# Chapter 4: Complementary Analyses

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## INTRODUCTION

An understanding of chemical composition, physical properties, and structural characteristics at an elemental, molecular, and functional group level is essential in unpacking coal formation and accurately predicting coal processing and conversion behaviour. Whilst petrography can provide a substantial amount of information as discussed in the previous chapters, it cannot provide all the information required to build a complete, holistic picture of coal. Hence the need for complementary and advanced analyses. This chapter briefly considers a variety of routine and non-routine analyses conducted on coal to assess chemical, physical, and structural properties. Chemical analyses, including proximate, ultimate analyses, and calorific value (CV) determination, are routine analyses conducted by coal laboratories. Coal is traded globally and domestically on its CV and ash content (determined during the proximate analysis). The physical properties of coal (Abrasive Index for abrasion and wear, Hardgrove Grindability Index for grindability, and drop shatter tests for friability) provide information required for coal handling and comminution (crushing to size). X-ray (XRD, XRF, tomography), laser (SEM, QEMSCAN, Raman), and infrared (NMR) techniques are used to determine the mineral component down to the elemental level, as well as information regarding the structural ordering of the carbon, revealing the heterogeneous structure of coal. Finally, analytical techniques crucial for characterizing metallurgical cokes are discussed. Many textbooks are available for further reference, including: van Krevelen (1961), Berkowitz (1985), Speight (2005, 2016), Willson *et al.* (2010), and Osborn (2013), amongst others.

## CHEMICAL ANALYSIS

### Calorific Value

Calorific value (CV) refers to the heat or energy content of coal, and is a vital parameter for coal-fired power stations in order to effectively predict heat energy input. Hence, CV is the most important commercial parameter and is, therefore, widely used for economic evaluation and marketing purposes. The higher the CV, the higher the monetary value of the particular coal. There is a direct correlation between CV and ash content (Figure 3.12).

To establish the CV, a known mass of coal (milled to a fine, representative sample) is burnt in pressurised oxygen in an isoperibol calorimeter (bomb calorimeter) under standardised conditions. The gross calorific value (GCV) is calculated from the rise in temperature of the water surrounding the vessel in the calorimeter and the mean effective heat capacity of the system. The result is given as the mean of duplicate determinations, reported to the nearest 0.01 MJ/kg, or kcal/kg or BTU/lb. CV can be determined by ISO standards at either constant volume or constant pressure, while CV by ASTM standards is determined at constant pressure. SANS 1928:2009/ISO 1928:2009 applies.

The net calorific value (NCV) is calculated from the GCV by calculation. NCV is generally reported on an ‘as received’ (ar) basis, and more closely represents the practical energy of a coal for a power station. It is therefore a common parameter for thermal coal sale contracts.

### Proximate Analysis

The term ‘proximate’ means ‘first’, and, thus, this analysis represents the first basis for coal characterisation and utilisation prediction. The analysis is conducted after crushing the coal sample to a nominal size of -95% passing 0.212 µm. When received by the laboratory, the coal is weighed and laid out as a thin layer on a tray for a specified length of time under controlled conditions in order to stabilise the moisture content of the coal in the laboratory atmosphere. After weighing again, the following analyses are undertaken on the coal sample:

* % moisture (reported as received, residual, inherent)
* % ash content
* % volatile matter (VM), and
* % fixed carbon (FC) (calculated by difference).

Each of the parameters is reported as a mean of duplicate determinations to the nearest 0.1% (weight %). A variety of ISO, ASTM, and country specific standards apply, which must be specified by the analytical laboratory when reporting the results; SANS 17246:2011/ISO 17246:2010 is appropriate for use in South Africa, amongst other standards listed for the individual analyses. Proximate determination by thermogravimetric (TGA) may also be undertaken (ASTM D7582 – 12).

**Moisture in coal:**

There are various types of moisture in coal, including *surface moisture* (stored in empty spaces between coal lumps and in pores, fractures, and cavities) and *inherent moisture* (attached physically to the coal in various forms, and typical of the coal in its natural state). As moisture content has a bearing on other parameters in the proximate suite of analyses, it is necessary to take account of the form of moisture and, therefore, the *moisture ‘basis’* upon which analyses are reported. This is particularly important when drawing up and meeting contract specifications. The different reporting bases for moisture, and other properties, are as follows:

* *As received (ar)* - total moisture, i.e. containing both surface and inherent forms of moisture.
* *Air dry (ad)* - the stable moisture content of the sample after it has achieved equilibrium with the humidity of the laboratory.
* *Dry (d)* –the analysis is reported based upon an assumed situation where the coal is completely free of moisture; this is a calculated value.
* *Dry ash-free (daf)* – again a calculated value representing the hypothetical condition that the sample is completely free of moisture and ash. This reporting basis allows for the assessment of a coal based solely on the organic matter in coal, namely the VM and FC contents, thus enabling standardisation of the organic components for more accurate comparison between samples.

Various equations allow the conversion of a given result to another on a different basis. Conversion equations may be found in many references, including Osborn (2013).

For moisture determination, the sample is brought to equilibrium with the humidity in the laboratory atmosphere. A known mass is then dried in an oven between 105-110oC in the presence of nitrogen. The moisture percentage is calculated from the loss of mass of the sample. The moisture content of a coal will change depending on the relative humidity of the atmosphere to which it is exposed; as humidity changes, so will the moisture content of the coal. For this reason, reproducibility for moisture content is not applicable.

**Ash content in coal:**

The ash content in coal is comprised of minerals which are the primary incombustible components in coal. Ash is the residue remaining after the complete combustion of all organic matter, and, thus, is considered a waste material (although certain forms of ash are sold for commercial purposes). Coal is traded globally based on CV, which is inversely proportional to the ash content (on an iso-rank basis), with the commercial categories being known as coal grade. The types of minerals included in coal are critical in determining beneficiation processes and the coal’s end use; the minerals are determined by XRD and SEM based techniques.

The standard procedure for determining the ash value of a coal involves heating a known mass of sample (usually 1 g) in a crucible in air to 500oC over 30 minutes, maintaining this sample at this temperature for 30 minutes and then heating to 815oC until the mass of the sample is constant. The percentage ash is calculated from the mass of residue remaining after combustion divided by the original mass of the sample used in the procedure. Some mineral species are altered when the coal is combusted and neo-formed minerals may occur. Carbon dioxide is released by carbonate minerals, SO3 arises from sulphides, and H2O is removed from clay minerals as water of crystallisation. X-ray analyses (XRF, XRD) provide more detail regarding the chemical composition and nature of minerals and ash present in a coal.

**Volatile matter:**

Volatile matter is the percentage loss in mass, adjusted for moisture, when coal is heated in the absence of oxygen under standardised conditions. It is a useful parameter when considering the reactivity of coal. In vitrinite-rich low ash coals there is a correlation between VM and coal rank such that VM may be used to infer the rank category of a coal, but caution is advised. Bituminous vitrinite-rich coals in close proximity to sills and dykes may possess low VM contents appearing to be high rank semi- or anthracitic coals, but are in fact locally burnt or heat-affected parts of seams. Similarly, coals rich in inert forms of inertinite will report considerably lower VM contents than reflected by the true rank of the coal (as defined by other means). Weathering and oxidation of coal may also reduce VM content. In power generation, VM aids the ignitability and burnout characteristics of coal by devolatilising when exposed to heat in the early phases of combustion. This is followed by rapid ignition of the volatiles, thereby supporting the ignition, combustion, and burnout of the solid carbon material (chars). In metallurgical coal, VM generates gas pores within the coke particles and provides heat in the furnace. To determine VM, 1 g of fine coal is placed into a lidded crucible (to prevent ingress of air) in a furnace at 900oC for 7 minutes. The mass loss difference accounts for the loss of VM less inherent moisture content.

**Fixed Carbon:**

Fixed carbon is the solid combustible residue remaining by calculation after the removal of moisture, ash, and VM from coal, expressed as a percentage. It is calculated by subtracting the percentage moisture, ash and VM from 100%. Hence, it is vital that all parameters used are on the same basis and accurately determined. FC is an indirect prediction of carbon content; C determination by ultimate analysis is a more accurate representation of the carbon in coal.

### Ultimate Analysis

The organic-derived components of coal are composed primarily of the elements: carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and organically bound sulphur (S). These components make up more than 99% of the organic and inorganic portions of coal, and as such, they are often reported as parts of the sum of 100% including moisture and ash. Determinations of C, H, and N are undertaken by an automatic non-dispersive infrared analyser. The sample undergoes combustion in pure oxygen at high temperatures in a small furnace, converting elemental C, H, and N into CO2, H2O, N2, and NOx. The gases pass through infrared cells to determine C and H content, and a thermal conductivity cell to determine N. The raw H analysis is corrected for moisture. From the ultimate analyses, C (% daf) may be used to predict rank in vitrinite-rich, low ash coals. Hydrogen is used in all NCV calculations, and N impacts on NOx formation and emissions. Oxygen is determined by difference. SANS 17247:2006/ISO 17247:2005 applies.

## PHYSICAL ANALYSIS

### Abrasion Index

Abrasion relates to the wear or erosion of plant parts by the coal components (organic and inorganic). Minerals such as pyrite and quartz cause a high wear rate in crushing, milling, and pulverising equipment. The Abrasion Index (AI) is a measure of the wear of the blades in the testing pot. A 2 kg sample of -6.7 mm sized material is placed in a mill in which four standard metal blades rotate at 1500 r/minutes for a duration of 12 000 revolutions. The AI is calculated from the loss in mass of the four blades during the test. Results are reported as the mean of duplicate determinations to the nearest 1 mg of metal lost per kilogram of coal. The values reported may range from an average of 200 mgFe/kg or less for normal coal and up to several 1000 mgFe/kg for coals containing sandstone or high pyrite contents.

### Hardgrove Grindability Index

The primary test for grindability is the Hardgrove Grindability Index (HGI) test which is used to characterise the ease by which a coal can be crushed and ground. It entails grinding a specific mass of coal with a specified particle size range (50 g of 16 x 30 mesh) in a mill for sixty revolutions.  The resulting coal is screened at 200 mesh, and sized, and the weight of the products recorded and compared against a standard. Values falling in the low 20s would imply a difficult to grind (hard) coal; values falling well above 60 implies a soft, friable, and easy to comminute coal.  Vitrite-rich bands in the bituminous range are known to provide higher HGI values (<50), and in-seam partings (sandstone or mudstone) when included with coal may result in HGI values as low as 28.  Weathered coals have been found to have HGIs as high as 70. SANS 5074:1994/ISO 5074:1994 applies.

### Drop Shatter Tests

The breakage properties of coal are of economic importance as sized material (such as peas, nuts, and cobbles) is required by users of coal in industry. During mining and transportation, coal breaks down to varying levels of size degradation, ultimately reaching a point beyond which little further breakage occurs naturally. Some coals retain large sizes until crushed in a preparation plant, while others crumble extensively once mined. It is relevant for coal producers and process engineers to establish to what extent coals will break naturally, or what forces are required to break coal particles to the required sizes.

To test this breakage property in a laboratory, coal is divided into sub-samples of less than 50 kg. Samples are then dropped from 2 metres and screened. This process is repeated until either all coal passes a nominated screen size aperture or until a point is reached at which the rate of breakage levels off. Vitrinite-rich bands are particularly brittle and would break off first, concentrating in the finer fractions, whereas fibrous inertinite forms and those bands of coal enriched in mineral matter would be more resistant to breakage and would therefore concentrate in the larger sizes. SANS 401:2010/ASTM D 440:2007 applies.

## MINERAL AND ASH COMPOSITION ANALYSIS

### X-Ray Diffraction (XRD)

X-ray diffraction (XRD) and X-ray fluorescence (XRF) techniques are used to determine the composition of minerals in coal. XRD can also assess the crystal structure of graphitic carbon. They are useful complementary techniques frequently used in conjunction with optical analyses (light or scanning microscopy, for example).

XRD is used to enhance the understanding of the minerals, inorganic, and organic matter in coal. The sample preparation for XRD analysis varies depending on the anticipated outcome, and the rapid analysis measures a bulk sample and assumes the sample is homogenous. The analysis is usually performed on coal, low-temperature-ashed coal, or on ash samples. The sample is exposed to x-rays, and the resultant diffraction patterns are representative of mineral phases. The analysis reveals both quantitative and qualitative information on mineral matter, depending on the software and methods used. Figure 4.1 represents an example of a typical spectrum generated for mineral identification in coal samples using XRD analysis. Quartz, clays, pyrite, muscovite, carbonates, and so on are readily determined, and the carbonaceous matter is approximated.

For quantitative analysis, the Rietveld method is applied to more accurately characterise the minerals in a sample. High temperature XRD analysis involves heating a sample within the XRD equipment and analysing changes as they occur. Thus, it is useful in predicting thermal behaviour of minerals in a boiler, for example.

For organic analysis, XRD involves the characterization of materials by means of assessing the atomic arrangement in the crystal lattice (Jenkins, 2000). This is a non-destructive and well established technique with good reproducibility. Coal structure is made up of highly disordered aromatic and aliphatic carbons, and, using XRD, the coal structure is determined by the presence of three Miller indices representing the interplanar spacing, namely: (i) d002, (ii) 110 and (iii) 100. The Miller indices are the reciprocals of the intersection distances in a unit cell. XRD studies use these Miller indices to determine the regular arrangement of atoms in crystals and the symmetry of their arrangement in a unit cell (Atkins and De Paula, 2006). The sharpness and intensity of the peaks provide an indication of the degree of order in the crystalline structure, indicative of the degree of graphitization (Verryn, 2012) (Figure 4.2).

**Figure 4.1: An XRD spectra showing mineral composition in a coal sample. The peaks represent positions where the X-ray beam has been diffracted by the crystal lattice, representing the unique fingerprint of that mineral (Ndhlalose, 2015).**

**Figure 4.2: A typical XRD spectra for coal when assessing the crystalline structure (Malumbazo, 2011).**

### X-Ray Fluorescence (XRF)

X-Ray Fluorescence (XRF) is a rapid, non-destructive analytical technique used for the determination of the elemental composition of coal. It enables the quantification of the major oxides and trace elements present in coal and ashed coal samples. The samples, ground to a fine powder, are mixed with a binder to form pellets / flat disks / fused beads. The prepared samples are bombarded with high energy x-rays, and fluorescent (or secondary) x-rays are emitted from the sample. The characteristic radiation is directly related to the amount of each element in the sample. The matrix effects are corrected.

Whilst light elements (e.g. beryllium, sodium) can, in principle, be analysed by XRF, instrumental limitations and low x-ray yields are problematic. More routinely, XRF is used to determine the major elements in ashed coal samples, including SiO2, Al2O3, TiO2, P2O5, CaO, MgO, Na2O, K2O, and SO3. The use of P2O5 as an indicator for phosphorous content is typically used in the coking industry. XRF is also a useful technique to determine chlorine levels in coal. The oxide values generated are typically used in slagging and fouling calculations. It must be noted that the overall accuracy of any XRF analysis depends in the accuracy of the peak and background measurements, as well as the instrument calibration.

### Sulphur Form Analysis

Understanding the sulphur content in coal is important for the prediction of sulphur-based emissions (such as SO2, H2S, and acid mine water) and coal beneficiation (sulphur removal), as well as interpreting depositional environments and the formation history of coal deposits. Thus, total sulphur determination is an important parameter in resource evaluations, with strict penalties applied in the market for high sulphur coals. Most coals globally fall in the range of 0.5 – 5 % total sulphur (or lower in Gondwana coals). Low-sulphur coals report less than 1% total sulphur; medium sulphur coals 1 – 3 % total sulphur, and high sulphur coals 3% or higher total sulphur content (Chou, 2012).

Total sulphur is determined in the suite of ultimate analyses, providing a bulk sulphur value and is not indicative of the sulphur form or its mode of occurrence. If the sulphur form and mode of occurrence is understood, then coal upgrading via conventional gravity separation, for example, may be possible. Sulphur occurs as pyritic (sulphides), organic, and sulphates, with the former two accounting for the bulk of sulphur in coal. Sulphates occur in weathered coals, and elemental sulphur is very rare.

Pyrite is the main sulphide, with marcasite, pyrrhotite, sphalerite, galena, and chalcopyrite known to occur. Plates 39 and 40 indicate several modes of occurrence of pyrite, as observed petrographically, from finely disseminated forms and framboids, to cleats, cell infillings, veins, and replacement minerals forms. Organic sulphur cannot be determined petrographically.

Sulphur form analysis is a geochemical analysis (ASTM D2492-2002, 1989; SANS 402:2005/ISO 157:1996) and determines sulphides and sulphates. Organic sulphur is traditionally calculated as the difference between total sulphur and the sum of sulphides and sulphate:

Organic sulphur = total sulphur – (sulphates and pyritic sulphur)

This means that any errors in the determination of the pyritic and sulphatic forms, as well as the total sulphur value, reflect in the organic sulphur value. HCl and HNO3 is used to extract sulphate and sulphides; organic sulphur is insoluble. The solution is assessed via atomic adsorption, where iron is determined as a measure of pyritic sulphur. Nitric acid determination may produce inaccurate sulphide values due to incomplete dissolution of pyrite or the presence of non-pyritic sulphides (Chou, 2012). Some researchers believe that organic sulphur is under reported, and direct determination by Qemscan or SEM-EDS is preferable.

### Trace Element determination

Trace elements (TE) in coal pose potential environmental hazards, specifically in terms of hazardous air pollutants (HAPS). The US Clean Air Act of 1990 lists eleven TEs which result directly from coal combustion and utilization: As, Be, Cd, Cr, Co, Pb, Hg, Mn, Ni, Sb, and Se. Swaine (2000) considered twenty-six elements found in coal to be of environmental concern with levels of toxicity decreasing from As, Cd, Cr, Hg, Pb, Se to B; Cl, F, Mn, Mo, Ni, Be, Cu, P, Th, U, V, Zn; and Ba, Co, I, Ra, Sb, Sn, and Ti. Finkelman (1994, 1995) considered the modes of occurrence of trace elements in coals, and Bergh *et al.* (2011), Wagner and Tlotleng (2012), Wagner and Hlatshwayo (2005) are recent publications pertaining to trace elements in South African coals. The reader is advised to consult Davidson and Clarke (1996), Ketris and Yudovich (2009), and Swaine (1990, 2000) for further information regarding TE in coals.

Whilst XRF can be used to determine TE in coals, the low detection levels create problems. Inductively coupled plasma mass spectrometry (ICP-MS) is the favoured method of TE analysis, excluding mercury determiantion. Mercury is typically determined via automated Hydride Generation-Flow Injection Mercury Systems or cold vapour atomic adsorption. All these techniques require the sample to be in solution, and hence the TE are extracted from the coal via destructive digestion or dissolution techniques. Coal may be ashed prior to extraction, but the more volatile TE may be lost during ashing (such as mercury, and some arsenic, cadmium, and selenium). Hence, sample preparation should be conducted in closed vessels to retain all gases. Sequential leaching or microwave digestion in closed teflon vessels are the preferred preparation techniques (Davidson and Clarke, 1996). SANS 406:2006, ASTM D6414-99, and ASTM D4606-95 also apply for sample preparation, as well as SANS 15237:2004 / ISO 15237:2003 for mercury determination. Density fractionation prior to anaysis is typically conducted to determine the TE affinities (organic or inorganic) (Hower *et al.,* 1996; Aktas *et al.,* 1998; Davidson, 2000; Querol *et al*., 2001; Wagner and Hlatshwayo, 2005; Bergh *et al*., 2011; Wagner and Tlotleng, 2012).

### Quantitative Evaluation of Materials using Scanning Electron Microscope

**Contribution by Dr Chris van Alphen**

Scanning electron microscopy (SEM), with or without emission detection systems (EDS, WDS), is a useful technique when assessing mineral occurrence in coal and ash. However, the detection of carbon is problematic. QEMSCAN (Quantitative Evaluation of Materials using Scanning Electron Microscope) is a scanning electron microscope configured to automatically characterise coal, fly ash, clinkers, and any particulate or deposit that is formed in a boiler (van Alphen, 2007). Traditional petrographic microscope characterises macerals based on reflectance of white light, whereas QEMSCAN characterises macerals and minerals based on atomic weight and elemental proportions. Light element detectors can measure elements with atomic numbers down to 6 (carbon), and, using a combination of back scattered images and x-ray spectral information, a particle image can identify the mineral, maceral or phase type (Lui *et al*; 2005). QEMSCAN is unique in that the resolution can achieve 2-3 µm, it is rapid (0.08 ms per point), and it can operate continuously, day and night. Image analysis provides the quantitative and qualitative information of different components and their size distribution. (Figure 4.3).

Carbon-coated carnauba wax polished sections are prepared for QEMSCAN analysis. Epoxy resin polished sections should not be used as the atomic weight contrast of macerals are the same as the epoxy resin; hence, QEMSCAN has difficulty discriminating between epoxy resin and coal.

Information derived from QEMSCAN analysis includes:

* Mass percent mineral and maceral proportions which are required to determine the total mineral matter content, mineral derived volatiles, and, finally the dry base ash content.
* Density distribution of coal particles. This provides valuable insight into the upgrade potential of a coal and the potential mineralogical characteristics of the product and discards.
* Slagging propensity and abrasive index of coal based on the deportment of minerals.
* Proportions of extraneous pyrite/calcite/dolomite cleats, stone (mudstone, siltstone and sandstone), carbominerites and dull/bright particles. This particle profile can be used to characterise a coal and predict its combustion characteristics.

**Figure 4.3: QEMSCAN false colour image of coal. Note the layers of included kaolinite (brown), inertinite (grey), and vitrinite-rich layers (light yellow). Dark blue represents dolomite cleats perpendicular to the bedding plane. Cracks (white) and oval secretinite inclusions (brown) are evident (Courtesy C. van Alphen).**

## **ADVANCED MOLECULAR AND STRUCTURAL ANALYSES**

Coal is a complex heterogeneous material made up of aromatic and aliphatic structures which are interconnected by both single carbon-hydrogen and double carbon-hydrogen bonded atoms. These aromatic clusters are linked to each other by bridges and form part of the secondary network of the coal structure. These bridges are formed from a variety of structures, made up of different kinds of bonding (covalent, donor-acceptor, or hydrogen bonds, poly-conjugated delocalizing electrons, van der Waals forces, *etc*.) (Krichko and Gagarin, 1990). Most of these bridges are believed to be aliphatic in nature, but may contain oxygen and sulfur functionality, depending on the origin of the coal (Spiro and Kosky, 1982). Bridges that contain oxygen as ethers are thought to have relatively weak bond strength. Other bridges are believed to be single bonds between the aromatic clusters, and these are known as bi-aryl linkages. On heating the aliphatic chains are the first to break, releasing the volatile elements whereas the aromatic forms are more difficult to break up. Liptinite is composed of abundant aliphatic chains and very little aromatic forms, whereas inert forms of inertinite are known to possess tightly bonded and disordered aromatic molecules (increasing in order with rank and temperature). These factors affect the degrees of difficulty in devolatilisation and ignition and the temperatures at which such macerals will combust. A variety of techniques have been developed to assess the functional groups in coal.

### Fourier-transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy, specifically FTIR, enables the identification the chemical bond configuration and to characterize functional groups in coal. Cannon and Sutherland (1945) were the first to characterize coal structure with FTIR. It was determined that coal contains functional groups such as OH (with hydrogen bonded) and CH (aliphatic and aromatic), C=O (in humic acids), and –C-C=C-C- of aromatic rings (Cannon and Sutherland*,* 1945). Further investigations revealed that coal contains aliphatic CH, CH2, and CH3 groups. Aromatic ring systems, -C-O- or C-O-C bonds, and associated OH and NH bonds can also be detected by FTIR. It can also show the presence of C=O groups and isolated C=C bonds (Van Vutch *et al.*, 1955).

Some researchers have used FTIR spectroscopy to characterize different maceral groups (Fujii *et al*., 1970; Kuehn *et al.,* 1982; Dyrkacz *et al.,* 1984). Liptinite has fewer aromatic CH bonds, more saturated CH bonds, and fewer aromatic CC bonds than vitrinite. Inertinite has fewer aromatic and aliphatic CH bonds, but more aromatic CC bonds when compared to vitrinite (Lowry, 1963). This is observed in Figure 4.4, where liptinite has an intense peak of C-H aliphatic at a wavelength of 2928 cm-1 as compared to inertinite and vitrinite. Inertinite and vitrinite have intense peaks for C=C aromatic bonds at the wavelength of 1613 cm-1 and at 875 cm-1 for C-H aromatic, whereas liptinite has less intense peaks at these wavelengths.

Infrared spectroscopy can also be utilized to determine a continuous transition from brown coals through bituminous coals and anthracites in vitrinite-rich coals as the functional groups that exist in such coals vary in their aromatic and aliphatic nature due to their degree of maturation. FTIR analysis is essential in determining the structural changes during coal conversion, as it can show functional groups that evaporate as the temperature increases. Therefore, FTIR data complements X-ray studies of aromatic carbons and provides information on the non-aromatic structure of coals.

### 13C Nuclear Magnetic Spectroscopy (13C NMR)

13C Solid state NMR is used to determine specific structural components in materials, including coal and carbons, and to obtain information pertaining to specific carbon functional group distribution. Cross-polarization (CP), magic-angle spinning (MAS), and dipolar dephasing (DD) are the techniques that allow for the characterization of a variety of average chemical structural features in coal samples. Usually these techniques are performed on coals to determine all of the carbon structural features associated with aromatic and aliphatic bonding. These features include the carbon aromaticity, the number of bridges and loops per cluster, the number of side chains per cluster, the fraction of carbons that are bridgeheads, the average number of carbons per aromatic cluster, and the average number of aliphatic carbons (Perry *et al.*, 2000). Figure 4.5 depicts a typical 13C NMR spectra for coal.

**Figure 4.4: Typical FTIR absorption bands for coal macerals (Chen *et al*, 2015).**

**Figure 4.5: A typical 13C NMR spectra for coals (Malumbazo, 2011).**

### X-Ray Computed Tomography (XCT)

X-ray computed tomography (XCT) is a non-destructive analytical technique with many applications, developed for the medical field and gaining popularity in materials science. Recent developments in geoscience applications, including coal, enable the 3D assessment of lump samples. The degree of porosity, mineral, and maceral distribution, fracture / cleat patterns, and so on, have been assessed in coals, and the results correlated with petrography (Naude *et al*., 2013). A sufficient amount of 2D X-ray radiographs are taken of a rotating sample and a 3D virtual image of the sample is reconstructed. A density map of the sample is generated, based on the relationship between X-ray attenuation (absorption and scattering of radiation) and atomic mass of the components. As minerals and macerals have different densities, it is easy to recognize these components; it is more difficult to separate the different macerals, but researchers are progressing in this area. Software also enables the slicing of the image to assess the entire particle, non-destructively. Naude *et al.* (2013) successfully utilized the technique to assess the porosity development (unconnected and connected pores) through a series of pyrolysed samples. Plackowski *et al.* (2015) applied the XCT images to obtain washability characteristics from coal lumps using semivariogram analysis, thus potentially replacing density fractionation (float-sink analysis) for coal washability predictions. The reader is referred to the report by Plackowski *et al.* (2015) for further information about the technique.

### Raman spectroscopy

**Contribution by Nthabiseng Maledi**

Macerals in coal differ from each other in terms of their morphology, optical properties, chemical composition, hardness, and micro-Raman signature (Jehlička *et al.,* 2003). Studies show that Raman spectroscopy as an analytical technique has substantial potential to be explored and used to characterize both the organic and inorganic matter in coal. The ability to probe materials at a molecular level, and to discriminate between different polymorphs, gives the technique an added advantage over bulk analytical techniques. Moreover, the technique offers additional benefits when used in conjunction with petrographic methods as it provides further information about the origins of a coal and its products. Raman spectroscopy is considered as a powerful analytical tool due to its sensitivity to crystalline and molecular structures, with a spatial resolution of 1µm (Beyssac *et al.,* 2002; Sheng, 2007). The coupling of an optical microscope to micro-Raman provides additional insight into the composition and nature of coals since the equipment can be focused on individual macerals and minerals (Green *et al.,* 1983; Marstalez and Bustin, 1993; Guedes *et al.,* 2005; Morga, 2011; Zhang *et al.,* 2015). The characterization of carbonaceous materials using Raman spectroscopy is well documented in literature (Tuinstra and Koenig, 1970; Zerda, 1981; Beyssac *et al*., 2002, 2003; Zickler *et al*., 2006, Guedes *et al*., 2008; Chabalala *et al*., 2011; and references therein), with a detailed review on the application of Raman spectroscopy to coal undertaken by Potgieter-Vermaak *et al*. (2011).

The first documented work of using Raman spectroscopy to characterize carbonaceous materials was reported by Tuingstra and Koenig (1970), who studied the structural behaviour of graphite (highest order of carbonaceous material). Any deviation from the observed spectra was considered to be due to structural abnormality, caused by the presence of defects in the microcrystalline lattices. Additional peaks are notable in highly disordered carbonaceous materials, such as coal. The two main Raman characteristic features of coal are the two main peaks at 1580 cm-1 and 1360 cm-1 wavelengths. The band at 1580 cm-1, within the first-order region, is referred to as the G-band and relates to the band in the graphitic structure (Beyssac *et al.,* 2002). This band is assigned to the E2g plane stretching vibration mode in the aromatic layers of graphite. The peak at 1360 cm-1 is called the D1 band, with the D denoting defects. The D1 band is assigned to the A1g symmetry, due to the presence of defects such as heteroatoms [Green *et al.,* 1983; Kelemen and Fang, 2001].

It was later discovered that deconvolution of the G and D bands showed that three additional peaks could be resolved at 1370 cm-1, 1580 cm-1, and 1620 cm-1 wavenumbers. The D1 band co-exists with the D2 band found at the 1620 cm-1 peak. The intensity of the D2 band is related to the ordering in the carbonaceous structure. Thus, the more ordered the material, the smaller the D2 peak. The D2 peak is assigned to the lattice vibration analogous to the G band. The D3 band is characterized by a broad peak around 1500 cm-1 to 1550 cm-1. The D3 band is assigned to the sp2 bonded form of carbon such as organic molecules, fragments, or functional groups. The D3 band is understood to be responsible for reacting sites and char reactivity in coals. The D4 band at 1150 cm-1 is found in highly amorphous materials such as soot and coal chars. The assignment of the D4 band has been debated, and assigned differently (Zhang *et al.,* 2015).

Raman parameters such as the intensity ratio between the D1 and the G band (ID/IG), frequency (ω), and the full width at half maximum (FWHM) of the G and D band have been correlated to the maturity of carbonaceous materials (Guedes *et al.,* 2012). An increase in the intensity of the G band and a decrease of the D band indicats the increased maturity of the carbonaceous material. The intensity of the D-band relative to G band is inversely proportional to the crystal lattice diameter, La (Johnson *et al.,* 1986). However, the relationship holds true only when La is below 2 nm (Zickler *et al.,* 2006). Figure 4.6 shows different Raman peaks determined on a coal and associated char products. Morga (2011) found a correlation between Raman parameters and volatile matter. In the study, it was concluded that a decrease in G band corresponded to a decrease in the volatile matter content and an increase in maceral reflectance. Chabala *et al.* (2011) determined that random vitrinite reflectance and Raman spectroscopy showed good correlations on char samples.

However, attentiveness must be exercised when using the technique. Although curve fitting has been extensively used to find Raman parameters (Zhang *et al.,* 2015) and related the parameters to coal intrinsic properties, it is important to note that the method can be biased and is subjected to operator involvement and manipulation of results. With an attempt to minimize operator involvement, Lünsdorf and Lünsdorf (2016) evaluated Raman spectra of carbonaceous matter by using an iterative curve fitting algorithm, and the results were found to be promising. The accuracy and reproducibility of Raman results rely on factors such as sample preparation, wavelength, and the effect of fluorescence. Beyssac *et al.* (2003) investigated the effect of grinding and polishing of the block mounts on the Raman spectrum. According to Lünsdorf and Lünsdorf (2016), other challenges encountered include the following:

* Thermal alteration of the coal structure due to heat from the laser source
* Structural defects due to polishing
* Orientation effects
* Spectral curve fitting method
* Wavelength dependency

**Figure 4.6: An example of Raman spectra generated from coal and combustion chars; spectra have been offset on the y-axis for clarity and the Raman intensity is referred as arbitrary units (Chabalala *et al*., 2011).**

## Combustion Performance Tests

In order to assess the suitability of a coal for combustion (to produce heat) or gasification (to produce heat, gases, liquids, or tars) or any other processes (for example pyrolysis), it is best to test the coal’s performance under laboratory conditions. More reactive coals require different engineering parameters compared to less reactive coals. The latter forms may require longer residence times or higher oxygen contents in their combusting environment and a high temperature furnace (different materials of construction), for example. The thermogravimetric analyser (TGA) and the drop tube furnace (DTF) enable the assessment of combustion characteristics at lab-scale and bench-scale levels respectively.

Thermogravimetry offers a comparatively easy assessment of coals. Combustion parameters such as temperatures at which devolatilisation begins, volatile and char ignition, peak temperature occurs (i.e. temperature where the rate of combustion is the greatest), burn out temperature (temperature at which the rate of combustion equals 1 wt% per minute), and burn out time. *T50* (the temperature at the level of 50% loss of combustibles) can be determined from the TGA curve generated, and its derivative (Figure 4.7).

**Figure 4.7: Derivative curves derived from thermogravimetric analysis to determine point of devolatilisation, ignition, peak temperature, and burnout properties. In this example, three different coals with different characteristics report variable ignition peaks (*pers comm* Samson Bada).**

Ignition occurs when a coal particle begins to glow while being heated in a stream of oxygen or oxygen-rich air. Kok (2012) demonstrated that peak and burn-out temperatures increased as the heating rate increased, and that the heating rates affected the measured heats of reactions of the coals studied. This implies that, whilst the TGA can provide useful information, it may be difficult to compare results using different test parameters. For true comparative studies, all operational functions in the TGA must be the same for all coals to be compared. Further information pertaining to the TGA and associated results may be found in Crelling *et al.* (1992), Sarkar *et al.* (2013) and Kok (2012), amongst others.

The drop tube furnace (DTF) provides parameters pertaining to ignition, combustion profiles, residence time, and burnout times of the coal particles. Typically, a DTF consists of a ceramic tube with three or more zones enabling sample collection. The zones are externally heated and the temperatures monitored. Heated [charred] pulverized coal is fed into the DTF, and the carbon burn out at each zone is calculated. The char samples can also be collected from each zone, and assessed optically (Plate 52). The information derived from the DTF (optically, physically, and chemically) indicates how a coal is likely to perform in a pf boiler, with the understanding that a boiler has many additional variables that may influence coal combustion. As with TGA results, it may be difficult to compare tests between DTF’s as different operating parameters may apply. For further information pertaining to the DTF and associated results refer to Bengtsson (1986), Card and Jones (1995), Wagner (1999), Cloke *et al.* (2002), Sarkar *et al.* (2013), amongst others.

## METALLURGICAL COAL AND COKE TESTS

### Crucible Swelling Number (CSN) or Free Swelling Index (FSI)

The Crucible Swelling Number (CSN) or Free Swelling Index (FSI) tests are determined by taking 1 g of -0.212 mm coal and heating it in a covered crucible to 820oC for 2.5 minutes.  The resultant coke “button” is compared to a series of standard profiles and given a number between 0 and 9.   A swelling number of 0 reflects a non-agglomerated and non-swelling coal, from 1 to 2.5 indicates a possible thermal coal, from 3 to 5 represents a possible weakly coking coal and 5.5 to 9 represents a possible coking coal.  While this is the easiest and most frequently applied test conducted on coals, it may not always reflect the true coking capacity of a coal.  Additional tests are recommended. SANS 501:2008 / ISO 501:2003 applies.

### Roga Index or Caking Index

The Roga (or Caking) Index was used in Europe to indicate coking capacity and as an alternate to crucible swelling number.  This has now been replaced by the Caking Index, G (ISO 15585).   In this test -0.2 mm coal is mixed with 5 g of anthracite and placed in a crucible.  A 100-115 g steel weight is placed on top of the coal sample and then the sample is pressed for 30 s under a 6 kg mass.  The sample is rapidly coked in an electric furnace to 850oC in 15 minutes.  The coke material is weighed, placed in a small drum and rotated for 5 minutes at a specific revolution. The coke residue is screened at 1 mm and the weight of the +1 mm is determined.  This +1 mm is tumbled a second time and the weight determined.  The Caking Index is reported as the mean of duplicate determinations of the mass of the sized products as calculated in a specific formula. This provides an indication of fusibility and swell. SANS 15585:2007/ISO 15585:2006 applies.

### Gieseler Plastometer

The Gieseler plastometer test is the only one which determines the actual extent of plasticity in the fluid phase of a coking coals.  This is determined by applying a constant torque to a standard stirrer placed in a crucible into which a sample of -0.425 mm coal with a minimum of fines is charged and uniformly packed.  The charge is heated uniformly through a temperature range from 300oC to 550oC (the plastic range).   The rate of movement of the stirrer is determined in relation to the increase in temperature.  The temperature and rate of maximum movement is recorded and the results reported as the maximum fluidity value expressed in dial divisions per minute (ddpm).  The higher the ddpm, the higher the plasticity.   This test is highly sensitive to the degree of oxidation in a coal and is strongly influenced by rank. SANS 737:2009/ISO 10329:2009 applies.

### Dilatation

Finely ground coal is compressed into the shape of a pencil and heated at a constant rate in a calibrated steel retort in a furnace. The vertical displacement of a piston resting upon the pencil is recorded continuously as a function of time and temperature.  The movement of the piston and resultant curve is characteristic of the swelling properties of the coal.   From this curve, the maximum upward and downward displacements and three characteristic temperatures are determined.   The maximum dilatation is the key parameter and the highest value possible is considered optimal.  Audibert-Arnu test and Ruhr test are slightly different dilatation tests, the difference being compaction of the pencil. The Ruhr test produces slightly higher dilatation maximum values than the Audibert-Arnu test.  This test, as in the case of the Gieseler test, is strongly influenced by rank.   SANS 6072:2009 applies.

### Grey-King Coke Type Test

Coal is heated in horizontal cylindrical retorts under standardised conditions to a final temperature of 600oC.  The coke residue obtained is classified by strength and degree of swelling against a standard set of characteristic profiles.  The values range from A (no coking characteristics at all) to G (superior coking properties). SANS 502: 1982 / ISO 502: 1982.

### Coke Strength and reactivity

Once coke has been produced, two properties become important, namely**, coke strength** (or stability) and **coke reactivity**. These two properties and determination are well reviewed by Suárez-Ruiz and Crelling (2008).  SANS 520:2007/ISO 556:1980 applies to the former.

In essence, coke strength (stability) is important for retaining the porosity and therefore permeability for gas throughout the burden within the blast furnace.  The reactivity of coke is an equally important property.   If coke is too reactive and is therefore used up too quickly, not only will this require an increase in higher coke feed but it will also reduce the strength of the coke by thinning the walls as carbon is removed.  This can lead to collapse of the cell walls, reduction in coke strength and increased permeability problems in the blast furnace.

Coke reactivity is measured as the weight loss of coke when it reacts with CO2 under given conditions and is reported as the Coke Reactivity Index (CRI).

Coke strength after reactivity is established by a mechanical strength test after reactivity with CO2.   This property is known as Coke Strength after Reactivity (CSR).