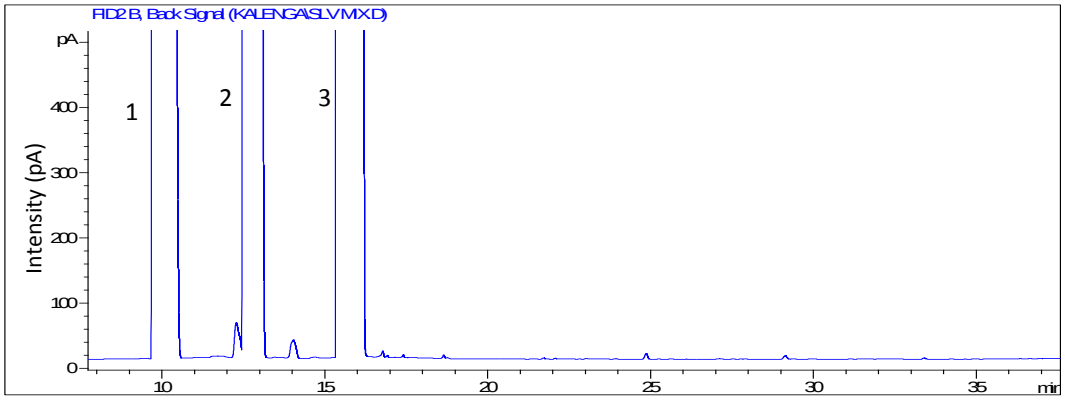


Figure A2: Chromatogram of mixture of solvents (1=dichloromethane, 2=toluene and 3= tetrahydrofurane)

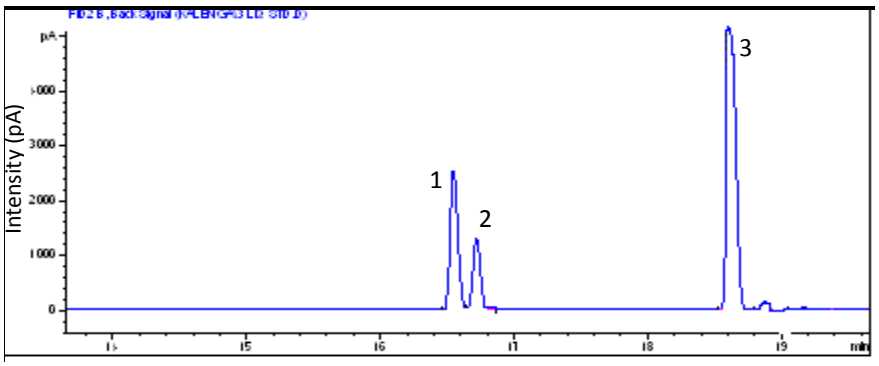


Figure A3: Standards of 2- MT, 3- MT and 2- ET (1,2 and 3 respectively) in dichloromethane.

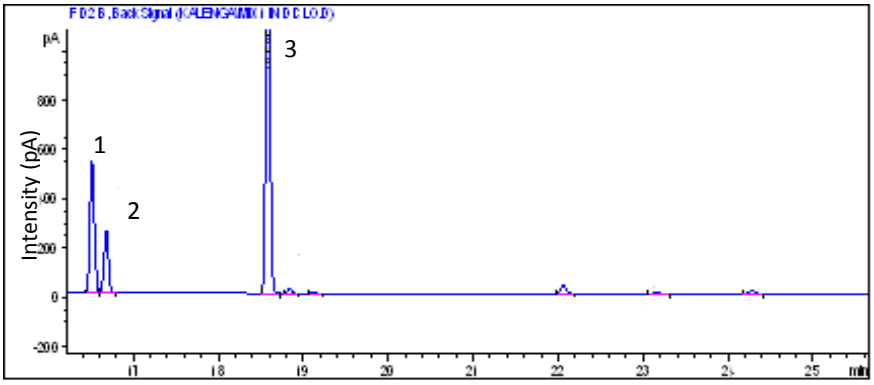


Figure A4: Mixture of 3 pure standards (2- MT and 3- MT and 2-ET) at concentration of 1000 mg l^{-1} in dichloromethane.

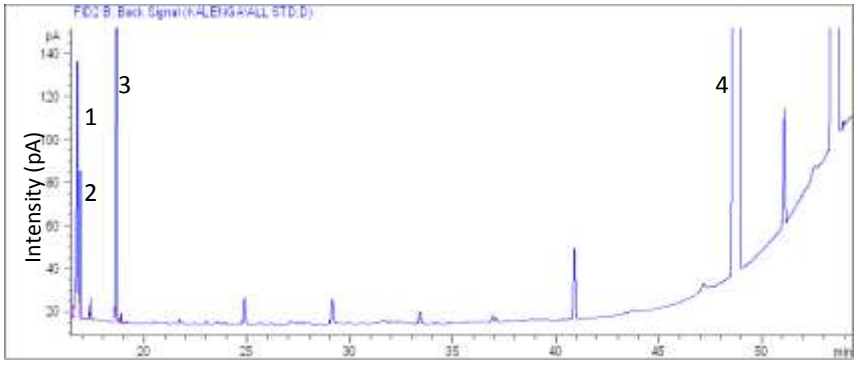


Figure A5: Chromatogram of all standards in dichloromethane (100 mg l^{-1})

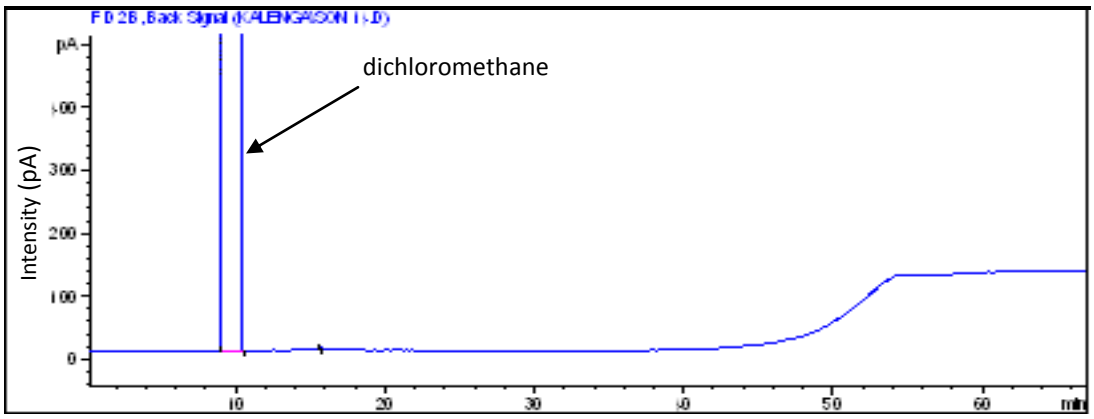
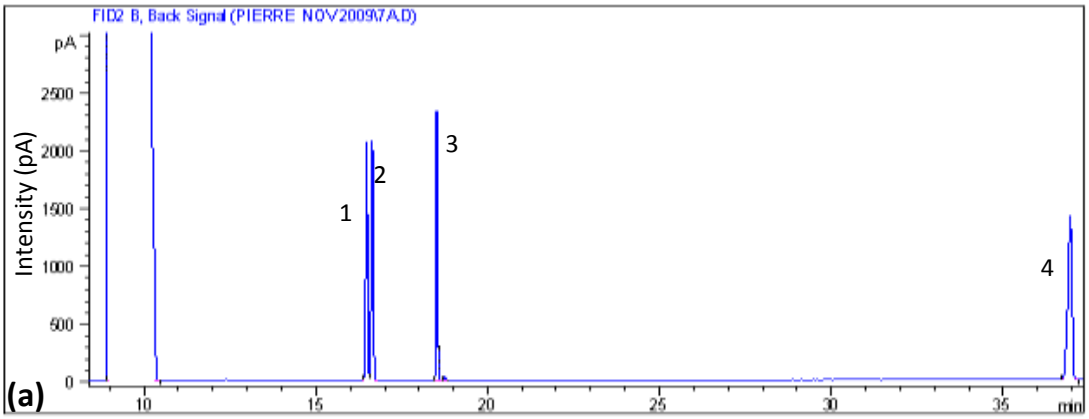
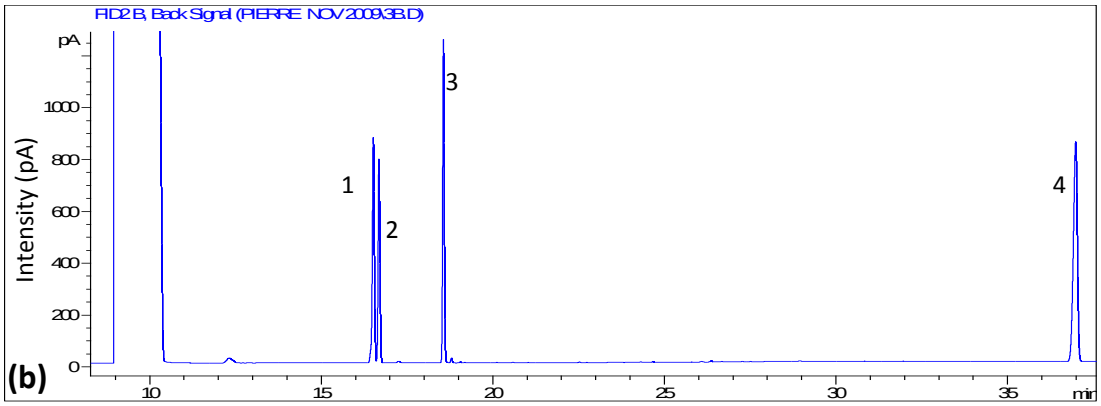


Figure A6: GC of Sonication extract from CRC sample in dichloromethane





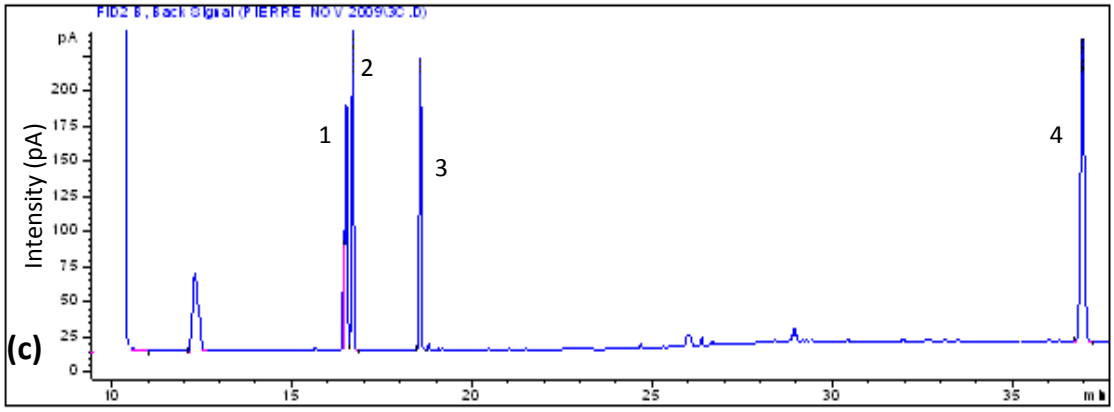
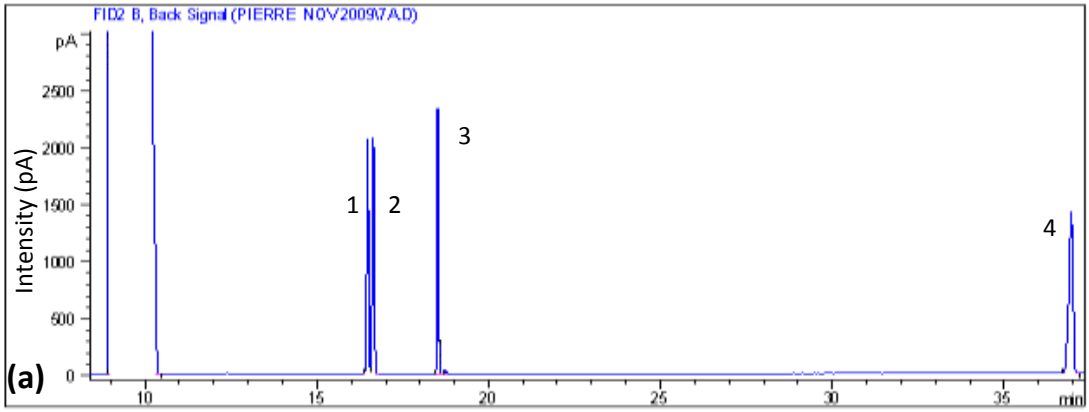
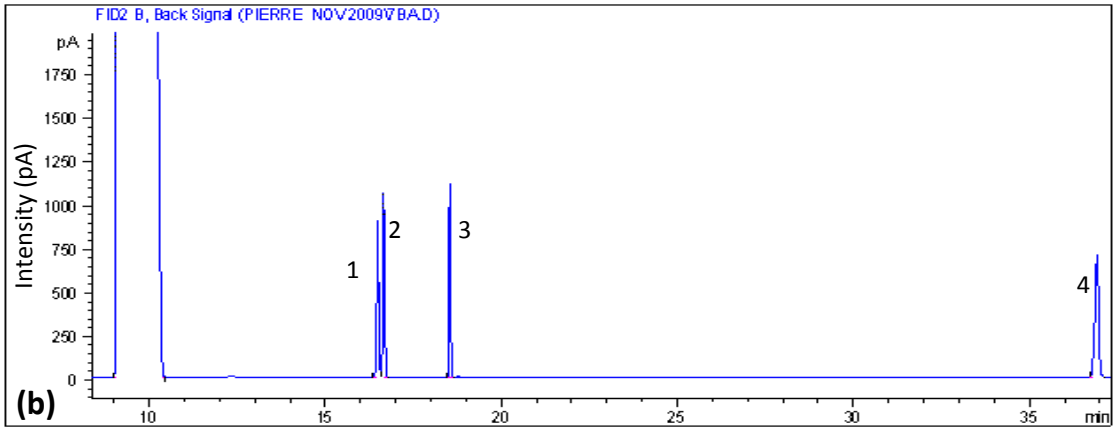


Figure A7: Chromatogram of organic sulphur compounds extracted from TRC sample with 17000 mg kg-1 (a), 8300 mg kg-1 (b) and 1700 mg kg-1 (c) spike. 1=2MT; 2=3MT; 3=2ET and 4=DBT.





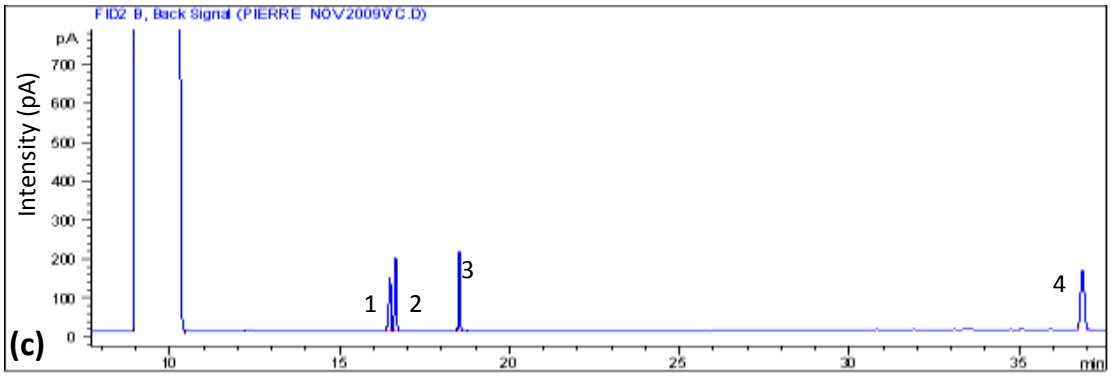


Figure A8: Chromatogram of organic sulphur compounds extracted from KRC sample with 17000 mg kg^{-1} (a), 8300 mg kg^{-1} (b) and 1700 mg kg^{-1} (c) spike. 1=2MT; 2=3MT; 3=2ET and 4=DBT.

Table $A1_a$: Extraction time effect on the recovery of 2-methyl thiophene in DRC sample.

Time (min)	spkd std (mg)	Peak area	2-MT (mg kg^{-1})	% Rec	Std area	Conc of Std	% Std Rec	Conc 2-MT in coal
75	50	5566	445.4	34.7	12902	1010	84.7	241.9
45	50	5952	387.7	27.5	15685	1011	70.7	97.3
15	50	7744	433.1	26.0	17504	979.7	56.8	11.5
45	5	2145	103	62.1	1110	102.3	73.7	97.3
75	5	903.6	86.4	52.0	1557	106.4	83.0	241.7
15	5	1991	110.9	61.4	1616	90.0	57.6	11.5

Table $A1_b$: Extraction time effect on the recovery of 3-methyl thiophene in DRC sample.

Time (min)	spkd std (mg)	Peak area	3-MT (mg kg^{-1})	% Rec	Std Area	Conc of Std	% Std Rec	Conc
75	50	6156	473.1	36.9	12811	985.6	82.8	nd
45	50	6812	420.6	29.9	15627	984.8	68.9	nd
15	50	9926	547.2	32.8	17808	996.5	57.8	nd
45	5	1062	63.9	49.2	1189	90.7	70.7	nd
75	5	1200	61.4	40.5	1994	112.2	80.8	nd
15	5	1348	58.3	32.7	2521	125.2	80.1	nd

Table $A1_c$: Extraction time effect on the recovery of 2-ethyl thiophene in DRC sample.

Time (min)	spkd std (mg)	Peak area	2-ET (mg kg^{-1})	% Rec	Std Area	Conc of Std	% Std Rec	Conc
75	50	7658	535	41.7	13115	949.8	79.8	nd
45	50	7535	431	30.6	16087	969.8	67.9	nd
15	50	8890	418.3	25.1	18788	933	54.1	nd
45	5	1671	80	61.6	2244	123.5	96.4	nd
75	5	2722	89.3	58.9	2823	134.2	96.6	nd
15	5	2568	89.6	50.2	3024	113.3	72.5	nd

Table $A1_d$: Extraction time effect on the recovery of dibenzo-thiophene in DRC sample.

Time (min)	spkd std (mg)	Peak area	DBT (mg kg^{-1})	% Rec	Std Area	Conc of Std	% Std Rec	Conc
75	50	9136	512.1	39.9	12305	996.7	83.7	nd
45	50	8902	490.3	34.8	13041	1014	71.0	nd
15	50	9567	491.8	29.5	15351	1010	58.6	nd
45	5	2978	86.4	66.6	2872	98.5	76.9	nd
75	5	2698	85.3	56.3	2978	90.0	64.8	nd
15	5	2387	89	49.8	3130	104.9	67.1	nd

Table $A2_a$: Spiked concentration effect on extraction of 2-methyl thiophene from coal samples

Sample	mg Std spkd	mg Std Spkd per kg coal	Peak Area	mg 2-MT	Rec from spkd sample	Std peak area	mg Std	Rec S std	Conc in coal ($mgkg^{-1}$)	% 2-MT in org S
TRC	50	17000	9739	33.43	66.86	7531	32.82	65.64	200.9	4.96
DRC	50	17000	8095	34.35	68.70	7531	32.82	65.64	507	15.0
KRC	50	17000	8164	34.43	68.86	7531	32.82	65.64	532.1	8.3
Mean	50	17000	8666	34.07	68.14	7531	32.82	65.64	413.3	9.42
TRC	25	8300	4359	13.66	54.64	3961	16.77	67.08	nd	nd
DRC	25	8300	4023	13.71	54.71	3961	16.77	67.08	nd	nd
KRC	25	8300	3459	13.75	55.00	3961	16.77	67.08	nd	nd
Mean	25	8300	3947	13.71	54.82	3961	16.77	67.08	nd	nd
TRC	5	1700	705.7	1.854	37.08	868.1	3.287	65.74	nd	nd
DRC	5	1700	856	2.17	43.42	868.1	3.287	65.74	nd	nd
KRC	5	1700	661.1	2.492	49.84	868.1	3.287	65.74	nd	nd
Mean	5	1700	740.9	2.172	43.46	868.1	3.287	65.74	nd	nd

Table $A2_b$: Spiked concentration effect on extraction of 3-methyl thiophene from coal samples

Sample	mg Std spkd	mg Std Spkd in kg coal	Peak Area	mg 3-MT	Rec from spkd sample	Std peak area	mg Std	Rec S std	Conc in coal (mg kg^{-1})	% 3 MT in org S
TRC	50	17000	8798	33.38	66.76	7650	33.13	66.3	nd	nd
DRC	50	17000	8070	34.01	68.02	7650	33.13	66.3	292.9	8.67
KRC	50	17000	7832	32.8	65.6	7650	33.13	66.3	nd	nd
Mean	50	17000	8233	33.40	66.81	7650	33.13	66.3	nd	nd
TRC	25	8300	3364	15.78	63.14	4119	17.11	64.4	nd	nd
DRC	25	8300	4032	16.24	64.96	4119	17.11	68.4	nd	nd
KRC	25	8300	3856	15.32	61.28	4119	17.11	64.4	nd	nd
Mean	25	8300	3751	15.78	63.12	4119	17.11	64.1	nd	nd
TRC	5	1700	881.9	2.87	57.39	899.5	3.504	70.1	nd	nd
DRC	5	1700	788.4	2.906	58.12	899.5	3.504	70.1	nd	nd
KRC	5	1700	718.2	2.835	56.7	899.5	3.504	70.1	nd	nd
Mean	5	1700	796.2	2.870	57.41	899.5	3.504	70.1	nd	nd

Table A2$_c$: Spiked concentration effect on extraction of 2- ethyl thiophene from coal samples

Sample	mg Std spkd	mg Std Spkd in kg coal	Peak Area	mg 2-ET	Rec from spkd sample	Std peak area	mg Std	Rec S std	Conc in coal (mg kg^{-1})	% 2-ET in org S
TRC	50	17000	10970	32.8	65.5	8023	33.13	66.26	nd	nd
DRC	50	17000	8388	33.52	67	8023	33.13	66.26	128.8	3.81
KRC	50	17000	7822	31.06	62.1	8023	33.13	66.26	nd	nd
Mean	50	17000	9060	32.46	64.55	8023	33.13	66.26	nd	nd
TRC	25	8300	4776	14.24	57	4106	16.11	64.44	nd	nd
DRC	25	8300	4659	14	56.0	4306	16.89	67.56	nd	nd
KRC	25	8300	3671	13.96	55.8	4106	16.11	64.44	nd	nd
Mean	25	8300	4369	14.07	56.4	4106	16.11	64.44	nd	nd
TRC	5	1700	928.4	2.616	52.3	741.7	3.504	70.08	nd	nd
DRC	5	1700	664.5	2.523	50.5	741.7	3.504	70.08	nd	nd
KRC	5	1700	705.4	2.57	51.38	741.7	3.504	70.08	nd	nd
Mean	5	1700	766.10	2.57	51.39	741.7	3.504	70.08	nd	nd

Table $A2_d$: Spiked concentration effect on extraction of dibenzo-thiophene from coal samples

Sample	mg Std spkd	mg Std Spkd in kg coal	Peak Area	mg DBT	Rec from spkd sample	Std peak area	mg Std	Rec S std	Conc in coal (mg kg^{-1})	% DBT in org S
TRC	50	17000	17408	31.46	62.92	11246	32.9	65.80	nd	nd
DRC	50	17000	12103	31.49	62.98	11246	32.9	65.80	524.8	15.5
KRC	50	17000	11278	31.90	63.80	11246	32.9	65.80	nd	nd
Mean	50	17000	13596	31.62	63.36	11246	32.9	65.80	nd	nd
TRC	25	8300	8640	16.35	65.47	5833	16.65	66.60	nd	nd
DRC	25	8300	6240	15.46	61.85	5833	16.65	66.60	118	3.49
KRC	25	8300	5423	14.56	58.24	5833	16.65	66.60	nd	nd
Mean	25	8300	6768	15.46	61.9	5833	16.65	66.60	nd	nd
TRC	5	1700	1654	3.162	63.24	1204	3.176	63.52	nd	nd
DRC	5	1700	1164	2.927	58.54	1204	3.176	63.52	nd	nd
KRC	5	1700	1205	3.03	60.69	1204	3.316	66.34	nd	nd
Mean	5	1700	1341	3.04	60.74	1204	3.316	66.34	nd	nd

Table A3: Calibration results for selected metals analysis on ICP-OES

Element and spectral line	Intensity(cps) at					Standard error (10^{-4} ppm)	Correlation coefficient	Detection limit (10^{-4} ppm)
	0.05 ppm	0.1 ppm	0.2 ppm	0.5 ppm	1.0 ppm			
As193.8	1750	3673	7832	19343	38483	3500	0.99996	133
Ba455.4	1764300	5391800	10486500	24917200	50287100	4420	0.99993	2.6
Ca396.9	2859570	6025800	10693400	25362100	50499200	8570	0.99985	4.1
Co 228.6	23752	47998	89114	229668	446047	6070	0.99988	18
Cr205.6	12824	25798	52179	130450	252646	5860	0.99986	10.1
Cu224.7	9920	18747	35424	85236	167264	4060	0.99992	50
Fe 238.2	36055	73955	141628	350950	675921	8360	0.99981	22
Hg194.2	3909	7654	15092	38913	81315	8750	0.99970	70
K766.3	9326	13879	21415	48021	96811	5500	0.99935	20
Mg279.6	980066	2070070	3932000	9683550	18776600	7420	0.99970	77
Mn257.6	208613	417452	808533	1980850	3850750	5070	0.99990	870

Table A3: Calibration results for selected metals analysis on ICP-OES (continued)

Element and spectral line	Intensity(cps)at					Standard error (10^{-4} ppm)	Correlation coefficient	Detection limit (10^{-4} ppm)
	0.05 ppm	0.1 ppm	0.2 ppm	0.5 ppm	1.0 ppm			
Na589.6	91543	353114	660063	1721490	3560560	9610	0.99998	28
Pb220.4	2517	6152	12489	32187	62837	5870	0.99986	85
S180.7	-1118	-867	-72	2172	6066	10300	0.99987	288.7
Sb206.8	957	1915	3718	9397	18639	1560	0.99999	257.2
Zn206.2	699	1459	3302	7940	15496	7250	0.99985	262.5