Coal sampling and analysis standards

Qian Zhu

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Author: Qian Zhu

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IEA Clean Coal Centre
Park House
14 Northfields
London SW18 1DD
United Kingdom

Telephone: +44(0)20 8877 6280

www.iea-coal.org

Preface

This report has been produced by IEA Clean Coal Centre and is based on a survey and analysis of published literature, and on information gathered in discussions with interested organisations and individuals. Their assistance is gratefully acknowledged. It should be understood that the views expressed in this report are our own, and are not necessarily shared by those who supplied the information, nor by our member countries.

IEA Clean Coal Centre is an organisation set up under the auspices of the International Energy Agency (IEA) which was itself founded in 1974 by member countries of the Organisation for Economic Co-operation and Development (OECD). The purpose of the IEA is to explore means by which countries interested in minimising their dependence on imported oil can co-operate. In the field of Research, Development and Demonstration over fifty individual projects have been established in partnership between member countries of the IEA.

IEA Clean Coal Centre began in 1975 and has contracting parties and sponsors from: Australia, Austria, Canada, China, the European Commission, Germany, India, Italy, Japan, New Zealand, Russia, South Africa, Thailand, the UK and the USA. The Service provides information and assessments on all aspects of coal from supply and transport, through markets and end-use technologies, to environmental issues and waste utilisation.

Abstract

Each year, billions of tonnes of coal are traded in regional and international market for use in power generation, steel and cement making, and many other purposes. In commercial operations, the price of coal not only reflects the quantity of coal but also reflects the relationship of a desirable property or a combination of properties to performance of the coal under service conditions. The properties of coal often form the basis of sale contracts, and payment for the coal is based on the analytical results. Coal is a very heterogeneous material containing various organic matter and inorganic (mineral) matter, and exhibits a wide range of physical properties. The analysis of coal is generally performed on the coal samples taken from the bulk material and not from the individual components. Given the extreme complexity of coal, coal sampling protocols must provide material that is representative of the lot sampled. To ensure a representative sample is collected, correct sampling procedures should be followed and certain rules adhered to. Also, analyses of coal need to be sufficiently accurate so as to preclude negative scientific or economic consequences. All coal analyses should follow standard procedures in order to obtain repeatable and reproducible results. This report reviews various aspects of coal sampling and analysis. It provides descriptions of standard procedures for coal sampling, preparation and routine tests of coal specified in the international Standards. The commonly used instrumental techniques for routine coal analysis and their recent developments are also reviewed in this report.

Acronyms and abbreviations

ad	air dry
AAS	atomic absorption spectroscopy
AES	atomic emission spectroscopy
AFS	atomic fluorescence spectroscopy
ar	as-received
ASTM	American Society for Testing and Materials
Btu/lb	British thermal units per pound
cal/g	calories per gramme
CCSEM	computer-contolled scanning electron microscopy
cm	centimetre
CV	calorific value
CVAAS	cold-vapour atomic absorption spectroscopy
daf	dry, ash-free
dmmf	dry, mineral-matter-free
DUET	dual-energy γ-ray transmission
EDS	energy dispersive x-ray spectrometer
EMPA	electron micro probe analyser
EPM	electron probe microanalysis
FAAS	flame atomic absorption spectroscopy
FTIR	Fourier transform infrared spectroscopy
g	gramme
GFAAS	graphite-furnace atomic absorption spectroscopy
HT	heating value
HHV	higher heating value
IC	ion chromatography
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectroscopy
in	inches
INAA	instrumental neutron activation analysis
ISO	International Organisation for Standardisation
J/g	joules per gramme
kcal/g	kilocalories per gramme
kcal/kg	kilocalories per kilogramme
kg	kilogramme
kJ/g	kilojoules per gramme
LHT	lower heating value
MAS	magic angle spinning
MJ/kg	megajoules per kilogramme
MJ/t	megajoules per tonne
ml/min	millilitres per minute
mm	millimetre
MR	Magnetic Resonance
MS	mass spectrometry
µm	micrometer
MS	Mössbauer spectroscopy
m/s	metres per second
MW	megawatts

NAA	neutron activation analysis
ng/g	nanograms per gramme
nm	nanometre
PFTNA	prompt-fast thermal neutron analysis
PGAA	prompt-gamma neutron activation analysis
PIXE	proton-induced x-ray emission analysis
PLC	programmable logic controller
rpm	revolutions per minute
SAXS	small angle x-ray scattering
SEM	scanning electron microscopy
t/h	tonnes per hour
vol%	volume percentage
wt%	percentage by weight
XAFS	x-ray absorption fine structure
XANES	x-ray absorption near edge structure
XRD	x-ray diffraction
XRF	x-ray fluorescence spectroscopy

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1 Introduction

Coal is used for power generation, steel making, cement production and many other purposes. Each year, billions of tonnes of coal are traded in local and international markets. In commercial operations, the price of coal not only reflects the quantity of coal but also reflects the relationship of a desirable property or a combination of properties to performance of the coal under service conditions. The properties of coal which have an impact on combustion and environmental performance often form the basis of sale contracts, and they include calorific value, volatile matter, moisture, sulphur, chlorine and ash (elemental composition) content of coal. These properties are all measured at samples taken during loading of the coal. Payment for the coal is based on the analytical results. Also, knowing the quality of coal is essential for the applications of that coal.

Coal sampling is performed whenever there is a need to analyse the coal. Coal sampling protocols must provide material which when analysed will provide results that are representative of the lot sampled. To ensure a representative sample is collected, correct sampling procedures should be followed and certain rules adhered to. Modifications to the standard procedures may have significant effects on the precision of the final results, which often lead to disputes between the seller and the customer.

Table 1 – Sampling and analyses normally required for coal evaluation (Speight, 2005)

Test/property	Results/comments
Sample information	
Sample history	Sampling date, sample type, sample origin (mine, location)
Sampling protocols	Assurance that sample represents gross consignment
Chemical properties	
Proximate analysis	Determination of the 'proximate' overall composition such as moisture, volatile matter, ash, and fixed carbon content
Ultimate analysis	Absolute measurement of the elemental composition such as carbon, hydrogen, Sulphur, nitrogen, and oxygen content
Sulphur forms	Chemically bonded sulphur: organic, sulphide, or sulphate
Ash properties	
Elemental analysis	Major and minor elements
Mineralogical analysis	Analysis of the mineral content
Trace element analysis	Analysis of trace elements; some enrichment in ash
Ash fusibility	Qualitative observation of temperature at which ash passes through defined stages of fusing and flow

The type of analysis normally requested by the coal mining and coal consuming industries may be a proximate analysis and/or an ultimate analysis, together with one or more of the miscellaneous analyses or tests as shown in Table 1. The primary reason for analysing coal is to determine whether it will meet the needs of a specific application, or to characterise the general quality of the coal for establishing the price of the coal, to control mine and cleaning operations or to determine plant efficiency. Assessment of any traits in coal properties is vital to ensuring a particular supply of coal is used in the most effective way. In general, the coal mining and coal consuming industries determine coal quality for immediate or near-term use.

Coal is highly heterogeneous in nature, and for this reason, several analytical techniques are needed for its characterisation in order to accurately predict its behaviour during applications such as coal combustion. The analyses need to be sufficiently accurate so as to preclude negative scientific or economic consequences. Coal has the tendency to gain or lose moisture and to undergo oxidation when exposed to the atmosphere. Also, many of the test methods applied to coal analysis are empirical in nature and therefore it is necessary that all coal analyses follow some kind of procedural guidelines in order to obtain repeatable and reproducible results. In other words, there is a requirement that reliable standard test methods be applied to coal analysis. Furthermore, the significant volume of coal traded among coal-producing and coal-consuming countries means that cross-referencing of standards for coal sampling and coal analysis accepted by both seller and buyer is a necessity. In fact, the use of standards is becoming more and more of a prerequisite to worldwide trade. As a result, international and various national standards for coal sampling and evaluation have been well established.

This report reviews the methods applied for coal sampling and for routine coal analysis. It begins with short introductions to the International Organisation for Standardisation, ASTM International, and the national standards organisations in some of the major coal producing and coal consuming countries in Chapter 2. Brief discussions of the Standards set up by these organisations and directions to where they can be found are provided. In Chapter 3, the objectives of coal sampling are discussed, including the procedures and rationale for collecting a representative sample. Standard methods for coal sampling under various conditions, and the recent developments in automatic coal sampling systems are presented. Standard procedures for sample preparation and bias tests are also covered in the chapter. The internationally accepted standard laboratory test methods that are used for coal analysis are discussed in Chapter 4. A complete review of the large number of test methods used for evaluation of coal and coal products would fill a considerable volume, and such detailed discussion is not the goal of this report. The focus here is on a description, with some degree of detail, of the test methods in common use for analysis of coal that is used for power generation/combustion.

Conventional coal test methods are well established and are widely used in laboratories worldwide. However, these methods often involve the use of wet analysis and can be time consuming. There are many relatively new approaches, usually based on modern sophisticated instrumentation, that have been shown to have wide applicability to coal analysis. Several such instruments are fast and can simultaneously determine carbon, hydrogen, and nitrogen and/or other elements in various samples. The use of instrumental analytical techniques has grown rapidly in recent years and instrumental analysis is now widely applied for analysis of coal and coal products. The commonly used instrumental techniques for routine coal analysis and their recent developments are reviewed in Chapter 5.

Laboratory measurements of parameters in coal are very well developed, but results can only be obtained twenty four hours after samples are taken. Online analysers provide an automatic, fast, relatively accurate, and instantaneous method of coal analysis for pricing, quality or process control, and SO_2 emissions control. The technologies applied by online analysers and the considerations when selecting an online analyser are also discussed in Chapter 5. A detailed review of online coal analysis systems for process

control in power plants can be found in a recent report published by the IEA CCC (Nalbandian, 2011). And finally, the discussions are summarised in Chapter 6.

Coal is an extremely complex, heterogeneous material that exhibits a wide range of physical and chemical properties. The rapid increase in coal utilisation in the twentieth century led to the development of a number of test methods for coal analysis so as to correlate coal composition and properties with its performance and behaviour during applications such as coal combustion and gasification. As a part of the multifaceted programme of coal evaluation, new methods are continually being developed and the accepted methods are modified/optimised to increase the accuracy of the technique as well as the precision of the results. However, it is only by assiduously careful analyses of coal that the various aspects of coal usage can be achieved in an effective and environmentally acceptable manner.

2 International and national standards

By definition, a standard is defined as a document, established by consensus and approved by a recognised body, that provides rules, guidelines, or characteristics for activities or their results for common and repeated use. Many industry bodies and trade associations require a product (for instance, coal) to conform to a standard or directive before it can be offered for sale. The use of standards is, in fact, becoming more and more of a prerequisite to worldwide trade. Much work, and the formation of various international and national standards organisations, have led to the development of standard methods for coal evaluation. Examples of the organisations for methods development and standardisation which operate at national or international level include the British Standards Institution (BSI), the German Institute for Standardisation (DIN), the International Organisation for Standardisation (ISO), and the American Society for Testing and Materials (ASTM). ISO and ASTM have carried out uninterrupted work in this field for many years while investigations on the development of the standardisation of methods of coal sampling and coal analysis have occurred in all of the major coal-producing countries.

2.1 ISO standards

Based in Geneva, Switzerland, ISO is the world's largest developer of voluntary International Standards. It is a network of national standards bodies. The national standards organisations make up the ISO membership and they represent ISO in their country. Today, ISO has members from 164 countries and 3368 technical bodies to take care of standard development.

ISO Standards regarding coal sampling, preparation and bias test, coal characterisation and coal analysis are in category ICS 73.040: Coals (including lignites) and ICS 75.160.10: Solid fuels. The full lists of coal related ISO Standards can be found on the ISO's website:

- ICS 73.040: Coals at http://www.iso.org/iso/home/store/catalogue_ics/catalogue_ics_browse.htm?ICS1=73&ICS2=040&
- ICS 75.160.10: Solid fuels at http://www.iso.org/iso/home/store/catalogue_ics/catalogue_ics_browse.htm?ICS1=75&ICS2=160&ICS3=10&

ISO Standards, with various modifications, have been adopted in many countries as national standard methods. In particular, ISO Standards are most widely accepted and applied in international markets for coal trade.

2.2 ASTM International

ASTM has recently changed its name to ASTM International. It develops and delivers voluntary consensus standards. Today ASTM International has over 30,000 technical experts and business professionals representing 150 countries.

Lists of coal standards and gas standards developed by ASTM can be found at ASTM's website (http://www.astm.org/Standards/coal-and-gas-standards.html). These standards are instrumental in the testing and chemical analysis of coal, coke, natural gas and other gaseous fuels, as well as the combustion residues of coal and coke. The materials specifically covered by these standards can be in the form of lump coke, pulverised coal, bituminous coal, coke and coal ash, reformed gas, and polishing and etching coal. These standards also include the thermophysical property tables for methane, ethane, propane, normal butane, and isobutane. These standards allow laboratories and other chemical facilities to examine and assess these fuels to ensure safe handling and use.

Despite the name change, ASTM coal standards are mainly adopted in the USA and Canada, and are accepted in the domestic coal markets or in the international coal market where US coal exporter are involved. However, these standards are widely used in universities and research laboratories for academic studies in coal, as well as in research and development of new analytical techniques for coal.

2.3 British standards

BSI, as the UK national standard body, is a prominent member of ISO. BSI is responsible for co-ordinating and facilitating the development of standards of UK origin, and has the right to adopt any international standard as a British Standard, but is not obliged to do so. BSI has a policy of adopting all international standards unless there are sound reasons to the contrary. Therefore, the majority of documents published as British Standards have their origin in international standards or European standards. The remainder are developed exclusively by BSI to meet particular needs in the UK (BSI, 2011). In the past, UK adoptions of ISO standards were given BS standard numbers which run in parallel with the relevant ISO numbers. Today, UK adoptions of ISO standards generally use their ISO numbers, although the year may be different to the ISO's depending on when they were adopted in the UK. Each UK adoption of an ISO standard has a national foreword BS which allows the UK authority to offer advice and guidance on applying the standard in a UK context. The British coal standards are in the *Coal* section of ICS Category of *Mining and Minerals*. The list of the British coal standards and a brief description of each standard can be found on the BSI's online shop at http://shop.bsigroup.com/ .

2.4 Chinese coal standards

The Standardisation Administration of China (SAC) is the national standard body that represents China in the ISO. SAC is responsible for organising the development and revision of national standards, and for the examination, approval, numbering and publication of national standards. Chinese Standards are divided into mandatory standards and voluntary standards. The code GB means these are mandatory national standards, whereas the code GB/T represents voluntary national standards. All China's coal standards are voluntary. These standards are in GB category D21. Many of China's standard test methods for routine coal analysis are adopted from the relevant ISO standards with various modifications. Information about China's coal standards can be found at SAC's website (http://www.sac.gov.cn/).

2.5 Indian standards

The Bureau of Indian Standards (BIS) is India's national standards body representing India, as a member body, in the ISO. BIS is responsible for development of national standards, certification, marking and connected matters. Indian coal standard numbers begin with code IS. Table 2 lists the Indian standards for coal sampling, characterisation and analyses, which are currently in force.

Table 2 – Indian standards for coal sampling, characterisation and analyses

Standard No	Title	Amendment	Year
IS 12891	Methods of determination of fusibility of ash of coal, coke and lignite		1990
IS 1350: Part 3	Methods of test for coal and coke: Part III Determination of sulphur	2	1969
IS 1350 : Part 4 : Sec 2	Methods of test for coal and coke: Part IV Ultimate analysis, Section 2 – Determination of nitrogen [superseding IS 1351:1959]	2	1999
IS 1350 : Part 1	Methods of test for coal and coke – Part I : Proximate analysis	1	1984
IS 1353	Methods of test for coal carbonisation – caking index, swelling and Grey-King assay (LT) coke types		1993
IS 1355	Methods of determination of chemical composition of ash of coal and coke	1	1984
IS 15438	Coal – Determination of forms of sulphur		2004
IS 15441	Solid mineral fuels – Determination of carbon and hydrogen – Liebig Method		2004
IS 4311	Method for the determination of mineral matter in coal		1967
IS 436 : Part 1 : Sec 1	Methods for sampling of coal and coke Part 1 : Sampling of coal Section 1 : Manual sampling		1964
IS 436 : Part 1 : Sec 2	Methods for sampling of coal and coke: Part I Sampling of Coal/Section 2: Mechanical sampling		1976
IS 437	Size analysis of coal and coke for marketing		1979
IS 4433	Method for determination of Hardgrove Grindability index of coal		1979
IS 5062 : Part 2	Methods of test for brown coals and lignites: Part II Determination of ash		1969
IS 9127 : Part 1	Methods of petrographic analysis of coal – Part 1 : Definition of terms relating to petrographic analysis of coal		1992
IS 9127 : Part 2	Methods for the petrographic analysis of bituminous coal and anthracite – Part 2 : Method of preparing coal samples		2002
IS 9127 : Part 3	Methods for the petrographic analysis of bituminous coal and anthracite – Part 3 : Method of determining maceral group composition		2002
IS 9127 : Part 4	Methods for petrographic analysis of coal – Part 4 : Method of determining microlithotype, carbominerite and minerite composition		2001
IS 9127 : Part 5	Methods for petrographic analysis of coal: Part 5 Microscopical determination of the reflectance of vitrinite		2004
IS 9949	Methods of test for abrasive properties of coal and associated minerals		1984
IS 1350 : Part 2	Methods of test for coal and coke – Part II : Determination of calorific value	1	1975
IS 1350 : Part 4 : Sec 1	Methods of test for coal and coke – Part IV : Ultimate analysis – Section I : Determination of carbon and hydrogen	1	1974
IS 5062 : Part 1	Methods of test for brown coals and lignites – Part I : Determination of moisture content by the direct volumetric method		1969

Some of the Indian coal standards are adopted from the relevant ISO standards.

2.6 South African national standards

As the national standards body, the South African Bureau of Standards (SABS) offers a full spectrum of standards development, information and conformity assessment services. SABS is a member body of the ISO, and has participated in the development of international standards. South Africa is one of the world's major coal producers and exporters. The coal industry plays an important part in the country's economy which has enhanced the role of the national coal standards in economic development. South Africa has established comprehensive national standards for coal sampling and analyses, which are largely based on ISO standards. All South African national standards are numbered with a national prefix SANS. The list of SANS coal standards with information and a preview of each one can be found at SABS's online store at: http://www.store.sabs.co.za/mining/coal?id=103&p=3 .

2.7 Australian standards

Recognised by the Australian Government as the nation's peak standards body, Standards Australia is the Australian member of the ISO. It is a not-for-profit, non-government organisation that co-ordinates standardisation activities and facilitates the development of Australian Standards. Through the Accreditation Board for Standards Development Organisations (ABSDO) other standards development organisations can be accredited to develop Australian Standards. The prefix AS is used to number the Australian Standards, and they are sold and distributed worldwide by SAI Global Limited. Information and previews of the Australian coal related standards are available on the SAI Global's website at http://www.saiglobal.com/ .

National Standards for coal sampling and coal analysis have also been established in many other countries but they will not be discussed here. Some of these Standards are also sold and distributed by SAI Global Limited and relevant information can be found at the company's website given above.

All Standards are subject to periodical review to consider any matters of concern raised at any other time, and to be updated in accordance with technical advances as new techniques are continually developed and existing methods are constantly improved and optimised.

It is appropriate that in any discussion of the particular methods used to evaluate coal or coal products, reference should be made to the relevant test. Accordingly, where possible, the relevant standard numbers should be included.

3 Coal sampling and sample preparation

The purpose of collecting and preparing a sample of coal is to provide a test sample which, when analysed, will provide test results representative of the lot sampled. This helps ensure an accurate characterisation of the coal from which the sample is taken. Proper sampling and sample preparation are critical for accurate analysis. Statistically, about 80% of the total variances involved at the different stages of sample collection, preparation and analysis come from errors during its collection. There are two criteria that must be followed when sampling to ensure the overall precision and accuracy of the results:

- ensure that the sample is representative of the bulk material, which means all parts of the material being sampled must have an equal probability of being collected and becoming part of the final sample for analysis, and
- ensure that the sample does not undergo any chemical or physical changes after completion of the sampling procedure and during the storage prior to analysis.

Coal is highly heterogeneous in nature consisting of particles of varied shapes and sizes each having different physical characteristics, chemical properties and residual ash content. It also has a tendency to segregate by size or mass. Sampling is further complicated by the sampling equipment available, the quantity to be represented by the sample mass, and the degree of precision required. In addition, the coal to be sampled may be a blend of different coal types. How the coal is blended, for instance whether it is intimately mixed or not, has a profound effect on the way a representative sample is obtained. As a result, coal is one of the most difficult materials to sample and the condition that a coal sample be completely representative of the whole as regards all aspects, is never fulfilled. National and international standards have been developed to provide guidelines to the coal sampling procedures under different conditions of sampling for the purpose of obtaining unbiased analysis samples.

The sampling of coal can take place from either stationary lots or from moving streams. Coal samples can be taken from a broad range of locations such as feed and product streams, conveyor belts, trucks, railway wagons, and stockpiles. Sampling can be carried out either manually or by mechanical sampling systems. Most coal samples require some kind of physical preparation prior to chemical analysis. The sample preparation process may include air drying, crushing, division, and mixing of a gross sample to produce the small individual portions required for laboratory analysis. Biased results can be introduced by the sampling procedure, during sample preparation and analysis. It is, therefore, important that all sampling systems are checked for bias. This chapter reviews the general principles of sampling, the methods and procedures of coal sampling, preparation and bias tests.

3.1 Sampling

How samples are collected is dependent on the aspect of mining and the purpose for which the coal is being tested. Samples may be required for technical evaluation, process control, quality control, and/or for commercial transactions. It is important, before collecting a sample, to decide what the purpose of the

sample will be, and then plan the sampling procedure accordingly so that it will be unbiased and sufficiently representative for the purpose.

3.1.1 General principles of sampling

The fundamental requirements of sampling include (OAR/EPA, 2009):

1. all particles of coal in the lot to be sampled are accessible to the sampling equipment and each individual particle shall have an equal probability of being selected and included in the sample;
2. the dimension of the sampling device used should be sufficient to allow the largest particle to pass freely into it;
3. the first stage of sampling known as primary increments is the collection of an adequate number of coal portions from positions distributed over the entire lot to reflect the variability of the coal. The primary increments are then combined into a sample, as taken or after reducing the mass of the sample to a manageable size. From this gross sample, the required number and types of test samples are prepared by a series of processes jointly known as sample preparation;
4. the minimum mass of the gross sample should be sufficient to enable particles to be present in the same proportions as in the lot of coal from which it is taken.

3.1.2 Establishing a sampling scheme

The sampling procedure will differ depending on the purpose and the nature of sample collection, for instance by mechanical or manual means, from moving belts or from stationary lots like wagons, and stockpiles. These different sampling techniques commonly follow a relevant national or international standard. The general procedure for establishing a sampling scheme is as follows (OAR/EPA, 2009):

- decide for what purpose the samples are taken, for example, plant performance evaluation, process control, commercial transactions;
- identify the quality parameters such as general analysis, total moisture content, size analysis, to be determined;
- define the lot;
- define the precision required;
- decide whether continuous or intermittent sampling is required;
- determine the number of sub-lots and the number of increments per sub-lot to achieve the required precision;
- determine or estimate the nominal top size of the coal;
- determine the minimum mass per increment and the minimum mass of the total sample;
- decide on the method of combining the different increments to produce the gross sample;
- decide on drawing common or separate samples for general analysis and moisture determination.

A sampling scheme has to be designed based on the purpose of sampling, and after ascertaining at what stage of the coal handling operation the sample is required. When designing a sampling scheme in order to meet a required precision of results, equations are necessary that link certain fuel and sampling

characteristics to that precision. The overall precision of the result is determined by the variability of primary increments, preparation and testing errors, the number of increments and samples taken to present the lot, and the mass of the samples. Issues that are to be determined when designing a sampling scheme include (ISO, 2001):

- division of lots: a lot may be sampled as a whole or a series of sub-lots. Each sub-lot will constitute one sample;
- basis of sampling: it can be either time-basis or mass-basis. In time-basis sampling, the sampling interval is defined in minutes/seconds and the mass is proportional to the flow rate at the time of taking the increment. In mass-basis sampling, the sampling interval is defined in tonnes and the mass of increments constituting the sample is uniform;
- precision of results: in all methods of sampling, sample preparation and analysis, errors may be introduced at every stage and the measured value may differ from the true value of the parameter. As the true value is not exactly known it is difficult to assess the accuracy of the results, but an estimate of precision of the results can always be made;
- bias of results: it is important to ensure, as far as possible, that the parameter to be measured is not altered by the sampling and sample preparation process or by subsequent storage prior to testing.

The required precision for a lot for each parameter has to be decided and then the number of sub-lots, number and mass of increment are to be estimated.

3.1.3 Precision of sampling

Precision is the closeness of the data to the true value in given conditions as indicated by the reproducibility of the unbiased results. Sampling precision depends on variability of coal, number of samples from a lot, number of increments comprising each sample, and mass of sample relative to the nominal top size.

A lot may be sampled as a whole, resulting in one gross sample, or divided into a number of sub-lots resulting in a gross sample from each. Such division may be necessary in order to achieve the required precision. Another important reason for dividing the lot is to avoid bias after taking the increment, particularly in order to minimise loss of moisture due to standing. After the precision has been decided, the necessary number of sub-lots, the minimum number of increments per sub-lot collected, and the average mass of the primary increments should be determined in accordance with the relevant standards. For example, according to the International Standards for mechanical sampling of hard coal from moving streams (ISO 13909–2:2001), the overall precision can be estimated using the following equations:

$$P_L = 2\sqrt{\frac{V_I}{n} + \left(1 - \frac{u}{m}\right)V_m + V_{PT}}{u}} \quad (1)$$

where:

- P_L is the estimated overall precision of sampling, sample preparation and testing for the lot at a 95% confidence level, expressed as percentage absolute;
- V_I is the primary increment variance;
- n is the number of increments per sub-lot;
- u is the number of sub-lots actually sampled;
- m is the number of sub-lots in the lot;
- V_m is the sub-lot variance;
- V_{PT} is the preparation and testing variance.

For continuous sampling, where u = m, equation (1) is simplified as follows:

$$P_L = 2\sqrt{\frac{\frac{V_I}{n} + V_{PT}}{m}} \quad (2)$$

The Standard also outlines the procedures for determining the minimum number of sub-lots required for practical reasons, and gives the following equations for estimating the number of increments, n, in each sub-lot for a desired precision:

for continuous sampling:

$$n = \frac{4V_I}{mP_L^2 - 4V_{PT}} \quad (3)$$

for intermittent sampling:

$$n = \frac{4V_I}{uP_L^2 - 4\left(1 - \frac{u}{m}\right)V_m - 4V_{PT}} \quad (4)$$

The Standard Practice for Collection of a Gross Sample of Coal (ASTM D2234/2234M) set by the ASTM, however, recommends that under general purpose sampling procedure, one gross sample represents a lot

with quantities up to 908 t for a 95% confidence level. For a lot with size over 908 t, either take separate gross samples for each 908 t lot of coal or fraction thereof, or one gross sample to represent the total tonnage (the lot size should not exceed 908 t) should be taken provided the number of primary increments are increased as follows:

$$N_2 = N_1 \sqrt{\frac{total\ lot\ size\ (t)}{908\ (t)}} \qquad (5)$$

where:

N_1 = number of increments specified in Table 3, and

N_2 = number of increments required.

A larger number of increments are required when sampling coal with greater variability or blends of different grades of coal. The increments should be spread uniformly on a tonnage basis throughout the mass of the lot or sub-lot so as to reflect the coal variability. Once the increments have been collected, they should be protected from contamination and changes in composition.

The minimum mass of a sample is dependent on the nominal top size of the coal, the precision required for the parameter concerned and the relationship of that parameter to particle size. There is an inverse relationship between sample mass and precision. In general, the higher the number of increments taken, the better the precision. Too few increments reduce precision since some of the quality variability may be missed. Increment sizes that are too small can introduce bias since there is a tendency to exclude the larger particles. Table 4 shows an example of the values for the minimum mass of samples for general analysis and determination of total moisture content as given in ISO 13909-2:2001. The minimum weight of samples recommended by ASTM D2234/2234M can be found in Table 3.

Table 3 – Number and weight of increments for general-purpose sampling procedure (ASTM D2234/2234M)

Top size, mm	**16**	**50**	**150***
Mechanically cleaned coal†			
Number of increments	15	15	15
Minimum weight of increments, kg	1	3	7
Raw (uncleaned) coal†			
Number of increments	35	35	35
Minimum weight of increments, kg	1	3	7

* For coal above 150 mm top size, the sampling procedure should be mutually agreed upon in advance by all parties concerned.

† If there is any doubt as to the condition of the preparation of the coal (for example, mechanically cleaned coal or raw coal) the number of increments for raw coal shall apply. Similarly, although a coal has been mechanically cleaned, it may still show great variation because of being a blend of two different portions of one seam or a blend of two different seams. In such cases, the number of increments should be as specified for raw (uncleaned) coal.

Table 4 – Minimum mass of sample for general analysis and determination of total moisture content (ISO 13909-2:2001)		
Nominal top size of coal, mm	**General-analysis samples and common samples, kg**	**Samples for determination of total moisture content, kg**
300	15,000	3,000
200	5,400	1,100
150	2,600	500
125	1,700	350
90	750	125
75	470	95
63	300	60
50	170	35
45	125	25
38	85	17
31.5	55	10
22.4	32	7
16.0	20	4
11.2	13	2.50
10	10	2
8.0	6	1.50
5.6	3	1.20
4.0	1.50	1.00
2.8	0.65	0.65
2.0	0.25	—
1.0	0.10	—

Note:

1. the masses for the general analysis and common samples have been determined to reduce the variance due to the particulate nature of coal to 0.01, corresponding to a precision of 0.2% ash;
2. extraction of the total-moisture sample from the common sample is described in ISO 13909–4:2001.Values in column 3 corresponds to minimum masses of divided samples for total moisture analysis, which are approximately 20% of the minimum masses for general analysis, subject to an absolute minimum of 0.65 kg.

Sampling should be carried out by systematically sampling either on a time-basis or on a mass-basis, or by stratified random sampling. The interval between primary increments depends on the size of the sub-lot and the number of primary increments in the sample, and should be determined in accordance with relevant standards. This interval should not be changed during the sampling of the sub-lot.

3.2 Methods of sampling

Coal samples can be taken at various locations from a moving stream or from a stationary lot either manually or by mechanical sampling systems. The selection of a sampling method depends upon factors such as the sampling purpose, accuracy desired, accessibility of the site and technical, economic and time constraints.

3.2.1 Sampling from moving streams

Sampling from a falling stream

The best location for sampling from a moving stream is at the discharge point of a conveyor belt or chute where the complete stream can be intersected at regular intervals. Sample increments are taken by an automatic mechanical sampler from the whole cross-section of a continuously moving stream at a transfer point. Mechanical cross-stream cutter type is widely accepted as providing a representative primary sample increment and is most commonly used. Various standards recommend that when samples are taken using a cross-stream cutter, the following design criteria should be met in order for representative and correct sampling:

1. the sample cutter should cut a complete cross-section of the stream;
2. the plane or surface of the cutter aperture should preferably be normal to the mean trajectory of the stream to maximise the effective cutter aperture;
3. the speed of the cutter should be constant and not exceed 0.6 m/s;
4. the ratio of cutter aperture to coal top size is a minimum of three, and the cutter opening should be wide enough to prevent bridging;
5. the cutter opening should have parallel edges;
6. the flowing stream to be sampled should be in free fall;
7. the sample cutter should completely retain or entirely pass the increment without loss or spillage and without any part of the cutter aperture ever being blocked or restricted by material already collected.

Depending on the design, there are different types of mechanical cross-stream cutters such as cutter-chute, cutter-bucket and swing-arm.

It is relatively straightforward to ensure that the cutter intercepts the complete stream. Also, it is easy to check visually that cross-stream cutters are operating correctly so the increment delimitation and extraction are correct. As a result, the need for bias tests is reduced.

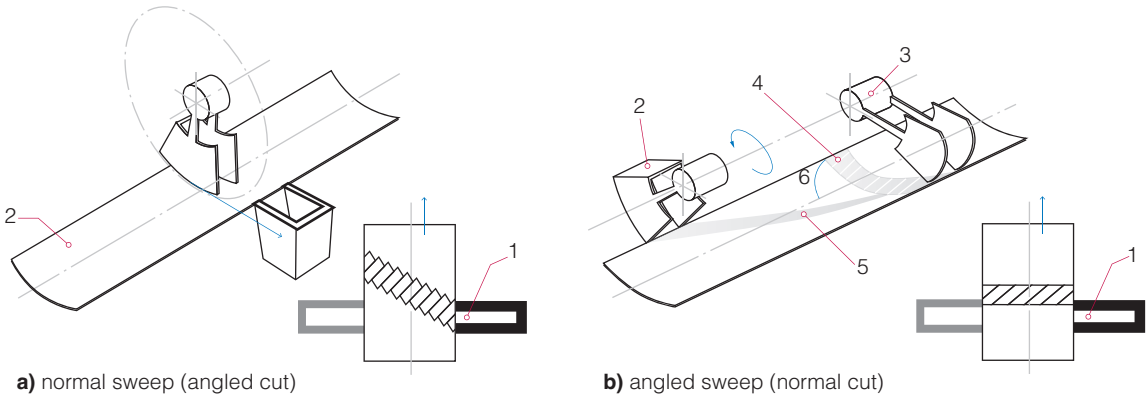
Sampling from a moving belt

It is preferred to use a sampler which cuts the full width of a falling stream of coal. However, where it is not possible, an alternative method is to scoop the sample from a moving conveyor belt using a cross-belt cutter. Cross-belt cutters are now widely used in the coal industry, partly because they are easier to retrofit than falling-stream samplers. They have a cutter that traverses the full width of the belt in a rotary motion. The leading edges of the cutter cut out an increment of coal being carried on the belt and the back plate pushes it off the belt. For representative and correct sampling the design of a cross-belt cutter should meet the following criteria:

1. the cutter lips should be parallel and cut the stream at a 90 degree angle to the centre-line of the convey being sampled;

2. the cutter should cut through the complete cross-section of the stream during one continuous operation with a uniform velocity and a minimum cutter velocity of 1.5 times the velocity of the belt;
3. the cutting aperture width of the cutter should be at least three times the nominal top size of the coal being sampled;
4. the cutter should have a capacity sufficient to accommodate the increment mass obtained at the maximum flow rate of the material;
5. the belt curvature should be profiled to form an arc which is matched by the cutter side plates to ensure that fines which tend to segregate to the bottom of the coal on the belt are included in the sample, and the gap between belt and side plates and/or back plates should be adjusted to the minimum required to safeguard against direct contact and consequential damage to the belt. In addition, the cutter should be equipped at the rear with an effective and durable wiper that sweeps off the bottom layer of coal cleanly;
6. any flexible blades, brushes or skirts fitted to the cutter should remain in close contact with the surface of the moving conveyor belt to ensure that the complete coal cross-section in the path of the cutter is collected from the belt.

There are two types of mechanical cross-belt samplers that are commonly used and they differ considerably as regards the movement of the cutter relative to the coal on the belt as illustrated in Figure 1. 'Square cutters' or 'hammer samplers' (*see* Figure 1a) have sides which are square to the belt. 'Skew cutters' (*see* Figure 1b) have sides set at an angle to the belt in order to reduce the amount of disturbance to the material on the belt which is near to the cutter but is not intended to be sampled. Both types of cutter are rotated about an axis which is parallel to the belt.



a) normal sweep (angled cut)
- cut is normal to belt movement

b) angled sweep (normal cut)
- cut is parrallel to belt movement

Figure 1 – Cross-belt samplers (Moodley and Minnitt, 2009)

For square cutter type samplers, the stream of coal on the upstream side of the cutters is held back, forming a wave of material which may enter the cutter body during the time the cutter cuts through the stream resulting in over-representation. Consequently, the relationship between belt velocity and cutter velocity relative to the coal is important. Also, the higher the cutter velocity is in relation to the belt velocity, the larger the effective aperture will be and the more favourable will be the sampling conditions.

However, the use of high cutter velocities may result in an unacceptable degree of breakage of sized coal. For these reasons, and also because the density of the material to be sampled is considerably higher than in cases of sampling from falling streams, various standards do not impose as strict limitations on cutter velocities as those applying to falling-stream samplers. The cutter velocity has to be carefully adjusted to avoid taking a biased sample. A commonly used rule is that the cutter speed should be at least 1.5 times belt speed (Robinson and others, 2010).

In order to avoid sampling bias, it is important to make sure the coal fines that tend to segregate and move closest to the conveyor belt are collected. To achieve this, the sampler needs to touch the belt. Understandably, the point of impact is an area of high wear and needs to be constantly adjusted to prevent a gap developing between the edge of the cutter and the conveyor belt.

Stopped-belt sampling

This method collects increments from a complete cross-section of the fuel on the conveyor belt by stopping the belt at intervals. Figure 2a shows a stopped-belt sampler. When properly collected, the stopped-belt increment can be considered as bias free. This method is labour and time consuming. Also, it disturbs plant operation and therefore it is no longer used in routine sampling. Today, stopped-belt sampling is recommended by several standards as a reference sampling method when carrying out a bias test procedure.

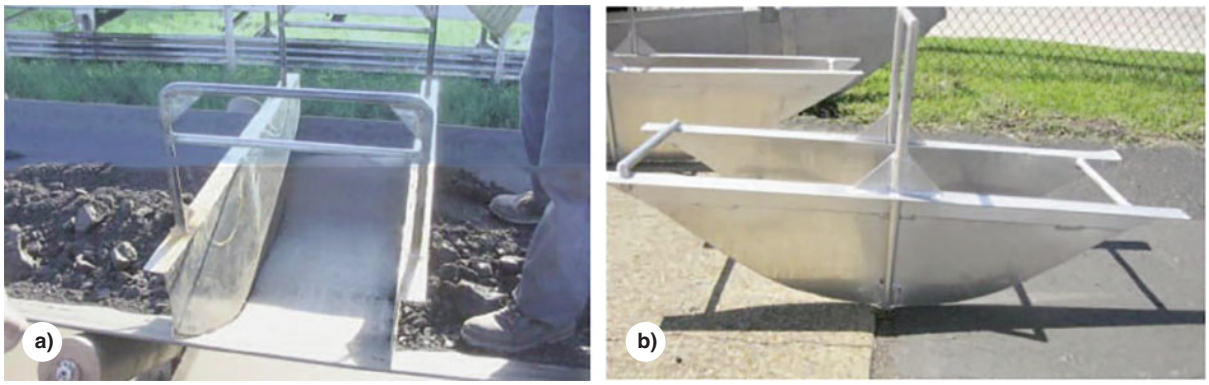


Figure 2 – A stopped-belt sampler (Renner, 2012)

Stopped-belt increments should be taken with a sampler such as a sampling frame (*see* Figure 2b) from a complete cross-section of coal on the belt at a fixed position, for a length along the belt which is at least three times the nominal top size of the coal. The sampler should be placed on the stationary belt at the predetermined position so that the separator plates at each end are in contact with the belt across its full width. All particles lying inside the sampling frame end plates should be swept into the sampling container.

3.2.2 Sampling from stationary coal

Sampling of material that is stationary such as a coal storage pile or railcars, is particularly problematic because in many cases it is not possible to ensure that all parts of the material are accessible and have an

equal probability of being collected and becoming part of the final sample for analysis. For large stockpiles, in particular, the material located in the centre of the pile will be inaccessible when conventional sampling techniques are used. Generally, samples taken around the pile will be limited by the depth of penetration of the sampling device into the stationary source.

Sampling from stockpiles

Coal samples can be taken by the methods for sampling of moving streams described above when a stockpile is laid down or picked up. If this is not possible, then increments can be taken regularly using manual probes, augers or scoops, from the working face of the stockpile, from the bucket of a front-end loader, or from a single discrete load delivered to, but before being pushed into, the main stockpile. This method can provide the best available sample, but it is clearly not an accurate or representative sample. The design of the equipment for manual extraction of increments should fulfil the following requirements (ISO 18283:2006):

- the width of the opening of the sampling device, which determines the minimum mass of increment, should be at least three times the nominal top size of the coal being sampled with a minimum dimension of 30 mm;
- the capacity of the device should be sufficiently large to contain at least the required minimum mass during the extraction of a single increment and to ensure it is not over filled;
- if the device is used for falling streams, the length of the entry aperture should be such as to ensure that the whole width of the stream is intercepted.

During the extraction of increments, large and hard pieces of coal or rock should not be pushed aside, and none of the coal should be lost from the device. Wet coal adhering to the devices should be minimised.

Examples of equipment for manually extracting increments are ladles, shovels/scoops, probes, augers, manual cutters, and sampling frames as illustrated in Figure 3. Probes and augers must not be used for coals that require size analysis; they should only be used for coals with a particle size of up to about 25 mm owing to the difficulty of insertion.

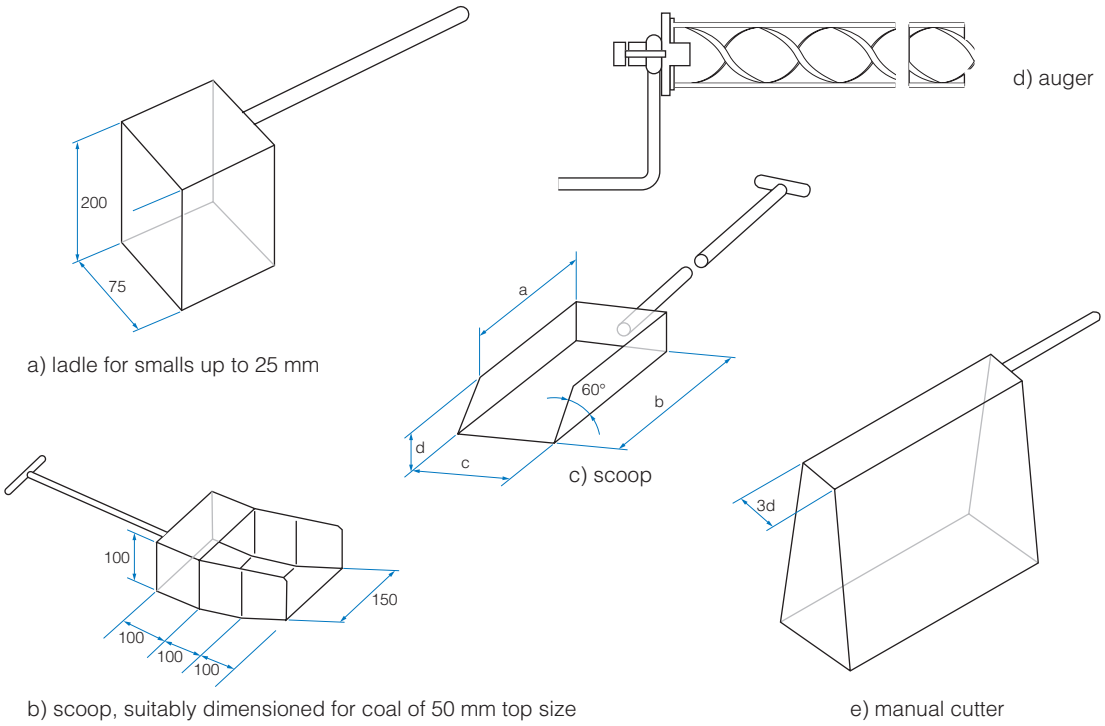


Figure 3 – Examples of equipment for manual sampling shown in ISO 18283:2006

Sampling the outer surface of a stationary or static stockpile is not recommended since the first principle of sampling (*see* Section 3.1.1) cannot be upheld. Results obtained from sampling static stockpiles are never correct nor representative and are merely indicative of the coal quality. Exposure, segregation and other causes mean that the surface layer of a coal stockpile is generally different in quality from the interior (Moodley and Minnitt, 2009). The sampling of a stockpile in situ should be used only if it is not possible to sample the coal as a moving stream. In such cases, various standards recommend the use of equipment (for example, a mechanical auger) that can penetrate to the bottom of the stockpile to ensure that a full column of coal is extracted so that a representative increment is obtained. Position of the boreholes should be chosen so that all parts of the stockpile are represented either by dividing the surface of the stockpile on a grid basis and a core taken from each section of the grid, or by carrying out an initial ground survey and then taking cores across the stockpile on the basis of sampling from equal volumes of coal (ISO 18283:2006).

Sampling from wagons, barges and ships

When coal is transferred to or from trucks, railway wagons, barges or ships, representative samples can be obtained from a moving stream as the vessels are filled or emptied. If this is not possible, the only way of extracting representative samples in-situ from vessels is full depth sampling where a number of full vertical columns are extracted from the vessels. The standards recommend that increments are taken using a suitable full-depth mechanical sampler (the use of an auger is preferred) that is driven down to the bottom of the vessel and then a full vertical column of material is extracted without any sample loss. An example of correct sampling from trucks is shown in Figure 4. Collecting coal from the tops of

fully-loaded barges, trucks or railway wagons before these are unloaded will not provide representative samples and is not permitted due to possible segregation or weather influences during transport (Holmes, 2010; Moodley and Minnitt, 2009). Sampling of stationary coal in the holds of large barges and large ships is impractical because of the difficulty of obtaining a full-depth representative sample. Therefore, the normal practice with large vessels is to sample the coal from a moving stream at port facilities during loading or unloading operations.

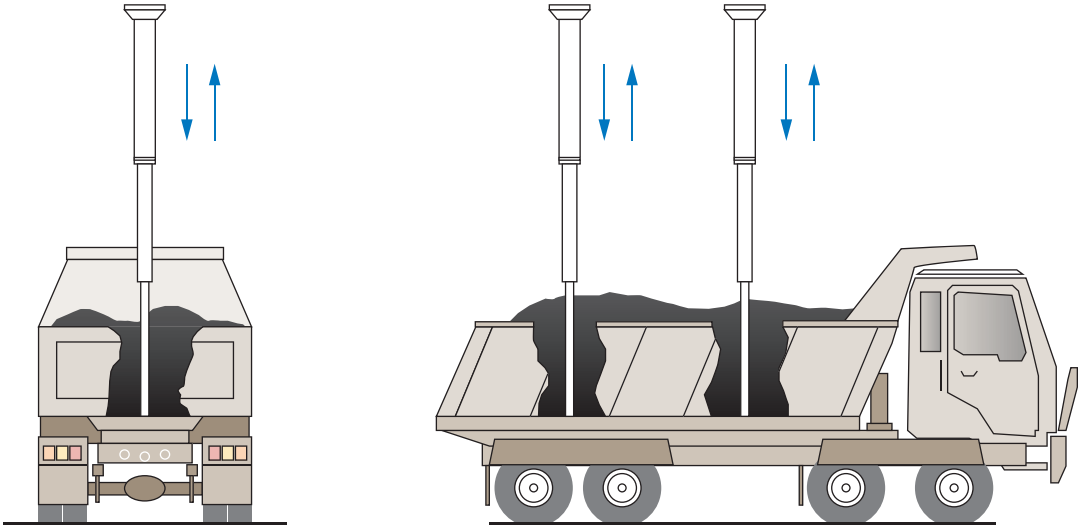


Figure 4 – An example of correct sampling of coal from trucks (Holmes, 2011)

Sampling from stationary lots is carried out on a mass-basis only. The standards specify the procedure of determining the number of sub-lots in the lot and the required number of increments in each sub-lot. A sub-lot can be one or any number of wagons, an entire barge, several barges or one hold of a barge. Depending on the number of increments required, at least one increment should be taken from each vessel. The position of increments within vessels should be evenly spaced and the selection of the position can be either systematic or random.

3.2.3 Manual sampling

Mechanical sampling from moving streams is the preferred method for sampling fuels. However, sometimes mechanical sampling systems are not available and manual sampling is the only alternative. While almost all major, well established loading terminals have mechanical sampling systems installed, there are many small ones that still depend on manual sampling. Moreover, for sized coal, mechanical sampling can be a problem because of degradation by the sampling system.

When sampling manually, conditions are usually far from ideal and the fundamental requirements of sampling that all fuel particles in the lot are accessible to the sampling instrument and that each individual particle has an equal probability of being selected and included in the sample are often not met. Manual sampling is subject to errors associated with human discretion. It is known to be incorrect and unreliable, generating biases that are unpredictable, inconsistent in time, and not readily quantifiable.

Therefore, manual sampling should always be avoided whenever possible and should only be applied if no possibility for mechanical sampling exists.

The extraction of increments should be carried out by suitably trained and experienced personnel using appropriate equipment. The sampler must understand the theory of sampling and be familiar with the relevant standards as well as the site specific standard operating procedures. The standards specify the design requirements of the equipment used for manual sampling. The international standards recommend that, in order to obtain the most representative sample that can be achieved, increments should be taken from fuel in motion such as from a transfer point of a continuously moving stream, during the process of building or reclaiming from a stockpile and during the process of loading/unloading barges, trucks or railcars (ISO 18283:2006). Sampling from a moving-belt or stationary lots is not recommended by ISO.

Samples taken from a moving stream by manual techniques are more precise than samples from a stationary source, but they are subject to human errors. The human factor involved in accurately repeating the cutting process adds to the sampling error. The sampling device should have an opening at least three times the top size of coal with a minimum dimension of 30 mm. The sampling device should cut through the full width of the stream, as far as possible at a constant speed of less than 0.6 m/s (ISO 18283), or 0.46 m/s (18 inches/s) (ASTM D2013). Collecting a sample from a conveyer with a coal flow rate of 500 t/h, could yield a sample weighing 100 – 150 kg. An increment this size would be very difficult to handle manually. Therefore, ASTM D6609-08 provides instructions for sampling by collecting individual increments from part of a cross section of a moving stream of coal. Although less precise than the full cross-stream procedure, multiple partial cross-sectional cuts should be taken at different locations until the entire stream has been sampled.

At mining operations without appropriate sampling technology, extracting increments from the grabs or front-end loaders may be the only solution to the problem of sampling, but the sample can never be representative. The operator of the grab or front-end loader is responsible for co-ordinating the extraction of the increments in an unbiased fashion. Manual probes, augers or scoops must be used to extract the samples as evenly spaced as possible over the surface of the front-end loader bucket or the grab. Such handling of coal results in accumulation of lumps at the bottom of large buckets (Moodley and Minnitt, 2009).

When sampling from stationary lots is necessary, the purpose of this sampling may be to get an indication of certain parameters or to estimate the quality of the stationary lot but the true values or any meaningful statistical inferences cannot be obtained. ISO recommends that a full column of fuel be extracted after the top surface of the fuel has been removed, whist ASTM recommends sampling beneath the exposed surface coal at a depth of approximately 61 cm (24 in) (ASTM D6883–04 (2012)).

When extracting increments, the manual probe/auger should be inserted at right angles to the surface of coal. Increments should be as evenly spaced out as possible.

3.3 Advances in mechanical sampling systems

Mechanical sampling systems started to gain widespread application in the early 1980s. Over the past 30 years, materials handling facilities have become larger, with higher throughput capacity and faster conveyer belt speeds. This fact, coupled with the increased emphasis on accuracy and precision, has led to a proliferation of mechanical sampling systems throughout the quality control chain. Modern mechanical sampling systems include some degree of preparation of the coal sample and are designed to accommodate the installation of an online coal analyser within its subsystem. Figure 5 illustrates an automatic cross-belt sampling system. Today, mechanical sampling systems range from single stage to multistage sampling systems incorporating crushing, discrete sub-sampling and reject handling. They can be found at mines, docks, ports, and power plants worldwide in sampling applications for coal, coke, a variety of ores and other materials.

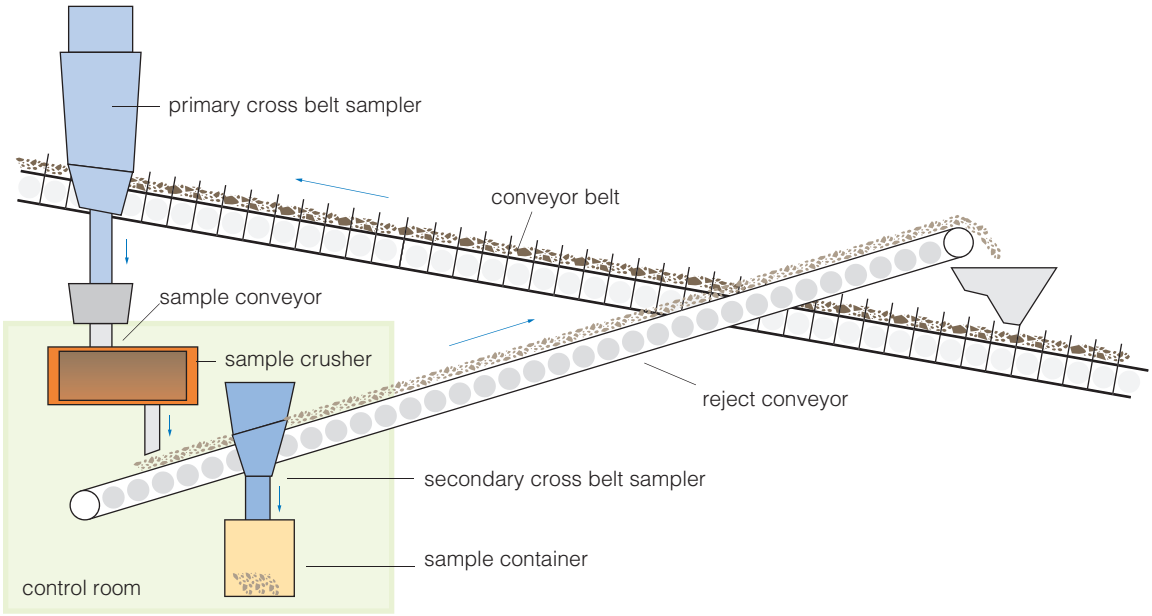


Figure 5 – An automatic (mechanical) cross-belt sampling system (McLanahan, 2013)

3.3.1 Automatic sampling systems

There are two basic types of automatic (mechanical) sampling systems: cross-stream sampler and cross-belt sampler. Both types of system include sub-systems of reduction (crushing) and division (riffling) of primary samples to produce a sample that represents the consignment but is small enough so the subsequent laboratory preparation prior to analysis is kept to a minimum.

While the size of primary increment is always a function of the tonnes per hour rate of the loading system, cross-stream samplers usually take much larger primary increments than cross-belt systems. A cross-stream cutter collects sample increments in a plane parallel to material flow, an orientation having a factor of 'time in flow' to the cross stream increment mass. When combined with cutter speed limitations recommended by Standards for the cross-stream cutter, the result is a primary increment mass of four to six times that of a comparable cross-belt systems on the same conveyor. On high capacity

conveyors, the mass of cross-stream primary increments can be higher than 1000 kg. For example, a cross-stream sampling system operated by Peabody Energy at one of its mine-sites with an average coal flow rate of 9980 t/h has an average of primary increment mass of 1380 kg (Rose, 2012). With substantially more primary coal sample to process, the downstream or sub-system components of cross-stream systems are usually larger in size and number, more complex and have higher costs.

Cross-belt samplers also enjoy a logistical advantage in location and accessibility. All they need for installation is sufficient room for the primary sampler at a point along the length of a conveyor belt and the downstream processing components can be located for easy access. As a result, retrofitting a cross-belt sampler on existing conveyors is relatively easy and economical. On the other hand, cross-stream samplers must always be located at the end of a conveyor belt and they additionally require sufficient height to accommodate the larger number of downstream processing components. As such, the cross-stream system is typically engineered at the same time that the conveyor belt system (with the needed transfer point) is designed and retrofit installations are rare (Reagan, 1999).

Despite these advantages, cross-belt samplers were slow to gain widespread acceptance for years after they were commercially available. However, in recent years improvements in the design and control of the cross-belt sampler have made this type of mechanical sampling device commonplace worldwide.

3.3.2 Collecting the full cross section

A cross stream cutter satisfies the requirement of obtaining a full cross section of the coal in each increment collected. However, in the early years, there was a reluctance to accept cross-belt samplers due to problems with their ability to collect a full cross section of coal.

Most conveyor belts are not configured in a perfect arc. The support idlers usually cause the belt to take on the shape of the idler racks and, without some modifications, the coal in the junction areas between the corners of the belt cannot be collected (*see* Figure 6). This problem is exacerbated if the conveyor idlers are placed far apart from the location of the cutter so the belt can sag between them resulting in a gap between the sample cutter and the belt (*see* Figure 7). As a result, part of the increment may potentially escape under the sampling device leading to sampling bias.

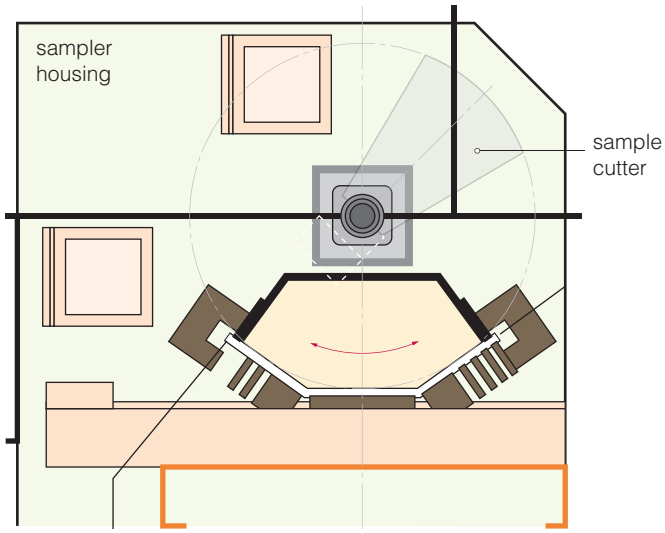


Figure 6 – Imperfect belt contour with corners in an unmodified sampling station (Reagan, 1999)

Figure 7 – The gap between the cross-belt cutter and the belt (Renner, 2011)

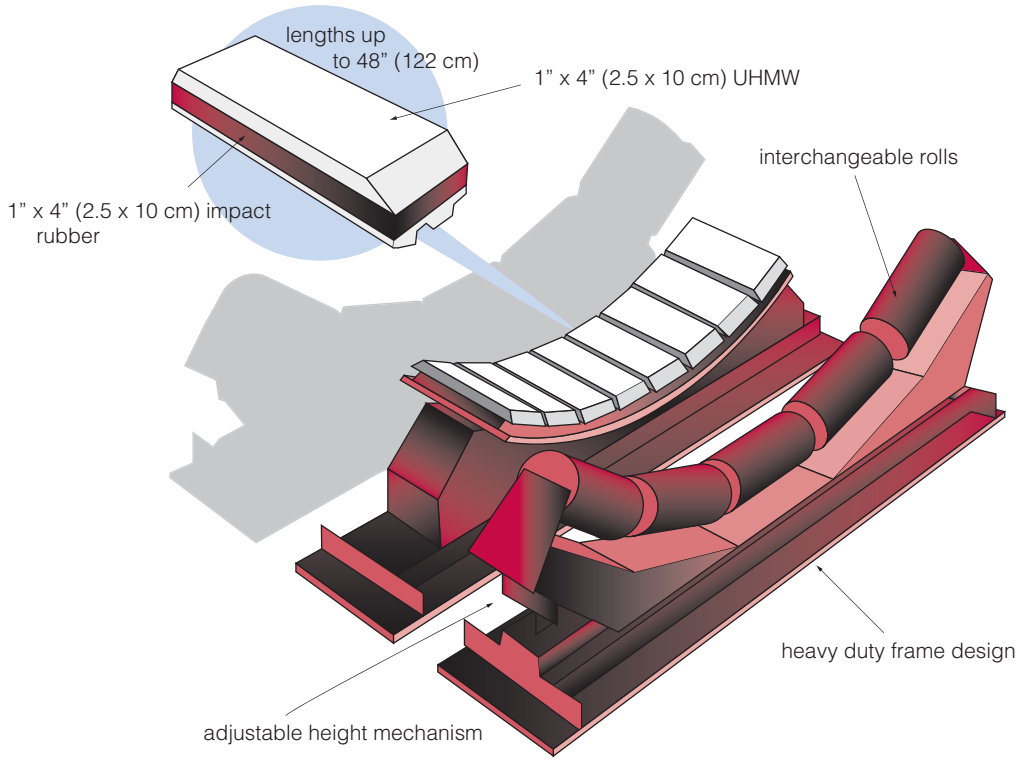


Figure 8 – Support mechanism for shaping the conveyor belt to the required contour for precise sampling (McLanahan, 2013)

In modern cross-belt sampling system designs a set of special impact idlers, or even a full impact 'saddle' is placed under the conveyor belt at the point of impact to prevent the conveyor belt from sagging. In addition, special idlers of a declining degree of angle are often added before and after the point of impact to reshape the contour of the belt to eliminate the corners. In an innovative approach, the conveyor belt is pneumatically lifted into a perfect contour shape for the brief time the increment is collected (Reagan, 1999). Figure 8 shows the support mechanism for shaping the conveyor belt to the required contour for precise sampling. Some designs also equip the sampler head with a brush on the trailing edge of the head to ensure that the belt is left clean and that a correct sample, corresponding to a clean diagonal swath of material being removed from the belt, is collected (Lyman and others, 2010).

3.3.3 The sampling system crusher

After the gross sample is collected, the next major challenge of mechanical sampling systems is to crush the coal to a top size suitable for laboratory analysis without influencing its moisture content. To accomplish this goal, the crusher needs to be free of plugging and easy to inspect, clean and repair.

Although it is necessary for all parts of the mechanical sampling system to operate properly and in sync, the crusher is one of the more critical mechanisms. When an unacceptable bias occurs in a sampling system it is most often due to a moisture bias. When a moisture bias occurs the first point to look at is the crusher. There are two types of crushers commonly used in mechanical sampling systems for coal: hammermill and double roll crusher. The majority of coal sampling systems today use hammermill

crushers. Hammermill crushers employ high speed internal rotors that rotate hammers and crush the coal by impact, driving it through a barrier (either a screen or a series of closely spaced bars). As a result, these crushers are very effective at producing coal of a low enough top size (≤4 mesh or 4.76 mm) so the need for further crushing at the laboratory is eliminated. However, crushing coal generates heat, and heat dries the sample. Also, the high rotor speed of the crushing hammers can create an air pressure differential in the upper and lower parts of the crusher and cause an airflow that can lead to moisture loss. In order to minimise the drying effect during crushing coal, the feed rate to the crusher should be optimised so the primary increment is processed as quickly as possible or the void time between increments is minimised. This can be achieved by increments batching or by increasing the number of primary increments. The feed rate is determined by several factors including the number of primary increments to be collected, the interval between the primary increments and the mass of the primary increments. If the primary increments collected are small resulting in a very low feed rate, the increments may be batched. As the increments are batched the sampling components, such as the crusher, can be turned off. In this case, the sampling system should be evaluated to determine how many batch increments can be collected based on chute capacity and the time required for the batch to be fed through the crusher before the next batch begins. Alternatively, the feed rate can be increased by increasing the number of primary increments collected.

Both ISO and ASTM recommend that the crushers should be designed and engineered in a way that the potential for any change in moisture content or loss of fine coal caused by induced air circulation in the equipment is minimised. The airflow created by the pressure deferential in the crusher can be reduced by lowering the rotor speed. The crusher rotor speed of 1200 rpm is generally accepted by the industry as the speed that the crusher can run with the least amount of drying although crushers operating at slower and faster speeds have also been tested and shown to obtain acceptable results (Campbell, 2013).

Another problem with hammermill crushers is wear. It is desirable that the crushers can produce a coal product with top size of 4 mesh (4.76 mm) or less. This can be very challenging with diverse characteristics found in coal from different seams and blends. The most important variable affecting the crusher performance is the size of the gap between the tip of the crushing hammer and the screen (or bars) against which the coal is crushed. As the hammers and screen wear, the gap grows and crusher efficiency declines leading to coarser coal and increased plugging. In recent years, hardened hybrid alloys have been employed to reduce wear of the crusher internal parts. Today, hammers and screens are available in a variety of special alloys for extreme duty applications. A quality control programme can also be introduced to monitor and maintain the correct top size of the material. In addition, a special mechanical wiping arm has been added to the crusher inlet chute, where plugging is most likely to happen, to periodically remove any coal build-up in this sensitive location (Campbell, 2013; Reagan, 1999).

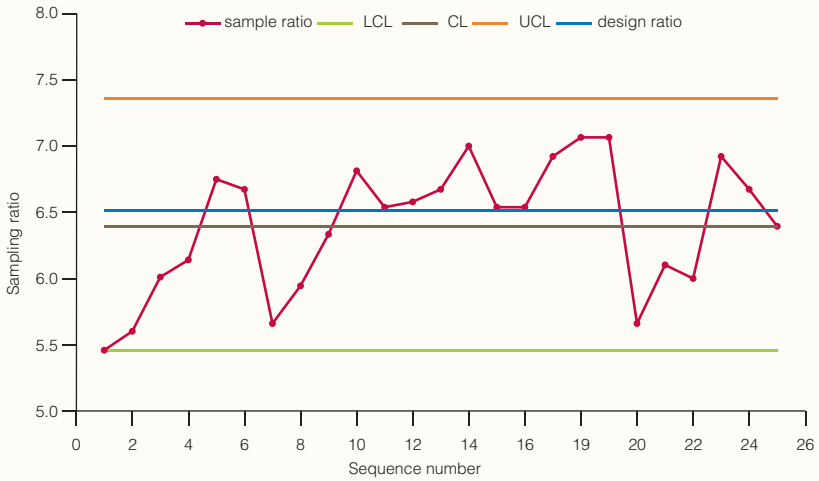
3.3.4 Command and control

One of the major advances in mechanical sampling systems has been the introduction of the programmable logic controller (PLC). The PLC is simply a computer installed with software programs that run and control the sampling system. Key data of the sampling operations are collected and transmitted. The data can then be printed out, displayed on a screen, and/or manipulated to produce sampling reports and quality control data such as date and time of the operation, number of primary cuts and number of secondary cuts. When combined with a scale for determining the sample mass, statistical process control charts can be produced automatically, further enhancing operations. An example control chart is shown in Figure 9.

A major advantage of PLC controls is its ease of use and speed of trouble shooting problems and malfunctions. PLC systems can be programmed to specifically identify the source of failure and automatically notify the operator when system problems occur and their source. With the use of the LED lights on the I/O (input/output) modules, the problem location time on PLC controlled systems is vastly reduced. Also a PLC can accumulate an operational history to explain special cause occurrences such as crusher pluggage or other issues (Reagan, 1999; Renner, 2013). Modern PLC systems allow operators to verify or modify the sampling operations simply by touch of screen or by pressing a few keys.

ACME PLANT

From: 02–Jan–14	**To: 26–Jan–14**	Number of Ratios:	25
Run of seven ratios on one side of line?	Yes	Design Ratio:	6.50
Run of ten out of eleven ratios on one side of line?	Yes	Avg Observed ratio:	6.40
Run of twelve out of fourteen ratios on one side of line?	No	%Difference:	1.55%
Run of seven ratios continually increasing or decreasing?	No	%CV	7.61%
Sample ID number(s) of OOC value(s)	None		



sequence number	sample ID	date	sample weight (lb)	Lot tons	sampling rate	moving range	LCL	CL	UCL
1	200001	02–Jan–14	8.2	1500	5.47	0.13	545	6.40	7.34
2	200002	03–Jan–14	8.4	1500	5.60	0.40	545	6.40	7.34
3	200003	04–Jan–14	9.0	1500	6.00	0.13	545	6.40	7.34
4	200004	05–Jan–14	9.2	1500	6.13	0.60	545	6.40	7.34
5	200005	06–Jan–14	10.1	1500	6.73	0.07	545	6.40	7.34
6	200006	07–Jan–14	10.0	1500	6.67	1.00	545	6.40	7.34
7	200007	08–Jan–14	8.5	1500	5.67	0.27	545	6.40	7.34
8	200008	09–Jan–14	8.9	1500	5.93	0.40	545	6.40	7.34
9	200009	10–Jan–14	9.5	1500	6.33	0.09	545	6.40	7.34
10	200010	11–Jan–14	10.2	1500	6.80	0.33	545	6.40	7.34
11	200011	12–Jan–14	9.8	1500	6.53	0.47	545	6.40	7.34
12	200012	13–Jan–14	9.4	1500	6.57	0.27	545	6.40	7.34
13	200013	14–Jan–14	100	1500	6.67	0.04	545	6.40	7.34
14	200014	15–Jan–14	9.8	1500	7.00	0.09	545	6.40	7.34
15	200015	16–Jan–14	9.8	1500	6.53	0.33	545	6.40	7.34
16	200016	17–Jan–14	9.8	1500	6.53	0.47	545	6.40	7.34
17	200017	18–Jan–14	10.4	1500	6.93	0.00	545	6.40	7.34
18	200018	19–Jan–14	10.6	1500	7.07	0.40	545	6.40	7.34
19	200019	20–Jan–14	10.6	1500	7.07	0.10	545	6.40	7.34
20	200020	21–Jan–14	8.5	1500	5.67	0.00	545	6.40	7.34
21	200021	22–Jan–14	9.1	1500	6.07	1.40	545	6.40	7.34
22	200022	23–Jan–14	9.0	1500	6.00	0.40	545	6.40	7.34
23	200023	24–Jan–14	10.4	1500	6.93	0.07	545	6.40	7.34
24	200024	25–Jan–14	10.0	1500	6.67	0.93	545	6.40	7.34
25	200025	26–Jan–14	9.6	1500	6.40	0.27	545	6.40	7.34

Figure 9 – An example of sampling ratio control chart (Renner, 2013)

3.3.5 Access to the sampling systems

Sampling systems need routine inspection, cleaning and preventive maintenance, especially on the high wear items. They also need rapid resolution when problems and malfunctions occur. When coal from multiple sources is sampled, the sampling system needs frequent and thorough cleaning. A poorly

maintained sampling system will lead not only to inefficient operation or reduced output, but also to erroneous samples. One of the long standing problems with mechanical sampling systems had been the poor access to the components, especially in the crushers. Given the wear and plugging described earlier, this poor access caused problems for sampling system operators. This key weakness has been addressed in recent crusher designs. Modern crusher designs allow complete access to the inside of the crusher for inspection and maintenance without disassembly of its drive or chute work, making it easy to change the screen plate or hammers. Other features include replaceable side liners, screen plates and impact liner. In addition, today's cross-belt samplers have access doors from which the operators can observe the system's operation, for instance if the cutters are correctly sized and shaped, are moving at the correct speed, and are not plugged (Reagan, 1999; McLanahan, 2013, JBLCo, 2013; Graham, 2002).

3.4 Sample preparation

The mass and top size of the gross sample collected by using the methods described above are usually too large for chemical or physical testing. Most often, samples are reduced and divided to provide a sample for analysis. The objective of sample preparation is to prepare one or more test samples from the primary increments for subsequent analysis. The sample preparation process may involve some or all of the following: constitution of samples, reduction (crushing), division, mixing and drying. The preparation helps to increase the sample surface area which enhances the efficiency of chemical reaction, and also aids in the homogenisation of the sample to ensure that the test sample analysed is representative of the entire sample (obtaining an unbiased analysis sample). The required mass and particle size of the test sample depend on the analysis to be carried out.

3.4.1 Constitution of a sample

Once primary increments have been collected, individual increments are usually combined to form a sample. A single sample may be constituted by combination of increments taken from a complete sub-lot or by combining increments taken from individual parts of a sub-lot. Under some circumstances, for instance, for size analysis or bias testing, the sample consists of a single increment which is prepared and tested. Figure 10 shows examples of the constitution of samples.

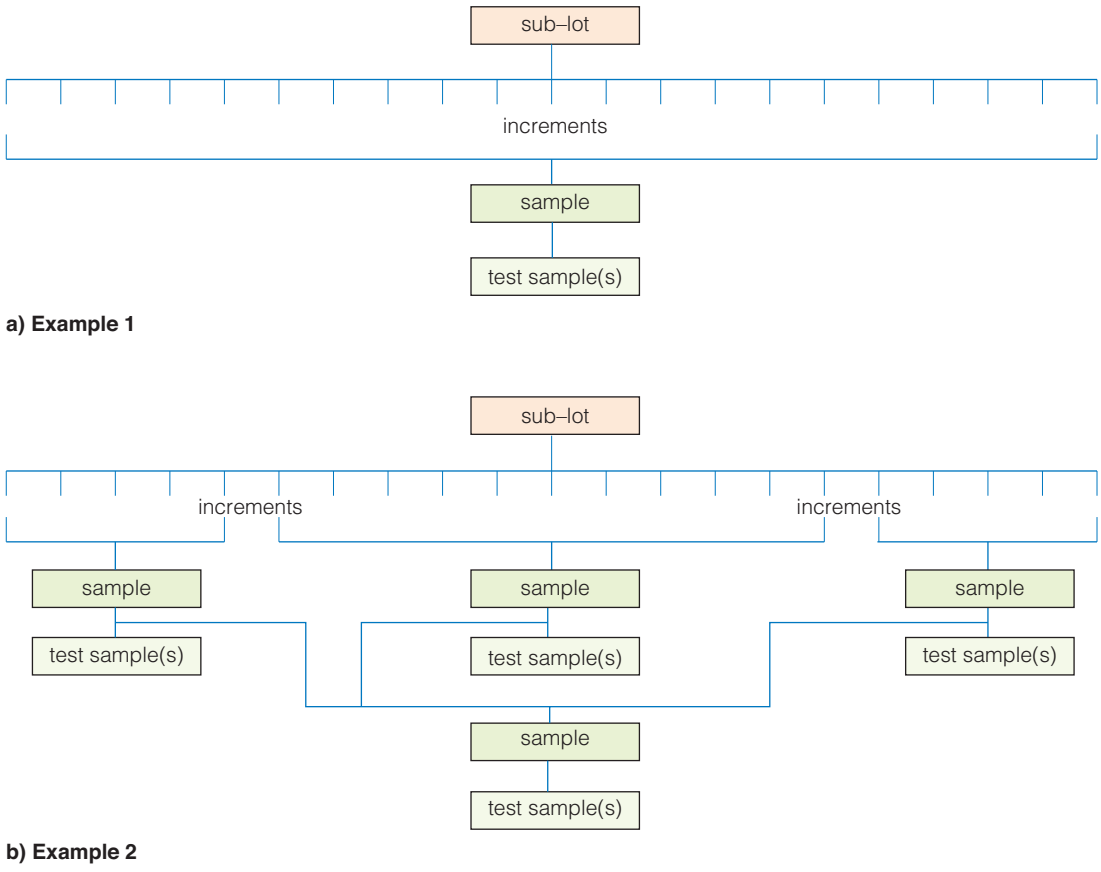


Figure 10 – Examples of the constitution of samples (ISO 13909-4)

The primary increments may be combined into a sample either directly as taken or after having been prepared individually to an appropriate stage by fixed-ratio division (discussed in Section 3.4.4). However, if the primary increments are not of almost uniform mass (that is the co-efficient of variation of the increment masses is more than 20% and there is a correlation between the flow rate at the time of taking the increment and the mass of the increment), they may only be combined into samples after having been divided individually by fixed-mass division.

When combining samples, the mass of the individual samples should be directly proportional to the mass of the coal from which they were taken in order to obtain a weighted mean of the quality characteristic for the sub-lot.

3.4.2 Air drying

When a coal sample is visibly wet it may not run freely through or may tend to adhere to the surfaces of sample reduction and dividing equipment. In such circumstances, it may be necessary to air-dry the sample in order to feed it properly through any subsequent reduction/dividing devices.

The purpose of air drying coal is to bring its moisture content to equilibrium with the atmosphere at ambient temperatures. The sample can be air dried either on a drying floor, or in an air drying oven. The sample is spread in a thin layer that should not exceed a thickness of twice (ASTM D2013) or 1.5 times

(ISO 13909–4) the nominal top size of the coal. Air drying on a drying floor will take much longer than air drying in an oven. ISO 13909–4 recommends drying time at a given temperature whilst ASTM D2013 recommends the air drying should stop when the loss in weight of the sample is less than 0.1%/h. If drying has been carried out at above ambient temperatures, the sample should be cooled until moisture equilibrium at normal ambient temperature is achieved before reweighing. The cooling period required will depend on the drying temperature. Drying temperatures above 40°C are not recommended by the Standards.

Several precautions are necessary to minimise the variance at this stage of sample preparation. Oxidation of coal during air drying must be avoided. Air drying of a sample on a drying floor should be carried out in a room free from dust and excessive wind currents. Excessive drying time should be avoided when a sample is air dried in an oven.

3.4.3 Sample reduction

Sample reduction is the process by which a coal sample is reduced in particle size without a change in weight. The test sample should be reduced to the particle size specified in the relevant test method and therefore the type of mill should be chosen to ensure that the required size is obtained. Mechanical equipment should be used to reduce the particle size but manual crushing is permitted for the breakage of large material to meet the maximum feed size acceptable to the first-stage mill. Mechanical mills that are commonly used include hammermill and double roll crusher.

As discussed in Section 3.3.3, heating of the sample and airstream effects should be minimised, particularly where the sample is to be used for the determination of total moisture, calorific value, and for coking tests. The correct top size and uniformity of particle size generated by the crusher should be regularly monitored and maintained. Also a uniform flow rate into the crusher should be maintained to avoid segregation by composition. Loss of sample or retention of material from previous samples, which might contaminate succeeding samples, should be minimised.

3.4.4 Sample division

Here the sample is reduced in weight without significant change in particle size. The reduction and division of the gross sample can be carried out either by an online mechanical process, or an offline mechanical or manual process, to a top size and mass suitable for subsequent testing.

Mechanical methods

Mechanical dividers are designed to extract one or more parts of the coal in a number of cuts of relatively small mass. Various types of mechanical divider are commercially available and examples of them are shown in Figure 11. The design of the mechanical dividers should meet the criteria specified by relevant standards. Accurate division can be achieved by extracting and compositing a large number of increments from the sample. ASTM D2013 specifies that at least 60 increments be taken at each stage of division. ISO 13909:4 specifies the minimum number of cuts for dividing an increment, which should be determined as follows:

- for fixed-mass division, a minimum of four cuts should be made when dividing primary increments. An equal number of cuts should be taken from each primary increment in the sub-lot;
- for fixed-ratio division, a minimum of four cuts should be made when dividing a primary increment of mean mass;
- for subsequent division of individual divided primary increments, a minimum of one cut should be taken from each cut from the preceding division.

Examples of procedures recommended by ISO for division of individual increments, and subsequent sample division are shown in Figure 12. The combined mass of all the divided increments in the sub-lot should, at each stage, have a minimum mass greater than the mass given in Table 5 corresponding to the type and top size of the sample. If the increment masses are too low to satisfy this requirement, the divided increment should be crushed prior to further division.

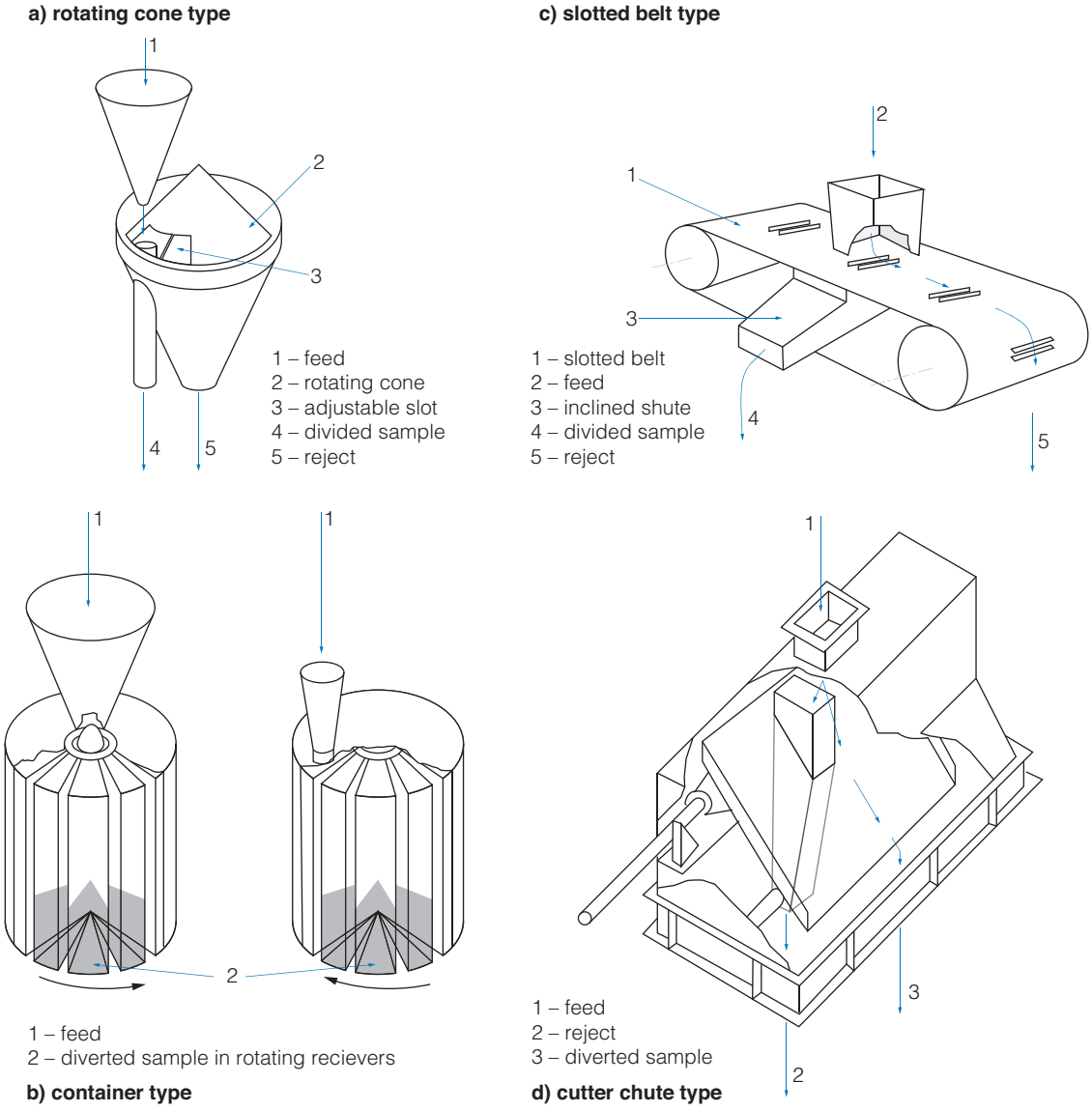
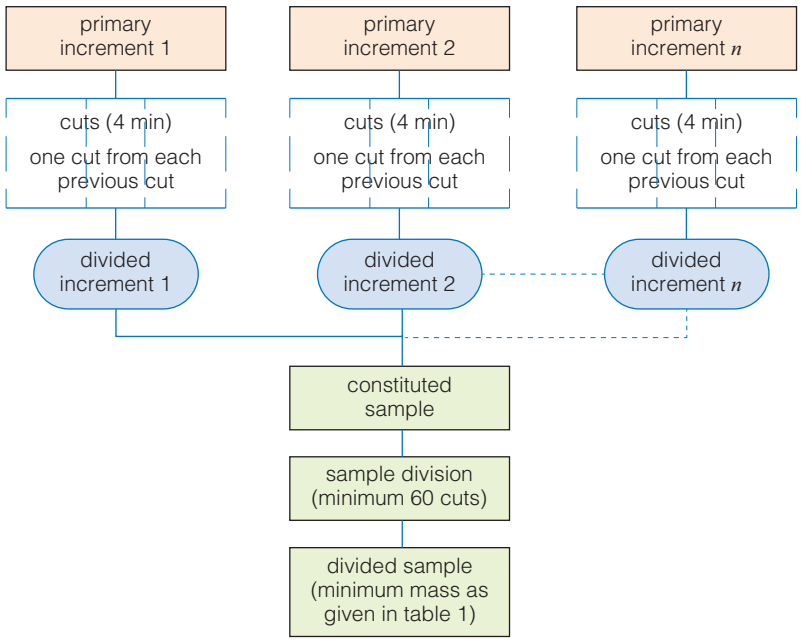
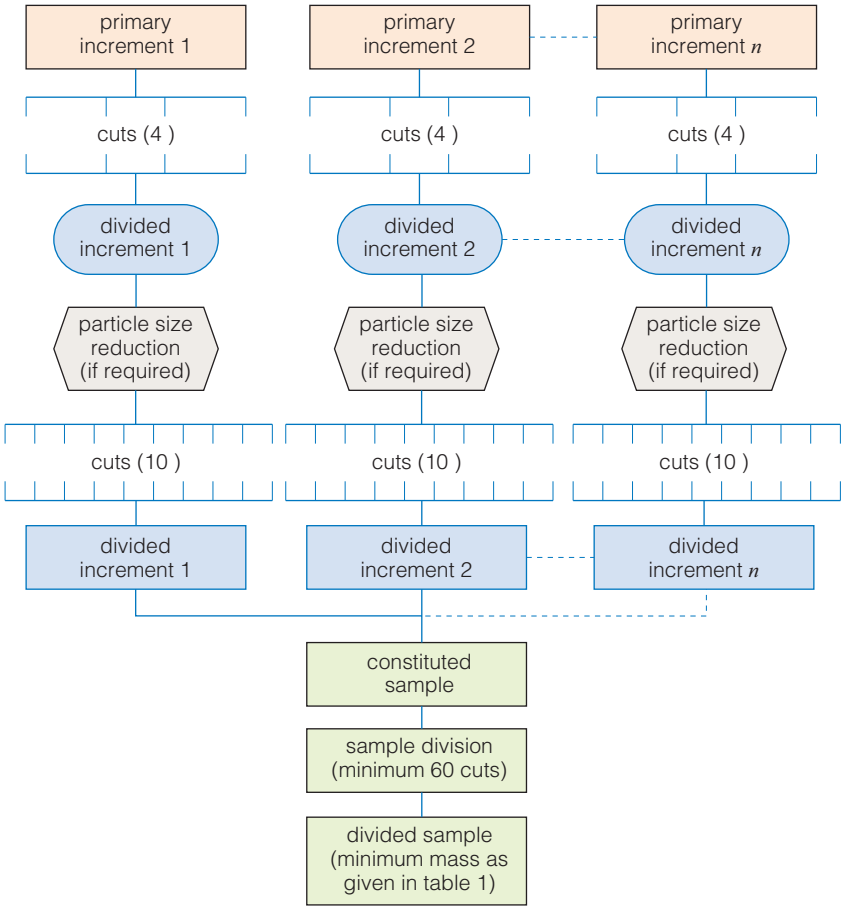


Figure 11 – Examples of mechanical dividers (ISO 13909:4)



a) Example of division of individual increments (minimum number of cuts)



a) Example of two-stage division of individual increments

Figure 12 – Examples of procedures for division of increments and samples (ISO 13909:4)

For dividing a sample constituted from all increments, or divided increments, ISO recommends that a minimum of 60 cuts be taken.

The minimum mass of divided samples is dependent on the nominal top size of the coal, the precision required for the parameter concerned and the relationship of that parameter to particle size. It should be noted that the attainment of the required minimum mass after division will not, in itself, guarantee the required precision, because division precision is also dependent on the number of cuts taken during division. For different types of test sample, the values for the minimum mass of divided samples of varying top size specified by ISO and ASTM are given in Table 5 and Table 6, respectively.

A complete sampling system generally includes a primary sampler, a secondary sampler, a crusher/crushers, and sometimes a tertiary sampler, which is known as a two- or three-stage sampling system. The primary increment is taken from the total lot of coal. The second increment is a full cross-stream cut of the primary increment. A crusher is used before and/or after the secondary sampler for sample reduction. Sample division may be accomplished by a tertiary sampler.

Table 5 – Values for the minimum mass of divided samples (ISO 13909:4)

Nominal top size of coal	General-analysis and common samples	Total-moisture analysis samples	Size-analysis samples	
mm	kg	kg	1%	2%
300	15000	3000	54000	13500
200	5400	1100	16000	4000
150	2600	500	6750	1700
125	1700	350	4000	1000
90	750	125	1500	400
75	470	95	850	210
63	300	60	500	125
50	170	35	250	65
45	125	25	200	50
38	85	17	110	30
31.5	55	10	65	15
22.4	32	7	25	6
16	20	4	8	2
11.2	13	2.5	3	0.7
10	10	2.0	2	0.5
8	6	1.5	1	0.25
5.6	3	1.2	0.5	0.25
4	1.5	1.0	0.25	0.25
2.8	0.65	0.65	0.25	0.25
2.0	0.25			
1	0.1			
<0.5	0.06			

Table 6 – Preparation of laboratory sample (ASTM D2013)		
Crush to pass at least 95% through sieve	Divide to a minimum weight of, g*	
	group A	group B
No. 4 (4.75 mm)	2000	4000
No. 8 (2.36 mm)	500	1000
No. 20 (850 µm)	250	500
No. 60 (250 µm) (100% through)	50	50

*if a moisture sample is required, increase the quantity of No. 4 (4.75 mm) or No.8 (2.36 mm) sieve subsample by 500 g.

Manual methods

A riffle is a sample divider that divides a sample stream into halves, one of which is discarded and the other remains as a sample for further splitting or analysis. For sample division, the coal is usually fed manually along its length, and as illustrated in Figure 13, adjacent slots feed opposite receivers. The riffle should be fed using a special pan that is exactly the same width as the top of the chute. It is important that the riffle slot width be at least 3 times the nominal top size of the coal. Each half of the riffle should have the same number of slots (at least eight and preferably more). All the surfaces on which the coal might rest shall have a slope of at least 60° to the horizontal. The coal should be fed into the riffle in a slow, uniform stream covering all of the slots of the riffle. The coal should not be allowed to build up in or above the riffle slots, and it should flow freely through the slots. When a staged sample division requires two or more steps or passes, the sample retained at each step should be taken alternately from each side of the riffle.

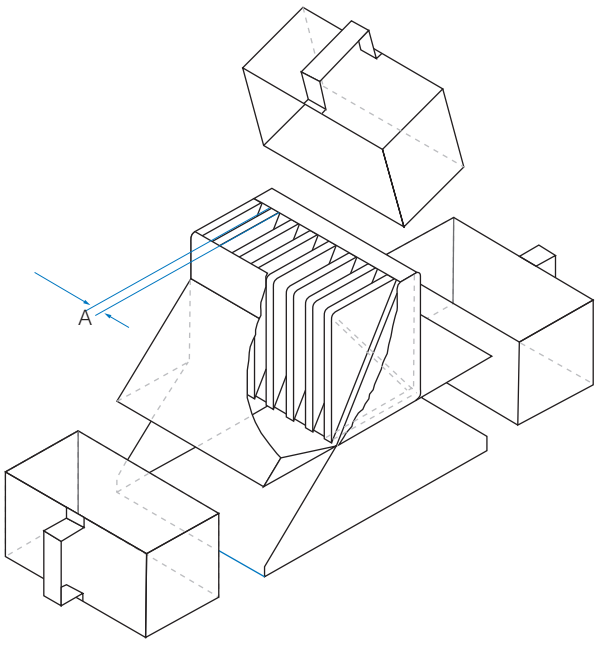


Figure 13 – A riffle sample divider

3.4.5 Sample mixing

The material should be mixed thoroughly to ensure the homogeneity of the test sample. In theory, thorough mixing of a sample prior to its division reduces errors due to sample preparation. In practice, however, this is not easy to achieve and some methods of hand mixing such as forming and reforming into a conical pile, can have the opposite effect leading to increased segregation. Mixing may also result in loss of moisture. Furthermore, mixing is not possible where samples or increments are flowing through any form of preparation system and is therefore restricted to offline preparation.

One method that can be used is to pour the sample through a riffle (*see* Figure 13) or a container-type sample divider (*see* Figure 11b) three times, reuniting the parts after each pass. If mechanical sample dividers are used in the course of preparation, an additional mixing step is not normally necessary to meet the required precision.

Mechanical mixing may be useful at the final stage of preparation of test samples. A mixing wheel can be used. The samples are in a number of closed containers that are attached to the rim of a wheel at an angle of 45° with the horizontal wheel shaft. The wheel is turned slowly so that the particles fall gently from top to bottom of the container, mixing the sample thoroughly. To obtain good mixing of the sample, the containers should be about half full and never more than two thirds full.

3.4.6 General rules of sample preparation

Any errors resulted from the sample preparation practice will remain in the final sample. Therefore, the standard procedure to be used for sample preparation should be carefully selected. Whenever possible, mechanical methods are preferable to manual methods to minimise human error. Sample preparation operations should be carried out by trained and experienced personnel. Before preparing the sample, the number and nature of the analysis and tests should be considered. A reserve sample is desirable in case a check analysis or test is required. The following precautions should be taken during sample preparation (Smith and others, 2010):

- in collecting, handling and preparing the sample, all operations should be done rapidly and in as few operations as possible to minimise possible coal oxidation and changes in coal moisture content;
- the sample should be protected from moisture change due to exposure to rain/snow, wind, sun, extreme temperatures, and from contamination on contact with other material;
- most coals oxidise on exposure to air and hence, the air-drying procedure should not be prolonged past the time necessary for air-drying (follow the procedure specified by the Standards). When the sample is air dried at above ambient temperatures, the sample should be allowed to attain ambient temperature before weighing and further reduction and division;
- whenever the sample is stored or transported, the sample bag/container should be weighed. The sample should be allowed to attain equilibrium to the new atmosphere by air-drying and the weight loss or gain should be used in the calculation of moisture content;

- the sample bag/container should be strong and large enough for the largest sample expected. After a sample is stored, the sample bag/container should be sealed properly;
- loss of material during sample preparation should be avoided.

3.5 Bias testing

3.5.1 Sampling error

The sampling error is by far the largest component of the total error – generally 80% of the total error arises from some aspect of sampling. A sampling error consists of random error and systematic error. Random error is caused by some chance occurrence in the sampling process. It may occur in both positive and negative directions around the mean value and tends to have an average value of zero. There are several ways to minimise the potential increase in variance due to a random error. For instance, a sampling method that takes a relatively large number of increments lessens the random error. Also, the sampling methods and techniques described in various standards are designed to decrease random errors.

A systematic error, also known as sampling bias, is a repetitive error usually caused by inaccuracies in the sampling mechanism and, as opposed to random, the results tend to be persistently higher or lower than those obtained using a reference sampling method which is intrinsically unbiased. A sampling system with a systematic error, or bias, will consistently misrepresent the actual coal in the same way, leading to inaccurate analytical results. Biased sampling can have a costly financial consequence. Table 7 shows an example of the costs of biased moisture measurements. It can be seen from Table 7 that for an annual coal supply contract of just over 4 million tonnes, even a small negative bias in coal moisture content could cost a coal company dearly.

Table 7 – Costs calculation of negatively biased moisture measurements (Renner, 2013)

Gross generating capacity of a utility	1500 MW
Gross capacity factor	88.0%
Unbiased coal heating value	130.26 MJ/t
Unbiased coal moisture content	8%
Average hourly coal requirement	539.0 tons/h (488.9 t/h)
Annual coal requirement	4,721,640 tons (4,282,527.5 tonnes)
Delivered cost of coal	$60.00/ton ($66.15/t)
Annual delivered cost	$283,298,400
Cost of 1% negative moisture bias	$2,834,252 annually
Cost of 0.19% negative moisture bias	$538,698 annually
Cost of 0.19% negative moisture bias	$0.114/ton ($0.126/t)

In 2008-09, 1,012,839.21 tons (918,645.16 tonnes) coal was shipped to the utility which submitted to the coal company for reimbursement of $115,463.66 for a 0.19% negative coal moisture bias identified during a bias test of the sampling system.

3.5.2 Methods of testing for bias

When a systematic error is considered, the bias present in the sampling mechanism must be known. Bias may be hardware induced, system logic induced, or a combination of both. To prevent sampling bias, a

sampling system should be bias tested to determine if it is introducing any systematic errors. In particular, a bias test is needed:

- upon installation of a new sampling system;
- after a system has been relocated;
- after modification which may affect particle size selection;
- after a conveyor from which the primary increments are collected is modified so as to change the speed troughing angle or discharge angle;
- after a system has been repaired from structural damage or deterioration, or lack of maintenance such that moisture content and/or particle size selection could have been affected.

It is a good practice to retest sampling systems periodically because some of the above mentioned are not readily determined (Renner, 2012).

All bias testing is based on a matched pairs experimental design. Bias is detected as a systematic difference between a test result and an accepted reference value. The accepted reference value is obtained by simultaneous sampling of the test coal by an accepted reference method and by the system under test. The preferred reference method is stopped-belt sampling (*see* Section 3.2.1). Both ISO and ASTM standards are built on this foundation but there are differences in test plan alternatives and differences in statistical analysis and interpretation of results. The bias testing design choice includes paired-increment or paired-batch test. The paired-increment test creates a close physical association between reference and system sample and can be used to test individual components of a sampling system. It is often not practicable to obtain single increment samples from the system so paired-batch test design can be used. Increments taken by the system can be compounded as samples, and compared with samples compounded from increments taken over the same period using the reference method. It is not necessary for the two samples to have the same number of increments or that they are of similar mass. The paired-batch test is the most frequently used method. ASTM D7430 also describes intraphase testing as a bias test design choice. In this case, surrogate samples can be used as reference samples for a dynamic phase of intraphase test.

Tests for bias can be carried out for ash, moisture or any other variable required. ASTM D7430 recommends bias tests for moisture, ash, sulphur content and heating value of coal. In ISO 13909:8, however, it is stated that the two parameters, moisture and ash, are sufficient for a bias test. This statement is supported by a recent study (Rose, 2012) and use of only two parameters simplifies the multivariate test calculations.

The ISO 13909:8 anticipates that the bias test may encompass the primary sampler alone, individual components or subsystems, or the entire system and gives instructions for carrying out such tests. Before the test, a detailed test procedure should be established. The design of the test will differ depending on the objectives and, therefore as the first step in planning, the objectives of the test should be clearly defined.

Bias testing can be a tedious and expensive process, especially when testing of the primary increment sampler is included. For this reason, a pre-test inspection of the sampling system and its operation, both static and under load, should be conducted. Any mechanical problems found during the inspection should be fixed and all conditions known to cause bias should be corrected to ensure that the system is operating correctly according to the standards so it is most likely to pass a bias test.

A minimum number of 20 pairs of observations is recommended by ASTM and ISO. For each pair, the difference between the analytical results is determined. The series of differences between the results reached is subject to a statistical analysis. Detailed step-by-step instructions for carrying out the statistical calculations and interpretation of the data are given in the national/international standards. The ASTM standards address bias testing of coal sampling systems using multivariate statistical methods whilst the existing bias test procedure specified in ISO standards uses only univariate statistical methods.

3.6 Comments

Automatic sampling systems are mechanical devices that require routine preventive maintenance. Operating a sampling system without a comprehensive operating and maintenance programme risks bias, availability issues and failure of audits by inspectors. Renner (2012, 2013) proposed a seven-step procedure to be incorporated to improve an existing sampling system and it can also be applied for commissioning a new one:

1. inspect the system while in service and while out of service. Check the pneumatic, hydraulic, electric and other components, measure cutter speeds, cutter operating intervals, sample flow rates, belt speeds, and note any mechanical problems;
2. fix the obvious mechanical problems and sample flow problems;
3. prepare a sample extraction table which includes the design sampling ratio, make corrections to the sampling parameters necessary to eliminate bias;
4. begin control charts of the sampling ratio;
5. identify and fix causes of out-of-control conditions;
6. after a stable condition has been reached, examine the co-efficient of variation (CV). If the CV is greater than 15%, identify and fix the causes of excessive variation;
7. continue to chart the sampling ratio and take action when indicated by the charts. After the system is stable and the CV is <15%, and the differences between the observed and design sampling ratio are <10%, bias test the system.

An extraction table is essential to verify sampling system operating parameters and system flow rates. Use of an extraction table allows the system operation to be mathematically evaluated providing a useful evacuation and planning tool. Use of the sampling ratio control chart is recommended by ASTM D7430 but is not discussed in ISO 13909. The charts have rules and limits and are process control charts that provide mathematical evidence of correct extraction of increments from the coal stream to be sampled. Renner believes that the seven-step procedure can provide the confidence of correct system operation.

4 Standard laboratory analysis of coal

Chemical analyses and testing of a coal sample are generally done off-site in a laboratory. The main purpose of coal sample analysis is to determine the quality or rank of the coal along with its intrinsic characteristics. Furthermore, these data will be used as the fundamental consideration for coal trading and its utilisation. General coal analysis and testing include the following:

1. Proximate analysis: moisture content, ash content, volatile matter, fixed carbon;
2. Ultimate analysis: carbon, hydrogen, oxygen, nitrogen, sulphur;
3. Ash analysis: major and minor elements in coal and coal ash;
4. Calorific value (also known as heating value or specific energy).

In addition, special coal analyses may also be performed on trace elements, coal hardness, ash fusion temperature, chlorine, fluorine, boron, arsenic, mercury, selenium, phosphorus, size analysis, and so on. Standardisation of the procedures and conditions is essential for obtaining results that are comparable within any one laboratory and between different laboratories. The standard test methods used in routine laboratory analyses of coal will be presented in the following sections. The variables are expressed as a percentage mass fraction (weight percent wt. %) and are calculated in several different bases. As received (ar) basis puts all variables into consideration and uses the total weight as the basis of measurement. Air dried (ad) basis neglects the presence of moisture other than inherent moisture while dry basis (d) leaves out all moisture, including surface moisture, inherent moisture, and other moisture. Dry, ash free (daf) basis neglects all moisture and ash constituents in coal while dry, mineral-matter-free (dmmf) basis leaves out the presence of moisture and mineral matters in coal, for example: quartz, pyrite, calcite. The differences in the bases of measurement used and the relationship of different analytical bases to various coal components are explained in more detail in a report published earlier by IEA CCC (Carpenter, 2002). Conversion from one basis to another can be performed using mass balance equations.

4.1 Proximate analysis

The proximate analysis of a coal determines the moisture content, volatile matter (VM), ash and, by difference, the fixed carbon within the coal sample. It is the simplest and most common form of coal evaluation, and constitutes the basis of many coal purchasing and performance prediction indices used by utility operators.

4.1.1 Moisture

Moisture may occur in various forms within a coal:

- surface or free moisture: water held on the surface of coal particles or macerals;
- inherent (residual) moisture: water held by capillary action within the pores/capillaries of coal;
- decomposition moisture: water produced from the thermal decomposition of organic constituents of coal;

- mineral moisture (water of hydration of mineral matter): water which comprises part of the crystal structure of hydrous silicates such as clays and inorganic minerals in coal.

There are various standardised tests to determine the moisture content of coal and they are classified depending upon the type of moisture content tested:

- equilibrium moisture (moisture-holding capacity);
- total moisture;
- moisture in air dried sample (residual moisture).

Proximate analysis of moisture determines the total and/or residual moisture content of coal. The total moisture content of coal consists of surface and inherent moisture, and is reported as a mass percentage of the coal on an as received basis. Residual moisture measures the moisture content of an air dried coal sample. Moisture determination depends on the extent of sample preparation and the condition of the coal sample. The entire procedure for determining the total moisture in coal, after collecting the gross sample, begins with preparing the sample for analysis. If the gross sample is sufficiently dry, it may be reduced immediately and then air dried. If the sample is too wet to reduce in size, it should be weighed and air dried, before size reduction, at ambient temperature. The coal sample must be reduced and divided to the size/mass specified for the test method used in accordance with relevant Standards. While air drying removes most of the surface moisture of coal, a temperature of approximately 107°C is needed to remove inherent (residual) moisture. The moisture content of coal can be determined by an indirect gravimetric method. This method involves oven-drying a known mass of coal sample to a constant mass at a temperature of 105 to 110°C in an atmosphere of either air (ASTM, ISO) or nitrogen (ISO). The moisture content is calculated from the loss in mass of the sample. ISO recommends that drying in a nitrogen atmosphere is suitable for brown coals/lignites and all hard coals, while drying in air is only suitable for hard coals not susceptible to oxidation. Indirect gravimetric method is recognised by ASTM and ISO as a standard method for determining moisture content in analysis sample of coal (ASTM D3173–11; ASTM D3302/D3302M–12; ISO 11722:2013; ISO 5068–2:2007). For other coal samples such as a gross sample, the Standards specify indirect gravimetric single-stage (ASTM D2961–11; ASTM D3302/D3302M-12; ISO 589:2008; ISO 5068–1:2007) and two-stage methods (ASTM D3302/D3302M–12; ISO 589:2008; ISO 5068–1:2007) for determining the total moisture in coal. In the single-stage method, a sample, prepared using a closed mill, is oven-dried to determine its total moisture content. In a two-stage method, a sample is coarsely ground and air dried. The sample is further crushed and then oven-dried to a constant mass under conditions described above. The total moisture content is calculated from the losses in mass during the two drying stages.

Other established procedures for measuring moisture in coal include direct gravimetric and direct volumetric method. In the direct gravimetric method, the analysis sample of coal is heated at 105–110°C in a stream of oxygen-free, dry nitrogen and the moisture driven off is collected in an absorption tube containing a desiccant. The increase in mass of the absorption tube (after deducting the result of a separate blank determination) is due to moisture in the sample of coal. The direct gravimetric method for

determining moisture content in coal was recognised by ISO as a standard method (ISO 331:1983) but the standard was withdrawn in 2004. In the direct volumetric procedure, the coal sample is heated under reflux conditions in boiling toluene. The moisture is carried by toluene to a graduated receiver where the moisture is condensed and separates from the toluene, allowing direct calculation of the volume of water released from the coal. The international standards describing the direct volumetric procedure as a standard method for determining moisture in hard coal (ISO 348:1981) and brown coals/lignites (ISO 1015:1992) were discontinued in 1990 and 2002, respectively.

Sample handling should be kept at a minimum during moisture determination to eliminate the potential for loss or gain of moisture during prolonged handling.

4.1.2 Ash

Ash is the residue remaining after the combustion of coal in air and is derived from inorganic complexes present in the original coal substance and from associated mineral matter. Therefore, the result of the determination is 'ash' and not 'ash content' as coal does not contain any ash. The ash yield is commonly used as an indication of the grade or quality of a coal since it provides a measure of the incombustible material.

Ash is determined by weighing the residue remaining after burning approximately 1 g of coal under rigidly controlled conditions of sample weight, temperature, time, atmosphere, and equipment specifications. The standard methods set by ASTM and ISO are similar but differ in detail. In the approach described in ISO 1171:2010, a general analysis test sample of coal (ground to pass a sieve of 212 µm aperture), accurately weighed, is heated in air in a furnace from room temperature to 500°C over a period of 60 minutes at a uniform heating rate and is held at this temperature for 30 minutes (60 minutes for brown coals/lignites). The sample is then heated to 815°C ± 10°C and maintained at this temperature for a minimum of 60 minutes until the sample is constant in mass. When the incineration period is complete, the sample is allowed to cool and then weighed. The results are reported as a percentage mass fraction on an air dried basis.

A similar two-stage heating process is also adopted by ASTM (D3174–12) but a lower incineration temperature is used. A weighed analysis sample of coal (with a top size of 250 µm) or a dried coal sample from the moisture determination is placed in a cold furnace and is heated, in air, gradually at such a rate that the temperature reaches 450–500°C in 1 hour. Heating of the coal sample continues so that a final temperature of 700–750°C is reached by the end of the second hour and the sample is maintained at this temperature for an additional 2 hours. The sample is then allowed to cool before being weighed. It is important to ensure that after incineration the sample is cooled under conditions which minimise moisture pickup.

Variations in the amount of ash arise from the retention of sulphur that originates from the pyrite. The amount of sulphur retained in the ash is in part dependent on the conditions of ashing and therefore, in

order to obtain values for the ash on a comparable basis, it is necessary to adhere strictly to the conditions specified in the relevant standard.

4.1.3 Volatile matter

Volatile matter (VM) in coal refers to the thermal decomposition products liberated when coal is heated at high temperature in the absence of air. The VM obtained during the paralysis of coal consists mainly of combustible gases such as hydrogen, carbon monoxide, hydrocarbons, tar, ammonia as well as incombustible gases like carbon dioxide and steam. VM content may be used to establish the rank of coals, to provide the basis for purchasing and selling, or to establish burning characteristics such as combustibility (reactivity) of a coal, and ease of ignition and hence flame stability. VM is determined by establishing the loss in weight resulting from heating a coal sample under rigidly controlled conditions. The measured weight loss, corrected for moisture as determined using standard methods, establishes the volatile matter content.

The methods for determining the VM content of a coal described in ISO and ASTM standards are based on the same principle and are similar. Approximately 1 g of a general analysis coal sample with top size of 212 µm (ISO) or 250 µm (ASTM) is heated in a covered crucible to a predetermined temperature for a total of exactly 7 minutes. The test method specified in ISO 562:2010 involves heating the coal sample to 900°C ± 5°C in a cylindrical silica crucible in a furnace, whilst the ASTM D3175-11 describes heating the coal sample to 950°C ± 25°C in a vertical platinum crucible. The results obtained from standard tests are expressed as a percentage mass fraction, generally on an air dried basis.

ISO 562 sets the standard test for VM in hard coals. For brown coals and lignites, ISO 5071-1:2013 (Brown coals and lignites – Determination of the volatile matter in the analysis sample – Part 1: Two-furnace method) applies. In this method, the coal is heated out of contact with air for 7 minutes at 400°C, then immediately transferred to another furnace and heated at 900°C for a further 7 minutes. The percentage of volatile matter is calculated from the loss in mass of the oven-dried sample or from the loss in mass of the analysis sample corrected for moisture.

ASTM D3175 applies to coals of all rank but provides a modified procedure for 'sparking' coals: the sample of a sparking coal is subjected to a preliminary gradual heating such that a temperature of 600°C ± 50°C is reached in 6 min. After this preliminary heating the sample is heated for exactly 6 minutes at 950°C ± 20°C. If sparking is then observed, the determination should be rejected and the test repeated until no sparking occurs either during the preliminary heating or during the 6-minute period at 950°C. 'Sparking' coals are defined as those coals that do not yield a coherent cake as residue in the VM test but do evolve gaseous products at a rate sufficient to carry solid particles mechanically out of the crucible when heated at the standard rate. Such coals normally include all low-rank non-caking coals and lignites but may also include some higher rank coals (Carpenter, 2002). Australian Standards set separate test procedures for determining VM content in high rank coals (AS 1038.3–2000) and low rank coals (AS 2434.2–2002), respectively. The method described in AS 1038 for determining VM in high rank coals is essentially similar to that of ISO 562. For determining VM in low rank coal, the test specified in AS 2434

involves heating the coal sample out of contact with air for 7 minutes at 400 °C and then at 900°C for a further 7 minutes.

The test is empirical. The variations in 1) the size, weight and material of the crucibles used, 2) the rate of temperature rise, 3) the final temperature, 4) the duration of heating; and 5) modifications that are required for coals which are known to decrepitate or which may lose particles as a result of the sudden release of moisture or other volatile materials can significantly affect the test results (Speight, 2012). In order to ensure reproducible results, it is essential that the standard procedures be followed closely. It is also essential to exclude air from the coal or coke during heating to prevent oxidation. The fit of the crucible lid is, therefore, critical. The moisture content of the sample is determined at the same time as the volatile matter so that the appropriate corrections can be made.

4.1.4 Fixed carbon

Fixed carbon in coal is the carbon that remains in the coal sample after volatile matter is driven off. This differs from the ultimate carbon content of the coal because some carbon is lost in hydrocarbons with volatiles. The ratio of fixed carbon to proximate VM, the fuel ratio, is used as a measure of combustion reactivity and burnout. Fixed carbon is not determined directly, it is calculated by subtracting from 100 the resultant summation of moisture, VM and ash, all as a percentage mass fraction on the same moisture reference basis.

4.2 Ultimate analysis

Ultimate analysis determines the percentage mass fraction of the major constituents of coal such as carbon, hydrogen, sulphur, nitrogen, and, usually by difference, oxygen. The ultimate analysis is used with the calorific value of the coal to perform combustion calculations such as the determination of coal feed rates, boiler performance and sulphur emissions.

4.2.1 Carbon and hydrogen

Carbon and hydrogen account for 70–95% and 2–6 wt.% (daf), respectively, of the organic substance of coal, and are thought by some to be the most important constituents of coal. The carbon determination includes carbon present as organic carbon occurring in the coal substance and any carbon present as mineral carbonate. The hydrogen determination includes hydrogen present in the organic materials and hydrogen in the free moisture accompanying the sample as well as hydrogen present as water of hydration of silicates.

The methods for determining carbon and hydrogen involve combustion of an exact amount of the coal in a closed system impervious to gases. All the hydrogen is converted to H_2O and all the carbon to CO_2. These products are absorbed by suitable reagents and determined gravimetrically. The combustion is usually accomplished by placing the coal in a stream of dry oxygen at specified temperatures. Complete conversion of the combustion gases to CO_2 and H_2O can be achieved by passing the gases through heated copper oxide. Chlorine (which may be released in significant amounts) and oxides of sulphur are usually

removed from the combustion gases by passage over lead chromate and silver while nitrogen oxides is removed by manganese dioxide.

This particular method of combustion analysis for carbon and hydrogen is used internationally although some modifications may have been made by the various national standards organisations. The sample size may vary from as little as 1 – 3 mg (microanalysis) to 100 – 500 mg (macroanalysis) with combustion temperatures from 850 – 900°C (Liebig method) to as high as 1350°C (high temperature combustion method) (Speight, 2012). In the Liebig method, approximately 0.2 g of test sample of coal is heated in a stream of pure oxygen to 850 – 900°C. The products of incomplete combustion are further burnt over copper oxide to ensure complete conversion of all the carbon and hydrogen to CO_2 and H_2O, respectively. The high temperature combustion method involves burning around 0.5 g of test sample of coal in a stream of pure oxygen at a temperature of 1350°C. ISO standards describe two standard tests for determining carbon and hydrogen: Liebig method (ISO 625:1996) and high temperature combustion method (ISO 609:1996, both ISO 625 and ISO 609 were reviewed and then confirmed in 2009). The Liebig method was also adopted by ASTM as a standard test method for carbon and hydrogen but the ASTM D3178-89 (2002) was withdrawn in June 2007 and replaced by ASTM D5373–08 which recommends instrumental determination of carbon, hydrogen, and nitrogen in laboratory samples of coal. ISO has also set standard ISO 29541:2010 (Solid mineral fuels – Determination of total carbon, hydrogen and nitrogen content – Instrumental method). In this test method, carbon, hydrogen and nitrogen are determined concurrently in a single instrumental procedure. The quantitative conversion of the carbon, hydrogen and nitrogen into their corresponding gases (CO_2, H_2O, N_2/NOx) occurs during combustion of the sample at an elevated temperature in oxygen. Combustion products which would interfere with the subsequent gas analysis are removed. Nitrogen oxides (NOx) produced during the combustion are reduced to N_2 before detection. The carbon dioxide, water vapour and elemental nitrogen in the gas stream are then determined quantitatively by appropriate instrumental gas analysis procedures.

4.2.2 Nitrogen

For years, the standard procedure of nitrogen determination by many laboratories was the Kjeldahl method. In the Kjeldahl method, pulverised coal is heated with concentrated sulphuric acid containing potassium sulphate, in the presence of a catalyst, to convert the nitrogen into ammonium sulphate. The ammonia is then released, recovered by distillation and determined by titration. The catalyst is usually a mercury salt, selenium or a selenium compound, or a mixture of the two. However, because this method mentions the use of mercury, in 2008 ASTM withdrew the D3179–02 (Standard test methods for nitrogen in the analysis sample of coal and coke) with no replacement. In 2010, ISO also withdrew its Standard ISO 333:1996 (Coal – Determination of nitrogen – Semi-micro Kjeldahl method). Some national standards organisations still recognise the Kjeldahl method as a standard test method for determination of nitrogen in coal. For instance, the German standard DIN 51722–1:1990-07 (Testing of solid fuels: determination of nitrogen content; semi-micro Kjeldahl method) and Australian AS 1038.6.2 – 2007 (Higher rank coal and coke – Ultimate analysis – Nitrogen) are currently valid.

As mentioned in Section 4.2.1 both ASTM and ISO set standards for instrumental determination of carbon, hydrogen, and nitrogen in coal. Nuclear reactions have been applied successfully to the determination of nitrogen in coal. Coal is irradiated with fast neutrons from a 14–MeV generator to produce nitrogen-13, which decays via positron emission and has a 10-minute half-life. Standard deviation for the nitrogen determinations was 0.07%. The instrumental neutron activation values were 6.8% higher (0.1% N) on average than those obtained using the standard Kjeldahl procedure. In the Kjeldahl procedure, loss of elemental nitrogen or nitrogen oxides or resistant heterocyclic nitrogen compounds can sometimes cause data errors, although most of these have been eliminated by application of modern laboratory procedures. Because results from instrumental neutron activation for nitrogen are independent of these factors, it has been suggested that the activation method is the more accurate of the two (Speight, 2005).

4.2.3 Sulphur

Sulphur is an important parameter for evaluating the fuel value of coal and its environmental impact since SO_2 emissions into the atmosphere are directly related to the sulphur content of the burned coal. For this, the sulphur content needs to be analysed with high precision. The three most widely used test methods for sulphur determination are the Eschka method, the bomb washing method, and the high-temperature combustion method. All these three methods are based on the combustion of the sulphur-containing coal to produce sulphate, which can be measured either gravimetrically or volumetrically.

In the Eschka method, a weighed analysis sample of coal and Eschka mixture (two parts by mass of magnesium oxide and one part of anhydrous sodium carbonate) are intimately mixed and heated together in an oxidising atmosphere gradually to a temperature of 800°C ± 25°C, and held at this temperature until oxidation of the sample is complete. The sulphur compounds evolved during combustion react with the magnesium oxide (MgO) and sodium carbonate (Na_2CO_3) and under oxidising conditions are converted to magnesium sulphate ($MgSO_4$) and sodium sulphate (Na_2SO_4). The sulphate is extracted with hydrochloride acid solution, and then, by adding barium chloride ($BaCl_2$) solution, precipitated from the resulting solution as barium sulphate ($BaSO_4$). The precipitate is filtered, ashed and weighed.

In the bomb washing method, sulphur is precipitated as barium sulphate from the washings from the oxygen bomb calorimeter following the calorimetric determination. After opening, the inside of the bomb is washed carefully, and the washings are collected. After titration with standard sodium carbonate solution to determine the acid correction for the heating value, the solution is heated and treated with ammonium hydroxide (NH_4OH) to precipitate iron ions as ferric oxide ($Fe(OH)_3$). After filtering and heating, the sulphate is precipitated with barium chloride and determined gravimetrically.

In the high-temperature combustion test method, a weighed sample of coal is burned in a tube furnace at a minimum operating temperature of 1350°C in a stream of oxygen to ensure complete oxidation of sulphur-containing components in the coal into predominantly sulphur dioxide (SO_2). The amount of SO_2 produced by burning the coal sample can be determined by various methods. In the acid–base titration method, the sulphur oxides formed are converted to sulphuric acid by reacting with hydrogen peroxide

and are then determined by titration with a standard base solution. The chlorine contained in the coal is also determined as the total sulphur measurement and, for accurate results, a correction must be made for the chlorine present in the sample. In the iodimetric titration procedure, the SO_2 formed is absorbed in an aqueous solution that contains iodine, reducing the trace iodine to iodide and thus resulting in an increase in resistance. Iodine titrant is then added proportionately until the trace excess of iodine is replenished and the solution resistance is reduced to its initial level. The volume of titrant expended is used to calculate the sulphur content of the coal. The infrared absorption detection procedure measures the SO_2 in the combustion gases by the absorption of infrared (IR) energy. SO_2 absorbs IR energy at a precise wavelength within the IR spectrum. Moisture and particulates are first removed from the gas stream by traps filled with anhydrous magnesium perchlorate. The gas stream is then passed through an infrared absorption cell. The IR energy absorbed is proportional to the amount of SO_2 in the combustion gases and therefore to the sulphur in the sample. Both iodimetric titration and infrared absorption detection procedures are empirical and therefore, the apparatus must be calibrated using the standard reference materials with sulphur percentages in the range of the samples to be analysed (Speight, 2005).

The three methods for determination of total sulphur in coal have all found application in various national and international standards. The ISO 334:1992 (Solid mineral fuels – Determination of total sulphur – Eschka method) has recently been revised and the revised ISO 334 is currently under publication. The ASTM D3177–02(2007) covers Eschka method and bomb washing method as standard test methods for determining total sulphur in an analysis sample of coal and coke but this standard was withdrawn in December 2012 and replaced with D4239–12. ASTM D4239 recognises the high-temperature combustion method as a standard test method for sulphur in the analysis sample of coal and coke. Two alternative procedures using high-temperature tube furnace combustion methods for rapid sulphur determination are described: A) high-temperature combustion method with acid base titration detection procedures, and B) high-temperature combustion method with infrared absorption detection procedures. When automated equipment is used, either method can be classified as an instrumental method. The high-temperature combustion method with acid base titration detection procedures is also covered in ISO 351:1996. However, in a recent review it has been proposed to withdraw this standard. ISO specifies the high-temperature combustion method with IR absorption procedures as a standard test method for determination of total sulphur in coals in ISO 19579:2006 (Solid mineral fuels – Determination of sulphur by IR spectrometry). ISO states that this method is applicable to coal samples having an ash yield of less than 40%. This standard has been reviewed and confirmed in 2010.

Although not normally part of an ultimate analysis, knowledge of the different forms of sulphur in coal can be useful in assessing how easily sulphur can be removed from coal (coal preparation) and is required for calculating coal properties to a mineral-matter-free basis. Sulphur occurs in coal in three main forms: inorganic sulphates or sulphate sulphur (sulphate minerals), pyritic sulphur (sulphide minerals) and organic sulphur. The standard methods used for the determination of the various forms of sulphur in coal are specified in ISO 157:1996 (reviewed and then confirmed in 2009) and ASTM D2492–02(2012), and they are based on the principle that sulphate sulphur is soluble in dilute hydrochloric acid

solution, whereas the pyritic and organic sulphur are not. Also, dilute nitric acid dissolves sulphate and pyrite sulphur quantitatively and attacks organic sulphur only slightly. Pyrite sulphur, however, is determined accurately by noting the quantity of iron extracted by dilute hydrochloric acid and subtracting this from the iron extracted by nitric acid, the difference being the iron present as pyrite iron (FeS_2), from which the equivalent quantity of pyrite sulphur can be calculated. Organic sulphur is then obtained by subtracting the combined percentages of sulphate sulphur and pyrite sulphur from the total sulphur determined, for example, by the Eschka method (Speight, 2005; Carpenter, 2002).

4.3 Calorific value

Calorific value (CV) is a direct indication of the heat content (energy value) of the coal. It is one of the most important parameters by which the coal is mined for combustion applications, and is the most commonly used benchmark of coal quality and hence its economic value. The CV is usually expressed as the gross calorific value (the higher heating value) or the net calorific value (the lower heating value). The difference between the gross calorific value (GCV) and the net calorific value (NCV) is the latent heat of condensation of the water vapour produced during the combustion process. The GCV assumes that all of the vapour produced from coal moisture during the combustion process is fully condensed. The NCV assumes that the water is removed with the combustion products without being fully condensed.

Standard methods for determining the CV of coal employ calorimeters and burning coal in oxygen under pressure in a closed system. The bomb calorimeter provides the most suitable and accurate apparatus for determination of the CVs of solid and liquid fuels, and is adopted in ASTM D5865-12 (Standard test method for gross calorific value of coal and coke) and ISO 1928:2009 (Solid mineral fuels – Determination of gross calorific value by the bomb calorimetric method and calculation of net calorific value). The procedures specified in the standards involve burning a weighed portion of the analysis sample of coal in high-pressure oxygen in a bomb calorimeter under specified conditions. The effective heat capacity of the calorimeter is determined in calibration tests by combustion of certified benzoic acid under similar conditions, accounted for in the certificate. The temperature measurements required for the evaluation of the corrected temperature rise are made during a fore-period, a main period (reaction period) and an after-period. For the adiabatic-type calorimeter (ASTM, ISO), the CV is calculated from the corrected temperature rises during the fore- and after-periods. For the isoperibol (isothermal jacket) (ASTM, ISO) and the static-jacket-type calorimeters (ISO), the CV is computed from the corrected temperature rise observed during the fore-, main- and after-period. Allowances are made for contributions from ignition energy, combustion of the fuse(s), for thermochemical corrections and, if appropriate, for heat losses from the calorimeter vessel to the water jacket. Water is added to the bomb initially to give a saturated vapour phase prior to combustion, thereby allowing all the water formed from the hydrogen and moisture in the sample to be regarded as liquid water. The result obtained is the GCV of the analysis sample at constant volume with all the water of the combustion products as liquid water, and is usually expressed in J/g (or kJ/g, MJ/kg), cal/g (or kcal/g, kcal/kg). Btu/lb is also used in some parts of the world such as the USA. In practice, fuel is burned at constant (atmospheric) pressure and the water is not condensed but is removed as vapour with the flue gases. Under these conditions, the operative heat of

combustion is the NCV of the fuel at constant pressure. The standards provide equations for converting GCV to NCV of the fuel at constant pressure and at consent volume.

4.4 Ash analysis

When coal is burned, the mineral constituents form an ash residue composed mainly of the oxides of silicon, aluminium, iron, calcium, magnesium, titanium, manganese, sodium and potassium, partly combined as silicates, sulphates and phosphates. Accordingly, the major and minor elements are usually quoted as their oxides in an ash analysis. Ash analysis is often useful in the total description of the quality of the coal because the composition of the mineral matter of a coal is often approached by analysing the chemical composition of the coal ash. Knowledge of ash composition is also useful in predicting the behaviour of ashes and slags in combustion chambers, and in consideration of the utilisation of the ash by-products of coal combustion. However, the chemical composition of laboratory-prepared coal ash may not exactly represent the composition of mineral matter in the coal or the composition of fly ash and slag resulting from commercial-scale burning of the coal. Table 8 lists the major inorganic constituents found in coal ash.

Table 8 – Major inorganic constituents of coal ash (Speight, 2012)

Constituents	Representative %
SiO_2	40–90
Al_2O_3	20–60
Fe_2O_3	5–25
CaO	1–15
MgO	0.4–4
Na_2O	0.5–3
K_2O	0.5–3
SO_3	0.5–10
P_2O_5	0–1
TiO_2	0–2

4.4.1 Preparation of coal ash

In the preparation of ash samples for analysis, slow burning of the coal samples is necessary to prevent the retention of sulphur as sulphate in the ash. The retention of sulphur as calcium sulphate ($CaSO_4$) in coal ash is related to a high amount of carbonates (calcite, $CaCO_3$), or pyrite (FeS_2), or both, in the coal and the ashing temperature to which it is subjected. Pyrite is oxidised to sulphur oxides and iron oxides at temperatures around 450 – 500°C. Iron oxides formed during oxidation of pyrite contribute to the catalytic oxidation of sulphur dioxide (SO_2) to sulphur trioxide (SO_3), which reacts with calcium to form calcium sulphate ($CaSO_4$) during the ashing process. If the rate of burning is too rapid, some of the sulphur oxides produced from burning pyrite may react with metal oxides to form stable sulphates. The result is that indefinite amounts of sulphur are retained, which introduces an error into all the analytical results unless all other oxides are corrected to the SO_3-free basis. Also, attempts must be made to ensure that important elements are not lost during the ashing procedure due to the higher temperatures used (Riley, 2007).

ASTM D1757 (Standard Test Method for Sulphate Sulphur in Ash from Coal and Coke) specifies procedures for determining sulphate sulphur in the ash and the result can be used to calculate the determined ash content or ash composition on a SO_3-free basis. However, D1757-03 was withdrawn in October 2009. An alternative method described in ASTM D5016-08e1 (Standard Test Method for Total Sulfur in Coal and Coke Combustion Residues Using a High-Temperature Tube Furnace Combustion Method with Infrared Absorption) allows for rapid determination of sulphur in the ash. The percent sulphur content of the coal ash can be calculated as SO_3 content, which can then be used to correct the measured ash content, ash composition or trace elements on a SO_3-free basis.

In selected ASTM test methods for determination of major and minor elements in coal ash, the ash is prepared by placing a weighed analysis sample of coal in a cold muffle furnace. The sample is heated gradually so that the temperature reaches 500°C in 1 hour and 750°C in 2 hours. Heating continues at 750°C until the sample reaches a constant weight. The ash produced is then cooled, ground to pass a 74 µm standard sieve, and reignited at 750°C for 1 hour. Materials previously ashed, fly ash, or bottom ash must be ignited until a constant weight is reached at 750°C and cooled in a desiccator.

For determination of trace elements in coal ash, the ash is prepared by placing a weighed analysis sample of coal in a cold muffle furnace and gradually heating to a temperature of 300°C in about 1 hour. Heating continues so that a temperature of 500°C is reached at the end of the second hour which is maintained for an additional 2 hours. After cooling and weighing, the ash is ground finely and reignited at 500°C for 1 hour. The sample is cooled and reweighed to calculate the percentage of ash. Immediately after ashing, the analysis sample is prepared or the dry ash stored in a vacuum desiccator.

ISO recommends that for determination of major and minor elements in coal ash, the analysis sample of coal should be ashed following the procedure specified in ISO 1171 (*see* Section 4.1.2). Coal ash received in the laboratory should be heated at 815°C for 15 minutes, and cooled immediately prior to weighing for analysis. It is recommended that boiler ash received in the laboratory be ground to a nominal top size of 63 µm, dried at 105°C for 1 hour and then stored in a desiccator.

4.4.2 Major and minor elements

Major, minor and trace elements in coals and ashes have concentrations that are detectable by most modern analytical techniques. Various instrumental methods have been applied in the analysis of ashes and ash deposits. These are commonly based on atomic absorption/emission spectroscopy (AAS/AES), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), ICP-mass spectroscopy (ICP-MS), atomic fluorescence spectroscopy (AFS), x-ray fluorescence spectroscopy (XRF) or a combination of these techniques. In all cases, the instruments can be supplied with automatic sample feeding devices and microprocessor-based data analysis and processing facilities. Table 9 shows the elements that can be detected by these techniques.

Table 9 – Analytical methods for major and minor elemental oxides in coal and coal combustion residues (Riley, 2007)	
Oxide	**Analytical methods**
SiO_2	AAS, XRF, ICP-AES
Al_2O_3	AAS, XRF, ICP-AES
Fe_2O_3	AAS, XRF, ICP-AES
CaO	AAS, XRF, ICP-AES
MgO	AAS, XRF, ICP-AES
Na_2O	AAS, XRF, ICP-AES
K_2O	AAS, XRF, ICP-AES
TiO_2	AAS, XRF, ICP-AES
MnO_2	XRF, ICP-AES
SO_3	XRF
P_2O_5	XRF, ICP-AES

ASTM recognises three different techniques as standard test methods for determining major and minor elements in coal ash. D3682–01(2006) (Standard Test Method for Major and Minor Elements in Combustion Residues from Coal Utilisation Processes) covers analysis of eight elements: aluminum, calcium, iron, magnesium, potassium, silicon, sodium, and titanium in laboratory coal ash and in combustion residues by AAS. The ash is fused within lithium tetraborate ($Li_2B_4O_7$) and heated to 1000°C for 15 minutes. The fused mixture is then dissolved in 2% HCl or appropriate dilutions made for AAS analysis. Instructions on background correction and analysis of standard reference materials (SRMs) or certified reference materials (CRMs) are given as essential parts of the procedures.

D4326-11 (Standard Test Method for Major and Minor Elements in Coal and Coke Ash By x-ray Fluorescence) specifies procedures for analysis of elements including Si, Al, Fe, Ca, Mg, Na, K, P, Ti, Mn, Sr, and Ba using XRF techniques. The ash is fused with $Li_2B_4O_7$ or other suitable flux agents and is then heated to 1000°C. The fused mixture is either ground and pressed into a pellet or cast into a glass disk. The pellet or disk is then irradiated by an x-ray beam of short wavelength (high energy). The X-radiation that is emitted or fluoresces, from the sample is characteristic of the elements in the sample. The X-radiation from the sample is dispersed and the intensities are measured at selected wavelengths by sensitive detectors. Detector output is related to concentration by calibration curves or by computerised data-handling equipment.

In the test method described in D6349-09 (Standard Test Method for Determination of Major and Minor Elements in Coal, Coke, and Solid Residues from Combustion of Coal and Coke by Inductively Coupled Plasma – Atomic Emission Spectrometry), the ash is fused with a fluxing agent followed by dissolution of the melt in dilute acid solution. Alternatively, the ash is digested in a mixture of hydrofluoric, nitric, and hydrochloric acids. Aqueous solutions of the samples are nebulised, and a portion of the aerosol that is produced is transported to the plasma torch, where excitation and emission occurs. Characteristic line emission spectra are produced by a radio-frequency inductively coupled plasma. A grating monochromator system is used to separate the emission lines, and the intensities of the lines are monitored by photomultiplier tube or photodiode array detection. The photocurrents from the detector are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of elements. Background must be

measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured.

The test method described in ASTM D2795–95 provides a rapid and inexpensive analysis of coal ash for major and minor elements. It determines silicon, aluminum, iron, titanium, and phosphorus colorimetrically, calcium and magnesium chelatometrically, and sodium and potassium by flame photometry. However, this standard was withdrawn in 2001 but is still used in some laboratories.

ISO adopts the XRF spectrometry as a standard method for the determination of silicon, aluminium, iron, calcium, magnesium, sodium, potassium, titanium, manganese, phosphorus and sulphur in hard coal ash. The procedure ISO sets out in ISO/TS 13605:2012 (Solid mineral fuels – Major and minor elements in hard coal ash and coke ash – Wavelength dispersive x-ray fluorescence spectrometric method) is similar to that described in ASTM D4326–11.

4.4.3 Trace elements

The trace elements of environmental interest include antimony, arsenic, beryllium, boron, cadmium, chlorine, chromium, cobalt, copper, fluorine, lead, manganese, mercury, molybdenum, nickel, selenium, thallium, vanadium, and zinc. The radioactive trace elements thorium and uranium can be added to this list. Various techniques can be used in determining the trace elements in coal and coal ash. The commonly used techniques include:

AAS	atomic absorption spectroscopy
AFS	atomic fluorescence spectroscopy
CVAAS	cold-vapour atomic absorption spectroscopy
GFAAS	graphite-furnace atomic absorption spectroscopy
IC	ion chromatography
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectroscopy
INAA	instrumental neutron activation analysis
PIXE	proton-induced x-ray emission analysis
XRF	x-ray fluorescence spectroscopy

ISO has not set up procedures for using a specific technique as a standard method of determination of trace elements in coal and coal ash. Instead, in its recently revised standard ISO 23380:2013 (Selection of methods for the determination of trace elements in coal) ISO provides guidance on the selection of the appropriate methods available to determine the common trace elements in coal.

ASTM has two different test methods for analysis of trace elements in coal ash. D3683–11 (Standard Test Method for Trace Elements in Coal and Coke Ash by Atomic Absorption) describes a procedure for the determination of beryllium, chromium, copper, manganese, nickel, lead, vanadium, and zinc in coal ash

using AAS. In the test method, the ash is dissolved by mineral acids and the individual elements is determined by AAS in which a solution of the sample is atomised and introduced into a flame in the path of radiation from the light source. A nitrous oxide/acetylene (N_2O/C_2H_2) flame can be used for beryllium, chromium, and vanadium, while an air/acetylene flame is used for cadmium, copper, manganese, nickel, lead, and zinc.

ASTM D6357–11 (Test Methods for Determination of Trace Elements in Coal, Coke, & Combustion Residues from Coal Utilization Processes by Inductively Coupled Plasma Atomic Emission, Inductively Coupled Plasma Mass, & Graphite Furnace Atomic Absorption Spectrometry) stipulates procedures for determining antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, vanadium, and zinc in coal and coal ash. In the test methods, the coal to be analysed is ashed under controlled conditions described in Section 4.4.1. The ash is digested by a mixture of aqua regia and hydrofluoric acid, and finally dissolved in 1% nitric acid. Coal combustion residues are digested on an as-received basis. The concentration of individual trace elements is determined by either ICP–AES or ICP–MS. Selected elements that occur at concentrations below the detection limits of ICP–AES can be analysed quantitatively by GFAAS. These methods may be applicable to the determination of other trace elements.

Table 10 – Sensitivity and detection limits for elements by AAS (Speight, 2012)

Elements	Sensitivity (µg/ml)	Range (µg/ml)	Detection limits	
			(µg/ml)	(µg/m^3)
Ag	0.036	0.5–5.0	0.003	0.1
Al	0.76	5–50	0.04	2
Ba	0.20	1–10	0.01	0.4
Be	0.017	0.1–1.0	0.002	0.08
Bi	0.22	1–10	0.06	3
Ca	0.021	0.1–1.0	0.005	0.02
Cd	0.011	0.1–1.0	0.006	0.03
Co	0.066	0.5–5.0	0.007	0.3
Cr	0.055	0.5–5.0	0.005	0.2
Cu	0.040	0.5–5.0	0.003	0.1
Fe	0.062	0.5–5.0	0.005	0.2
In	0.38	5–50	0.05	2
K	0.010	0.1–1.0	0.003	0.1
Li	0.017	0.1–1.0	0.002	0.08
Mg	0.003	0.05–0.5	0.0003	0.01
Mn	0.026	0.5–5.0	0.003	0.1
Na	0.003	0.05–0.5	0.0003	0.01
Ni	0.066	0.5–5.0	0.008	0.3
Pb	0.11	1–10	0.02	0.8
Rb	0.042	0.5–5.0	0.003	0.1
Sr	0.044	0.5–5.0	0.004	0.2
Ti	0.28	5–50	0.02	0.8
V	0.88	10–100	0.1	4
Zn	0.009	0.1–1.0	0.002	0.08

Table 11 – Detection limits for various elements by XRF (Speight, 2012)

Element	Detection limit*	Element	Detection limit*	Element	Detection limit*
Ag	1.2	Ga	0.01	Si	170 ppm
Al	5.0	Hg	0.24	Sm	4.1 µg/ml
As	0.11	In	1.1	Sn	3.9 ppm
Au	0.001 cm^{-2}	K	0.52	Sr	0.00007
Ba	0.12	La	0.12	Tb	159 µg/ml
Bi	0.61	Mn	0.0015	Te	0.12
Ca	0.100	Mo	0.072	Th	6.5 µg/ml
Cd	0.40	Nd	0.30	Ti	0.001
Ce	0.17	Ni	0.06	U (as UO_2)	0.72
Co	0.05	P	0.001	U	0.00002
Cr	0.00006	Pb	0.0003	Y	0.22
Cs	0.15	Rb	0.0075	Yb	6.8 µg/ml
Cu	0.00002	Rh	103 µg/ml	Zn	0.00004
Eu	0.66	Sc	0.38	Zr	0.00002
Fe	0.0085	Se	0.020 cm^{-2}		

*in µg except as noted.

Table 12 – Sensitivity of various elements to INAA (Speight, 2012)

Sensitivity (g)	Elements
$10^{-13} – 10^{-12}$	Dy, Eu
$10^{-12} – 10^{-11}$	Au, In, Mn
$10^{-11} – 10^{-10}$	Hf, Ho, Ir, La, Re, Rh, Sm, V
$10^{-10} – 10^{-9}$	Ag, Al, As, Ba, Co, Cu, Er, Ga, Hg, Lu, Na, Pd, Pr, Sb, Sc, U, W, Yb
$10^{-9} – 10^{-8}$	Cd, Ce, Cs, Gd, Ge, Mo, Nd, Os, Pt, Ru, Sr, Ta, Tb, Th, Tm
$10^{-8} – 10^{-7}$	Bi, Ca, Cr, Mg, Ni, Rb, Se, Te, Ti, Tl, Zn, Zr
$10^{-7} – 10^{-6}$	Pb
$10^{-6} – 10^{-5}$	Fe

Table 13 – Concentration ranges and repeatability and reproducibility limits for various elemental oxides in coal and coal ash by ICP-AES (ASTM D6349)

Elemental oxide	Concentration range	Repeatability limit	Reproducibility limit
SiO_2	2.04–73.73, %	-0.13 + 0.09 †	2.00 + 0.10 †
Al_2O_3	1.04–29.54, %	0.17 + 0.06 †	0.86 + 0.07 †
Fe_2O_3	0.39–47.94, %	0.13	0.23
MgO	0.40–7.29, %	0.02 + 0.08 †	0.11 + 0.11 †
CaO	1.04–44.03, %	0.11	0.25
TiO_2	0.06–1.47, %	0.02 + 0.07 †	0.05 + 0.12 †
K_2O	0.09–2.53, %	0.06 + 0.11 †	0.14 + 0.30 †
$P2O_5$	0.10–1.34, %	0.01 + 0.18 †	0.11 + 0.31 †
Na_2O	0.17–7.44, %	0.06 + 0.09 †	0.10 + 0.17 †
MnO_2	198–834, mg/kg (ppm)	0.16	0.42
BaO	266–950, mg/kg (ppm)	0.07	190
BaO	0.13–3.00, %	0.17	0.30
SrO	285–104 60, mg/kg (ppm)	33 + 0.076 †	73 + 0.164 †

† is the average of two test results

Comments

Analytical techniques recognised by ASTM and ISO as standard test methods of examining the major, minor and trace elements which occur in coals and coal ashes have been discussed here. However, they are by no means the only applicable methods for ash analysis. There are several other techniques that have found considerable use as means by which various elements in coal can be measured qualitatively and quantitatively. Each method has different detection limits for the different elements as shown in Table 10–13. The interested reader is refereed to the critical review of the advantages and limitations of these methods by Carpenter (2002). It is essential to recognise the limitations of the individual methods before any attempts is made to interpret the data.

4.5 Miscellaneous analysis

4.5.1 Chlorine

The chlorine content of coals may be useful in the evaluation of slagging problems, corrosion in engineering processes, and in the total analysis of coal. The chlorine content of coal is normally low, usually only a few tenths of a percent or less. It occurs predominantly as sodium, potassium, and calcium chlorides, with magnesium and iron chlorides present in some coals.

Tests for determination of chlorine are performed by burning a coal in oxygen, and the chlorine formed is collected and analysed. ASTM sets two standard methods of determining chlorine in coal. The D2361–02 (Standard Test Method for Chlorine in Coal) offers a choice of two procedures for combusting the coal sample. In the first procedure, a weighed analysis sample of coal, mixed with Eschka mixture, is burned in an oxygen bomb. An ammonium carbonate solution is added to the bomb to trap the chloride-containing species produced in the combustion. The bomb interior is washed with hot water, the washings are then collected in a beaker and acidified with nitric acid. In the second procedure, a weighed coal sample is mixed Eschka mixture in a suitable crucible. This mixture is covered with additional Eschka mixture to ensure that no chlorine is lost during combustion. The mixture is then ignited gradually in a muffle furnace by raising the temperature to 675 ± 25°C within 1 hour and maintaining this temperature for 1 hour. The incinerated mixture is washed with hot water and the washing is collected into a beaker and is acidified with nitric acid. The amount of chloride is determined by either a modified Volhard or by a potentiometric titration with silver nitrate solution. This standard was withdrawn in October 2008 without replacement.

In the test method specified in ASTM D4208–13 (Standard Test Method for Total Chlorine in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method), total chlorine is determined by combusting a weighed analysis sample in a high pressure bomb in oxygen (2–3 MPa). A diluted base solution (2% Na_2CO_3 solution) is added to the bomb to trap the chloride-containing species produced. The bomb is rinsed into a beaker with water and following the addition of an ionic strength adjuster ($NaNO_3$ solution), the chloride is determined by measuring the potential of the solution with a chlorine ion-selective electrode.

The procedure for standard test method specified in ISO 587:1997 (Solid mineral fuels – Determination of chlorine using Eschka mixture) is essentially similar to the second procedure of ASTM D2361. A known mass of sample is ignited in intimate contact with Eschka mixture in an oxidising atmosphere to remove combustible matter and to convert the chlorine to alkaline chlorides. These are extracted with nitric acid or water and determined by either the Volhard or the Mohr method, or by potentiometric titration using an Ion Selective Electrode (ISE). However, it has been proposed to discontinue this standard. The proposed new standard for determination of chlorine content in solid mineral fuels provides instructions for two coal combustion procedures: high temperature combustion in oxygen and bomb combustion. In the high temperature combustion procedure, the sample is combusted at high temperature (1250 ± 25°C) in an oxygen atmosphere. The gaseous combustion products, including the formed chloride, are collected in a trap filled with water, in which they are dissolved. In the bomb combustion procedure, the sample is combusted in a high pressure bomb in oxygen (≤4 MPa). The formed chloride is collected in an absorption solution inside the bomb. The chloride content in the digestion solution is determined by ion chromatography, although the use of other equivalent methods is allowed (Carpenter, 2013).

4.5.2 Mercury

Mercury is one of the most toxic trace element naturally occurring in coal and it can be released during coal combustion causing an environmental concern. Knowing the mercury content in the coal prior to combustion is critical in controlling its emissions from the combustion process. The commonly used analytical methods for the determination of mercury in coal and combustion residue involve wet digestion or thermal decomposition of coal sample followed by detection of mercury using AAS. The standard procedures of wet digestion/CVAAS are described in the ASTM D6414 – 01(2006) (Standard Test Methods for Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapour Atomic Absorption). D6414 offers a choice of two wet digestion methods. In method A, the mercury in the analysis sample of coal is dissolved by heating the sample at a specified temperature in a mixture of nitric and hydrochloric acids. The acid solutions produced are transferred into a vessel in which the mercury is reduced to elemental mercury. The mercury content is then determined by flameless CVAAS. The method B involves solubilisation of the mercury by heating the sample in a mixture of nitric acid and sulphuric acid with vanadium pentoxide. The acid solution is then transferred into a vessel in which the mercury is reduced to elemental mercury and is determined by flameless CVAAS. However, mercury and mercury salts can be volatilised at low temperatures, and precautions against inadvertent mercury loss should be taken when using this method (Speight, 2005).

ISO considers that the determination of the total mercury content of coal cannot be accomplished satisfactorily by traditional ashing and digestion procedures because of the volatility of the element and therefore the thermal decomposition method is adopted in ISO 15237:2003 Solid mineral fuels – Determination of total mercury content of coal (confirmed in 2009). This method involves burning a weighed analysis sample of coal in an oxygen bomb, the mercury species formed during combustion being absorbed in water. The mercury species present in the water are reduced by stannous chloride and quantified by flameless CVAAS. A similar procedure is adopted by ASTM in Standard Test Method for

Total Mercury in Coal by the Oxygen Bomb Combustion/Atomic Absorption Method (D3684–01(2006)). Instead of water, dilute nitric acid is used inside the bomb to absorb the mercury vapours. The bomb is rinsed into a reduction vessel with dilute nitric acid. All mercury present is oxidised to the mercuric form by adding potassium permanganate ($KMnO_4$) solution until the permanganate colour persists and a stable solution is created. Immediately before analysis, hydroxylamine hydrochloride is added to remove any excess oxidant, and the mercuric mercury is reduced to metallic mercury by stannous chloride. The mercury is then determined by the flameless CVAAS.

The determination of mercury in coal and coal ash can also be accomplished by a simpler analysis procedure set in ASTM D6722–11 (Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis) which involves thermal decomposition of the sample combined with catalytic conversion, amalgamation and quantitative determination by AAS. The analysis sample of coal is weighed into a combustion boat, which is first dried and then decomposed thermally and chemically in a furnace in an oxygen atmosphere. Mercury and other combustion products are released from the sample and carried by a flow of oxygen to the catalytic section of the furnace, where oxidation is completed and nitrogen and sulphur oxides as well as halogens and other interfering compounds are removed. The remaining decomposition products are carried to a gold amalgamator that traps mercury selectively. After the system is flushed with oxygen to remove any remaining decomposition products, the amalgamator is heated rapidly, releasing mercury vapour. Flowing oxygen carries the mercury vapour through cells positioned in the optical path of the spectrophotometer, where it is quantitatively measured by atomic absorption at 253.7 nm.

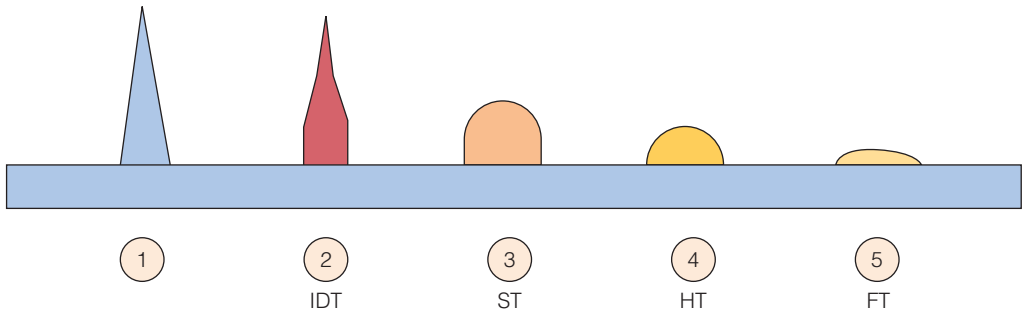
4.5.3 Mineral matter in coal

The analytical techniques used to measure mineral matter in coal are virtually the same as those to measure trace elements in coal and coal ash. Therefore, consideration of standardised method for the determination of mineral matter in coal has not been given priority by ASTM, whereas ISO does have a standard: ISO 602:1983 (Coal – Determination of mineral matter). In this method, the coal sample is partially demineralised by treatment with hydrochloric and hydrofluoric acids under such conditions the coal substance remains unaffected. The loss in mass of the coal due to acid treatment is recorded and the undissolved part of the mineral matter is determined by ashing the partially demineralised coal. In addition, the iron content of the ash is determined so that the pyrites present in the extracted coal can be calculated. The amount of hydrochloric acid absorbed by the coal substance is also determined. ISO 602 was reviewed in 2013 and the decision is pending.

4.5.4 Ash fusibility

Design of most coal combustion and coal conversion equipment anticipates that the ash either remains solid or assumes some degree of fluidity, depending on the particular design. Ash fusion temperatures predict whether the ash will perform properly in the process for which the coal is chosen. The ash fusibility determination is an empirical test designed to simulate as closely as possible the behaviour of coal ash when it is heated in contact with either a reducing or an oxidising atmosphere. The test is

intended to provide information on the fusion characteristics of the ash. It gives an approximation of the temperatures at which the ash remaining after the combustion of coal will sinter, melt, and flow. The critical temperature points are measured by observation of the behaviour of triangular pyramids (cones) prepared from coal ash when heated at a specified rate in a controlled atmosphere as illustrated in Figure 14.



1 – cone before heating
2 – DT initial deformation temperature (first rounding of cone tip)
3 – ST softening or sphere temperature (cone height = cone width)
4 – HT hemispherical temperature (cone height = $\frac{1}{2}$ cone width)
5 – FT fluid or flow temperature (cone height = 1.6 mm (ASTM D 1857))

Figure 14 – Critical temperature points of the ash fusion test (Carpenter, 2002)

The test method for determining the fusibility of coal ash involves an observation of the temperatures at which characteristic changes of shape occur (*see* Figure 14) when heated at a specified rate in controlled, mildly reducing, and where desired, oxidising atmospheres. In the Standard Test Method for Fusibility of Coal and Coke Ash described in ASTM D1857/D1857M–04(2010), to obtain the ash for the test, an analysis sample of coal with nominal size of 250 µm is heated gradually to a temperature of 800 to 900°C to remove most of the combustible material. The ash is ground in an agate mortar to a top size of 75 µm, spread on a suitable dish, and ignited in a stream of oxygen for approximately 1 hour at 800 to 850°C. The ash is mixed thoroughly and moistened with a few drops of dextrin binder and worked into a stiff plastic mass. The mass is then formed into a cone using a cone mould. The cone is dried, mounted on a refractory base, and heated at a specified rate in a furnace under either oxidising or reducing conditions.

The ISO 540:2008 Hard coal and coke – Determination of ash fusibility (reconfirmed in 2011) covers a similar test procedure. The ash is prepared according to the method specified ISO 1171 (*see* Section 4.1.2). The ash is ground to a top size of 75 µm (< 63 µm is recommended), and moistened with demineralised water or dextrin solution to make a paste. A paste of ash is moulded into (pyramid, cube, upright cylinder or truncated cone) shape with sharp edges and/or tip, allowed to dry and any organic matter removed by heating the test piece slowly to around 850°C. The test piece is then transferred into a furnace and heated at a specific rate under either oxidising or reducing conditions. The shape of the specimen is recorded at intervals of temperature change not greater than 20°C until the maximum temperature of the furnace is reached or the flow temperature of the specimen has been attained.

Proper control of the atmosphere surrounding the test sample is probably the greatest issue encountered in determining ash fusibility, particularly when a reducing atmosphere is used. A mildly reducing atmosphere is specified since it is believed that this more closely approximates to conditions existing in several types of combustion equipment. Lower softening temperatures are obtained with a mildly reducing atmosphere than in strongly reducing or oxidising atmospheres. With a mildly reducing atmosphere, the iron in the ash is present predominantly in the ferrous state, whereas in a strong reducing atmosphere, some of the iron may be in the metallic state. In an oxidising atmosphere the iron is in the ferric state. Both ferric iron and metallic iron increase the refractory quality of the ash, resulting in higher fusion temperatures. Softening temperatures may vary by as much as 150 to 200°C, depending on the atmosphere in which the test is made (Speight, 2005). A mixture of 60 vol% CO and 40 ± 5 vol% CO_2 is recommended in ASTM D1857 to produce a mildly reducing atmosphere in the furnace, while ISO 540 recommend the use of a mixture of 55–65 vol% CO and 35–45 vol% CO_2, or 45–55 vol% H_2 and 45–55 vol% CO_2.

4.5.5 Coal swelling property

Knowledge of the swelling property of a coal can be used to predict or explain the behaviour of the coal during carbonisation or in other processes such as gasification, liquefaction, and combustion.

The free-swelling index is a measure of the volume increase of a coal when heated under specific conditions and is reported in numbers from 0 to 9, with higher values considered superior from a coking standpoint. The result may be used as an indication of the caking characteristic of the coal when burned as a fuel. The procedures of the test method specified in ASTM D720–91(2010) (Standard Test Method for Free-Swelling Index of Coal) and that in ISO 501:2012 (Hard coal – Determination of the crucible swelling number) are essentially similar. Approximately 1 g of freshly ground analysis sample of coal is placed in a silica crucible with a prescribed size and shape, and the surface of the sample in the crucible is levelled by light tapping on a hard surface. Cover the crucible with the unpierced lid. The crucible is then heated at such a rate that the inner temperature of the crucible reaches 800 ± 10°C in 1 minute and 820 ± 5°C in 1 minute (ASTM D720), or 800 ± 10°C in 1.5 minute and 820 ± 5°C in 2.5 minutes (ISO 501). The heating continues for such time as is required for the flame of the burning volatile matter to die out. Turn off the heat and allow the crucible to cool. The test can be carried out in a furnace (D720), or using either electric or gas heating (D720 and ISO 501). The shape of the coke button formed in the crucible is classified by comparison with a chart of standard profiles and corresponding swelling index numbers. At least three buttons are made for each sample, and the average of the profile numbers is taken as the free-swelling index. The standard profiles and corresponding swelling number are shown in Figure 15.

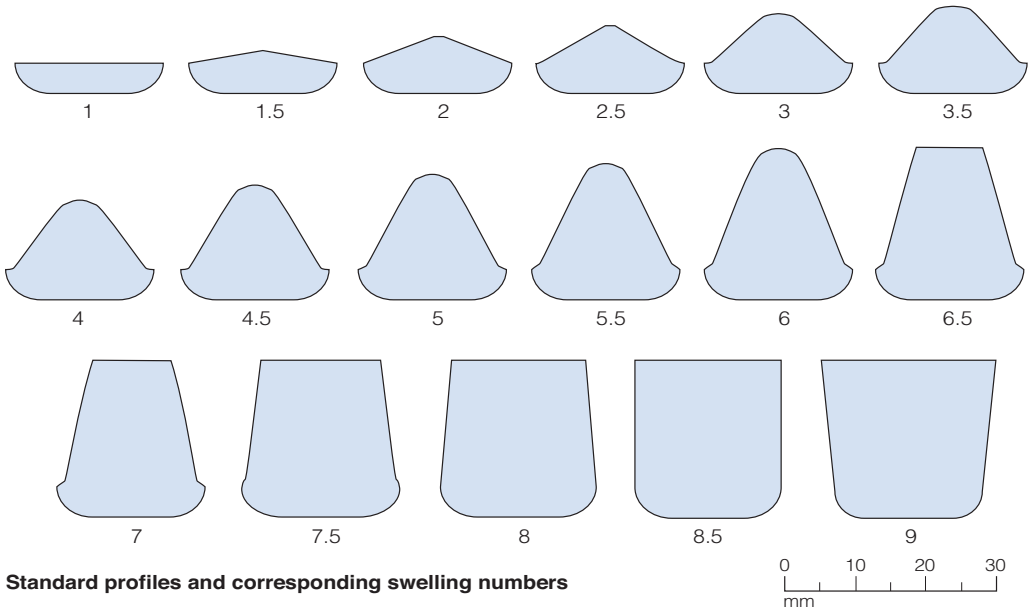


Figure 15 – Determination of free-swelling index – Standard profiles (actual size) and corresponding swelling numbers (ISO 501:2012)

The swelling property of hard coal/bituminous coal can be measured using a dilatometer. This test method is limited in applicability to coal that has a free-swelling index ≤1. ASTM D5515-97(2010) covers the procedure of Standard Test Method for Determination of the Swelling Properties of Bituminous Coal Using a Dilatometer. The principle of the method is that the final volume of char obtained at the conclusion of a standard dilatation test is dependent on the mass of coal in the coal pencil and on the radius of the retort tube. This test method incorporates a procedure that determines the mass of air dried coal in the coal pencil, provides a means to measure the average retort tube radii; and employs a means to report coal expansion on an air dried coal mass basis (Speight, 2005).

ISO sets two different standard procedures for measuring the dilatation of coal: the Ruhr dilatometer (ISO 8264:1989 Hard coal – Determination of the swelling properties using a dilatometer, confirmed in September 2013) and the Audibert-Arnu dilatometer (ISO 349:1975 Hard coal – Audibert-Arnu dilatometer test, confirmed in December 2010). The methods are very similar, having the same basic apparatus and heating rate but using different initial masses of coal arising from the method of pencil preparation. The ISO 23873:2010 (Hard coal – Method for the measurement of the swelling of hard coal using a dilatometer) combines the two previous procedures by adjusting the equipment specification to define a single acceptable method. In the test procedure described in ISO 23873, a test piece, in the form of a pencil, prepared from powdered coal is heated in a steel retort positioned in a furnace from a starting temperature of 300°C (or 30°C below the expected softening temperature if this is known) at a constant rate of 3°C/min to a temperature up to 500°C. The temperature monitoring system should have been previously calibrated using two reference metals of known melting points. The change in level of a piston resting upon the test piece is observed continuously, and a record is produced which is characteristic of the swelling properties of the coal.

4.5.6 Hardgrove Grindability index

Grindability is an indication of the relative ease with which a coal may be pulverised in comparison with coals chosen as standards. Determination of grindability of coal using a Hardgrove machine has been accepted as the standard method. The standard procedures for determination of Hardgrove Grindability index of coal specified in ASTM D409/D409M–12 (Standard Test Method for Grindability of Coal by the Hardgrove-Machine Method) and ISO 5074:1994 (Hard coal – Determination of Hardgrove Grindability index, this standard was last confirmed in 2007 and is now under review) are essentially the same. The test utilises a Hardgrove machine which is a ball-and-ring type of mill in which a sample of sized coal is ground for specified number (usually, 60) of revolutions. The change in size is determined by sieving and the grindability index is calculated. In the test, 50 ± 0.01 g of air dried analysis sample of coal with practical size range 1.19 and 0.595 mm is evenly distributed in the grinding bowl of the Hardgrove machine. The bowl is fastened into position and the load is fully applied to the driving spindle. The machine is turned on and after 60 ± 0.25 revolutions it stops automatically. The grinding bowl is removed from the machine and all the coal particles are brushed onto 200 Mesh sieve (with 0.074 mm openings) with a close-fitting receiving pan. The sieve is covered and shaken mechanically for exactly 10 minutes and the underside of the sieve is brushed carefully into the receiver. This shaking and cleaning is repeated for two 5–minute periods. The two portions of coal remaining on the sieve and passing the sieve are weighed separately to the nearest 0.01 g; the Hardgrove Grindability index of the coal is then determined using a calibration chart.

Each Hardgrove machine should be calibrated by use of standard reference samples of coal with grindability indexes of approximately 40, 60, 80, and 110. These numbers are based on an original soft coal chosen as a standard coal whose grindability index was set at 100. High grindability index numbers indicate easy-to-grind coals (Riley, 2007).

4.6 Accuracy and precision

In any form of analysis, accuracy and precision are required, especially when the analytical data are used for commercial operations where coal is sold on the basis of quality. The word accuracy is used to indicate the reliability of a measurement or an observation. However, it is more specifically a measure of the closeness of agreement between an experimental result and the true value. On the other hand, precision is a measure of the degree to which replicate data and/or measurements conform to each other, the degree of agreement among individual test results obtained under prescribed similar conditions. Therefore, it is possible that data can be very precise without necessarily being correct or accurate.

Precision is commonly expressed inversely in terms of standard deviation or variance and, by definition, does not include systematic error or bias. Accuracy is often expressed inversely in terms of the standard deviation or variance, and includes both the random error and any systematic error or bias. The effect of bias on the standard deviation is to inflate it. In the measurement of coal quality for commercial purposes, accuracy expressed in this manner is generally of less interest than is bias itself. When bias is reduced to a magnitude that is not of practical importance, accuracy and precision can become meaningful parameters

for defining truly representative sampling and for interpretation of the results of various test methods (Speight, 2005). Therefore, it is important that the various test methods used for evaluation of a coal provide acceptable reproducibility and repeatability of the analytical data. In the national and international standards for test methods, in addition to the procedural guidelines, the required reproducibility and repeatability (precision) for each test method are specified. Formula or formulae for calculation of the results are also given and the method of reporting the results is outlined as well in the standards.

Due to the heterogeneous nature of coal, there are many problems associated with the analysis of coal such as the tendency of coal to gain or lose moisture and to undergo oxidation when exposed to the atmosphere. In addition, the large number of tests and analyses required to characterise coal adequately also raise issues. Furthermore, many of the test methods applied to coal analysis are empirical in nature, and hence strict adherence to the standard procedures is necessary to obtain repeatable and reproducible results. It should be noted that the ASTM or ISO may have withdrawn some of the test methods as indicated in the previous sections. However, these test methods are still being used, for whatever reason, in many analytical laboratories.

5 Instrumental analytical techniques

Conventional coal analysis involves the use of wet analysis or the use of typical laboratory bench-scale apparatus. While this trend may continue for the foreseeable future, there are many relatively new approaches, usually based on modern sophisticated instrumentation, that have shown wide applicability to coal analysis. The introduction of microprocessors and microcomputers in recent years has led to the development of a new generation of instruments for coal analysis. In particular, automated instrumentation has been introduced that can determine moisture, ash, volatile matter, carbon, hydrogen, nitrogen, sulphur, oxygen, and ash fusion temperatures in a fraction of the time required to complete most standard laboratory procedures, and the tests can be carried out in situ where the coal is mined, processed, transported or utilised.

The use of instrumental analytical techniques has been growing rapidly in recent years and the instrumental analysis is now being widely applied for analysis of coal and coal products. Many such instrumental methods have been adopted by national and international standard organisations as standard test methods for coal analysis. Other instrumental test methods have been applied to coal analysis by companies and in laboratories in many parts of the world although they have not been developed into standard test methods. Some of the techniques that are widely used in routine coal analysis and their recent advances are reviewed in the following sections of this chapter.

5.1 X-ray spectroscopy

When an electron from the inner shell of an atom is lost due to some sort of excitation, it is replaced with an electron from the outer shell. X-rays (KeV photons) are emitted during electronic transitions to the inner shell states. These x-rays have characteristic energies related to the atomic number, and each element therefore has a characteristic x-ray spectrum. The elemental composition of a specimen can be determined by comparing the x-ray emission spectrum of the specimen with spectra of standard materials of known composition (after some mathematical corrections for absorption, fluorescence and atomic number). X-rays can be excited by a high-energy beam of charged particles such as electrons (as in electron microscope) or protons (as in proton-induced x-ray emission), or a beam of x-rays (as in XRF). These methods enable elements from the entire periodic table to be analysed, with the exception of H, He and Li. There are two main techniques for analysing the spectrum of characteristic x-ray radiation: energy-dispersive x-ray spectroscopy and wavelength dispersive x-ray spectroscopy.

5.1.1 X-ray diffraction

The x-ray diffraction (XRD) analysis is probably the best developed and most widely used method for identifying mineral phases and minerals in coal. It is a powerful analytical technique for identifying and characterising unknown mineral matter in coals. XRD of coal reveals important qualitative and quantitative information on the mineral matter composition of coal and the interaction of mineral matter during conversion processes. It is a rapid, nondestructive technique that requires minimal sample

preparation and, in most cases, it provides an unambiguous mineral determination. XRD has been used to obtain the structural information of coal/char and coal ash.

There are two types of XRD: single crystal diffraction and powder or polycrystalline diffraction. The latter is used in coal analysis. All XRD methods are based on generation of x-rays in an x-ray tube. These x-rays are directed at the sample, and the diffracted rays are detected/measured. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this. For qualitative analysis, the specimen is scanned over a wide angular range to ensure that all the major diffraction peaks of the component minerals are recorded. Diffraction spacings are then calculated from the peak positions, and the elements present in the sample are determined by using standard tables of diffraction spacing.

XRD has benefited from recent developments in computer processing that allow the technique to be used for more precise quantitative determination of mineral percentages. These advances are largely based on the Rietveld methodology, which involves computational adjustment of mineral XRD patterns to allow for variations in crystal structure, preferred orientation and other mineralogical or analytical parameters. An example of the new developments is the SIROQUANT, a computer software program developed by CSIRO Energy Technology (Australia) that is based on Rietveld methods of diffraction pattern analysis for quantitative XRD evaluation. The SIROQUANT calculates a theoretical XRD profile and fits it to the measured pattern by full-matrix least-squares refinement of the following Rietveld parameters: phase scales, line asymmetry, phase preferred orientation, phase line widths, instrument zero, the line shape parameter for each phase, and the phase unit cell dimensions. A calculated XRD pattern of each mineral could be generated from its known crystal structure, and the sum of all calculated patterns can be fitted to the observed XRD pattern of a multi-mineral sample by least squares analysis to find the optimum individual phase scales. These are then used to determine the mineral percentages (Ward, 2001; Pinetown and Boer, 2006). The developer claimed that the detection limits for most minerals in low-temperature ashes using XRD with SIROQUANT was around 0.1%. The detection limits for individual minerals in raw coals were around 0.2%, which were not substantially affected by the dilution of the mineral matter with the organic material. The value of quantitative XRD analysis was demonstrated in the determination of minerals in various streams of a coal preparation plant. This allowed the partitioning of minerals in the process to be determined and has important implications for coal preparation (Dale and others, 1998).

Researchers at Australian University of New South Wales used XRD combined with SIROQUANT to determine the mineral percentages in a range of coals from Australia and USA, low-temperature ashes and in some cases higher-temperature ashes prepared by heating the coals in air to around 370°C, as well as US Argonne Premium Coals reference set. They found that the inferred ash composition from the SIROQUANT data was very close to the actual chemical composition of the ash from the same coal samples, confirming that the quantitative XRD results were consistent with other indicators of mineral matter constitution. Independent checks against pyritic sulphur and carbonate CO_2 also confirmed the SIROQUANT results for the particular minerals concerned (Ward, 2001).

Pinetown and Boer (2006) also studied the mineralogical composition of South African coal using XRD with SIROQUANT. They found that the measurements on low-temperature ash were more accurate in identifying minerals, especially those occurring as rare constituents since the organic material in coal tends to obscure interpretations from raw coal XRD results.

Winburn and others (1998) at US North Dakota State University independently developed and tested a quantitative XRD method based on Rietveld methodology for coal ash analysis. They reported that the results obtained were accurate to within ±15% of the actual values and typically within ±10%. The presence of large amounts of an amorphous phase did not significantly alter the accuracy of the results. Microabsorption contributed to the error associated with the method, but care needed to be taken when correcting for its effects.

To determine the effectiveness of direct XRD analysis on raw coal and the determination of major/minor mineral phases as a routine job, Benzel and others (2010) compared the results from XRD analysis of whole coal and low-temperature ash. The coals were selected from five major coal basins in the USA each having a unique mineralogy that reflects the depositional setting and later authigenic alteration. The relative concentrations of identified minerals were determined on these largely amorphous samples (65–95%) by running Rietveld analysis. The results showed that air-drying and grinding of whole coal generates less secondary dehydrated minerals when compared to low-temperature ash. Direct analysis of whole coal reduces preparation time and more accurately reflects the true mineralogy of the coal.

More recently, Soundarrajan and others (2013) studied the transformation of mineral matter in bituminous coal fractions during gasification using AES, computer-contolled scanning electron microscopy (CCSEM) and XRD with Rietveld method. Both XRD and CCSEM were used to measure the major minerals in the coal and gasified chars. They found that the measured values were within acceptable ranges from both techniques and the composition of iron minerals were further corroborated by Mössbauer spectroscopy. Their work showed the usefulness of the XRD technique as a fast and comparably accurate method for qualitative and quantitative study of the crystalline and amorphous transformation during coal conversion that might have significant implications in fly ash formation.

It is important to note that the researchers or analysts are required to have substantial knowledge and experiences in the field in order to make correct interpretations of the obtained XRD spectra using Rietveld methodology. The best precision for this method is only 10% due to problems in obtaining uniform mixing of the sample and standard materials, orientation problems, and difficulty in obtaining representative standards.

5.1.2 X-ray fluorescence

X-ray fluorescence (XRF) is the emission of characteristic 'secondary' (or fluorescent) x-rays from a material that has been excited by bombarding with high-energy 'primary' x-rays or gamma rays. This phenomenon has been widely used for elemental analysis and chemical analysis. XRF is a mature technology and has the advantage of being nondestructive, rapid, simple, and cost-effective, which is

probably unsurpassed by any other method when used for multi-elements determinations in the same prepared coal sample. This technique has been adopted by both ASTM and ISO as a standard test method for determining major and minor elements in coal ash (*see* Section 4.4.2). XRF has also been used extensively for determining sulphur in coal.

XRF spectrometry can be undertaken by two distinct methods, energy dispersive XRF (ED-XRF) and wavelength dispersive XRF (WD-XRF). The ED–XRF is more cost effective compared to WD–XRF. It also allows for smaller units with fewer components resulting in a cheaper and more reliable instrument. Such instruments can be easily tailored to the needs of different customers, integrated with industrial installations, and also miniaturised for the purpose of in-situ analysis. Detection precision and accuracy of an XRF instrument are driven by several factors including x-ray excitation source and strength, type of detector used, time exposure, sample surface conditions, physical and chemical matrix effects, as well as primary elements of interest and inherent x-ray spectral line interference from element overlap. Today, bench-top or portable XRF elemental analyser or XRF sulphur analyser for coal/coal ash are widely available from a number of manufacturers. Figure 16 shows an example of a bench-top ED-XRF elemental analyser by Applied Rigaku Technologies, Inc (USA). In the ED–XRF method, the coal sample is air dried and ground to required particles size. Approximately 7 or 8 gram of homogeneous coal powder is pressed into even, compact sample holder or a pellet. The secondary x-rays emitted by the sample are directed into a solid-state detector. Incoming photons ionise the atoms within the detector, producing electrical pulses which are proportional to the levels of energy being detected. These pulses are amplified and interpreted using a computer that calculates the elemental composition of the sample. The resulting information is then enhanced by referencing an onboard database and/or user defined information that provides additional data about the sample. The spectrum of the sample are adjusted for a number of other variables that might distort the results including (Niton UK, 2013):

- geometric effects caused by the sample's shape, surface texture, thickness and density;
- spectral interference such as a variety of scattering effects originated within the sample;
- sample matrix effects such as absorption of the characteristic x-rays of one element by other elements in the sample, and secondary and tertiary x-ray excitation of one or more elements by other elements in the sample.

Instrumentation

model	Rigaku NEX QC
x–ray tube	4 W Ag-anode
detector	semiconductor
sample type	coal (powder)
film	Mylar
analysis time	300 seconds 240 seconds for S 60 seconds for Ca, Ti, Fe
environment	air
options	autosampler manual sample press

Figure 16 – A bench-top ED-XRF elemental analyser (Rigagu, 2013)

In an inter-laboratory study carried out by the US Electric Power Research Institute (EPRI), the analytical methods for measuring Hg and Cl in coal were evaluated and compared. The study found that the Cl values obtained using an XRF analyser were in excellent agreement with the consensus values. A lower quantitative limit for Cl could be achieved with XRF compared to standard test methods. However, the determination of Cl using XRF suffered interferences from sulphur in coal. This interference became significant for coals with sulphur content greater than 1% (EPRI, 2000). Wang and others (2005) evaluated the determination of iodine in coal using XRF and found that under optimum conditions, coal samples with iodine concentrations higher than 5 ppm can be determined using this ED-XRF method. Song and others (2006) used XRF to simultaneously determine As, P, S, Cl in coal. They found that the measured values of As, P, S, Cl in the coal samples agreed well with the results obtained from standard test methods, and the test limit of the XRF were 1.2 μg/g for As, 22 μg/g for S, 2.1 μg/g for P and 2.0 μg/g for Cl. However, x-rays are unable to penetrate the coal particles beyond 3.175 mm and therefore this method requires finely ground homogeneous samples, limiting its applications in online analysis as only the material surface can be analysed, prohibiting a sound representation of the entire product (Willett and Corbin, 2011).

XRF is a rapid, simple and accurate method of determining the concentration of major and minor elements in coal ash. The coal ashing procedure removes most of the combustible and volatile components. XRF analysis of whole coal is more challenging. One problem is that calibration standards for XRF analysis of whole coal must themselves be whole coals. Only a few coal standards exist, and these are certified for only a few elements. Non-metals like S, P, B and C are difficult or impossible to determine using XRF. This technique is also greatly affected by matrix effects and numerous standards are required in order to match the sample matrix (Davidson and Clarke, 1996; Huggin, 2002). Recent advances in excitation and detection have made it possible to determine light elements and non-metals such as S. This has been done by the use of a Rh end window tube as a universal tube and light elements can be excited effectively by Rh L radiation (Khuder and others, 2007).

The development of polarised ED-XRF offers additional improvement in the technique, especially for extending the XRF technique to trace elements or for carrying out the analysis on whole coal samples. The use of polarised incident radiation reduces background fluorescence radiation thereby increasing the signal/noise ratio resulting in significantly lowered detection limits for determining trace elements in coal. Recently, Moriyama and others (2010) investigated the use of an ED–XRF spectrometer with polarised optics and new quantification software for trace elements determination. They claimed that accurate analysis down to ppm level could be achieved even in complex sample composition with the quantification software which estimates non-measuring sample matrices using scattering intensities and full profile fitting method combined with the Fundamental Parameter (FP) method. The scattering FP method corrects for non-measuring components in samples such as coal fly ash, soils and biological samples by using Compton and Thomson scattering intensities from a Mo secondary target. The measured concentrations of the trace hazardous elements (As, Cd, Cr, Hg, Pb, and Se) and major elements in a coal fly ash sample using the ED-XRF spectrometer with secondary targets, polarised optics, and high speed detector with pile-up rejection demonstrated good agreements with the certified values.

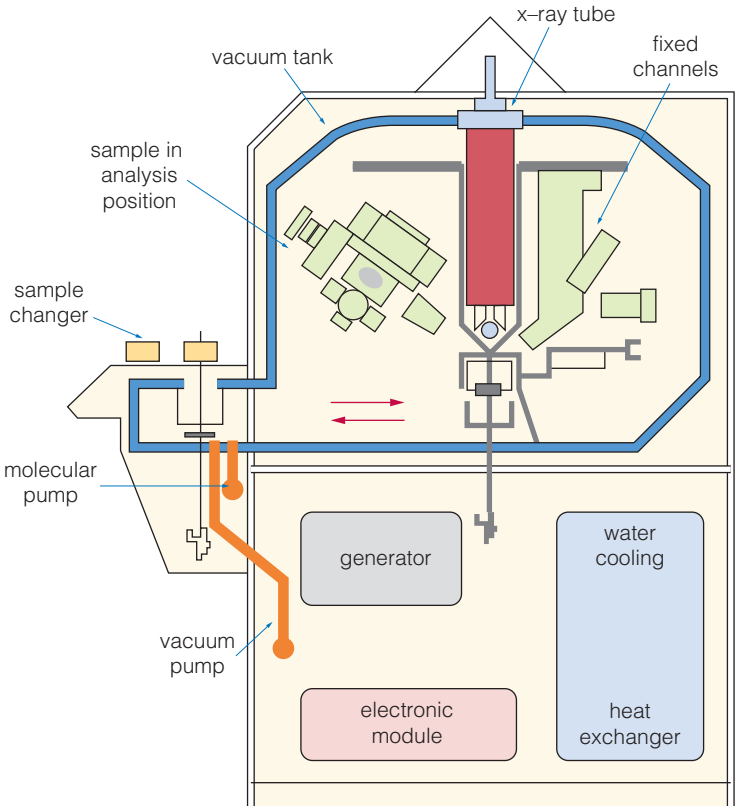


Figure 17 – The integrated XRF and XRD spectrometer (Bonvin and others, 1998)

Bonvin and others (1998) proposed an integrated XRD–XRF system for online process control applications. The combined XRD and XRF instrument, as illustrated in Figure 17, has separate proportional counters to detect diffracted beams and fluorescence radiation. A standard XRD platform is used with fixed geometry goniometer and an energy dispersive x-ray detector for the XRF analysis. This

approach has been applied in industrial processes such as iron and steel, and cement making but is yet to be tested and validated for coal analysis.

5.1.3 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) is the measurement of the x-ray absorption co-efficient of a material as a function of energy. x-rays of a narrow energy resolution are shone on the sample and the incident and transmitted x-ray intensity are recorded as the incident x-ray energy is incremented. Through mathematical analysis of the number of x-ray photons that are transmitted through a sample and the number of x-ray photons shone on the sample, one can obtain local structural information for the atom in question.

XAS is a unique tool for studying, at the atomic and molecular scale, the local structure around selected elements that are contained within a material. Very often, the term XAFS (x-ray absorption fine structure) is used which is a broad one that comprises several different techniques: EXAFS (extended XAFS); XANES (x-ray absorption near edge structure); NEXAFS (near edge XAFS); and SEXAFS (surface EXAFS). Although the basic physics of these techniques is fundamentally the same, different approximations, techniques, terminology, and theoretical approaches may be employed in different situations, particularly in the low-energy (soft x-ray) and high-energy (hard x-ray) regimes.

In the initial studies that concentrated on arsenic and chromium in coal, Huffman and others (1994) demonstrated that XAFS spectroscopy with a solid-state multi-element germanium detector was capable of providing speciation information at realistic concentration levels of 10–100 ppm. Two main forms of As were observed in coal: As contained in pyrite As(V) and in arsenate (AsO_4^{-3}), while Cr in coal and in ash was observed to be present predominantly (>95%) in the Cr^{3+} state. Their results also showed that chromium oxyhydroxide was the standard compound whose XAFS spectrum most closely resembled that of Cr in coal. Huggins and others (2000) compared the speciation of As in a bituminous and a lignite coal determined using XAFS spectroscopy and sequential extraction by aqueous solutions. In order to facilitate a more direct comparison of the two methods, the arsenic XAFS spectra were obtained from aliquots of the coal prepared after each stage of the leaching procedure. They showed that the results from the two methods were consistent and complementary.

Huggins and Huffman (1996) examined the mode of occurrence of selected trace elements in coal using XAFS. They found that for elements between calcium and molybdenum in the periodic table, information relating to the mode of occurrence could be deduced from the XAFS spectrum provided the concentration of individual element exceeded about 5 ppm. The XAFS data indicated that Mn, Zn, As and Br were largely organically associated in certain coals, and As, and to a lesser extent, Se would oxidise over time once the coal had been exposed to air. Their results showed that this spectroscopic method was capable of providing information on element forms dispersed in the organic fraction of coal as well as on the mineralogical forms of the element.

XAFS spectroscopy is now widely applied to characterise various elements in coal and coal-derived products. There have been a number of investigations into the sulphur, chlorine and other hazardous elements in coal and coal combustion products using XAFS and/or XANES (Bao and others, 2009; Huggins and Huffman, 1995; Huggins, 2011; Huggins and Huffman, 2002; Shah and others, 2007). The major drawback of the XAFS technique is that it requires synchrotron light as a source, which is expensive and not easily available.

5.1.4 Small-angle x-ray scattering

Small-angle x-ray scattering (SAXS) is a small-angle scattering (SAS) technique where the elastic scattering of x-rays by a sample that has heterogeneity in the nanometre-range, is recorded at very low angles (typically 0.1–10°). This angular range contains information about the shape and size of macromolecules, characteristic distances of partially ordered materials, pore sizes, and other data. SAXS is an attractive alternative and more reliable technique to evaluate the porosity of coal because x-rays readily penetrate the entire sample, all pores are accessible to investigation including closed pores that are not connected to a pore leading to the particle surface. SAXS can trace the development of coal porosity based on degree of metamorphism. Recent investigations into the pore structures of different rank coals and the structural changes with treatment of the coal under varying temperatures and pressures using SAXS and gas (for instance N_2, CO_2) adsorption/desorption isotherms showed the usefulness of SAXS in evacuating the pore shape and the pore size distribution (Cai and others, 2013; Winans and others, 2013). Information on the surface geometry of coal such as the surface fractal dimension and the diffuse interfacial layer of coal can also be obtained using SAXS (Winans and others, 2013; Liu and others, 2011).

5.2 Electron microscopy

An electron microscope is a type of microscope that uses an electron beam to illuminate a specimen and produce a magnified image. There are several types of electron microscope such as transmission electron microscope (TEM), scanning electron microscope (SEM), and reflection electron microscope (REM), with SEM being most extensively used in coal analysis.

5.2.1 Scanning electron microscopy

The SEM produces images by probing the specimen with a focussed electron beam that is scanned across a rectangular area of the specimen (raster scanning). When the electron beam interacts with the specimen, it loses energy by various mechanisms. The lost energy is converted into alternative forms such as emission of low-energy secondary electrons and high-energy backscattered electrons, light emission or x-ray emission, which provide signals carrying information about the properties of the specimen surface, such as its topography and composition. SEM has been extensively used to study the morphology and cross section of coal and coal char/ash, and analysis of the SEM image can provide valuable information such as particle size, swelling of the particles during conversion, and the structure of char/ash. This information can be correlated to the fundamental properties of parent coal and the process parameters.

SEM with energy dispersive x-ray spectrometer (EDS) has been widely used to identify the composition and nature of minerals in coals and to determine the associations of the minerals with each other. Examinations can be made of samples resulting from ashing techniques or whole coal. With this technique it is possible to identify the elemental components and deduce the mineral types present in coal samples. Figure 18 shows an example of the SEM image of a cross-section of a bituminous coal and its x-ray spectrum obtained using an SEM-EDS. Recent studies on iron sulphide minerals in coals, minerals in coals, and transformation of minerals during coal conversion all used SEM as the primary analytical tool (Kgabi and others, 2009; Zhu and others, 2002; Manoj, 2013; Manoj and others, 2009; Oliveira and others, 2011; Ma and others, 2013).

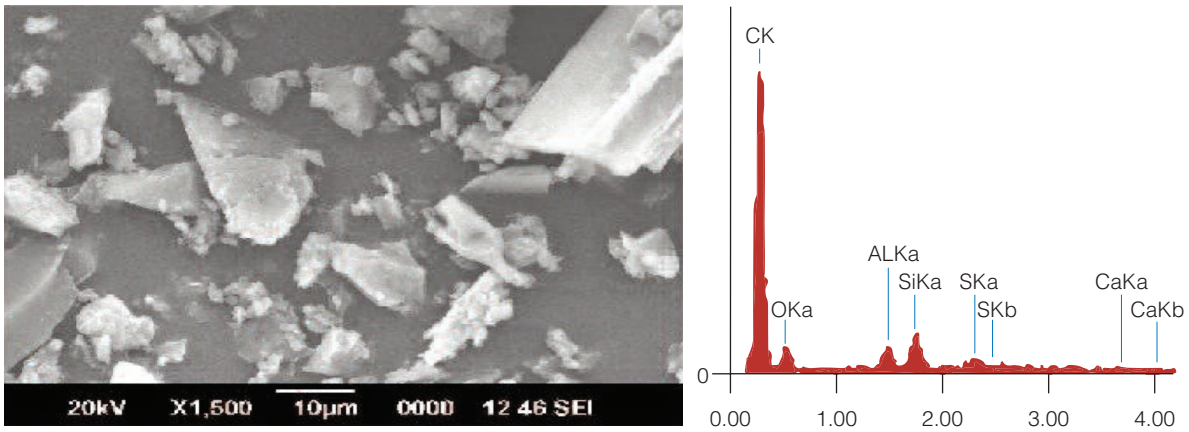


Figure 18 – SEM-EDS characterisation of an Indian bituminous coal (Manoj, 2013)

Advantages of a SEM include its wide-array of applications, the detailed three-dimensional and topographical imaging and the versatile information garnered from different detectors. SEMs are easy to operate, work fast, and require minimal sample preparation. In addition, the technological advances in modern SEMs allow for the generation of data in digital form. However, SEMs are expensive, large and must be housed in an area free of any possible electric, magnetic or vibration interference. Special training is required to operate an SEM as well as to prepare samples as the preparation of samples can result in artifacts. Also, SEMs carry a small risk of radiation exposure associated with the electrons that scatter from beneath the sample surface.

Recently, computer-controlled SEM (CCSEM) to evaluate SEM images have been developed to determine the size, quantity, distribution, and semi-quantitative composition and association of mineral grains in coal mine dusts, coals, coal ashes and in coal liquefaction residues. With this information, the impacts of coal properties on wear of system components, slag flow, fouling of heat exchangers, fine-particle collection, and ash handling can be assessed and predicted.

A CCSEM instrument consists of an SEM that is interfaced with a computer-controlled acquisition and data-collection system. The system can measure several thousand different mineral particles, which appear randomly placed in a polished section of the coal embedded in resin or wax. In the SEM, the electron beam is under the control of a computer and is stepped across the field-of-view in a relatively

coarse grid in order to locate mineral particles in the coal/resin (or wax) matrix. The back-scattered electron intensity is used to discriminate between mineral particles and the background of coal macerals and resin or wax mounting medium. Once a mineral particle is located, the grid spacing is greatly reduced. The cross-sectional area of the particle is measured by extending eight diagonals through the centre of the particle to the edge of the particle and summing the areas of the triangles so produced. After the area is measured in this manner, the electron beam is positioned at the centre of the particle and an EDS spectrum is obtained. The chemical information contained in this spectrum is then used to identify the mineral. By analysing several thousand particles in the coal section in this manner, a reasonably quantitative description of the coal mineralogy can be obtained (Gupta, 2007). A diagram of a CCSEM system is shown in Figure 19.

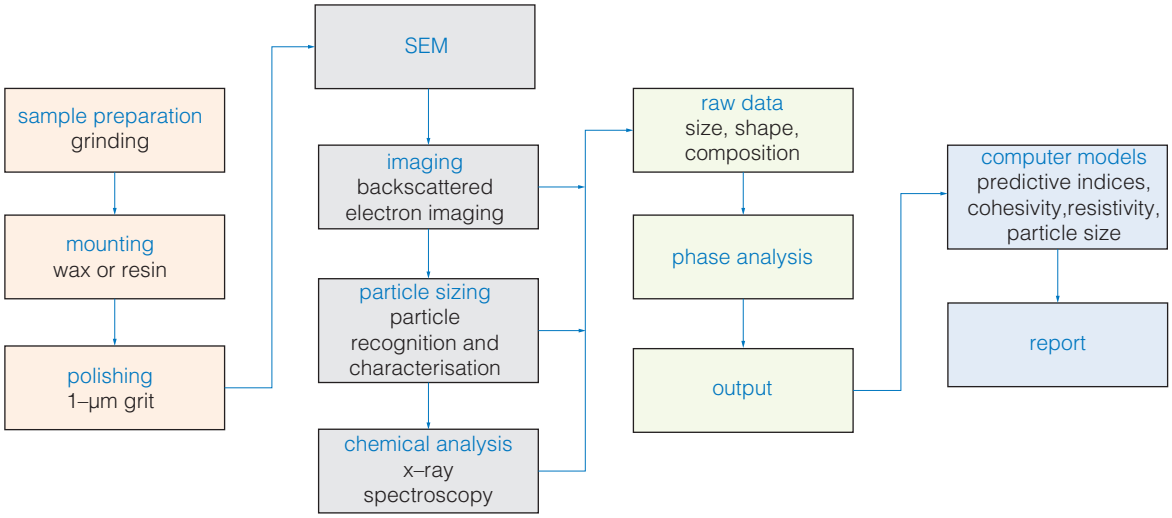


Figure 19 – A diagram of a CCSEM system (MTI, 2012)

An international co-operative study on the accuracy of a CCSEM system for analysis of minerals in coal found that the main factors affecting the accuracy of CCSEM analysis were the coal sample preparation technique and the number of mineral grains analysed. The differences of the CCSEM systems including their operating conditions only played a minor role to account for the discrepancy of CCSEM measurements, as different laboratories gave similar CCSEM results on the same coal sample stub. The results from this study indicated that the sample preparation technique that mixes crushed coal and wax into a pressed pellet produced an optimum particle distribution. If a coal sample contained coarse minerals, then a greater number of grains comprising large size minerals would need to be analysed (Gupta and others, 1999). Improved procedures for sample preparation and CCSEM analysis were developed and described by Cieplik and others (2003) in which Carnauba wax was used as embedding material for increased contrast between embedding material and the organics in coal to distinguish between free mineral particles and those included in the organic coal matrix. Optimised particle distribution and mass fraction were also obtained using the procedures. Since CCSEM was developed around 20 years ago, it has been refined, enhanced, and continuously advanced. One of the improvements has been to move from single elemental analysis at a central point to an average elemental analysis

derived from several analyses obtained at a number of points on a grid imposed on each particle. This accounted for variation in the mineral composition within a mineral grain. The mineral recognition programme and general data handling have also been extensively developed over recent years (Gupta, 2007). Recent investigations have shown CCSEM to be a valuable means of identifying phases of minerals in coal and coal ashes (Soundarrjan and others, 2013; Cprek and others, 2007).

5.2.2 Electron probe microanalysis

An electron microprobe (EMP), also known as an electron probe microanalyser (EPMA) or electron micro probe analyser (EMPA), is an analytical tool used to non-destructively determine the chemical composition of small volumes of solid materials. It is essentially a hybrid instrument combining the capabilities of both the SEM and an XRF, with the added features of fine-spot focussing (approximately 1 micrometer), optical microscope imaging, and precision-automated sample positioning. Electron probe microanalysis (EPM) is based on the principle that a sample will produce x-rays characteristic of the elements present in the sample when exposed to a finely focussed electron beam. The electron column and basic instrumentation for EPM are very similar to those from SEM. The major difference is that, while SEM describes the surface morphology by visual magnification of the surface, EPM is able to describe the chemical composition of the sample. A scanning electron microscope, when equipped with an x-ray spectrometer, can carry out the same analysis as that of an EPM. Modern scanning electron microscopes are commonly equipped with energy dispersive x-ray spectrometers (EDS) that allow qualitative and quantitative chemical analysis. EMP can be used as a powerful analytical tool in coal research if used in conjunction with other analytical techniques such as SEM, transmission electron microscopy (TEM) and optical microscopy, XRD, and Mössbauer spectroscopy (Gupta, 2007).

EPMA equipped with an energy-dispersive x-ray detector can be used to simultaneously determine the morphology and the constitution elements (within a microscopic size volume) of coal. The procedures for quantitative analysis of coal and elemental contents of coal using SEM and EMPA have been described in detail by Karner and others (nd). However, until recently a major drawback of EPMA was its inability to routinely and precisely analyse samples for the low-energy (light) elements such as C, N, O, and F. This was because of 1) the absorption of the long-wavelength and low-energy X-radiation in the specimen, the analyser crystal and the detector window; 2) the low cross-sections for ionisation; and 3) spectral interference from higher-energy elements. The resulting low count-rates and generally low peak-to-background ratios place a heavy demand on the detection process. Matrix-correction programs must be substantially more robust than those for higher-energy (heavier) elements (Raudsepp, 1995). Over the last decade, both the technology and the data evaluation methods of x-ray spectra analysis and quantitative determination of sample composition have been improved for EPM. One of the major advances in this field has been the introduction of commercial silicon-based spectrometers equipped with thin polymer windows which improve the transmission of low-energy x-rays, as well as newly designed high resolution energy dispersive detectors such as microcalorimeters. Another important improvement is the development of evaluation models for quantitative analysis, which can handle various types of target samples. Recently, a low-energy EPMA and energy-dispersive x-ray detector with an ultra-thin

window was developed allowing quantitative determination of the concentrations of low-energy elements, as well as the higher-energy elements that can be analysed by conventional EPMA. Furthermore, by varying the excitation voltage (the so-called 'beam variation' EPMA), useful information on the heterogeneity with respect to chemical composition of individual particles can be obtained (Ro, 2005).

5.2.3 Transmission electron microscopy

A transmission electron microscopy (TEM) utilises energetic electrons to provide topographical, morphologic, compositional and crystallographic information on samples. TEM is a microscopy technique in which a beam of electrons is transmitted through a specimen forming an image in the process. The image is magnified and focussed onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a camera. High resolution TEM (HR–TEM) can be used to deduce the structure of coal at atomic level. The lattice fringe image obtained from HR–TEM provides direct coal or char atomic structural information. TEM with EDS is another method that has been used to identify and characterise the phases of minerals, and to determine the distribution of elements in coal and coal ash (in atomic or weight percentages).

TEM offers the most powerful magnification, potentially over one million times or more. Similar to SEM, TEM has a wide range of applications. It can provide information on surface features, shape, size and structure as well as element and compound structure. It is easy to operate with proper training. Like SEM, TEM is large, expensive, and requires special housing to prevent any possible electric, magnetic or vibration interference. Sample preparation in TEM can be a complex procedure. Glikson (2001) reviewed the TEM technique and its applications including sample preparation, a topic also described by Chen and others (2005). TEM has been extensively applied in studies in morphology and composition of coal and coal ash, especially ultra-fine fly ash (Chen and others, 2005; Linak and others, 2006; Silva and da Boit, 2011; van der Merwe and others, 2011; Oliveira and others, 2011; Wu and others, 2013; Damoe and others, 2012).

5.3 Atomic spectroscopy

Atomic spectroscopy is an analytical technique that measures the concentration of chemical elements in a sample. When elements are transformed into atomic vapour at high temperatures, emission or absorption of light may occur and this can be accurately measured at a unique resonant wavelength, which is characteristic of the emission/absorption lines of the elements concerned. The science of atomic spectroscopy has yielded three techniques for analytical use: atomic absorption, atomic emission, and atomic fluorescence.

5.3.1 Atomic absorption spectroscopy

Atomic absorption spectroscopy (AAS) uses the absorption of light to measure the concentration of gas-phase atoms. Since samples are usually liquids or solids, the analyte atoms or ions must be vaporised in a flame or graphite furnace. The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. The analyte concentration is determined from the amount of absorption. AAS has

many uses in different areas of chemistry due to its high sensitivity, low instrumental detection limits, and ability of multi-elements analysis on an individual sample. It has been widely used to determine major, minor and trace elements in coal and coal ash.

AAS requires that the analyte atoms be in the gas phase. Ions or atoms in a sample must undergo dissolution and vaporisation in a high-temperature source such as a flame or graphite furnace. Depending on the atomiser used there are several types of AAS such as flame AAS (FAAS), graphite furnace AAS (GFAAS, also known as electrothermal atomic absorption spectroscopy), cold-vapour AAS (CVAAS). Flame AAS can only analyse solutions, while graphite furnace AAS can accept solutions, slurries, or solid samples.

Flame Atomic Absorption Spectroscopy (FAAS)

The FAAS typically makes use of a flame to atomise the sample. A solution of the sample is nebulised by the flow of gaseous oxidant, mixed with a gaseous fuel, and carried into a flame where atomisation occurs. When irradiated with light of their own characteristic resonance wavelength, these atoms will absorb some of the radiation by excitation of the electrons, and the absorbance is proportional to the population density of atoms in the flame, thereby permitting a quantitative analysis. FAAS has been used in coal research/analysis laboratories worldwide as an effective means for determining trace elements, as well as major and minor elements in coal and coal ash (Bartoòová and others, 2002; Baysal and Akman, 2011; Sager, 1993; Yigmatepe and others, 2010; Anawar, 2012). FAAS is a well-developed, mature technique and the standard procedures for determining elements such as Ca, Fe, K, Mg, Mn, Na, Co and Li in coal ash, as well as indirect measurement of pyritic sulphur concentration in coal by determining the iron concentration in a separated fraction by FAAS have long been established (USGS, 1989; USGS, 1997).

It is required for FAAS that the sample be introduced into the excitation source in the form of a solution, most commonly an aqueous one. Some common methods used for decomposition and dissolving samples for atomic absorption methods include acid extraction, wet oxidation, combustion in an oxygen bomb or other closed container to avoid loss of analyte, low or high temperature ashing, and high-temperature fusion. The decomposition and dissolution steps are often more time consuming and introduce more errors than the spectroscopic measurement itself. For these reasons, there is considerable interest in the development of analytical methods which allow the direct analysis of solid samples. Some attempts have been made at solid sampling by FAAS. An example was sample introduction as slurries by means of a nebuliser (Alves and others, 2000). Based on a direct solid sampling technique for determining Cu and Cd in biological samples by FAAS, Flores and others (2004) developed a device for direct solid sampling by FAAS for coal analysis. In this method, a finely ground, dry coal sample (≤50 μm) is carried by a constant flow of air to a quartz T-cell, where it is burnt in the flame and atomised. The free atoms then pass the optical path and are measured with atomic absorption. Using this device, the use of concentrated acid is eliminated and the sample pretreatment is reduced basically to two steps: grinding and drying. The Mn concentration in three standard coal samples of varying ranks was measured using direct solid sampling FAAS and GFAAS. Good agreements between the measured and the certified values were obtained with the precision being better than 6%. However, when using slurry or solid sampling, the spectral and/or

chemical interferences are much more abundant than with liquid samples. Also, problems related to the slurry/solid transport and clogging of the nebuliser may arise and thereby more work is needed in order to apply solid sampling by FAAS for coal analysis.

FAAS is currently the most widely used of all the atomic spectroscopic methods due to its simplicity, effectiveness, and relatively low cost. However, its sensitivity is lower and it needs larger amount of sample compared with GFAAS.

Graphite Furnace Atomic Absorption Spectroscopy

GFAAS is a technique that is very suitable for the analysis of metals at trace levels – the detection limits fall in the ppb (parts per billion) range for most elements. Free atoms of most elements can be produced from samples by the application of high temperatures. A small amount of a sample to be analysed, is injected into a graphite furnace. The furnace is heated with a special temperature programme. First the solvent of the solution is evaporated, followed by ashing of the sample, which removes most of the sample-matrix. The last stage of the heating programme is the atomisation-phase, which creates a cloud of free atoms in the graphite furnace. The concentration of free atoms in the furnace is measured by absorption of element specific irradiation through the graphite furnace. This irradiation is produced by a hollow cathode lamp, which contains the element of interest in its cathode. The amount of absorption is a measure of the concentration of the element in the sample-solution.

With the use of a graphite furnace as an atomiser, it is possible to analyse solid samples by GFAAS. A way of performing such measurements is to weigh the finely ground sample into a graphite boat and insert the boat manually in the furnace. Another way is to prepare a slurry of the powdered sample by ultrasonic agitation in an aqueous medium. The slurry is then pipetted into the furnace for atomisation. The methods of direct solid sampling and slurry sampling were reviewed and compared by Bendicho and de Loos-Vollebregt (1991). Direct solid and slurry sampling are now widely applied in measurements of trace elements in coal, coal bottom ash and fly ash using GFAAS (Vale and others, 2001; Silva M and others, 1999, Silva A and others, 2004, 2005; Borges and others, 2006).

Recently, the use of a modifier to eliminate or reduce spectral and/or chemical interferences has been investigated. The selection of the modifier depends on the element to be determined. A water soluble liquid modifier is mixed and homogenised with the sample solution before atomisation. The modifier acts by suppressing the signal of interfering element/elements or moving its peak to a higher or lower temperature and thereby the element of interest can be measured with improved accuracy and precision when the absorbance is recorded as a function of time and temperature. By monitoring absorbance signal intensity and its changes with temperature additional information on occurrence of the molecular species during heating was obtained (Kozliak and others, 2011). For analysis of solid samples, a method was developed in which the graphite tube wall or the surface of the graphite sampling platform was coated with a chemical modifier. Modifying the graphite sampling platform surface also allowed the optimised pyrolysis and atomisation temperature to be used to minimise the structured background absorption (Silva and others, 2005; 2004; Maia and others, 2002). Furthermore, the use of high-resolution

continuum source GFAAS was investigated. This new instrumental concept makes the whole spectral environment in the vicinity of the analytical line accessible, providing a lot more data than just the change in absorbance over time available from conventional instruments (Borges and others, 2006; Silva and others, 2004, 2005).

Compared with FAAS, GFAAS offers greater sensitivity and requires less sample, but has lower accuracy and precision. In addition, GFAAS is slow – typically requiring several minutes per element, and has relatively lower analytical range.

Cold Vapour Atomic Absorption Spectroscopy (CVAAS)

CVAAS is very useful for determination of mercury in coal and coal combustion products. This technique is applicable only to the determination of mercury because it is the only metallic element that has an appreciable vapour pressure at ambient temperature. This unique property gives rise to the possibility of measuring mercury without the additional thermal energy supplied by a flame or electrothermal heating. CVAAS uses reducing agents, such as $SnCl_2$ or $NaBH_4$, to convert the ionic Hg^{2+} in solution into Hg^0 in gas phase. The liberated gaseous Hg is introduced into the absorption cell of an AAS where it is detected (López-Antón and others, 2012). CVAAS is more sensitive than FAAS, reaching mercury detection limits in the ppb range. A major advantage of the technique is the inherent separation of the mercury from the matrix.

Hydride generation atomic absorption spectroscopy (HGAAS)

Hydride generation is an effective analytical technique that separates hydride forming metals, such as As and Se, from a range of matrices by conversion to their volatile hydride. It offers a route to the analysis of several important trace elements which have specific problems when analysed by conventional methods. Separating the elements from the matrix can improve the sensitivity of the AAS technique and avoids physical, matrix and spectral interferences. The separation of the hydride from the matrix allows for high efficiency of analyte introduction into the AAS. The concentration effect, the added sensitivity and relatively interference free as compared to GFAAS make FGAAS particularly useful for determining those elements in fossil fuel that form stable covalent hydrides. It is now applied to the determination of antimony, arsenic, bismuth, germanium, lead, mercury, selenium, tellurium and tin in a wide range of matrices including coal and its combustion products (Geng and others, 2010; Matusiewicza and Krawczyka, 2008; USGS, 1997; Iwashita and others, 2007; Vieira and others, 2002; Moscoso-Pérez and others, 2003; Moreda-Piñeiro and others, 2002a,b).

5.3.2 Atomic emission spectroscopy

Atomic emission spectroscopy (AES, also called optical emission spectroscopy or OES) uses the intensity of the light emitted from excited atoms to determine the concentration of an element in a sample. AES was one of the first multi-element techniques applied to trace elements determination in fossil fuels. As with AAS, depending on the atomisation method used, there are several types of AES such as flame AES, inductively coupled plasma AES (ICP–AES), spark or arc AES.

ICP–AES is one of the most commonly used techniques for elemental analysis. Its high specificity, multi-element capability and good detection limits result in the use of the technique in a large variety of applications. In ICP–AES method, excitation is achieved by high temperature plasma, usually argon, flowing in a quartz tube surrounded by an induction coil. A schematic of an ICP–AES is shown in Figure 20. A plasma source is used to dissociate the sample into its constituent atoms or ions, exciting them to a higher energy level. They return to their ground state by emitting photons of a characteristic wavelength depending on the element present. A spectrometer separates this light into the characteristic wavelengths, which are measured and recorded by a multi-element detector. When calibrated against standards the technique provides a quantitative analysis of the original sample. The strengths and weaknesses of ICP–AES are outlined in Table 14.

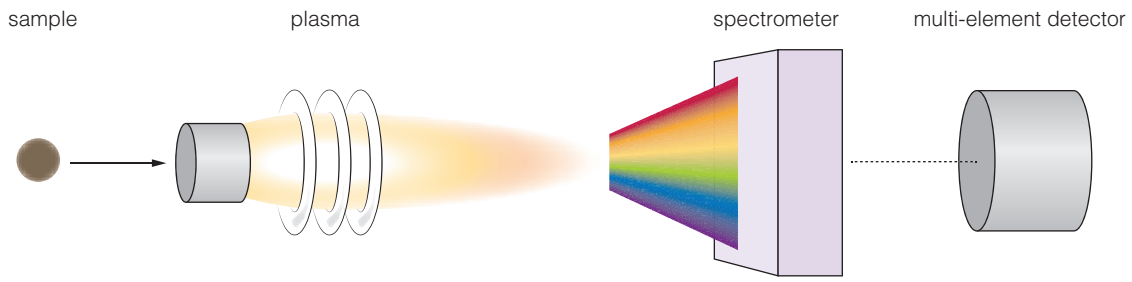


Figure 20 – Schematic of an ICP-AES (Philips, 2008)

Table 14 – The strengths and weaknesses of ICP-AES (Hieftje, 2007)	
Strength	**Weakness**
10^8 counts/s^{-1} per atom leading to high sensitivity	Overlap of sensitive lines due to: Spectral clutter ('rich' spectral) Spectral interferences
Rich spectrum; choice of spectral lines	High background (continuum, bands)
Atom and ion lines can be used	Detector noise (low work function)
Straightforward spatial averaging	Cannot 'see' some oxides, multiply charged ions
Convenient diagnostics for checking performance	
Smple instrumentation	

ICP–AES requires sample preparation, the type of which depends mainly on the sample introduction system available. Solution nebulisation, which is the most commonly adopted technique, requires transfer of analytes from the solid phase into solution by either acid dissolution or fusion. Microwave assisted dissolution of coal has been developed as a rapid and safe sample preparation method (Sun and Hoffman, 1996; Wang and others, 2012; Saydut, 2010; Mujuru and others, 2009; Rodushkin and others, 2000). Various acids and acid mixtures, including HNO_3, HCl, HF, $HClO_4$, H_2SO_4, H_3BO_3 and H_2O_2, have been used for coal samples. The limitation of acid-based sample preparation is incomplete digestion due to some mineral fractions in coal are resistant to acid dissolution processes while the fusion method enables resistant samples to be dissolved more easily after they have been fused. An alternative method of slurry nebulisation/atomisation has been developed which uses an aqueous suspension of fine powder of coal/ash samples injected into the ICP–AES. Slurry atomisation provides advantages including that it eliminates complex dissolution procedures, avoids the use of hazardous chemicals, and analyte loss as

well as reagent consumption are minimal compared to sample dissolution. Slurry atomisation has been applied in elemental analysis of coal and coal ash (Santos and Nobrega, 2006; Maia and others, 2003; 2000; Rodushkin and others, 2000) and a range of other samples such as cement and gypsum. Direct introduction of pulverised coal into the ICP-AES has also been attempted as a possible methods to avoid the drawbacks associated with ashing and dissolution. However, the precision and reproducibility of the element determinations are generally not as good as from a solution (Huggings, 2002)

ICP–AES is well developed and is now the technique of choice for multi-element analysis of coal and coal combustion products. A major advantage of ICP–AES is the relatively rapid, low cost and simplicity of instrumentation. The operation of an ICP–AES is well automated for multi-sample operation. It is widely used for determination of major, minor and trace elements in coal and coal ash both in research and in commercial analytical laboratories. The major disadvantage is that the analysis is best done on solutions of coal ash or on acid-digested coal rather than on coal directly.

5.3.3 Comments

Earlier work investigated the use of other types of AES such as Spark AES and arc AES for determining elements in coal and coal ash (Dreher and Schleicher, 1975; Mills, 1983; Swaine, 1990). These techniques, regarded as semi-quantitative, are still in use today (Szabo and others, 2013; Huggins, 2002). However, ICP-AES is largely superceding other AES techniques because of the better properties of the ICP as an excitation source. Both the detection limits and precision for the determination of trace elements in coal/coal ash by ICP-AES are superior to those for other AES techniques.

AAS and AES are well developed techniques and have been widely used in coal research and for routine analysis of coal. FAAS is sensitive for many elements and is the simplest of the different variations of AAS. GFAAS is an especially attractive method for trace elements as it has the best sensitivity of the four variations discussed above. CVAAS is very useful for determination of Hg as the other AAS methods do not determine this element reliably. HGAAS is generally useful for those volatile elements in coal that form stable covalent hydrides, such as As, Bi, Pb, Sn, and Te. The ICP–AES and AAS techniques are readily available, have relatively low costs, and they have been adopted by various national and international standard organisations as standard methods for determination of major, minor and trace elements in coal and coal combustion products.

5.4 Mass spectrometry

Mass spectrometry (MS) works by ionising chemical compounds to generate charged molecules or molecule fragments and measuring their mass-to-charge ratios. In an MS procedure, a sample is ionised, usually to cations by loss of an electron or electrons. The ions are accelerated so that they all have the same kinetic energy. The ions are then deflected by a magnetic field according to their masses as well as the number of charges. The separated ions are measured and the results displayed as spectra of the relative abundance of ions as a function of the mass-to-charge ratio. The atoms or molecules can be

identified by correlating known masses to the identified masses or through a characteristic fragmentation pattern.

Techniques for ionisation have been key to determining what types of samples can be analysed by MS. There are a number of ionisation techniques applicable to MS, among which the spark source MS (SSMS), glow-discharge MS (GDMS) and ICP–MS have found applications in coal analysis.

5.4.1 Spark source mass spectrometry

SSMS utilises a high voltage electric discharge, or spark, to ionise solid samples within a vacuum. SSMS was the first MS technique applied to the determination of trace elements in coal. Whole coal samples, as well as ash residues, fly ash, and respirable coal dust have been analysed using this technique (Guidoboni, 1973; Sharkey and othrs, 1975; Pilate and Adams, 1981; Conzemius and others, 1984). A different approach to the determination of trace elements in coal is to apply isotope dilution to SSMS (Carter and others, 1977). In this technique, an enriched isotope, usually of low abundance in the original coal or ash, is mixed with the sample in a known amount and the isotopic ratio for the element of interest is then determined, from which the abundance of the element can be calculated upon comparison with a sample that is unspiked in the enriched isotope. This method is limited to elements that have two or more naturally occurring or long-lived isotopes. However, it provides very sensitive and precise determination compared to SSMS (Huggins, 2002).

SSMS is rapid and covers a wide range of elements. Detection limits of 0.02 ppm or better for some elements can be achieved with SSMS but it is liable to inference by multiple charges and complex ions. The technique is generally regarded as semi-quantitative with experimental errors that are typically as large as ±50% for elements in coal without standards. Coal samples require preliminary treatment to remove carbon and hydrogen (Swaine, 1990; Huggins, 2002; Speight, 2005).

5.4.2 Glow-discharge mass spectrometry

In GDMS, the conducting solid sample serves as a cathode for a direct current glow discharge in argon. For elemental analysis of coal or coal ash, the sample is mixed with silver powder and is pressed into the shape of a pin to serve as a conducting electrode in a low-pressure argon plasma ionisation chamber. Sample atoms are sputtered into the plasma and then ionised. The plasma is a constant matrix in which the ionisation efficiencies of the elements also remain constant. The ionisation efficiencies expressed as relative sensitivity factors are used to convert ion intensities to elemental concentrations. The application of this technique to coal and coal ash particles has been demonstrated (Jacobs and others, 1995; US DOE, 1994; Luo and Huneke, 1992).

GDMS is more sensitive and precise than SSMS with detection levels for many elements in the sub-ppb range and accuracies in the order of ±20%, even for standardless application. SSMS and GDMS are well suited for semi-quantitative survey studies, and the sample preparation and analysis time are not demanding. With the use of relative sensitivity factors to correct the measured ion beam ratios, GDMS could become a reasonably quantitative method for rapid analysis of trace elements in coal ash (Huggins,

2002; King and others, 1995). However, more research is needed on direct use of coal in GDMS, as low-rank coals in particular, appear to give rise to significant problems (Luo and Huneke, 1992).

5.4.3 Inductively coupled plasma-mass spectrometry

Like ICP–AES, the ICP as an atomic vaporisation process also makes it an excellent source of ions for use in a MS, enhancing the precision and accuracy of the MS technique. The energy of the ions created in the plasma is also optimum for separation in a quadruple MS. ICP–MS is capable of multi-elemental analysis, has wide dynamic range and low instrumental detection limits. It has, over the years, become one of the most common techniques used for elemental analysis of coal and coal products (Fadda and others, 1995; USGS, 1997; Richaud and others, 1999, 2000a; Díaz-Somoano and others, 2004).

As for AAS and AES techniques, the performance and quantitative precision of ICP–MS are significantly better if the analytes are introduced into the MS in the form of solution or liquid. As a result, ashing is considered a necessary step in preparing suitable analytes. The sample preparation methods for ICP-MS are essentially the same as those for ICP–AES. The ICP–MS analysis of ash offers several benefits:

- it is fast, quantitative multi-element analysis that can be done within a few minutes;
- it is sensitive, detection limits for many elements are in the ppt (parts per trillion) range;
- it is highly selective, isotopic interferences are relatively few;
- it is easy to calibrate, stock solutions of various elemental abundance levels can be used to generate calibration data or standard reference materials can be used.

The major disadvantage to this method is that the analyte signal is very susceptible to variation in the plasma nebuliser flow and the radio-frequency power applied to the plasma. The instrumental drift can also be a problem as the instrument ‘warm up’ over the first hour or two of operation (Huggins, 2002). Furthermore, for volatile elements such as Hg, ICP–MS often has a pronounced memory effect resulting in a positive bias in the results. This is due to retention of the volatile elements in multiple locations such as the sample introduction tubes, the nebuliser and the spray chamber (López–Antón and others, 2012).

Attempts have been made to develop techniques for direct measurements on coal rather than ash, so that the problem of loss of volatile elements during ashing may be avoided. One such technique developed involves combining a laser ablation process on coal with an ICP–MS (LA–ICP–MS). In this process, a pulse of laser operated at the primary wavelength of 1068 nanometre is used for laser ablation. Samples of coal for the laser ablation process are prepared from finely ground coal pressed to form pellets. The laser ablation process forms very fine particles that are then swept by a stream of argon into the ICP, where the analytes are vaporised and ionised for the MS determination (Huggins, 2002).

The use of the scanning mode of LA-ICP-MS allows direct analyses of micron-sized coal components down to the ppm level using polished coal sections or blocks. Lyons and others (1990), and Spears and others (2007) used the scanning mode of LA-ICP-MS to analyse trace elements in coal macerals. The elements analysed were known to have some organic association. Using LA–ICP–MS, both the concentration and the distribution of the trace elements in coal were determined. The scanning mode of the LA-ICP-MS was

also adopted for the analysis of fly ash particles (Spears. 2004). The data were statistically analysed to overcome a problem associated with the small mean grain size of the particles (10 μm).

Kleiber and others (2002) studied inorganic constituents in different coals using LA–ICP–MS analyses of coal pellets and ICP–MS analyses of solutions prepared using microwave-assisted digestion of the coals. Their results showed that the LA–ICP–MS could be used for quantitative multi-elements determination in coal with precision of around 10% being achieved. Recently, Boulyga and others (2007) investigated the direct measurement of Cl, S, Hg, Pb, Cd, U, Br, Cr, Cu, Fe, and Zn in powdered coal samples using isotope dilution LA–ICP–MS. Four certified reference coals were used in the study and the results showed that this method was fast, sensitive and accurate.

Elements ranging from lithium to uranium, and including major elements such as carbon, can be analysed by ICP–MS. Detection limits for many trace elements are in the range of 5–100 ng/g. Accuracy and precision appears to be limited principally by sample homogenisation as typically >5 mg of coal is consumed in the analysis. The ICP–MS has relatively high costs but it is well suited for a laboratory environment as no radiation source is needed (Huggins, 2002).

5.5 Neutron activation analysis

Neutron activation analysis (NAA) is a sensitive, nondestructive multi-element analytical technique used for both qualitative and quantitative analysis of major, minor, trace and rare elements. The sample is bombarded with neutrons, causing the elements to form radioactive isotopes. The radioactive emissions (gamma rays) and radioactive decay paths for each element are well known. Using this information, it is possible to study spectra of the emissions of the radioactive sample, and determine the concentrations of the elements within it.

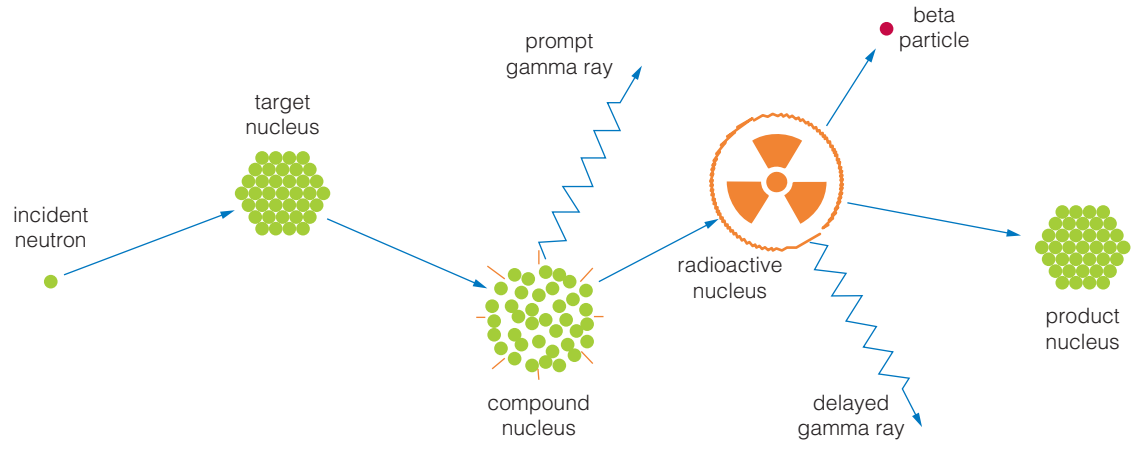


Figure 21 – Diagram illustrating the process of neutron capture by a target nucleus followed by the emission of gamma rays

The NAA technique falls into two categories according to whether the radioactive emissions are measured during neutron irradiation (prompt gamma ray) or at some time after the end of the irradiation (delayed gamma ray), as illustrated in Figure 21. The former is termed prompt-gamma neutron activation

analysis (PGNAA) and the latter is called delayed-gamma neutron activation analysis (DGNAA), also known as conventional NAA. If NAA is conducted directly on irradiated samples it is termed instrumental neutron activation analysis (INAA). In some cases irradiated samples are subjected to chemical separation to remove interfering species or to concentrate the radioisotope of interest, this technique is known as radiochemical neutron activation analysis (RNAA). NAA allows discrete sampling of elements as it disregards the chemical form of a sample, and focuses solely on its nucleus. Therefore, sample preparation requirement is minimal.

5.5.1 Instrumental neutron activation analysis

Detailed description of INAA and its applications in elemental analysis of coal and coal ash can be found in the literature (USGS 1989; Dams, 1992; Palmer, 1990; Abel and Rancitelli, 1975). Around 40 elements in coal and ash can be determined simultaneously by INAA. The detection limit of an element strongly depends on several factors such as the cross-section, the half-life of the isotope produced and the abundance of the γ-rays emitted. As a result the detection limits for the different elements vary over many orders of magnitude. The introduction of the high resolution Lithium-drifted Germanium (Ge(Li)) and more recently the High-Purity Germanium (HPGe) γ-ray detectors made a good differentiation between radioisotopes possible. Data reduction in INAA involves comparison of the γ-ray spectrum obtained from the coal or ash with that of a standard material of established elemental composition. The application of microcomputer assisted data reduction of the gamma spectra further opened the way to a multi-elemental analysis. With automatic data reduction of γ-spectra, large numbers of similar samples can be processed routinely fairly rapidly if only the most intense radioisotopes are measured (Dams, 1992).

The analysis of the whole coal sample by INAA is especially useful in determination of elements that might be volatilised during ashing, such as bromine. Other advantages of INAA include very low detection limits for many elements, significant matrix independence, easily automated, and provides precise data for many major, minor, and trace elements. In spite of its major advantages, INAA also has some considerable drawbacks: (1) for best precision, a neutron reactor should be used as the source of the thermal neutron flux, which is a serious limitation on the availability of the technique; (2) some elements, notably B, Be, Cd, Cu, F, Hg, Mo, Ni, Pb and Tl, are not easily analysed by INAA due to their low cross-sections, insufficient γ-intensities or unfavourable half-lives, and thereby, these elements have relatively large detection limits; and (3) the technique tends to have a long turnaround time because it is typical practice to perform γ-ray counting immediately after irradiation and then again some hours, or days, or even months later so that interference from short-lived radioactive species are eliminated and better precision can be obtained on longer-lived species (Huggins, 2002). In addition, while many elements present in coal and ash can be determined using INAA, no information is provided about the chemical state of the element, which is of vital importance in studying the behaviour and/or environmental impact of the elements during coal utilisation. Despite these limitations, INAA has been widely used to obtain concentration data on major, minor and trace elements in coal and coal ash. Recent INAA studies on coal and ash include investigations on Chinese coals (Ren and others, 1999), Korean coal and its combustion

products (Lim and others, 2013), on fly ash of Malaysian coals (Al-Areqi and others, 2008), on bituminous coals from Indonesia and Australia (Saleh and Suhaimi, 2008), Nigerian coal and coal ash (Ogugbuaja and James, 1995; Ewa and others, 1996), and German and US coals (Palmer and Lyons, 1996).

For the detection of particular elements, with less favourable sensitivity or present in extremely low concentrations radiochemical neutron activation analysis (RNAA), or special irradiation and counting systems can be applied. In RNAA, a radiochemical separation is performed after the neutron irradiation is done to enhance the precision of a determination of an element present in low concentration by avoiding or minimising elemental interferences. Various RNAA methods for the determination of Sb, As, Br, Cd, Cs, Ga, Hg, Rb, Se, U, and Zn in coal have been described in detail by Frost and others (1975).

5.5.2 Prompt-gamma neutron activation analysis

PGNAA is a rapid, nondestructive multi-elemental analysis technique. Most PGNAA analysers use californium–252 (Cf–252) as the neutron source. Typically, the sample will not acquire significant long-lived radioactivity. The response time for measurements is of the order of 1 minute. PGNAA may provide elemental contents and depth profiling for major and minor elements in coal such as H, C, N, P, S, Al, Fe, Ca, Na, K, Si, Cl, as well as B, Cd, Pb and some rare earth elements, especially Sm and Gd. Most of these elements either cannot, or cannot easily, be determined with normal NAA. Oliveira and Salgado (1993) measured elemental concentrations of H, C, N, Cl, Si, Ti, Al, Fe, Ca, Na, K, and S in six coals using PGNAA and compared the results with those obtained by conventional analysis. They found that, except for N, K, S and Ca, the values obtained from the two methods agreed well.

One of the typical applications of PGNAA is an online belt elemental analyser or bulk material analyser used in cement, coal and mineral industries.

5.5.3 Prompt fast thermal neutron analysis

Prompt fast thermal neutron analysis (PFTNA) uses a pulsed deuterium-tritium (d–T) sealed tube generator that produces 14 MeV neutrons in pulses several microseconds long and with a frequency of several kilohertz (kHz). In PFTNA, a coal sample is irradiated with fast neutrons. Some of the fast neutrons are moderated by the coal or moderators placed external to the coal, thereby producing a field of thermal and epithermal neutrons in the coal. Neutrons interacting with nuclei in the coal, results in the emission of γ-rays that have energies unique to each element. The millisecond pulsing of neutrons with a frequency of a few kHz allows the measurement of γ-rays originating from neutron inelastic scattering, thermal neutron capture, and neutron activation. Three separate gamma ray spectra are acquired: one spectrum is acquired during the neutron burst (‘fast spectrum’) and two spectra are acquired in between the neutron bursts (‘thermal spectrum’ and ‘activation spectrum’). By acquiring the gamma rays in three different time windows, there is a significant reduction of the background as compared with the spectra taken with a radioisotopic source. The elemental content of the material is deduced by analysing the γ-ray spectra using a least-squares spectrum deconvolution method.

The use of fast high-energy neutrons has two unique advantages: 1) the neutrons irradiating the material have a wide range of energies, from thermal energies to 14 MeV. The wide energy range opens up many reaction channels such as neutron capture, inelastic scattering and inelastic reactions allowing the direct determination of elements such as O, C, and Na, in addition to all the other elements determined by PGNAA from thermal neutron interactions in coal; 2) because the 14 MeV neutrons are isotropic, multiple experimental setups can be arranged around the neutron generator to determine groups of elements with the highest sensitivity (Dep and Vourvopoulos, 1997). However, the limited life-time of the neutron generator tube restricts its use to a selected number of applications. The amount of radiation generated by PFTNA technology also necessitates a high level of shielding during operation.

Work has been carried out to develop an online elemental analyser based on PFTNA technology (Dep and Vourvopoulos, 1997; Belbot and others, 1999; Vouropoulos, 1999). Recently, a PFTNA online elemental coal analyser developed by Western Kentucky University's Applied Physics Institute (WKU) was demonstrated at a coal-fired power plant. The analyser and associated sampling equipment were located on the main conveyor that feeds the plant coal storage bunkers. The coal analyser identified and quantified the elements of ash formation along with moisture, sulphur, and heat content of the coal being fed to the bunkers. The test results indicated that the PFTNA technology is viable for coal analysis (EPRI, 2008).

5.6 Miscellaneous methods

5.6.1 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a technique used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. The term Fourier transform infrared spectroscopy reflects the fact that a Fourier transform (a mathematical process) is required to convert the raw data into the actual spectrum.

FTIR is a powerful tool for probing the functional groups in coal, ash and chars. As a nondestructive analytical method, it identifies molecular vibration, both stretching and bending, due to the absorption of infrared radiation. A sample exposed to continuously changing wavelengths of infrared radiation absorbs light when the incident radiation corresponds to the energy of a particular molecular vibration. Energies of the stretching vibrations correspond to infrared radiation with wave numbers between 1200 and 4000 cm^{-1}, while the bending vibration is in the range of 500–1200 cm^{-1}. This part of the infrared spectrum is particularly useful for detecting the presence of functional groups, because these groups have characteristic and invariant absorption peaks at these wavelengths (Gupta, 2007). FTIR has been used in the identification of the chemical structure of coal (Li and others, 2012; Saikia and others, 2007; Gilfillan and others, 1999; Cloke and others, 1997). Earlier work found that by using diffuse-reflectance FTIR as a rapid characterisation technique it was possible to predict coal reactivity (Gilfillan and others, 1999; Cloke and others, 1997). Rein and others (2013) determined the quality of fifteen Eastern European coals

using an FTIR system with diffuse reflectance sample interface. By measuring the amount of silicate minerals and the amounts of aliphatic CH stretch in the hydrocarbon region of the coals, they successfully determined the qualities of coals from different parts of the same coal mine and from different coal producing regions.

Figure 22 – A portable Agilent 4100 ExoScan FTIR system (Rein and others, 2013)

Recently, a portable FTIR system has been made available for use in non-laboratory environments. Figure 22 shows a handheld FTIR system by Agilent Technologies. When it is used for in-situ analysis of coal, all instrument functions are executed using the attached PDA. An automated, on-board method for the verification of coal quality is initiated by simple touch screen commands and results are clearly displayed on the PDA (Rein and others, 2013).

FTIR can be coupled to other instruments such as gas chromatographic (GC) or thermogravimetric (TG) analysers, opening up new areas of application. For example, in a study of natural oxidation/weathering of coal, MacPhee and others (2004) used TG–FTIR to measure all the organic oxygen in both fresh and oxidised coal by simultaneous measurement of the three main oxygen-containing gases H_2O, CO and CO_2 evolved during rapid pyrolysis.

5.6.2 Nuclear magnetic resonance spectroscopy

Commonly known as NMR spectroscopy, this technique exploits the magnetic properties of certain atomic nuclei for determining the physical and chemical properties of atoms or the molecules in which they are contained. The solid state ^{13}C NMR spectroscopy is a useful tool for the study of composition and structure of whole coal. In particular, four functional types of carbon in coal can be resolved and recognised: polycondensed aromatic, simple aromatic, oxygen-bound aliphatic and simple aliphatic. Coal is thought to consist of a matrix of aromatic clusters connected by aliphatic bridging groups, aliphatic and carbonyl side chains attached to the aromatic cluster, and solvent-extractable components referred to as the 'mobile phase'. The carbon NMR spectra are derived from the resonance of the C-13 isotope of carbon, which is the only carbon isotope with a magnetic moment. ^{13}C NMR has been used to quantify the average carbon skeletal structure of a given coal with 12 parameters that describe the aromatic and aliphatic regions of the coal matrix. From these structural parameters, combined with an empirical relationship between bridgehead carbons and aromatic carbon per cluster, a description of the lattice structure of coal

can be attained. Useful structural parameters determined from these analyses include the number of carbons per cluster, the number of attachments per cluster, the number of bridges and loops, the ratio of bridge to total attachments, the average aromatic cluster molecular weight, and the average side chain molecular weight (Wemmer and others, 1981; Gupta, 2007). There are several variations in the NMR techniques used for the study of coal and coal chars which include multi-nuclear single-pulse excitation- and cross-polarisation-magic angle spinning (SPE/MAS and CP/MAS, respectively), and hydrogen spin-lattice relaxation. A detailed discussion of characterisation of coal and oil shale using different NMR techniques can be found elsewhere (Maciel and Erbatur, 1994). Solid state NMR spectroscopy has been extensively used in studying chemical structure of coal (Mao and others, 2013; Kalaitzidis and others, 2006; Georgakopoulos, 2003; Straka and others, 2002; Chen and others, 1997). Attempts have also been made to characterise coal ash using NMR spectroscopy (Metsel, 1991; Burchill and others, 1991). Burchill and others (1991) extended the applications of NMR techniques to the characterisation of the inorganic structure of coal. They studied the chemical environments of inorganic elements Na, Al, Si, P and B in coal by measuring the MAS NMR spectra of ^{23}Na, ^{27}Al, ^{29}Si, ^{31}P and ^{11}B. Using the same methods on coal ashes and boiler deposits, they were able to investigate the transformations of these elements in combustion processes.

A recent development is the use of proton NMR (^{1}H NMR) spectroscopy for coal characterisation. The sensitivity of hydrogen atoms to magnetic resonance, the ease in measuring the spectra, and fast data acquisition on relatively cheap low-field NMR instruments makes this characterisation technique particularly useful. Research conducted on Australian coals has produced promising relationships between NMR measurements and coal properties (Harmer and others, 2001). The ^{1}H low field NMR has also been used to characterise the pore structure of coal and to determine coal moisture content (Liu and others, 2013; Yao and Liu, 2012; Yao and others, 2010; Guo and others, 2007).

The NMR imaging technique has found useful applications in studying the swelling property of coal in solvent (French and others, 1993; Ma and others, 1996). Recently, Saito and Kato (2006) developed an in-situ NMR imaging technique that enables the direct observation of coal softening and melting behaviour during heating.

5.6.3 Raman spectroscopy

Raman Spectroscopy is a vibrational spectroscopy technique used to collect a unique chemical fingerprint of molecules. Each molecule has a different set of vibrational energy levels, and the photons emitted have unique wavelength shifts. Vibrational spectroscopy involves collecting and examining these wavelength shifts and using them to identify what is in a sample. Different peaks in the spectrum correspond to different Raman excitations. Raman spectroscopy is a useful tool for characterisation of the structural features of coal and coal-derived products. Raman spectral characteristics, mainly those of the G (graphite) band to crystalline graphite and D (Disorder) bands to any type of structural disorder in the graphitic structure, were used to investigate the coal/char structure and its correlation to other characteristics (for instance the coal rank, the variation in the 'graphite' crystalline size). For coal analysis,

the information gained by Raman investigations has been used to describe char evolution as a function of temperature, and different conversion conditions (Li and Li, 2005; Guedes and others, 2012). In addition, Raman spectral characteristics can be correlated to coal maturation, rank/grade and many other aspects of interest (Kelemen and Fang, 2001; Manoj and Jose, 2011; Manoj and Kunjomana, 2010; Guedes and others, 2012; Li and Li, 2005; Li and others, 2012). A recent review of the work published on the Raman characterisation of the natural organic matter of coals is available (Potgieter-Vermaak and others, 2011). Raman spectroscopy has also been used to identify the inorganic matter such as pyrite in coal and coal derived products (Oliveira and others, 2011; McCarty and others, 1989).

Raman spectroscopy is a nondestructive analytical method that requires minimal sample preparation. It is sensitive to many amorphous compounds and can be used for in-situ analysis.

5.6.4 Laser-induced breakdown spectroscopy

Laser-induced breakdown spectroscopy (LIBS) is technically very similar to a number of other laser-based analytical techniques such as Raman and fluorescence spectroscopy. LIBS is an atomic emission spectroscopy technique which uses highly energetic laser pulses to provoke optical sample excitation. The interaction between focussed laser pulses and the sample creates plasma composed of ionised matter. Plasma light emissions can provide spectral signatures of chemical composition of many different kinds of materials in a solid, liquid, or gaseous state. In principle, LIBS can detect all elements, limited only by the power of the laser as well as the sensitivity and wavelength range of the spectrograph and detector. In particular, LIBS has the ability to detect low-atomic number elements that are difficult to detect using alternative direct analysis techniques for solid samples. If the constituents of a material to be analysed are known, LIBS may be used to quantify the content of each constituent element. LIBS can provide an easy, fast chemical analysis with reasonable precision, detection limits, and cost. Additionally, as there is no need for sample preparation, it is well suited to online and in-situ chemical analysis.

LIBS has found applications in a wide range of fields. For coal analysis, a LIBS system was first developed to analyse low-ash lignites from Victoria (Australia). The elemental analysis of this material posed a particular analytical problem due to its high moisture (up to 70%) and low ash content (around 1%). The LIBS system consisted of a pulsating laser, optical spectrometer, CCD (charge-coupled device) detectors, a data processing computer, and was fully software-controlled. Coal received from the mines was crushed and mixed prior to analysis. The crushed coal was loaded into a sample holder that allow pressing of the sample and direct transfer into the analyser without further handling. The detectable elements in this lignite variety included: Al, C, Ca, H, K, Mg, Na, Fe, and Si. The test results showed that the LIBS system could measure the inorganic components in coal in a matter of seconds. The detection limits were of the order of 0.01% by weight and measurement repeatability and accuracy within ±10%. The technique was further extended to determining bulk properties of coal such as moisture content and calorific value with the use of multivariate analysis of the data to correlate the measured sample fluorescence (from all the elements and molecules observed) to other bulk properties of the material. The commercial units of this

LIBS system were later installed and operated in coal-fired power plants in Australia and Indonesia (Chadwick and others, 2003).

Recently, extensive research work has been carried out worldwide to develop a LIBS approach for coal analysis. Much of the efforts have been focussed on developing a LIBS online coal analyser (Wang and others, 2009; Levy, 2011; Yin and others, 2009; Zhang and others, 2012; Yuan and others, 2012, 2013). For determination of the elements in coal both qualitatively and quantitatively using LIBS, a key step is the proper identification of each emission line of a particular element in a neutral or ionised state and data processing/calibration procedure for quantitative determination. Mathematical models have been developed to process the data obtained from LIBS measurement to identify and subsequently quantify the elements of interest. Work is continuing to improve/optimise the models for better accuracy of the results or to extend the data processing to produce more information on the coal analysed (Yin and others, 2009; Zhang and others, 2012; Romero and others, 2010; Yuan and others, 2013). For instance, Romero and others (2010) developed and tested a LIBS system for analysis of coal ash composition. They also developed a concept to predict coal slagging potential via fusion temperature artificial neural network (ANN) models based on LIBS emission intensity measurements.

The applications of LIBS in the analysis of coal dusts and coal ashes have also been investigated (Ctvrtnickova and others, 2010; Stipe and others, 2012).

LIBS systems are subject to variation in the laser spark and resultant plasma which often limits reproducibility. The latest research in LIBS has tried to improve the accuracy of quantitative chemical analysis.

5.6.5 Mössbauer spectroscopy

Mössbauer spectroscopy (MS) is a useful technique for the analysis of iron-bearing minerals in coal and coal ash. It is well-known that the iron bearing minerals play an important role in slag formation in a coal combustion system. MS provides quantitative information on the occurrence of Fe in different oxidation states, the identification of Fe-bearing phases and the distribution of Fe among those phases. An earlier review providing comprehensive information on the application of MS in coal analysis is available (Huggins and Huffman, 1979). This method is now widely used to analyse Fe and Fe-bearing minerals in coal and coal ash (Patel and others, 2013; Oliveira and others, 2011; Kgabi and others, 2009; Kolker and Huggins, 2007; Bayukov and others, 2005; Medina and others, 2006).

5.7 Online analysis systems

Online coal analysers were developed in the USA, Australia and Europe during the late 1970s and early 1980s, and they have been in use in coal mines, preparation plants and coal-fired power plants for almost thirty years. Online analyses provide automatic, continuous, rapid and relatively accurate process data in real time. Online analysers enable feed forward control to be applied in mines and preparation plants for sorting, blending purposes and stockpile management or to ensure the coal quality meets the contract requirements, as well as in power plants to adjust feed rate, blends or other critical controllable

parameters to meet specific boiler requirements and/or to comply with emission regulations. Commercial online analysers are now available from a number of manufacturers. These analysers apply a wide range of technologies including nuclear, microwave, ultrasonic and optical to deliver an appropriate online solution. The instruments can be integrated into the plant central control system and incorporate the latest web based control technology for remote administration and diagnosis.

5.7.1 Technologies

There are three types of online coal analysers:

- online moisture meters, most of them employing microwave technology but magnetic resonance is also used for moisture determination;
- online ash gauges mostly using gamma ray attenuation technology;
- elemental analysers for ash, sulphur, and sometimes ash constituent analyses. Various technologies can be used for elemental analysis. When combined with a moisture meter, as is generally the case, moisture, calorific value and sulphur content of coal can also be determined.

5.7.1.1 Moisture measurement

Microwave attenuation is the most commonly used technique for measurement of moisture in coal. The moisture meter is installed with the transmitter and the receiver placed across the coal under test. An electromagnetic wave is generated and passed through the coal by the transmitter. Water molecules in the coal absorb the electromagnetic energy and attenuate the transmitted signal, and the amount of electromagnetic energy absorbed is detected by the receiver. Despite the complexity of the physical structure of coal, there is usually a simple linear relationship between the moisture content and the amount of energy absorbed (at least in a limited range of moisture content).

Recently, the emerging technology of Magnetic Resonance (MR) has been applied to moisture meters offering a more direct measurement. This technique is based on the same scientific phenomenon as Magnetic Resonance Imaging (MRI). MR operates by the rapid application and removal of radio frequency electrical pulses within a magnetic field. Water content is analysed through the MR signal induced by hydrogen atoms in water molecules placed in magnetic fields. MR provides precise hydrogen proton measurements leading to very accurate moisture measurement and hydrogen proton inputs into the calorific value determination. While microwave measures only free moisture, MR measures all (both free and bound) moisture. However, MR instruments have historically been large, sophisticated, and expensive.

Moisture meters are often found in conjunction with elemental analysers, but sometimes are used alone, or in conjunction with ash gauges.

5.7.1.2 Ash determination

Two common techniques employed by ash gauges are dual-energy γ-ray transmission (also called dual-gamma or low-energy transmission LED), and natural gamma detection.

Dual-energy γ-ray transmission (DUET)

DUET is the most commonly used technique in online coal ash analyses. It is based on the fact that ash constituents have a considerably different atomic number to the combustible matter (C, H, N, O) in coal. The technique consists of measuring the transmission of both high and low energy gamma rays through coal. The transmission of high energy gamma rays, which are mainly Compton scattered, depends on the mass per unit area of coal in the beam. The transmission of low energy gamma rays, which are subject to both Compton scattering and photoelectric absorption, is sensitive to both the mass per unit area and the ash content.

DUET uses two gamma ray sources of differing energy levels (the high-energy source, usually americium 241 and the low-energy source either cesium 137 or barium 133) and measuring the relative attenuation of the gamma rays passing through the coal. The attenuation of the high-energy gamma ray is roughly proportional to the mass of material between the source and the detector. On the other hand, the low-energy gamma ray is attenuated differently according to the atomic number of the atoms between the source and detector. The low-energy gamma ray is attenuated more by the elements found in coal ash such as Al, Si, Fe, Ca but not as much by C, H, N and O in coal. When the two gamma sources are used in combination, one tends to act as a normaliser, accounting for mass flow changes, whereas the other can detect variations in ash content. Figure 23 shows a diagram of a DUET ash analyser.

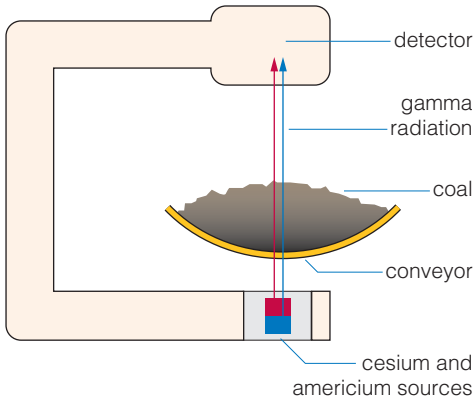


Figure 23 – A DUET ash analyser (Realtime Group at www.realtimegrp.com)

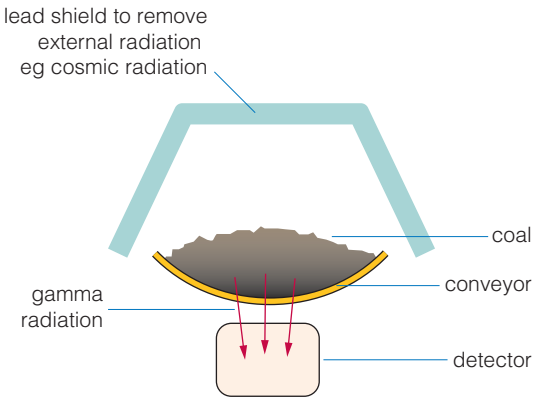


Figure 24 – A natural gamma ash analyser (Realtime Group at www.realtimegrp.com)

The main advantages of a DUET ash gauge is its ability to measure the ash content of coal directly on a conveyor belt independently of the mass of coal on the belt and of the belt speed. However, it is very sensitive to, and incapable of detecting, changes in the percentage of ash that is iron oxide (Fe_2O_3). A change in the Fe_2O_3 percentage of ash as little as 1% in a 10% ash bituminous coal will cause an error in total ash determination of about 0.6%. This phenomenon is proportional to the total ash amount, so for a typical raw coal of 25% ash, the impact is far greater (about 1.5%) (Woodward, 2007). Prior to use, the ash gauge needs to be calibrated based on ash composition of the coal to be analysed. If the percentages of Fe or Ca in the ash changes significantly, the calibration will need to be redone.

Natural gamma detection

This technique relies on the tendency of some coals to possess, as a fairly constant part of the ash, isotopes of potassium (K), uranium (U) and thorium (Th), which are natural gamma emitters. Thus, as the ash levels increase, the amounts of these gamma rays and the amount of their signal received by the detector also increase. This method uses a sensitive scintillation detector (typically sodium iodide) that detects the radio-nuclides emitted by K, U and Th. Through a suitable calibration, the gamma signal is converted into an ash percentage reading. This technique does not use any radioactive sources, eliminating some costs and issues associated with many of the other radio-nuclide based analysers. As the measurement is unaffected by Fe and Ca content, it is ideal for coals with highly variable compositions of these elements which can dramatically affect the results of DUET systems. This technique has lower costs. The obvious limitation of the natural gamma ash gauge is that it relies on the assumption that the naturally radioactive K, U or Th is a constant percentage of the ash, which is clearly untrue. The measurement attained with the natural gamma technology is less accurate than some other technologies. A further drawback is the significant shielding requirements necessary to prevent false readings from other naturally occurring radiation sources (Willett and Corbin, 2011; Woodward, 2007). A schematic of a natural gamma ash analyser is shown in Figure 24.

5.7.1.3 Elemental analysers

In coal the elements of interest are S, Cl, Si, Al, Fe, Ca, Ti, K and Na. Elements such as Si, Ca, Al, Fe make up the major ash oxides and by summing the ash oxides the percentage of ash in the coal can be determined.

Measurement of S is dictated by the control of SO_2 emissions from coal-fired power plants. Determination of elements such as C, H, O, N. and S allows for the calculation of heating value and plant efficiency. Elements like Na and Cl have harmful effects on boilers, causing fouling and slagging. There are a few different technologies used in online elemental analysis of coal. Prompt fast thermal neutron analysis (PFTNA), x-ray fluorescence (XRF) and prompt gamma neutron activation analysis (PGNAA) are the most widely used techniques. LIBS has also shown its potential applications in online coal analysis.

Prompt fast thermal neutron analysis (PFTNA)

PFTNA is capable of measuring the major and minor elements contained in coal. It utilises nuclear reactions produced from fast and thermal neutrons, and isotopes with half-lives of seconds or minutes. A key feature of the analyser is its ability to analyse automatically three distinct gamma ray spectra, and produce the elemental content of coal as it moves through a coal chute or conveyor. The main advantages of the analyser include self calibration independent of the coal rank, and better accuracy in the determination of elements such as C, O, and Na. The minimum detection limit of Na is close to 200 ppm. Also, because there is no radioactive source being used, this technology is quite safe when it is not powered up. However, it faces challenges due to tube disposal issues, safety during operation and the size of the equipment. Neutron generator tubes are also costly to manufacture and have a limited life.

Prompt gamma neutron activation analysis (PGNAA)

Online coal analysis by PGNAA usually uses Californium–252 as the neutron source (thermal energies of 2.4 MeV) and a sodium iodide detector to measure gamma rays emitted by thermal reactions. It is capable of measuring almost all elements but is typically used to determine the major elements (except for O) in coal, S, Si, Al, Fe, Ca, Ti, K and, if the percentage in coal is high enough, Na. PGNAA equipment is usually combined with a moisture meter to complete the determination of coal properties. PGNAA penetrates the entire sample volume thereby representatively analysing the full stream of coal. The density is measured and is used for bed depth correction. Smaller bed depths result in a reduced gamma ray signal from the coal. The analyser calibration is independent of the coal seam. This method can be sensitive and accurate depending on the element analysed. It is the most widely used technology for full elemental coal analysis, particularly when it is important to know some of the coal's specific elements, such as sulphur. The biggest drawback is the requirement of maintaining a nuclear isotope source to provide the neutrons. This draws extra costs in handling, training, meeting regulatory requirements, and replenishing the source. Like PFTNA, the neutron generation tubes of PNGAA are expensive and have limited life. High level shielding is required so the equipment is bulky.

x-ray fluorescence (XRF)

The XRF online analyser measures ash, sulphur, calorific value and a complete proximate analysis. It can be coupled with a microwave moisture meter to monitor moisture. In the past, detector technology limited the application of XRF technology primarily for detecting elements with atomic numbers greater than about 20. Silicon photo iodide (Si PIN) detectors, which are electrically cooled, are now employed and the improved detector technologies have extended the useful range into the characterisation of

elements with lower atomic numbers of central importance for coal analysis However, an XRF online analyser is unable to detect elements with atomic number smaller than 10 and therefore it cannot measure C, H, N, and O in coal. XRF is primarily a 'surface measurement technology' as the x-rays are unable to penetrate the entire sample volume thereby representatively analysing the full stream of coal. This method requires finely ground homogeneous samples and a carefully prepared stream of material. The system requires no radioactive source, which increases reliability and safety with no special shielding. XRF cannot match the precision of PGNAA but has low costs so it can be economically viable for selected applications (Moodley and Minnitt, 2009; Willett and Corbin, 2011).

Laser induced breakdown spectroscopy (LIBS)

LIBS is emerging as a potential competitor for technology for online coal elemental analyser. LIBS can detect all elements by using a highly energetic laser pulse. It can measure the major ash constituents in coal such as Si, Al, Fe, Ca, K and Ti, as well as Na, Mg which PGNAA cannot in most coals. Studies have been performed to determine the feasibility of replacing PGNAA analysers with LIBS analysers. A trial was arranged at Optimum Colliery (South Africa) in which a LIBS analyser was installed in line with a PGNAA analyser and laboratory data served as reference in the assessment of analytical accuracy. The trial was carried out over a four-month period. Comparisons between the LIBS and PGNAA measurements revealed an average standard error between the two of only 0.32% (Gaft and others, 2008). Recently, an online coal analyser based on LIBS technology coupled with a MR moisture meter, developed by Progression, Inc (USA), was installed and tested at a Powder River Basin (PRB) mine. As the mine already had a two-stage sampling system on the silo feed belt, comparisons of the results from laboratory analysis and those obtained by the analyser were carried out for a three-week period during February to March 2012. It was claimed that LIBS achieved accuracies comparable to those of other elemental analysis technologies (primarily PGNAA) for S and Si, Al, Fe, Ca, K and Ti. The system outperformed PGNAA analysers in determining the calorific value and moisture of coal, and in particular, in Na_2O since sodium levels in PRB coals lie below the detection threshold for PGNAA analysers (Woodward, 2013; Davis, 2013).

The LIBS analyser does not use a radioactive source so no special shielding is required. As a result, the system is more compact with a small footprint, light in weight and easy to install compared with PGNAA analysers. This technique is fast and sensitive. Commercial LIBS online coal analysers are now available. The main disadvantage is that a LIBS analyser analyses surface chemistry of the coal exclusively and not the volume as the laser pulse ablates a small amount of material from the coal surface. Therefore, like XRF analysers, it requires finely ground homogeneous samples.

5.7.2 Location of an online analyser

An online analyser can be installed on a coal conveyor belt (cross-belt online analyser) or on a sample stream of the online sampling system (sample-stream online analyser). The cross-belt elemental analysers are used for process control and sample-stream elemental analysers for quality control.

The cross-belt elemental analysers are less accurate than sample-stream elemental analysers, but they do carry many advantages such as little or no sampling requirement, lower cost and quicker installation and probably greater uptime. Also, the analyser can be located where it is needed, not where there is a place for a sampling system. With their simple design, it is much easier to relocate the analysers when needed and they are easy to maintain. Field performance has shown these devices to be of adequate accuracy for many applications. If properly used and maintained, they offer the utility a cost-effective solution to many process challenges (Moodley and Minnitt, 2009).

However, with all the advantages there are also some limitations associated with the cross-belt online analysers that include (Moodley and Minnitt, 2009; Woodward and others, 2003):

- whereas a sample-stream analyser has an optimal and constant cross-section for elemental analysis, the cross-belt analyser must accommodate whatever belt loading and cross-sectional profile it receives leading to reduced accuracy;
- obtaining physical samples to calibrate and compare to the analyser is a challenge. Because of the size of the standards required, the use of reference blocks is also more difficult, particularly in wide belt applications.

Two primary factors should be considered when choosing an analyser location. If the coal is sorted, the analyser should be located close to, but obviously upstream of, the sorting point. A coal complex consisting of numerous coal flow paths may need more than one analyser with the preferred sites determined by the greatest variability in coal quality. In a blending application, the analyser is preferred immediately downstream of the point at which all the coal streams come together. Careful consideration of size and access requirements will be required when determining the optimum location for placing an analyser. Unfortunately, the ideal process location is often unavailable due to the second key factor namely, physical or environmental constraints. Such constraints may include the lack of a sampling system (to either feed the analyser or to be able to obtain occasional physical samples for analyser comparison purposes), lack of headroom or horizontal space limitations, inconvenience of running utilities, and inadequate protection from the elements. As a result, the choice of analyser location is often compromised (Moodley and Minnitt, 2009).

5.7.3 Selecting an online analyser

The choice of the type of an analyser is mainly between an ash gauge and an elemental analyser, whether or not coupled with a moisture meter. Criteria of greatest importance in choosing between ash gauges and elemental coal analysers include parameters of interest, coal complexity and coal quality variability, and accuracy requirement. There is a large gap in price and performance between elemental analysers and ash gauges. The economics and choice of technology will depend on why the system is being installed. If the coal producer or utility is interested primarily in ash, moisture, and calorific value, and there is no need to measure sulphur online, the simple ash gauges coupled with moisture analysers, both mounted over the existing conveyor, may be adequate for the task and cost only around one third that of elemental analysers. In multiple seam applications and in cases where the iron fraction in the ash varies

significantly, a dual gamma ash gauge is unlikely to perform acceptably. As the accuracy requirements become more stringent or if the determination of sulphur is required, the choice may be a cross-belt elemental analyser or, for the best accuracy possible, a sample-stream elemental analyser (Moodley and Minnitt, 2009; Woodward and others, 2003).

When choosing between the sample-stream analyser and the cross-belt analyser, although it is related to the quality requirement, sample-stream analysers are more appropriate for load out situations where quality is paramount. Further upstream, where control decisions can be less exact, a cross belt analyser is often more appropriate. Proximity to, or existence of, a sampling system will also determine the appropriateness of the technology. The sample-stream analyser is an appropriate technology if a complementary sampling system is already available; where no proximal sample position is available, a cross-belt analyser becomes relatively more attractive.

In selecting appropriate technology, the main decision criteria usually include the objective of the installation, system performance and pricing. In choosing between the PGNAA and PFTNA technologies, if the major ash constituents Si, Al, Fe, Ca, Ti, K, and S as well as ash, volatile matter and CV are the main interests then a PGNAA instrument may be sufficient. If measurement of the elements Na, Cl, C, O are also required, then PFTNA is the more suitable option. Na, Cl and C can be measured by PGNAA only if their concentration in coal is sufficiently high.

In choosing between XRF and PGNAA, the advantages of XRF over a PGNAA system are: (1) the cost is lower, (2) the technique does not use neutron sources. The energy levels of the x-rays used are low, and they can be easily stopped by the steel enclosure; (3) easier to calibrate and to maintain. The main disadvantages of the technology are: (1) it is less precise than PGNAA; (2) it does not provide full elemental analysis; (3) it measures surface composition only. Table 15 and Table 16 compare the XRF and PGNAA instruments, and their capabilities, respectively.

Table 15 – Comparison of PGNAA and XRF (Hallee, 2010)

PGNAA	XRF
Californium source: • average 2 year lifetime	x-ray tube: • more than 6 year lifetime
High maintenance cost	Low maintenance cost
Difficult licensing	Easy licensing
Measures nearly all elements (no Oxygen)	Measures elements with atomic number >10
Better precision	Less accurate than PGNAA
Non-integral volume measurement	Surface measurement
Dependent on the load below the saturation volume	Independent of the load
Difficult to calibrate, large samples required	Easy to calibrate, small samples required

Table 16 – Elemental measurement capabilities of PGNAA and XRF (Hallee, 2010)		
Measurements	**PGNAA**	**XRF**
Proximate analysis		
Moisture	✓	✓
Ash	✓	✓
Sulphur	✓	✓
CV	✓	✓
SO_2	✓	✓
Elemental analysis		
C	✓	-
H	✓	-
N	✓	-
S	✓	✓
Cl	✓	✓
Si	✓	✓
Al	✓	✓
Fe	✓	✓
Ti	✓	✓
Ca	✓	✓
K	✓	✓

When compared with PGNAA, LIBS has advantages which include: (1) it can measure elements such as O, Na, Mg which PGNAA cannot or has difficulty to measure; (2) it is fast; (3) has lower costs; and (4) it does not use a radioactive source. No heavy shielding is required so it is light, has a small footprint and is easy to install. The major disadvantage of LIBS is that it measures only the surface of the coal particles.

Because XRF and LIBS only analyse the surface of coal particles, for best accuracy, the preferred location for XRF and LIBS online elemental analysers is on the sample stream conveyor where the coal has been ground to a fine particle size and homogenised.

Comments

Certain coal properties (for instance, the elemental composition of coal) can be determined by several instrumental methods. Each method has its advantages and limitations. In general, no single method yields a complete analysis of coal and it is often necessary to employ a combination of methods. A disadvantage of some of the instrumental methods is the small sample size used which may not be representative of the quantity of coal being analysed. In addition, most instruments need careful calibration in order to perform precise and accurate, and bias free coal analysis. Most often, the accuracy of the results is highly dependent on the quality and suitability of the standard materials used to standardise the instruments.

6 Summary

With coal being a major source of fuel in many parts of the world and large volumes of coal traded locally and internationally every year, there is a need to understand the fundamental properties of coal so as to establish the price of the coal, and for quality and process control. Also, there is a continued interest in the efficient use of coal and the development of clean coal technologies, making the area of coal evaluation of paramount importance.

Standards

A large number of test methods for evaluation of coal and coal products have been developed and some of the well established test methods are recognised by various standards organisations as standard methods for coal evaluation/characterisation. International and various national standards have been set up to provide procedural guidelines for coal sampling and sample preparation, coal analysis and bias tests for sampling and analytical systems. The ISO Standards are internationally accepted and many national standards are largely based on the ISO Standards. The ASTM Standards are mainly adopted in the USA and Canada, and are widely used in universities and research institutions in the study of coal and in developing new analytical techniques of coal.

Coal sampling

Coal is highly heterogeneous in nature consisting of particles of varied shapes and sizes each having different physical characteristics, chemical properties and residual ash content. Proper sampling and sample preparation are critical for accurate analysis. Obtaining a representative sample implies that every particle has an equal chance of being selected. A correct and representative sample requires that every particle in a lot being sampled is equally represented. A representative sample is collected by taking a definitive number increments, periodically throughout the entire coal lot being sampled. The number and weight of increments required for a desired degree of precision depends on the variability of the coal which increases with increasing impurities. The sampling of coal can take place from either stationary lots or from moving streams. Sampling from stationary lots is particularly problematic because in many cases it is not in compliance with the fundamental sampling principle stipulating that all parts of the lot being sampled must be accessible for physical sampling. Therefore, sampling from moving streams is preferred. The best location for sampling from a moving stream is at the discharge point of a conveyor belt or chute, that is a falling stream where the complete stream can be intersected at regular intervals. However, cross-belt cutters are now more popular and are widely used in the coal industry. The stopped-belt sampling, when properly executed, is considered as bias free and is recommended by several standards as a reference sampling method when carrying out a bias test procedure.

Sampling can be carried out manually or mechanically. Manual sampling is subject to human errors and is known to be incorrect and unreliable. Whenever possible, mechanical sampling from moving streams should be the choice for coal sampling.

Whichever sampling method is used, the sampling equipment used should meet the design criteria set by the relevant Standards and correct procedures must be followed in order for representative and correct sampling.

Advances in technologies have led to automated mechanical sampling systems ranging from single stage to multistage sampling systems incorporating crushing, discrete sub-sampling and reject handling. Modern mechanical sampling systems are more accurate and precise, and are designed to accommodate the installation of an online coal analyser within its subsystem..

Sample preparation and bias testing

The sample preparation process may involve constitution of samples, reduction (crushing), division, mixing and drying, or all or a combination of these. Issues such as loss or gain of moisture, improper mixing of constituents, improper crushing and grinding, and oxidation of coal may arise during the sampling and sample preparation processes. To minimise moisture contamination, all standard methods include an air-drying stage in the preparation of the analysis sample to provide a stabilised sample that is not subject to further moisture change. The sample is then reduced and divided to provide an analysis sample. Sample division can be carried out mechanically or manually. Various types of mechanical divider are commercially available which meet the design criteria specified by relevant standards. The minimum mass of divided samples depends on top size and is specified in the relevant standards. In general, the coal preparation steps should be done rapidly, and in as few steps as possible. The sample should be protected from moisture change, oxidation and contamination.

Testing for bias in a coal sampling system is an essential part of coal analysis and is of significant importance. Bias testing on sampling systems should be carried out periodically. All bias testing is based on a matched pairs experimental design. A minimum number of 20 pairs of observations is recommended by international standards. Tests for bias can be carried out for ash, moisture or any other variable required but two parameters, moisture and ash, are thought to be sufficient for a bias test.

Standard laboratory analysis of coal

Routine coal analysis and testing generally include proximate analysis, ultimate analysis, ash analysis and heating value. In addition, special coal analyses such as determination of trace elements, coal hardness, ash fusion temperature may also be executed. The proximate analysis of coal is an assay of the moisture, ash, volatile matter, and fixed carbon as determined by series of prescribed or standard test methods. Moisture, volatile matter, and ash are all determined by subjecting the coal to prescribed temperature levels for prescribed time intervals. The losses in weight are, by stipulation, due to loss of moisture and, at the higher temperature, loss of volatile matter. The residue remaining after ignition at the final temperature is called ash. Fixed carbon is the difference of these three values summed and subtracted from 100.

Ultimate analysis determines the percentage mass fraction of the major constituents of coal like carbon, hydrogen, sulphur, nitrogen, and, usually by difference, oxygen. Carbon and hydrogen are determined by

combustion of weighed sample of coal in dry oxygen in a closed system at specified temperatures to convert all the hydrogen to H_2O and all the carbon to CO_2. These products are absorbed by suitable reagents and determined gravimetrically.

The Kjeldahl method for determining nitrogen in coal has been used for many years. However, the international standards that describe the procedures of the Kjeldahl method have recently been withdrawn but some national standard organisations still recognise this method as a standard test method for nitrogen. International and various national standards recommend that the total carbon, hydrogen and nitrogen contents be determined by instrumental methods.

The three most widely used test methods for sulphur determination are the Eschka method, the bomb washing method, and the high-temperature combustion method, all based on combustion of the sulphur-containing coal to produce sulphate, which can be measured either gravimetrically or volumetrically. Total sulphur values alone are not adequate in assessing a cleaning process for reducing the sulphur content of coal. Methods for determination of the different forms of sulphur in coal are specified by various standards.

The calorific value is determined in a bomb calorimeter either by a static (isothermal) method or by an adiabatic method, with a correction made if net calorific value is of interest.

The ash is prepared by heating the coal under different prescribed conditions depending on the standard test methods selected for determination of major and minor and/or trace elements in coal ash. The elemental composition of coal can be determined by instrumental analysis methods such as AAS/AES, ICP-AES, ICP-MS, AFS, XRF or a combination of these techniques.

The analytical techniques used to measure mineral matter in coal are virtually the same as those used to measure trace elements in coal and coal ash.

Tests for determination of chlorine are performed by burning a coal in oxygen, and the chlorine formed is collected and analysed. There are two standard methods of determining chlorine in coal, oxygen bomb combustion/ion selective electrode method and combustion methods with or without Eschka mixture. Several techniques can be used for the determination of Hg in coal and combustion residue. Various methods are selected by different standards organisations as standard methods.

The ash fusibility determination is an empirical test designed to simulate as closely as possible the behaviour of coal ash when it is heated in contact with either a reducing or an oxidising atmosphere. The free-swelling index is a measure of the volume increase of a coal when heated under specific conditions and is reported in numbers from 0 to 9, with higher values considered superior from a coking standpoint. The swelling property of hard coal/bituminous coal can be measured using a dilatometer. The grindability of coal is determined using a Hardgrove machine.

Due to the heterogeneous nature of coal and the fact that many of the test methods applied to coal analysis are empirical in nature, strict adherence to the standard procedures is necessary to obtain repeatable and reproducible results.

Instrumental analytical techniques

A large number of instrumental analytical techniques have been shown to have wide applicability to coal analysis and are now widely applied for analysis of coal and coal products. These techniques are based on a wide range of technologies including x-ray spectroscopy, electron microscopy, atomic spectroscopy, mass spectrometry, neutron activation analysis, Fourier transform infrared spectroscopy, and laser-induced breakdown spectroscopy. Many of these techniques are fast, sensitive, simple to operate, have low detection limits, and if properly calibrated, accurate. In particular, many of the instruments are capable of determining multi-elements simultaneously. Additional information such as chemical forms of the elements may be obtained. Some instruments require minimal sample preparation and can be used for in-situ measurements. Many of such instrumental methods have been well developed and adopted by national and international standard organisations as standard test methods for coal analysis. Other instrumental test methods have been applied to coal analysis by companies and in laboratories in may parts of the world although they have not obtained Standard status.

Online analysers provide an automatic, fast, relatively accurate, and instantaneous method of coal analysis for pricing, quality or process control, and SO_2 emissions control. There are three types of online coal analysers: moisture meters, ash gauges and elemental analysers. Various technologies can be applied. Most moisture meters employ microwave technology but magnetic resonance is also used for moisture determination. Microwave moisture meters are low cost, simple to use and reliable. MR measures all (both free and bound) moisture but it is large, sophisticated and expensive. Two common techniques employed by ash gauges are dual-energy γ-ray transmission (also called dual-gamma or low-energy transmission LED), and natural gamma detection. DUET is the most widely used due to its ability to measure the ash content of coal directly on a conveyor belt independently of the mass of coal on the belt and of the belt speed. However, it is incapable of detecting changes of iron oxide (Fe_2O_3) in ash and its results are affected by changes in the percentages of Fe or Ca in the ash. Natural gamma detection is ideal for coals with highly variable compositions of Fe and Ca and is cheaper. However, it is less accurate than some other technologies that requires significant shielding.

Technologies used in online coal elemental analyse include PFTNA, XRF and PGNAA and more recently LIBS. PGNAA is capable of measuring most of the major elements (except for O, and Na if its percentage in coal is low) in coal. PGNAA can be sensitive and accurate depending on the element analysed. Its calibration is independent of the coal rank. It is the most widely used technology for full elemental coal analysis. The biggest drawback is the requirement of maintaining a nuclear isotope source to provide the neutrons. PFTNA is capable of measuring the major and minor elements contained in coal. The main advantages of the PFTNA include self calibration independent of the coal rank, and better accuracy in the determination of elements such as C, O, and Na, which PGNAA cannot or has difficulty in detecting. XRF

cannot match the precision of PGNAA, and is unable to measure C, H, N, and O in coal. However, it has low costs so it can be economically viable for selected applications. LIBS is emerging as a potential competitive technology for online coal elemental analysers. LIBS can detect the major ash constituents in coal such as Si, Al, Fe, Ca, K and Ti, as well as Na, Mg which PGNAA cannot in most coals. The main disadvantage is that a LIBS analyser, like XRF analysers, analyses surface chemistry of the coal particles and therefore requires finely ground homogeneous samples.

An online analyser can be installed on the coal conveyor belt (cross-belt online analyser) or on the sample stream of the online sampling system (sample-stream online analyser). The cross-belt analysers are less accurate but they have advantages such as little or no sampling requirement, lower cost and quicker installation. Also, the analyser can be located where it is needed, not where there is a defined place. However, they also have some limitations like the difficulty in obtaining physical samples to calibrate and diminished accuracy due to changes in belt loading and cross-sectional profile. Careful consideration of size and access, and application requirements is required when determining the optimum location for placing an analyser.

The choice of an analyser is mainly between an ash gauge and an elemental analyser, whether or not coupled with a moisture meter. Criteria of greatest importance in choosing a suitable online analyser include the purpose of the installation, coal complexity and coal quality variability, accuracy requirement and costs.

A disadvantage of most of the instrumental methods is the small sample size used which may not be representative of the quantity of coal being analysed. In addition, most instruments need careful calibration in order to perform precise, accurate, and bias free coal analysis. Most often, the accuracy of the results is highly dependent on the quality and suitability of the standard materials used to standardise the instruments.

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