Trace and minor elements in coal.

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TRACE AND MINOR ELEMENTS IN COAL

presented by

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Abstract of a thesis in part fuflilment for the degree of Doctor of Philosophy by William Charles Pearce, entitled:

Trace and Minor Elements in Coal

Several instrumental techniques have been evaluated for the determination of trace and minor elements in coal.

Electrothermal atomisation and atomic-absorption spectroscopy using coal slurries gave accurate results for the determination of arsenic, despite the identification of aluminium spectral interferences. Selenium determined using the method with deuterium arc background correction produced 'structured' backgrounds which were corrected by the Smith-Hieftje system. The method has wide application for trace metal analysis.

Scanning electron microscopy and energy-dispersive X-ray analysis produced accurate results for the determination of chlorine and minor elements in pellets of coal powders. The determination of sulphur was inaccurate because this element occurs in different mineralogical forms in coal. Total elemental analyses were also successfully correlated with ash contents of coal.

Wavelength dispersive X-ray fluorescence analysis of pellets of powdered coal gave precise and accurate results for determinations of chlorine and phosphorus. The different fluorescent yields of organic and inorganic sulphur in coal caused inaccuracy in determinations of this element. Backscattered radiation was used to estimate ash content and the possibility of multi-element analysis of coal was indicated.

Inductively coupled plasma-optical emission spectroscopy was used for multi-element analysis of coal ash. The method gave a five-fold increase in speed of analysis, without loss in accuracy or precision, compared to BS procedures and is recommended for trace element determinations.

All these techniques should be regarded as complementary and can be expected to make a significant contribution to coal analysis.

The importance of the mode of occurrence of elements in coal has been illustrated by studies of chlorine. Long-held views have been disproved and the likelihood is that chlorine is present in one form, uniformly distributed and linked ionically to coal but evolved as hydrogen chloride at low temperatures. It has no relationship with nitrogen, sodium or other alkali-metals in coal.

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CONTENTS

1.1 BRIEF HISTORY, OCCURRENCE AND FORMATION OF COAL

1.1.1 History

Coal is the most abundant of the fossil fuels and its formation occurred several hundred million years ago by the action of heat and pressure on buried decaying vegetable matter. A comprehensive treatise of coal formation and composition was given by Francis.[1]

Coal has been known from ancient times even though in the ages preceding the industrial revolution it did not play a part of any great importance. During several hundred centuries B C the Chinese mined and utilised coal. (Chengi mines). Much later Marco Polo mentioned coal as one of the curiosities he found in China. The Greek philosopher Theophrastos, a pupil of Aristotle knew coal and called it 'anthrax', from which the word anthracite was derived. When the Romans invaded Gaul they noted that a 'flammable earth' was being excavated from the mountains.

In the middle-ages coal was rediscovered in Europe and the oldest documents on coal mining date from the twelfth century. The use of coal was prohibited in many places on account of 'the evil smelling smoke'. It was not until the end of the eighteenth century that coal assumed a significant role in the economy which it has maintained. The UK national production increased to a maximum of 287 million tonnes in 1913 which represented virtually the total energy demand of the country. In Britain today the National Coal Board is a very large organisation, produces some 120 million tonnes of coal per year and employs some 250,000 people.

1.1.2 Occurrence

It is extremely difficult to make estimates of the world's coal reserves and therefore figures published on this subject are disputable. However it is generally accepted that approximately 80 percent of all extractable coal reserves occur in North America, Asia and the USSR. The coal resources of China and USA together equal those of the USSR. Western Europe has less than 10 percent of the estimated reserves, the United Kingdom with 150×10^9 tonnes accounting for about one half of this amount.

1.1.3 Origin

Coal originated through the accumulation of plant debris that was later covered, compacted and changed over a period of millions of years into the 'organic rock' that we find today. Most bituminous coal seams were deposited in swamps that were regularly flooded with nutrient containing water that supported peat-forming vegetation. The lower levels of the swamp waters were anaerobic and acidic; this environment promoted structural and biochemical decomposition of the plant remnants. This microbiological and chemical alteration of the cellulose, lignin and other plant substances, and later the increasing depth of burial, resulted in a decrease in the percentage of moisture and a gradual increase in the percentage of carbon. This change from peat through the stages of lignite, (brown coal) bituminous coal and ultimately anthracite, (the process called "coalification") is characterised physically by decreasing porosity and increasing gelification and vitrification.

Some schools of thought regard the high pressures exerted by overburden strata as most important for the chemical changes in coalification, others regard bacterial decomposition as the main agency,[2,3,4,5,6] but the universally recognised factor involved in coalification is undoubtedly temperature.[7] The time-temperature relationship, with the temperature increasing with increasing depth, accounts for the general truth of Hilts rule,[8] which states that coals from greater depth have undergone greater coalification. The degree of coalification is often signified by the coal 'rank'. The disagreement concerning the origin, and in particular the metamorphosis of coal, is further exacerbated by the question as to whether cellulose or lignin of plant tissues became the principal coal forming material. It is however without doubt that both these constituents are the major precursors of coal.[9,10,11.]

1.2 PETROGRAPHY OF COAL

The banded appearance of coal has attracted the attention of several scientists and detailed examination revealed quite distinct coal types. At the beginning of this century two serious attempts to classify coal types were made, one in England,[12] the other in America.[13] The work carried out in England was based on the visual study of bituminous coals, and the outcome was generally accepted by coal scientists here and in Europe. The American study using microscopy attempted to relate the distinguishable components of coal with the plant materials from which they originated. Although the two systems have been compared the sets of terms are not really equivalent and a true correlation cannot be attained. The Stopes[12] nomenclature is used by the National Coal Board and it identifies the following principal components:

vitrain:-	" coherent and uniform, brilliant, glossy, vitreous in texture, breaking with conchoidal fracture. "
clarain:-	" smooth glossy shine when broken at right angles to the bedding plane, finely banded surface lustre. "
durain:-	" hard with close firm texture which appears granular. A broken face has a lumpy matt appearance. "
fusain:-	" occurs chiefly as patches or wedges, it consists of powdery, friable, readily detachable fibrous strands. "

In addition to the above types there are also boghead and cannel coals. These have a dull metallic-like lustre and break with a conchoidal fracture. A splinter of these coals can be ignited with a naked flame which will continue to burn. Boghead coal has a dull brownish colour whilst cannel coal is black. The latter two types are thought to have originated from the coalification of vegetable mud deposited at the bottom of swamps.

The introduction of microscopic examination of coal using transmission[14] and reflected light oil immersion techniques[15] prompted Stopes to update her original classification[16] and the expression 'coal macerals' was first introduced. The above account is of necessity only a brief description of coal maceral identification and terminology, and for a more detailed description the reader is referred to the appropriate texts.[7,17,18]

1.3 CLASSIFICATION OF COAL

In view of the wide variation in the properties and composition of coals it is not surprising that its classification has proven complex. As many as fourteen bases[17] have been used for coal classification ranging from as widely different parameters as visual appearance, to sharpness of X-ray diffraction peaks. The most useful classification for coal scientists is based upon a combination of chemical analysis and physical properties. The first attempt to establish some ordered system to coal classification was by Regnault[19] who with Grüner[20] published work based on the percentage of residue obtained when coal is heated (carbonisation). This terminology is still used in France.

Early work was also carried out in Germany[21,22] and in the USA[23,24] but it was not until Parr[25] combined calorific value with volatile matter and fixed carbon that the coal classification currently used in the USA first began to take shape. A very detailed account of the historical development of the classification of American coals is given by Rose.[26]

In Great Britain Seyler[27,28,29,30] produced what is still regarded as a masterpiece of scientific coal classification. His system was based on elementary composition, viz. carbon, hydrogen and oxygen, which may be the reason why it has never met with ready acceptance in commercial or technical circles. The National Coal Board has introduced an entirely different system,[31] which is based on volatile matter content and caking properties. The method involves assessing the Gray-King coke type and volatile matter[32] and uses the misnomer of 'coal rank code' classification. The system is illustrated in Fig. 1.1. It is quite possible as the trace element content of coal becomes more widely established that further methods of classification may be suggested, until one which satisfies the needs of the producer, user and coal scientist is obtained.

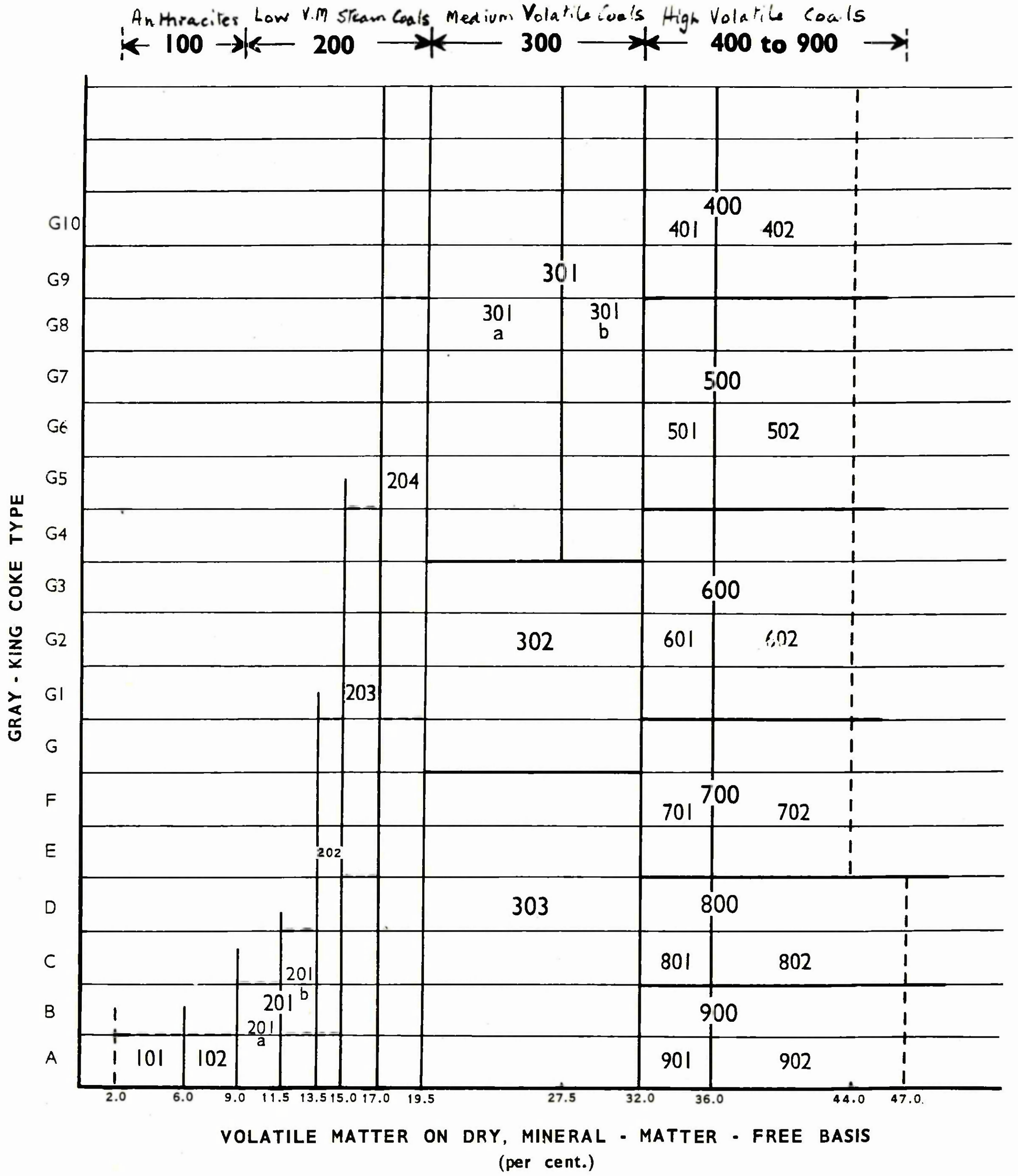
1.4 OCCURRENCE OF ELEMENTS WHICH ARE PRESENT IN COAL

Coal, although predominantly carbon, contains the elements hydrogen, oxygen, nitrogen, sulphur and other minor and trace elements. These elements can either be an integral part of the coals structure (inherent) or be present as extraneous mineral matter.

Figure 1.1

COAL CLASSIFICATION SYSTEM USED BY N.C.B.

(Revision of 1964)



- - - - Defines a general limit as found in practice, although not a boundary for classification purposes.

——— Defines a classification boundary.

NOTES

1. Coals that have been affected by igneous intrusions ('heat-altered' coals) occur mainly in classes 100, 200 and 300, and when recognized should be distinguished by adding the suffix H to the coal rank code, e.g. 102H, 201bH.
2. Coals that have been oxidized by weathering may occur in any class, and when recognized should be distinguished by adding the suffix W to the coal rank code, e.g. 801W.

The types of vegetation which flourished in the carboniferous era were of simpler structure, but generally of much greater size than those predominant today. Classification of the main plant groups and their chemical constituents is well documented,[1,33] and it is evident from the components listed (carbohydrates, lignins, proteins, fats, waxes and resins), that coal-forming matter is composed largely of the elements carbon, hydrogen, oxygen and to a lesser extent nitrogen and sulphur. It is moreover generally accepted that the various elements, present in coal are likely to have been derived from three principal sources.[34,35]

(i) Elements originally present as constituents of the coal-forming vegetation.

(ii) Dissolved or suspended minerals introduced by water percolating through the decaying vegetation during coal formation. This process is called 'syngenesis' and is the coalification of plant material up to and including the establishment of rank.

(iii) Dissolved or suspended minerals introduced by water percolating through the pores, cracks and fissures in the coal after its formation. This process is called "epigenesis", in which the changes are due to outside influences subsequent to the establishment of rank.

The occurrence of minor and trace elements in coal has been known for at least 48 years.[36] Trace elements are usually found in $\mu g\ g^{-1}$ levels in coal whereas minor constituents have concentrations of approximately 0.05 to 1.0 percent. The mode in which they are present is important when suggestions for their removal or control are to be postulated. The research described in Chapter 4 clearly illustrates how detailed studies concerning the mode of occurrence of a particular minor element in coal are essential when control strategies for that element are being considered.

1.5 THE SIGNIFICANCE OF MINOR AND TRACE ELEMENTS IN COAL UTILISATION

The significance of minor and trace element release during the combustion of coal is far from clear. Depending on the researcher the evaluation can differ widely, as can be illustrated by the following contrasting quotations:

(i) "Possibly one of the most dangerous and certainly one of the most insidious forms of pollution arises from the mobilisation (release) of toxic elements such as As, Fe, Be, Pb, Sb, Hg, Ti and V in our environment. The majority of living organisms possess little or no tolerance for these elements, whose presence in the environment is unseen and often undetected. It is well established that many trace elements are mobilised in association with airborne particles derived from high temperature combustion sources such as fossil fueled power plants."[37]

(ii) "The effect of fly ash deposition upon water quality and vegetation (via root uptake) is insignificant in the vicinity of the Mojave generating plant after 50 years operation."[38]

Both statements cannot be correct. One obvious answer is that the analytical methods used to collect data for evaluation are unreliable and imprecise.

A £5 million programme of 'acid rain' research, recently funded by the National Coal Board and the Central Electricity Generating Board, should establish reliable information about this international environmental topic, which has provided so much emotional speculation and conjecture. The five year programme will concentrate on the causes of acidification of surface waters in Norway and Sweden, and will be carried out by the Royal Society with the Norwegian Academy of Science and Letters, and the Royal Swedish Academy of Science. If one proposal to restrict sulphur emissions throughout Europe, which would mean a three-fold reduction from UK power stations, were put into operation, the capital cost to the CEGB is estimated at £4 billion with an additional operating cost of £700 million a year. This would increase the cost of electricity by up to 15 percent.

The importance of rapid, accurate and precise methods of coal analysis cannot be over emphasised if satisfactory conclusions to such investigations are to be drawn. Considering the very large tonnages burnt at power stations the sensitivity of detection of such techniques needs to be 10^{-9} - 10^{-12}g and the development of such methods is essential.[39,40]

Elements which in excess could be harmful to man, and which are known to occur in traces in coal include As, Se, Mn, Sb, B, Cd, Cr, Cu, Pb, Mg, Ni, V and Zn.[41] Whether or not their release by combustion could, in fact, be harmful will depend on the distribution and dispersion of waste products and whether concentration has occurred, rather than the total quantities produced. With the data available at the present time it is reasonable to accept that the ranges of trace element concentrations in British coals are similar to those in US coals, where more information is available,[42,43,44] but higher than in Australian coals.[45]

The significance of minor and trace element concentrations in coal cannot be overlooked in modern utilisation technologies such as liquification, gasification and fluidised bed combustion.[46,47,48] These processes not only need detailed studies of coal structure but also information concerning the inherent and extraneous elements present. The use of pressurised fluidised bed combustion is critically affected by elemental composition, but when successfully developed will dramatically reduce the emission of coal combustion products into the atmosphere.

1.6 THE HISTORICAL DEVELOPMENT OF ANALYTICAL METHODS FOR COAL ANALYSIS IN BRITAIN

The British Standards Institution (BSI) was founded in 1901 and incorporated by Royal Charter in 1929. The first published method in 1930 for the sampling and analysis of coal for export was BS No.404.[49] This was followed the subsequent year by BS No.420[50] 'The sampling and Analysis of Coal for Inland Purposes'. The Solid Fuel Industry Committee supervised the compilation of these standards with the help of some twenty-one Government, scientific and industrial organisations. Recognising the need for coal analysis standards, 1932-1936 saw the production of further British Standards for the determination of fusion temperature of coal ash,[51] sampling and analysis of Coke,[52] sampling of large run-of-mine coal,[53] determination of phosphorus in coal and coke,[54] analysis of coal and coke ash,[55] ultimate analysis of coal and coke[56] and the crucible swelling test for coal.[57]

Using the methods previously described in these BS publications and the Government Department of Scientific and Industrial Research paper on the methods of analysis of coal and coke,[58] BS 1016, 'Analysis and testing of Coal and Coke',[59] was first issued in 1942 and also a second comprehensive specification BS 1017, 'The sampling of Coal and Coke'.[60] In order to keep abreast of progress, the British Standard Specifications are subject to periodic review. The process of nationalisation of the coal industry in 1947 possibly delayed the revision of the first of these until 1957 when BS 1016 was separated into 16 parts[32] covering the proximate, ultimate analysis and physical testing of coal and coke. This method of presentation permitted the revision of any part of the standard with the minimum of delay. Most modifications to the methods or introduction of new methods were aimed at reducing the considerable time taken for most of the analyses. It is interesting to note that in the subsequent reviews of methods certain tests were changed frequently for example the determination of volatile matter.[32] Other tests such as the Gray-King Coke type[32] and the Eschka chemical analysis for sulphur and chlorine in coal[32] have remained virtually unchanged to the present day.

Part 14, 'The Analysis of Coal and Coke Ash' was completely revised in 1963[32] with increased speed of analysis in mind. The method developed by the British Coal Utilisation Research Association was adopted[61] but in addition an alternative, less precise, method outlining the use of a Hilger large quartz spectrograph was appended.[62] The acceptance of the latter method was therefore somewhat limited and this coupled with the non-acceptance as a British Standard in 1960 of the Leitz 'Heating' Microscope for the measurement of coal ash fusibility, became the chief contributing influences to the lack of interest of coal scientists in the introduction of instrumental methods for coal and ash analysis. Since 1979 five additional parts have been introduced into the British Standards:

(i) Part 17, 'Size Analysis of Coal, 1979'[32]
(ii) Part 18, 'Size Analysis of Coke, 1981'[32]
(iii) Part 19, 'Abrasion Index of Coal and Coke, 1980'[32]
(iv) Part 20, 'Hardgrove Index of Coal, 1981'[32]
(v) Part 21, 'Moisture Holding Capacity of Coal, 1981.[32]

By their very nature BS methods are conservative. The tendency has been to retain conventional methods because new ones require expensive instrumentation. However, with the resistance to technological advances declining, one of the major aims of the work described in this thesis, is to develop rapid instrumental methods for coal and coal ash analysis with the same degree of precision as the current methods so that they can eventually achieve BS status.

1.7 INSTRUMENTAL TECHNIQUES FOR COAL ANALYSIS

Conventional chemical techniques for coal and coal ash analysis lack the sensitivity needed to measure trace quantities of certain elements in samples of manageable size, and minor element determination can also pose problems because of analysis time and poor method precision. The introduction of instrumental techniques which use the principle of some physical characteristic e.g. emission of electromagnetic radiation which differs for each element, offers great scope for improvement. Such methods are highly sensitive with detection limits of 10^{-10} to 10^{-12} g. The main features of the instrumental methods generally used for elemental analysis are outlined below.

Nuclear Activation Analysis (NAA) measures emission from unstable isotopes generated by nuclear irradiation. Several grammes of sample are used, which reduces the risk of heterogeneity and the sample processing is minimal since carbon does not interfere - both of which are advantages when dealing with coal.[63,64] Numerous papers have been reported outlining the analysis of coal but a limitation is that potentially toxic elements such as Cd, Cu, Hg, Pb, Ni and Zn are not easily determined.

Scanning Electron Microscopy and Energy Dispersive X-ray Analysis (SEM/EDXA) uses a beam of electrons to generate secondary electrons (image) and characteristic X-rays (analysis) from the specimen surface. The technique requires minimum sample preparation and can provide structural information, element distributions as well as chemical analyses. This novel method for coal analysis has not been used previously to the extent reported here in Chapter 3.

X-ray fluorescence spectroscopy (XRF) also requires minimal preparation of solid-samples. The limitation as with SEM/EDXA is that only a small volume of the sample surface is analysed. Bombardment of the sample by a beam of X-rays ejects electrons from the inner shells of some atoms which then emit secondary X-rays (fluorescence) of characteristic frequency as outer shell electrons move to fill gaps. Self-adsorption, enhancement and effects of particle size all interfere with the quantitative emission of secondary X-rays, but can be corrected by calculation. As with NAA the method is potentially capable of multi-element analysis and only the very light elements are difficult to detect. Although there was considerable interest in this technique for coal analysis between 1960 and 1970,[65,66] there was little progress beyond the research stage.

Spark Source Mass Spectrometry (SSMS) ionises the sample and then separates the ions according to their mass/charge ratios. It covers a wide range of elements but is liable to interference by multi-charged and complex ions. The sample analysed is very small with consequent risk of errors when dealing with non-homogeneous materials. Practical instrumentation is slow to use, for example coal samples require preliminary treatment to remove carbon and hydrogen.[67,68]

Atomic Emission Spectroscopy (AES) measures the intensity of light emitted at wavelengths characteristic of individual elements when atoms are excited in an 'atom cell'. This can be a flame, plasma or electrically heated carbon tube. It is rapid and sensitive but liable to spectral interference both from 'overcrowding' of lines when many elements are present and from broad molecular bands. Samples normally need to be dissolved which ensures that they are homogeneous but this also involves eliminating carbon from coals.[69] Solid-samples have been used but generally with poorer precision than solution analysis.[70] Care is also needed to avoid changes in the concentration of excited atoms due to changes in flame temperature.

Atomic-Absorption Spectrometry (AAS) is inexpensive and the most frequently used of modern instrumental methods for trace metal analysis. Samples are vaporised and atomised in a flame or an electrically heated graphite device or via conversion to volatile hydrides.[71] Light from a line source, usually emitting a single elemental spectrum is passed through the vapour and the degree of absorption measured. Absorption, which depends on the concentration of ground-state atoms present is much less sensitive to 'atom cell' temperature than the emission from excited species used for atomic emission spectrometry; it is, however, still liable to spectral interference. Sample preparation, including elimination of carbon from coals, is also usually needed before all three methods of injection.[72] For the commonest, flame vaporisation, this involves solution of the samples which has the advantage of ensuring homogeneity but at some risk of contamination. The use of solid-sample introduction into a graphite furnace[73] is reported in Chapter 2 of this study and shows that with careful control of the furnace conditions acceptable results can be obtained.

Other physical analytical methods, e.g. photo-electron spectrometry, ion-microprobe mass spectrometry, auger electron spectrometry, proton bombardment for inducing X-ray emission (PIXE), can be used to determine trace element distributions within individual particles. These are more specialised methods and are not considered as practically useful at this time because there are simpler less sophisticated alternative techniques available. The methods described generally have high sensitivity and good reproducibility, although (NAA) has been shown to give large imprecision in the analysis of fly ash[74] (ranges from ± 1.7 to ± 33.3 percent).

1.8 AIMS AND OBJECTIVES OF THE PRESENT STUDY

Coal analysis can thus be shown to be a branch of analytical chemistry with an honorable history. Methods have been developed which have achieved widespread acceptance, British Standard recognition and partly because of this and the traditional nature of the industry's product there has perhaps not been as rapid an acceptance of new instrumentally based methodologies as in some of the younger industries.

Recent technological developments in coal utilisation and environmental awareness are causing tighter and more comprehensive specifications to be developed for coal. The understanding of the effects of minor and trace elements has increased but the mode of occurrence of these elements is very often important when strategies for their control or removal are to be postulated. This together with the common need to speed analytical procedures and to release manpower means that it is timely to study the application of instrumental methods to coal analysis.

Given the pressures discussed above and the nature of coal it is possible to identify the desirable features of any new analytical methods:

(i) high sensitivity for the elements of concern, as often only trace levels may be deleterious and when high tonnages are used the mass flow of such elements may still be high;

(ii) speed, to meet customers strict quality requirements many samples are submitted for analysis in laboratories with constraints upon manpower, as coal can be troublesome to bring into solution methods directly applicable to powdered coal are preferred as are multi-element methods;

(iii) acceptable precision and accuracy.

A further important consideration is the likely availability of instrumentation in the relevant laboratories e.g. this was considered to eliminate NAA and SSMS.

The aims of this study have been to:

(i) identify promising new analytical methodologies for coal analysis;

(ii) investigate the fundamental application of these to coal analysis;

(iii) develop suitable methodologies for routine coal analysis.

To these ends the following techniques were assessed as being worthy of extensive study:

(i) atomic-absorption spectrometry using electrothermal atomisation and coal slurries;

(ii) scanning electron microscopy and energy dispersive X-ray analysis of coal powders;

(iii) quantitative multi-element analysis of coal powders by wavelength dispersive automated X-ray fluorescence spectrometry;

(iv) multi-element optical emission spectrometry of solutions of coal ash by inductively coupled plasma.

None of these techniques determine all the elements and none can be considered accurate in an absolute sense as all require calibration. Choice between them is generally based on convenience or utility and the analytical coal scientist will employ several techniques to achieve his objective of precise, accurate and rapid analysis.

CHAPTER 2

DIRECT DETERMINATION OF TRACE ELEMENTS IN COAL BY ATOMIC-ABSORPTION SPECTROMETRY USING SOLID-SAMPLING AND ELECTROTHERMAL ATOMISATION

2.1 INTRODUCTION

The increase in sensitivity obtained using electrothermal atomisers instead of flames for atomic-absorption spectroscopy is now widely accepted. Fuller[75] gives a useful account of conventional electrothermal atomisation for atomic-absorption spectrometry. The general applicability of electrothermal atomisers for solid samples has been shown by several groups of workers.[76–80] In particular Langmyhr and Aadalen[81] reported the direct determination of copper, nickel and vanadium in coal and petroleum coke by graphite furnace atomic-absorption spectroscopy. Marks, Welcher and Spellman[82] atomised directly, chips of complex alloys and successfully determined traces of selenium, lead, bismuth, tellurium and thallium. The molecular absorption from matrix salts usually associated with the analyte was eliminated in this procedure and therefore improvements in signal to background noise were claimed when results were compared with atomisation from acid solutions of the same alloys.

The aim of this chapter is to develop methods for the determination of certain trace elements of concern in coal viz. arsenic and selenium by using conventional graphite furnace atomic-absorption spectroscopy and then to extend these into a method for their direct determination in coal by solid-sampling.

The toxic and carcinogenic properties of arsenic and its compounds are well known.[83] Although the toxicological significance of different levels and forms of exposure may not be fully appreciated, control of such exposure is obviously desirable. There is therefore an established need to monitor the levels of arsenic entering the environment. Coal contains arsenic at trace levels and the National Coal Board monitors closely the arsenic content of fuel supplied to food manufacturers where contamination may occur, e.g. sugar refiners, maltsters and brewers. Typically it is recommended that the arsenic content of the fuel supplied to these industries should not exceed 6 $\mu g\ g^{-1}$.

Selenium is similar to arsenic in toxicity and reactivity.[84] A precise knowledge of the selenium content in the environment and food products is therefore necessary. The analytical determination of selenium is difficult and additionally the colorimetric reagent often used (diaminobenzidine) is a carcinogen and stringent regulations must be adhered to in order to ensure its safe use.[85]

Even though fume and dust may be removed from stack gases using electrostatic precipitators, arsenic and selenium fumes may be gaseous at low temperature and this, together with the increased large-scale burning of pulverised coal for power generation, may pose problems of environmental pollution.

The existing British Standard method[86] for the determination of arsenic in coal is time consuming and requires an experienced analyst. The precision of the method is poor and, probably because the procedure involves a hydride generation stage, was also found to give low results for certain coals including National Bureau of Standards certified samples. The repeatability by the same analyst for this method is given as $1.0\ \mu g\ g^{-1}$ for coals with arsenic content (as As_2O_3) less than $6\ \mu g\ g^{-1}$ and $1.5\ \mu g\ g^{-1}$ for coals with arsenic content of $6\ \mu g\ g^{-1}$ or greater. This degree of precision, particularly for high-arsenic coals, is difficult to achieve.

Selenium on the other hand is not determined by the NCB on a routine basis and no BS method for its determination has been suggested. Hence there is a requirement for a rapid, sensitive and precise method for determining both arsenic and selenium in coal.

The obvious attraction of an instrumental technique to determine arsenic and selenium directly in coal is that complex error-prone sample preparation stages are eliminated. Neutron-activation analysis has the sensitivity to perform this determination but the equipment is not readily available to most laboratories. X-ray spectroscopic analysis does not possess sufficient sensitivity for direct trace element analysis of coal. Atomic-absorption spectroscopic equipment is available in most laboratories but conventional flame spectroscopy is not sufficiently sensitive for the routine monitoring of low arsenic levels. If, however, arsine is generated using sodium tetrahydroborate (III) and the hydride swept to a flame or heated tube atomiser, the sensitivity of the method is greatly improved.[87]

Unfortunately, the hydride generation technique suffers from a number of interferences,[87,88] and is only applicable after the sample has been brought into solution.

The use of graphite furnace atomisation provides one of the most suitable methods for trace element analysis of coal. However, the large increase in sensitivity over flame atomic-absorption is offset by a substantial increase in background absorption levels. This increase in background absorption is caused by an increase in both molecular absorption and light scattering from particles in the atomic vapour. The particular difficulty in electrothermal atomisation is that the distribution of the atomic vapour being measured and the background reading are not reproducible from one atomisation cycle to the next. Two additional difficulties were encountered in this study.

(i) wavelengths in the UV range of the electromagnetic spectrum are used for the analyte lines causing a further increase in background absorption levels;

(ii) the use of solid-samples increases matrix concentration levels, poses problems with calibration and sampling precision.

In all the background correction systems known at the present time two measurements have to be made; one incorporating the atomic-absorption signal and background; the other the background alone. The difference between these two measurements gives the true atomic-absorption signal. The most suitable methods for background correction in electrothermal atomisers are briefly discussed in the subsequent paragraphs. For a more comprehensive study reference should be made to Newstead, Price and Whiteside.[89]

2.1.1 Continuum Source Method

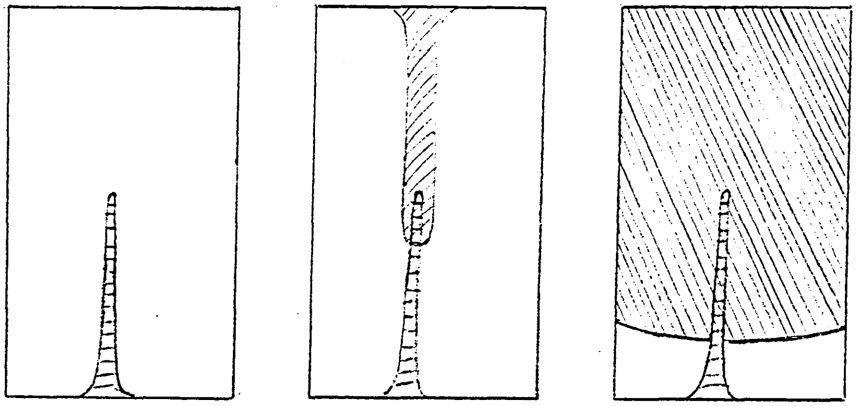
This is by far the most common of the background correction systems available. The continuum source may be either a hollow cathode lamp e.g hydrogen or tungsten, or a deuterium arc (D_2 arc). The latter gives a more intense source but has different geometry to a line source and is therefore much more difficult to optically align in the spectrometer. The D_2 arc emission spectrum is quite intense up to 400 nm but reduces to almost zero in the visible wavelength range.

The principle of background correction using a continuum source is simply explained by Ebdon.[71] When using a line source such as a hollow cathode lamp we observe specific atomic-absorption in the atom cell, absorption from molecular species and light scattering from particulates (non-specific absorption). When using a continuum source the amount of atomic-absorption observed is negligible, but the same amount of non-specific absorption is seen. Thus if the signal observed with the continuum source is subtracted from that observed with the line source, the error is removed. This correction procedure is very simply illustrated in Figure 2.1.

The problems with continuum background correction are emphasised when using electrothermal atomisation and were first described by Massmann.[90,91] The band-pass of the monochromator is typically two orders of magnitude wider than the atomic-absorption line. The background measurement is an averaged reading over this band-pass and may differ from the actual background absorption at the atomic-absorption line. This variation in background within the band-pass can be caused by the fine structure of molecular electronic spectra or the broadened edges of other elemental atomic-absorption lines particularly when that element is present in high concentrations. This latter occurrence is however uncommon. This type of background problem is referred to as "structured" background. Depending upon the characteristic shape of the background, when its averaged absorption is subtracted from the atomic-absorption signal it can result in under or over compensation (negative absorption reading).

It is also evident that if the atomic-absorption line was broadened then problems would arise. The width of absorption lines of analyte atoms are generally considered to be governed by Doppler and Lorentz effects. The former arises from the random thermal motion of atoms whilst the latter arises from collisions of atoms with other atoms or molecules of a different kind. The centre of the line is broadened primarily by the Doppler effect whilst the wings are broadened by the Lorentz effect. For resonance lines, self-absorption broadening can be very important. The maximum absorption occurs at the line centre and proportionally more intensity is lost here by self-absorption than at the wings. Thus, as the concentration of atoms increases in the atom cell not only does its intensity increase, but its profile changes.

Figure 2.1 Continuum source background correction[71]

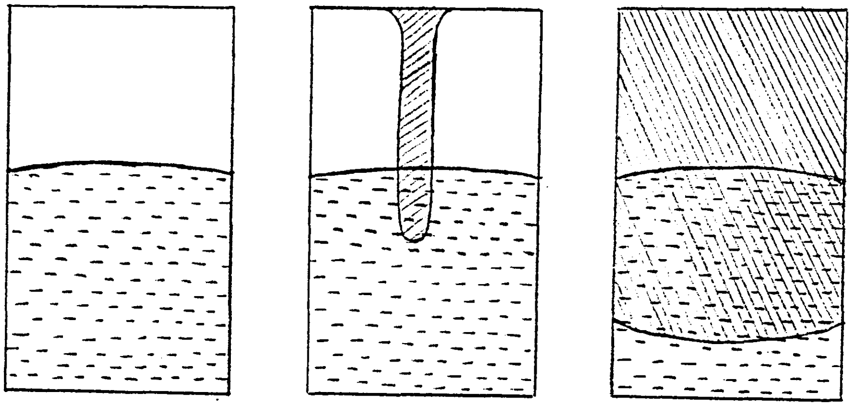


Observed
absorption
= AA + molecular
absorption

Radiation detected using a line source e.g. hollow cathode lamp

Atomic-absorption of line source ~ 30%

Molecular absorption of the line source ~ 50%



Observed
absorption
= molecular
absorption

Radiation detected using a continuum source, e.g. deuterium arc or hydrogen hollow cathode lamp

Atomic-absorption of continuum source ~0.01%

Molecular absorption of continuum source ~50%

Corrected atomic-absorption =

Absorption observed using line source - absorption observed using continuum source

This is simply illustrated in Figure 2.2. High atom concentrations give rise to appreciable self-absorption and can actually result in 'self-reversal'. This characteristic is made use of in one of the background correction methods discussed later.

Despite these problems the continuum source method of background correction is widely used and many successful applications have been reported.[89]

2.1.2 Zeeman Method

The principle and use of this method of background correction has been suitably explained by several authors.[71,92,93] Its usefulness when determining arsenic and selenium in geological samples has been described recently by Pruszbowska, Giddings and Barratt.[94]

An atomic spectral line when generated in the presence of a strong magnetic field can be split into a number of components of slightly different wavelengths ($\sim$ 0.004 nm). The magnetic field can be applied to the source or atom cell but greater instability problems have been found with the former type. In a 'normal' Zeeman effect the line appears as three components when viewed perpendicular to the magnetic field. A typical example of 'normal' Zeeman splitting is given in Figure 2.3. The π component is situated at the 'normal' wavelength of the line, but the σ^+ and σ^- components lie an equal distance either side. This 'normal' Zeeman splitting is uncommon and complex 'anomolous' patterns are more usually obtained giving large reductions in sensitivity. The σ components are linearly polarised perpendicular to the magnetic field whilst the π component is polarised in a plane parallel to the magnetic field.

If the magnetic field is placed around the atomiser and a rotating polariser positioned between the light source and the sample, the π component, which gives both the atomic-absorption of the element and background absorption can be measured separately from the σ signal which gives only the background absorption. Subtraction of the σ signal from the π signal produces the true analyte absorption. This type of correction, because of the very small displacement from the atomic-absorption line, in order to measure background, should frequently correct for 'structured' background described in 2.1.1. A difficulty found with this correction

Figure 2.2 Effect of self-absorption on line profile with increasing concentration 1 to 5.

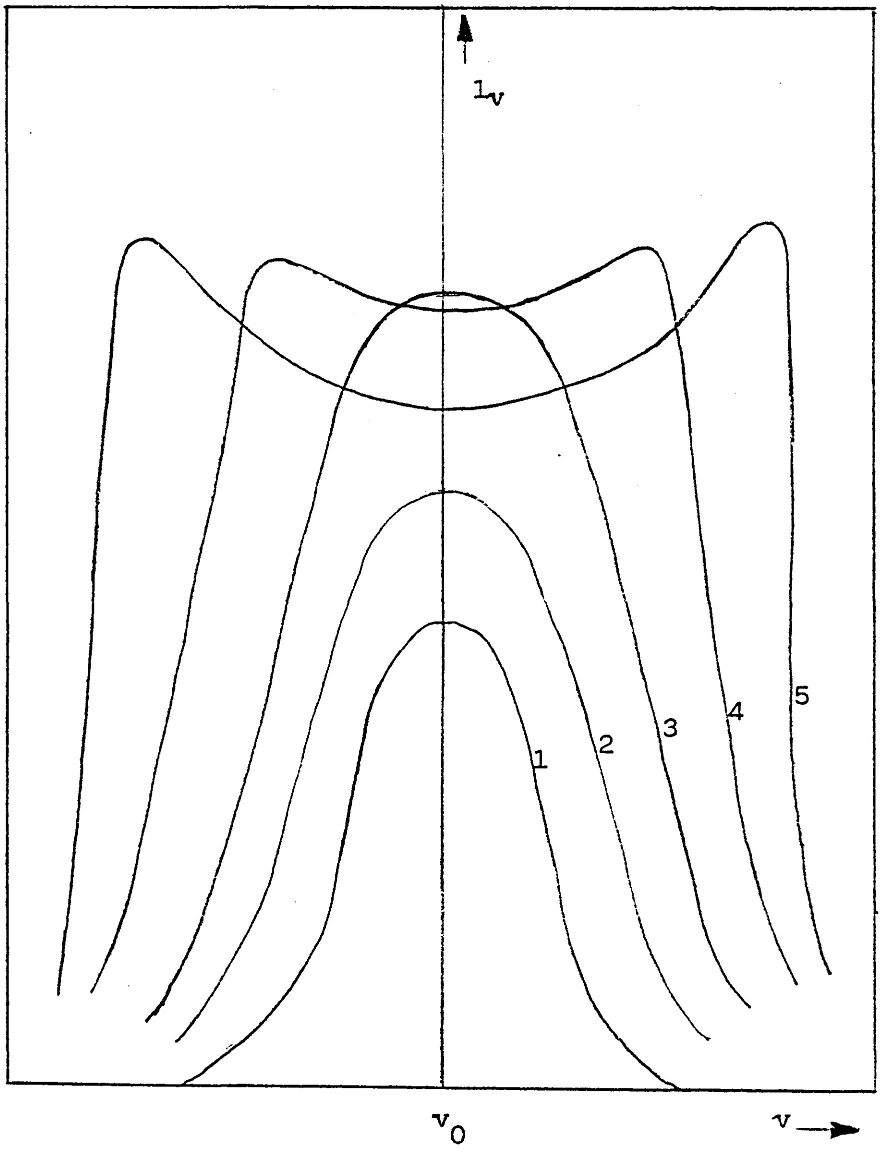
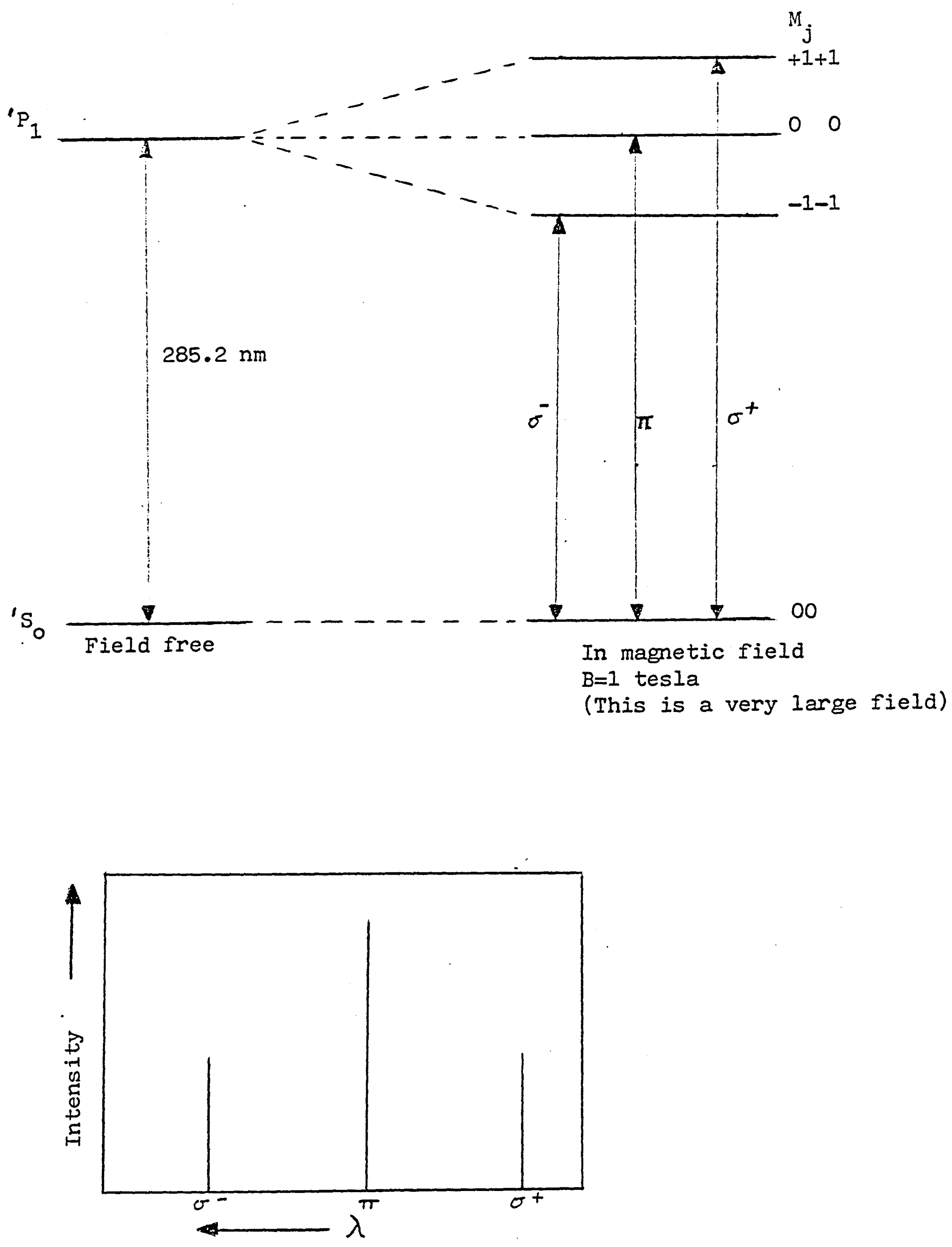


Figure 2.3 Normal Zeeman effect for Magnesium at the 285.2 nm line



(The diagram exaggerates the separation of components for clarity. In this instance, it would be 0.0038 nm.)

method is that widely differing concentrations of the analyte can produce the same corrected atomic-absorption reading. As the concentration of the analyte increases, the σ components broaden[92] and begin to absorb more and more of the perpendicular component of the source radiation. This analyte absorption therefore appears as background and can be so large that when substracted from the π component can actually reverse the curve.[95] This effect is often referred to as 'roll over' and limits the useful analytical working range to about 0.5 absorbance units. It is illustrated in Figure 2.4.

2.1.3 Smith - Hieftje Method

This background correction system recently developed uses the concept that when excessive current is passed through a hollow cathode lamp self-reversal occurs.[96] This is because unexcited atoms in the lamp absorb radiation at the atomic spectral line. The lamp is first run at low current giving a signal from the sample element and background. A brief pulse of higher current is then applied to the lamp reducing the atomic-absorption of the sample to a minimum, but without changing the background absorbance intensity. The true absorbance of the element is obtained using the difference of the two signals. The effect of self-reversal upon an atomic line has already been explained and is illustrated in Figure 2.2.

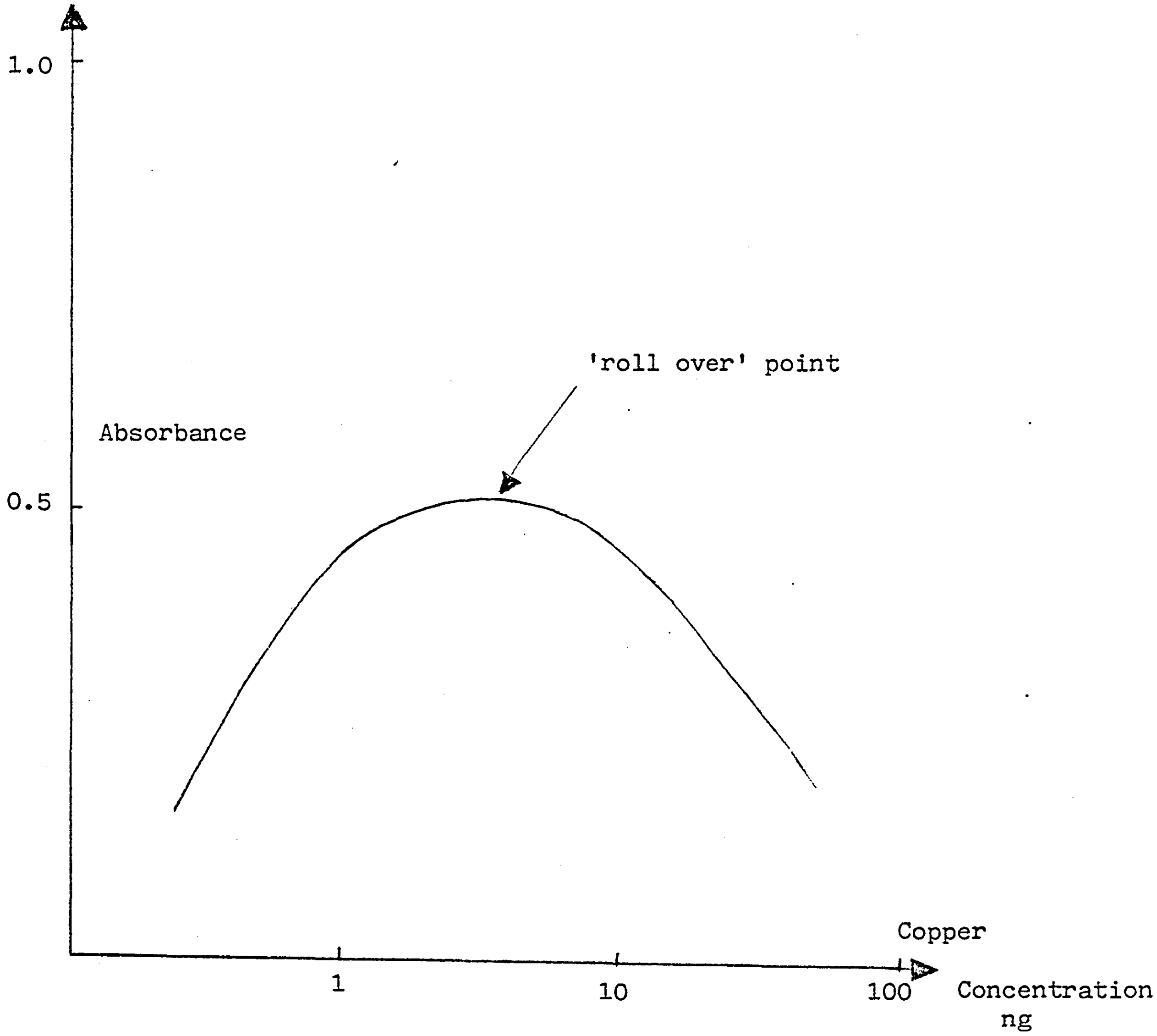
This system has the advantages that background correction can be made anywhere in the spectrum range and that it should correct 'structured' background and spectral interferences. It is claimed to compensate for background absorbances of as high as 3.0 units. The three main disadvantages are:

(i) the sensitivity of the absorption signal can be reduced by large amounts;

(ii) although inexpensive itself, the electronics necessary in the spectrometer make it impossible to use with existing atomic-absorption instruments;

(iii) with concentration broadening in the atom cell non-linear calibration curves can again present problems.

Figure 2.4 The effect of increasing copper concentration upon calibration using Zeeman background correction



Deuterium arc background correction was used extensively in this work, primarily because of its availability. When background problems were encountered, particularly with the determination of selenium, it was necessary to evaluate the performance of the Zeeman and Smith-Hieftje correction systems.

2.2 EXPERIMENTAL

2.2.1 Reagents

Hydrochloric acid (1 M, Aristar grade)
Hydrofluoric acid (48% V/V, Aristar grade)
Nitric acid (concentrated, Aristar grade)
Hydrogen peroxide (30% m/V, Aristar grade)
Ethanol (AnalaR grade)
Magnesium nitrate ($Mg(NO_3)_2 \, 6H_2O$, AnalaR grade)
Nickel nitrate ($Ni(NO_3)_2 \, 6H_2O$, AnalaR grade)
Aluminium solution spectrosol 1000 mgl^{-1}
Iron solution spectrosol 1000 mgl^{-1}

All chemicals were obtained from BDH Chemicals, Poole, Dorset.

2.2.2 Preliminary Studies

Coal is a notoriously difficult matrix to destroy without loss of volatile metals.[97] The extraction of arsenic from powdered coal was first attempted using hydrochloric acid (1 M). The arsenic content of the filtered leachate was determined by electrothermal atomisation using nickel nitrate as matrix modifier.[98] The results, although reproducible for a given sample, were low when compared to the standard method. Therefore, various other digestion procedures were investigated. Dissolution can be achieved speedily using perchloric acid, but the use of this reagent is discouraged for routine analysis by the National Coal Board. British Standard 1016[86] recommends the use of concentrated sulphuric acid/concentrated nitric acid, but this is both slow and leaves undigested silica suspended in solution. The alternative British Standard 1016 dry oxidation method[86] using potassium permanganate, magnesium oxide and oxygen, yields low arsenic recoveries.

Some workers favour the use of PTFE-lined steel pressure bombs and a mixture of fuming nitric acid and hydrofluoric acid.[99] In this laboratory some problems were encountered with acid migration and subsequent attack upon the steel casing of the bomb. In addition, a maximum of only 100 mg of coal could be digested on each occasion, a serious limitation for the determination of arsenic and selenium. The most successful approach was based upon a dry-ashing procedure (with magnesium and nickel nitrates as ashing aids) followed by acid digestion, first reported by Haynes[100] for combustible municipal wastes. The dry-ashing procedure was either accomplished in a similar manner to that described by Haynes, or by using a low-temperature plasma asher. The ash was then taken up in a mixture of concentrated nitric acid, hydrofluoric acid and hydrogen peroxide, with nickel nitrate as volatilisation suppressor. Following the successful evaluation of this digestion procedure it was adapted to allow the direct injection into the furnace of coal slurried in nitric acid containing magnesium and nickel nitrates. The arsenic and selenium levels in the coal were determined following an optimised furnace heating cycle.

2.2.3 British Standard Procedure

This was performed as laid down in BS 1016[78] (wet oxidation method).

2.2.4 Digestion of coal for electrothermal atomisation

Coal (2g) was heated in a platinum crucible with 10% m/V magnesium nitrate solution (15 cm^3), 25% m/V nickel nitrate solution (5 cm^3) and ethanol (3 cm^3) according to the method described by Haynes.[100] After drying at 120°C for 2 hours, the mixture was heated at 160°C for 4 hours and then at 450°C for 4 hours. After cooling, water (5 cm^3), concentrated nitric acid (10 cm^3) and concentrated hydrofluoric acid (2 cm^3) were added. The solution was heated to dryness. Further nitric acid (10 cm^3) and hydrogen peroxide (30% mV, 10 cm^3) were added to complete the dissolution. The digest was made up to 100 cm^3.

As an alternative to the first ashing stage the coal (2 g) may be placed in a low-temperature plasma asher (Plasmaprep 100; Nanotech (Thin Films) Ltd., Prestwich, Manchester). The activated stream of oxygen gas decarbonised the sample completely in 48 hours at 20 watts forward power. The ash was then digested with nitric and hydrofluoric acid as above after the addition of 25% m/V nickel nitrate solution (5 cm^3) as a volatilisation suppressor.

2.2.5 Slurry atomisation method

Coal (0.5 to 1 g) ground to less than 45 μm, using a mill (Type MS400; Retsch Spectromill, Glen Creston Ltd., Stanmore, Middlesex) was weighed accurately into a 50 cm^3 polypropylene screw-cap bottle and 10 cm^3 of a reagent solution (containing 10 gl^{-1} each of nickel and magnesium nitrate, 50 $cm^3 l^{-1}$ of concentrated nitric acid and 100 $cm^3 l^{-1}$ ethanol) were added. A magnetic stirrer bar was inserted, the bottle sealed and the contents stirred for 5 minutes. Aliquots of the suspension (5 to 20 μl) were taken using a precision micro-pipette (Gilson Pipetman P; Anachem Ltd, Luton, Bedfordshire) while continuously stirring.

2.2.6 Atomiser Parameters

A double-beam atomic-absorption spectrometer (Model 460; Perkin-Elmer Ltd., Beaconsfield, Bucks.) fitted with a carbon furnace atomiser having a silicon photodiode temperature sensor and four stage programme unit (Model 76(b), Perkin-Elmer Ltd.) was used. An arsenic and a selenium electrodeless discharge lamp (EDL) and power supply from the same manufacturer were also employed. The spectrometer was fitted with a deuterium arc simultaneous background corrector and a furnace fume extraction unit. Signals were displayed on a multi-range chart recorder (Model Speedomax XL681, Leeds and Northrup, Birmingham).

Samples were injected into the furnace either using the 0-20 μl adjustable precision micro-pipette or a tantalum solid-sampling spoon (Perkin-Elmer Ltd.).

The following parameters were used for the determination of arsenic and selenium by electrothermal atomisation.

Arsenic
Wavelengths: 193.7 nm and 197.2 nm
Slit width: 0.7 nm (alternate)

Furnace conditions:
Dry : 200°C for 50s, very slow ramp-rate (1 x 30)
Char : 900°C for 50s, slow ramp-rate (30)
Ash : 1200°C for 50s, slow ramp-rate (30)
Atomise : 2200°C for 6s, maximum power-rate (0)
Argon internal gas flow-rates: normal 140 cm^3 min^{-1}
mini-flow 25 cm^3 min^{-1}
Time for complete analysis cycle 185s

Selenium
Wavelengths: 196.0 nm and 204.0 nm
Slit width: 0.7 nm (alternate)

Furnace conditions:
Dry : 200°C for 50s, very slow ramp-rate (1 x 30)
Char : 900°C for 50s, slow ramp-rate (30)
Ash : 1200°C for 50s, slow ramp-rate (30)
Atomise : 2000°C for 5s, maximum power rate (0)
Argon internal gas flow-rates: normal 140 cm^3 min^{-1}
mini-flow 25 $cm^3 min^{-1}$
stopped-flow 0 $cm^3 min^{-1}$

Time for complete analysis cycle 184s

2.2.7 Analysis of the residue remaining after the Haynes digestion procedure was carried out on a high-ash coal

On standing, a sample of a high-ash coal (MK) digested by the procedure described in section 2.2.4 produced a white crystalline deposit. In high-ash coal digests, such deposits were always observed. The solution was filtered and the deposit examined qualitatively using the techniques of Scanning Electron Microscopy and Energy Dispersive X-ray Analysis (SEM/EDXA) (Camscan 330 ADP scanning electron microscope; Cambridge Scanning Company, Bar Hill, Cambridge and Link 860 Series I X-ray analysis equipment; Link Systems, High Wycombe, Bucks.)

The sample was mounted on an aluminium stub using non-aqueous carbon dag (LEIT-C) and dried. The characteristic X-rays were generated from the sample using an electron beam accelerating voltage of 20 Kev. The X-rays were detected with a solid-state silicon/lithium crystal and processed using pulse-height discrimination.

2.3 RESULTS AND DISCUSSION

2.3.1 Determination of arsenic in coal by dissolution and electrothermal atomisation

Selected coal samples, including NBS Standard Reference Material 1632a (National Bureau of Standards, Washington, USA) were digested using the full digestion procedure of Haynes[100] outlined in Section 2.2.4. The amount of hydrofluoric acid recommended was increased for some high-ash coals to ensure that all the silica was digested. The NBS sample was also plasma ashed prior to digestion. The results obtained are given in Table 2.1 where they are compared with results obtained by three different laboratories using the BS method.[86] Using the full digestion procedure, good agreement was found with the certified value for NBS SRM 1632a with acceptable precision. The result obtained following plasma ashing appears to be low and experience suggests that it is necessary to control very carefully the operation of the asher to prevent losses of volatile elements such as arsenic. Agreement with the results obtained by the BS method[86] is not so good and the problems with this method will be discussed later.

The programme cycle was shown to give no "memory" effect for the determination of arsenic. Nickel nitrate effectively prevented loss of arsenic during the char and ash stages. The use of pyrolytically coated tubes reduced the peak height and distorted peak shapes, and therefore uncoated tubes were preferred. These effects would appear to be in accord with the mechanisms of arsenic atomisation and stabilisation recently reported.[101] Peak-height measurements were used in calibration and for all determinations. However, to obtain sharp peak profiles it was found necessary to use the maximum power heating mode (5.6 watts) in the atomisation stage. With this rapid initial heating some means of temperature control is necessary to monitor the power application and prevent overshoot of temperature. A silicon photodiode temperature sensor achieves this by monitoring the light emission from the outside wall of the graphite tube.[102]

TABLE 2.1

Comparison of the determination of arsenic in coal following dissolution

	Arsenic content/µg g^{-1} (air-dried basis)					
Coal Sample	BS method[a]			Digestion/Graphite Furnace		
	Different Laboratories			Separate Digests		
	1	2	3	1	2	3
A	4.9	5.0	4.6	3.9	3.6	3.8
B	17.0	20.9	17.1	27.5	26.4	27.5
C	7.8	6.3	7.6	5.2	5.2	5.9
D	6.1	5.0	5.3	8.1	8.5	8.7
NBS SRM 1632(a)	CERTIFIED 9.3 ± 1.0			9.8	9.6	9.0
Plasma ashed 1632(a)	CERTIFIED 9.3 ± 1.0			7.6	8.4	-

[a] method according to BS1016[86]

This sensor is easily calibrated for the atomisation temperature selected.

Reagent blanks were found to be low and it was not necessary to apply any correction. The miniflow mode was used to reduce the internal argon flow-rate during the analysis of low-arsenic coals. Calibration graphs were slightly curved for both the normal and miniflow modes but working ranges of 1 to 8.0 ng and 0.5 to 2.5 ng of arsenic, respectively, were obtained. The upper amounts correspond to absorbances of approximately 0.2 and 0.15 unit and 20.0 $\mu g.g^{-1}$ and 6.5 $\mu g\ g^{-1}$ arsenic in coal, respectively, using a 20 µl injection. The lower end of the working range for this technique was estimated to be 0.1 $\mu g\ g^{-1}$ of arsenic in coal, using a 50 µl injection.

2.3.2 Determination of arsenic in coal by solid-sampling and electrothermal atomisation

Following this success in determining arsenic in coal after ashing and dissolution, attempts were made to extend the method so that the matrix was destroyed *in situ* in the furnace. Initially, milligram amounts of coal powdered to less than 45 µm were added directly to the furnace tube using a specially designed solid-sampling spoon. The coal was then wetted with nickel nitrate and magnesium nitrate before the programme cycle was commenced. The results obtained, however, were not reproducible. It was then decided to investigate the use of slurried coal samples. The slurries were prepared in a solution containing nickel nitrate (to form nickel arsenide and prevent losses during the lengthy ashing and charring necessary), magnesium nitrate (to act as an ashing aid), nitric acid (to provide an acidic medium) and ethanol (to act as a wetting agent).

The precision of the micropipette for the delivery of distilled water and the slurry was determined and found to be within the manufacturer's specifications. The pipette was found in a run of 10 determinations, at the 20 µl level, to deliver 20.029 mg of distilled water with a standard deviation of 0.163 mg (0.8% relative), giving 95% confidence level limits of 20.326 to 19.674 µl.

The precision of the slurry-sampling and atomisation was also found to be satisfactory. Ten replicates of a 10 µl injection of a coal slurry (0.5 g in 10 cm^3) gave an average chart deflection of 11.50 units (approximately 1.15 mV) with a standard deviation of 0.60 unit (5.2% relative).

Comparative results for the analysis of arsenic in coal by this solid-sampling method and the BS method[86] are given in Table 2.2. An encouraging agreement between results obtained by the BS method, calibration with aqueous arsenic standards (matched for nickel and magnesium content) and calibration with aliquots of coal sample A, can be seen for the coal samples A–H. These samples, all from the East Midlands Coalfield, have similar compositions being bituminous low-rank (802, 902) coals. Agreement was not so good for samples I and J which are European coals, of unknown rank but high ash and the National Bureau of Standards SRM bituminous coal, which was also found to have a high ash content. When the NBS SRM 1632(a) coal was taken as the standard and the arsenic content recalculated, the contents of coals I and J were determined as 9.4 and 9.1 µg g^{-1} respectively, in much better agreement with those obtained by the BS method.

When a larger sample of British coals was taken from various coalfields, the results presented in Table 2.3 were obtained. Examination of this table shows reasonable agreement between the BS method results and those obtained using coal standards and direct slurry atomisation. The results using aqueous calibration are not in such good agreement.

2.3.3 Determination of arsenic in coal by the British Standard method[86]

As the evidence that all the discrepancies observed arose from problems with the slurry atomisation technique was not convincing, it was decided to investigate the performance of the BS method[86] with a high-arsenic coal sample. In outline, the BS method involves the digestion of a sample of coal ground to less than 212 µm, in concentrated nitric and concentrated sulphuric acids.

TABLE 2.2

Comparative results for the determination of arsenic in coal using the slurry atomisation method

Coal Sample	Arsenic content/$\mu g\ g^{-1}$ (air-dried basis)		
	BS method[a]	Slurry with reagent calibration[b]	Slurry with coal A as standard[c]
A	4.8	5.0	-
B	18.3	20.5	16.9
C	7.2	7.5	6.4
D	5.5	6.0	5.4
E	11.6	12.5	9.9
F	7.3	9.2	7.7
G	24.2	22.0	18.0
H	5.0	4.3	3.7
I	10.1	25.5	20.7
J	9.2	24.5	20.1
NBS SRM 1632(a)	9.3[d]	25.1	20.5

[a] Method according to BS1016[86]

[b] Calibrated with aqueous reagents matched for nickel and magnesium content

[c] Calibrated with aliquots of coal A as 4.8 $\mu g.g^{-1}$ arsenic content

[d] Certificate value 9.3 ± 1.0

TABLE 2.3

Determination of arsenic in coal using the slurry atomisation method for coals from various British fields

Sample		Arsenic content/µg g^{-1} (air-dried basis)		
		BS method[a]	Slurry with reagent calibration[b]	Slurry with coal as standard
Wales	C507	1.0	1.2	-
	C508	1.9	2.6	2.0[c]
	C509	3.0	4.1	3.2[c]
	C510	4.3	5.5	4.3[c]
	C511	3.8	6.6	5.1[c]
	C553	1.0	1.4	0.9[c]
Yorkshire	358	2.0	2.1	1.5[d]
	359	6.0	9.2	-
	360	16.0	25.4	15.6[d]
	361	23.0	49	31[d]
	362	29.0	96	93[d]
Scotland	KH	9.7	16.8	10.1[e]
	MT	5.9	13.1	7.4[e]

[a] Method according to BS1016[86]

[b] Calibrated with aqueous reagents matched for nickel and magnesium content

[c] Calibrated with aliquots of coal C507 as 1.0 µg g^{-1} arsenic content

[d] Calibrated with aliquots of slurried coal 359 as 6.0 µg g^{-1} arsenic content

[e] Calibrated with aliquots of slurried coal MK (see Table 2.4) as 16.7 µg g^{-1} arsenic content

This form of attack was preferred to the alternative dry oxidation procedure which gives low arsenic recoveries. Arsine is evolved from the digest, using granulated zinc and the in situ sulphuric acid, following prior reduction of arsenic to arsenic (III) with tin (II) chloride and potassium iodide. The evolved arsine is collected in dilute iodine solution and then treated with ammonium molybdate and hydrazine sulphate to form the blue molybdo-arsenate complex. The absorbance of the complex at 835 nm is measured. The results of this investigation on 13 different samples of the same coal gave a range of values of 18.6 to 31.9 $\mu g\ g^{-1}$, with a standard deviation of 3.53 $\mu g\ g^{-1}$ (14% relative). The 95% confidence limits were $25.2 \pm 7.1\ \mu g\ g^{-1}$. These results are not untypical of the BS method for high-arsenic coal samples.

Recently considerable attention has been given to the determination of arsenic by hydride generation followed by atomic-absorption spectrometry[87]. Some interferences observed in this technique might also be expected to affect the BS method. In the determination of arsenic in coal digests by arsine generation atomic-absorption spectroscopy low recoveries have been observed if undigested silica is allowed to remain suspended in solution and if metal ions such as copper and nickel are present.[103] In this latter work the interference from silica was removed by prolonged boiling or elevated digestion temperatures, which age the silica, and that of transition metal ions by a lanthanum hydroxide co-precipitation step from ammoniacal solution. It is clearly prudent to ensure that the effect of silica is minimised in the BS method and hence an alternative digestion procedure with a faster boiling rate at 310°C was evaluated. The results are given, in brackets, in column two of Table 2.4.

Given these potential problems with the standard method and the evident poor precision of this method a comparison was sought of results obtained by the slurry method for arsenic with several other analytical methods.

TABLE 2.4

Comparison of results for the determination of arsenic in coal by various methods (air-dried basis)

Coal Sample	Arsenic content/$\mu g\ g^{-1}$ (air-dried basis)						
	BS method[a,b]		Hydride AAS[c]	NAA[d]	Graphite Furnace Slurry method		
					(e)	(f)	(g)
MK	16.7		18.5	28.0	17.7	-	48
SK	14.1	(16.6)	16.7	20.0	22.7	19.0	49
TY	13.2	(17.0)	17.3	32.0	22.7	16.0	44
CT	7.0	(6.9)	8.4	11.3	14.3	12.5	45
TY T/H	2.9	(2.8)	4.6	-	6.7	4.8	19
TY H/H	10.8	(12.6)	15.2	-	13.5	8.9	34

[a] Method according to BS1016[86]

[b] Figures in brackets according to BS1016 but with a faster boiling rate

[c] Arsine generation from perchloric acid digest, following lanthanum hydroxide co-precipitation, with flame atomic absorption finish[97]

[d] Neutron activation analysis

[e] Calibrated with aqueous reagents matched for nickel and magnesium content

[f] Calibrated with aliquots of slurried coal MK as 16.7 $\mu g\ g^{-1}$ arsenic content

[g] Calibrated with standard additions of aqueous arsenic

2.3.4 Comparison of results for determination of arsenic in coal by several analytical methods

A comparison of arsenic figures for six different coals from the East Midlands coalfield by the BS method,[86] hydride generation, atomic-absorption spectrometry,[103] neutron-activation analysis and the graphite furnace direct slurry atomisation procedure is given in Table 2.4. The problem with precision using the BS method is clearly shown for high-arsenic coals, (viz. greater than 6 $\mu g\ g^{-1}$) in columns two and three of Table 2.4. The results obtained by hydride generation, the modified BS method and the direct slurry atomisation method calibrated with slurried coal are in reasonable agreement. The figures obtained by neutron-activation are generally high, and as this was performed elsewhere under contract the reason for this is not clear. It does seem to be generally true that when arsenic values for standard coals are reported, activation analysis results are often higher than those obtained by other methods.[104] Unfortunately, papers presenting such results frequently do not discuss these figures or offer comparisons with alternative procedures.[105-109]

The results obtained by the standard additions procedure are clearly high. Obviously arsenic in aqueous solution added to a coal slurry behaves differently in the graphite furnace to that bound in the coal. For the same reasons, the best calibration appears to be obtained by using different amounts of a slurried coal sample of a similar nature and with a known arsenic content. In the light of these results, it was decided to investigate the somewhat anomalous arsenic figures for some coals. In particular, results that show least agreement appear to involve coals with a high-arsenic and a high-ash content, suggesting some mineralogical origin of the discrepancies. The coals selected are listed in Table 2.5.

2.3.5 Effect of coal type on direct slurry atomisation method

The ash, total sulphur (and pyritic sulphur) contents of several coal samples were determined and compared with the arsenic content as determined by the BS method.[86] These figures are given in Table 2.5. The composition of the ash for most of these coals was also determined and these results are presented in Table 2.6.

TABLE 2.5

Ash and Sulphur contents of samples analysed for arsenic (air-dried basis)

Coal Sample	Ash % m/m	Total Sulphur % m/m	Pyritic Sulphur % m/m	Arsenic content/µg g^{-1}[a]
A	4.6	1.14	-	4.8
B	7.9	2.17	-	18.3
C	3.8	1.37	-	7.2
D	4.5	1.21	-	5.5
E	5.9	0.82	-	11.6
F	8.0	1.18	-	7.3
G	5.9	2.46	-	24.2
H	3.1	1.43	-	5.0
I	16.4	1.45	-	10.1
J	16.4	1.08	-	9.2
NBS SRM 1632(a)[b]	21.7	1.62	-	9.3 (Cert)
C507	2.3	1.07	-	1.0
C508	3.2	1.05	-	1.9
C509	4.0	1.30	-	3.0
C510	2.5	1.25	-	4.3
C511	3.7	1.63	-	3.8
C553	2.3	1.08	-	1.0
358	3.1	1.43	-	2.0
359	8.6	1.88	-	6.0
360	27.5	2.58	-	16.0
361	28.2	3.18	-	23.0
362	38.2	3.17	-	29.0
MK	18.4	2.14	1.16	16.7
SK	15.7	1.76	0.89	16.6
CT	16.5	0.80	0.23	6.9
TY	14.7	1.55	0.66	17.0
TY T/H	5.6	1.01	0.18	2.8
TY H/H	4.5	1.25	0.33	12.6
MT	21.3	0.62	0.28	5.9
KH	11.6	1.13	0.48	9.7

TABLE 2.5 continued

Coal Sample	Ash % m/m	Total Sulphur % m/m	Pyritic Sulphur % m/m	Arsenic content/μg g^{-1} [a]
Western 1.3 S.G [c]	3.3	1.60	0.48	2.3
1.3-1.4 S.G [c]	7.7	2.78	1.88	11.1
1.4-1.5 S.G [c]	17.9	3.79	3.07	23.1
1.5-1.6 S.G [c]	26.5	3.91	3.28	34.5
1.6-1.7 S.G [c]	35.0	4.26	3.94	55
1.7-1.8 S.G [c]	41.5	5.32	5.11	65

- Not determined

[a] Determined by BS method[86]

[b] National Bureau of Standards SRM 1632(a)

[c] Specific gravity separated coal fractions

TABLE 2.6

Major and minor ash constituents of coals analysed for arsenic content

						Ash Composition % m/m								
Sample	Arsenic/[a] µg g^{-1}	Ash %m/m	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	Mn_3O_4	P_2O_5	SO_3	TOTA
A	4.8	4.6	40.9	25.5	17.4	0.7	1.7	1.3	4.5	2.8	<0.1	0.2	4.0	99.
B	18.3	7.9	40.3	21.3	21.3	0.6	1.6	1.1	3.2	2.6	<0.1	0.3	5.5	97.
C	7.2	3.8	36.1	23.1	19.4	0.7	3.9	0.9	5.1	2.1	<0.1	1.0	7.5	100.
D	5.5	4.5	46.4	27.8	15.0	0.6	1.8	0.6	1.9	2.0	<0.1	1.0	2.0	99.
E	11.6	5.9	37.4	28.4	10.4	1.5	7.1	2.4	2.4	1.1	0.3	0.6	5.3	96.
F	7.3	8.0	36.7	24.3	13.3	1.7	8.4	4.6	1.8	1.0	0.4	0.1	7.8	100.
G	24.2	5.9	14.3	3.9	54.6	0.9	12.8	3.9	1.1	5.6	0.1	0.2	5.4	102.
H	5.0	3.1	21.6	17.8	38.0	0.7	11.4	2.6	0.4	1.0	0.1	0.1	7.0	100.
I	10.1	16.4	50.8	28.0	9.7	0.2	1.0	1.5	1.6	4.3	0.1	<0.1	0.8	98.
J	9.2	16.4	49.8	26.1	10.0	0.6	1.5	1.5	2.8	4.4	0.1	<0.1	1.5	98.
NBS	9.3	21.7	59.5	17.9	9.7	1.0	6.5	3.3	0.6	1.8	0.1	0.3	0.8	99.
TY T/H	2.8	5.6	48.9	31.5	6.1	0.8	3.7	1.2	6.4	1.2	<0.1	0.3	2.9	102.
TY H/H	12.6	4.5	40.4	18.6	14.6	0.5	8.0	1.9	7.9	1.5	0.1	0.3	9.4	103.
SK	16.6	15.7	50.7	26.8	10.8	0.8	2.2	1.5	1.7	3.2	0.1	0.3	1.1	99.
MK	16.7	18.4	49.2	28.1	11.3	0.9	2.6	1.5	1.0	3.1	0.1	0.3	1.4	99.
CT	6.9	16.5	48.1	28.2	6.8	1.3	4.6	2.3	1.1	2.1	0.2	0.4	3.2	98.

TABLE 2.6 continued

Sample	Arsenic/[a] μg g^{-1}	Ash %m/m	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	Mn_3O_4	P_2O_5	SO_3	TOTA
					Ash Composition % m/m									
TY	17.0	14.7	48.0	27.6	9.3	0.8	4.0	1.5	2.4	3.2	0.1	0.2	2.8	99.
358	2.0	3.1	41.5	25.0	18.5	1.1	2.2	1.5	5.7	3.0	ND	ND	ND	–
359	6.0	8.6	45.5	25.6	16.8	1.1	1.8	1.5	2.8	3.2	ND	ND	ND	–
360	16.0	27.5	47.0	26.5	15.5	1.1	1.6	1.5	1.7	3.3	ND	ND	ND	–
361	23.0	28.2	48.8	27.5	13.8	1.0	1.4	1.5	1.2	3.5	ND	ND	ND	–
362	29.0	38.2	49.4	28.5	11.9	1.0	1.3	1.5	1.0	3.8	ND	ND	ND	–
KH	9.7	11.6	59.8	27.3	6.1	1.2	1.4	1.5	0.1	1.9	ND	0.2	0.5	100.
MT	5.9	21.3	51.5	24.6	8.6	0.9	4.1	1.9	0.5	3.3	ND	0.2	3.6	99.

[a] Determined by BS method[86]

ND = Not determined

Correlation coefficients of 0.68, 0.84 and 0.95 were found between ash, total sulphur, and pyritic sulphur, respectively, and the arsenic content of coal. The strong correlation of arsenic with pyritic sulphur may indicate the presence of the mineral arsenopyrite (mispickle) in coal. It may be possible to identify arsenopyrite in coal using the techniques of scanning electron microscopy and energy dispersive X-ray analysis. The correlation coefficients for the difference in the arsenic level as found by the BS method[86] and the slurry atomisation method with the percentage ash constituent values are shown in Table 2.7. Clearly none of these correlations is significant.

Analysis of a low-ash coal directly in the furnace tube after a high-ash coal determination did not produce any significant change in the observed absorption. It was therefore concluded that the apparent increase in the response by direct electrothermal atomisation with increased ash content of coal was not caused by build-up of ash in the tube. The major ash constituent in coal is silica, and to test the suggestion that silica can occlude arsenic in electrothermal atomisation, pure quartz and amorphous silica (less than 3 μm) were added to coal slurries in concentrations of up to 5 percent of the coal, without any measurable effect on the absorption signal.

Recently several workers have reported considerable success in using graphite platforms in graphitefurnace atomisers to overcome a variety of interferences.[110] The use of such a platform ensures that the analyte atoms are released from the platform into a hotter environment, thus more nearly approaching the ideal of isothermal atomisation and reducing vapour-phase interferences. When small platforms were made from old graphite tubes and samples pipetted onto them, there was no improvement in the results obtained by the standard additions technique. The only changes observed were some broadening of the absorption peak, indicating, as expected, a slower release of arsenic relative to the rapid atomisation mode normally used. That the platform technique did not remove differences in the atomisation of arsenic from coal and from aqueous calibration solutions is a further confirmation that the interferences do not occur in the vapour phase.

TABLE 2.7

Correlation Coefficients for the difference in arsenic values by the BS method[86] and the slurry atomisation technique versus percentage ash constituents

Ash Constituent	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	Mn_3O_4	P_2O_5	SO_3
Correlation Coefficient	0.14	0.22	0.01	0.16	0.30	0.01	0.28	0.41	0.07	0.11	0.31

Fuller et al[111] have drawn attention to the effects that particle size may have on the electrothermal atomisation of solid-samples; particularly the sampling errors that may arise with particles larger than 25 µm. All samples in this work were ground to pass through a 45 µm sieve. The particle size distributions of samples A-J and NBS SRM 1632(a) were examined using a Coulter Counter. In each instance 98% of the particles were found to be less than 40.3 µm in size, with most of the particles being in the range 20.16 to 10.08 µm. The particle size fractions were fairly consistent for all the samples and therefore within a suitable range for solid electrothermal atomisation.

2.3.6 Aluminium spectral interference at the arsenic 193.7 nm line

The direct atomisation of coal slurries requires accurate measurement of the background absorption, which may be in the range 0.4 to 0.8 absorbance units. The conventional continuum source dual beam background correction system, such as the deuterium arc used in this work will not correct for 'structured' background or spectral interferences.

Recently an aluminium spectral interference at the arsenic 193.7 nm absorption line has been described by Riley.[112] This interference was reported to be from Al^{+} lines at 193.47 and 193.45 nm and the Al^{2+} line at 193.58 nm on the arsenic 193.7 nm resonance line used. Given the very narrow widths of atomic-absorption lines this seems at first unlikely. When it is recalled that a solid-sampling technique was used and that aluminium was present at levels up to about 6% in the coal (60,000 $\mu g\, g^{-1}$) it will be seen that very considerable broadening of the aluminium lines can be expected and some problems from overlap of the wings of these broadened lines might be possible.

Such an interference was not indicated by the correlation coefficient (0.22) shown in Table 2.7 A possible explanation is that only a proportion of the aluminium present in coal is digested, whereas the correlation was established using the total aluminium content.

The precipitation of $MgAlF_5.xH_2O$[113,114] would remove the aluminium from solutions of coal prepared by the Haynes digestion procedure[100] and should thus effectively reduce this aluminium spectral interference to negligible levels. The SEM/EDX analysis of the filtered Haynes digestion residue for a high-ash coal (MK) is shown in Figure 2.5. The presence of fluoride, magnesium and aluminium is indicated and accepting the poor sensitivity of this technique for the determination of fluoride it is not unreasonable to suggest that most of the aluminium has been precipitated from solution as $MgAlF_5.xH_2O$.

To investigate further, 5 µl of a 1 µg $cm3^{-1}$ aluminium solution were added to a number of low-ash coals digested by the Haynes procedure and this resulted in large signal enhancements. This confirmed that aluminium at high concentrations does cause interference at the arsenic 193.7 nm line. A selection of high-ash coals, including NBS reference materials were analysed as previously described but at the alternative 197.2 nm resonance line, which is reported to be free of aluminium interference.[112]

2.3.7 Analysis of arsenic at the 197.2 nm resonance line

The 197.2 nm line is generally less intense than the 193.7 nm line and consequently more noise was encountered. Aqueous calibration standards showed the linear working range to extend to approximately 10 ng of arsenic using the mini-flow mode of 25 cm3 min^{-1} argon (c.f 2.5 ng for the 193.7 nm line). The lower limit of the useful working range was about 2 ng, again a four-fold increase.

Several high-ash coals, powdered and then slurried as previously described were then re-analysed at 197.2 nm by slurry atomisation using aqueous calibration standards matched only for nickel and magnesium nitrate content. The results are given in Table 2.8. Clearly many of the major discrepancies shown in Tables 2.2, 2.3 and 2.4 have been eliminated. Good agreement is found with values obtained by the standard method up to and including 4% m/m aluminium in the coal. In the one case where good agreement is not obtained the ash content is so high, almost 40%, that perhaps complete confidence cannot be maintained in the hydride formation step of the BS method.

Figure 2.5 Energy dispersive X-ray spectrum from scanning electron microscope for filtered Haynes digestion residue for a high-ash coal (MK) at 20 KeV, 25 seconds at 30° take-off angle

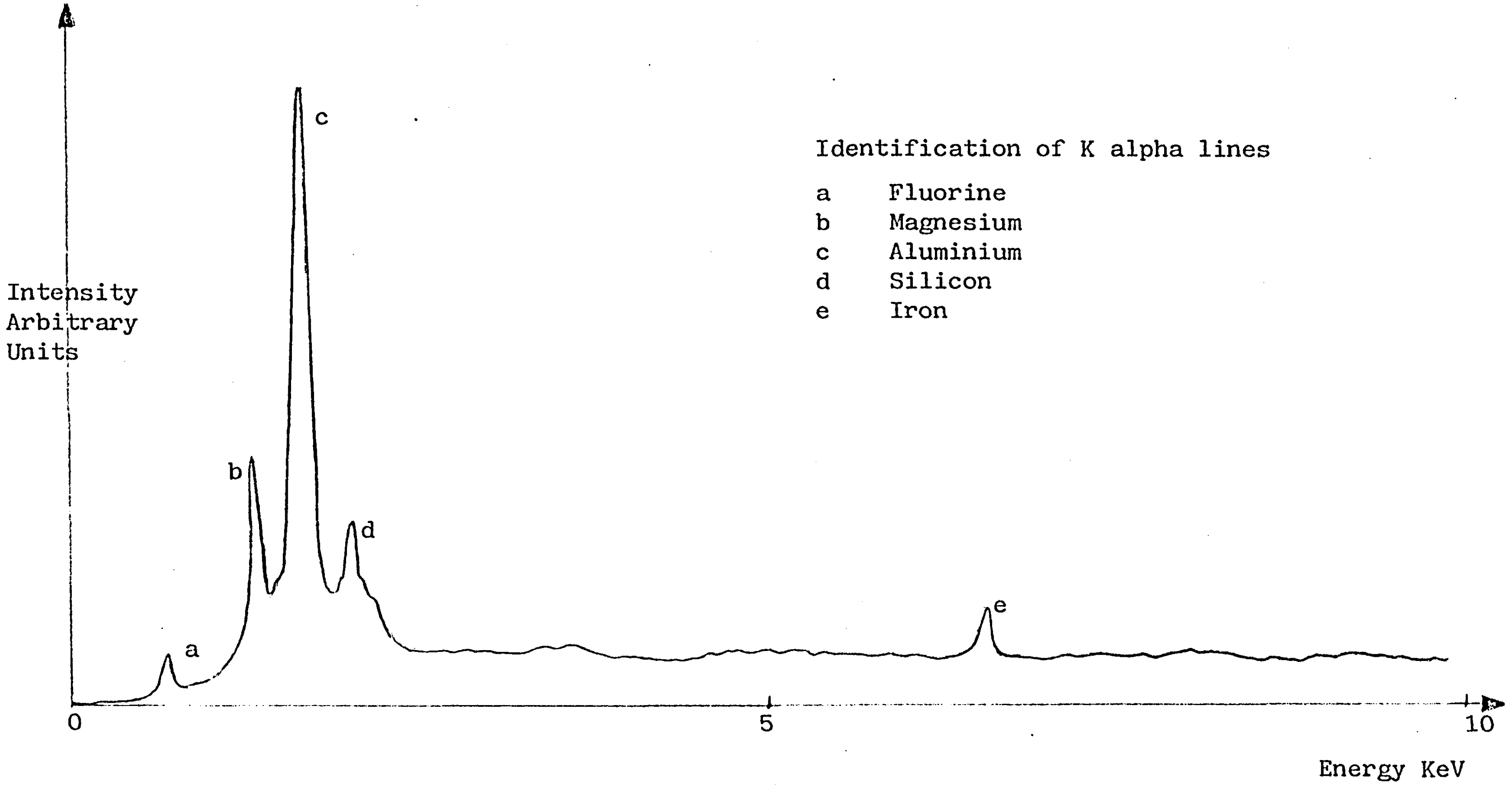


TABLE 2.8

Determination of arsenic in coal using the 197.2 nm resonance line (air-dried basis)

Coal Sample	Aluminium Content % m/m in coal	Ash % m/m	As previously found at 193.7 nm/ $\mu g\ g^{-1}$	BS method/ $\mu g\ g^{-1}$	As found at 197.2 nm/ $\mu g\ g^{-1}$
NBS SRM 1632(a)	2.06	21.7	25.1	9.3 ± 1.0*	8.5
NBS SRM 1635	0.32	5.2	ND	0.42 ± 0.15*	0.75
KH	1.67	11.6	16.8	9.7	7.7
360	3.85	27.5	25.4	16.0	12.9
361	4.12	28.2	49	23.0	23.5
362	5.77	38.2	96	29.0	39
MK	2.74	18.4	17.7	16.7 [18.5]'	14.4
CT	2.46	16.5	14.3	7.0 (6.9)† [8.4]'	8.3
SK	2.21	15.7	22.7	14.1 (16.6)† [16.7]'	14.6
TY	2.15	14.7	22.7	13.2 (17.0)† [17.3]'	14.5

' Figures in square brackets obtained by hydride generation AAS, see ref. 97.

* Certificate value

† Figures in parentheses obtained according to BS 1016 but with a faster boiling rate.

ND Not determined

Attempts to improve upon the agreement shown in Table 2.8 by the standard addition method of calibration were not successful. Indeed positive errors and poor precision were obtained with this method. This is perhaps not surprising since the success of the standard addition method depends upon adding analyte in a form similar to that present in the sample. Adding aqueous arsenic solutions to a coal slurry does not meet this criterion.

The results presented in Table 2.8 clearly indicate that arsenic can be determined directly in a wide range of coals using slurry atomisation and aqueous calibration standards, providing the 197.2 nm resonance line is used. It seems likely that a very broadened aluminium line is responsible for a spectral interference which gives rise to positive errors at the 193.7 nm line.

Correction for such a spectral interference was not achieved using the conventional continuum source approach used in this work but possibly a spectral background correction device based on the Zeeman effect or the Smith-Hieftje principle would have eliminated this interference. Choice of the alternative 197.2 nm resonance line, still provides adequate sensitivity, removes the necessity to look at alternative background correction systems, and markedly extends the utility and versatility of a very rapid analytical procedure.

2.3.8 Characteristics of the Method

The above results using the 193.7 nm line show that it is not possible to determine arsenic in coals using solid-sampling electrothermal atomisation with aqueous solution calibration but that it is possible to determine the arsenic content of coals by calibration with a coal of the same type and of known arsenic content. Such arsenic figures can be provided by the digestion/conventional electrothermal atomisation procedure described above.

The results using the alternative 197.2 nm resonance line with aqueous solution calibration for coal slurry analyses, show very good agreement with certified reference coal standards and samples analysed by BS procedures. These results make it unnecessary to investigate the use of other types of background correction systems.

The total time for a complete analysis of ground coal was less than ten minutes.
Using aqueous injection of 20 µl and the 'miniflow' internal gas-flow mode for the 193.7 nm line 0.05 ng of arsenic gave an absorbance of 0.0044, whilst for the 197.2 nm line 0.2 ng of arsenic gave the same absorbance i.e (1%). When a 10% m/V slurry was used the detection limit was less than 0.5 $\mu g\ g^{-1}$ for both these lines. Thus, the method is well suited to cover the normal range of arsenic contents of 1 to 25 $\mu g\ g^{-1}$ found in coal. The working range can be further extended by making a more dilute slurry, enabling coals of high arsenic content to be determined.

2.3.9 Determination of selenium in coal by dissolution and electrothermal atomisation

This trace element found in coal, is not analysed on a routine basis by the NCB and therefore a comparison for accuracy of the method could only be made with the two NBS/SRM coals.

Calibration graphs using aqueous selenium solution in a nickel and magnesium nitrate matrix, with and without a platform in the graphite tube for the miniflow mode at the 196.0 nm line, are given in Figures 2.6 and 2.7. The graphs show an approximate linear working range up to 12.5 ng and 15 ng of selenium respectively.

Analyses of coals digested by the Haynes procedure[100] are given in Table 2.9. The results clearly show poor precision for certain coals, although the values obtained for the NBS SRM 1632(a) coal are acceptable and in good agreement with the certified value.
The signal response for digested coals was characterised by a negative-absorption, presumably caused by overcompensation of the background using the D_2 arc. This often indicates the presence of 'structured' background, a problem described in Section 2.1.1. The absorption profile is illustrated in Figure 2.8. This profile made it difficult to evaluate the true atomic-absorption signal.

The formation of volatile SeF_6, or even H_2Se, during the digestion procedure is a possibility and could be the reason for poor repeatability observed for the results given in Table 2.9.

Figure 2.6 A calibration curve of selenium using mini-flow mode at the 196.0 nm line

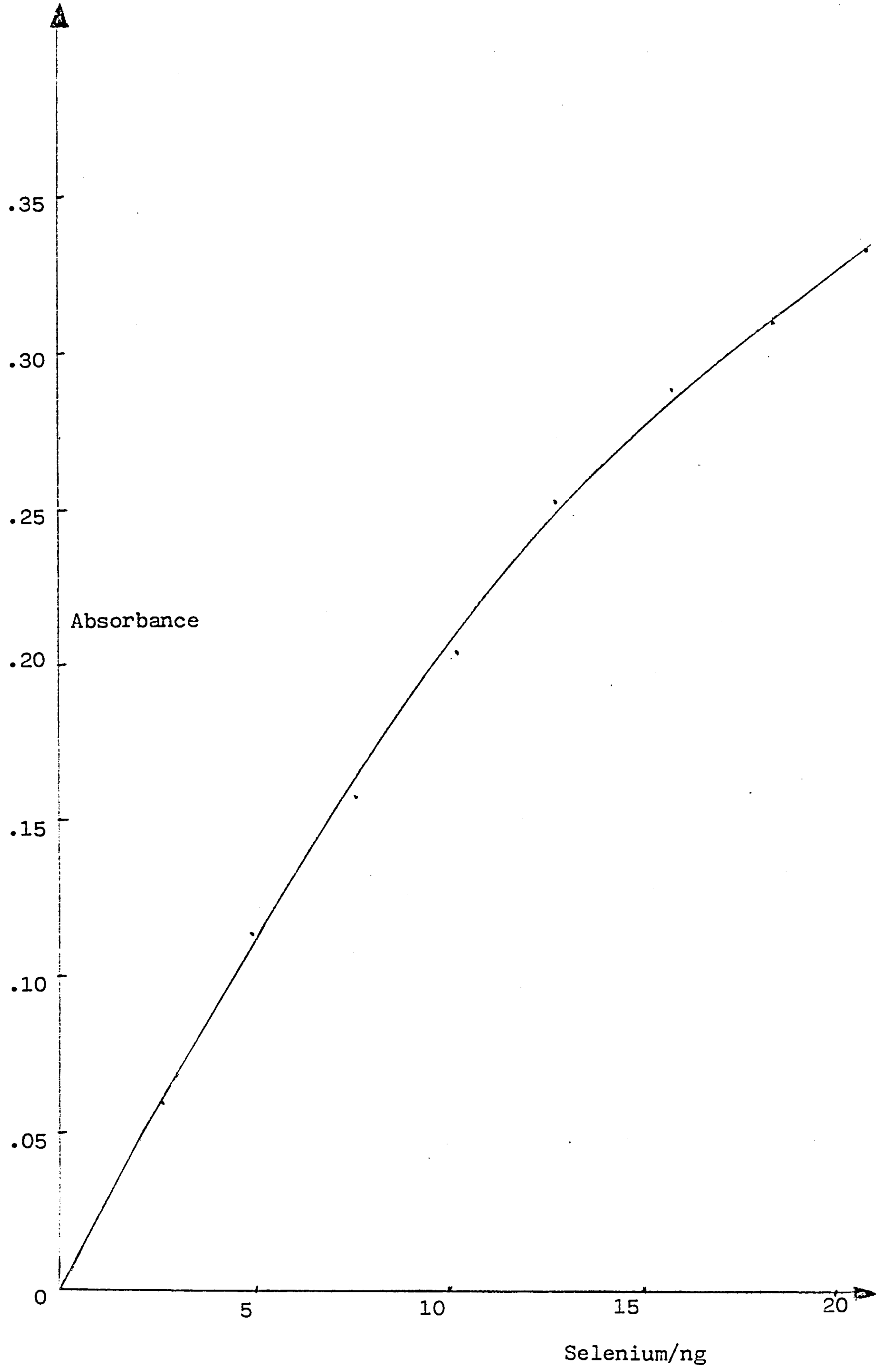


Figure 2.7 A Calibration curve of selenium using a platform insert in the tube and mini-flow mode at the 196.0 nm line

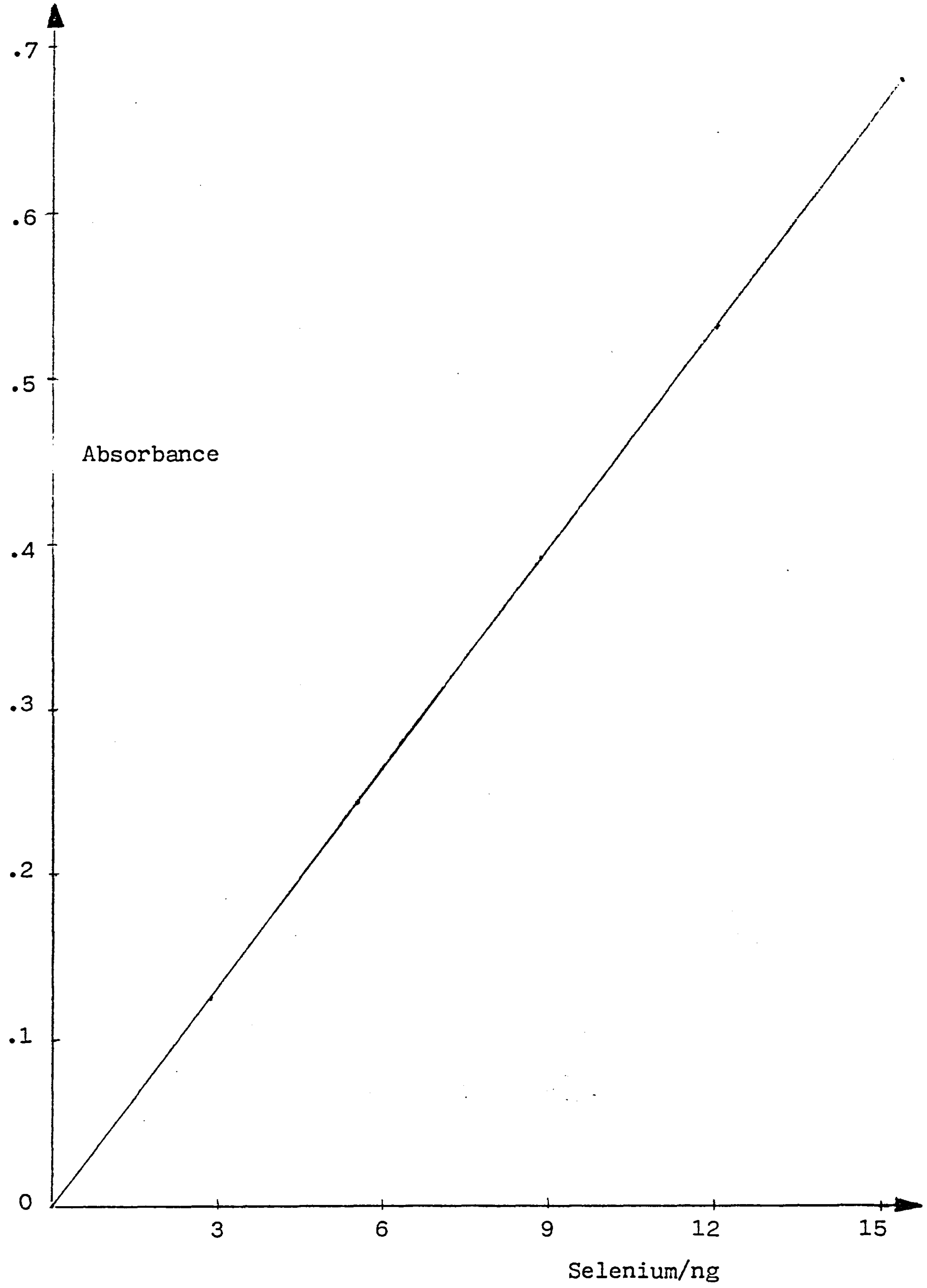


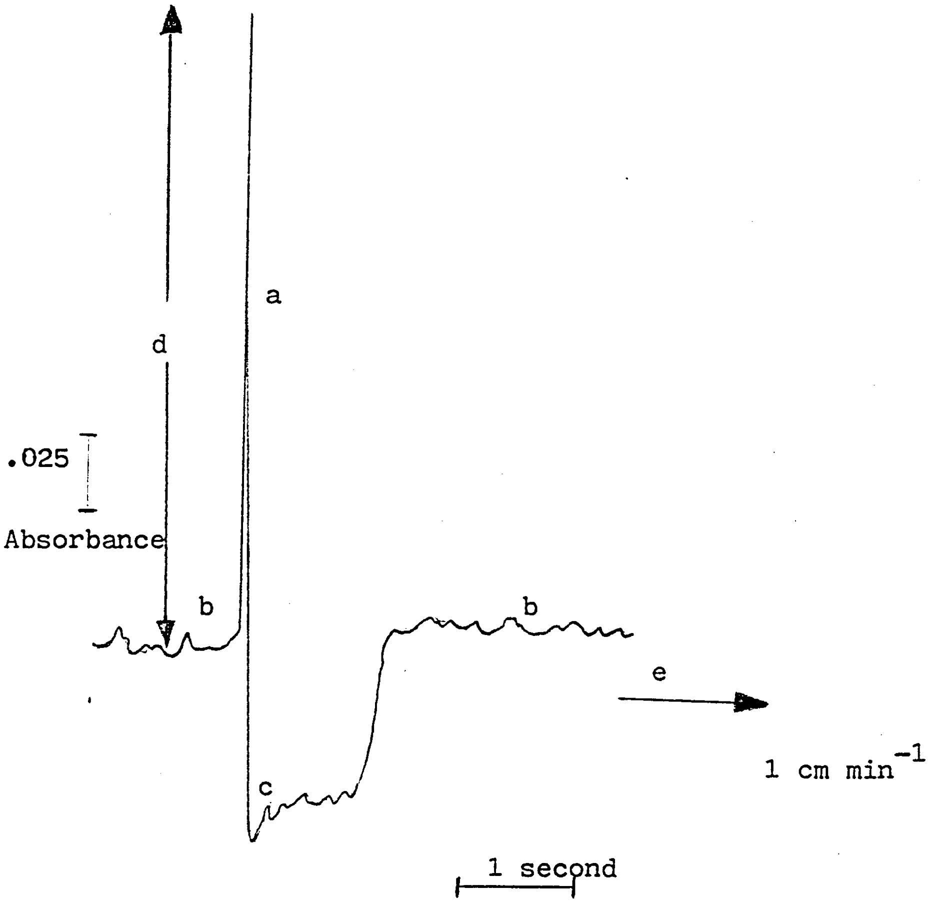
TABLE 2.9

Determination of selenium in coal using the Haynes digestion procedure

Coal Sample	Cert. Value µg g^{-1}	Selenium content/µg g^{-1} (separate digests air-dried basis)		
		1	2	3
1632(a)	2.6 ± 0.7	2.6	3.3	2.8
1635	0.9 ± 0.3	1.2	2.4	-
MK	-	0.3	0.9	1.5
E	-	2.7	0.5	1.2
F	-	1.4	0.5	-
KH	-	0.8	0.3	-

- Not determined

Figure 2.8 Characteristics of the absorption signal for selenium at 196.0 nm using aqueous digestion of coal



a Absorption signal

b Base-line

c Overcompensation caused by deuterium arc background correction system

d Measured signal response

e Chart direction

The use of slurried coal samples, to eliminate possible digestion problems produced even larger over compensation of the atomic-absorption signal than that illustrated in Figure 2.8. This made absorption measurements impossible.

Spectral interference from atoms of iron at the selenium 196.0 nm atomic line has been reported by Saeed when analysing blood serum.[115] Such an interference was confirmed by the addition of iron solution (20 μl of 1000 mg l^{-1}) to selenium standards matched for nickel and magnesium nitrate contents. These additions produced overcompensation of the atomic-absorption signal as shown in Figure 2.8.

The alternative but less sensitive 204.0 nm line was then examined using both aqueous digests and slurried coal samples. Overcompensation of the atomic-absorption signal was once again found.

A background measurement problem was found for slurried coal samples using an alternative instrument, (Instrumentation Laboratory model 517, Instrumentation Laboratory (UK) Ltd, Warrington, Cheshire WA3 7PB). This equipment uses deuterium arc background correction and the analyses were performed using a platform insert in the graphite tube.

Thus, with the equipment available at both the collaborating and sponsoring establishments, it was not possible to achieve satisfactory background correction for the determination of selenium in coal. With the kind co-operation of two instrument manufacturers, background correction systems that have been suggested as being capable of compensating for 'structured' background (see Section 2.1) were investigated for the determination of selenium in coal.

2.3.10 Determination of selenium in coal using electrothermal atomisation and the Zeeman background correction system

2.3.10.1 Analytical conditions

A Perkin-Elmer (PE) model 5000 atomic-absorption spectrometer fitted with graphite furnace atomisation and Zeeman background correction was used in the study. The following parameters were selected after optimisation of the signals obtained for selenium in solutions of nickel and magnesium nitrates (Haynes[100] digestion concentrations).

Wavelength	196.0 nm (EDL)
Slit width	0.7 nm

Furnace conditions

Dry $110^{\circ}C$ ramp for 20 seconds
$110^{\circ}C$ hold for 20 seconds

Char $800^{\circ}C$ ramp for 20 seconds
$800^{\circ}C$ hold for 30 seconds

Atomise $2000^{\circ}C$ max power rate 5 seconds

Time for complete analysis cycle 95 seconds.

2.3.10.2 Results and Discussion

The calibration for selenium in a nickel and magnesium nitrate solution matrix[100] was linear up to 100 $\mu g\ l^{-1}$. A solution of NBS SRM 1632(a) coal (2g 100 $cm^{3\ -1}$) was found to give no measurable signal response for a 20 μl injection into the furnace. Spiking selenium solutions with large excesses of iron solution produced a considerable depression in the absorption signal viz:

Solution ($\mu g\ l^{-1}$)	Peak height measurement(mm)	
100 Se	111	110
100 Se + 100 Fe	67	68

The background correction system did not apparently correct for interferences from iron atoms. When slurried samples of NBS SRM 1632(a) coal were analysed, a variable signal was obtained which could not be measured. The equipment traces a background signal in addition to the atomic-absorption response for an element. This background signal was greater for the 100 $\mu g\ l^{-1}$ selenium solution than for the same amounts of both selenium and iron solutions. This is not easy to explain unless there was an equipment fault. The background correction system was not capable of removing iron interference at the selenium 196.0 nm atomic line, and could not be used for the analysis of coal slurries.

The digested coal solution appeared to have lost selenium, supporting the possible formation of volatile SeF_6 or H_2Se in the digestion procedure.

Evaluating equipment under such limited trials is not satisfactory and it may be that the instrument was malfunctioning. A second evaluation was carried out some two months later but the results obtained did not change the conclusions already made.

2.3.11 Determination of selenium in coal using the Smith-Hieftje background correction system

2.3.11.1 Analytical conditions

An Instrumentation Laboratory (IL) model Video 22, dual channel, double-beam atomic-absorption spectrometer fitted with graphite furnace atomisation and both Smith-Hieftje and deuterium arc background correction systems was used in this study. I am indebted to others for these results[116] which are included to illustrate the nature of the problems encountered in selenium determination.

The equipment was optimised for the determination of selenium using the method previously described in section 2.3.10.1. The conditions were found to be different from those used previously with the (PE) equipment.

Wavelength	196.0 nm
Clean	on
High-flush	on
Pyrolytically	coated tube

Furnace conditions

Time(s)	30	25	30	-	5
Temp (^oC)	79	115	800	2030	2030

Time for complete analysis cycle 90 seconds

2.3.11.2 Results and Discussion

The calibration for selenium in the nickel and magnesium nitrate solution matrix[100] was linear up to 100 $\mu g\ l^{-1}$. Coal slurries only were examined using the equipment, because of the previously reported difficulty in obtaining repeatable results on solutions of coal prepared by the Haynes digestion procedure.[100] The results obtained for the two NBS reference coals are given in Table 2.10. The values obtained are in reasonable agreement with the certified values and suggest that this type of background correction system is capable of removing spectral interference from atoms of iron at the 196.0 nm resonance line.

Table 2.10

Determination of selenium using Smith-Hieftje background correction and slurried coal sampling

	Selenium content/$\mu g\ g^{-1}$ (air-dried basis)	
NBS Sample	Cert. Value	This work[116]
1632(a)	2.6 ± 0.7	1.6
1635	0.9 ± 0.3	1.1

The results obtained using the Smith-Hieftje system should be considered tentatively because of the limited number of results available for evaluation. However, this background correction device was also used for the determination of arsenic at the 193.7 nm atomic line using coal slurries.[116] The reported aluminium spectral interference at this line was completely eliminated and the results obtained for the NBS SRM coals were in very good agreement with the certified values. Graphical plots illustrating this work are given in Figure 2.9.

It appears that the Smith-Hieftje system does have a greater potential for application to the direct determination of selenium in coal than the Zeeman method of background correction, but I was not convinced that the Zeeman equipment was indeed functioning correctly.

2.4 CONCLUSION

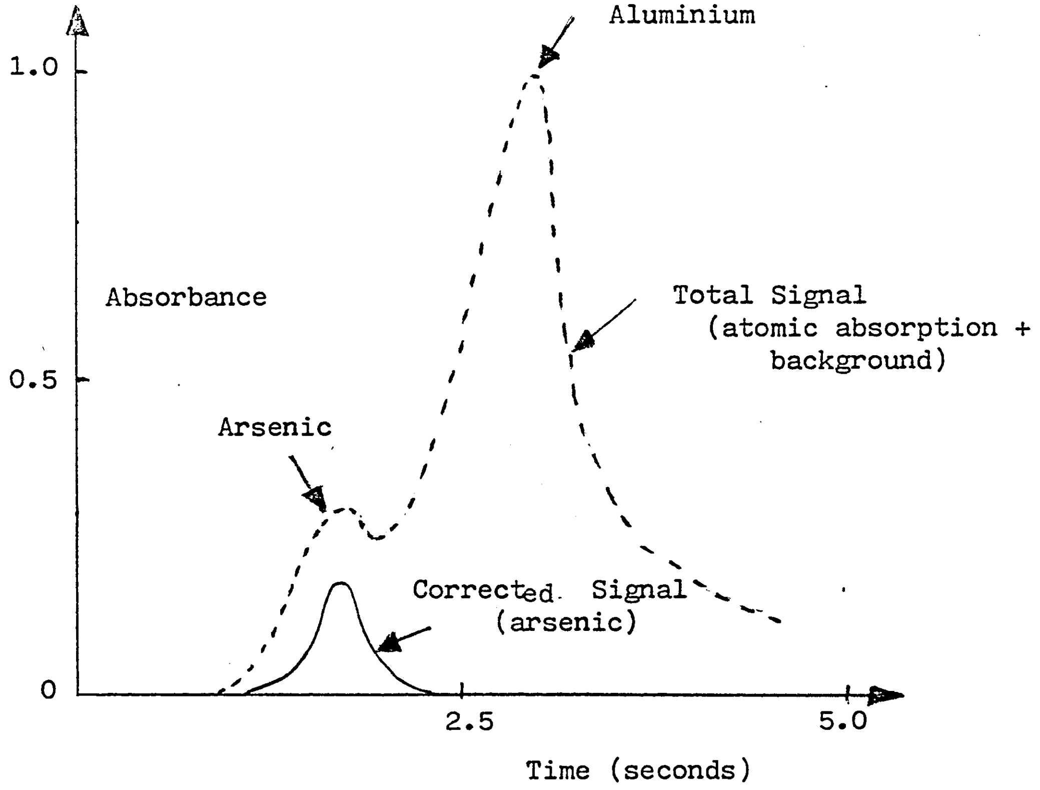
The method of solid-sampling and electrothermal atomisation for coal analysis has been shown to be very successful for the determination of arsenic. The difficulties encountered using the method applied to selenium, were that background interference problems occurred using a deuterium arc at the two most sensitive selenium lines.

The method avoids digestion problems for trace metal analysis of coal, such a problem with selenium has clearly been identified in this study. However, the use of solid-samples increases matrix concentrations and the consequential atomic line broadening may generate background absorption measurement problems, particularly when using a continuum source method of correction. The wings of broadened atomic lines near to the analyte line will cause an incorrect background measurement when using a continuum source method.

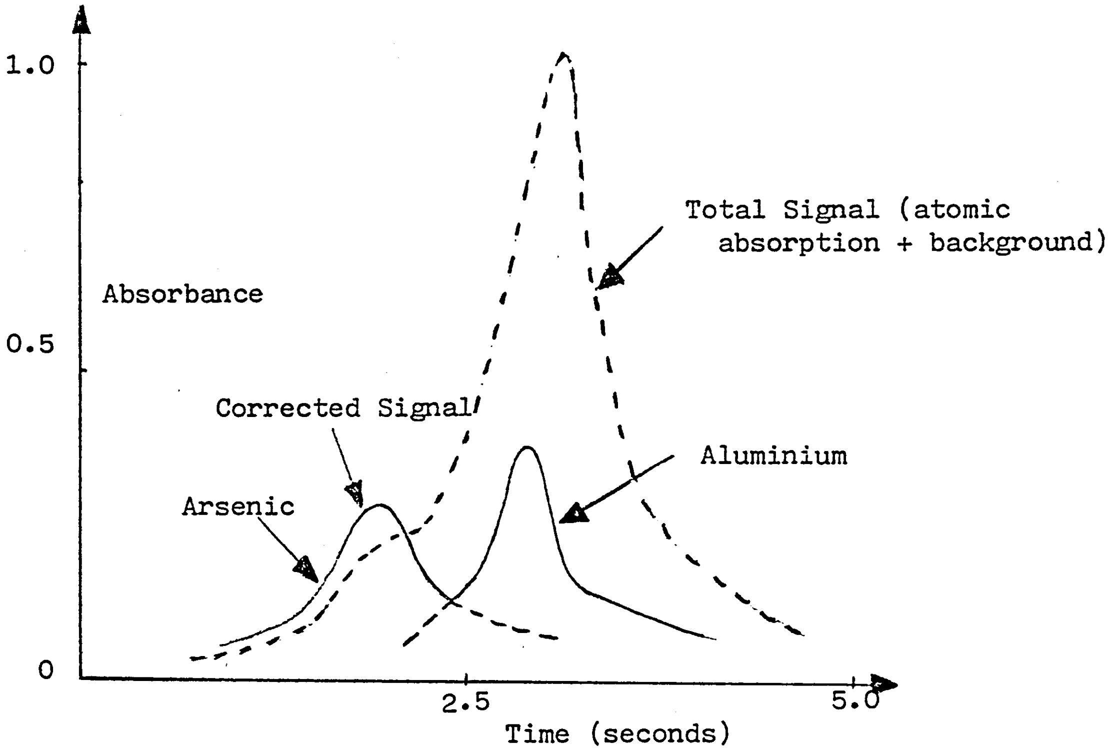
The use of Zeeman and Smith-Hieftje background correction systems, which are suggested as capable of compensating for spectral overlaps and 'structured' background showed some success, particularly when using the Smith-Hieftje principle.

Figure 2.9 Comparison of D_2 arc and Smith-Hieftje background correction for the determination of arsenic in slurried samples of NBS SRM 1632(a)

a) Smith-Heiftje correction



b) Deuterium arc correction



An additional problem in the study was the unavailability of coals with accurately determined selenium contents.

The method should, however, have a wide application for trace metal analysis in coal, particularly if careful background correction and matrix modification are employed.

CHAPTER 3

THE APPLICATION OF SCANNING ELECTRON MICROSCOPY AND ENERGY-DISPERSIVE X-RAY ANALYSIS TO POWDERED COALS

3.1 INTRODUCTION

Coal combustion is likely to be the major energy source well into the next century and therefore efficient utilisation as well as environmental considerations are active fields of research. Sulphur, chlorine and other volatile minor and trace elements present in coal can produce potentially harmful materials such as sulphur dioxide and hydrogen chloride. The attractions of direct instrumental techniques for elemental coal analysis are speed and accuracy, achieved by elimination of error-prone, time-consuming, preparation stages.

The scanning electron microscope and complementary energy-dispersive X-ray analysis equipment (SEM/EDXA) can be used for non-destructive quantitative micro-analysis.[117,118,119] The technique is normally employed on highly polished metallic specimens. Recently energy-dispersive X-ray fluorescence spectroscopy was applied for seam location differentiation of coal specimens using trace element concentrations.[120]

A micro-analysis technique such as SEM/EDXA would be useful to demonstrate the uniform micro-distribution of certain elements found in coal, in particular chlorine, whose mode of occurrence is no longer thought to be as alkali metal salts present in the mineral matter.[121,122]

Quantitative analysis of a range of coals by the SEM/EDXA technique is reported here. Twelve elements were determined simultaneously, i.e. chlorine, sulphur and the major constituents of coal ash. The results for chlorine and sulphur are compared to those obtained by the current British Standard methods[123] and by those obtained potentiometrically with the appropriate ion-selective electrodes (ISE).[124] For the other elements, comparisons are presented where possible with figures obtained by the atomic-absorption spectroscopic, colorimetric and gravimetric analyses of solutions prepared from the same coals ashed at 815°C.[123] Two National Bureau of Standards reference coals have also been analysed. Correlations between these results, the conventional ash content[123] and the SEM/EDXA elemental sum, excluding chlorine and sulphur, are also investigated in this chapter.

3.2 EXPERIMENTAL

3.2.1 Instrumentation

3-30 ADP Scanning electron microscope (SEM) (CamScan, Bar Hill, Cambridge).

860 Series I Energy-dispersive X-ray (EDX) analysis system with solid state Silicon (Lithium) detector (30 mm^2 active area, resolution FWHM at 5.9 keV of 155 eV at 10,000 cps) and fully quantitative ZAF4/FLS and ZAF/PB software. (Link Systems, High Wycombe, Bucks).

Double beam atomic-absorption spectrometer, Model 460, (Perkin-Elmer Ltd., Beaconsfield, Bucks).

Manually operated press Type 5100-4599 (15 tonnes) (Perkin-Elmer Ltd., Beaconsfield, Bucks).

Micro-mill, Type MS 400, Retsch Spectromill, (Glen Creston, Stanmore, Middlesex).

Cobalt and multi-element standards, Leit-C carbon dag, (Agar Aids, Stansted, Essex).

Coulter Counter Model TA II, (Coulter Electronics Ltd., Luton Beds).

Carbon fibre vacuum deposition equipment, (Nanotech, Prestwich, Manchester).

3.2.2 Sample Selection

Three pillar sections of coal from the National Coal Board, East Midlands Region were selected to give a range of ash contents, and chlorine contents in coal of 0.2-0.8 percent. The seams chosen are shown in the coal pillar photographs (Plates 3.1, 3.2 and 3.3) and details of the routine analyses are given in Tables 3.1, 3.2 and 3.3. In addition, two National Bureau of Standards reference coals, 1632a and 1635 and six well analysed bituminous coal standards were examined.

3.2.3 Sample Preparation

Each sampled coal pillar was separated into two approximately equal sections along its length, one half being sealed in plastic bags and retained. The other half was sub-divided and its seam profile and analysis are illustrated in Tables 3.1, 3.2 and 3.3.

PLATE 3.1 COAL PILLAR SECTION 60

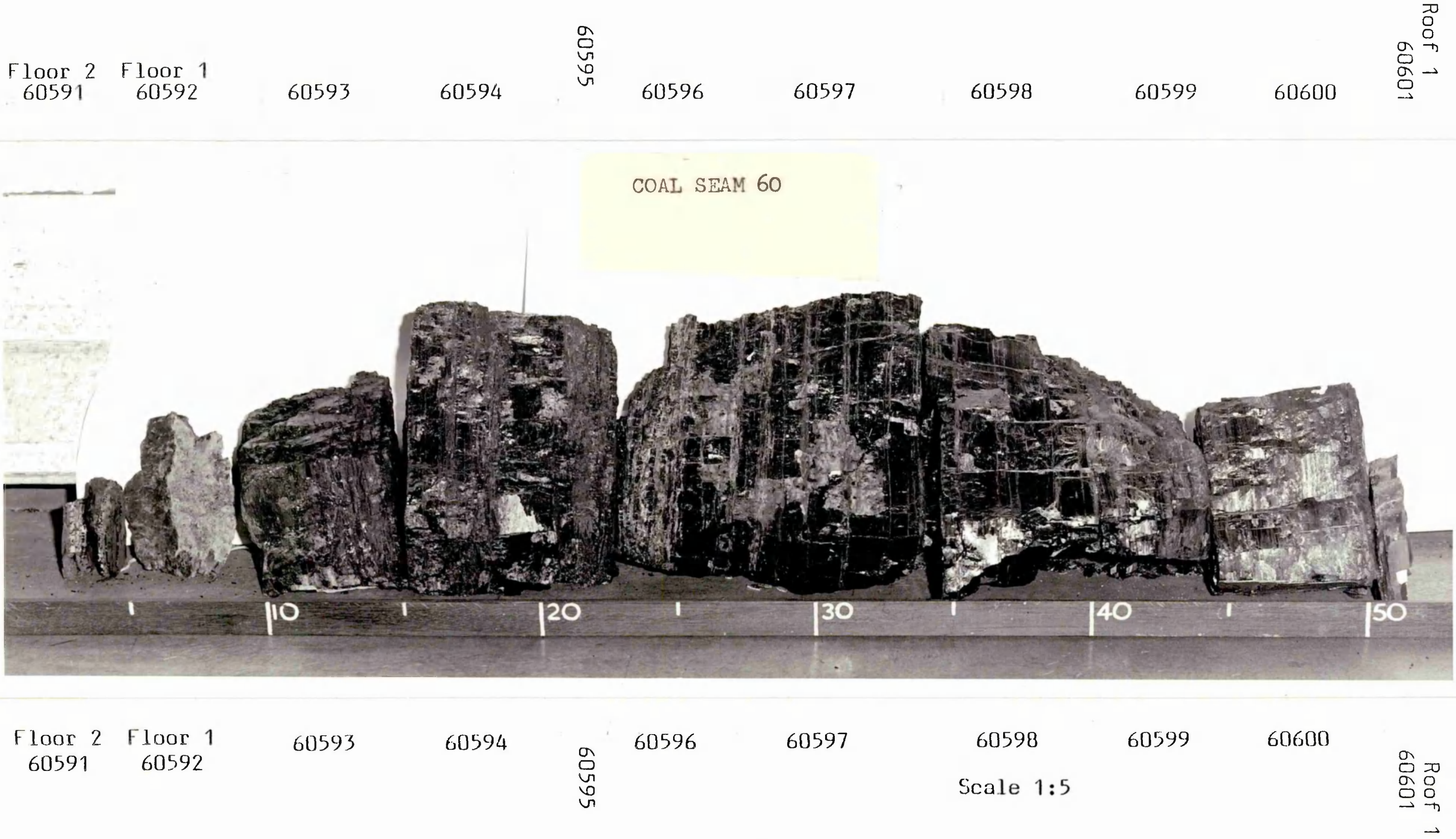
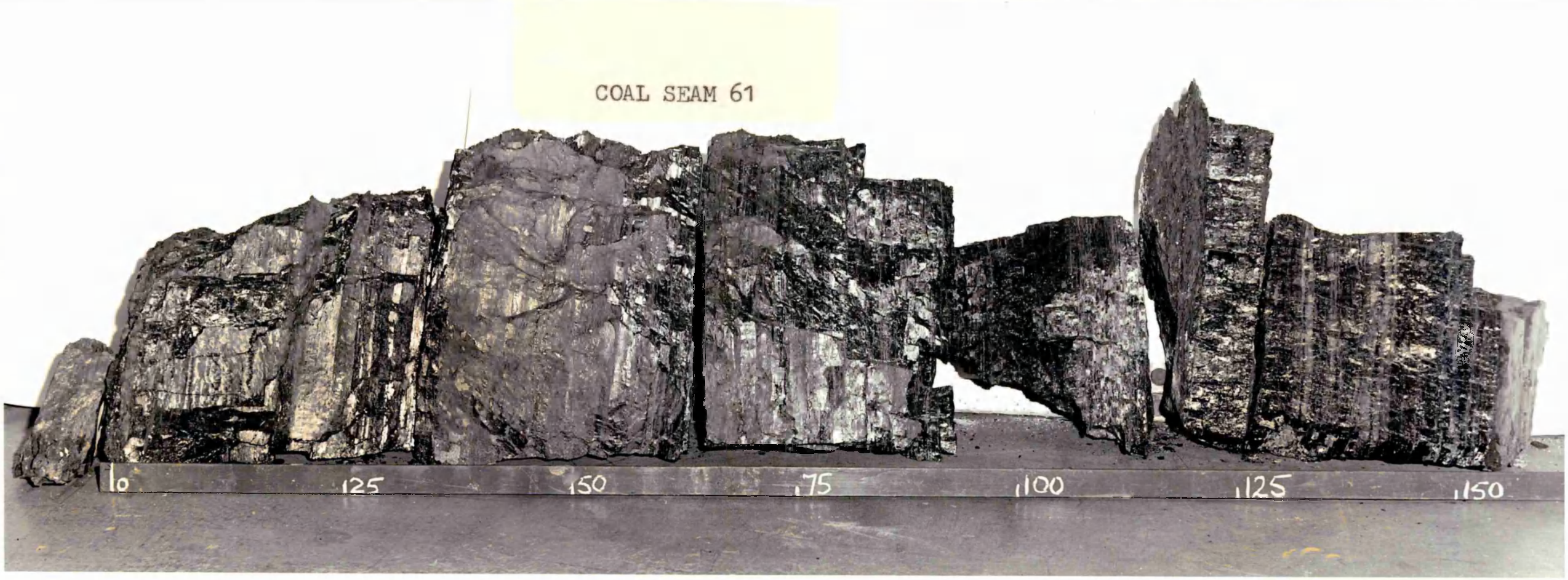
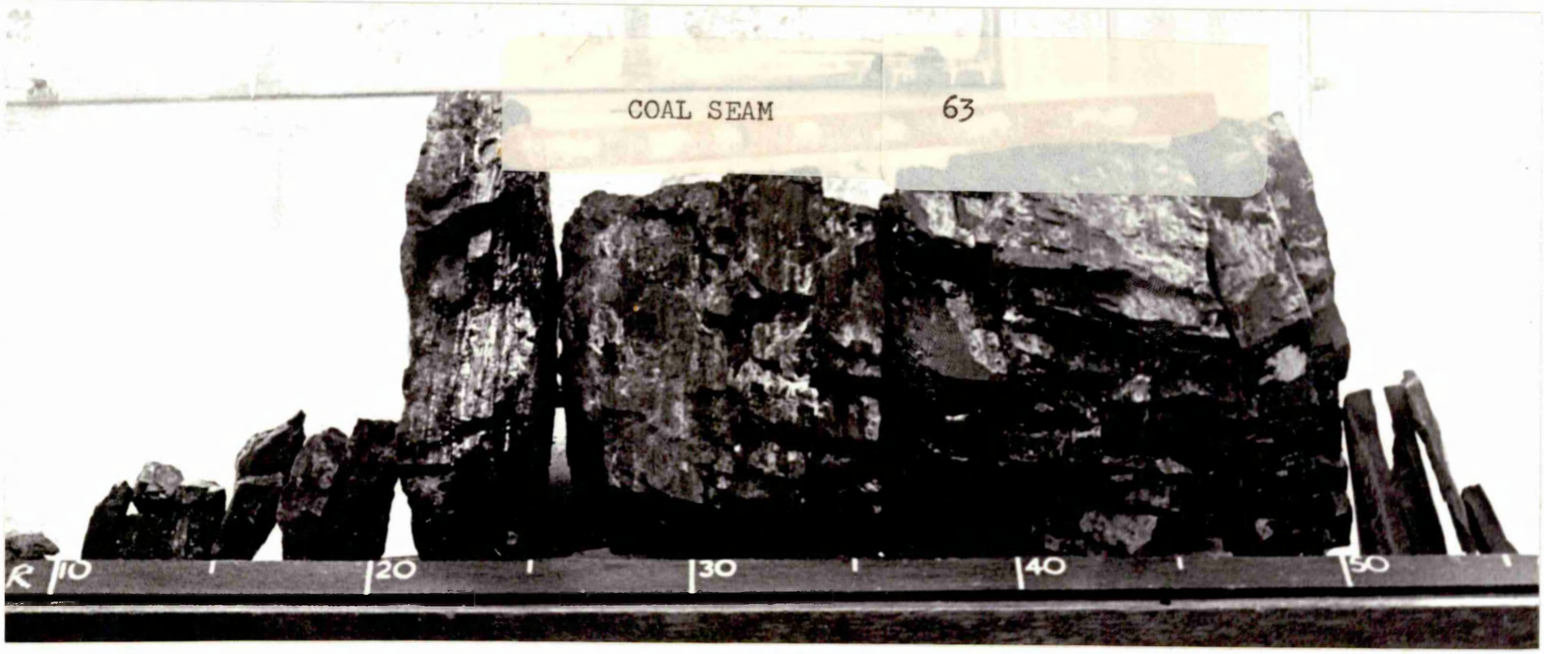


PLATE 3.2 COAL PILLAR SECTION 61



Scale 1 : 7

PLATE 3.3 COAL PILLAR SECTION 63



Scale 1 : 10

TABLE 3.1

Seam profile analysis of coal pillar 60

Coal Pillar 60

	ANALYSIS (air dried)						DESCRIPTION
	Sect	th cm	sp gr -72's	ash %	sulphur %	chlorine %	
Roof 2		-	2.50	87.3	0.11	0.11	Mudstone, grey, with ironstone bands, darker in basal 20cm (200cm examined).
Roof 1		3	1.73	45.4	0.40	0.34	Interleaved mudstone and bright coal.
60600 H		12	1.36	7.1	0.72	0.60	Bright coal with many thin dull streaks.
60599 G		10	1.34	4.9	0.84	0.57	Top 8cm bright coal with dull streaks; 1cm dull coal; basal 1cm bright coal.
60598 F		15	1.32	3.8	0.86	0.56	Bright coal with ankerite in the cleat.
60597 98cm E		16	1.31	3.9	0.74	0.56	Bright coal with ankerite in the cleat.
60596 D		10	1.33	5.0	0.83	0.61	Bright coal with several fusain pockets and partings.
60595 C		4	1.36	5.2	0.76	0.78	Very fusainous bright coal with dull streaks.
60594 B		18	1.34	5.5	1.38	0.64	Bright coal with fusain pockets and ankerite in the cleat. Wafer dirt partings at base.
60593 A		15	1.37	8.9	1.82	0.57	Bright coal.
Floor 1		20-24	2.34	82.8	0.30	0.21	Seatearth, mudstone, grey, listric (Thickness variable 20-24cm)
Floor 2		8	1.64	38.5	1.72	0.39	Interleaved bright coal and mudstone.
Floor 3		2	2.20	76.6	0.35	0.21	Seatearth, mudstone, dark grey, with coal streaks.
Floor 4		-	2.52	89.8	0.11	0.12	Seatearth, mudstone, light grey (10cm examined).

Scale 1:10

TABLE 3.2

Seam profile analysis of coal pillar 61

Coal Pillar 61

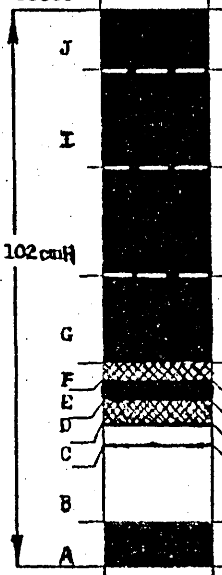
	Sect	th cm	sp gr -72's	ash %	sulphur %	chlorine %	DESCRIPTION
	Roof	-	2.45	85.6	0.31	0.16	Mudstone, grey, shaly, darker in basal 5 cm (50 cm examined)
61122 M		7	1.36	7.4	4.96	0.38	Bright coal with some fibrous pyrites.
61121 L		20	1.30	2.8	2.22	0.38	Top 6 cm bright coal; 1 cm dull coal; 6 cm bright coal; 1 cm dull coal; basal 6 cm bright coal.
61120 K		8	1.32	5.6	3.48	0.34	Bright coal with some flake pyrites.
61119 J		7	2.45	85.4	0.26	0.16	Seatearth, mudstone, brownish-grey.
61118 I		9	1.38	8.8	4.80	0.34	Bright coal with several dirt faces and thin pyritic lenses.
61117 H		15	1.30	3.4	3.34	0.34	Bright coal.
61116 G		16	1.31	4.0	3.22	0.35	Bright coal.
61115 F		8	1.33	2.6	1.42	0.50	Banded bright and dull coal.
61114 E		9	1.30	2.8	1.28	0.36	Top 4 cm bright coal; 1 cm dull coal; basal 4 cm bright coal.
61113 D		19	1.30	3.2	0.82	0.38	Dull coal with bright streaks.
61112 C		16	1.31	4.4	0.95	0.37	Top 10 cm bright coal; 2 cm dull coal; basal 4 cm bright coal.
61111 B		2	2.08	64.9	3.86	0.20	Seatearth mudstone, dark grey, some pyrites.
61110 A		15	1.37	9.4	3.56	0.34	Bright coal with several dirt faces and pyritic lenses.
61109	Floor	-	2.54	88.4	0.18	0.20	Seatearth, mudstone, grey (10 cm examined)

Scale 1:10

TABLE 3.3

Seam profile analysis of coal pillar 63

Coal Pillar 63



		ANALYSIS (air dried)						
		Sect.	th. cm	sp.gr. -72's	ash %	sulphur %	chlorine %	DESCRIPTION
63505		Roof	-	2.52	85.2	3.31	0.05	Mudstone, silty, dark grey, fissile, containing Lingula. (150cm examined).
63503	J		11	1.42	11.4	4.44	0.23	Bright coal with a few dirt partings and pyritic lenses.
63502	I		18	1.35	5.7	2.38	0.24	Bright coal with pyritic lenses.
63501	102cm H		20	1.34	5.2	1.36	0.28	Bright coal.
63500	G		16	1.38	6.8	1.52	0.32	Bright coal with many fusain partings in top 2cm and basal 3cm.
63499	F		3	1.59	17.9	1.42	0.35	Very fusainous bright coal.
63498	E		4	1.38	5.2	1.20	0.30	Bright coal with many fusain partings.
63497	D		4	1.51	20.6	1.21	0.21	Dirty dull coal with much compressed fusain.
63496	C		4	1.94	55.8	0.84	0.09	Seatearth mudstone, carbonaceous.
63495	B		14	2.31	76.8	0.38	0.06	Seatearth mudstone, slightly silty, grey.
63494	A		8	1.40	11.2	2.90	0.21	Bright coal with many dirt partings.
63493		Floor 1	28	2.56	89.0	0.34	0.06	Seatearth mudstone, grey, listric.
		Floor 2	3+	-	-	-	-	Seatearth, sandstone (fine).

Scale 1:10

For each subsection two representative 200g samples of < 212 μm coal plus one 200g sample of < 2.8 mm coal were prepared. The coarser sample was retained for stock whilst the other two samples were used for SEM/EDX analysis and British Standard chlorine, sulphur and ash analysis.[123,124]

For SEM/EDX analysis 250-500 mg portions of air-dried coal were placed in a 13 mm diameter die under vacuum, and a load of 10 tonnes applied for 3 minutes. This produced a coherent coal disc of approximately 2-3 mm thickness. This disc was mounted on a 13 mm diameter stereoscan stub using non-aqueous carbon dag (LEIT-C) which was then allowed to dry in air. A number of coals prepared in this way were coated with a thin film of carbon using the carbon fibre deposition equipment.

A special holder supplied by the microscope manufacturer enabled a cobalt reference standard and five coal discs to be mounted together in the microscope chamber. This arrangement took approximately 15-20 minutes to pump down to the required vacuum of 10^{-5} torr before analysis. The total time involved for the multi-element analysis of a single sample of <212 μm coal is estimated as less than 30 minutes.

Ash analysis on the residue after incineration of selected coal samples at 815°C was carried out according to standard procedures.[123]

3.2.4 Methods of Analysis

The method for quantitative analysis by SEM/EDXA using a polished multi-element standard is well documented.[117,118,125]

It is usual practice to carbon-coat a non-metallic sample with a thin film of carbon for quantitative analysis.[125] This prevents build-up of electrons at the specimen surface and maintains stability of X-ray excitation. It also reduces thermal damage and movement of ions within the specimen which may change the surface composition.

It was unclear whether pressed discs of coal powder would be sufficiently conducting to prevent this charging effect, since coal is basically eighty percent carbon, it was initially assumed that charging effects would be negligible.

Cobalt and elemental spectra generated from polished standard materials were stored and processed using the energy-dispersive analysis equipment. Two different methods of processing the X-ray energy spectra of coal were evaluated in this study. The first method used corrected absolute intensities from the elements present and has been available commercially for about four years (ZAF4/FLS).[126,127] The second method ratios the peak to local background counts for each element and at the time of writing has been available commercially for only a few months (ZAF/PB).[128,129] The work reported here can be regarded therefore as evaluating the technique for coal analysis.

When both calibrations were carried out the geometry conditions were such that the specimen was not tilted towards the X-ray detector. This position was chosen to give the take-off angle best suited to the design of the instrument and hence optimum X-ray collection efficiency. However, these conditions have the disadvantage that the specimen cannot be tilted without changing the azimuth, elevation and cosine angles.

3.2.4.1 ZAF4/FLS Software

This software uses net intensities from the elements. It was set up for a processing time of 20 μs and 20 eV per channel and then proceeded with according to the manufacturers instructions. The elemental calibration list was chosen to include all the major and minor constituents found in coal. A typical analysis print-out is shown in Table 3.4. Careful examination of this table shows that the geometry, operating voltage and reference parameters are entered first. The ZAF4/FLS software offers a choice of sub-routines prompted by the words 'PROGRAM' 'OPTION' and 'NEXT' which allow various analytical operations to be performed. From a choice of possible schemes for the analytical calculations, an option was selected which gave one element by difference. Thus, a missing, i.e. undetectable, element is made to account for the difference in composition of all the detected elements from one hundred percent. The X-rays of the elements hydrogen, carbon, oxygen and nitrogen are all absorbed by the beryllium window (0.008 mm thick) of the detector but of these carbon was chosen as the 'element by difference' since the coal matrix is predominantly organic in nature.

TABLE 3.4

Computer print-out of SEM/EDX analysis of coal using ZAF4/FLS software

```
*  791* ZAF4/FLS  REV01-LINK SYSTEMS LTD.-1978

TILT=  .00/  ELEVATION=35.00/  AZIMUTHAL ANGLE= .00/
COSINE= .966/  KV= 20.00/
EV/CH=20/  CALIBRATION ELMT:CO/  PEAK ENERGY(KEV)=  6.9242/
LABEL (20 CHAR. MAX.):26/10/83

PROGRAM=
1=DATA ANALYSIS  2=ANALYSER  3=DISK LISTING
4=EDIT STANDARD FILE  5=CHARACTERISATION  6=CHANGE SNO,SN1
7=SAVE/RETRIEVE PROFILE LIBRARY

PROGRAM=1

E.D.S.  ANALYSIS? YES
OPTION=
0=STANDARDS OR SPECTRUM TREATMENT ONLY
1=ALL ELMTS  2=1 ELMT BY DIFF.  3=1 ELMT BY STOICH.
4=ALL ELMTS,NORMALISED  5=ELMT BY STOICH.,NORMALISED

OPTION=2  UNANALYSED ELMT:  C  LIVETIME=100

ELMT   LINE    STD
 CL     K       1
 S      K       1
 FE     K       1
 SI     K       1
 AL     K       1
 CA     K       1
 MG     K       1
 NA     K       1
 K      K       1
 TI     K       1
 MN     K       1
 P      K       1
 C      K       1

ANALYSE CO ?NO
TRACK NO.(CO)=6
 COBALT  3 LIVETIME 100S                LIVETIME =  100
 ENERGY        RES         AREA
-    6.6     104.15      71495
  6912.9     170.22     173426
TOTAL AREA=      401916      GF=  49.966

ANALYSES? NO
TRACK NO.=7
 NBS 1632  A (1)                   LIVETIME(SPEC)=  100
 ENERGY        RES         AREA
-    7.0     103.69      72508
TOTAL AREA=    96757
......
```

TABLE 3.4 (continued)

```
FIT INDEX=  .80

ELMT       APP.CONC      ERROR(WT%)
 CL          .073          .029
 S          1.080          .042
 FE          .514          .052
 SI         4.587          .064
 AL         2.679          .068
 CA          .220          .032
 MG          .109          .059*  < 2 SIGMA*
 NA          .084          .085*  < 2 SIGMA*
 K           .451          .037
 TI          .171          .032
 MN          .026          .037*  < 2 SIGMA*
 P    -      .025          .052*  < 2 SIGMA*


 [ 1 2 ZAF/S]
20.00 KV  TILT=  .00 ELEV=35.00  AZIM=  .00  COSINE=  .966
SPECTRUM:  NBS 1632 A (1)          26/10/83
LAST ELMT BY DIFFERENCE

ELMT        ZAF        %ELMT
 CL        1.078        .068
 S         1.123        .962
 FE         .879        .586
 SI        1.111       4.128
 AL        1.138       2.354
 CA        1.092        .201
 MG        1.102        .099
 NA         .962        .087
 K         1.171        .385
 TI         .905        .188
 MN         .868        .030
 P         1.595        .000
 C          .354        .000
TOTAL                  9.088

NEXT=
1=MORE ANALYSES  2=ADD MORE ELMTS  3=STD.CALIBRATION
4=CHANGE ELEMENTS  5=SAME ANALYSIS,CHANGE OPTION
6=VIEW DEVIATIONS(MID SCREEN=3.6 SIGMA)

NEXT=
```

The corrections for atomic number (Z), absorption (A) and fluorescence (F)[125] were made on the basis of this assumption. The elements to be determined, including the element by difference, are then entered with their selected X-ray lines and standard numbers.

Cobalt was used as an intermediate reference standard in order to compensate for drift in instrument operating conditions such as the beam current. A spectrum of pure cobalt (area scanned $\simeq 0.04$ mm^2 magnification $\sim$1000) was first processed at given instrument settings and then the unknown coal sample analysed for an area scanned $\simeq 0.8$ mm^2, (= magnification $\sim$ 200), taking care not to change any instrument settings other than the specimen stage Z control to focus the sample. This maintains a fixed object to lens distance which preserves the same geometry. Changes in electron optical conditions made it advisable to re-calibrate with cobalt after three coal disc analyses.

Examination of results in Table 3.4 shows that the computer first prints out the analysed element symbol, the apparent concentration and the error (% m/m) which is the standard deviation. When the apparent concentration is less than twice the error then '< 2 sigma' is printed, which indicates the result is not statistically significant. This was the case for a number of elements normally determined in routine coal ash analysis. The ZAF4/FLS programme performs two operations upon each unknown spectrum. Firstly, the filtered least squares (FLS)[126,127] peak deconvolution routine is executed. This routine first compensates for any drift in the spectrum, by reference to the cobalt standard, removes silicon escape peaks, then applies a digital filter to the spectrum. The peaks in the resulting filtered spectrum are then fitted using a least squares algorithm and a library of stored standard element spectra to determine the contribution of each element emission line to the unknown spectrum.[127] Secondly, the resulting elemental peak areas are corrected, using the ZAF routine in the package, to yield the required elemental composition.

The X-rays generated from the cobalt standard and coal samples were generally counted for a computer live-time of 100 seconds although in some cases longer periods were used to improve limits of detection. The cobalt calibration statistics were chosen such that the average 'dead time' (the time X-rays cause pulse pile-up in the processor) was less than 40%.

In addition to the ZAF correction factors and the elemental composition, the programme yields a measure of the systematic versus random errors in the processed spectrum. Thus a figure of merit for the 'goodness of fit' ('fit index')[127] is produced and the residuals from the peak fit may be viewed in order that any unexpected elements, or regions of poor fit, may be identified and investigated.

3.2.4.2 ZAF/PB Software

The ZAF/PB programme enables quantitative analyses to be estimated for particles and bulk specimens of uncertain geometry e.g. powders, deposits on filters, etc. The peak to local background ratio for each element is calculated and the ratio of these values to the peak to background ratios from known standards are used in an iteration procedure to calculate the composition of the unknown.[128,129]

The advantage of using this ratio method is that peak to background measurements are less geometry dependent. However, statistical errors in the estimation of background are relatively high and therefore the method should not be expected to give the same precision as the ZAF4/FLS procedure. Table 3.5 shows a print-out of the ZAF/PB analysis procedure for the same spectrum as shown in Table 3.4.

Geometry and operating voltage are entered first, followed by a request for, 'Analysis of particles?' In most cases the reply is 'No', the exception being for widely dispersed particles where X-ray fluorescence is assumed to be negligible. The fluorescence correction in the ZAF procedure is not applied in this case. An analysis livetime of 100 seconds is generally used with a matrix option, where carbon as the chosen element, accounts for the difference between the total of all the elements determined and one hundred percent. Cobalt is used as the intermediate reference standard as described in the ZAF4/FLS method.

TABLE 3.5

Computer print-out of SEM/EDX analysis of coal using ZAF/PB software

```
*  287* ZAFPB REV01-LINK SYSTEMS LTD.-1979

TILT=  .00/  ELEVATION=35.00/  AZIMUTHAL ANGLE=  .00/
COSINE=  .966/  KV= 20.00/
ANALYSIS OF PARTICLES?NO
EV/CH=20/  CALIBRATION ELMT:CO/  PEAK ENERGY(KEV)=  6.9242/
LABEL (20 CHAR. MAX.):15/11/83 COAL DISCS

PROGRAM=
1=DATA ANALYSIS  2=ANALYSER   3=DISK LISTING
4=EDIT STANDARD FILE  5=CHARACTERISATION  6=SET SYSTEM RESOLUTION
7=PROFILE UTILITIES
8=EDIT MATRIX FILE   9=CALCULATOR

PROGRAM= 1

SPECTRUM ANALYSIS? YES  LIVETIME=100
OPTION=
0=SPECTRUM TREATMENT ONLY  1=ALL ELMTS ANALYSED
2=ELMTS IN KNOWN MATRIX  3=ANALYSIS OF STANDARD(IN MATRIX)
4=ELMT BY STOICHIOMETRY
10-HOLDER  11=GRID

OPTION=2 MATRIX NO.=2:  CARBON

ELMT     LINE    STD
 CL        K      1
 S         K      1
 FE        K      1
 SI        K      1
 AL        K      1
 CA        K      1
 MG        K      1
 NA        K      1
 K         K      1
 TI        K      1
 MN        K      1
 P         K      1

ANALYSE CO ?NO
TRACK NO. (CO)=6
 COBALT  3 LIVETIME 100S    LIVETIME=  100  I/P RATE= 4019 CPS
 ENERGY     RES      AREA
-    6.6  104.15    71495
  6912.9  170.22   173426
TOTAL AREA=  401916    GF=  49.966
```

TABLE 3.5   (continued)

```
ANALYSE?  NO
TRACK NO.=7
 NBS 1632 A (1)          LIVETIME(SPEC)=  100
TILT= .00/ ELEV=35.00/  AZIM=  .00/
 ENERGY      RES        AREA
-   7.0   103.69       72508
TOTAL AREA=   86757  ......   FIT INDEX=  .90

 4 ITERATIONS   G-FACTOR= 3.544

 20.00 KV  TILT=  .00   ELEV.=35.00   AZIM.=  .00 COSINE= .966

SPECTRUM:  NBS 1632 A (1)          15/11/83COAL DISCS
ELMTS IN MATRIX: CARBON

ELMT      -AREA            AREA/BGND          %CONC         FST
CL K    322 +- 126      .036 +-   .014          .14        1.952
S  K   4508 +- 172      .444 +-   .018         1.67        2.726
FE K   1179 +- 117      .383 +-   .038          .82        3.330
SI K  18206 +- 252     1.624 +-   .036         5.14        1.509
AL K   7539 +- 190      .755 +-   .025         2.93        1.455
CA K    857 +- 123      .126 +-   .018          .29        1.884
MG K    194 +-  94      .031 +-   .015          .14        1.451
NA K     70 +-  53      .024 +-   .018          .16        1.966
K  K   1692 +- 137      .220 +-   .018          .52        1.632
TI K    604 +- 111      .110 +-   .020          .25        2.823
MN K     66 +-  93      .018 +-   .025          .04        3.149
P  K    -64 +- 141     -.006 +-   .014         -.02        3.164
MATRIX                                        87.93
                                         TOT= 100.00

NEXT=
1=MORE ANALYSES  2=ADD MORE ELMTS   3=GAIN CALIBRATION
4=DATA ANALYSIS  5=CHANGE OPTION.KEEP SAME ELMTS
6=VIEW RESIDUAL SPECTRUM

NEXT=
```

The coal analysis spectrum is entered along with the coal disc geometry parameters. The 'Fit Index' is calculated which is a measurement of the quality of fit of the unknown spectrum to stored standard peak profiles and is related to the normalised chi-squared for the fit.[127] The background ratios for all elements are determined and these values are subjected to an iterative calculation process in which the G-factor i.e. the relative efficiency of the bremsstrahlung production given by:-

$$G = \sum \frac{C_i Z_i^2}{A_i}$$

where Ci = Mass fraction
Zi = Atomic number
Ai = Atomic weight of element i in material

and inter-element corrections are determined. When the calculation stage is complete, the number of iterations and the G-factor are printed followed by the analysis condition, option label and the table of results. The element symbol is printed first, followed by the 'AREA' which is the net total counts after the least squares fitting routine ± one standard deviation. This is followed by the 'AREA/BGND', which is the ratio of deconvoluted peak area to estimated background per KeV ± one standard deviation; the percentage concentration and finally the FST. The FST (factor for standard treatment) is calculated from the standard profiles and is a correction factor for the particular standard used in calibration. As in the ZAF4/FLS procedure, after the results have been printed the prompt 'NEXT=' is issued. The spectrum analysis procedure is illustrated in Figures 3.1 and 3.2.

3.2.4.3 Novel method using a Coal Standard

It is possible using the ZAF/PB software to utilise a spectrum from a well characterised reference coal as a standard. This should allow more accurate peak to background ratios to be estimated for unknown coal matrices. The procedure involves collecting a cobalt spectrum and then a coal standard spectrum for 100 seconds counting time. These spectra are then processed using the option to calculate FST and RST (Ratio for standard treatment) values for the coal standard.

Figure 3.1 Schematic diagram of spectrum processing and data correction - ZAF/PB

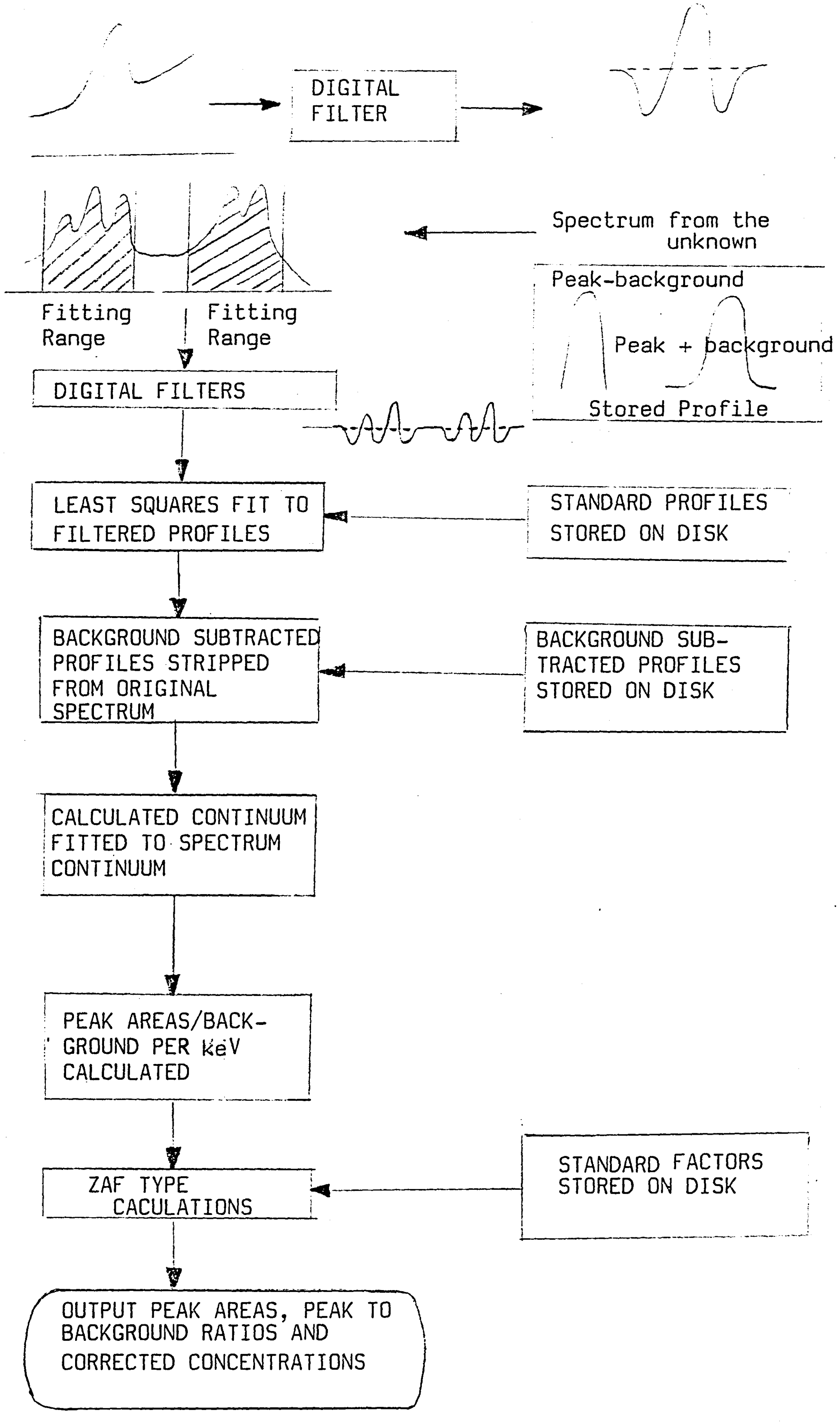
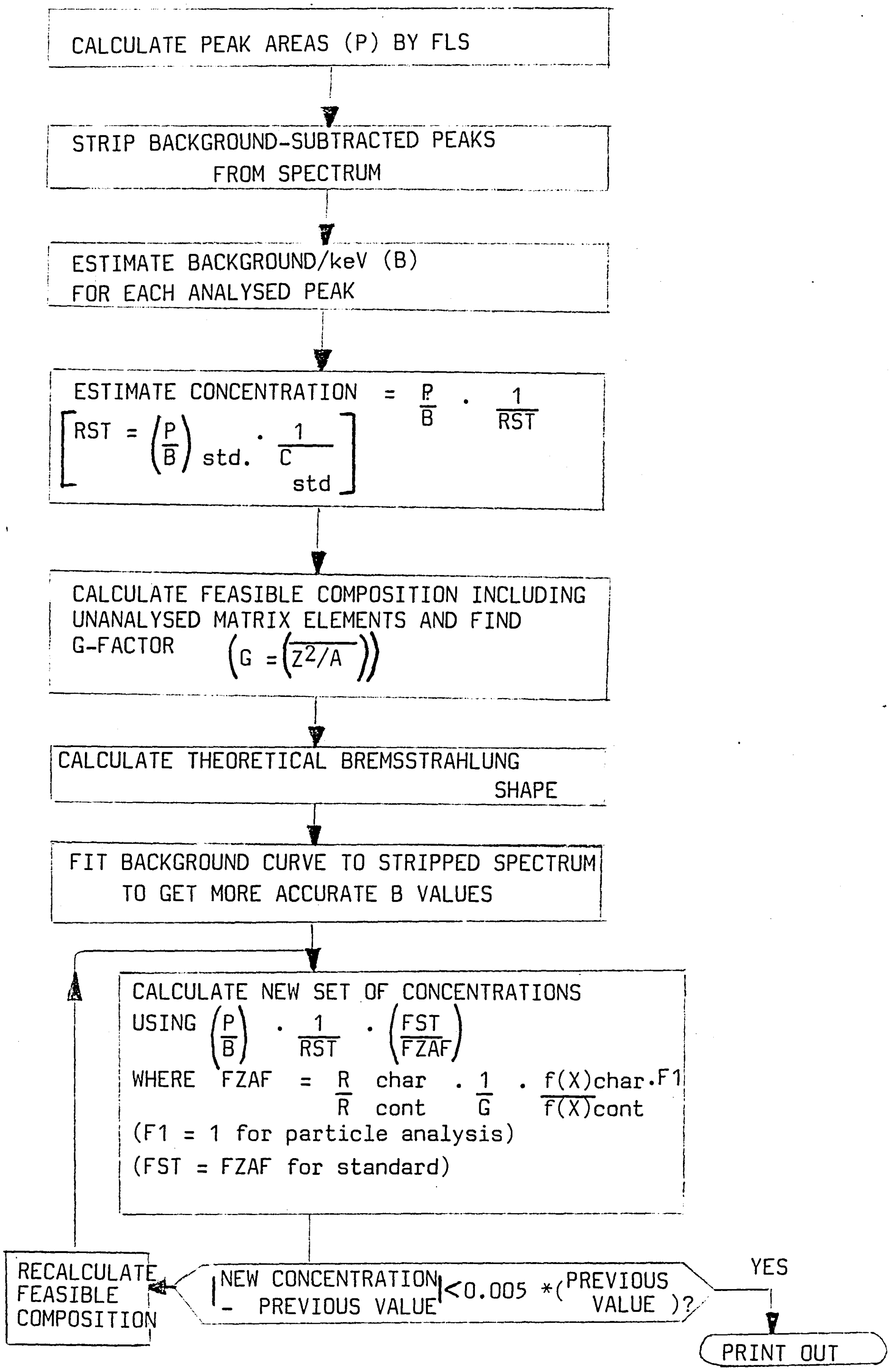


Figure 3.2 Schematic diagram of spectrum and data processing - ZAF/PB



The values and the percentage concentration of the elements are stored in the standards file. The analysis of unknown coals is carried out as described in section 3.2.4.2 except that the peak profile from the coal is used as the standard.

3.2.5 Particle Size Reduction

To establish the effect of fine grinding of coal on the precision and accuracy of the results obtained using SEM/EDXA, approximately 3g of two samples (60593 and 61118) were ground separately for 20 minutes in the micromill. The resultant coal passed easily through a 45 µm sieve and was then pressed into duplicate pellets for analysis.

3.3 RESULTS AND DISCUSSION

3.3.1 ZAF4/FLS Programme

3.3.1.1 Chlorine

The results of duplicate chlorine determinations by the three chemical methods and of three single replicate determinations by SEM/EDXA are given in Tables 3.6, 3.7 and 3.8, together with the respective averages. The samples analysed included 29 sub-sections predominantly of coal (less than 50% ash) and 12 of dirt (over 50% ash content). Comparing the averages of the three chemical determinations with those of the three SEM/EDXA determinations, the difference exceeds 0.04 percent for only two of the coal sub-sections and five of the dirts. Clearly a calculation method which assumes the major residual element to be carbon will perform less satisfactorily on samples containing more than 50% ash, but for coal samples the overall procedure can be considered to give results in very good agreement with traditional methods. This very good agreement between bulk chemical methods and the SEM/EDXA micro-analytical technique provides positive evidence for the uniform distribution of chlorine in coal lithotypes, and its probable existence in one bonding form.[125] The limit of detection was about 0.4 mg g^{-1}.

TABLE 3.6

Comparison of Chlorine Analyses (air-dried basis)

SEAM 60

Sample No.	Ash % m/m	Chlorine % m/m Average of Duplicates			Average Chlorine % m/m	SEM/EDXA Chlorine % m/m			SEM/EDXA Average Chlorine % m/m
		Eschka[a]	High Temp[b]	I S E[c]		(1)	(2)	(3)	
60603	87.3	0.12	0.14	0.11	0.12	0.33	0.30	0.26	0.30
60601	45.4	0.36	0.38	0.39	0.38	0.35	0.37	0.41	0.38
60600	7.1	0.65	0.61	0.67	0.64	0.64	0.68	0.64	0.65
60599	4.9	0.60	0.60	0.61	0.60	0.59	0.56	0.58	0.58
60598	3.8	0.53	0.55	0.55	0.55	0.47	0.50	0.50	0.49
60597	3.9	0.60	0.59	0.62	0.60	0.56	0.54	0.58	0.56
60596	5.0	0.63	0.64	0.66	0.64	0.63	0.61	0.64	0.63
60595	5.2	0.79	0.83	0.81	0.81	0.82	0.85	0.86	0.84
60594	5.5	0.66	0.68	0.70	0.68	0.66	0.62	0.63	0.64
60593	8.9	0.57	0.58	0.61	0.59	0.55	0.55	0.54	0.55
60592	82.8	0.24	0.23	0.24	0.24	0.26	0.30	0.25	0.27
60591	38.5	0.41	0.40	0.42	0.41	0.41	0.41	0.41	0.41
60590	76.6	0.25	0.24	0.24	0.24	0.30	0.25	0.26	0.27
60589	89.8	0.14	0.16	0.14	0.15	0.25	0.24	0.21	0.23

[a] Eschka method as defined in BS 1016 Part 8[123]

[b] High temperature method as defined in BS 1016 Part 8[123]

[c] Direct potentiometry by ion-selective electrode (ISE) on a solution of absorbed gases evolved from coal after high temperature incineration.[124]

TABLE 3.7

Comparison of Chlorine Analyses (air-dried basis)

SEAM 63

Sample No.	Ash % m/m	Chlorine % m/m Average of Duplicates			Average Chlorine % m/m	SEM/EDXA Chlorine % m/m			SEM/EDXA Average Chlorine % m/m
		Eschka[a]	High Temp[b]	I S E[c]		(1)	(2)	(3)	
63505	83.2	0.06	0.05	0.04	0.05	0.10	0.07	0.07	0.08
63503	11.4	0.21	0.23	0.24	0.23	0.20	0.21	0.20	0.20
63502	5.7	0.26	0.24	0.23	0.24	0.22	0.21	0.21	0.21
63501	5.2	0.24	0.26	0.27	0.26	0.20	0.23	0.20	0.21
63500	6.8	0.35	0.32	0.36	0.34	0.35	0.37	0.36	0.36
63499	17.9	0.35	0.35	0.38	0.36	0.39	0.41	0.39	0.40
63498	5.2	0.33	0.31	0.34	0.33	0.36	0.35	0.37	0.36
63497	20.6	0.21	0.21	0.22	0.21	0.20	0.24	0.20	0.21
63496	55.8	0.09	0.09	0.09	0.09	0.14	0.12	0.13	0.13
63495	76.8	0.06	0.06	0.05	0.06	0.14	0.14	0.16	0.15
63494	11.2	0.20	0.21	0.20	0.20	0.18	0.18	0.17	0.18
63493	89.0	0.08	0.09	0.07	0.08	0.05	0.09	0.09	0.08

[a] Eschka method as defined in BS 1016 Part 8[123]

[b] High temperature method as defined in BS 1016 Part 8[123]

[c] Direct potentiometry by ion-selective electrode (ISE) on a solution of absorbed gases evolved from coal after high temperature incineration.[124]

TABLE 3.8

Comparison of Chlorine Analyses (air-dried basis)

SEAM 61

Sample No.	Ash % m/m	Chlorine % m/m Average of Duplicates			Average Chlorine % m/m	SEM/EDXA Chlorine % m/m			SEM/EDXA Average Chlorine % m/m
		Eschka[a]	High Temp[b]	I S E[c]		(1)	(2)	(3)	
61124	85.6	0.18	0.16	0.17	0.17	0.11	0.10	0.10	0.10
61122	7.4	0.38	0.37	0.41	0.39	0.40	0.40	0.38	0.39
61121	2.8	0.41	0.39	0.43	0.41	0.45	0.46	0.45	0.45
61120	5.6	0.35	0.34	0.38	0.36	0.31	0.34	0.37	0.34
61119	85.4	0.18	0.16	0.19	0.18	0.14	0.12	0.17	0.14
61118	8.8	0.36	0.35	0.38	0.36	0.38	0.42	0.40	0.40
61117	3.4	0.35	0.35	0.36	0.35	0.35	0.35	0.36	0.35
61116	4.0	0.35	0.35	0.38	0.36	0.33	0.38	0.36	0.36
61115	2.8	0.56	0.51	0.57	0.55	0.51	0.54	0.52	0.53
61114	2.8	0.37	0.36	0.41	0.38	0.39	0.35	0.36	0.37
61113	3.2	0.41	0.39	0.44	0.41	0.42	0.44	0.43	0.43
61112	4.4	0.39	0.37	0.42	0.39	0.38	0.40	0.38	0.39
61111	64.9	0.17	0.20	0.19	0.19	0.20	0.23	0.20	0.21
61110	9.4	0.36	0.35	0.38	0.36	0.35	0.39	0.32	0.35
61109	88.4	0.19	0.20	0.19	0.19	0.23	0.25	0.26	0.25

[a] Eschka method as defined in BS 1016 Part 8[123]

[b] High temperature method as defined in BS 1016 Part 8[123]

[c] Direct potentiometry by ion-selective electrode (ISE) on a solution of absorbed gases evolved from coal after high temperature incineration.[124]

3.3.1.2 Sulphur

Little agreement is apparent between the total sulphur contents determined chemically and by SEM/EDXA shown in Tables 3.9, 3.10 and 3.11. The closest approach occurs in coal samples where the pyritic sulphur is virtually absent viz. (samples 61109, 61112, 61113, 61119, 60589, 60592 and 60595-60601 inclusive). This is consistent with the understanding that organic sulphur, like chlorine, is uniformly distributed within the coal, while pyritic and sulphate sulphur may occur in discrete areas of comparatively high concentration. On the other hand, all the SEM/EDXA estimates are lower than the total sulphur determined by the BS 1016 high temperature method.[123] It might have been expected that the random selection of sample area scanned would give rise to some abnormally high estimates where pyritic particles were included in the field of view, but this is not apparent from a consideration of the sets of three replicates reported for each sample. It must therefore be concluded that the pyrites is fairly uniformly disseminated, either in its natural occurrence or in the process of grinding the samples to $< 212\ \mu m$ prior to analysis.

An explanation is required for the repeatable but very low estimate of sulphur content by SEM/EDXA when more than a trace of pyrites is present. The reproducibility of the calibration for sulphur using an iron sulphide (FeS_2) standard was confirmed (as shown in Table 3.12). Thus the accuracy of calibration must be queried, this may also explain some low results obtained for iron in the same coals detailed below. Mineralogical effects on the analysis of samples using the similar technique of X-ray fluorescence have previously been reported.[130] Such mineralogical effects may also be present here.

The limit of detection for sulphur was found to be about 0.6 mg g^{-1}.

TABLE 3.9

Comparison of Sulphur Analyses (air-dried basis)

SEAM 60

Sample No.	Ash % m/m	Forms of Sulphur[a] Sulphur % m/m			Total Sulphur % m/m	SEM/EDXA Total Sulphur % m/m			SEM/EDXA Average Sulphur % m/m
		Pyritic	Organic (By Diff)	SO_4		(1)	(2)	(3)	
60603	87.3	0.13	<0.01	0.01	0.12	0.11	0.10	0.12	0.11
60601	45.4	0.10	0.33	0.01	0.44	0.35	0.41	0.38	0.38
60600	7.1	0.12	0.66	<0.01	0.78	0.66	0.72	0.65	0.68
60599	4.9	0.07	0.86	<0.01	0.93	0.91	0.94	0.77	0.87
60598	3.8	0.10	0.80	0.01	0.91	0.70	0.70	0.72	0.71
60597	3.9	0.11	0.69	<0.01	0.80	0.68	0.64	0.62	0.65
60596	5.0	0.09	0.78	0.01	0.88	0.80	0.75	0.70	0.75
60595	5.2	0.05	0.74	<0.01	0.79	0.69	0.70	0.73	0.71
60594	5.5	0.42	0.99	0.02	1.43	1.22	1.19	1.20	1.20
60593	8.9	0.99	0.96	0.04	1.99	1.53	1.56	1.56	1.55
60592	82.8	0.09	0.21	<0.01	0.30	0.21	0.21	0.22	0.21
60591	38.5	1.22	0.63	0.01	1.86	1.19	1.18	1.21	1.19
60590	76.6	0.19	0.15	0.01	0.35	0.25	0.33	0.36	0.31
60589	89.8	0.08	0.01	<0.01	0.09	0.05	0.08	0.11	0.08

[a] Determined chemically according to BS 1016 Part 6[123]

TABLE 3.10

Comparison of Sulphur Analyses (air-dried basis)

SEAM 63

Sample No.	Ash % m/m	Forms of Sulphur[a] Sulphur % m/m			Total Sulphur % m/m	SEM/EDXA Total Sulphur % m/m			SEM/EDXA Average Sulphur % m/m
		Pyritic	Organic (By Diff)	SO_4		(1)	(2)	(3)	
63505	83.2	3.14	0.24	0.12	3.50	1.62	1.82	1.57	1.67
63503	11.4	3.55	0.77	0.27	4.59	2.42	2.50	2.12	2.34
63502	5.7	1.49	0.82	0.12	2.43	1.08	1.15	1.16	1.13
63501	5.2	0.52	0.85	0.02	1.39	0.63	0.64	0.62	0.63
63500	6.8	0.75	0.72	0.03	1.50	0.92	0.85	0.99	0.92
63499	17.9	1.07	0.30	0.05	1.42	1.00	0.98	1.03	1.00
63498	5.2	0.50	0.69	0.02	1.21	0.90	0.80	0.92	0.87
63497	20.6	0.71	0.50	0.03	1.24	0.92	0.86	0.75	0.84
63496	55.8	0.54	0.31	0.01	0.86	0.50	0.52	0.48	0.50
63495	76.8	0.17	0.22	0.01	0.40	0.22	0.22	0.25	0.23
63494	11.2	1.90	0.91	0.10	2.91	1.42	1.71	1.64	1.59
63493	89.0	0.14	0.22	0.01	0.37	0.23	0.26	0.28	0.26

[a] Determined chemically according to BS 1016 Part 6[123]

TABLE 3.11

Comparison of Sulphur Analyses (air-dried basis)

SEAM 61

Sample No.	Ash % m/m	Forms of Sulphur[a] Sulphur % m/m			Total Sulphur % m/m	SEM/EDXA Total Sulphur % m/m			SEM/EDXA Average Sulphur % m/m
		Pyritic	Organic (By Diff)	SO_4		(1)	(2)	(3)	
61124	85.6	0.17	0.16	0.01	0.34	0.18	0.16	0.12	0.15
61122	7.4	3.89	0.99	0.10	4.98	2.01	2.11	2.05	2.06
61121	2.8	0.96	1.25	0.02	2.23	1.63	1.71	1.56	1.63
61120	5.6	2.13	1.27	0.04	3.44	2.03	2.06	1.94	2.01
61119	85.4	0.03	0.25	0.01	0.29	0.25	0.23	0.24	0.24
61118	8.8	3.34	1.28	0.22	4.84	2.79	3.10	3.12	3.00
61117	3.4	1.90	1.40	0.06	3.36	2.11	2.20	2.11	2.14
61116	4.0	1.80	1.36	0.07	3.23	1.97	2.05	2.03	2.02
61115	2.8	0.48	0.91	0.04	1.43	0.97	0.95	0.95	0.96
61114	2.8	0.35	0.93	0.02	1.30	0.87	0.95	0.89	0.90
61113	3.2	0.04	0.79	0.01	0.84	0.74	0.74	0.71	0.73
61112	4.4	0.07	0.86	0.02	0.95	0.75	0.85	0.81	0.80
61111	64.9	3.54	0.44	0.02	4.00	1.15	1.08	1.09	1.11
61110	9.4	2.40	1.16	0.08	3.64	2.20	2.13	2.18	2.17
61109	88.4	0.02	0.10	0.06	0.18	0.05	0.12	0.08	0.08

[a] Determined chemically according to BS 1016 Part 6[123]

TABLE 3.12

Repeat SEM/EDX chlorine and sulphur analyses (air-dried basis)

Iron Pyrite Standard - Second calibration

Coal Sample No.	Chlorine % m/m					Sulphur % m/m				
	1	2	3	Average	Previous SEM Average	1	2	3	Average	Previous SEM Average
60596	0.66	0.64	0.62	0.64	0.63	0.77	0.72	0.77	0.75	0.75
63503	0.22	0.19	0.19	0.20	0.20	2.16	2.17	2.20	2.20	2.34
61120	0.34	0.39	0.34	0.36	0.34	2.14	2.12	2.02	2.09	2.01
61111	0.24	0.20	0.22	0.22	0.21	0.98	1.11	1.05	1.05	1.11

3.3.1.3 Other Elements

Tables 3.13, 3.14 and 3.15 show the percentage contents of silicon, aluminium, iron, titanium, calcium, magnesium, sodium and potassium in each of the 41 subsections. A comparison of these subsection percentage contents with those determined by standard atomic-absorption spectroscopic, colorimetric and gravimetric procedures on solutions of coal ash[123] is given in Table 3.16. The agreement is fairly good, although the SEM/EDXA procedure lacks sensitivity for certain trace elements and results for iron and calcium are often low. As additional checks standard coals NBS SRM 1632a and 1635 (National Bureau of Standards, Washington, D.C.) and five reference coals were subjected to SEM/EDXA as well as conventional analysis. The results shown in Tables 3.17 and 3.18 indicate good agreement for several elements (notably chlorine, aluminium, potassium and titanium)while the agreement is poorest for iron, sulphur and silicon. Again the poor agreement for iron and sulphur may be due to effects caused by the presence of iron pyrite. The levels of magnesium, sodium, manganese and phosphorus observed are generally below the detection limits. The detection limits for the major and minor elements found in coal were estimated for counting periods of 100 and 250 seconds and are listed in Table 3.19. Examination of this table shows that detection limits are improved slightly by increasing the counting time from 100 seconds to 250 seconds.

An interesting comparison, between the ash content as normally determined at 815°C[123] and the SEM/EDXA estimate of the ash-forming elements present can be made. The calculation of an ash content to represent the residue left on combustion at 815°C using the elemental composition of the original coal is difficult because the proportion of sulphur retained in the ash is not predictable. Using these combustion conditions all the chlorine is volatilised and none remains in the ash. As an alternative, however, the relationship between the conventional ash content and the sum of the elements determined by SEM/EDXA excluding chlorine and sulphur altogether can be demonstrated as in Figure 3.3. The correlation coefficient is 0.997.

TABLE 3.13

Elemental Analysis of Coal using SEM/EDXA (air-dried basis)

SEAM 60

Element	Si % m/m			Al % m/m			Fe % m/m			Ti % m/m			Ca % m/m			Mg % m/m			Na % m/m			K % m/m			Average Corrected Total Elemental Composition %m/m
Determination	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	
60603	21.08	17.27	17.51	11.13	8.98	9.36	4.32	3.74	3.63	0.65	0.55	0.62	0.23	0.17	0.23	0.79	0.56	0.70	0.42	0.30	0.37	3.47	2.91	3.01	37.56
60601	10.11	8.93	8.84	5.74	4.97	5.00	1.74	1.45	1.52	0.24	0.21	0.27	0.23	0.17	0.10	0.40	0.31	0.19	0.44	0.20	<0.16	1.81	1.59	1.55	18.73
60600	1.15	1.09	1.13	0.70	0.69	0.73	0.27	0.30	0.22	<0.06	<0.06	<0.06	0.37	0.56	0.39	<0.12	0.16	0.14	0.18	0.31	0.27	0.17	0.14	0.19	3.18
60599	0.19	0.19	0.24	<0.14	0.17	0.20	0.23	0.33	0.19	<0.06	<0.06	<0.06	0.37	0.53	0.45	<0.12	0.11	0.13	<0.16	<0.16	0.21	<0.07	<0.07	<0.07	1.34
60598	0.13	<0.12	0.13	<0.14	0.16	0.16	0.10	0.10	0.22	<0.06	<0.06	<0.06	0.25	0.26	0.34	<0.12	<0.12	<0.12	<0.16	0.20	<0.16	<0.07	<0.07	<0.07	0.77
60597	0.15	0.16	<0.12	0.14	0.15	<0.14	0.16	0.15	0.20	<0.06	<0.06	<0.06	0.41	0.28	0.35	<0.12	<0.12	<0.12	<0.16	0.16	0.19	<0.07	<0.07	<0.07	0.97
60596	0.14	0.12	0.23	0.18	0.17	0.19	0.27	0.19	0.22	<0.06	<0.06	<0.06	0.62	0.44	0.46	0.11	<0.12	<0.12	0.23	<0.16	0.15	<0.07	<0.07	<0.07	1.32
60595	0.32	0.35	0.39	0.30	0.30	0.35	0.25	0.29	0.35	<0.06	<0.06	<0.06	0.74	0.46	0.64	0.13	0.13	0.13	0.34	0.30	0.28	<0.07	<0.07	<0.07	2.16
60594	0.38	0.31	0.38	0.32	0.33	0.40	0.45	0.49	0.48	<0.06	<0.06	<0.06	0.38	0.39	0.46	<0.12	<0.12	<0.12	0.17	0.28	0.25	<0.07	<0.07	<0.07	1.98
60593	0 65	0.71	0.81	0.62	0.61	0.74	0.91	0.93	0.83	0.23	<0.06	<0.06	0.56	0.45	0.60	0.16	0.13	0.18	<0.16	0.24	<0.16	0.07	<0.07	0.13	3.28
60592	15.94	16.91	17.24	9.26	9.71	9.81	1.68	1.77	1.78	0.41	0.48	0.52	<0.06	0.11	0.14	0.41	0.35	0.38	0.18	<0.16	0.36	2.68	2.96	2.90	32.16
60591	7.05	6.84	6.87	4.42	4.30	4.33	1.51	1.63	1.58	0.19	0.16	0.17	0.14	0.17	0.12	0.24	0.15	0.16	<0.16	0.19	<0.16	1.30	1.23	1.20	14.67
60590	13.62	16.73	13.70	8.04	9.53	7.98	2.27	1.73	2.31	0.40	0.49	0.41	0.19	0.16	0.12	0.40	0.34	0.38	0.29	0.32	<0.16	2.70	2.94	2.65	29.25
60589	19.96	18.73	19.38	9.95	9.45	9.76	3.30	3.14	3.39	0.64	0.62	0.61	0.13	0.11	<0.06	0.71	0.69	0.68	<0.16	0.27	0.28	3.14	3.01	3.22	37.18

NOTE: Neither Manganese nor Phosphorus could be detected in any of the above samples

TABLE 3.14

Elemental Analysis of Coal using SEM/EDXA (air-dried basis)

SEAM 63

Element	Si % m/m			Al % m/m			Fe % m/m			Ti % m/m			Ca % m/m			Mg % m/m			Na % m/m			K % m/m			Average Corrected Total Elemental Composition %m/m
Determination	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	
63505	16.27	17.91	16.75	7.63	8.45	7.80	4.20	4.24	4.11	0.57	0.56	0.56	0.16	0.15	0.19	0.65	0.72	0.55	0.34	0.34	<0.16	2.48	2.71	2.53	33.48
63503	1.51	1.34	1.45	0.91	0.68	0.80	1.87	1.89	1.88	<0.06	<0.06	<0.06	0.22	0.19	0.37	<0.12	<0.12	<0.12	<0.16	<0.16	0.16	0.23	0.21	0.24	4.88
63502	0.19	0.26	0.26	0.14	0.12	0.16	0.43	0.54	0.53	<0.06	<0.06	<0.06	0.21	0.24	0.20	<0.12	<0.12	<0.12	<0.16	<0.15	<0.16	<0.07	<0.07	<0.07	1.32
63501	0.17	0.18	0.14	0.17	0.17	0.14	0.19	0.25	0.23	<0.06	<0.06	<0.06	0.24	0.37	0.26	<0.12	<0.12	<0.12	<0.16	<0.16	<0.16	<0.07	<0.07	<0.07	1.04
63500	0.24	0.19	0.28	0.22	0.23	0.30	0.51	0.57	0.57	<0.06	<0.06	<0.06	0.62	0.68	0.76	0.12	0.15	0.18	<0.16	0.21	0.19	<0.07	<0.07	<0.07	2.10
63499	0.33	0.39	0.33	0.33	0.43	0.33	1.49	1.49	1.36	<0.06	<0.06	<0.06	2.76	2.62	2.61	0.48	0.49	0.45	<0.16	0.16	0.18	<0.07	<0.07	<0.07	5.61
63498	0.40	0.37	0.39	0.39	0.36	0.31	0.44	0.40	0.49	<0.06	<0.06	<0.06	0.39	0.40	0.46	0.15	<0.12	<0.12	0.25	<0.16	<0.16	0.07	<0.07	<0.07	1.93
63497	4.10	4.05	3.45	2.81	2.76	2.46	0.67	0.57	0.59	0.14	<0.06	0.08	0.10	0.11	0.11	<0.12	<0.12	<0.12	0.24	0.16	<0.16	0.42	0.39	0.32	7.99
63496	10.62	10.46	9.80	6.35	6.22	5.66	0.86	0.88	0.88	0.44	0.39	0.38	0.13	0.10	<0.06	0.22	0.14	<0.12	<0.16	<0.16	<0.16	1.21	1.16	1.15	19.25
63495	12.84	13.86	13.21	8.56	9.07	8.75	1.39	1.62	1.57	0.58	0.47	0.47	0.20	0.15	0.21	0.34	0.29	0.23	0.20	0.30	0.37	1.68	1.87	1.72	26.71
63494	1.28	1.30	1.36	1.17	1.28	1.29	0.90	0.92	0.64	<0.06	<0.06	<0.06	0.24	0.32	0.18	<0.12	<0.12	<0.12	0.18	<0.16	<0.16	0.13	0.12	0.09	3.89
63493	18.90	19.56	19.15	9.74	9.93	9.83	2.13	2.18	2.10	0.57	0.69	0.69	<0.06	<0.06	<0.06	0.43	0.48	0.46	<0.16	<0.16	<0.16	2.87	2.91	2.84	35.36

NOTE: Neither Manganese nor Phosphorus could be detected in any of the above samples

TABLE 3.15

Elemental Analysis of Coal using SEM/EDXA (air-dried basis)

SEAM 61

Element	Si % m/m			Al % m/m			Fe % m/m			Ti % m/m			Ca % m/m			Mg % m/m			Na % m/m			K % m/m			Average Corrected Total Elemental Composition %m/m
Determination	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	
61124	14.94	15.33	15.11	9.14	9.39	9.11	2.48	2.63	2.56	0.41	0.46	0.46	<0.06	<0.06	<0.06	0.58	0.62	0.56	<0.16	0.27	0.26	3.40	3.41	3.46	31.70
61122	0.41	0.42	0.42	0.30	0.32	0.26	1.02	1.03	0.94	<0.06	<0.06	<0.06	0.10	0.10	0.08	<0.12	<0.12	<0.12	0.17	<0.16	0.20	<0.07	<0.07	<0.07	2.17
61121	0.33	0.32	0.35	0.32	0.31	0.40	0.53	0.59	0.51	<0.06	<0.06	<0.06	0.08	0.09	<0.06	<0.12	<0.12	<0.12	<0.16	0.23	<0.16	<0.07	<0.07	<0.07	1.58
61120	0.40	0.49	0.38	0.42	0.42	0.32	0.78	0.82	0.84	<0.06	<0.06	<0.06	0.08	0.12	0.08	<0.12	<0.12	<0.12	<0.16	0.21	<0.16	<0.07	<0.07	<0.07	1.93
61119	14.36	14.80	14.09	10.79	11.18	10.77	1.46	1.45	1.53	0.52	0.53	0.49	<0.06	0.12	<0.06	0.59	0.38	0.32	0.52	<0.16	0.28	3.25	3.52	3.49	31.60
61118	0.71	0.78	0.69	0.68	0.69	0.68	1.84	1.74	2.05	<0.06	<0.06	<0.06	<0.06	0.09	0.11	<0.12	<0.12	<0.12	<0.16	<0.16	0.22	0.10	0.14	0.09	3.65
61117	0.15	0.20	0.16	0.19	0.19	0.18	0.95	1.07	1.02	<0.06	<0.06	<0.06	<0.06	0.09	0.12	<0.12	<0.12	<0.12	<0.16	<0.16	<0.16	0.08	<0.07	<0.07	1.59
61116	0.21	0.20	0.25	0.25	0.21	0.19	1.01	1.17	1.04	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.12	<0.12	<0.12	<0.16	<0.16	<0.16	<0.07	<0.07	<0.07	1.76
61115	0.26	0.33	0.32	0.39	0.27	0.35	0.28	0.20	0.27	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.12	<0.12	<0.12	0.17	<0.16	0.19	<0.07	<0.07	<0.07	1.22
61114	0.32	0.38	0.32	0.31	0.30	0.30	0.17	0.30	0.20	<0.06	<0.06	<0.06	<0.06	0.10	<0.06	<0.12	<0.12	<0.12	<0.16	<0.16	<0.16	<0.07	<0.07	<0.07	1.09
61113	0.54	0.55	0.53	0.50	0.54	0.54	<0.10	<0.10	<0.10	<0.06	<0.06	<0.06	0.08	0.10	<0.06	<0.12	<0.12	<0.12	<0.16	<0.16	<0.16	<0.07	<0.07	<0.07	1.36
61112	0.75	0.68	0.69	0.69	0.66	0.79	<0.10	<0.10	<0.10	<0.06	0.09	<0.06	0.09	0.08	0.08	<0.12	<0.12	<0.12	0.19	<0.16	<0.16	<0.07	<0.07	<0.07	1.80
61111	11.79	11.85	11.25	8.53	8.61	8.09	2.10	2.02	2.04	0.52	0.58	0.54	<0.06	0.11	0.12	0.32	0.39	0.33	0.24	0.29	<0.16	1.83	1.98	1.85	25.25
61110	1.03	1.11	1.10	1.02	1.04	1.01	1.24	1.06	1.15	<0.06	<0.06	<0.06	0.16	0.09	0.09	<0.12	<0.12	<0.12	<0.16	<0.16	<0.16	0.12	0.08	0.11	3.67
61109	19.02	18.74	18.67	10.01	10.10	10.09	2.13	2.06	2.15	0.62	0.59	0.53	0.18	0.13	0.16	0.54	0.62	0.52	0.29	0.29	0.31	3.39	3.26	3.30	35.92

NOTE: Neither Manganese nor Phosphorus could be detected in any of the above samples

TABLE 3.16

Comparison of SEM/EDX coal analysis with analysis of a solution of the coal ash (dry basis)

Sample No.	Ash (% m/m)	Si (% m/m)		Al (% m/m)		Fe (% m/m)		Ti (% m/m)		Ca (% m/m)		Mg (% m/m)		Na (% m/m)		K (% m/m)		Mn (% m/m)		P (% m/m)		Sample No.
		1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	
60603	87.8	24.12	19.06	12.54	10.06	3.99	3.99	0.53	0.60	0.25	0.22	1.11	0.70	0.33	0.37	3.44	3.21	0.06	<0.09	0.04	<0.12	60603
60601	44.9	12.22	9.69	6.67	5.47	1.54	1.64	0.22	0.25	0.26	0.18	0.60	0.31	0.30	0.26	1.83	1.72	<0.01	<0.09	<0.01	<0.12	60601
60600	7.2	1.24	1.19	0.72	0.75	0.44	0.28	0.03	<0.08	0.75	0.47	0.26	0.14	0.22	0.26	0.17	0.18	0.04	<0.10	<0.01	<0.13	60600
60599	5.0	0.17	0.22	0.15	0.18	0.59	0.27	0.01	<0.09	1.25	0.48	0.32	0.12	0.17	<0.13	0.01	<0.07	0.05	<0.10	<0.01	<0.13	60599
60598	4.0	0.13	0.12	0.10	0.16	0.43	0.15	<0.01	<0.09	0.92	0.30	0.24	<0.11	0.09	<0.14	0.01	<0.08	0.05	<0.11	<0.01	<0.14	60598
60597	3.9	0.16	0.15	0.12	0.15	0.48	0.18	<0.01	<0.09	0.98	0.37	0.27	<0.11	0.12	0.16	0.01	<0.07	0.04	<0.10	<0.01	<0.13	60597
63493	88.9	26.38	19.59	11.57	10.02	2.05	2.18	0.48	0.66	0.19	<0.08	0.75	0.47	0.26	<0.12	2.89	2.93	<0.06	<0.09	0.04	<0.12	63493
63494	11.0	1.72	1.40	1.38	1.33	1.77	0.88	0.03	<0.09	0.57	0.27	0.06	<0.11	0.07	0.18	0.17	0.12	0.01	<0.10	0.03	<0.13	63494
63495	76.3	22.50	13.71	11.38	9.06	1.34	1.58	0.51	0.53	0.16	0.20	0.46	0.29	0.28	<0.12	2.05	1.81	<0.06	<0.09	0.03	<0.12	63495
63496	56.0	17.06	10.66	7.73	6.28	1.21	0.91	0.34	0.42	0.12	0.11	0.27	0.15	0.25	0.30	1.35	1.21	<0.04	<0.09	<0.02	<0.12	63496
63497	20.4	5.72	4.06	3.02	2.81	0.84	0.64	0.15	0.15	0.15	0.12	0.11	<0.10	0.14	<0.13	0.41	0.40	0.01	<0.09	0.02	<0.13	63497
63498	4.9	0.48	0.41	0.33	0.37	0.73	0.46	0.01	<0.08	0.71	0.44	0.24	<0.11	0.13	<0.13	0.02	<0.07	0.04	<0.09	0.02	<0.13	63498
61124	84.9	22.14	15.56	13.57	9.47	2.73	2.64	0.41	0.45	0.18	<0.08	1.07	0.61	0.38	0.22	3.96	3.52	<0.09	<0.09	0.04	<0.12	61124
61122	7.3	0.50	0.43	0.31	0.30	3.40	1.03	0.03	<0.08	0.16	0.09	0.02	<0.10	0.09	0.17	0.06	<0.07	<0.01	<0.09	<0.01	<0.12	61122
61121	2.9	0.34	0.33	0.29	0.35	0.84	0.55	0.01	<0.08	0.10	0.09	0.01	<0.10	0.09	<0.12	0.03	<0.07	<0.01	<0.09	<0.01	<0.12	61121
61120	5.7	0.61	0.43	0.56	0.40	1.94	0.83	0.02	<0.08	0.13	0.10	0.02	<0.10	0.09	<0.12	0.09	<0.07	<0.01	<0.09	<0.01	<0.12	61120
61119	85.2	20.78	14.93	16.05	11.29	1.67	1.53	0.51	0.53	0.21	<0.08	1.03	0.45	0.57	0.32	4.62	3.54	<0.06	<0.09	0.04	<0.12	61119
61118	8.9	1.01	0.75	0.83	0.70	3.20	1.93	0.03	<0.08	0.06	0.10	0.04	<0.10	0.11	<0.12	0.16	0.11	<0.01	<0.09	<0.01	<0.12	61118

1. Atomic Absorption and Colorimetric Analysis of Solution of the Coal Ash

2. SEM/EDX Analysis

TABLE 3.17

Determination of elements in standard coals NBS SRM 1632a[a] and 1635[a] (dry basis) using ZAF4/FLS software

NBS SRM 1632a[a]

Element	Concentration % m/m						
	SEM/EDXA[b]				Digestion AAS[c]	Certified Value	Gladney[d]
	1	2	3	Average			
Cl	0.07	<0.06	0.07	0.07	-	-	0.076 ± 0.005
S	0.96	0.96	0.95	0.96	(1.55)[e]	1.62 ± 0.03	1.45 ± 0.23
Fe	0.59	0.54	0.51	0.55	1.11	1.11 ± 0.02	1.13 ± 0.03
Si	4.13	4.14	4.04	4.10	5.89	-	5.9 ± 0.02
Al	2.35	2.38	2.28	2.34	3.04	(3.1)[f]	2.97 ± 0.04
Ca	0.20	0.17	0.17	0.18	0.26	0.23 ± 0.03	0.23 ± 0.01
Mg	<0.12	<0.12	<0.11	<0.12	0.10	(0.1)[f]	0.095 ± 0.035
Na	<0.17	<0.16	<0.16	<0.16	0.08	0.084 ± 0.004	0.076
K	0.40	0.36	0.36	0.37	0.45	0.42 ± 0.02	0.41 ± 0.01
Ti	0.19	0.19	0.14	0.17	0.14	(0.18)[f]	0.165 ± 0.013
Mn	<0.07	<0.07	0.10	<0.07	0.05	0.0028 ± 0.0002	0.0031 ± 0.0002
P	<0.10	<0.10	<0.10	<0.10	0.03	-	0.028

NBS SRM 1635[a]

Element	Concentration % m/m						
	SEM/EDXA[b]				Digestion AAS[c]	Certified Value	Gladney[d]
	1	2	3	Average			
Cl	<0.06	<0.06	<0.06	<0.06	-	0.0003	0.0003
S	0.15	0.11	0.13	0.13	(0.38)[e]	0.33	0.40 ± 0.13
Fe	<0.10	<0.10	<0.10	<0.10	0.24	0.239 ± 0.005	0.24 ± 0.03
Si	0.31	0.18	0.23	0.24	0.76	-	0.64 ± 0.13
Al	0.25	0.18	0.21	0.21	0.34	0.32	0.32 ± 0.02
Ca	0.23	0.11	0.16	0.17	0.58	-	0.56 ± 0.02
Mg	<0.12	<0.12	<0.12	<0.12	0.10	-	0.10
Na	<0.16	<0.16	<0.16	<0.16	0.18	-	0.25 ± 0.03
K	<0.07	<0.07	<0.07	<0.07	0.04	-	0.01
Ti	<0.06	<0.06	<0.06	<0.06	0.02	0.02	0.021 ± 0.003
Mn	<0.07	<0.07	<0.07	<0.07	0.002	0.002	0.002
P	<0.10	<0.10	<0.10	<0.10	0.006	-	0.012

[a] National Bureau of Standards, Washington D.C, U.S.A. Standard Reference Material 1632a Coal (Bituminous) and 1635 (sub-bituminous) Coal.

[b] Results from this work

[c] Result by atomic absorption or colorimetry after HF digestion of the coal ash.[123]

[d] Gladney results.[131]

[e] Analysis by BS 1016, Part 6.[123]

[f] Non-certified value.

TABLE 3.18

Determination of elements in reference coals using ZAF4/FLS software

Element	Concentration % m/m (air-dried basis)														
	Ref. Coal Sample No. 20					Ref. Coal Sample No. 29					Ref. Coal Sample No. 44				
	SEM/EDXA[a]				Digestion AAS[b]	SEM/EDXA[a]				Digestion AAS[b]	SEM/EDXA[a]				Digestion AAS[b]
	1	2	3	Average		1	2	3	Average		1	2	3	Average	
Cl	0.48	0.43	0.42	0.44	(0.55)[c]	0.29	0.24	0.30	0.26	(0.27)[c]	0.23	0.22	0.22	0.22	(0.23)[c]
S	1.29	1.30	1.34	1.31	(2.32)[d]	1.42	1.30	1.42	1.38	(2.28)[d]	1.45	1.40	1.43	1.43	(2.06)[d]
Fe	1.11	1.12	1.01	1.08	1.78	1.37	1.22	1.30	1.30	1.84	1.59	1.63	1.54	1.58	2.22
Si	3.88	3.57	3.78	3.74	4.72	5.16	4.83	5.23	5.07	6.19	3.66	3.64	3.66	3.66	4.38
Al	2.58	2.61	2.72	2.64	2.64	3.08	3.04	3.16	3.09	3.34	2.34	2.31	2.29	2.31	2.27
Ca	0.16	0.26	0.11	0.18	0.30	0.27	0.24	0.21	0.24	0.40	0.32	0.38	0.36	0.35	0.63
Mg	<0.12	0.16	0.18	0.17	0.21	<0.12	0.24	<0.12	<0.12	0.21	0.28	0.14	0.16	0.19	0.23
Na	<0.16	<0.16	<0.16	<0.16	0.22	<0.16	0.20	<0.16	<0.16	0.20	0.16	<0.16	<0.16	<0.16	0.13
K	0.56	0.56	0.57	0.56	0.50	0.76	0.70	0.81	0.76	0.66	0.55	0.53	0.54	0.54	0.45
Ti	0.12	0.09	<0.06	0.10	0.11	0.14	0.13	0.16	0.14	0.13	0.11	0.13	<0.06	0.12	0.13
	Ref. Coal Sample No. 47					Ref. Coal Sample No. 68									
Cl	0.22	0.23	0.22	0.22	(0.21)[c]	0.45	0.44	0.47	0.45	(0.44)[c]					
S	1.46	1.43	1.48	1.45	(2.29)[d]	1.58	1.55	1.58	1.57	(2.44)[d]					
Fe	1.18	1.09	1.11	1.13	1.89	1.94	1.95	1.78	1.89	2.60					
Si	4.28	4.23	4.21	4.25	5.09	8.28	8.04	8.03	8.12	9.72					
Al	3.06	3.00	2.99	3.01	3.49	5.42	5.33	5.36	5.37	5.56					
Ca	0.20	0.14	0.12	0.15	0.26	0.26	0.22	0.26	0.25	0.26					
Mg	0.16	0.15	0.15	0.15	0.20	0.24	0.38	0.29	0.30	0.40					
Na	<0.16	<0.16	<0.16	<0.16	0.19	0.22	0.35	0.23	0.27	0.36					
K	0.62	0.62	0.62	0.62	0.62	1.22	1.27	1.12	1.20	1.08					
Ti	0.12	0.09	0.14	0.12	0.12	0.29	0.25	0.22	0.25	0.28					

Manganese and phosphorus were below the limit of detection.

[a] Results from this work

[b] Results by atomic absorption or colorimetry after HF digestion of the coal ash[123]

[c] Analysis by BS 1016, Part 8[123]

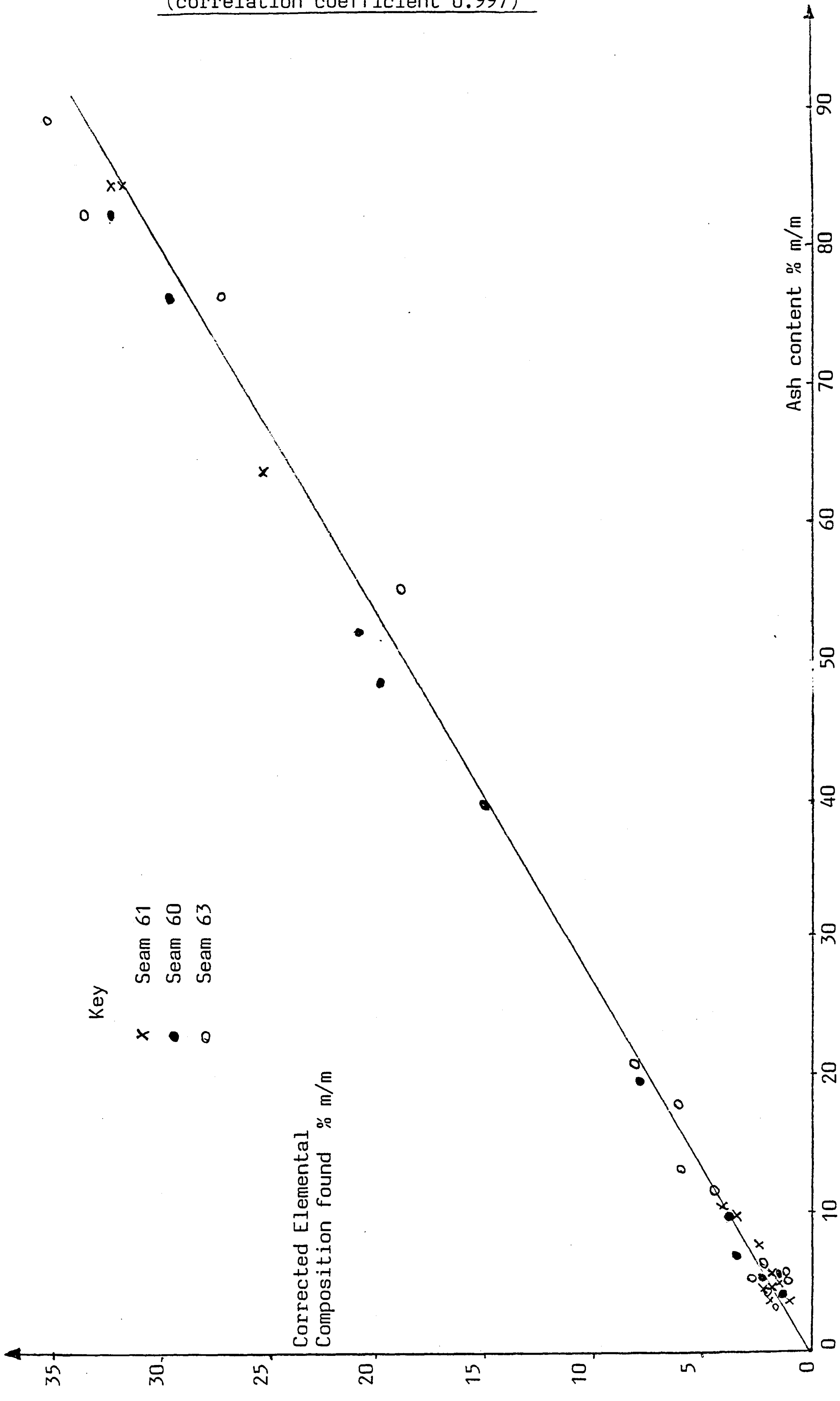
[d] Analysis by BS 1016, Part 6[123]

TABLE 3.19

Estimated detection limits for counting periods of 100 and 250 seconds using ZAF4/FLS software for coal discs (air-dried basis)

Element	Counting period 100 seconds Detection limit % m/m	Counting period 250 seconds Detection limit % m/m
Cl	0.06	0.04
S	0.08	0.06
Fe	0.10	0.07
Si	0.12	0.08
Al	0.14	0.09
Ca	0.06	0.04
Mg	0.12	0.08
Na	0.16	0.11
K	0.07	0.05
Ti	0.06	0.04
Mn	0.07	0.05
P	0.10	0.07

Figure 3.3 Calibration of SEM/EDXA corrected minor element composition and conventional ash content (correlation coefficient 0.997)



3.3.1.4 Precision of Chlorine and Sulphur Determinations

The precision of the SEM/EDXA technique for chlorine and sulphur determinations was assessed from twenty replicate analyses of sample 60596, chosen for this purpose because it contained practically no pyritic sulphur. The same area of the sample disc was analysed each time, with a cobalt calibration check after every three sample scans. The relative standard deviations (coefficients of variation) were calculated to be 2.5 and 4.9 percent for chlorine and sulphur respectively (the mean values being 0.636 % m/m chlorine and 0.711 % m/m sulphur).

3.3.1.5 Effect of Particle Size of Coal

To investigate whether the particle size of the coal influenced the result of the SEM/EDXA determination of chlorine or sulphur two samples (60593 and 61118) were ground separately in the micro-mill. This produced a material which passed easily through a 45 μm sieve, and particle size determinations using a Coulter Counter have shown that only ten percent of the coal particles produced were in fact greater than 20 μm in size. Duplicate discs prepared from each sample were analysed in the manner already described and the results are given in Table 3.20.

The mean chlorine contents (0.56 and 0.37 percent) agree well with the figures determined at <212 μm size (means 0.55 and 0.40 percent) and with the means of the three chemical methods of analysis (0.59 and 0.36 percent). On the other hand the estimates of sulphur content (means 1.43 and 2.90 percent) are slightly lower than the corresponding figures at <212 μm (1.55 and 3.00 percent) and much lower than by chemical methods (1.99 and 4.84 percent). Grinding to finer than 45 μm can at least be said to be without effect on the chlorine determinations. Reproducibility between discs also appears to be acceptable.

TABLE 3.20

Duplicate micro-analysis of coal milled to less than 45 μm (air dried basis)

(Area analysed ~14 mm^2)

	Sample 60593		Sample 61118	
	Element % m/m		Element % m/m	
Element	Disc A	Disc B	Disc A	Disc B
Cl	0.55	0.56	0.36	0.38
S	1.38	1.47	2.88	2.92
Fe	0.82	1.02	1.78	1.97
Si	0.55	0.52	0.64	0.73
Al	0.48	0.48	0.57	0.60
Ca	0.71	0.86	<0.06	<0.06
Mg	0.11	0.17	<0.12	<0.12
Na	0.15	0.21	<0.16	<0.16

Potassium, manganese, phosphorus and titanium were all below the limit of detection.

3.3.1.6 Effect of Sample Area Scanned

Table 3.21 lists the single determinations of chlorine and sulphur made on three samples (60593, 60596 and 61113) for different areas analysed in the range 1.40 x 10^7 μm^2 to 1.41 x 10^1 μm^2. The corresponding magnifications are also shown. A magnification of 50000 was the highest at which acceptable focussing could be achieved for coal discs under the chosen operating conditions. The depth of penetration was not measured, but with the electron beam accelerating voltage used (20 kV) it would be a few µm only.

The chlorine values show no particular trend, and the relative standard deviations are similar to those mentioned above. For sulphur there is a downward trend with decreasing area of scan for sample 60593 (0.99 percent pyritic sulphur) shown in Figure 3.4. This trend is barely noticeable for the other two samples which contain less than 0.1 percent pyritic sulphur. This downward trend for sample 60593 can be attributed to a reduction in the pyritic sulphur present in the area analysed.

It would appear from the SEM/EDXA sulphur results of the samples in which pyrites is virtually absent, that the results are in close agreement with the organic sulphur determined by difference, using British Standard methods.[123] The practical use of this is limited however, because the majority of coals contain pyrites.

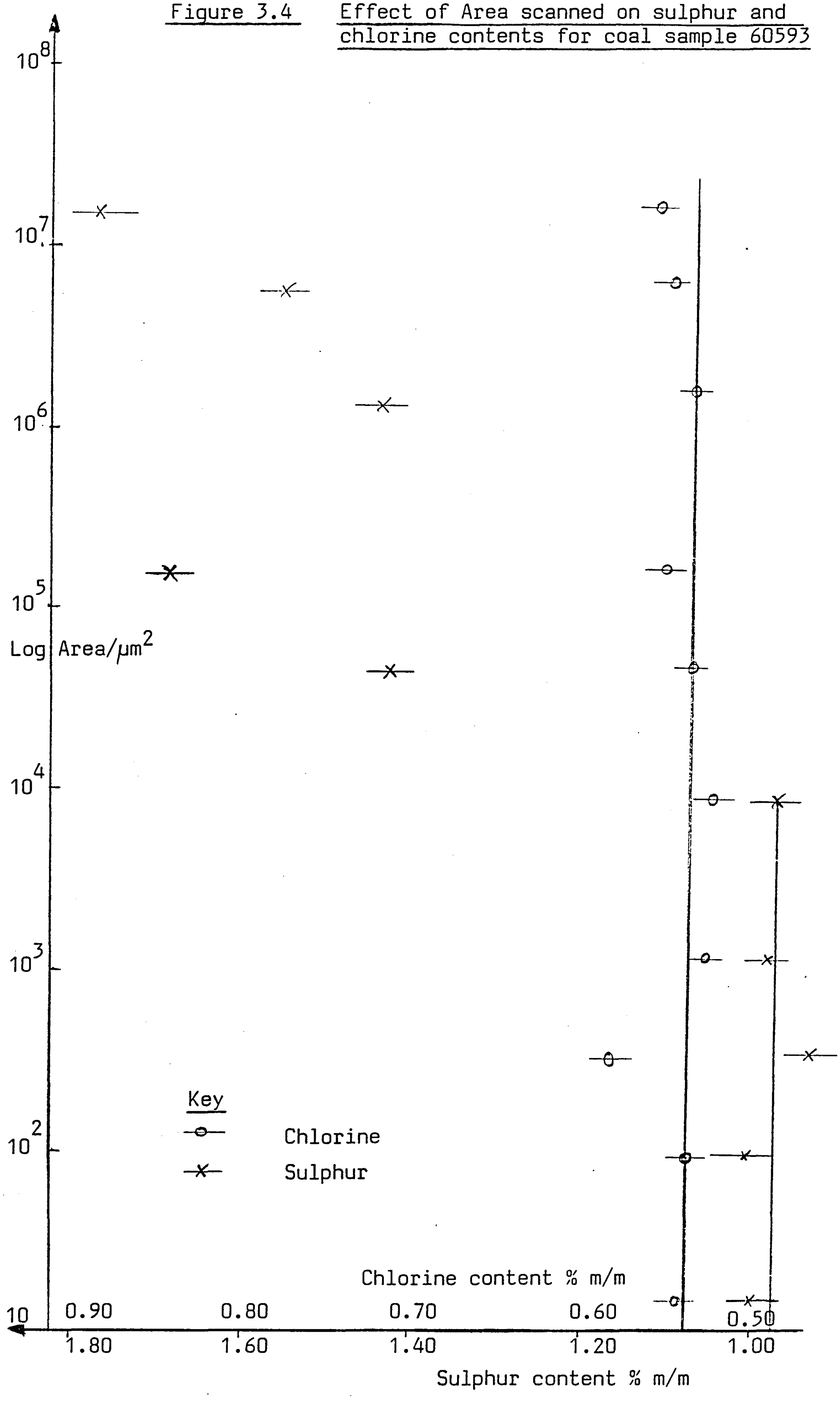
It was observed using the SEM that iron pyrite was found in coal usually as sub-micron particles or agglomerates (framboids) (Plates 3.4 and 3.5). It was impossible in the majority of cases to resolve a field of view for analysis without inclusion of iron pyrite. Increasing the magnification to greater than 2000 times for sample 60593 enabled a field of view to be selected without pyritic inclusions, but this was the exception rather than the rule.

TABLE 3.21

Effect of sample area scanned on chlorine and sulphur determinations (air-dried basis)

Magnification	Area µm^2	Sulphur % m/m			Chlorine % m/m		
		60593	60596	61113	60593	60596	61113
X 50	1.40×10^7	1.74	0.75	0.71	0.56	0.63	0.44
100	3.50×10^6	1.55	0.73	0.69	0.55	0.62	0.42
200	8.80×10^5	1.47	0.74	0.69	0.53	0.61	0.43
500	1.43×10^5	1.68	0.70	0.71	0.55	0.63	0.45
1000	3.56×10^4	1.42	0.73	0.70	0.53	0.61	0.42
2000	8.91×10^3	0.98	0.71	0.65	0.52	0.65	0.45
5000	1.41×10^3	1.00	0.71	0.66	0.52	0.66	0.47
10000	3.52×10^2	0.95	0.64	0.71	0.58	0.61	0.43
20000	8.80×10^1	1.02	0.65	0.62	0.53	0.62	0.42
50000	1.41×10^1	1.00	0.64	0.63	0.54	0.64	0.40
Average		1.28	0.70	0.68	0.54	0.63	0.43
Range		0.95- 1.74	0.64- 0.75	0.62- 0.71	0.52- 0.58	0.61- 0.66	0.40- 0.47
Std. Dev		0.32	0.04	0.03	0.02	0.02	0.02
95% Confidence Limits		1.28± 0.64	0.70± 0.08	0.68± 0.06	0.54± 0.04	0.63± 0.04	0.43± 0.04
Relative Std.Dev (%)		25.0	5.7	4.4	3.7	3.2	4.7

Figure 3.4 Effect of Area scanned on sulphur and chlorine contents for coal sample 60593



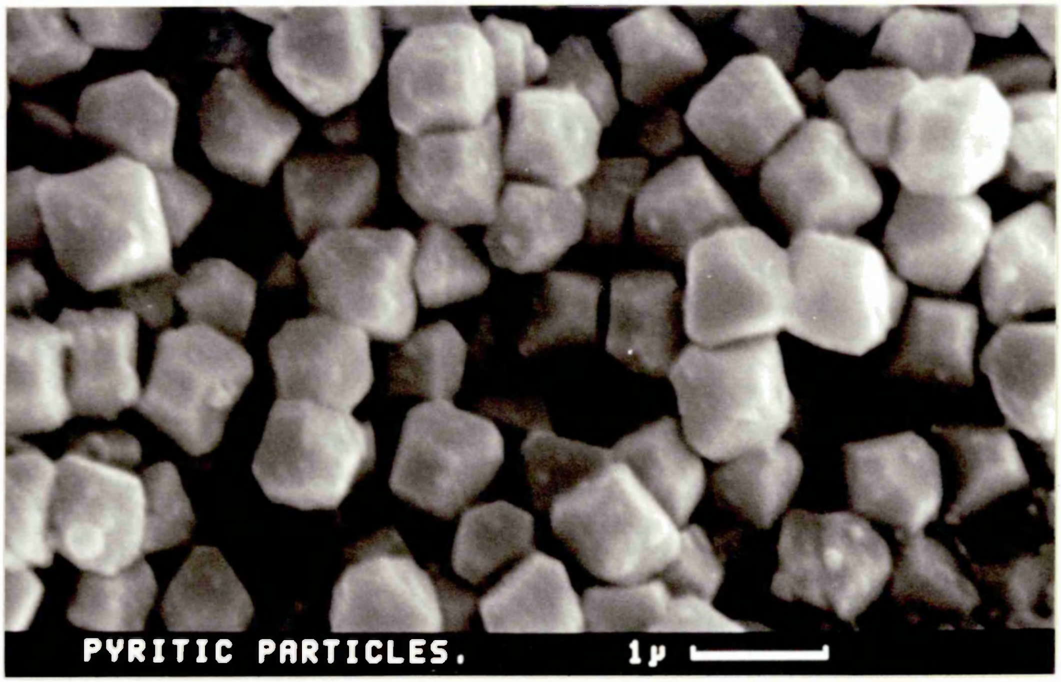


PLATE 3.4

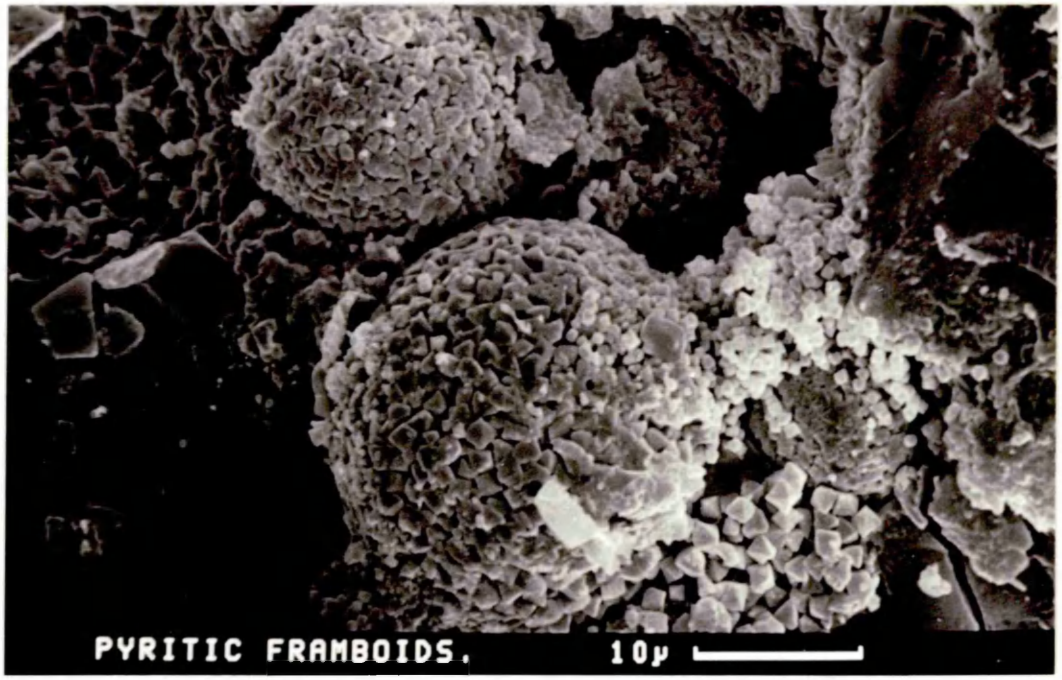


PLATE 3.5

3.3.1.7 Effect of Coal Disc preparation pressure

The analysis of pressed discs of the same coal subjected to varying amounts of applied pressure during preparation has been investigated. The method of preparation has been detailed in section 3.2.3. The results of these analyses are given in Table 3.22.

A change in load from one to eight tonnes applied to the disc results in no apparent effect upon the subsequent SEM/EDX analyses and the relative standard deviations for chlorine and sulphur are in good agreement with previously reported figures. All the discs produced were coherent and hence this sample preparation procedure does not influence the SEM/EDX analytical result.

3.3.1.8 Effect of carbon coating of coal

The low sulphur results for coals containing a substantial amount of iron pyrite may have been due to charging of the mineral surface during analysis. To investigate this, duplicate discs of samples 61120 and 61121 (coal pillar 61) were examined. One disc of each sample was carbon-coated using the carbon fibre deposition equipment. The thickness of coating was not measured but as carbon has a low X-ray absorption the reduction in X-ray emission was considered minimal.

The average results for three determinations using the ZAF4/FLS software are given in Table 3.23. Carbon coating produces results which are slightly lower than uncoated coal discs and which show no improvement in accuracy when compared to chemical analyses. These lower results for carbon-coated samples are probably due to the small amount of X-ray emission absorbed by the carbon film.

It can be seen from the results in Table 3.23 that the non-conducting nature of the mineral matter in coal is not responsible for the poor analysis of certain elements viz. iron and sulphur. In fact aluminium and silicon, which are chiefly present in the mineral matter, show little difference whether the coal disc has been coated with carbon or not.

TABLE 3.22

Variation in SEM/EDX analyses with load applied to coal discs during preparation (< 212 µm coal) (air-dried basis)

Chemically determined values[123]

0.77% Cl Chlorine
0.95% S Sulphur

Element / Load Applied/ tonnes	Cl (%)(Average)	S(%)(Average)	Fe(%)(Average)	Na(%)(Average)
1	0.73 0.71 0.71(0.72)	0.74 0.75 0.75(0.75)	0.13 0.16 0.11(0.13)	0.27 0.25 0.24(0.25)
3	0.78 0.76 0.78(0.77)	0.81 0.91 0.86(0.86)	0.16 0.19 0.17(0.17	0.23 0.33 0.31(0.29)
6	0.76 0.79 0.78(0.78)	0.83 0.85 0.76(0.81)	0.17 0.17 0.14(0.16)	0.27 0.16 0.35(0.26)
7	0.73 0.71 0.75(0.73)	0.80 0.76 0.79(0.78)	0.20 0.14 0.13(0.16)	0.24 0.23 0.29(0.25)
8	0,78 0.76 0.79(0.78)	0.80 0.80 0.77(0.79)	0.19 0.19 0.16(0.18)	0.29 0.27 0.22(0.26)
Average	0.755	0.799	0.161	0.263
Range	0.71-0.79	0.74-0.91	0.11-0.20	0.22-0.35
Std.Dev	0.030	0.048	0.026	0.048
95% Conf. Limits	0.755 ± 0.060	0.799 ± 0.096	0.161 ± 0.052	0.263 ± 0.096
Rel.Std. Dev. (%)	4.0	6.0	16.3	18.2

TABLE 3.23

Effect of carbon coating of coal discs

Element	Average Concentration % m/m (air-dried basis)					
	Sample 61120			Sample 61121		
	Uncoated	Carbon Coated	Digestion AAS[a]	Uncoated	Carbon Coated	Digestion AAS[a]
Cl	0.35	0.34	(0.36)[b]	0.41	0.38	(0.41)[b]
S	2.34	2.19	(3.44)[c]	1.67	1.62	(2.23)[c]
Fe	1.11	1.10	1.78	0.58	0.53	0.83
Si	0.51	0.46	0.51	0.26	0.25	0.31
Al	0.47	0.41	0.47	0.28	0.23	0.28

Ca, Mg, Na, K, Ti, Mn and P were below the limit of detection

[a] Result by atomic absorption or colorimetry after HF digestion of the coal ash.[123]

[b] Analysis by BS 1016, Part 8.[123]

[c] Analysis by BS 1016, Part 6.[123]

3.3.2 ZAF/PB Programme

This programme has only been available for a short time and was not evaluated as extensively as the ZAF4/FLS software. Ten coals including two certified reference samples NBS 1632a and 1635 were analysed. Two methods of using this software were investigated and are discussed in the following sections.

3.3.2.1 Normal method using polished chemical standards

Five reference coals and NBS SRM 1632a and 1635 were analysed using ZAF/PB for a 100 second counting time, as described in section 3.2.4.2. The results for the two NBS coals are given in Table 3.24 and the five reference coals in Table 3.25. Chlorine results are very poor with the average values very much higher than the chemically determined values. This is surprising, one would expect that an element which gives good results for ZAF4/FLS would also give good results for ZAF/PB. The reason may be error in the calculation of peak to background ratios for chlorine.

On the other hand, sulphur results are improved compared to the chemical results, particularly in the case of NBS SRM 1632a and reference coals 44 and 68.

For other elements, iron and silicon are still low when compared to the chemical values but greatly improved when compared to ZAF4/FLS results. The other elements show no particular trend. The detection limits for the elements determined by ZAF/PB in coal are listed in Table 3.26. They are generally poorer than those found for the corresponding counting periods of 100s and 250s using ZAF4/FLS. This is probably due to uncertainty in estimation of the background.

TABLE 3.24

Determination of elements in standard coals NBS 1632a[a] and 1635[a] using ZAF/PB software

NBS SRM 1632a[a]

Element	Concentration % m/m (dry basis)						
	SEM/EDXA[b]				Digestion AAS[c]	Certified Value	Gladney[d]
	1	2	3	Average			
Cl	0.14	0.10	0.15	0.13	-	-	0.076 ± 0.005
S	1.67	1.65	1.64	1.65	(1.55)[e]	1.62 ± 0.03	1.45 ± 0.23
Fe	0.82	0.68	0.69	0.73	1.11	1.11 ± 0.02	1.13 ± 0.03
Si	5.14	5.30	4.93	5.12	5.89	-	5.9± 0.2
Al	2.93	3.13	2.80	2.95	3.04	(3.1)[f]	2.97 ± 0.04
Ca	0.29	0.22	0.24	0.25	0.26	0.23 ± 0.03	0.23 ± 0.01
Mg	0.14	<0.12	<0.12	<0.12	0.10	(0.1)[f]	0.095 ± 0.035
Na	<0.24	<0.24	<0.22	<0.24	0.08	0.084 ± 0.004	0.076
K	0.52	0.46	0.48	0.49	0.45	0.42 ± 0.02	0.41 ± 0.01
Ti	0.25	0.25	0.18	0.23	0.14	(0.18)[f]	0.165 ± 0.013
Mn	<0.11	<0.11	<0.11	<0.11	0.05	0.0028 ± 0.0002	0.0031 ± 0.0002
P	<0.08	<0.08	<0.08	<0.08	0.03	-	0.028

NBS SRM 1635[a]

Element	1	2	3	Average	Digestion AAS[c]	Certified Value	Gladney[d]
Cl	0.11	0.18	0.17	0.15	-	0.0003	0.0003
S	0.41	0.39	0.39	0.40	(0.38)[e]	0.33	0.40 ± 0.13
Fe	0.16	0.22	0.25	0.21	0.24	0.239 ± 0.005	0.24 ± 0.03
Si	0.56	0.43	0.44	0.48	0.76	-	0.64 ± 0.13
Al	0.47	0.41	0.39	0.42	0.34	0.32	0.32 ± 0.02
Ca	0.53	0.41	0.46	0.47	0.58	-	0.56 ± 0.02
Mg	<0.14	<0.14	<0.13	<0.14	0.10	-	0.10
Na	<0.24	<0.26	<0.24	<0.25	0.18	-	0.25 ± 0.03
K	<0.08	<0.09	<0.09	<0.09	0.04	-	0.01
Ti	<0.14	<0.12	<0.13	<0.13	0.02	0.02	0.021 ± 0.003
Mn	<0.12	<0.20	<0.17	<0.16	0.002	0.002	0.002
P	<0.07	<0.10	<0.10	<0.09	0.006	-	0.012

[a] National Bureau of Standards, Washington D.C, U.S.A.
Standard Reference Material 1632a Coal (Bituminous) and 1635 (sub-bituminous) coal.

[b] Results from this work.

[c] Result by atomic absorption or colorimetry after HF digestion of the coal ash.[123]

[d] Gladney results.[131]

[e] Analysis by BS 1016 Part 6.[123]

[f] Non-certified value

TABLE 3.25

Determination of elements in reference coals using ZAF/PB software

Element	Concentration % m/m (air-dried basis)														
	Ref. Coal Sample No. 20					Ref. Coal Sample No. 29					Ref. Coal Sample No. 44				
	SEM/EDXA[a]				Digestion AAS[b]	SEM/EDXA[a]				Digestion AAS[b]	SEM/EDXA[a]				Digestion AAS[b]
	1	2	3	Average		1	2	3	Average		1	2	3	Average	
Cl	0.82	0.85	0.75	0.81	(0.55)[c]	0.46	0.37	0.44	0.42	(0.27)[c]	0.37	0.40	0.37	0.38	(0.23)[c]
S	1.91	2.05	1.85	1.94	(2.32)[d]	2.06	1.97	2.06	2.03	(2.28)[d]	2.06	2.10	1.96	2.04	(2.06)[d]
Fe	1.26	1.32	1.30	1.29	1.78	1.51	1.55	1.53	1.53	1.84	1.83	1.87	1.83	1.84	2.22
Si	4.54	4.45	4.47	4.49	4.72	5.86	6.15	5.60	5.87	6.19	3.94	4.19	3.87	4.00	4.38
Al	3.00	3.27	3.18	3.15	2.64	3.77	3.94	3.61	3.77	3.34	2.64	2.86	2.91	2.80	2.27
Ca	0.23	0.23	0.24	0.23	0.30	0.31	0.34	0.28	0.31	0.40	0.48	0.49	0.46	0.48	0.63
Mg	0.31	0.28	0.26	0.28	0.21	0.31	0.29	0.24	0.28	0.21	0.19	0.17	0.16	0.17	0.23
Na	0.43	0.30	0.31	0.35	0.22	0.25	0.34	0.23	0.27	0.20	0.22	0.19	0.13	0.18	0.13
K	0.68	0.67	0.65	0.67	0.50	0.85	0.90	0.95	0.90	0.66	0.67	0.69	0.57	0.64	0.45
Ti	0.12	0.11	0.11	0.11	0.11	0.14	0.19	0.13	0.15	0.13	0.09	0.15	0.10	0.11	0.13
	Ref. Coal Sample No. 47					Ref. Coal Sample No. 68									
Cl	0.34	0.35	0.34	0.34	(0.21)[c]	0.80	0.82	0.80	0.81	(0.44)[c]					
S	2.30	2.08	2.12	2.17	(2.29)[d]	2.29	2.40	2.36	2.35	(2.44)[d]					
Fe	1.31	1.44	1.49	1.41	1.89	2.04	2.81	2.22	2.37	2.60					
Si	4.88	4.77	5.14	4.93	5.09	9.82	9.84	10.33	10.00	9.72					
Al	3.45	3.45	3.88	3.59	3.49	6.66	6.65	6.69	6.67	5.56					
Ca	0.22	0.18	0.26	0.22	0.26	0.24	0.34	0.28	0.29	0.26					
Mg	0.25	0.27	0.34	0.29	0.20	0.57	0.49	0.45	0.50	0.40					
Na	0.24	0.31	0.32	0.29	0.19	0.40	0.35	0.37	0.37	0.36					
K	0.81	0.69	0.69	0.73	0.62	1.34	1.27	1.40	1.34	1.08					
Ti	0.16	0.14	0.14	0.15	0.12	0.30	0.35	0.36	0.34	0.28					

Manganese and phosphorus were below the limits of detection.

[a] Results from this work

[b] Results by atomic absorption or colorimetry after HF digestion of coal ash[123]

[c] Analysis by BS 1016, Part 8[123]

[d] Analysis by BS 1016, Part 6[123]

TABLE 3.26

Estimated detection limits for counting periods of 100 and 250 seconds using ZAF/PB software for coal discs (air-dried basis)

Element	Counting period 100s Detection limit % m/m	Counting period 250s Detection limit % m/m
Cl	0.10	0.07
S	0.12	0.09
Fe	0.15	0.10
Si	0.14	0.10
Al	0.14	0.10
Ca	0.08	0.05
Mg	0.12	0.09
Na	0.24	0.16
K	0.08	0.06
Ti	0.09	0.06
Mn	0.11	0.08
P	0.08	0.06

3.3.2.2 Novel method using a coal standard

Reference coal 59 was used as the standard coal for calibration using the method described in section 3.2.4.3. Eleven analyses of coal 59 were then performed using the coal standard and the results are given in Table 3.27. These results show good agreement between the averaged values and the chemically determined values for silicon, aluminium and iron. Sulphur and chlorine were not in such good agreement. The range of values was wider than expected. The results for the same spectra analysed using the normal polished chemical standard method of calibration are given in Table 3.28. The accuracy using this calibration for chlorine, sulphur and iron is poor and therefore its use is not recommended.

Two coals taken from pillar section 61 were analysed as unknowns using coal 59 as the calibration standard. The results are given in Table 3.29 and show some improvement compared to previous results, particularly for sulphur. Investigation using coals as standards with similar composition to unknowns may effectively show the wider applicability of this novel calibration procedure.

3.4 CONCLUSIONS

A rapid, precise and accurate method for the determination of chlorine in coal has been established using the ZAF4/FLS software of the SEM/EDXA system, with a relative standard deviation of 2.5% but a detection limit of 0.4 mg g^{-1} compared with 0.2 mg g^{-1} for the British Standard Eschka method.[123]

TABLE 3.27

Elemental Analysis of Coal 59 using ZAF/PB software with Coal 59 as standard

Coal 59 Determination	Concentration % m/m (air-dried basis)				
	Si	Al	Fe	S	Cl
59A	0.60	0.47	1.46	2.25	0.26
59B	0.55	0.41	1.23	2.16	0.26
59C	0.56	0.47	1.36	2.20	0.28
59D	0.52	0.51	1.35	2.20	0.30
59E	0.59	0.42	1.23	2.33	0.28
59F	0.62	0.48	1.17	2.32	0.31
59G	0.61	0.41	1.17	2.32	0.29
59H	0.57	0.48	1.34	2.24	0.28
59I	0.63	0.44	1.32	2.37	0.29
59J	0.60	0.50	1.28	2.30	0.27
59K	0.61	0.49	1.41	2.22	0.26
Average	0.59	0.46	1.30	2.26	0.28
Range	0.52-0.63	0.41-0.51	1.17-1.46	2.16-2.37	0.26-0.31
Std.Dev.	0.03	0.04	0.09	0.07	0.02
95% Confidence Limits	0.59±0.06	0.46±0.08	1.30±0.18	2.26±0.14	0.28±0.04
Relative Std. Dev. (%)	5.1	8.7	6.9	3.1	7.1
Digestion AAS	0.59	0.48	1.26	2.35[d]	0.32[c]

The following elements were below the limit of detection

Element	Concentration % m/m (air-dried basis)						
	Ca	Mg	Na	K	Ti	Mn	P
ZAF/PB value	0.08	0.16	0.24	0.07	N D	N D	N D
Digestion AAS	0.07	0.03	0.08	0.06	0.02	0.003	0.004

N D - Not determined

[c] Analysis by BS 1016 Part 8.[123]

[d] Analysis by BS 1016 Part 6.[123]

TABLE 3.28

Elemental Analysis of Coal 59 using ZAF/PB software with normal polished chemical standard

Coal 59 Determination	Concentration % m/m (air-dried basis)				
	Si	Al	Fe	S	Cl
59A	0.66	0.65	1.04	2.61	0.57
59B	0.60	0.58	0.88	2.51	0.57
59C	0.62	0.65	0.97	2.56	0.62
59D	0.57	0.72	0.96	2.55	0.66
59E	0.65	0.59	0.88	2.72	0.63
59F	0.69	0.68	0.84	2.70	0.68
59G	0.68	0.58	0.83	2.70	0.65
59H	0.63	0.67	0.95	2.60	0.62
59I	0.70	0.62	0.94	2.76	0.64
59J	0.66	0.71	0.91	2.68	0.60
59K	0.68	0.69	1.00	2.58	0.57
Average	0.65	0.65	0.93	2.63	0.62
Range	0.57-0.70	0.58-0.72	0.83-1.04	2.51-2.76	0.57-0.68
Std.Dev.	0.04	0.05	0.07	0.08	0.04
95% Confidence Limits	0.65±0.08	0.65±0.10	0.93±0.14	2.63±0.16	0.62±0.08
Relative Std. Dev. (%)	6.2	7.7	7.5	3.0	6.5
Digestion AAS	0.59	0.48	1.26	2.35[d]	0.32[c]

The following elements were below the limit of detection

Element	Concentration % m/m (air-dried basis)						
	Ca	Mg	Na	K	Ti	Mn	P
ZAF/PB value	0.08	0.16	0.24	0.07	N D	N D	N D
Digestion AAS	0.07	0.03	0.08	0.06	0.02	0.003	0.004

N D - Not determined

[c] Analysis by BS 1016 Part 8.[123]

[d] Analysis by BS 1016 Part 6.[123]

TABLE 3.29

Determination of elements in coals 61120 and 61121 using coal 59 as a standard and ZAF/PB software

Coal Sample	Element	Concentration % m/m (air-dried basis)				
		SEM/EDXA[a]				Digestion AAS[b]
		1	2	3	Average	
61120	Cl	0.45	0.42	0.38	0.42	(0.36)[c]
	S	3.48	3.52	3.41	3.47	(3.44)[d]
	Fe	2.13	2.22	2.15	2.17	1.78
	Si	0.64	0.67	0.59	0.63	0.56
	Al	0.54	0.48	0.53	0.52	0.49
	Ca	0.11	0.13	<0.08	0.12	0.12
	Mg	0.14	<0.12	<0.12	<0.12	0.02
	Na	<0.24	<0.24	<0.24	<0.24	0.21
	K	<0.08	<0.08	<0.08	<0.08	0.08
	Ti	<0.09	<0.09	<0.09	<0.09	0.09
61121	Cl	0.42	0.48	0.48	0.46	(0.41)[c]
	S	2.44	2.52	2.47	2.48	(2.23)[d]
	Fe	1.16	1.15	1.12	1.14	0.83
	Si	0.36	0.31	0.32	0.33	0.31
	Al	0.32	0.26	0.37	0.32	0.28
	Ca	<0.08	<0.08	0.08	<0.08	0.08
	Mg	<0.12	<0.12	0.12	<0.12	<0.01
	Na	<0.24	<0.24	<0.24	<0.24	0.21
	K	<0.08	<0.08	<0.08	<0.08	0.02
	Ti	<0.09	<0.09	<0.09	<0.09	0.04

Manganese and phosphorus were below the limits of detection.

[a] Results from this work

[b] Results by atomic absorption or colorimetry after HF digestion of coal ash.[123]

[c] Analysis by BS 1016 Part 8.[123]

[d] Analysis by BS 1016 Part 6.[123]

On the other hand, sulphur cannot be determined accurately in coal using ZAF4/FLS except where pyrites and sulphate-sulphur are virtually absent. The relative standard deviation for sulphur is about 5% with a detection limit of 0.6 mg g^{-1}. In a coal sample which contains pyrites the sulphur content is found to decrease with decreasing area scanned. The finely disseminated nature of pyrites makes it impossible, except in isolated cases, to analyse fields of view excluding this mineral.

The use of a ratio of peak to background intensities in the ZAF/PB software significantly improves the results for sulphur. The most accurate sulphur results are obtained when a reference coal is used as a standard in this software.

Chlorine and organic sulphur appear to respond similarly to SEM/EDXA in as much as the determined concentrations (within focussing limitation) are virtually independent of the area analysed.

The SEM/EDXA results for chlorine therefore suggest that this element is evenly distributed within the organic part of coal in one bonded form.

The implications of this distribution are studied in greater detail in chapter 4.

The major ash forming elements found in coal can be determined simultaneously, with detection limits ranging from 0.4 to 1.1 mg g^{-1}. A correlation coefficient of 0.997 has been found for the relationship between the conventional ash content and the sum of the elements determined by the ZAF4/FLS software, excluding chlorine and sulphur. The agreement between the observed values and those obtained by standard procedures where the levels of constituent permit SEM/EDXA determination, is fairly good.

Some improvement in the accuracy of the results, particularly for aluminium, silicon and iron was found using the ZAF/PB software. The use of a coal standard did not appear to improve the accuracy of the results for these elements determined by ZAF/PB, but this method may give some improvement if a coal with a similar elemental composition to unknowns is used as the standard.

A reduction in particle size of coal from less than 212 μm to less than 45 μm has little or no effect on the elemental analyses obtained using the SEM/EDXA method.

The applied pressure in the range of one to eight tonnes used to prepare coal discs, was found not to affect the SEM/EDXA analytical result.

No evidence has been produced in this work to suggest that it is necessary to carbon coat discs of coal to obtain satisfactory SEM/EDX analysis.

The detection limits of the SEM/EDXA technique are improved slightly by increasing the counting time from 100s to 250s and also when using the ZAF4/FLS software instead of ZAF/PB.

The availability of the two software options described in this chapter, greatly increases the versatility and usefulness of a novel technique for the direct analysis of coal powders.

CHAPTER 4

INVESTIGATIONS INTO THE MODE OF OCCURRENCE OF CHLORINE IN COAL

4.1 INTRODUCTION

This chapter discusses the likely mode of occurrence of chlorine in coal mentioned briefly in chapter 3, where accurate chlorine analyses were achieved using SEM/EDXA. The mode of occurrence and behaviour of trace and minor elements are important when strategies for their removal or control in combustion processes are suggested.

The development of rapid, sensitive and accurate methods of coal analysis is the main aim of this thesis. However, as these methods are developed the paucity of knowledge as to the mode of occurrence of trace and minor elements is exposed. Thus, a second but important aim is to investigate the bonding of elements in coal and hence indicate possible control strategies to minimise harmful effects. Such considerations are clearly illustrated in this chapter for the particularly deleterious element chlorine.

Although chlorine is present in minor quantities in coal (less than one percent m/m) it is extremely troublesome, corroding tubes and furnaces in coal combustion and coal conversion processes.[132,133,13] In addition, because of the large tonnages involved in the UK (viz. 75 million tonnes) hydrogen chloride emissions from power-station stacks may be harmful to the environment.[135] It is anticipated that chlorine may soon be included in the price structure for coal supplied for electricity production in the UK. A monetary penalty will be imposed for high chlorine content coals.

The estimated increase in chlorine levels by development of further deep-mined seams, emphasises the importance of understanding the forms or form in which chlorine is bound in coal, so that harmful environmental effects may be avoided.

Earlier researchers, De Waele[136] Crossley[137] and Nelson[138] suggested that chlorine occurs in coal in the form of alkali chlorides, principally sodium chloride. Later studies by Edgcombe,[121] Daybell and Pringle[122] and Daybell[139] proposed that chlorine was not wholly present as inorganic chlorides and suggested possible ionic chloride to coal linkages. Skipsey[140,141] provided evidence for a relationship between chlorine content of coal and rank. He proposed that the soluble sodium and chlorine present in coal were adsorbed from hypersaline strata waters which permeated the coal substance after the rank pattern had been established. In the USA Gluskoter and Rees[142] reported that they could not extract all the chlorine from finely ground Illinois coals by aqueous leaching.

More recent studies by Saunders,[143] suggested concentration of chlorine in the vitrinite maceral (bright coal) with a strong correlation between the sodium content of that maceral and the water extractability of chlorine. She suggested that chlorine is present in at least two forms in coal, one of which is sodium chloride 'solution' in vitrinite pores. This concentration and even distribution in the vitrinite maceral was confirmed by Spears.[144] Chakrabarti[145] has put forward evidence for the presence of organic chlorine in Indian coals and actually proposed a method for its estimation. Caswell[146] using a silver nitrate staining technique, related the degree of water leachability of chlorine to the different coal macerals and also showed that the exinite (dull coal) and inertinite (fusainous coal) rich regions allow access of leaching solvents to a greater extent than vitrinite (bright coal).

An attempt to explain some of the earlier inconsistencies in the literature is given by Hodges, Ladner and Martin[147] in a recent review. It is worthy of note that this review was first published internally within the NCB[148] with reference to the work described here. Certainly some of the assumptions and conclusions drawn by Hodges from conflicting literary evidence are tenuous without the confirmatory work reported here.

The object of the work described in this chapter therefore is to resolve some of these inconsistencies in the literature, and the experiments are primarily concerned with the presence of chlorides in coal and investigations into the physical and chemical characteristics of the chlorine-coal bond. This study applies the technique of elemental mapping using SEM/EDXA to establish the likely presence of metallic chlorides in coal. British Standard and instrumental methods of coal analysis are used to evaluate chlorine reactions, on heat treatment and/or chemical treatment. The aim therefore is to establish the mechanism by which chlorine is bound within the coal substance.

4.2 EXPERIMENTAL EQUIPMENT

3-30 ADP Scanning electron microscope (SEM) (CamScan, Bar Hill, Cambridge.)

860 Series I, Energy-dispersive X-ray (EDX) analysis system with solid state silicon (Lithium) detector and fully quantitative ZAF4/FLS software. (Link Systems, High Wycombe, Bucks.)

Manually operated press, type 5100-4599 (15 tonnes). (Perkin Elmer Ltd., Beaconsfield, Bucks.)

Micro-mill type MS 400, Retsch Spectromill and 'Shatterbox' grinding mill. (Glen Creston, Stanmore, Middlesex.)

Double beam atomic-absorption spectrometer, Model 460 (Perkin Elmer Ltd., Beaconsfield, Bucks.)

Cobalt and Multi-element standards. (Agar Aids, Stansted, Essex.)

Plasmaprep 100 r.f. activated oxygen low-temperature asher. (Nanotech, Prestwich, Manchester.)

Microwave plasma detector MPD 850, (Applied Chromatography Systems Ltd., Luton, Bedfordshire.)

Coulter Counter Model TAII, (Coulter Electronics Ltd., Luton, Beds.)

Gas detector tubes, (Dräeger Safety, Chesham, Bucks.)

4.3 STUDIES USING SCANNING ELECTRON MICROSCOPY AND ENERGY DISPERSIVE X-RAY ANALYSIS (SEM/EDXA)

4.3.1 Presence of alkali metal chlorides in coal

The combined techniques of scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDXA) were utilised to ascertain the presence of alkali metal chlorides in freshly fractured pieces of coal (< 6.4 mm) and pressed coal powders (< 212 μm). The examination used the facility of X-ray mapping, whereby dots generated from characteristic X-rays of an element coincide with the spatial distribution of that element. For example, sodium and chlorine X-ray dots generated from a crystal of sodium chloride would have the same distributions of much higher density than the background X-ray counts.

Using this technique, chlorine was found not to be associated with sodium, potassium or calcium and to be evenly distributed in coals of various ranks and origins. Micrographs of a typical X-ray elemental map showing the chlorine distribution and the micrograph of the same freshly fractured surface are shown in Plate 4.1.

In order to prove that the technique of X-ray elemental mapping was capable of detecting discrete particles of sodium chloride in coal, crystallites of AnalaR sodium chloride of size less than 45 μm were added to a sample of Littleton Park coal (< 212 μm) and thoroughly mixed. The admixture, having a calculated chlorine content of 1.22 percent compared with 0.72 percent (m/m) for the coal alone, was examined as previously described. Numerous sodium chloride crystallites over 10 μm in size could be detected, and some as small as 3 μm were seen. Micrographs illustrating one of the larger particles are shown in Plate 4.2.

It can thus be argued that if sodium chloride is present as such, it must exist as particles less than 3 μm in diameter, probably less than 1 μm, taking into account the reported detection limit for the SEM/EDX apparatus.[118]

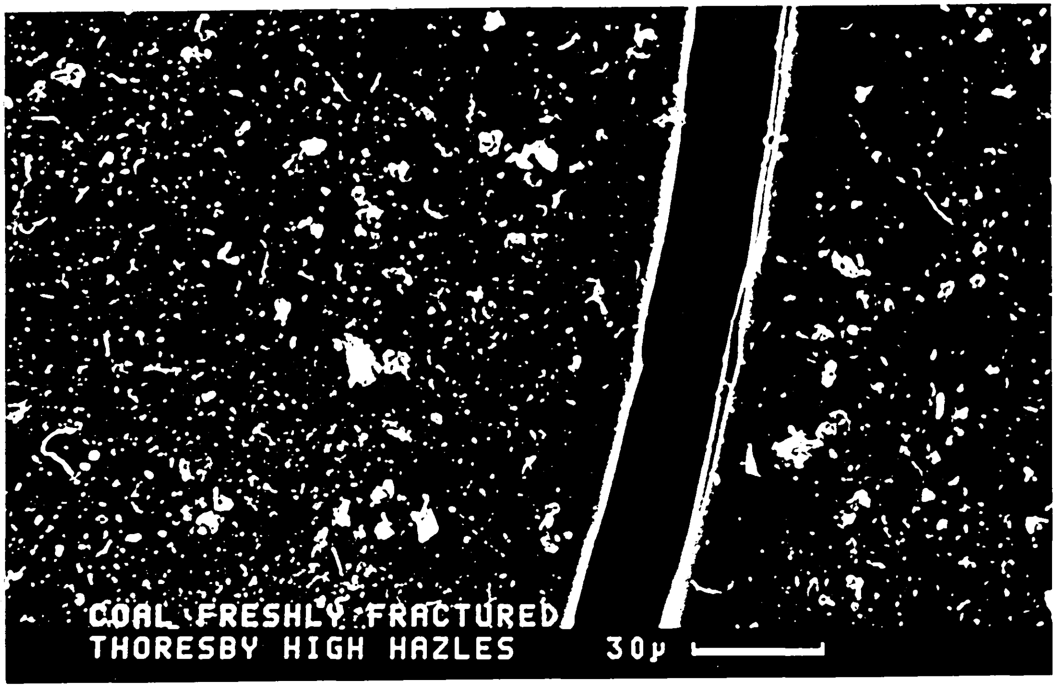


PLATE 4.1(a)
Scanning Electron Micrograph

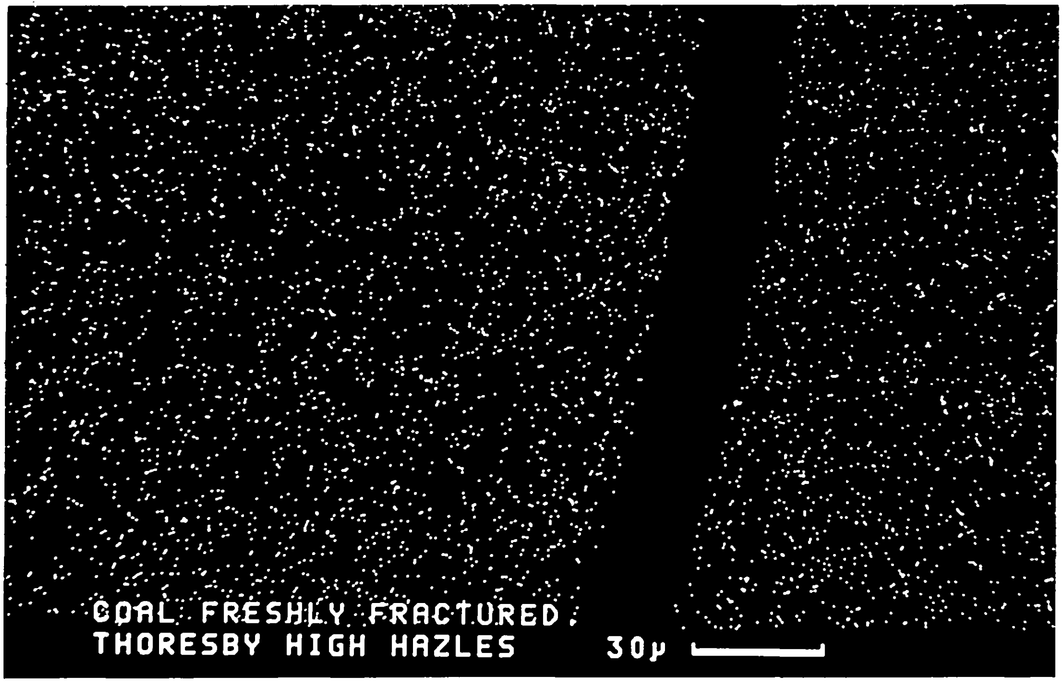


PLATE 4.1(b)
Chlorine X-ray Distribution Map of same area

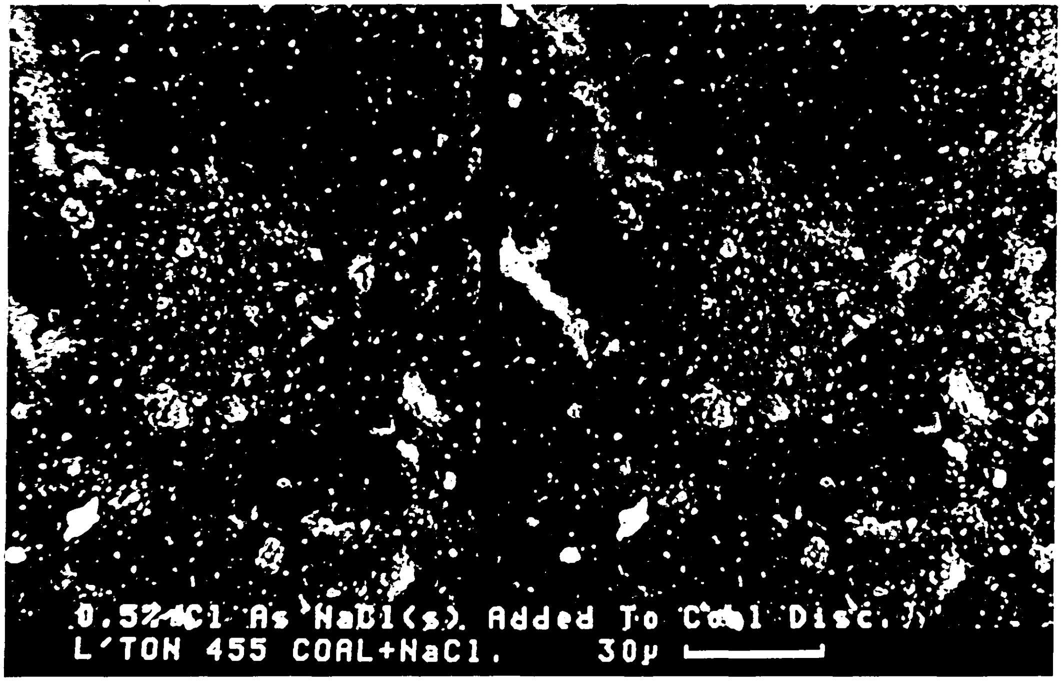


PLATE 4.2(a)
SEM micrograph of Littleton coal pressed disc with 0.5% chlorine added as sodium chloride (< 45 µm)

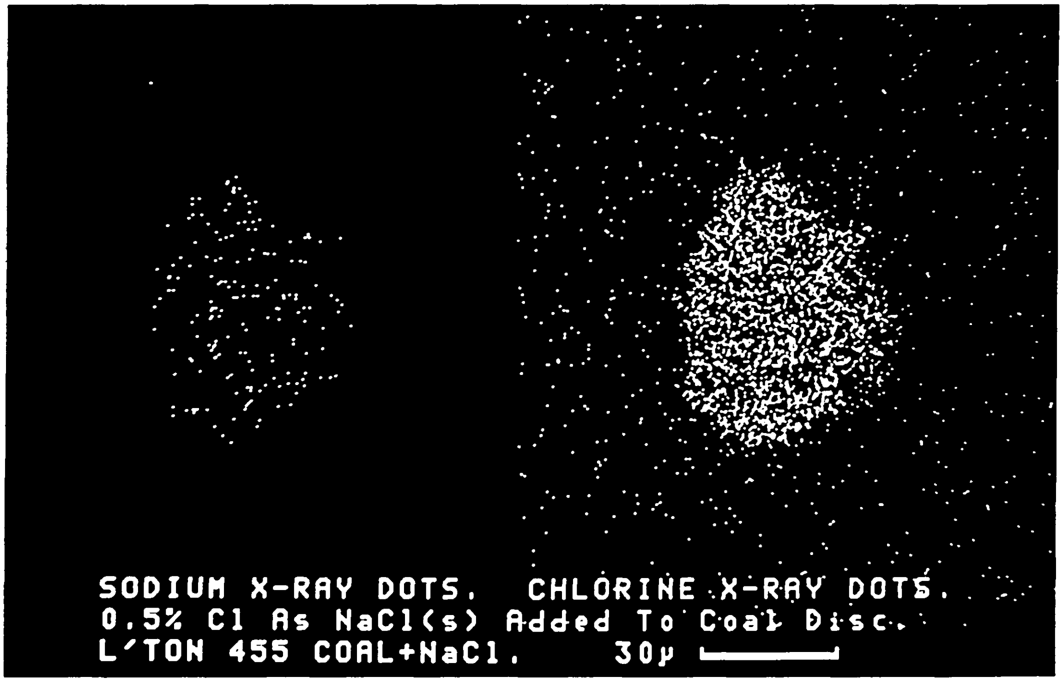


PLATE 4.2(b)
As above with image enhanced sodium/chlorine X-ray distribution only

4.3.2 SEM/EDXA of coal powders

Independent but indirect evidence for the uniformity of chlorine distribution in coal has been provided by the development of a procedure for the quantitative determination of chlorine by SEM/EDXA using compressed pellets of powdered coal. This procedure has been described in Chapter 3.

Analyses using this method were performed on several air-dried coals of different origins and ranks. Sulphur and chlorine determined by B S methods[149] are compared to determinations of the same elements by SEM/EDXA in Table 4.1. The total SEM/EDXA elemental determinations are listed in Appendix 4.1.

The replicates of chlorine results by SEM/EDXA given in Table 4.1 show good reproducibility and agreement with B S values. Sulphur analyses, however, show poor reproducibility and are invariably lower than the chemically determined values, often by appreciable amounts. These results (Table 4.1) indicate that chlorine is uniformly distributed within the organic part of coal, is independent of the area analysed and is probably present in one bonding form. On the other hand, sulphur is known to occur in coal as organic, pyritic and sulphate sulphur forms. SEM/EDX determinations using ZAF4/FLS software of an element present in more than one bonding form in a coal sample, were shown in Chapter 3 to give inaccurate results.

The results listed in Appendix 4.1 show good precision and reasonable agreement with B S values for the other minor elements, except iron, which is found in variable amounts in coal, commonly as iron pyrite.

Thus by using the technique of SEM/EDX analysis and X-ray elemental mapping no positive evidence for the existence of sodium, potassium or calcium chloride crystallites was found in this wide range of coals.

TABLE 4.1

SEM/EDXA of selected coals (air-dried basis)

Coal	Chlorine % m/m					Sulphur % m/m				
	SEM/EDXA				Average BS1016 Value %m/m	SEM/EDXA				Average BS1016 Value %m/m
	1	2	3	Average		1	2	3	Average	
Florence Rowhurst	0.98	0.97	0.98	0.98	0.99	0.49	0.53	0.50	0.51	0.59
Cortonwood/ Silkstone	0.12	0.12	0.11	0.12	0.11	0.95	1.02	0.97	0.98	1.50
South Durham 'C' Seam	0.25	0.24	0.24	0.24	0.25	0.57	0.61	0.63	0.60	0.92
Cadley Hill (Bright Coal)	0.42	0.44	0.43	0.43	0.45	1.33	1.34	1.34	1.34	3.02
Cadley Hill (Dull Coal)	0.37	0.37	0.37	0.37	0.39	1.15	1.28	1.18	1.20	2.33
Tilmanstone Milyard	0.12	0.10	0.10	0.11	0.13	0.86	0.82	0.88	0.85	1.50
Thoresby Top Hard	0.81	0.83	0.85	0.83	0.89	0.73	0.71	0.73	0.72	0.87
Thoresby Top Hard Resample	0.83	0.85	0.83	0.84	0.84	0.86	0.94	0.80	0.87	1.31
Thoresby High Hazles	1.00	0.97	1.03	1.00	1.02	0.90	0.95	0.98	0.94	1.02
Lea Hall Shallow	0.95	1.01	0.99	0.98	0.97	0.73	0.75	0.78	0.75	1.22

4.4 HEAT TREATMENT

The behaviour of chlorine on heat treatment of coal is considered extensively in the following sections to ascertain its stability, nature of its release and the effects upon the coal residue.

4.4.1 Dependence on temperature of heating

Samples (500 mg) of two selected coals were heated separately in alumina boats within a tube furnace for one hour with air and three hours with nitrogen, at a flow rate of 500 $cm^3 min^{-1}$ over the temperature range 160-220°C. A third coal was heated for one hour in air alone. The chlorine loss was estimated by analysis of the effluent gas collected in neutralised hydrogen peroxide.[149] The residual chlorine in the coal sample was determined by the high temperature BS method.[149] The results are given in Table 4.2 and plotted in Figure 4.1.

The chlorine losses for two of the coals are very similar in air and nitrogen, with the threshold temperature for chlorine release, being 180°C in both cases. The third sample, Blidworth High Hazles coal, had a slightly lower threshold temperature of 170°C and three times the chlorine loss at 200°C of the two other samples. The losses in air agree well with findings of Edgecombe[121] but not the losses in nitrogen. The losses at 200°C in both air and nitrogen confirm that the majority of chlorine evolved is unlikely to have been derived from the decomposition of alkali chloride (eg Sodium chloride, m.pt 801°C, b.pt 1413°C).

Sulphur determinations were also carried out on the samples using BS procedures.[149] The loss of sulphur in the majority of cases was less than 0.02 percent with a maximum of 0.03 percent. This precludes the involvement of oxides of sulphur with the chlorine loss under mild heat treatment. It also contradicts the findings of Gluskoter and Rees.[142]

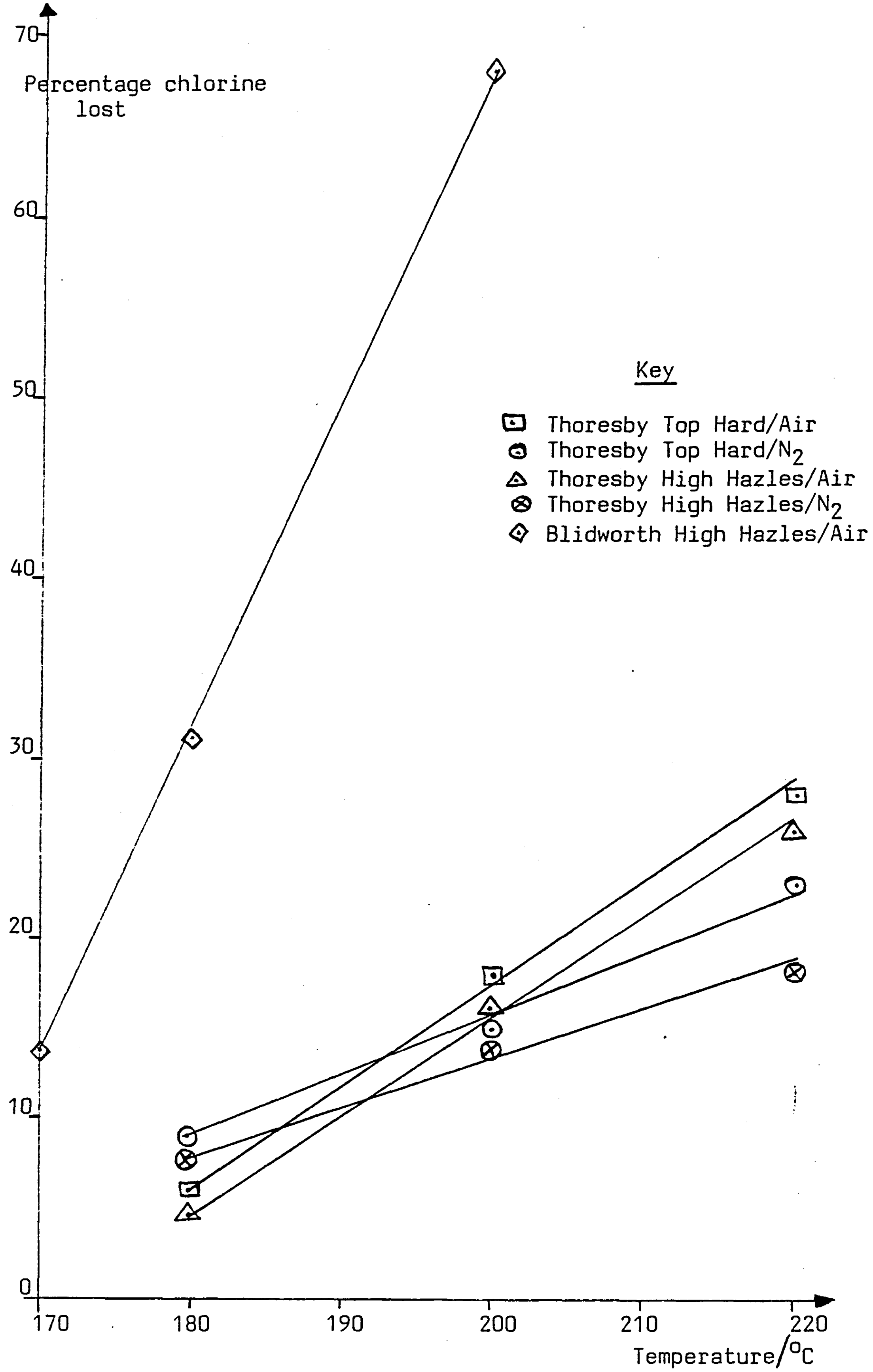
TABLE 4.2

Temperature dependence of chlorine loss in air for 1 hour and nitrogen for 3 hours (air-dried basis)

Sample/Total Chlorine % m/m	Tube Furnace Temp: ^{o}C	Loss in Air Time: 1 hour Chlorine % m/m		Percentage Chlorine Lost	Loss in Nitrogen Time: 3 hours Chlorine % m/m		Percentage Chlorine Lost
		Lost	Retained		Lost	Retained	
Blidworth	160	< 0.02	ND	< 3	ND	ND	ND
High Hazles/	170	0.09	ND	14	ND	ND	ND
0.65	180	0.20	ND	31	ND	ND	ND
	200	0.44	ND	68	ND	ND	ND
Thoresby	160	< 0.02	0.80	< 2	< 0.02	0.82	< 2
Top Hard/	170	< 0.02	0.82	< 2	< 0.02	0.79	< 2
0.82	180	0.05	0.72	6	0.07	0.68	9
	200	0.15	0.64	18	0.12	0.71	15
	220	0.23	0.59	28	0.19	0.63	23
Thoresby	160	< 0.02	0.85	< 2	< 0.02	0.82	< 2
High Hazles/	170	< 0.02	0.87	< 2	< 0.02	0.80	< 2
0.87	180	0.04	0.83	5	0.07	0.78	8
	200	0.14	0.65	16	0.12	0.73	14
	220	0.23	0.60	26	0.16	0.68	18

ND = Not determined.

Figure 4.1 Loss of chlorine with temperature from coals heated in air and nitrogen



4.4.2 Dependence on time of heating

Samples (500 mg) of three selected coals were heated separately in a tube furnace at 210 ± 5°C for periods of between 1 and 72 hours in air, and also in nitrogen. The loss of chlorine and sulphur were estimated by analysis of the effluent gas[149] and the chlorine and sulphur contents of the residual coals were also determined.[149] The results are given in Table 4.3 and plotted in graphical form in Figures 4.2, 4.3 and 4.4.

The results show a rapid initial loss of chlorine in air, with a substantial loss after 72 hours. In nitrogen the chlorine loss/time curve is of similar shape, and also characteristic of the simultaneous and independent decomposition of a mixture of materials.[150] The fact that a loss of chlorine occurs in nitrogen tends not to support Edgcombe's suggestion that chlorine loss involves an oxidation reaction mechanism.[121] Nor is there much support for the proposal that organic sulphur oxidising to sulphur dioxide assists in the liberation of chlorine. The substantial loss of chlorine at this comparatively low temperature argues against the presence of alkali chlorides, except possibly in trace amounts.

In a further experiment portions of two of the same coals were heated at 210 ± 5°C in an air oven for longer periods, and also after grinding to a finer particle size (approximately 80 percent between 12 and 20 μm). The results are given in Table 4.4.

If chlorine were present in more than one bonding form, e.g. ionically and covalently in proportions suggested by the sodium/chlorine ratio,[121]

$$\text{sodium/chlorine ratio} = \frac{\text{water soluble sodium (chlorine equivalent)}}{\text{water soluble chlorine}}$$

one form might be expected to be stable at the chosen temperature of 210 ± 5°C and prolonged heating at this temperature would not reduce the chlorine content below a certain minimum. The high proportion which is evidently lost suggests that it occurs mainly in one bonding form.

TABLE 4.3

Chlorine loss with time on heating at 210 ± 5°C

Thoresby Top Hard Eschka[a] (air-dried basis): S = 0.95% m/m
Cl = 0.82% m/m

Time of Heating (hours)	In Air					In Nitrogen				
	Chlorine % m/m		Percentage	Sulphur % m/m		Chlorine % m/m		Percentage	Sulphur % m/m	
	Lost	Retained	Chlorine Lost	Lost	Retained	Lost	Retained	Chlorine Lost	Lost	Retained
1	0.20	0.57	24	0.04	0.95	0.07	0.70	9	nil	0.96
3	0.36	0.46	44	0.06	0.90	0.12	0.63	15	0.01	0.97
6	0.44	0.35	54	0.11	0.81	0.16	0.60	20	0.02	0.95
18	0.50	0.32	61	0.21	0.79	0.23	0.59	28	0.02	0.91
72	0.59	0.21	72	0.27	0.72	0.39	0.43	48	0.03	0.88
Thoresby High Hazles Eschka (air-dried basis): S = 1.09% m/m Cl = 0.87% m/m										
1	0.23	0.65	26	0.03	1.12	0.07	0.79	8	0.01	1.13
3	0.34	0.49	39	0.07	0.98	0.11	0.69	13	0.02	1.03
6	0.44	0.40	51	0.09	0.98	0.14	0.66	16	0.03	1.07
18	0.50	0.37	57	0.11	1.08	0.23	0.60	26	0.03	1.07
72	0.62	0.23	71	0.22	0.95	0.34	0.49	39	0.04	1.08
Blidworth - High Hazles Eschka (air-dried basis) : S = 0.90% m/m Cl = 0.65% m/m										
1	0.29	0.32	45	0.04	0.82	0.07	0.59	11	nil	0.90
3	0.39	0.22	60	0.05	0.81	0.14	0.53	22	nil	0.96
24	0.50	0.12	77	0.16	0.74	0.27	0.39	42	nil	0.87
72	0.55	0.11	85	0.21	0.72	0.30	0.34	46	nil	0.95

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[a] Eschka method as described in ref.[149] a sodium carbonate/magnesium oxide fusion followed by chloride titration using Volhard's method.

Loss of chlorine at 210 ± 5°C in air and nitrogen

Key

△—△ Loss in air

○—○ Loss in nitrogen

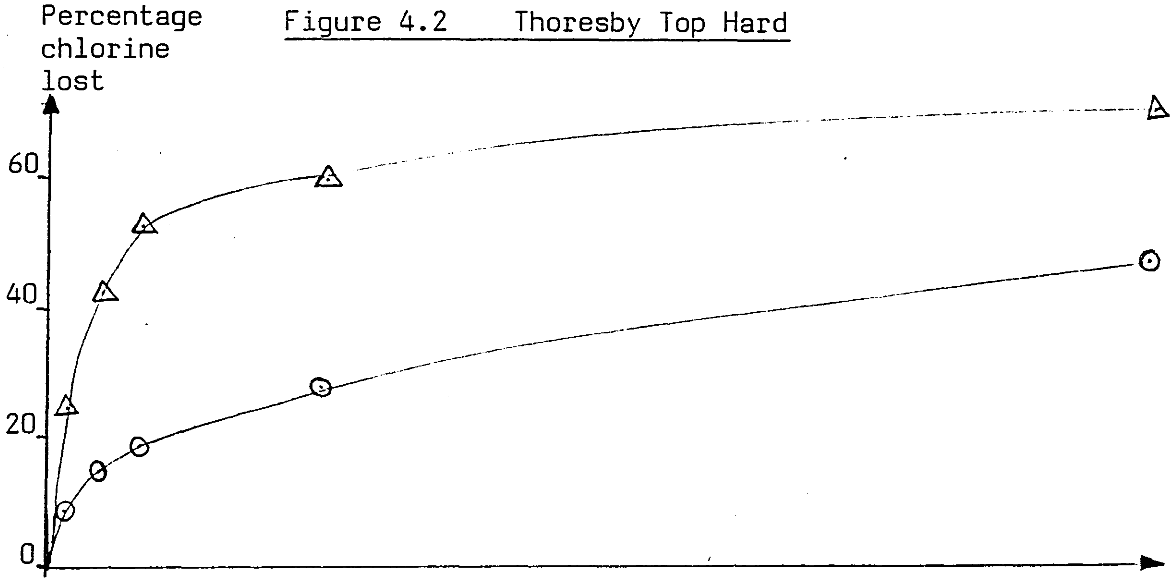


Figure 4.2 Thoresby Top Hard

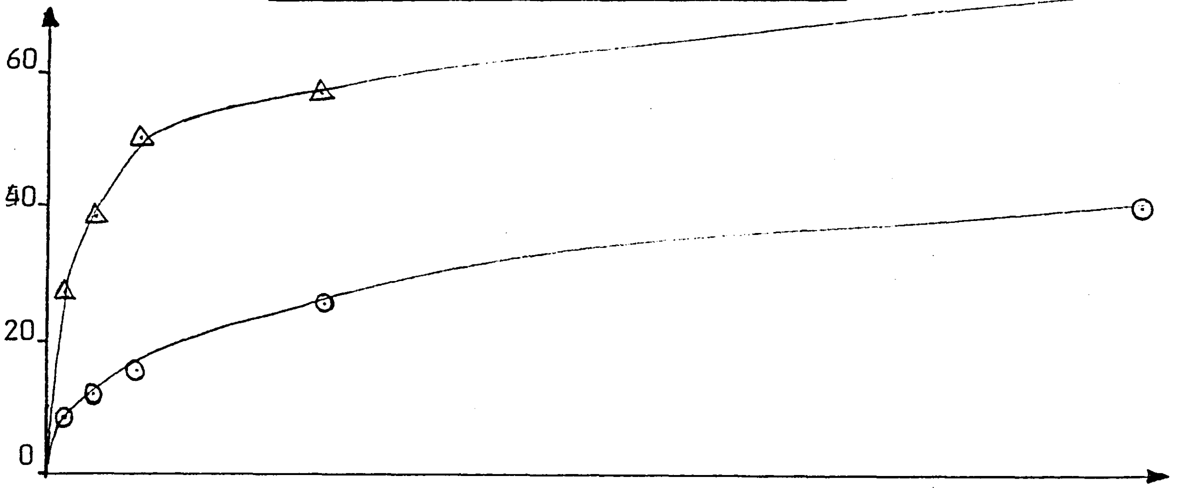


Figure 4.3 Thoresby High Hazles

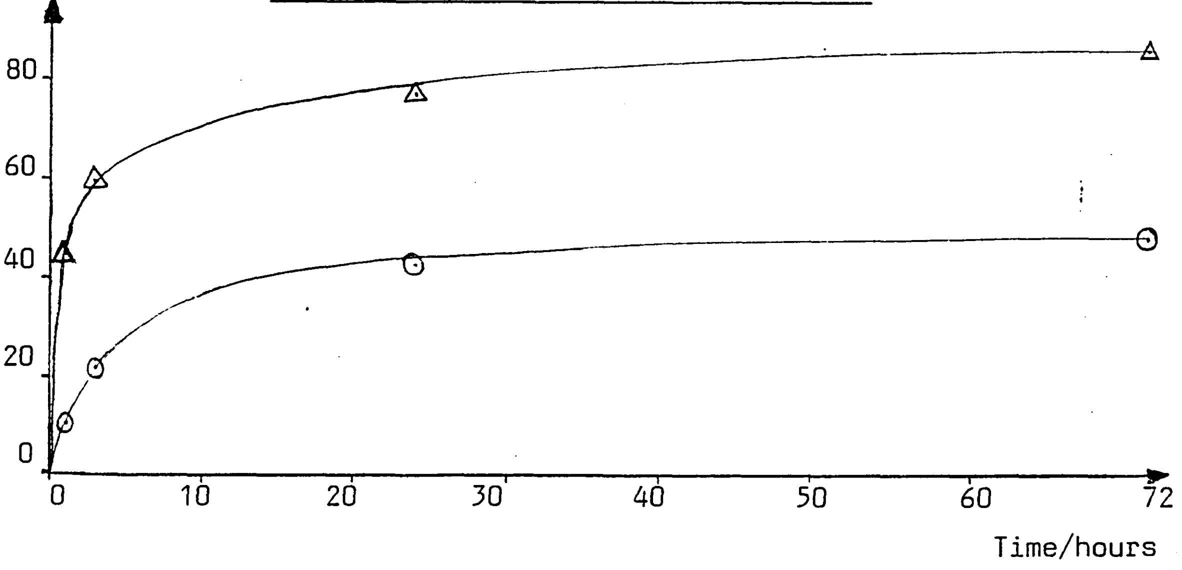


Figure 4.4 Blidworth High Hazles

TABLE 4.4

Loss of chlorine on prolonged heating (air-dried basis)

Thoresby coal	Particle size/ μm	Original chlorine content % m/m	Heating period/ days	Chlorine remaining after heating % m/m	Chlorine lost %
Top Hard	< 212	0.80	4	0.12	85
" "	< 212	0.80	16	0.10	87
" "	< 45	0.80	16	0.07	92
High Hazles	< 212	0.93	4	0.16	83
" "	< 212	0.93	16	0.12	87
" "	< 45	0.93	16	0.08	91

In addition, the range of samples heated at 205°C was increased to include coals of different ranks and origins and low chlorine contents. The results are given in Table 4.5 and clearly show that the loss of chlorine is independent of the coal's origin or the amount of chlorine it contains. The higher percentage loss at the smaller particle size (over 90 percent) is perhaps an indication that physical limitation may be a retarding factor at larger particle sizes.

4.4.3 Calorific value loss associated with loss of chlorine after heat treatment

Any attempt to exploit the lability of the chlorine atom to reduce the chlorine content of coal by thermal treatment (e.g preheating of pulverised fuel in a counter current flow of power station flue gas) would be accompanied by some reduction in calorific value, depending on the oxygen content of the treatment medium. In order to estimate the losses incurred, static samples of coal were heated in air, nitrogen and a simulated flue gas for different periods.

Two sets of experiments were carried out on the two Thoresby coal samples, of which the basic analysis is given in Table 4.6.

(i) Heating in a tube-furnace

In the first set, 500 mg samples of $< 212\ \mu m$ coal were heated individually at 210 ± 5°C in a tube furnace with air or a simulated flue gas for one hour or with nitrogen for three hours, at gas flow rates of 500 $cm^3\ min^{-1}$. The effluent gases were passed through neutralised hydrogen peroxide and the chlorine and sulphur contents determined.[149] The residual coal was transferred quantitatively to a 15 mm diameter capsule and the calorific value determined.[149]

The results are given in Table 4.7.

TABLE 4.5

Analysis of coal samples ($< 212\ \mu m$) before and after heating in an air-oven for 16 days @ 205 ± $5^{o}C$ (air-dried basis)

Colliery - Seam	Original Chlorine Content % m/m	Chlorine Remaining after heating % m/m	Average chlorine lost %
Florence - Rowhurst	0.99	0.15 0.16	84
Cortonwood - Silkstone	0.11	0.02 < 0.02	82
South Durham - 'C' Seam	0.25	0.03 0.05	84
Cadley Hill - (Bright Coal)	0.45	0.05 0.05	89
Cadley Hill - (Dull coal)	0.39	0.03 0.05	90
Tilmanstone - Milyard	0.13	0.02 < 0.02	85
Thoresby - Top Hard	0.89	0.14 0.14	84
Thoresby - Top Hard Resample	0.84	0.12 0.14	85
Thoresby - High Hazles	1.02	0.13 0.11	88
Lea Hall - Shallow	0.97	0.17 0.17	82

TABLE 4.6

Analysis of Thoresby coals (air-dried basis)

Thoresby Coal	Sulphur % m/m	Chlorine % m/m	Moisture % m/m	Ash % m/m	Calorific Value kJ/kg	Calorific Value (DAF basis) kJ/kg
Top Hard	0.95	0.77	5.9	4.4	30010	34120
High Hazles	1.12	0.83	6.9	8.4	28290	33400

TABLE 4.7

Loss of chlorine and calorific value in a tube furnace at 210 ± 5^{o}C (air-dried basis)

Thoresby Coal	Gas used	Time of heating hours	Effluent Analysis		Residual Coal Analysis		CV loss %	Chlorine loss %
			Sulphur % m/m	Chlorine % m/m	Calorific Value kJ/kg	Calorific Value (DAF) kJ/kg		
Top Hard	Air	1	0.02	0.18	26350	29380	13.9	24
High Hazles	Air	1	0.03	0.17	25190	29740	11.0	20
Top Hard	Nitrogen	3	0.02	0.15	30220	33690	1.2	19
High Hazles	Nitrogen	3	< 0.02	0.12	28340	33460	< 1.0	15
Top Hard	Simulated Flue Gas	1	< 0.02	0.16	29100	32440	4.9	21
High Hazles	Simulated Flue Gas	1	0.05	0.15	27380	32330	3.2	18

(ii) Heating in an air-oven

In the second set, 10 g samples of each coal were heated in an air-oven at 210 ± $5^{o}C$ for 1 hour. The coals were then allowed to equilibrate with the laboratory atmosphere, and moisture, ash, sulphur, chlorine and calorific value determined. The results are shown in Table 4.8.

The results for both coals show an insignificant loss of calorific value on heating in the tube furnace in nitrogen for 3 hours, with an approximate chlorine loss of 17 percent. In air, both in the tube furnace and in the oven, the loss in calorific value is approximately ten percent. Using a simulated flue gas of composition by volume of 12% CO_2, 7% O_2 and 81% N_2, the calorific loss was found to be less than 5 percent. The corresponding chlorine loss was 21 percent for the Top Hard and 18 percent for the High Hazles coals respectively. The experimental conditions, however, are far removed from those which would occur in power-station practice, where mixing would be more intimate and contact time much less.

Laboratory scale tests on a dynamic chlorine release process could be undertaken to study these effects, but before the principle is seriously advanced, methods for separating the hydrogen chloride-laden flue gas from the fuel and dealing with its corrosive properties must be proposed and assessed.

4.4.4 Identification of effluent gases from the low temperature heating of coal

If indeed sodium chloride crystallites are present in coal their disappearance on heating must be explained by occlusion in a more volatile decomposition product, or by chemical reaction to produce a more volatile chlorine compound e.g

$$NaCl + NH_4NO_3 \rightleftharpoons NH_4Cl \uparrow + NaNO_3$$

These two possibilities are considered below.

TABLE 4.8

Loss of chlorine and calorific value in an air-oven at 210 ± $5^{o}C$ (air-dried basis)

Thoresby Coal	Sulphur % m/m	Chlorine % m/m	Moisture % m/m	Ash % m/m	Calorific Value kJ/kg	Calorific Value (DAF) kJ/kg	CV loss %	Chlorine loss %
Top Hard	0.88	0.56	6.3	4.2	27300	30500	10.6	27
High Hazles	1.04	0.58	7.2	8.1	25560	30180	9.7	28

4.4.4.1 Effluent from coal heated in air at 210 ± 5°C

The results of analysing the effluent gases from four coals in a current of air at 210 ± 5°C for 3 hours are given in Table 4.9. The figures show that substantial amounts of chlorine were found in the neutralised hydrogen peroxide through which the effluent gases had been passed. Neither sodium nor potassium could be detected in this solution. It follows that the chlorine was not lost from coal on heating as sub-micron size particles of sodium or potassium chloride.

The probability that the chlorine was evolved as hydrogen chloride gas was supported by qualitative tests made with gas detector tubes on the atmosphere inside an air-oven where about 15 g of Thoresby High Hazles coal were spread out on a 20 cm diameter watch glass and heated at 210 ± 5°C for 15 minutes. Hydrogen chloride was detected at 25 ppm while chlorine and chlorine dioxide were undetectable (minimum detectable concentration 0.2 ppm).

4.4.4.2 Formation of a volatile chlorine-nitrogen compound

The hypothesis that the ammonium ion or nitrogen[121,122], was involved in the loss of chlorine from coal on low temperature heating was tested. The coal samples were treated in two ways: heating in an air oven for 96 hours at 210 ± 5°C, and plasma-ashing at below 150°C. The residues and the original coals were analysed for total nitrogen by the standard method[149] involving sulphuric acid digestion in the presence of a catalyst and steam distillation of ammonia.

The results are given in Table 4.10.

There is no appreciable loss of nitrogen to account for the known loss of chlorine at 210 ± 5°C. Nitrogen could not be detected in the plasma ash and evidently fixation to nitrate does not occur with these samples under the conditions employed.

TABLE 4.9

Analysis of the effluent from coals heated in air at 210 ± $5^{o}C$ for three hours

Coal	Analysis of absorbing solution for effluent gases as % m/m (air-dried basis)			
	Sulphur	Chlorine	Sodium	Potassium
Thoresby Top Hard	0.11	0.39	< 0.01	< 0.01
Thoresby High Hazles	0.02	0.48	< 0.01	< 0.01
Lea Hall Shallow	0.15	0.48	< 0.01	< 0.01
Hem Heath Yard/Ragman	0.14	0.37	< 0.01	< 0.01

TABLE 4.10

Loss of nitrogen on heating coal in air at 210 ± $5^{o}C$ and on plasma ashing

Coal	Nitrogen % m/m (air-dried basis)		
	In coal	In residue after 96 hours at 210 ± $5^{o}C$ (air-oven)	In plasma ash
Thoresby Top Hard	1.58	1.54	< 0.02
Thoresby High Hazles	1.68	1.64	< 0.02
Lea Hall Shallow	1.24	1.24	< 0.02
Hem Heath Yard/Ragman	1.24	1.24	< 0.02

These results do not, of course, preclude the existence of chlorine-nitrogen linkages in the coal at temperatures below 200°C, which are easily ruptured above that temperature.

4.4.4.3 Microwave plasma detection of chromatographically separated gaseous products from coal heated at 210 ± 5°C

Notwithstanding the general acceptance that nearly all the chlorine in coal is lost as hydrogen chloride on heating, a gas chromatograph with a microwave plasma detector was used to identify any traces of chlorine-containing organic decomposition products which might also be evolved.

Portions (1 g) of Thoresby Top Hard and High Hazles coals were heated separately in a tube furnace at 210 ± 5°C in an air or nitrogen flow of 100 cm^3 min^{-1}. The effluent gases were scrubbed with distilled water to remove hydrogen chloride and then passed through a short length of Tenax gas chromatographic adsorbent on which any organic compounds would be expected to be retained. A degree of concentration was ensured by passing one tenth of the gas flow through the adsorbent for a 20 minute period, and duplicate collections were made. Any adsorbed gases were then thermally desorbed on to a 50 m length of squalane-coated capillary column with a helium carrier as the column temperature was raised from 25 to 105°C at 4°C min^{-1}. Detector response to carbon and chlorine in the column effluent was recorded.

The same nine peaks occur in the chlorine chromatograms for each coal heated in air. Five were tentatively identified as follows:

Dichloromethane
Chloropropane
Trichloromethane
1-Chlorobutane
Chlorobenzene

Fewer peaks were observed when the coals were heated in nitrogen. High Hazles coal gave larger peaks than Top Hard, but no estimate of concentration has been attempted, nor is it possible to say whether these compounds originate as fragments of the coal structure or were formed by reaction between the coal and the hydrogen chloride evolved during heating. The latter has been shown to be unlikely by passing a standard mixture of hydrocarbons in air through the system in the presence of a flow of 200 ppm hydrogen chloride in air: no evidence of chlorination was observed.

No evidence has been found so far to disprove the labile nature of the chlorine-coal bond on heating nor its lack of bonding association with the cations present in coal.

4.4.5 Loss of chlorine on low-temperature plasma ashing

Further proof of the absence of alkali chloride in coal is given by the ease with which chlorine is released by ashing in an oxygen plasma. Using the Plasmaprep 100 equipment, 16 coals (< 212 µm) were dried in nitrogen[149] and exposed in 1-2 g amounts, spread evenly on 9 cm diameter petri-dishes, to an atmosphere of radio-frequency excited oxygen. The instrument was set at 20 watts forward power, such that the reflected power was a minimum and the temperature of the sample did not exceed 150°C. Samples were ashed to constant weight for up to 60 hours and then analysed for chlorine using BS procedures.[149]

The effect of plasma ashing on the chlorine content of the samples is given in Table 4.11. The average loss of chlorine ranged from 90-100 percent and therefore virtually all the chlorine present in these samples can be considered volatile under these conditions.

4.4.6 Determination of 'Organic' chlorine in coal

This method[151,152] differentiates between inorganic chlorine (as in crystalline sodium chloride) and organic chlorine (as in trichlorophenol). It has been applied to the two Thoresby coal samples.

TABLE 4.11

Chlorine loss from plasma ashed coal samples ($<$ 212 μm air-dried basis)

Colliery - Seam	Original chlorine content % m/m	Plasma ash % m/m	Average chlorine in plasma ash % m/m	Average chlorine in plasma ash (air-dried coal basis) % m/m	Average loss of chlorine %
Florence - Rowhurst	0.99	9.2	0.26	0.02	98
Cortonwood - Silkstone	0.11	8.9	0.12	< 0.02	90
South Durham - 'C' Seam	0.25	3.2	0.39	< 0.02	95
Cadley Hill - (Bright Coal)	0.45	8.8	0.35	0.03	93
Cadley Hill - (Dull Coal)	0.39	7.3	0.20	< 0.02	96
Tilmanstone - Milyard	0.13	5.9	< 0.26	< 0.02	~100
Thoresby - Top Hard	0.89	16.2	0.38	0.06	93
Thoresby - Top Hard Resample	0.84	6.6	< 0.21	< 0.02	~100
Thoresby - High Hazles	1.02	7.9	0.48	0.04	96
Lea Hall - Shallow	0.97	3.5	0.40	< 0.02	99
Lea Hall - Yard	0.53	36.8	< 0.06	< 0.02	~100
Lea Hall - Deep	0.69	15.9	0.13	0.02	97
Littleton- Shallow	0.45	14.4	< 0.14	< 0.02	~100
Littleton - Park	0.72	21.9	0.11	0.02	97
Hem Heath - Yard/Ragman	0.48	31.7	0.05	0.02	97
Hem Heath - Winghay	0.60	42.5	0.07	0.03	95

The principle involved is the release of chlorine compounds by thermal decomposition in a hydrogen/ammonia atmosphere, followed by total conversion to hydrogen chloride in the presence of a nickel catalyst and fixation as ammonium chloride. The ammonium chloride deposited on the walls of the quartz reaction tube is dissolved in water and titrated using the Volhard technique.[153] The results are given in Table 4.12.

The results of the calibration tests show that the procedure is capable of differentiating between organic (trichlorophenol) and inorganic chlorine (sodium chloride), and to be virtually unaffected by the presence of pyrites.

In both coal samples almost all the chlorine present was evolved and detected as ammonium chloride. Omission of the nickel catalyst produced no reduction in the recovery of chlorine from coal, but with trichlorophenol about a one-third reduction in chlorine recovered was observed. A similar result was apparent using argon/ammonia carrier gas instead of hydrogen/ammonia. Thus although about 70 percent of the chlorine in trichlorophenol is released as hydrogen chloride on heating the remainder requires reduction by the catalyst, whereas almost all the chlorine in coal is evolved as hydrogen chloride. This conclusion agrees with the findings of Iapalucci et al,[154] who condensed and analysed the flue gases from a laboratory scale pulverised fuel combustor. These findings are consistent with chlorine in coal being present as an organic species or volatile ionic compound yielding hydrogen chloride on heating.[121,122,155]

4.4.7 Behaviour of coal with added sodium chloride on heating and plasma ashing

This section discusses the effect of low temperature heating and plasma ashing upon sodium chloride added as a control to coal, in the form of a solid or in solution.

To 1 g samples of each of 4 coals ($< 212\ \mu m$) in porcelain crucibles were added known amounts of solid sodium chloride ($< 45\ \mu m$) or sodium chloride solution. These, together with samples of the unadulterated coal, were heated in an air oven at 210 ± 5^{o}C for 96 hours and the residual chlorine contents of the whole sample determined by the Eschka method.[149]

TABLE 4.12

Determination of 'Organic' chlorine in coal

Results of calibration with Trichlorophenol (TCP)

Carrier gas	Wt of TCP/g	Wt of NaCl Added/g	Wt of Pyrites added/g	Percentage Cl in TCP determined (theoretical 53.9% m/m)
Using Nickel Catalyst				
1. Hydrogen	0.1036	-	-	53.3
2. Hydrogen	0.1001	0.0870	-	53.3
3. Hydrogen	0.0553	0.0510	0.1053	52.4
Without Nickel Catalyst				
1. Hydrogen	0.1010	-	-	38.6
2. Hydrogen	0.1004	-	-	37.2
3. Argon	0.1006	-	-	40.4

Results with Coal
(0.5 g air-dried coal (< 63 μm) was used for each test)

Thoresby coal sample	Total Cl % m/m	Carrier Gas	'Organic' chlorine % m/m	Chlorine in residue % m/m	'Organic' chlorine as percent of total
Using Nickel Catalyst					
1. Top Hard	0.75	Hydrogen	0.72	0.03	96
2. Top Hard	0.75	Hydrogen	0.70	0.04	93
3. High Hazles	0.91	Hydrogen	0.89	0.03	98
4. High Hazles	0.91	Hydrogen	0.87	0.03	96
Without Nickel Catalyst					
1. Top Hard	0.75	Hydrogen	0.72	0.02	96
2. Top Hard	0.75	Argon	0.75	< 0.02	100
3. High Hazles	0.91	Hydrogen	0.90	0.03	99
4. High Hazles	0.91	Argon	0.90	0.02	99

The results are given in Table 4.13.

Assuming that the loss of original chlorine from each coal is independent of the admixture there is no indication that any significant proportion of the added chlorine has been expelled under the conditions of the experiment.

After drying in a nitrogen atmosphere at 105°C further portions of the 4 samples were subjected to activated oxygen decarbonisation using the low temperature plasma ashing equipment at a temperature below 150°C for 48 hours.

The results are given in Table 4.14.

Again, there is no indication that any significant loss of added chlorine has occurred.

The possibility remains that some of the sodium chloride could become reactive on heating or plasma ashing if it penetrated the micro-pores of coal by impregnation. This suggestion is considered further by the tests described later in section 4.5.5 of this chapter.

4.5 CHEMICAL TREATMENT

This section describes the removal of chlorine from coal and associated strata by aqueous leaching and its likely association with other soluble cations. The possibility of an anion-exchange reaction of chlorine in coal is also investigated. A comparison of the reactions of coal with polar and non-polar solvents is given. The treatment of coal with perklone and sodamide in xylene is discussed.

The method of vacuum impregnation of coal with sodium chloride described, has been used to indicate the nature of the chlorine-coal bond. Chemical methods of fixing the evolved hydrogen chloride produced on heating coal have also been assessed.

Finally, the section evaluates an X-ray radiographic technique to assess coal porosity.

TABLE 4.13

Loss of chlorine from coals with added sodium chloride on heating at 210 ± 5^{o}C (air-dried basis)

	Thoresby Top Hard			Thoresby High Hazles		
	No Addition	Solid Addition	Liquid Addition	No Addition	Solid Addition	Liquid Addition
Chlorine in original coal % m/m	0.80	0.80	0.80	0.93	0.93	0.93
Chlorine added % m/m	-	0.85	0.85	-	0.86	0.85
Total chlorine in mixture % m/m	0.80	1.65	1.65	0.93	1.79	1.78
Total chlorine in residue after heating at 210^{o}C % m/m	0.12	0.97	0.95	0.16	0.98	1.01
Net chlorine loss % m/m	0.68	0.68	0.70	0.77	0.81	0.77
Loss of added chlorine %	-	nil	0.02	-	0.04	nil

	Lea Hall Shallow			Hem Heath Yard/Ragman		
	No Addition	Solid Addition	Liquid Addition	No Addition	Solid Addition	Liquid Addition
Chlorine in original coal % m/m	0.74	0.74	0.74	0.49	0.49	0.49
Chlorine added % m/m	-	0.82	0.91	-	0.72	0.75
Total chlorine in mixture % m/m	0.74	1.56	1.65	0.49	1.21	1.24
Total chlorine in residue after heating at 205^{o}C % m/m	0.14	0.92	1.07	0.16	0.85	0.91
Net chlorine loss % m/m	0.60	0.64	0.58	0.33	0.36	0.33
Loss of added chlorine %	-	0.04	(-0.02)	-	0.03	nil

TABLE 4.14

Loss of chlorine on plasma-ashing coal with added sodium chloride (air-dried basis)

	Thoresby Top Hard			Thoresby High Hazles		
	No Addition	Solid Addition	Liquid Addition	No Addition	Solid Addition	Liquid Addition
Chlorine in original coal % m/m	0.80	0.80	0.80	0.93	0.93	0.93
Chlorine added % m/m	-	0.87	0.85	-	0.87	0.85
Total chlorine in mixture % m/m	0.80	1.67	1.65	0.93	1.80	1.78
Total chlorine in plasma ash % m/m	0.03	0.87	0.85	0.03	0.86	0.85
Net chlorine loss % m/m	0.77	0.80	0.80	0.90	0.94	0.93
Loss of added chlorine %	-	0.03	0.03	-	0.04	0.03

	Lea Hall Shallow			Hem Heath Yard/Ragman		
	No Addition	Solid Addition	Liquid Addition	No Addition	Solid Addition	Liquid Addition
Chlorine in original coal % m/m	0.74	0.74	0.74	0.49	0.49	0.49
Chlorine added % m/m	-	0.81	0.91	-	0.74	0.77
Total chlorine in mixture % m/m	0.74	1.55	1.65	0.49	1.23	1.26
Total chlorine in plasma ash % m/m	< 0.02	0.80	0.89	< 0.02	0.72	0.79
Net chlorine loss % m/m	0.74	0.75	0.76	0.49	0.51	0.47
Loss of added chlorine %	-	0.01	0.02	-	0.02	nil

4.5.1 Aqueous leaching experiments

These have been designed to classify the ease with which chlorine can be leached from coal and also its possible relationship with water soluble sodium or other cations.

4.5.1.1 Standard test for the classification of the aqueous leachability of chlorine from coal

A selection of coals from the UK coalfields of the NCB were classified according to the ease with which chlorine could be removed by leaching. The method developed involved placing a representative 200 g of ¼" by 1/8" fraction of coal in a stainless steel basket and suspending this in a two litre beaker, containing one litre of distilled water. The basket was shaken manually for 5 minutes and the liquid stirred using a magnetic stirrer for 24 hours. After 10, 120 and 1440 minutes 100 cm^3 of the suspension were abstracted by means of a pipette. The suspension was filtered to remove fine coal and the chloride content of the filtrate determined by Mohr's method.[153]

The results of these tests are given in Table 4.15 and displayed as a bar chart in Figure 4.5. The basic analytical data relating to the coals used is given in Appendix 4.2.

Classification using the total extraction of chlorine after 24 hours is not easy although it has been suggested that coals could be separated into two distinct types: the so called 'easy' to leach coals typified by Lea Hall Shallow and the 'difficult' to leach coals typified by Cortonwood Silkstone. Certainly a coal seam with less than twenty percent of its total chlorine extractable after 24 hours using the test could be considered as 'difficult' to leach.

The analytical reproducibility of the leaching test for nine coal samples was assessed using independent analyses from the NCB Western Area Laboratory and the Central Electricity Board's Research Establishment. The results given in Table 4.16 and displayed in the form of a bar chart in Figure 4.6 show excellent agreement.

TABLE 4.15

24 hour leaching tests on ¼" x 1/8" coal samples (air-dried basis)

Colliery/Seam	Total chlorine % m/m	Leaching time/ mins	Chlorine leached %	Water solubles % m/m				
				Cl	Na	K	Ca	Mg
Florence/Rowhurst	0.99	10	2.7	0.027	0.011	< 0.001	0.004	< 0.001
		120	5.7	0.056	0.025	0.001	0.010	0.002
		1440	9.1	0.090	0.039	0.006	0.019	0.003
Cortonwood/Silkstone	0.11	10	3.6	0.004	0.002	< 0.001	< 0.001	< 0.001
		120	6.4	0.007	0.005	< 0.001	< 0.001	< 0.001
		1440	8.7	0.010	0.008	< 0.001	< 0.001	< 0.001
South Durham/'C' Seam	0.25	10	1.4	0.004	0.003	< 0.001	< 0.001	< 0.001
		120	2.6	0.007	0.004	< 0.001	0.001	< 0.001
		1440	4.0	0.010	0.007	0.001	0.002	< 0.001
Cadley Hill (Bright Coal)	0.45	10	3.1	0.014	0.010	< 0.001	0.003	0.001
		120	9.8	0.044	0.029	0.001	0.008	0.003
		1440	23.4	0.106	0.065	0.001	0.019	0.009
Cadley Hill (Dull Coal)	0.39	10	4.6	0.018	0.012	<0.001	0.002	< 0.001
		120	13.3	0.052	0.033	0.001	0.004	0.002
		1440	25.2	0.098	0.062	0.001	0.009	0.004
Tilmanstone/Milyard	0.13	10	21.5	0.028	0.014	< 0.001	0.004	< 0.001
		120	33.1	0.043	0.021	< 0.001	0.009	0.001
		1440	33.5	0.047	0.021	< 0.001	0.013	0.001
Lea Hall/Shallow	0.97	10	5.7	0.056	0.027	0.001	0.005	<0.001
		120	16.3	0.158	0.078	0.002	0.013	<0.001
		1440	35.2	0.343	0.164	0.003	0.026	0.004
Babbington/Blackshale	0.45	10	5.6	0.025	0.015	<0.001	0.003	<0.001
		120	12.0	0.054	0.024	0.001	0.006	0.001
		1440	21.7	0.098	0.044	0.001	0.010	0.003
Babbington/Tupton	0.76	10	11.1	0.084	0.035	<0.001	0.011	0.023
		120	21.4	0.163	0.063	< 0.001	0.021	0.049
		1440	32.1	0.244	0.102	0.001	0.041	0.008
Bilsthorpe/Low Main	0.74	10	12.0	0.089	0.040	<0.001	0.010	0.002
		120	18.6	0.138	0.061	<0.001	0.018	0.004
		1440	27.7	0.205	0.086	<0.001	0.035	0.006
Bilsthorpe/Parkgate	0.70	10	8.0	0.056	0.023	<0.001	0.005	0.001
		120	16.6	0.116	0.106	<0.001	0.013	0.003
		1440	35.9	0.251	0.240	0.001	0.036	0.006
Thoresby/Top Hard[a]	0.80	10	2.9	0.023	0.010	< 0.001	0.002	0.001
		120	6.3	0.051	0.023	< 0.001	0.006	0.001
		1440	18.8	0.151	0.071	0.001	0.019	0.005
Thoresby/Top Hard[b] *	0.89	10	10.0	0.089	0.046	0.001	0.009	0.002
		120	22.8	0.203	0.110	0.002	0.027	0.005
		1440	42.5	0.379	0.178	0.004	0.044	0.008
Thoresby/Top Hard[b] (Resampled)	0.84	10	14.6	0.123	0.056	0.001	0.016	0.003
		120	31.1	0.261	0.110	0.002	0.034	0.006
		1440	48.6	0.408	0.172	0.003	0.063	0.010
Thoresby/High Hazles[a]	0.93	10	6.5	0.060	0.030	< 0.001	0.009	0.002
		120	16.1	0.150	0.075	0.001	0.020	0.005
		1440	36.1	0.336	0.173	0.001	0.048	0.008
Thoresby/High Hazles[b]	1.02	10	7.4	0.075	0.037	0.002	0.009	0.002
		120	21.6	0.220	0.104	0.004	0.027	0.005
		1440	44.6	0.455	0.208	0.009	0.062	0.010
Thoresby/Parkgate	0.73	10	9.5	0.069	0.029	<0.001	0.006	0.001
		120	18.5	0.135	0.062	0.001	0.015	0.003
		1440	31.3	0.229	0.107	0.001	0.033	0.005

* Sample suspected to be contaminated with Dust Suppression water

[a] Sampled in July 1980

[b] Sampled in June 1982

NB Water soluble iron was less than 0.1 mgl^{-1} in all the samples

Figure 4.5 Chlorine leachability with time for selected coals

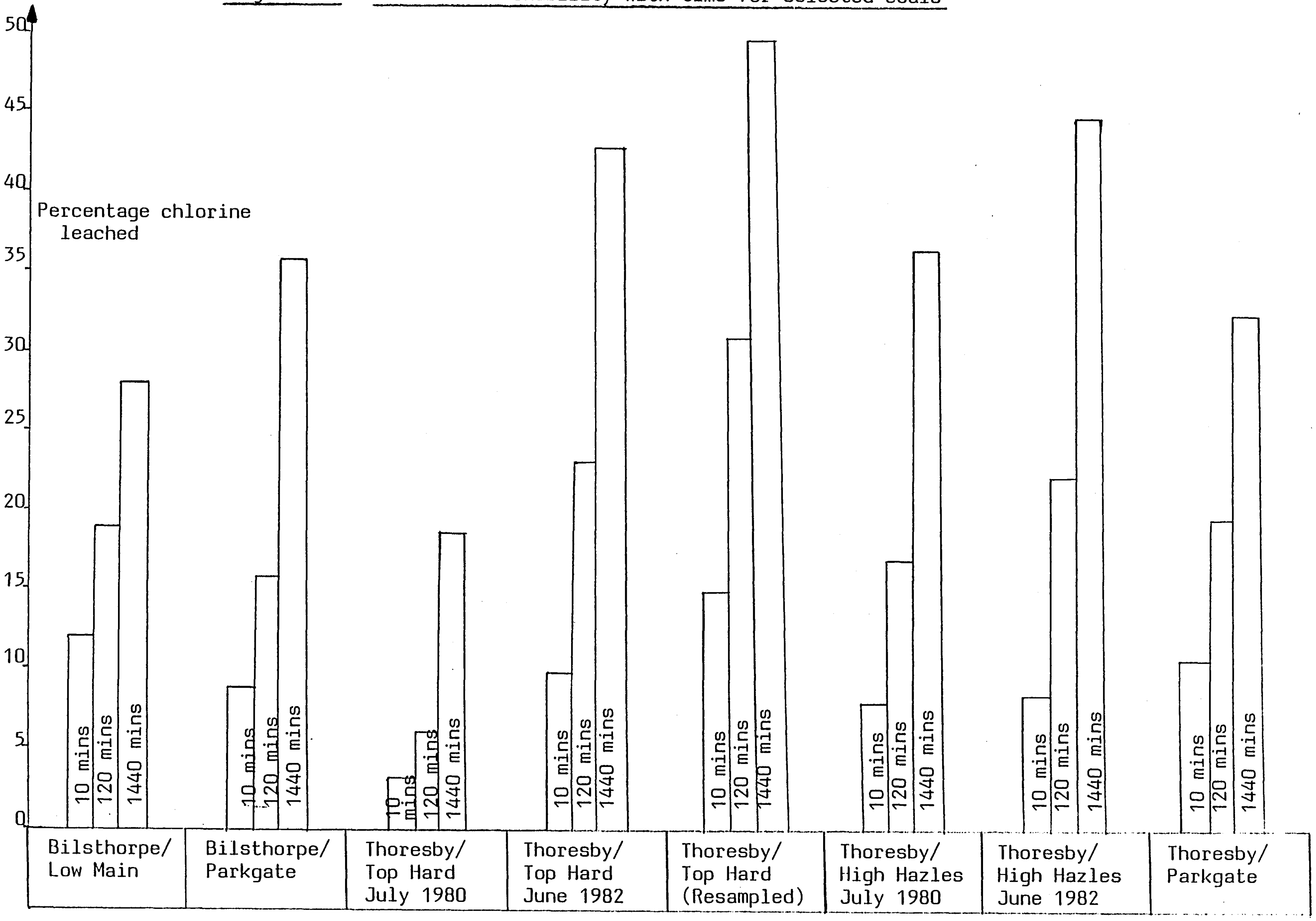


Figure 4.5 Chlorine leachability with time for selected coals (continued)

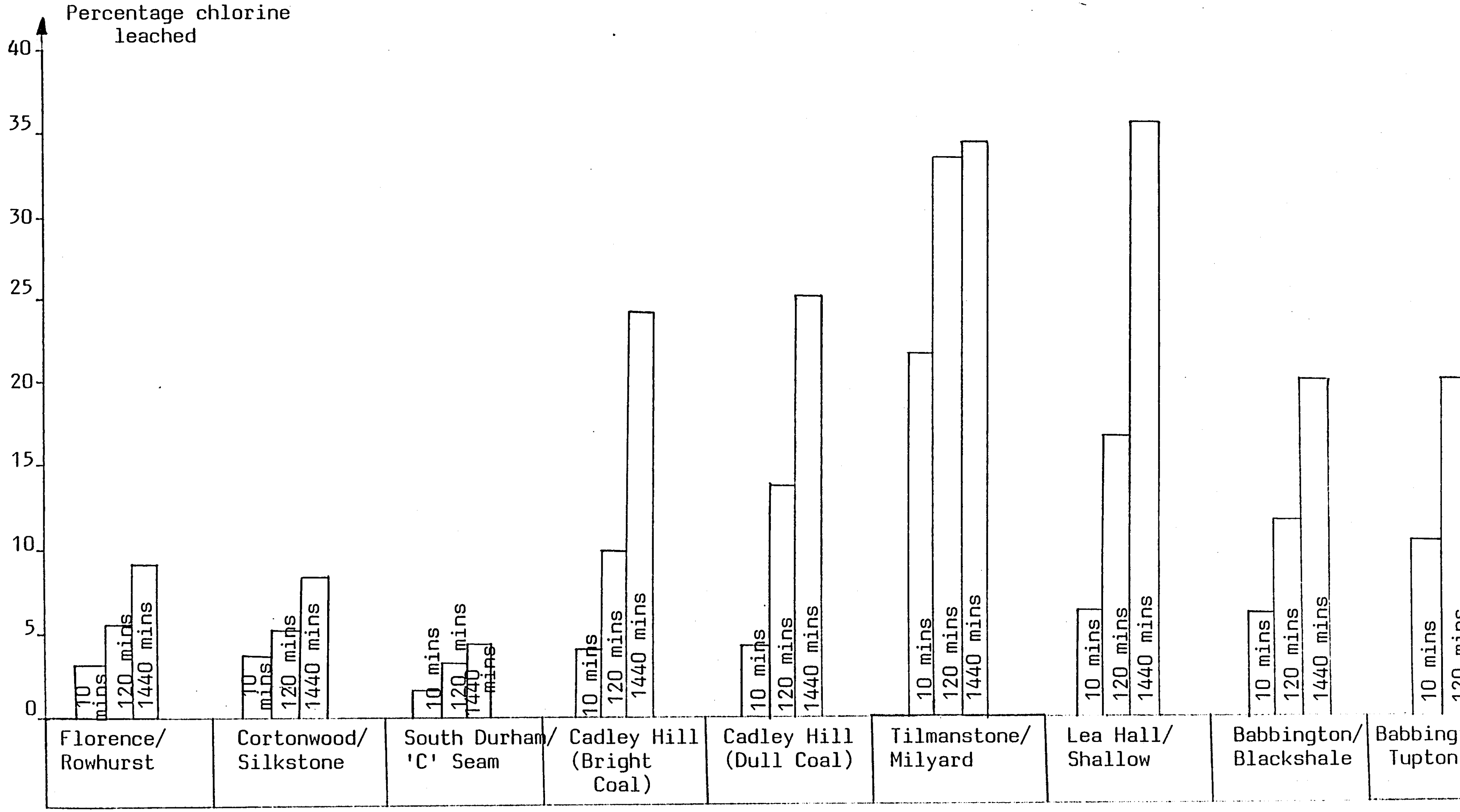


TABLE 4.16

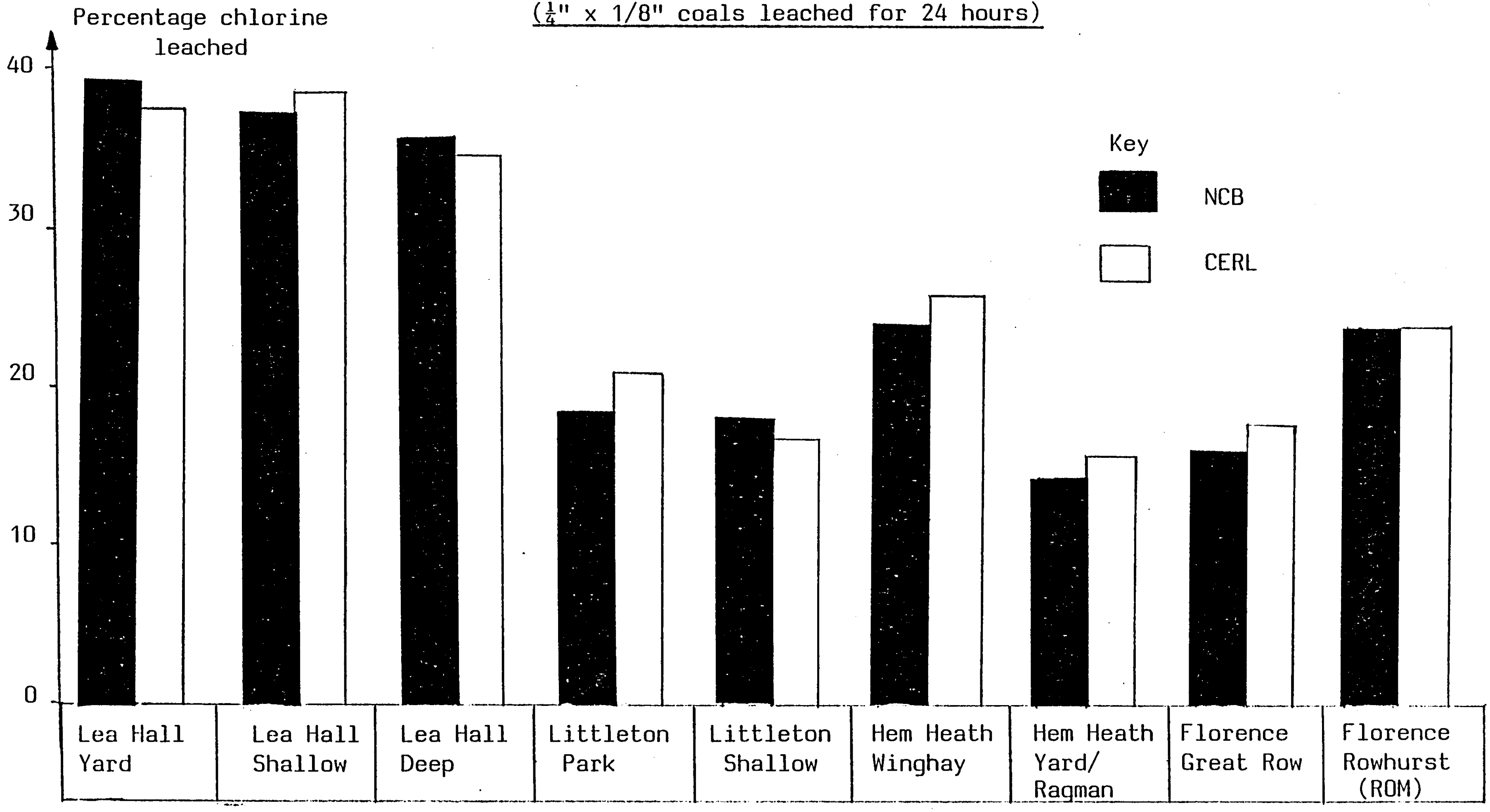
Comparison of leachability of selected Western Area coals performed by NCB and CERL

24 hour leaching tests (¼"-1/8" coals)
(CERL total chlorine figures given in brackets)

Colliery	Seam	Total chlorine % m/m	Leach time/ mins	Percentage chlorine leached		NCB water solubles/mg 1-1 (in leachate)				
				NCB	CERL	Cl	Na	K	Ca	Mg
Lea Hall	Yard	0.53	10	9.4	9.9	100	75.5	7.5	3.9	0.7
		(0.52)	120	19.8	22.3	233	162.8	13.3	3.3	0.9
			1440	39.2	37.5	502	296.0	22.0	10.7	2.5
	Shallow	0.61	10	6.5	6.4	80	43.3	4.2	8.6	1.0
		(0.66)	120	18.4	18.1	249	135.0	9.1	25.0	3.2
			1440	37.4	38.9	571	296.0	17.4	71.4	9.2
	Deep	0.69	10	7.5	8.2	103	51.1	4.2	12.0	1.7
		(0.73)	120	19.8	21.3	304	148.0	9.1	35.7	5.2
			1440	35.6	34.8	613	310.8	13.7	72.2	10.8
Littleton	Park	0.72	10	6.1	6.8	88	53.3	5.8	3.5	0.9
		(0.74)	120	12.6	11.2	201	118.4	10.0	5.8	1.5
			1440	18.4	21.0	331	196.1	14.9	19.4	4.5
	Shallow	0.45	10	3.0	3.1	27	18.5	2.5	5.6	0.3
		(0.48)	120	8.5	7.8	79	51.8	5.0	9.9	0.7
			1440	17.9	17.0	201	118.4	10.0	34.7	2.2
Hem Heath	Winghay	0.60	10	16.1	16.6	193	140.6	8.3	9.3	1.2
		(0.58)	120	22.3	23.4	297	229.4	12.0	7.1	1.2
			1440	23.9	26.0	356	296.0	16.2	9.1	1.2
	Yard/Ragman	0.48	10	7.5	8.0	72	46.6	5.0	2.5	0.5
			120	12.8	14.4	137	92.5	7.5	0.8	0.2
			1440	14.5	15.8	174	133.2	7.5	0.7	0.2
Florence	Great Row	0.57	10	11.2	10.4	127	96.2	6.2	4.4	0.6
		(0.54)	120	15.3	15.5	193	155.4	9.1	1.3	0.2
			1440	15.4	17.5	219	192.4	10.8	1.5	0.4
	Rowhurst (ROM)	0.46	10	17.1	15.1	157	111.0	6.2	0.4	0.1
		(0.51)	120	21.2	20.8	228	151.7	7.5	0.5	0.1
			1440	22.0	22.0	253	185.0	9.1	0.4	0.1

N B Water soluble iron was less than 0.1 mg 1^{-1} in all the samples

Figure 4.6 Comparison of the leachability of selected Western Area coals performed by NCB and CERL.
($\frac{1}{4}$" x 1/8" coals leached for 24 hours)



At the same time it seemed prudent to examine seam consistency. Therefore, three seams were sampled and analysed by the standard test approximately two years after their first assessment. The results are given in Table 4.17 and displayed in the form of a bar chart in Figure 4.7.

Although good agreement is obtained for the two 'easy to leach' seams (Thoresby High Hazles and Lea Hall Shallow) the Thoresby Top Hard seam results appear anomalous. The resample taken for this seam (March 1982) confirmed that its classification had changed from 'difficult' to 'easy' to leach.

This tends to discredit any attempt to classify coal seams according to their leachability with water or to propose leaching mechanisms as suggested by Bettleheim and Hann[156] which can be generally accepted for a seam.

4.5.1.2 Sodium to chlorine ratio (SCR)

The above ratio is calculated for coal using the percentage aqueous extractions of chlorine and sodium, the ratio being given by:

$$\frac{\text{Water soluble sodium (chlorine equivalent)}}{\text{Water soluble chlorine}}$$

If chlorine were present wholly or chiefly as sodium chloride then this ratio would approach or equal unity. A number of researchers[121,157] have suggested that all chlorine can be extracted from coal with water providing the coal has been finely ground but this is contrary to the findings of Gluskoter and Rees.[142] In order to clarify the position (and estimate SCRs), about ten grammes of ten coals of various ranks and origins were ground separately for fifteen minutes in a 'shatterbox.' Using a Coulter Counter the mean particle size of these ultrafine coals was found to be approximately 10 μm.

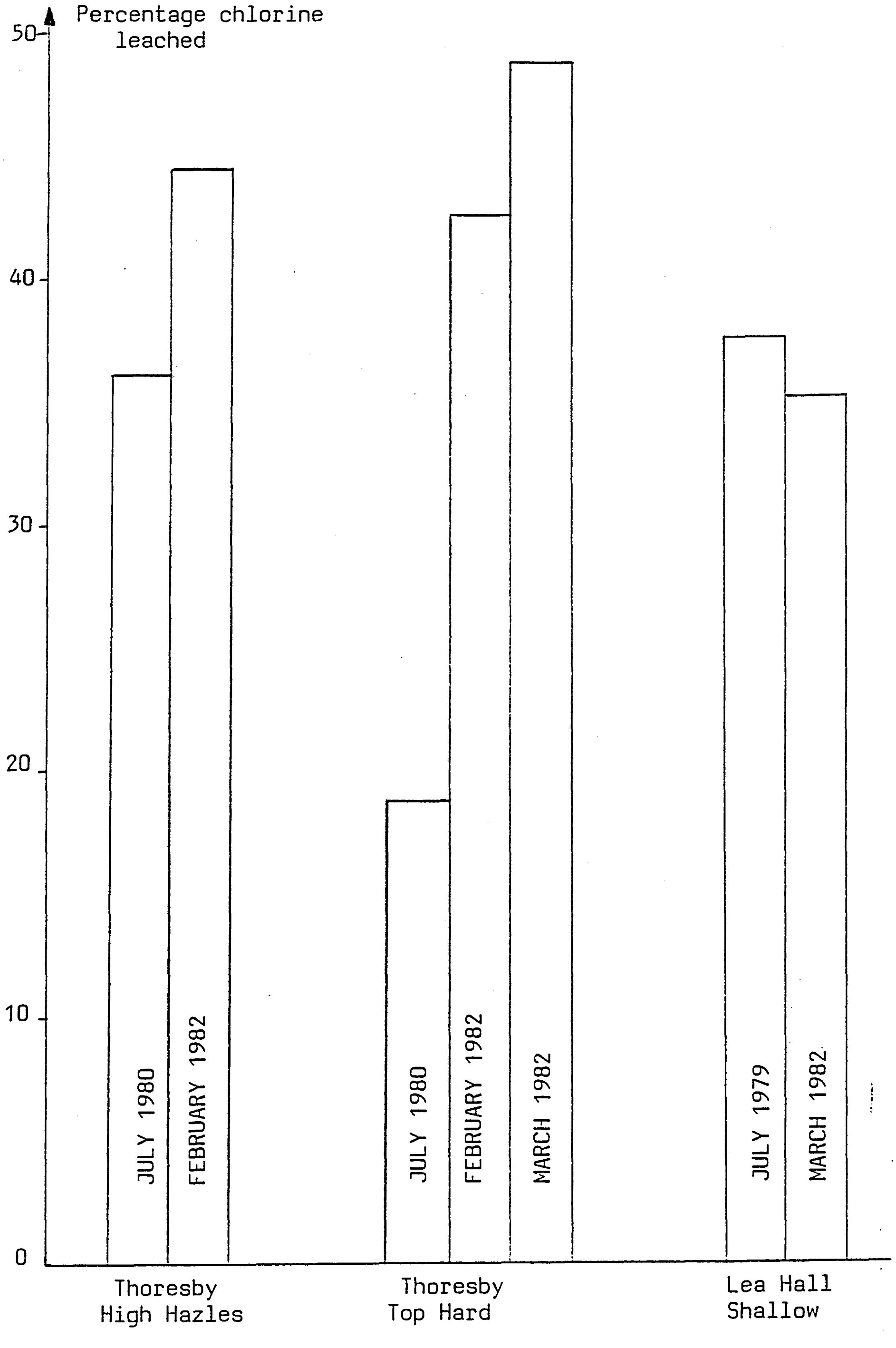
Finely ground coal (2.5g) was refluxed with deionised water (100 cm^3) for 90 minutes. The resulting suspension was cooled and filtered. The filtrate and washings were then made up to 250 cm^3 in a graduated flask.

TABLE 4.17

Comparison of leachability of ¼" x 1/8" coal samples from three seams taken at different times

Colliery	Seam	Date Sampled	Total chlorine % m/m	Chlorine leached after 24 hours %
Thoresby	High Hazles	July 1980	0.93	36.1
	High Hazles	February 1982	1.02	44.6
Thoresby	Top Hard	July 1980	0.80	18.8
	Top Hard	February 1982	0.89	42.5
	Top Hard Resample	March 1982	0.84	48.6
Lea Hall	Shallow	July 1979	0.61	37.4
	Shallow	March 1982	0.97	35.2

Figure 4.7 Comparison of leachability of ¼" x 1/8" samples from three seams taken at different times



Aliquots of this solution were taken for the determination of chloride (Mohr titration)[153] sodium, potassium, calcium and iron (atomic absorption spectrometry). The results and the calculated SCRs are given in Table 4.18.

Chlorine was quantitatively extracted from all the coal samples examined. The SCRs ranged from 0.196 to 0.559, providing further evidence that chlorine is not present in coal chiefly as sodium chloride. In addition, the soluble cations sodium, potassium, calcium and magnesium do not stoichiometrically balance the soluble chloride ions (i.e TCC ratio[‡]) except for Cadley Hill bright coal. The electroneutrality is presumably maintained by hydrogen ions (H^+). This adds support to Daybell and Pringles[122] suggestion as to the presence of chloride ion, held by ion-exchange linkages to coal. This possibility will be examined in more detail in a later section.

[‡] $$\text{TCCR} = \frac{\text{Total water soluble alkali cations (chlorine equivalent)}}{\text{water soluble chlorine}}$$

4.5.1.3 Presence of sodium chloride in fusain-enriched coal sections

It was decided to ascertain the effect of water leaching samples from the East Midlands Coalfield of fusain-enriched coals ground to $< 212\ \mu m$. Fusainous coal is very porous, powdery and water should therefore ingress its micropore structure easily. Seven coals were air-dried and their proximate composition determined[149] (Table 4.19.) Representative 20g increments of these coals were then leached with 100 cm^3 of distilled water in a stoppered 250 cm^3 conical flask. A few drops of methylated spirit were added as a wetting agent and the coals were continuously stirred using a magnetic stirrer for a 24-hour period. The samples were filtered using a Whatman 541 filter paper under vacuum and the filtrate analysed for chlorine by Mohr's method,[153] sodium and potassium by flame photometry and calcium and magnesium by atomic-absorption spectrometry. The results on an air-dried coal basis and the calculated sodium to chlorine ratios (SCR) are given in Table 4.20.

TABLE 4.18

Analysis of ultrafine coal refluxed with distilled water (air-dried basis)

Colliery/Seam	Total Chlorine % m/m	Water solubles % m/m					Chlorine = Soluble Sodium	Chlorine = Total alkali Soluble Cations	SCR[c]	TCCR[b]
		Cl	Na	K	Ca	Mg				
Florence/Rowhurst	0.99	0.99	0.126	0.124	0.396	0.048	0.194	0.728	0.196	0.735
Cortonwood/Silkstone	0.11	0.11	0.015	0.012	0.008	0.007	0.023	0.051	0.209	0.464
South Durham/'C' Seam	0.25	0.25	0.052	0.008	0.056	0.024	0.080	0.172	0.320	0.688
Cadley Hill/Bright Coal	0.45	0.45	0.141	0.013	0.150	0.057	0.217	0.445	0.482	0.989
Cadley Hill/Dull Coal	0.39	0.38	0.134	0.008	0.042	0.012	0.207	0.269	0.542	0.708
Thoresby/Top Hard[a]	0.89	0.88	0.319	0.066	0.133	0.031	0.492	0.715	0.559	0.813
Thoresby/High Hazles	1.02	1.00	0.319	0.033	0.283	0.014	0.492	0.793	0.492	0.793
Tilmanstone/Milyard	0.13	0.12	0.023	<0.001	0.058	<0.001	0.036	0.087	0.300	0.725
Thoresby/Top Hard (Resampled)	0.84	0.84	0.252	0.017	0.093	0.026	0.389	0.524	0.463	0.624
Lea Hall/Shallow	0.97	0.97	0.267	0.012	0.092	0.011	0.412	0.520	0.425	0.536

[a] Sample suspected to be contaminated with dust suppression water

[b] $$\text{TCCR} = \frac{\text{Total water soluble alkali cations (chlorine equivalent)}}{\text{Water soluble chlorine}}$$

[c] $$\text{SCR} = \frac{\text{Water soluble sodium (chlorine equivalent)}}{\text{Water soluble chlorine}}$$

TABLE 4.19

Analysis of Fusain-enriched coal samples (air-dried basis)

Sample Colliery/Seam	Moisture % m/m	Ash % m/m	Sulphur % m/m	Chlorine % m/m
Babbington/Blackshale	13.0	18.9	7.50	2.50
Calverton/Low Bright/Brinsley	7.5	8.5	0.80	2.92
High Moor/Two Foot	1.7	13.5	0.61	0.44
Linby/High Hazles	10.7	14.4	0.54	0.78
Cotgrave/Blackshale	1.9	12.4	4.15	0.67
Ollerton/Parkgate	3.4	10.0	2.15	2.56
Sherwood/Deep Hard/1st Piper	6.6	9.9	0.33	4.08

TABLE 4.20

Results of leaching fusain-enriched coal samples (< 212 μm) with water (air-dried basis)

Colliery/Seam	Total chlorine % m/m	Water solubles % m/m (air-dried basis)					Chlorine equivalent to soluble sodium % m/m	SCR[a]	Chlorine = total alkali soluble cations	TCCR[b]	Chlorine in residual coal % m/m
		Chlorine	Sodium	Potassium	Calcium	Magnesium					
Babbington/Blackshale	2.50	2.20	0.94	0.01	0.11	0.04	1.45	0.66	1.62	0.74	0.39
Calverton/Low Bright/Brinsley	2.92	2.63	1.08	0.02	0.13	0.04	1.67	0.63	1.87	0.71	0.27
High Moor/Two Foot	0.44	0.31	0.16	< 0.01	< 0.01	< 0.01	0.25	0.81	0.25	0.81	0.10
Linby/High Hazles	0.78	0.58	0.16	< 0.01	0.03	0.02	0.40	0.69	0.46	0.79	0.13
Cotgrave/Blackshale	0.67	0.53	0.27	< 0.01	0.07	0.02	0.42	0.79	0.51	0.96	0.16
Ollerton/Parkgate	2.56	2.21	1.10	0.01	0.37	0.06	1.70	0.77	2.13	0.96	0.26
Sherwood/Deep Hard/1st Piper	4.08	3.56	1.50	0.02	0.64	0.10	2.32	0.65	3.06	0.86	0.39

^{a} SCR $= \dfrac{\text{Water soluble sodium (chlorine equivalent)}}{\text{Water soluble chlorine}}$

^{b} TCCR $= \dfrac{\text{Total water soluble alkali cations (chlorine equivalent)}}{\text{Water soluble chlorine}}$

The total chlorine contents of four of the samples are very much higher than normally found in bituminous coals from the East Midlands coalfield and the SCR's range from 0.63-0.81 with a mean value of 0.71.

SEM/EDX elemental mapping described in section 4.3.1 showed the presence of sodium chloride crystallites in the samples; one such particle, approximately 30 μm in diameter is shown in Plate 4.3. Quantitative estimates of the samples using SEM/EDXA are given in Table 4.21. The results of plasma-ashing on two of the samples (Ollerton Parkgate and Sherwood Deep Hard/Piper) are given in Table 4.22. These results are indicative of the presence of sodium chloride crystallites in varying proportions in fusain-enriched coal sections.

Comparing the total chlorine contents given in Table 4.20 with those in Table 4.21 the results for Calverton Low Bright/ Brinsley and Sherwood Deep Hard/Piper seams appear odd, on the basis that the SEM/EDXA results are usually lower than chemical results when the determinant is present in more than one chemical form.[125] The SEM/EDXA figure is an average of measurements made on several different areas of the sample, and in these two cases the explanation may be that the areas examined contained chlorine predominantly in one form, i.e. sodium chloride.

4.5.1.4 Presence of sodium chloride in mudrock and sandstone roof and floor strata associated with coal measures

If the chlorine present in coal has been derived from contact with hypersaline strata water after the rank has been established, as suggested by Skipsey[140,141] then sodium chloride should be found in the strata associated with coal measures. The tests described in this section are designed to establish this presence.

To determine the total water soluble ions, twelve samples of roof and floor sandstone, siltstone and mudrock were ground to < 212 μm, air-dried and then leached with distilled water as described in the previous section. The results are given in Table 4.23. The results of plasma ashing four of these samples are given in Table 4.24.

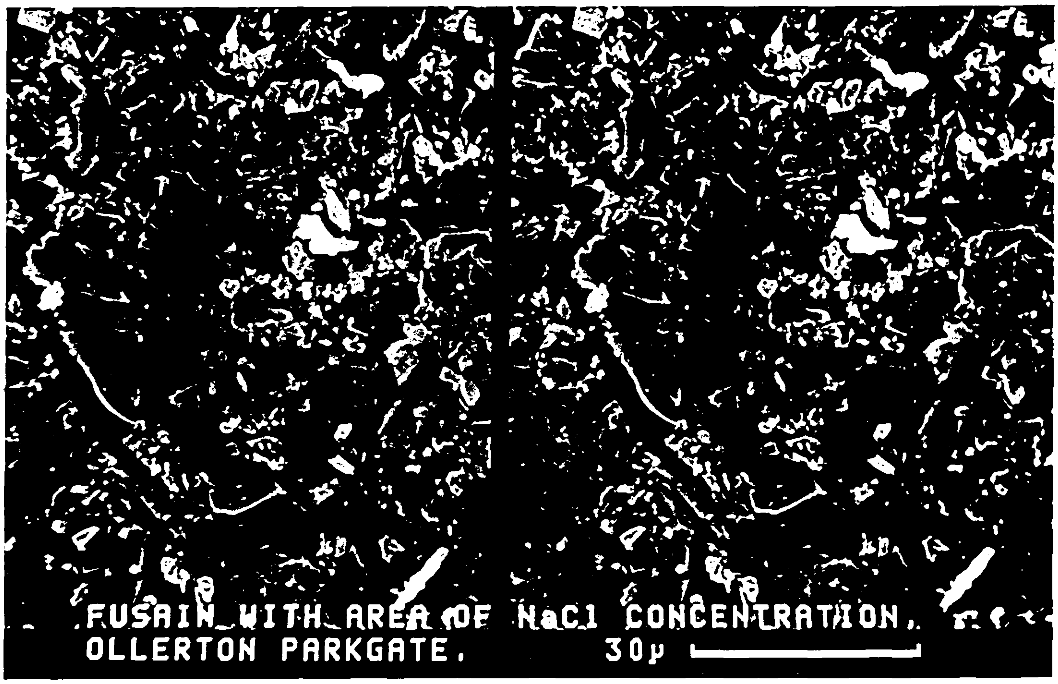


PLATE 4.3(a)
Scanning Electron Micrograph

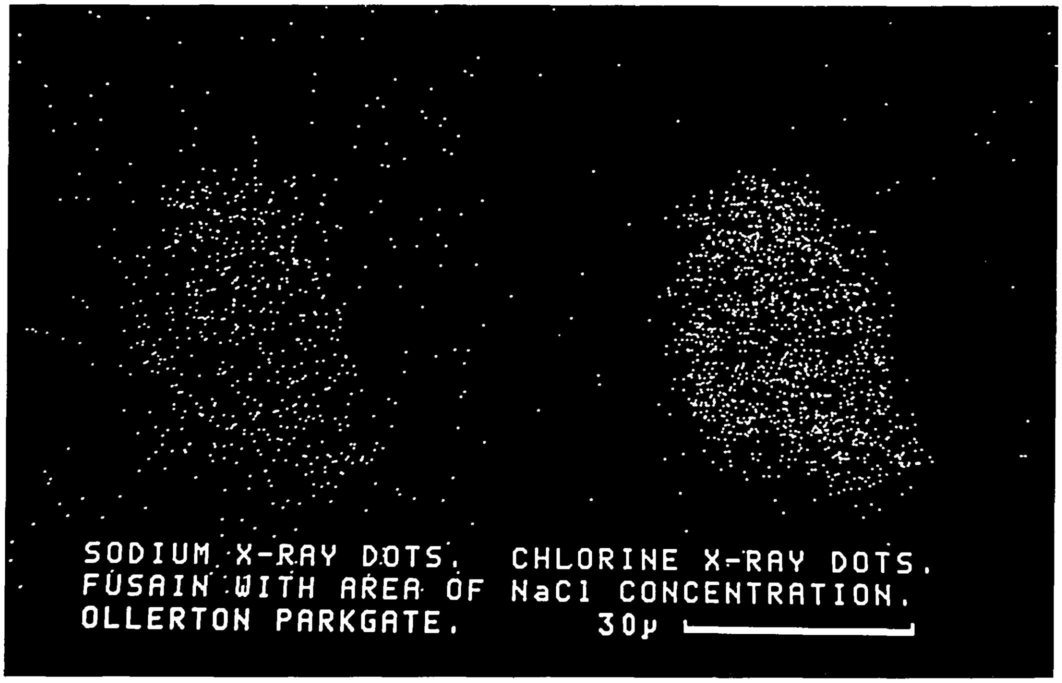


PLATE 4.3(b)
Sodium and Chlorine X-ray
Distribution of same area

TABLE 4.21

SEM/EDXA of Fusain-enriched coal samples (air-dried basis)

Colliery/Seam	Chlorine % m/m	Sodium % m/m	Potassium % m/m	Calcium % m/m	Magnesium % m/m	Iron % m/m	Silicon % m/m	Aluminium % m/m	Phosphorus % m/m	Sulphur % m/m
Babbington/Blackshale	1.73	0.31	<0.08	0.53	0.19	5.16	0.46	0.39	<0.14	4.16
Calverton/Low Bright /Brinsley	2.90	1.10	<0.08	0.67	0.12	0.97	0.81	0.77	<0.14	0.64
High Moor/Two Foot	0.40	0.17	<0.08	1.86	0.15	0.54	0.60	0.50	<0.14	0.42
Linby/High Hazles	0.59	0.17	0.15	0.46	<0.10	0.77	1.32	1.27	<0.14	0.47
Cotgrave/Blackshale	0.54	0.18	<0.08	0.45	<0.10	1.55	0.31	0.35	0.14	1.48
Ollerton/Parkgate	1.78	0.61	<0.08	0.91	0.15	1.73	0.54	0.55	0.17	1.63
Sherwood/Deep Hard/1st Piper	4.22	1.74	<0.08	1.25	0.28	0.43	0.92	0.84	<0.14	0.28

TABLE 4.22

Chlorine retained in fusain-enriched coal samples after plasma ashing for 48 hours at < 150°C (air-dried basis)

Colliery/Seam	Water soluble chlorine % m/m	Total chlorine % m/m	Percentage chlorine retained	Plasma ash % m/m
Ollerton/Parkgate	2.21	2.56	57.4	20.5
Sherwood/Deep Hard/ 1st Piper	3.56	4.08	66.2	19.7

TABLE 4.23

Results of leaching roof and floor strata (< 212 μm) associated with coal measures (air-dried basis)

Sample		Ash % m/m	Sulphur % m/m	Total chlorine % m/m	Water solubles % m/m (air-dried basis)					Chlorine equivalent to soluble sodium	SCR*	Percentage chlorine leached
Pillar section no.	Description				Chlorine	Sodium	Potassium	Calcium	Magnesium			
81471	Seatearth mudstone (floor)	70.6	0.27	0.26	0.19	0.15	0.003	0.002	< 0.001	0.23	1.21	73
81470	Seatearth siltstone fine (floor)	92.9	0.21	0.14	0.14	0.10	0.004	0.001	< 0.001	0.15	1.07	67
81133	Mudstone (roof)	85.2	0.27	0.22	0.19	0.15	0.006	0.003	0.001	0.23	1.21	86
80772	Siltstone fine(roof)	92.2	0.10	0.15	0.15	0.08	0.004	0.001	< 0.001	0.12	0.80	100
81484	Seatearth siltstone coarse (floor)	95.6	0.06	0.04	0.04	0.03	0.002	0.001	0.001	0.05	1.25	100
81273	Sandstone fine (roof)	86.4	0.32	0.46	0.49	0.28	0.014	0.060	0.013	0.43	0.88	100
83750	Sandstone	94.6	0.09	0.27	0.23	0.12	0.006	0.05	0.02	0.19	0.83	85
82210	Sandstone	95.1	0.04	0.41	0.37	0.19	0.008	0.10	0.07	0.29	0.78	90
82094	Sandstone	95.2	0.06	0.43	0.39	0.21	0.007	0.13	0.04	0.32	0.84	91
83584	Mudstone	54.9	0.50	0.45	0.32	0.18	0.012	0.28	< 0.01	0.28	0.83	71
83575	Mudstone	63.7	0.74	0.42	0.28	0.18	0.010	0.02	< 0.01	0.28	1.00	67
82999	Mudstone	58.1	0.61	0.43	0.29	0.18	0.009	0.35	0.05	0.28	0.97	67

$$* \quad \text{SCR} = \frac{\text{Water soluble sodium (chlorine equivalent)}}{\text{Water soluble chlorine}}$$

TABLE 4.24

Chlorine retained in roof and floor strata after plasma ashing for 48 hours at <150°C (air-dried basis)

Sample		Total chlorine % m/m	Retained chlorine % m/m	Chlorine retained-percentage of original	Ash % m/m	Water soluble chlorine % m/m
Pillar section no.	Description					
81273	Sandstone	0.46	0.41	89	86.4	0.49
82210	Sandstone	0.41	0.36 0.40	93	95.1	0.37
82094	Sandstone	0.43	0.38	89	95.2	0.39
83575	Mudstone	0.42	0.18 0.16	40	63.7	0.28

Extrapolation of figures from Table 4.23 plotted in Figure 4.8 shows that as the carbonaceous nature of these strata samples increases then the water extractable chlorine as a percentage of the total decreases. The calculated SCR's range from 0.78-1.25 with a mean value of 0.98.

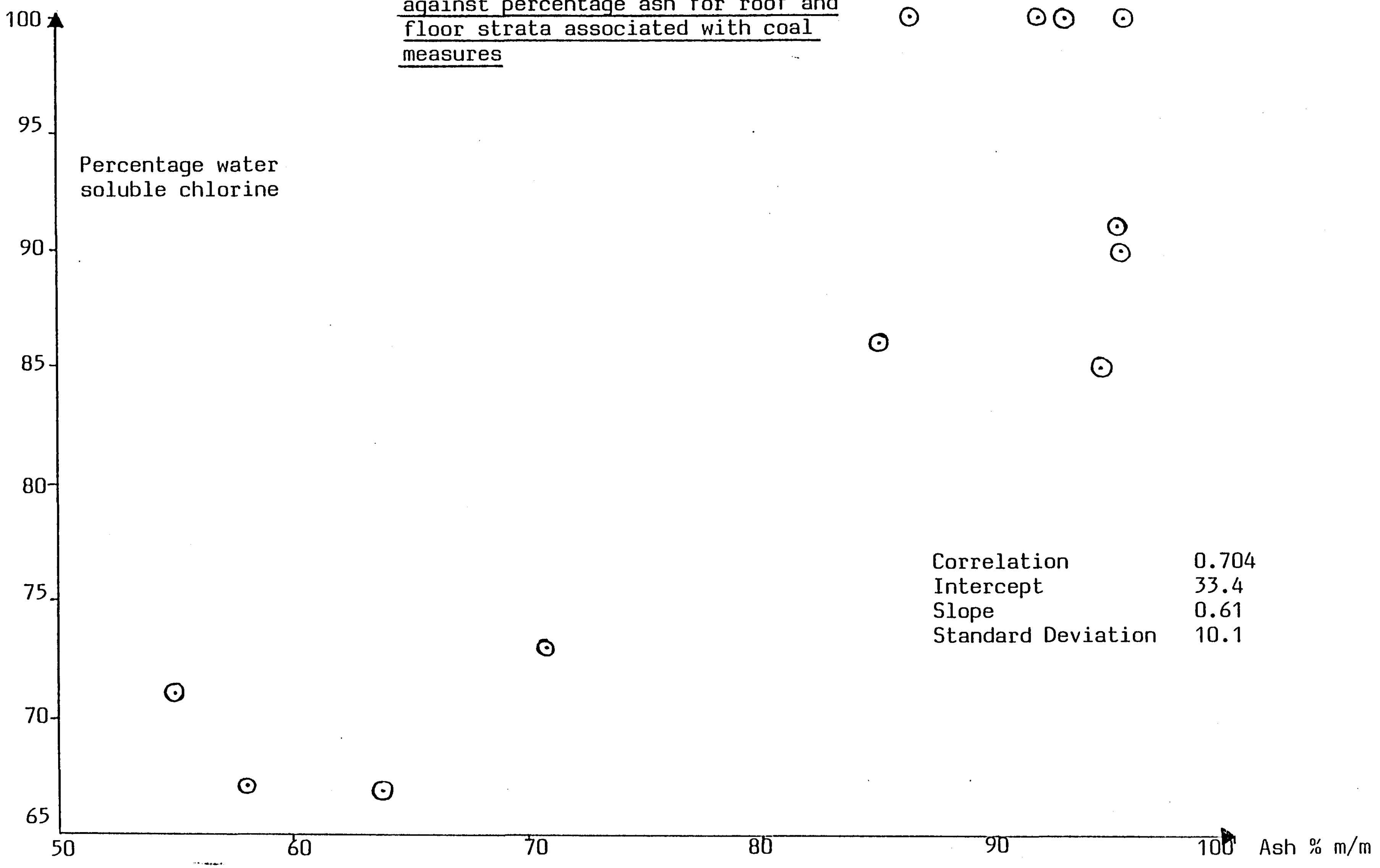
Table 4.24 shows that on plasma ashing the four selected samples the majority of chlorine present is retained in the ash in all but sample 83575. This mudstone sample is atypical ie. carbonaceous with an ash content of 63.7 percent. These results suggest that all the water soluble chloride present is associated with sodium, presumably as sodium chloride solution in the pore water. SEM/EDX examination of the samples demonstrated the presence of sodium chloride crystallites. A cluster of such crystallites is illustrated in Plate 4.4 the smallest having a diameter of approximately 2 μm. These results and those in section 4.5.1.3 support the previous assumption[140,141] that chlorine in coal has been derived, in part, from contact with percolating brine, subsequent to the coal's formation.

4.5.1.5 Leaching characteristics of low ash and low chlorine coals

In order to determine if sodium could be water extracted from coal in excess of the water extractable chloride the following test was performed.

Six samples of low ash and low chlorine pillar section coal samples, were ground to <45 μm using the Retsch Spectromill. Ground material (20 g) was placed in a 250 cm^3 conical flask and 100 cm^3 of distilled water added, plus a few drops of methylated spirit. The flask was stoppered and the contents magnetically stirred for 24 hours. The suspension was filtered under vacuum using a Whatman 542 filter paper and the soluble sodium, chlorine and potassium determined on the filtrate as described in section 4.5.1.3. The results are given in Table 4.25. As expected the water soluble chloride is low. The water soluble sodium and potassium are also very low. It would follow therefore that low chlorine coals would have low water extractable sodium contents and possibly low total sodium contents as suggested by earlier workers.[117,122,139]

Figure 4.8 Percentage water soluble chlorine against percentage ash for roof and floor strata associated with coal measures



Correlation	0.704
Intercept	33.4
Slope	0.61
Standard Deviation	10.1

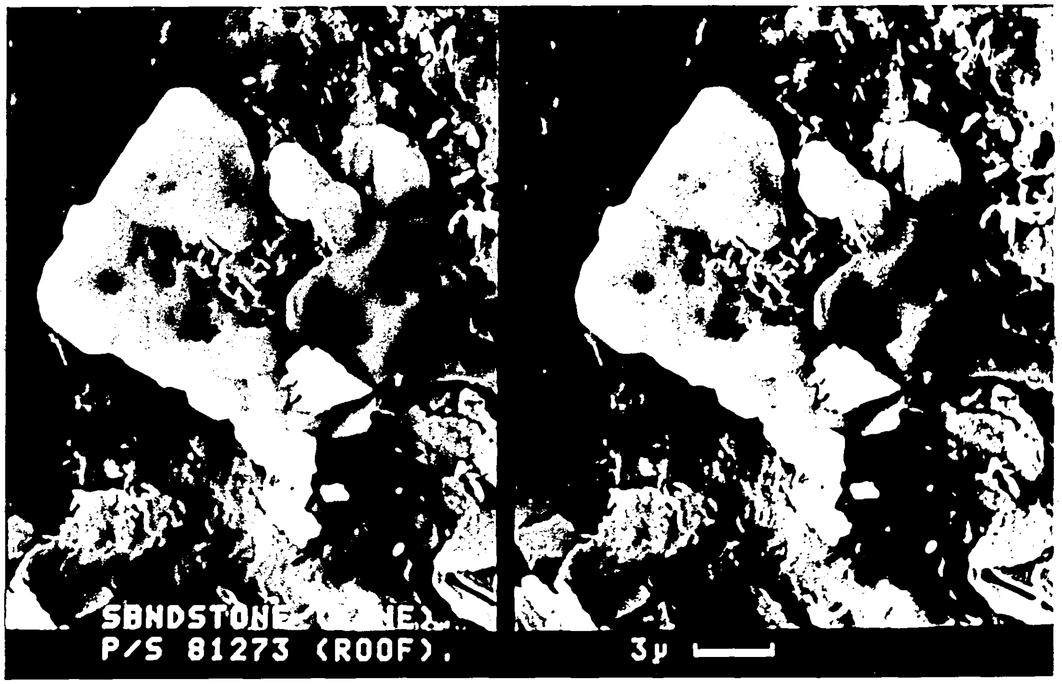


PLATE 4.4(a)
Scanning Electron Micrograph showing NaCl Crystallites

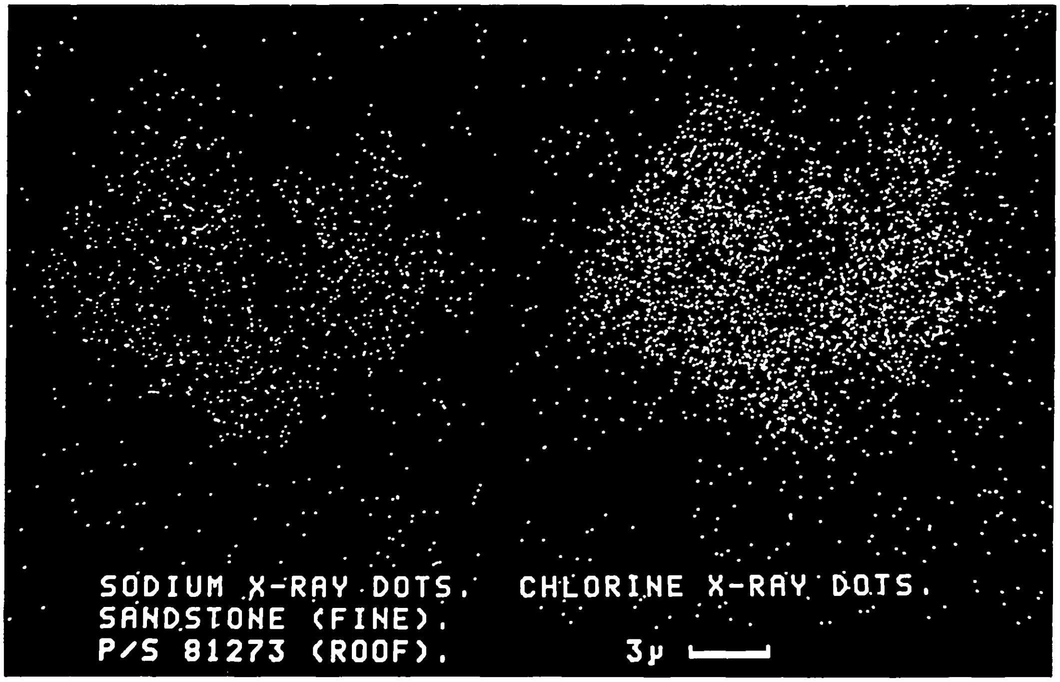


PLATE 4.4(b)
Sodium and Chlorine X-ray
Distribution of same area

TABLE 4.25

Leaching of low chlorine coals to assess sodium-chlorine ratio (SCR) (air-dried basis)

Coal sample number	Ash % m/m	Chlorine in original coal % m/m	Water soluble analyses % m/m			
			Cl	Na	K	SCR
77888	8.2	0.09	0.02	0.01	0.001	0.90
77928	13.8	0.09	0.03	0.02	0.001	1.03
77929	8.5	0.07	0.03	0.02	0.001	1.24
77930	6.7	0.06	0.03	0.02	0.001	0.98
77931	7.2	0.08	0.03	0.01	0.001	0.77
77932	10.6	0.04	0.03	0.02	0.005	1.30

Although the SCR's may be indicative as to the presence of sodium chloride crystallites in these coals, none could be identified using SEM/EDXA.

4.5.2 Anion-exchange property of the chlorine-coal bond

If the chlorine-coal bond exhibited an anion exchange reaction with a weakly basic property it would be exchanged by the following anions in order of reactivity:

$$OH^- > PO_4^{3-} > SO_4^{2-} > Cl^-$$

whereas if the chlorine-coal bond exhibited a strongly basic anion exchange property, it would <u>not</u> be displaced by hydroxyl and the order of reactivity would be:

$$PO_4^{3-} > SO_4^{2-} > Cl^- > OH^-$$

The ten coals selected as reference samples were ground to less than 212 μm and treated with solutions of 0.01-1.00 molar sodium hydroxide, ammonium hydroxide, nitric, sulphuric and phosphoric acids as described below.

The air-dried coal (2g of $<$ 212 μm) was magnetically stirred for two hours in a stoppered 500 cm^3 flask with 100 cm^3 of distilled water (or aqueous reagent) plus a few drops of methylated spirit as a wetting agent. The suspension was vacuum filtered and the water extract titrated for chloride content by Volhard's method[153]. The chlorine content of the filtered coal residue was determined on an air-dried basis by the Eschka method.[149] The percentage chlorine extracted or exchanged was then calculated. The results given in Table 4.26 are not indicative of any anion-exchange property, at the particle size examined. This finding agrees with unpublished studies by Peterson and Brown.[158]

It is interesting to note that for Cadley Hill, Thoresby and Lea Hall samples the use of sulphuric and phosphoric acids extracts less chlorine than distilled water alone. It may be that the mechanism of leaching with water is different for certain coals in the presence of these large and highly charged ions.

TABLE 4.26

Comparison of chlorine extractions for reference coals using anion exchange

Sample	Chlorine extracted % of total								
Reagent	Florence Rowhurst	Cortonwood Silkstone	South Durham 'C' Seam	Cadley Hill (Bright)	Cadley Hill (Dull)	Tilmanstone Milyard	*Thoresby Top Hard	Thoresby High Hazles	Lea Hall Shallow
Distilled Water	20.2	10.0	15.9	46.7	37.5	50.0	56.8	58.0	46.1
M/100 NaOH	20.2	8.3	16.0	45.6	45.0	50.0	58.2	67.6	53.9
M/10 NaOH	20.4	10.0	16.0	51.1	48.7	50.0	59.7	68.0	58.0
M/100 LiOH	21.2	10.0	16.7	50.0	50.0	50.0	57.6	64.4	57.4
M/10 LiOH	20.6	10.0	15.9	50.0	51.2	50.0	59.3	67.6	60.0
M/10 NH_4OH	20.6	8.3	15.9	51.1	51.2	50.0	59.7	68.0	63.4
M/1 NH_4OH	21.0	8.3	16.0	51.1	52.4	46.2	61.2	68.6	65.6
M/100 HNO_3	20.6	8.3	16.7	50.0	50.0	50.0	65.2	66.7	62.6
M/10 HNO_3	21.2	8.3	17.3	51.1	53.6	50.0	67.0	67.3	68.0
M/100 H_2SO_4	20.8	8.3	16.0	29.2	31.4	50.0	50.5	56.7	45.0
M/10 H_2SO_4	21.6	8.3	16.0	29.2	31.4	50.0	51.0	56.7	43.6
M/100 H_3PO_4	20.8	8.3	15.9	29.8	31.4	50.0	50.5	50.0	40.4
M/10 H_3PO_4	19.7	10.0	16.0	30.4	32.6	50.0	50.5	49.5	37.8

* Sample believed to be contaminated with dust suppression water

It is likely that the solvation of the chlorine-coal bond will be restricted by the accessibility of chlorine to the solvent and hence is dependent on the pore size of coal. It has been confirmed, however, that fine grinding of coal enables all the chlorine to be extracted by distilled water alone. (see section 4.5.1.2)

4.5.3 Solubility of chloride in polar and non-polar solvents

If chlorine were attached to nitrogen in coal as an amine hydrochloride, quaternary or pyridine salt,[122] i.e. as a strongly ionic compound, then it would be expected to be insoluble in non-polar solvents.

Samples of the two Thoresby coals (2g of < 212 μm) were magnetically stirred for 2 hours in a stoppered 500 cm^3 flask with 100 cm^3 of each solvent (diethyl ether and water) plus 5 drops of ethanol as a wetting agent. The solutions were filtered and the water extract titrated for chloride content by Mohr's method.[153] The diethyl ether extract was evaporated on alumina and the chloride determined by the high temperature method,[149] as were the chlorine contents of the original coals and the residues after extraction.

The results are given in Table 4.27.

The figures indicate that none of the chlorine present in the coals examined is soluble in cold diethyl ether. This evidence confirms that the chlorine-coal bond is strongly ionic.

4.5.3.1 Reaction of coal with sodamide in xylene (Tschitschibabin reaction)

If chlorine is bonded to coal covalently then polarisation of the carbon-chlorine bond might be expected. Such a bond could exhibit nucleophilic substitution and hence displacement of chlorine. The following experiment was used to establish if such a reaction occurred.

TABLE 4.27

Solubility of chloride in polar and non-polar solvents

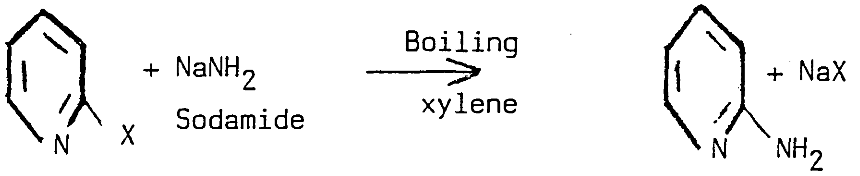
Water extraction

Sample	Total chlorine % m/m		Chlorine in residue % m/m		Chlorine in leachate % m/m		% of total chlorine extracted	
	1	2	1	2	1	2	1	2
Thoresby								
Top Hard	0.81	0.81	0.57	0.57	0.27	0.27	33.3	33.3
High Hazles	0.83	0.80	0.48	0.49	0.37	0.37	57.8	61.3
Diethyl ether extraction								
Thoresby								
Top Hard	0.81	0.81	0.83	0.87	<0.02	< 0.02	N D	N D
High Hazles	0.83	0.80	0.83	0.85	<0.02	< 0.02	N D	N D

N D   Not detectable

Two selected coals were refluxed for 3 hours with a xylene/ sodamide mixture in a soxhlet-type arrangement (Tschitschibabin reaction).[159]

The general scheme of this reaction is:



where X = halogen

The results of analysis of these samples are given in Table 4.28, and they do not show any appreciable loss of chlorine by this treatment. The attack on the chlorine-coal bond by sodamide in xylene would be by nucleophilic substitution and therefore this does not occur. The slight reduction in sulphur content is attributed to the dissolution in boiling xylene of some organic compounds present in coal.

The evidence so far suggests that the probable mechanism of attachment of chlorine to coal is addition, producing a loose ionic linkage.

4.5.3.2 Reaction of coal with perklone ($CCl_2=CCl_2$)

The effect of treating coal with a chlorinated hydrocarbon has been determined in the following test. Perklone was the selected solvent because of its common use in gravity separation procedures for coal.

A sample of Calverton Low Bright coal ($< 212\ \mu m$) was soaked in Perklone (boiling point 121°C) at room temperature for 24 hours and then dried above perklone's boiling point at 130°C for 24 hours. A sample of untreated coal was also dried at 130°C for 24 hours and both samples were then analysed.[149] The results are given in Table 4.29. The significance of results from one sample only should not be over-estimated, but it would appear that the treated coal retained 55 percent more chlorine than the untreated coal when both were heated above the boiling point of perklone. No explanation of this phenomenon is given here and it is suggested that more coal samples and other chlorinated hydrocarbon solvents could be examined similarly.

TABLE 4.28

Reaction of coal with sodamide in xylene (Tschitschibabin)

Coal	Chlorine content % m/m[a]		
	Original	After refluxing in xylene (3 hours)	After refluxing in xylene with $NaNH_2$ (3 hours)
Thoresby Top Hard	0.78	0.76	0.73
Thoresby High Hazles	0.82	0.78	0.74

Coal	Sulphur Content % m/m		
	Original	After refluxing in xylene (3 hours)	After refluxing in xylene with $NaNH_2$ (3 hours)
Thoresby Top Hard	1.01	0.89	0.93
Thoresby High Hazles	1.19	0.99	1.04

[a] High temperature BS 1016[149]

TABLE 4.29

Take-up of chlorine by coal from perklone ($CCl_2 = CCl_2$)

Coal sample - Calverton Low Bright

Chlorine content % m/m[a]								
Original Sample			Dried at 130°C (24 hours)			Mixed with perklone and dried at 130°C (24 hours)		
1	2	Av.	1	2	Av.	1	2	Av.
0.50	0.51	0.51	0.53	0.54	0.54	0.79	0.79	0.79

Percentage of chlorine taken up:	55% of original
Boiling point of perklone:	121°C

[a] High temperature BS 1016[149]

In addition the thermal characteristics of chlorinated coals could be ascertained.

4.5.4 Radiographic assessment of coal porosity

Porosity clearly plays an important part in the absorption of chlorine within the coal's structure and in the facilitation of removal by leaching. Whilst the test for leaching described in 4.5.1.1 is satisfactory in practice, an alternative and less time-consuming method of demonstrating differences in porosity, and perhaps of classifying coals for leachability, has been investigated.

Beeching in 1938[160,161] showed that samples of coal standing in contact with solutions of lead salts and subsequently X-rayed at 55 Kv, 50 mA for 0.15 seconds produced definite and distinct impregnation patterns. He applied the technique to a number of different coal types and calculated a mean pore radius from the theoretical equation:

$$h^2 = \frac{Trt}{8\eta} \quad \ldots\ldots\ 1$$

Where h = height solution risen (cm)
t = time (secs)
r = mean pore radius (cm)
T = surface tension of solution (dynes cm^{-1})
η = viscosity of solution (poises)

Samples of coal from different sub-sections of Thoresby Top Hard and High Hazles were taken from various positions within the seam. Pieces of coal were prepared from the subsection with approximately the following dimensions:- 6½ cm wide, 7½ cm high and 1 cm thick, all with their bases parallel to the bedding plane. These samples were stood vertically in Pyrex beakers, (125 cm^3) arranged in batches of twelve on perspex shelves and X-rayed. The samples were then removed, 10 cm^3 of 40 percent lead nitrate solution was added to each beaker and the coal samples replaced carefully in the solution. The beakers were covered to prevent evaporation and X-rayed initially at frequent intervals, and then less frequently, over a period of seven days.

A quite remarkable difference in impregnation rate is observed between these two coal seams. A photograph of a batch of twelve seam sub-sections in contact with lead nitrate for 7 days is shown in Plate 4.5 with Plate 4.6 showing a comparison between a Top Hard sample and a High Hazles sample. Impregnation of the High Hazles coal was complete in 20 minutes whilst the Top Hard coal was impregnated to only a quarter of its height after 7 days. Definite distances of impregnation could be measured from the X-ray contact prints and using equation 1 the mean pore radius was calculated for both coals. Plate 4.7 shows typical contact prints of X-ray plates for two of the samples (actual size), before and after impregnation.

Calculations using equation 1

(i) Top Hard Coal: mean pore radius $r = \dfrac{(1)^2 \times 8 \times 0.033}{86400 \times 80} = 3.8 \times 10^{-8}$ cm

(ii) High Hazles Coal: mean pore radius

$$r = \frac{(6.5)^2 \times 8 \times 0.033}{1200 \times 80} = 1.2 \times 10^{-4}\,\text{cm}$$

The precise numerical values are of course unimportant and are obviously not a true measure of pore size since this calculation would include any macro-fissuring within the samples, but the significant point is that the two coals differ by several orders of magnitude. This difference may be compared with the difference between the chlorine leachabilities of the Top Hard and High Hazles coals, determined on the ¼ x 1/8 inch fraction from the whole seam section (less dirt) by the procedure described earlier, (see Table 4.15 and Figure 4.5). The figures are 19 and 36 percent respectively.

At the very least the method shows a striking difference in the way specimens from two seams absorb concentrated lead nitrate solution.

The general applicability of this method to classify coal seams in order of leachability has been tested by using nine seam samples from the East Midlands coalfield. The results are given in Table 4.30.

T/H M	T/H M	T/H J	T/H J
T/H J	T/H F	T/H F	T/H F
H/H D	H/H D	H/H A	H/H A

T/H = Top Hard
H/H = High Hazles

PLATE 4.5

Subsections in contact with lead nitrate solution for 7 days

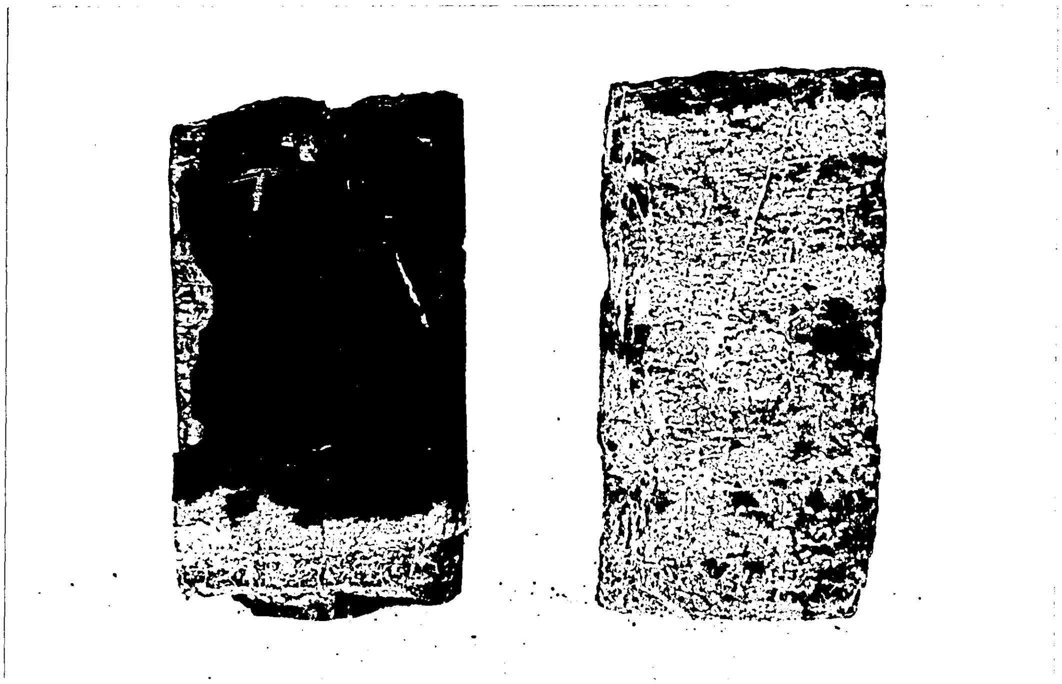


PLATE 4.6

Thoresby Top Hard
Subsection J

Thoresby High Hazles
Subsection A

Thoresby coals after contact for 7 days in lead nitrate solution

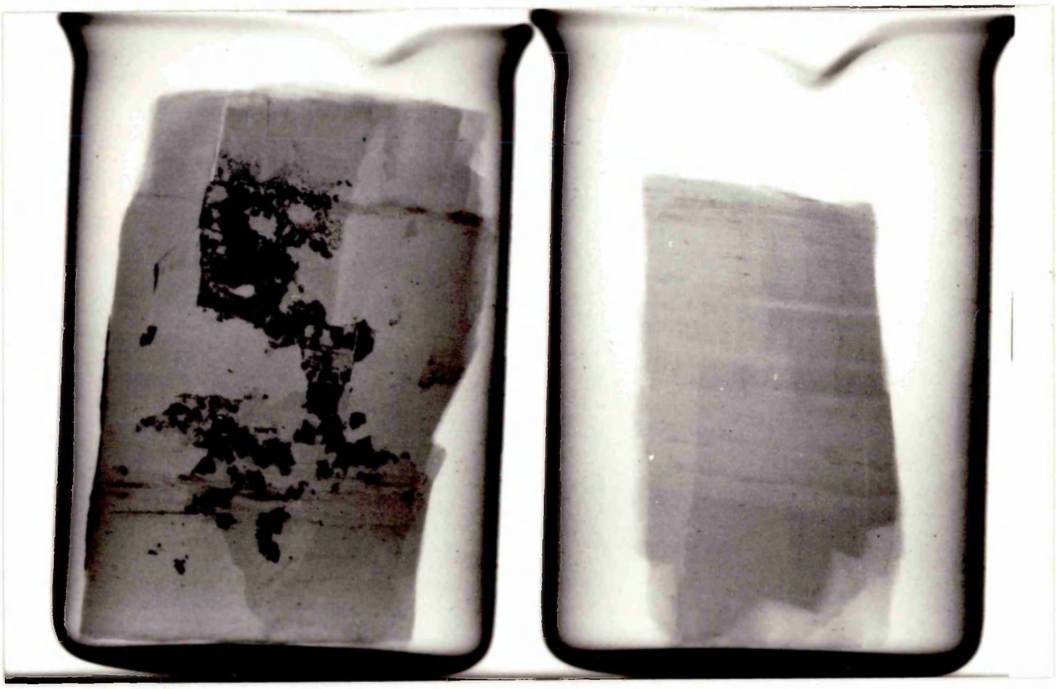


PLATE 4.7 (a)

Thoresby Top Hard
Subsection J

Thoresby High Hazles
Subsection F

X-ray film contact prints before addition of lead nitrate solution for 7 days

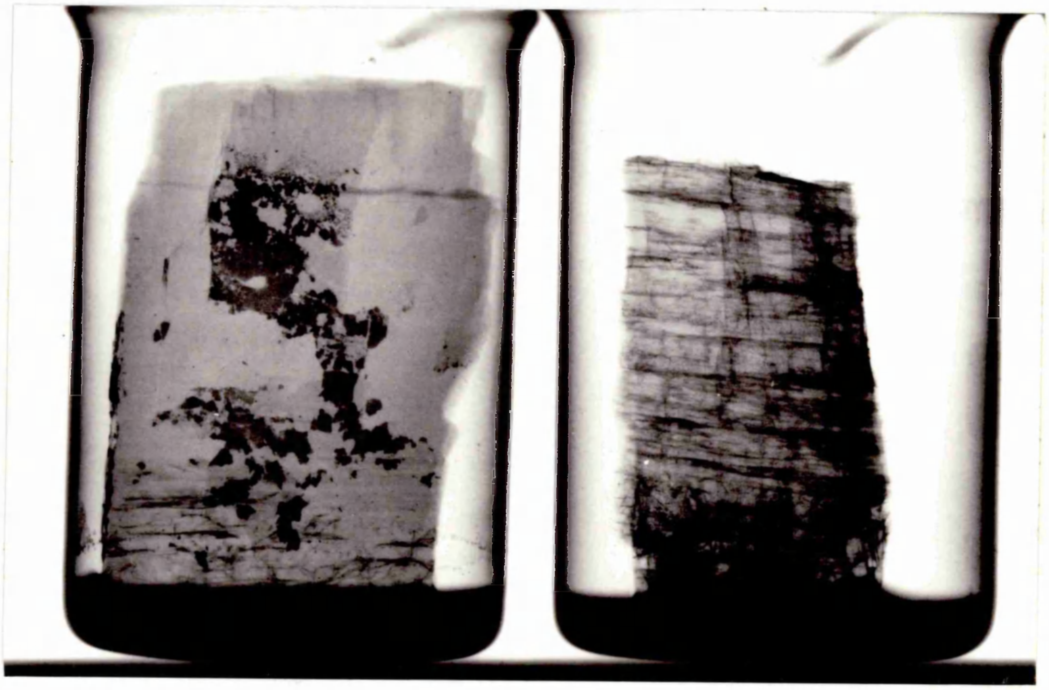


PLATE 4.7 (b)

Thoresby Top Hard
Subsection J

Thoresby High Hazles
Subsection F

X-ray film contact prints after addition of lead nitrate solution for 7 days

TABLE 4.30

X-ray radiographic examination of coal

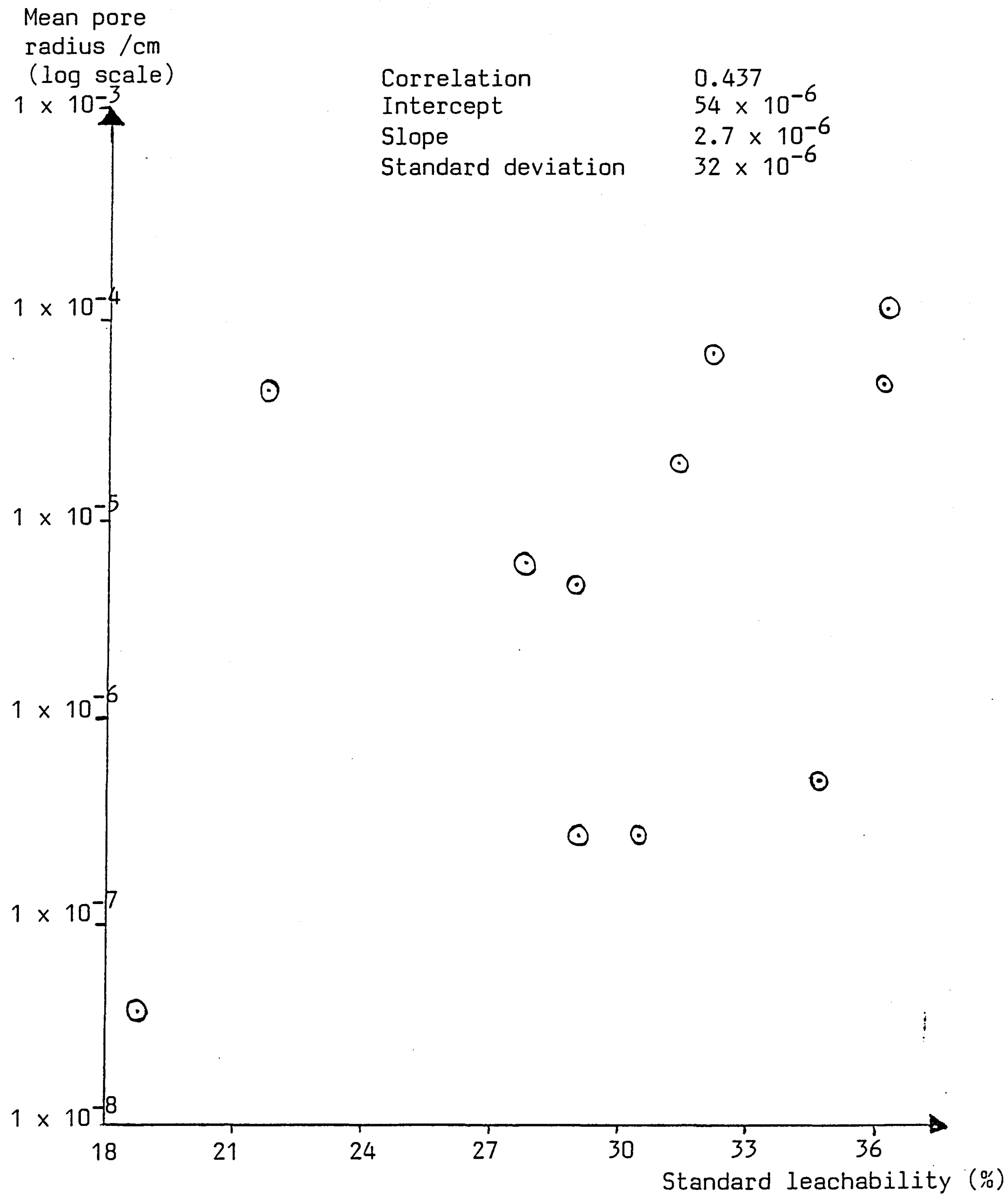
Sample No.	Colliery	Seam	Sub-section	Estimated mean pore radius /cm	Average pore radius /cm	Leachability order from estimated pore radius	Standard leachability %	Leachability order from standard leachability
1	Babbington	Blackshale	J	4.8×10^{-7}	4×10^{-5}	4	21.7	10
			J	3.4×10^{-5}				
			F	(4% sulphur - not measurable)				
			B	2.3×10^{-7}				
			B	1.4×10^{-4}				
2	Babbington	Tupton	E	Canneloid	7×10^{-5}	2	32.1	4
			C	2.8×10^{-5}				
			C	2.8×10^{-5}				
			B	1.1×10^{-4}				
			B	1.1×10^{-4}				
3	Bevercotes	Parkgate	H	4.7×10^{-7}	3×10^{-7}	10	30.4	6
			H	8.6×10^{-8}				
4	Bilsthorpe	Low Main	J	9.8×10^{-6}	6×10^{-6}	6	27.7	9
			J	1.5×10^{-5}				
			E	5.8×10^{-7}				
			E	4.8×10^{-7}				
5	Bilsthorpe	Parkgate	P	9.8×10^{-5}	5×10^{-5}	3	35.9	2
			P	1.6×10^{-9}				
			L	8.0×10^{-5}				
			L	5.3×10^{-6}				
6	Ollerton	Parkgate	M	3.2×10^{-8}	3×10^{-7}	8	29.1	7
			M	(Not measurable)				
			K	6.1×10^{-7}				
			K	2.4×10^{-7}				
7	Rufford	High Hazles	E	4.7×10^{-7}	5×10^{-7}	10	34.6	3
			E	8.6×10^{-8}				
			B	1.4×10^{-6}				
			B	2.4×10^{-7}				
8	Thoresby	High Hazles	F	1.2×10^{-4}	1×10^{-4}	1	36.1	1
			D	1.2×10^{-4}				
			A	1.2×10^{-4}				
9	Thoresby	Parkgate	E	3.7×10^{-5}	2×10^{-5}	5	31.3	5
			E	3.8×10^{-5}				
			C	5.3×10^{-6}				
			C	3.4×10^{-7}				
10	Thoresby	Top Hard	M	3.8×10^{-8}	4×10^{-8}	11	18.8	11
			J	3.8×10^{-8}				
			F	3.8×10^{-8}				
11	Welbeck	Top Hard	I	5.0×10^{-6}	5×10^{-6}	7	28.9	8
			I	5.0×10^{-6}				

This table attempts to compare the order of leachability by the standard procedure described in section 4.5.1.1 with the estimated average mean pore radius calculated using the X-ray method. The results although exhibiting the same general pattern show several anomalies which prevent a satisfactory correlation. (Figure 4.9). The anomalies may be due to the presence of different lithotypes within the seam.

The need to test specimens from at least each lithotype of coal present in the seam has been investigated. A sub-section taken from the Babbington Tupton seam showed no penetration of lead salt even after seven days, but the overall seam's leachability by the standard test was fairly good. Examination of this sub-section alone using the standard test (4.5.1.1) produced a very low chlorine extraction. The standard leaching test results for this sub-section and two other Babbington sub-sections are given in Table 4.31 and displayed in the form of a bar chart in Figure 4.10. The basic analyses for these sub-sections are given in Appendix 4.3. The X-ray film contact prints for sub-sections E and C are also shown in Plate 4.8. Examination of Table 4.31 shows that sub-sections B and C have very similar leaching characteristics whilst those for sub-section E are much lower. The results in Appendix 4.3 show a difference in basic analysis for sub-section E when compared to analysis for sub-section B and C and it was later established that sub-section E was in fact composed of cannel coal.

The assessment of chlorine extractability for the seam as a whole either by the standard test or by the X-ray radiographic method must therefore give due weight to the differing extractabilities of the different lithotypes present. A further problem using the X-ray radiographic technique is the presence of dirt bands or pyrites in the sample. Such inclusions obscure the radiographic representation and make measurement of the lead salt's penetration difficult. It is therefore necessary to select low ash, low sulphur samples to obtain the best results. Despite these difficulties and the evidently complex nature of the pore system in coal established by Bettleheim and Hann[156] it is still thought that the method gives a rapid guide to a subsection's leachability and a clear picture of the macrofissuring present.

Figure 4.9 Estimated mean pore radius (lead nitrate test) compared with results using the standard leachability test.



Correlation	0.437
Intercept	54×10^{-6}
Slope	2.7×10^{-6}
Standard deviation	32×10^{-6}

TABLE 4.31

Results showing leachability of $\frac{1}{4}$" x 1/8" coal subsections from Babbington Tupton (percentage chlorine leached based on Eschka chlorine figures)

Sub-section	Total chlorine (Eschka) % m/m	Leaching time/ minutes	Chlorine leached %	Water solubles in leachate/ mgl^{-1}					
				Cl	Na	K	Ca	Mg	Fe
B	0.65	10	7.5	97	40	0.8	13.6	2.6	<0.1
		120	23.5	306	117	1.5	43.0	8.8	0.1
		1440	40.2	522	184	2.1	77.8	15.2	0.1
C	0.77	10	10.6	164	171	1.2	27.2	5.0	<0.1
		120	22.6	347	180	2.0	56.6	11.4	<0.1
		1440	41.8	643	204	2.3	88.0	17.0	0.1
E	0.56	10	1.8	20	34	0.7	3.5	0.6	<0.1
		120	3.4	38	50	0.5	6.1	1.1	<0.1
		1440	8.0	90	70	0.9	12.1	2.2	0.1

Figure 4.10 Comparison of the leachability of various subsections taken from Babbington Tupton seam

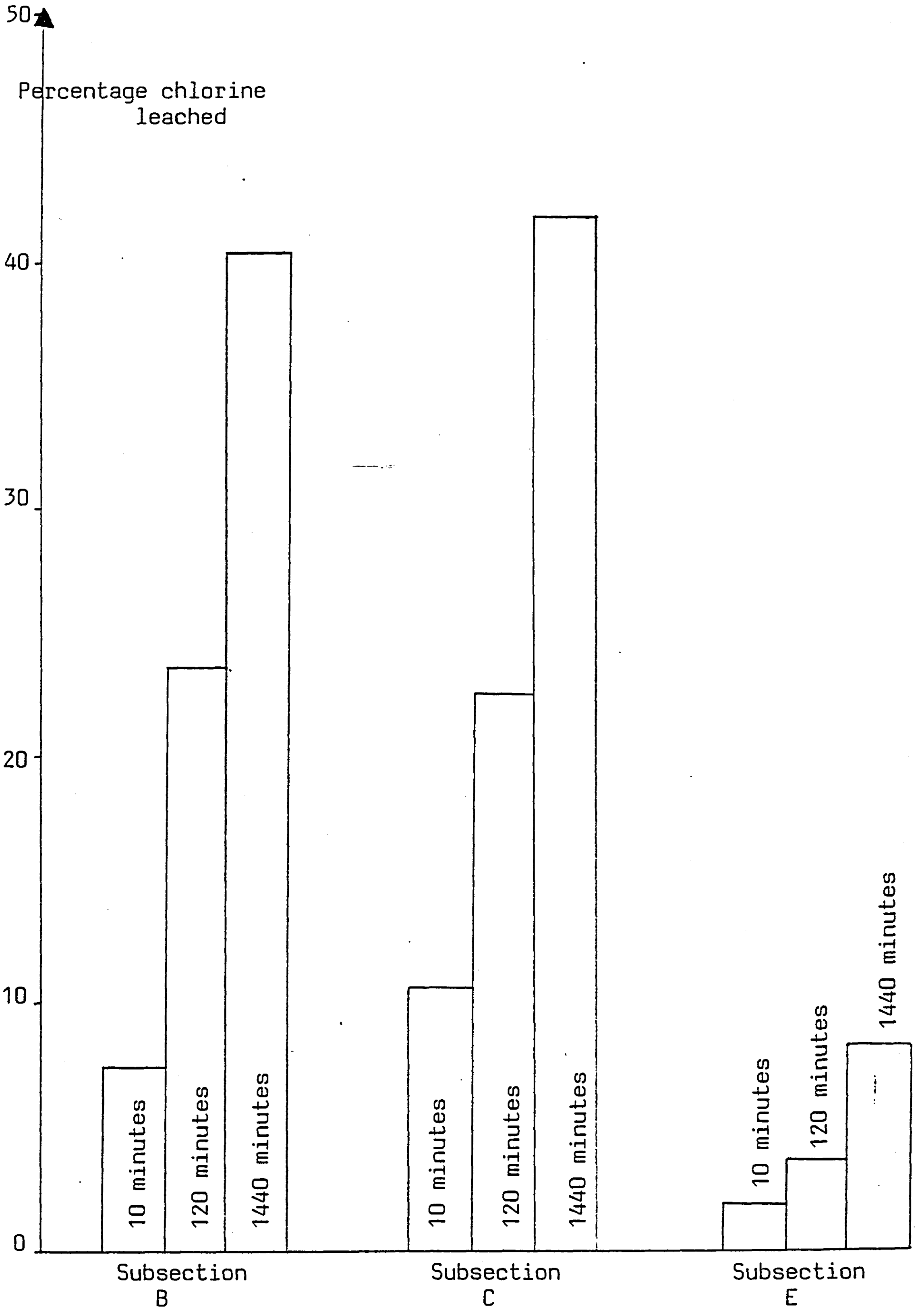


PLATE 4.8 (a)

Babbington Tupton
Subsection E

Babbington Tupton
Subsection C

X-ray film contact prints before addition of lead nitrate solution for 7 days

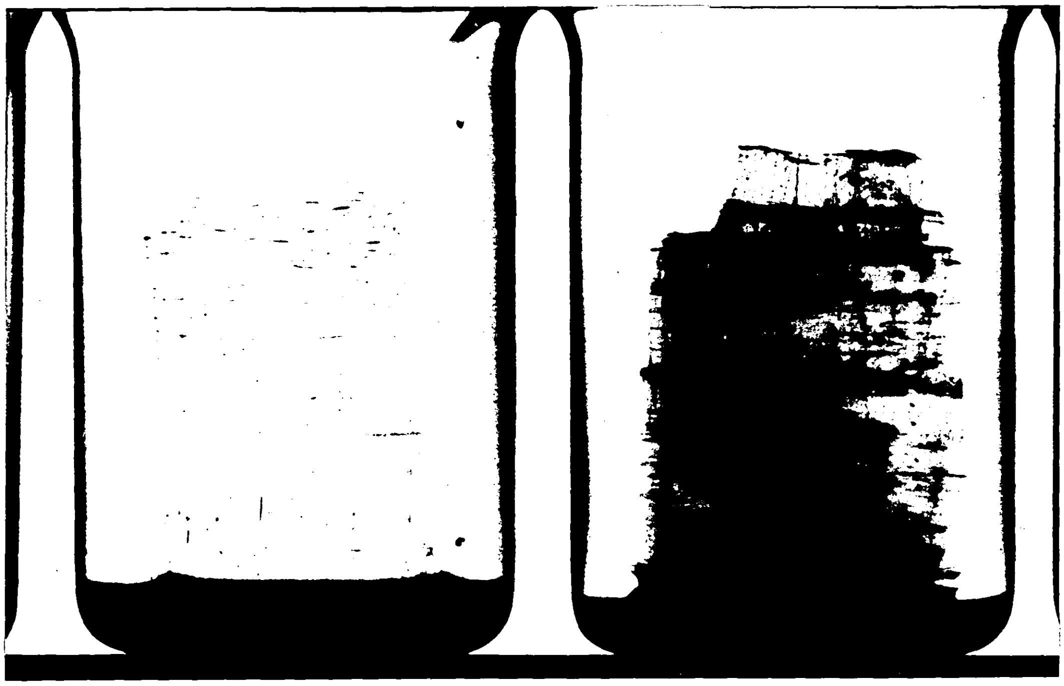


PLATE 4.8 (b)

Babbington Tupton
Subsection E

Babbington Tupton
Subsection C

X-ray film contact prints after addition of lead nitrate solution for 7 days

The complications explained above however, do not allow the method to be used universally or indiscriminately for the assessment of leachability. The variation within subsections of a seam may explain the discrepancy already mentioned when the standard leaching test was repeated on different samples of the Thoresby Top Hard seam (see section 4.5.1.1). This observation throws into disarray any attempt to classify coal seams according to their leachability with water.

4.5.5 Impregnation of coal with sodium chloride

The possibility that sodium chloride might react within the micropore structure of coal, mentioned in section 4.4.7, has been investigated by impregnating coal with sodium chloride solution under vacuum. The coals examined included samples which had previously been leached with water using the standard test to remove soluble chlorine. It was thought that treatment with sodium chloride solution should at least replace this water soluble chloride.

In addition the use of radioactive chlorine as a radiotracer in the vacuum impregnation experiment and the involvement of nitrogen in the bonding mechanism of chlorine to coal, are assessed. The fate of sodium associated with chloride in the impregnation reaction is also determined.

4.5.5.1 Sodium chloride introduced by solution impregnation under vacuum

Duplicate samples (10 g) of air-dried coal (< 212 μm) were placed in round-bottomed flasks (125 cm^3) with side arms. The flasks were evacuated for 48 hours and the internal pressure measured using a Pirani gauge. The vacuum approached 10^{-2} Torr for each sample before impregnation. The side arm of the flask was sealed and quickly immersed in 20% NaCl solution prepared with de-aerated distilled water. The seal was broken and the solution completely filled the flask. The side arm was resealed and the flask contents left for 16 days for the sodium chloride solution to impregnate the coal. The contents were vacuum filtered and the coal air-dried for 2 days. Each sample was then thoroughly mixed and the following tests performed.

1) Moisture, ash and Eschka chlorine contents[149] of impregnated and unimpregnated samples.

2) Plasma ashing of each sample at a temperature below 150°C followed by Eschka chlorine determination on the residue.

3) Heating samples at 210 ± 5°C for 36 days and determining the chlorine content of the residue by the Eschka method.

4) Qualitative and quantitative examination by SEM/EDXA.

The results are given in Tables 4.32 - 4.36.

1) Take-up of chlorine on impregnation

Examination of Table 4.32 shows that the leached coal samples impregnate to a greater degree than the unleached coals, the amount of chlorine take-up varying in the range 2.0 - 3.5 percent (m/m), with a corresponding increase in 815°C ash content of 0.5 - 1.0 percent (m/m).

2) Loss of chlorine in plasma-ashing

The results of plasma ashing leached and unleached impregnated coals (Table 4.33) show that about 20-25 percent of the extra chlorine take-up on impregnation is lost from unleached samples and 25-30 percent from previously leached samples. The chloride ion in solution has evidently reacted with the coal substance to form either an addition or substitution product which readily loses chlorine on plasma ashing. The work carried out in section 4.5.3.1 suggests that the most likely method of attachment of chlorine to coal is addition, to produce a loose ionic linkage. An alternative theory that some sodium chloride remains in the micro-pore structure of the coal as a 'liquid solution'[143] seems unnecessary to account for its presence, since at some stage of the evaporation/drying process sodium chloride would be deposited on the coal surface and behave as the salt.

TABLE 4.32

Average moisture, ash and chlorine contents of Thoresby coal samples (air-dried basis)

Sample No.	Thoresby coal	Moisture % m/m	Ash % m/m 815°C	Eschka chlorine % m/m			
				1	2	3	Mean
1	High Hazles	7.2	9.4	0.88	0.87	0.87	0.87
2	Top Hard	5.9	4.6	0.81	0.82	0.81	0.81
3	High Hazles leached	6.3	7.6	0.56	0.60	-	0.58
4	Top Hard leached	4.2	6.3	0.62	0.60	-	0.61
5	High Hazles impregnated A	7.0	10.0	3.43	3.22	3.09	3.25
6	High Hazles impregnated B	6.9	9.9	2.84	2.94	2.85	2.88
7	Top Hard impregnated A	5.9	5.4	3.56	3.94	3.39	3.46
8	Top Hard impregnated B	5.3	5.1	3.10	3.24	3.10	3.15
9	High Hazles leached and impregnated A	6.0	8.1	3.61	3.37	3.69	3.56
10	High Hazles leached and impregnated B	5.6	8.1	3.16	3.16	3.44	3.25
11	Top Hard leached and impregnated A	4.1	7.4	3.63*	4.29	4.47	4.38
12	Top Hard leached and impregnated B	4.2	7.3	4.39	3.76*	4.35	4.37

* Spillage suspected. Figure omitted from calculation

TABLE 4.33

Chlorine loss from plasma-ashed impregnated coal (air-dried basis)

Sample No.	Thoresby coal	Total chlorine % m/m	Chlorine added % m/m	Plasma ash % m/m	Chlorine in plasma ash % m/m	Chlorine in plasma ash (air-dried coal basis) % m/m			Added chlorine lost %
						1	2	Mean	
1	High Hazles	0.87	-	10.6	0.38	0.04	-	0.04	-
2	Top Hard	0.81	-	6.1	0.66	0.04	-	0.04	-
3	High Hazles leached	0.58	-	8.0	0.25	0.02	-	0.02	-
4	Top Hard leached	0.61	-	5.7	0.70	0.04	-	0.04	-
5	High Hazles impregnated A	3.25	2.38	13.7	13.4	1.83	-	1.83	23
6	High Hazles impregnated B	2.88	2.01	13.5	10.1	1.37	1.58	1.48	26
7	Top Hard impregnated A	3.46	2.65	10.0	20.7	2.07	-	2.07	22
8	Top Hard impregnated B	3.15	2.34	9.8	18.3	1.79	1.86	1.83	22
9	High Hazles leached and impregnated A	3.56	2.98	12.3	13.4	1.65*	2.14	2.14	28
10	High Hazles leached and impregnated B	3.25	2.67	12.5	14.1	1.87	1.73	1.80	32
11	Top Hard leached and impregnated A	4.38	3.77	13.3	19.4	2.58	2.77	2.68	29
12	Top Hard leached and impregnated B	4.37	3.76	13.3	20.4	2.71	2.65	2.68	29

* Spillage suspected. Figure omitted from calculation

The classical work of Frech and Cedergren[162,163] who used both experimental results and thermodynamic calculations to estimate hydrogen chloride losses from chloride impregnated graphite furnace tubes (GFAAS) when they were heated to high temperatures, might explain the decomposition of sodium chloride. However, the reactions involved are complex and because of interferences of other ions not all elements behaved in the experiments quite the same as was predicted by calculation. The likelihood of such equilibrium reactions occurring at 150°C during plasma ashing or at 205°C in an air-oven seems very remote.

Some of the 70-80 percent added chlorine not lost on plasma ashing can readily be identified as NaCl crystallites on the surface of coal using SEM/EDX analysis.

Nitrogen-containing groups might be the means of attachment of chloride ions to form an 'organic' salt. If this were so, a greater susceptibility to chloride impregnation and/or subsequent loss of chlorine on plasma ashing (or heating at 210°C in air) might be observed in coals of greater nitrogen content, or more particularly in coals of greater 'basic' nitrogen content. This suggestion is explored later in this section.

3) Loss of chlorine on prolonged heating

Taking into account the loss of chlorine from coal at 210 ± 5°C over extended heating periods (Table 4.4) it was assumed for calculation (Table 4.34) that 90 percent of the original chlorine present in coal would be lost on heating after 36 days. The results (Table 4.35), although inconsistent, show once again a loss of some of the impregnated chlorine for each sample. Although errors due to sample transfer were eliminated in this test and in the plasma ashing test, agreement between duplicates is not good.

TABLE 4.34

Estimated loss of chlorine from untreated Thoresby coals on prolonged heating (air-dried basis)

Assume 90 percent of the original chlorine is lost after heating at 210 ± 5^{o}C for 36 days (see Table 4.4)

Sample No.	Thoresby coal	Chlorine content % m/m	Estimated chlorine loss after 36 days % m/m
1	High Hazles	0.87	0.78
2	Top Hard	0.81	0.73
3	High Hazles leached	0.58	0.52
4	Top Hard leached	0.61	0.55

TABLE 4.35

Actual loss of chlorine from impregnated coal on prolonged heating

Sample No.	Thoresby coal	Estimated chlorine average % m/m	Estimated chlorine content after heating @ 210 ± 5^{o}C for 36 days % m/m	Determined chlorine content % m/m			Impregnated chlorine lost %
				1	2	Av.	
6	High Hazles impregnated B	2.88	2.10	2.02	1.95	1.99	5
7	Top Hard impregnated A	3.46	2.73	2.21	2.34	2.28	16
8	Top Hard impregnated B	3.15	2.42	2.23	1.99	2.11	13
9	High Hazles leached and impregnated A	3.56	3.04	2.09	1.86	1.98	35
10	High Hazles leached and impregnated B	3.25	2.73	1.84	2.13	1.99	27
11	Top Hard leached and impregnated A	4.38	3.83	3.01	3.76	3.40	11
12	Top Hard leached and impregnated B	4.37	3.82	3.05	2.73	2.87	25

(Note: Insufficient of sample 5 for test)

4) Quantitative examination by SEM/EDX analysis

With a few exceptions, mainly in the case of sodium, agreement between replicate analyses by the SEM/EDX analysis technique (Table 4.36) is reasonably good. Agreement between Eschka and SEM estimates of chlorine content for the unimpregnated coals (samples 1-4 inclusive) is very good (cf. Table 4.32) but for the remainder the SEM figures are only about half those determined by Eschka.

Discrepancies of this kind are not unknown in the similar technique of X-ray fluorescence analysis when the element sought exists in more than one bonding form in the material under examination.[130] Sodium chloride crystallites were shown to be present by SEM/EDXA and the presence of the labile form was proven by its loss on low-temperature heating, and plasma ashing. A similar effect was observed in the case of sulphur in the previous chapter, when using the same SEM/EDXA method the Eschka estimates showed more sign of agreement in the absence of pyritic and 'sulphate' sulphur.

4.5.5.2 Involvement of nitrogen in the high vacuum impregnation of coal using aqueous sodium chloride

To assess the possible involvement of nitrogen in the impregnation reaction mentioned previously in 4.5.5.1, twelve carbonaceous samples were impregnated as described in that section, except that the flasks were evacuated for a reduced time of seven hours. The selected samples covered a range of nitrogen contents and analyses of their plasma ashes are given in Table 4.37.

TABLE 4.36

SEM/EDX Analysis of Thoresby Top Hard and High Hazles NaCl (aq) impregnated coals (air-dried basis)

Sample No.	Thoresby coal	Chlorine % m/m				Sodium % m/m				Sulphur % m/m			
		1	2	3	Mean	1	2	3	Mean	1	2	3	Mean
1	High Hazles	0.90	0.90	0.84	0.88	0.35	0.28	0.26	0.30	1.09	1.07	1.01	1.05
2	Top Hard	0.81	0.84	0.81	0.82	0.29	0.20	0.37	0.29	0.85	0.78	0.79	0.81
3	High Hazles leached	0.59	0.56	0.58	0.58	0.22	0.18	0.13	0.18	0.80	0.82	0.83	0.82
4	Top Hard leached	0.59	0.60	0.58	0.59	0.22	0.17	0.14	0.18	0.80	0.79	0.81	0.80
5	High Hazles impregnated A	1.78	1.86	1.71	1.79	1.22	1.18	1.24	1.21	0.87	0.84	0.76	0.82
6	High Hazles impregnated B	1.75	1.75	1.70	1.73	1.04	1.02	0.99	1.01	0.78	0.80	0.90	0.82
7	Top Hard impregnated A	2.19	2.11	2.20	2.17	1.29	1.25	1.21	1.25	0.73	0.75	0.77	0.75
8	Top Hard impregnated B	1.95	1.90	1.86	1.89	1.19	1.02	1.00	1.07	0.64	0.72	0.80	0.72
9	High Hazles leached impregnated A	1.71	1.69	1.74	1.71	1.07	1.00	0.98	1.00	0.87	0.81	0.83	0.84
10	High Hazles leached impregnated B	1.58	1.71	1.66	1.65	0.95	1.21	1.18	1.10	0.94	0.92	0.90	0.92
11	Top Hard leached impregnated A	1.76	1.76	1.72	1.73	0.81	0.89	0.87	0.86	0.79	0.78	0.69	0.75
12	Top Hard leached impregnated B	1.56	1.68	1.61	1.68	0.92	0.72	0.83	0.82	0.79	0.74	0.76	0.76

TABLE 4.37

Average moisture, ash, total nitrogen, chlorine and plasma ash contents with chlorine loss on plasma ashing of selected samples (air-dried basis)

Sample No.	Sample	Moisture % m/m	Ash % m/m	Total nitrogen % m/m	Chlorine % m/m	Plasma ash % m/m	Chlorine in plasma ash % m/m	Chlorine in plasma ash (air-dried coal basis) % m/m
1	Thoresby High Hazles coal	7.2	8.6	1.54	0.92	10.6	0.38	0.04
2	Thoresby Top Hard coal	6.2	4.3	1.55	0.82	6.1	0.66	0.04
3	Thoresby High Hazles leached coal	6.3	7.6	1.57	0.58	8.0	0.25	0.02
4	Thoresby Top Hard leached coal	4.2	6.3	1.53	0.61	5.7	0.70	0.04
5	Manvers (6645D) coal	1.8	4.4	1.76	0.18	6.2	0.23	< 0.02
6	Yorkshire I coal	2.0	4.2	1.60	0.34	5.7	0.59	0.03
7	Yorkshire II coal	0.5	1.8	1.50	0.05	2.7	1.34	0.04
8	Daw Mill (7140D) coal	5.7	9.0	1.11	0.20	10.8	0.27	0.03
9	Russian Anthracite coal	4.8	6.8	0.70	0.04	9.7	<0.17	<0.02
10	German Brown coal	17.6	4.1	0.60	0.04	11.1	<0.16	<0.02
11	Activated charcoal	4.9	0.5	0.24	0.08	N D	N D	N D
12	Graphite	4.0	0.3	1.44	< 0.02	N D	N D	N D

N D = Not determined

The results of the analyses of these samples after impregnation and the effect of plasma ashing them are given in Table 4.38. The results of heating the impregnated samples in an air-oven at 210 ± 5^{O}C appear in Table 4.39. The SEM/EDXA results for the coals before and after impregnation are given in Table 4.40 with the abstracted average results for chlorine, sodium and sulphur given in Table 4.41. Ash analyses of all the samples after incineration at 815^{O}C are shown in Table 4.42.

It can be seen from Table 4.37 that the amount of chlorine retained in the samples on plasma ashing ranged from less than 0.02 percent to a maximum of 0.04 percent.

Analyses after impregnation (Table 4.38) showed that the chlorine taken up by the samples ranged from 1.97 percent for Daw Mill coal to 9.3 percent for graphite. On subsequent plasma ashing an average loss of 20 percent of the added chlorine was found, the maximum loss being 49 percent for the activated charcoal sample. These results confirm the previous findings that a proportion of the chlorine added to coal as NaCl, on impregnation becomes unstable and is lost on plasma ashing. The uptake of chlorine does not relate to the nitrogen content of the samples (correlation coefficient 0.39). The sample of activated charcoal lost approximately 50 percent of its added chlorine on plasma ashing with a nitrogen content much lower than the Thoresby coal samples (3 and 6 percent loss). These observations do not support the hypothesis that the mechanism binding chlorine to coal involves nitrogen. The most likely method of attachment is by sorption of ions into the coal structure.

Examination of Table 4.39 shows that the average loss of added chlorine, on heating the samples at 210 ± 5^{O}C for 16 days is approximately 8 percent, the range being from nil for the Yorkshire I coal to 27 percent for activated charcoal. Although the losses are smaller than those obtained by plasma ashing, this is not surprising since during the latter process all the carbonaceous matter is destroyed. However, the results do show the same trend as indicated in Figure 4.11.

TABLE 4.38

Average moisture, ash, chlorine and plasma ash contents with chlorine loss on plasma ashing of selected impregnated samples (air-dried basis)

Sample No.	Impregnated sample	Moisture % m/m	Ash % m/m	Total chlorine % m/m	Added chlorine % m/m	Plasma ash % m/m	Chlorine in plasma ash % m/m	Chlorine in plasma ash (air-dried coal basis) % m/m	Added chlorine lost %	Total nitrogen (air-dried coal) % m/m
13	Thoresby High Hazles coal	7.3	9.8	3.23	2.31	13.0	17.3	2.25	3	1.45
14	Thoresby Top Hard coal	5.6	5.2	4.51	3.69	9.8	35.5	3.48	6	1.38
15	Thoresby High Hazles leached coal	7.6	8.2	2.87	2.29	10.8	17.0	1.84	20	N D
16	Thoresby Top Hard leached coal	6.3	7.6	4.98	4.37	13.1	27.1	3.55	19	N D
17	Manvers (6645D) coal	1.8	6.1	2.36	2.18	11.4	16.3	1.86	15	N D
18	Yorkshire I coal	1.4	5.5	2.53	2.19	8.8	19.1	1.68	23	N D
19	Yorkshire II coal	0.8	2.3	2.46	2.41	7.4	23.9	1.77	27	N D
20	Daw Mill (7140D) coal	5.1	9.9	2.17	1.97	14.9	10.7	1.59	19	N D
21	Russian Anthracite coal	4.4	7.5	2.18	2.14	10.3	13.1	1.35	37	N D
22	German Brown coal	14.6	5.2	3.72	3.68	12.3	25.2	3.10	16	N D
23	Activated charcoal	31.0	8.9	9.03	8.95	10.0	45.6	4.56	49	N D
24	Graphite	5.6	14.2	9.30	9.30	16.4	54.2	8.88	5	1.17

N D = Not determined

TABLE 4.39

Loss of chlorine from impregnated selected samples heated in an air oven @ 210 ± 5°C for 16 days

Sample No.	Impregnated sample	Total chlorine % m/m	Added chlorine % m/m	Average chlorine content after heating @ 210 ± 5°C for 16 days % m/m	Average chlorine content after heating the un-treated samples @ 210 ± 5°C for 16 days % m/m	Estimated added chlorine lost % m/m (based upon loss from untreated coal)	Impregnated chlorine lost %
13	Thoresby High Hazles coal	3.23	2.31	2.38	0.12	0.05	2
14	Thoresby Top Hard coal	4.51	3.69	3.72	0.10	0.07	2
15	Thoresby High Hazles leached coal	2.87	2.29	2.17	0.06	0.18	8
16	Thoresby Top Hard leached coal	4.98	4.37	4.10	0.06	0.33	8
17	Manvers (6645D) coal	2.36	2.18	2.14	0.02	0.06	3
18	Yorkshire I coal	2.53	2.19	2.27	0.02	nil	nil
19	Yorkshire II coal	2.46	2.41	2.30	< 0.02	0.11	5
20	Daw Mill (7140D) coal	2.17	1.97	1.83	0.03	0.17	9
21	Russian Anthracite coal	2.18	2.14	1.94	< 0.02	0.20	9
22	German Brown coal	3.72	3.68	3.00	< 0.02	0.68	18
23	Activated charcoal	9.03	8.95	6.58	0.05	2.42	27
24	Graphite	9.30	9.30	8.98	0.02	0.32	3

Figure 4.11 Loss of impregnated chlorine with heating at 210 ± 5°C and plasma ashing of selected samples

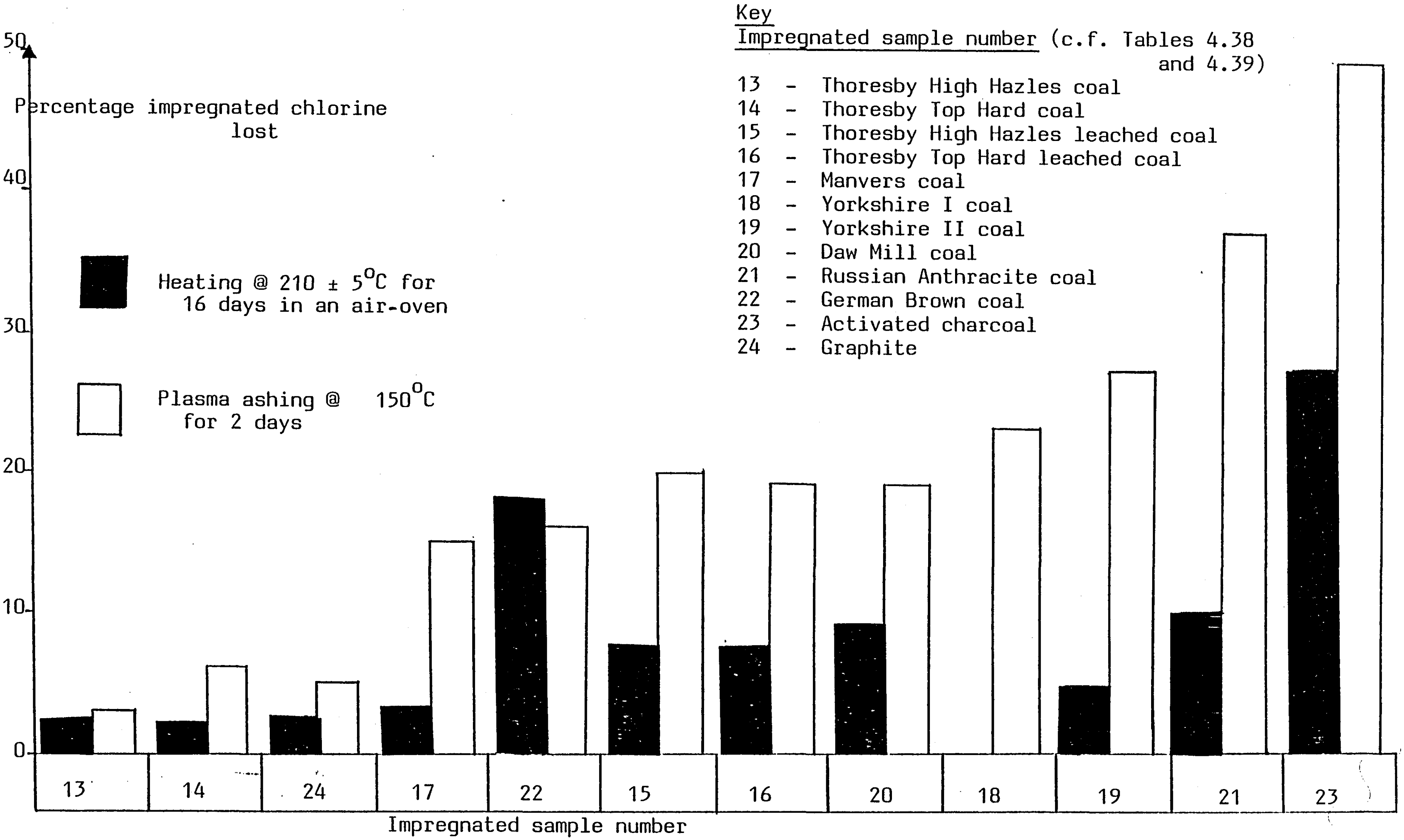


TABLE 4.40

SEM/EDXA of original and impregnated selected samples (air-dried basis)

Element determinations	Cl % m/m		S % m/m		Si % m/m		Al % m/m		Fe % m/m		Ti % m/m		Ca % m/m		Mg % m/m		Na % m/m		K % m/m		Total element comp. %	Calculated ash % from SEM/EDXA (Chapter 3)	Actual 815°C ash %
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2			
Original samples																							
Thoresby High Hazles	0.91	0.89	1.01	1.08	1.99	1.94	1.45	1.53	0.30	0.40	<0.08	<0.08	0.25	0.28	<0.10	<0.10	0.32	0.39	0.37	0.33	6.82 6.77	13.2	8.6
Thoresby Top Hard	0.83	0.82	0.77	0.85	0.80	0.80	0.80	0.78	0.10	0.10	<0.08	<0.08	0.16	0.17	<0.10	<0.10	0.27	0.33	0.07	0.07	3.97 3.83	6.2	4.3
Thoresby High Hazles leached	0.58	0.59	0.83	0.80	1.09	1.09	0.88	0.90	0.21	0.17	0.11	<0.08	0.09	<0.08	<0.10	<0.10	0.13	0.22	0.08	0.07	4.01 4.00	7.1	7.6
Thoresby Top Hard leached	0.60	0.59	0.79	0.80	1.09	1.02	0.92	0.86	0.17	0.15	<0.08	0.11	0.13	0.09	<0.10	0.10	0.17	0.22	0.07	0.07	3.98 3.98	7.0	6.3
Manvers (6645D)	0.21	0.22	1.23	1.27	0.71	0.80	0.57	0.64	0.53	0.46	<0.08	<0.08	<0.08	<0.08	<0.10	<0.10	<0.12	<0.12	0.07	0.07	3.46 3.65	5.7	4.4
Yorkshire I	0.33	0.33	0.99	0.87	0.82	0.81	0.60	0.60	0.27	0.26	<0.08	<0.08	<0.08	<0.08	<0.10	<0.10	<0.12	<0.12	0.07	0.07	3.28 3.19	5.4	4.2
Yorkshire II	0.10	0.11	0.62	0.66	0.33	0.37	0.24	0.30	<0.10	<0.10	<0.08	<0.08	<0.08	<0.08	<0.10	<0.10	<0.12	<0.12	0.07	0.07	1.46 1.66	2.2	1.8
Daw Mill (7140D)	0.20	0.25	1.18	1.10	1.33	1.44	1.20	1.11	0.41	0.33	<0.08	<0.08	<0.08	<0.08	0.13	0.17	0.15	0.23	0.12	0.11	5.51 5.38	7.4	9.0
Russian Anthracite	0.15	0.09	1.62	1.79	1.09	1.28	0.71	1.58	1.15	1.20	<0.08	<0.08	0.30	0.44	<0.10	<0.10	<0.12	<0.12	0.07	0.07	5.45 5.85	10.4	6.8
German Brown	0.10	0.14	<0.10	<0.10	<0.08	<0.08	0.12	0.15	<0.10	<0.10	<0.08	<0.08	<0.08	<0.08	<0.10	<0.10	<0.12	<0.12	0.07	0.07	0.35 0.45	1.0	4.1
Activated Charcoal +	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Graphite *	0.05	0.08	<0.10	<0.10	<0.10	<0.10	0.33	0.46	0.11	0.16	<0.08	<0.08	<0.08	<0.08	<0.10	<0.10	<0.12	0.12	0.25	0.37	0.84 1.43	2.9	0.3
Impregnated samples																							
Thoresby High Hazles	1.62	1.51	0.82	0.79	1.33	1.34	1.01	1.07	0.21	0.23	<0.08	<0.08	0.11	<0.08	<0.10	<0.10	1.04	1.04	0.19	0.25	6.45 6.35	11.0	9.8
Thoresby Top Hard	1.81	1.90	0.73	0.75	0.66	0.69	0.66	0.68	0.10	0.13	<0.08	<0.08	<0.08	<0.08	<0.10	<0.10	1.06	0.95	<0.07	0.07	5.17 5.20	7.0	5.2
Thoresby High Hazles leached	1.47	1.61	0.77	0.75	1.26	1.26	0.99	1.00	0.21	0.25	<0.08	<0.08	<0.08	<0.08	<0.10	<0.10	1.13	1.07	0.20	0.21	6.18 6.27	10.7	8.2
Thoresby Top Hard leached	1.70	2.00	0.77	0.82	1.01	1.17	0.88	0.87	0.17	0.11	<0.08	<0.08	<0.08	<0.08	<0.10	<0.10	0.99	1.04	0.10	0.10	5.20 5.80	7.9	7.6
Manvers (6645D)	1.19	1.04	1.12	1.06	0.68	0.61	0.54	0.55	0.45	0.34	<0.08	<0.08	<0.08	<0.08	<0.10	<0.10	0.77	0.77	0.09	0.10	4.88 4.56	6.9	6.1
Yorkshire I	1.20	1.05	0.63	0.92	0.42	0.87	0.32	0.56	0.11	0.33	<0.08	<0.08	<0.08	<0.08	<0.10	<0.10	0.90	0.60	<0.07	<0.07	3.81 4.56	6.4	5.5
Yorkshire II	1.15	1.23	0.61	0.58	0.34	0.35	0.30	0.28	<0.10	<0.10	<0.08	<0.08	<0.08	<0.08	<0.10	<0.10	0.82	0.86	<0.07	<0.07	3.50 3.56	4.7	2.3
Daw Mill (7140D)	1.18	1.37	1.01	0.96	1.41	1.38	1.20	1.29	0.48	0.36	0.13	<0.08	0.60	0.65	0.13	0.13	0.90	0.95	0.18	0.16	7.22 7.35	13.8	9.9
Russian Anthracite	2.22	2.30	0.40	0.38	0.36	0.26	0.27	0.19	0.21	0.23	<0.08	<0.08	<0.08	<0.08	<0.10	<0.10	1.67	1.91	0.10	<0.07	5.34 5.35	7.3	7.5
German Brown	2.16	1.84	0.11	0.10	<0.08	<0.08	0.15	0.09	<0.10	<0.10	<0.08	<0.08	0.10	0.11	0.11	<0.10	3.97	3.62	<0.07	<0.07	6.70 5.89	11.4	5.2
Activated Charcoal+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Graphite *	10.15	11.44	<0.10	<0.10	<0.08	<0.08	<0.08	<0.08	<0.10	<0.10	<0.08	<0.08	<0.08	<0.08	<0.10	<0.10	7.22	8.00	<0.07	0.07	17.80 19.91	21.9	-

* Made up with Boric Acid to form coherent disc   + Would not form coherent disc

TABLE 4.41

SEM/EDXA of original selected samples used in impregnation tests (air-dried basis)

Sample No.	Sample	Average Chlorine % m/m	Average Sodium % m/m	Average Sulphur % m/m
1	Thoresby High Hazles coal	0.90	0.36	1.05
2	Thoresby Top Hard coal	0.83	0.30	0.81
3	Thoresby High Hazles leached coal	0.59	0.18	0.82
4	Thoresby Top Hard leached coal	0.60	0.20	0.80
5	Manvers (6645D) coal	0.22	< 0.12	1.25
6	Yorkshire I coal	0.33	< 0.12	0.93
7	Yorkshire II coal	0.11	< 0.12	0.64
8	Daw Mill (7140D) coal	0.22	0.19	1.14
9	Russian Anthracite coal	0.12	< 0.12	1.71
10	German Brown coal	0.12	< 0.12	< 0.10
11	Activated Charcoal	-	-	-
12	Graphite	0.06	< 0.12	< 0.10

SEM/EDXA of impregnated selected samples (air-dried basis)

13	Thoresby High Hazles coal	1.57	1.04	0.81
14	Thoresby Top Hard coal	1.86	1.01	0.74
15	Thoresby High Hazles leached coal	1.54	1.10	0.76
16	Thoresby Top Hard leached coal	1.85	1.02	0.80
17	Manvers (6645D) coal	1.15	0.77	1.09
18	Yorkshire I coal	1.13	0.75	0.77
19	Yorkshire II coal	1.19	0.84	0.60
20	Daw Mill (7140D) coal	1.22	0.92	0.99
21	Russian Anthracite coal	2.26	1.79	0.39
22	German Brown coal	2.00	3.80	0.11
23	Activated Charcoal	-	-	-
24	Graphite	10.80	7.61	< 0.10

- Not determined

TABLE 4.42

Selected samples - Analysis of 815°C ash

Sample No.	Sample	SiO_2 % m/m	Al_2O_3 % m/m	Fe_2O_3 % m/m	TiO_2 % m/m	CaO % m/m	MgO % m/m	Na_2O % m/m	K_2O % m/m	P_2O_5 % m/m	Mn_3O_4 % m/m	SO_3 % m/m	Cl % m/m	Total % m/m
1	Thoresby High Hazles	42.6	23.0	6.3	1.6	12.9	1.6	5.5	3.8	0.2	0.1	4.3	0.2	101.6
13	Thoresby High Hazles impregnated	39.8	21.9	5.6	1.0	2.1	1.0	22.0	1.3	0.2	0.1	6.4	0.2	101.3
2	Thoresby Top Hard	38.5	34.5	5.4	1.2	6.4	1.5	8.7	0.7	0.2	0.1	4.3	0.2	101.4
14	Thoresby Top Hard impregnated	32.2	24.8	4.3	0.9	2.8	0.7	26.0	0.4	0.2	0.1	9.4	0.7	102.4
3	Thoresby High Hazles leached	44.9	27.1	5.6	0.9	6.8	1.5	5.1	3.7	0.3	0.1	4.6	0.2	100.5
15	Thoresby High Hazles leached impregnated	37.8	24.4	4.9	0.8	2.6	1.0	22.1	1.5	0.3	0.1	4.2	0.2	99.6
4	Thoresby Top Hard leached	44.5	28.7	10.0	1.5	2.8	0.6	7.3	1.7	0.7	0.1	0.5	0.2	98.3
16	Thoresby Top Hard leached impregnated	37.0	21.8	6.9	1.4	1.8	0.4	22.0	0.5	0.2	0.1	9.4	0.7	102.1
5	Manvers (6645D)	41.3	26.4	24.6	1.1	1.0	1.9	1.9	2.8	0.1	0.1	1.2	0.2	102.3
17	Manvers (6645D) impregnated	35.5	24.5	15.8	0.5	0.4	0.6	22.6	1.2	0.1	0.1	1.3	0.3	102.9
6	Yorkshire I	43.0	24.6	24.2	1.8	1.5	1.8	3.2	1.6	0.2	0.1	0.9	0.2	102.8
18	Yorkshire I impregnated	35.6	21.1	8.6	1.0	0.9	0.7	32.8	1.2	0.1	0.1	0.9	0.2	102.9
7	Yorkshire II	43.5	35.2	4.1	1.1	1.7	1.7	8.1	5.0	0.2	0.1	0.2	0.2	100.8
19	Yorkshire II impregnated	35.0	25.9	3.3	1.0	0.8	0.9	31.1	0.9	0.1	0.1	0.2	0.2	99.2
8	Daw Mill (7140D)	43.6	23.0	9.2	1.3	12.7	2.1	1.7	1.6	0.1	0.4	5.2	0.2	100.9
20	Daw Mill (7140D) impregnated	35.8	19.5	8.1	0.7	8.0	1.7	16.9	0.9	0.1	0.3	5.2	0.2	97.2
9	Russian Anthracite	34.3	12.5	31.2	0.7	9.6	2.5	1.9	2.1	0.5	0.3	5.9	0.2	101.5
21	Russian Anthracite impregnated	28.3	10.2	23.6	0.3	4.7	1.9	16.1	0.6	0.3	0.2	5.9	5.1	97.2
10	German Brown	7.4	2.6	12.0	0.6	55.2	8.7	0.7	< 0.1	0.3	0.1	10.4	0.2	97.9
22	German Brown impregnated *	-	-	-	-	-	-	-	-	-	-	-	-	-

* Results invalid - attack of both silica and platinum crucibles.

The anomalous nature of the German brown coal (sample number 22) may be attributed to its high calcium content (see Table 4.42). It is shown later in this chapter (section 4.5.6.2) that calcium oxide has some success in fixing chlorine as calcium chloride at low temperatures (205°C).

The SEM/EDX analyses given in Tables 4.40 and 4.41 show that after impregnation the elemental concentrations, excepting sodium and chlorine, decrease; and that total chlorine analyses on the impregnated samples compared with chemical method results are low, an observation that has been mentioned earlier. The analyses of the samples ashed at 815°C given in Table 4.42 show a range of elemental compositions and it is interesting to note that Russian anthracite retains approximately 5 percent chlorine after ashing at this temperature. The chemical attack on platinum crucibles at 815°C by the German brown coal impregnated sample (number 22) demonstrates the highly corrosive nature of calcium oxide and sodium chloride mixtures.

It should be borne in mind in considering impregnation results that sodium chloride may remain on the surface of coal.

This problem of superficial sodium chloride has prompted the suggestion to use radioactive ^{36}Cl in sodium chloride solution to investigate further the exchange of chlorine in the chlorine-coal reaction. An attempt to perform such experiments is described in a subsequent section.

4.5.5.3 Water extraction of carbonaceous samples before and after impregnation with aqueous sodium chloride

When coal or carbonaceous samples are impregnated with sodium chloride solution a proportion of the chloride added to the coal becomes unstable at low temperature. The fate of the sodium associated with the chloride under these conditions has not yet been established.

Samples of coal and activated charcoal were impregnated using the standard procedure and the chlorine contents of the original and impregnated samples determined by the Eschka method. Subsamples of each (500 mg) were placed in a conical flask (100 cm^3) and distilled water (30 cm^3), plus a few drops of methylated spirit were added. The flask was stoppered and its contents magnetically stirred for 24 hours. The suspension was centrifuged for 30 minutes at 3000 r.p.m. and the supernatant liquid analysed for chloride by Mohr's method[153] and for sodium by flame photometry. The results are given in Table 4.43. The SCR ratio allowing for the water soluble sodium and chlorine originally present in the coals can be seen to be unity for the impregnated samples, suggesting that sodium remains in the coal after impregnation, probably as adsorbed ions, and both sodium and labile chloride ions thus introduced are accessible to subsequent water-leaching.

This conclusion may be used to further the arguments for the suggestion that sodium chloride solution resides in the coal's microstructure[143]. However this theory explains neither the low temperature instability of chlorine but not sodium, nor the different water extraction characteristics of chlorine compared with sodium. The most likely explanation is that chloride ions are adsorbed onto reactive sites within coal's microstructure producing a loose ionic bond, unassociated with sodium. The physical and chemical evidence so far established suggests that the vast majority of chlorine is present in coal in this form.

4.5.5.4 Vaccum impregnation of coals using ^{36}Cl in sodium chloride solution as a radioactive tracer

The radiochemistry facilities at Sheffield City Polytechnic have been used to impregnate four coal samples simultaneously with radioactive ^{36}Cl in a 20 percent sodium chloride solution. ^{36}Cl is an emitter of negative beta particles (E_{max} = 0.714 MeV) with a long half-life of 3×10^5 years.

TABLE 4.43

Water extraction of selected carbonaceous samples before and after impregnation with NaCl (aq)

Sample No. (cf Tables 4.38 and 4.39)	Sample	Water soluble analyses % m/m						SCR*
		Sodium	Sodium -(control)	Impregnated sodium (chlorine equivalent)	Original sodium (chlorine equivalent)	Chlorine	Chlorine -(control)	
1	Thoresby High Hazles original (control)	0.25	-	-	0.39	0.78	-	0.50
13	Thoresby High Hazles impregnated	2.16	1.91	2.95	-	3.73	2.95	1.00
2	Thoresby Top Hard original (control)	0.13	-	-	0.20	0.48	-	0.42
14	Thoresby Top Hard impregnated	3.12	2.99	4.62	-	5.00	4.52	1.02
3	Thoresby High Hazles leached original (control)	0.09	-	-	0.13	0.42	-	0.31
15	Thoresby High Hazles leached impregnated	1.65	1.56	2.41	-	2.88	2.46	0.98
15	Thoresby High Hazles leached impregnated	2.10	2.01	3.10	-	3.49	3.07	1.01
4	Thoresby Top Hard leached original (control)	0.09	-	-	0.13	0.36	-	0.36
16	Thoresby Top Hard leached impregnated	2.52	2.43	3.75	-	3.96	3.60	1.04
16	Thoresby Top Hard leached impregnated	3.24	3.15	4.80	-	5.00	4.64	1.03
10	German Brown coal	0.02	-	-	0.02	0.04	-	0.50
22	German Brown impregnated coal	2.63	2.61	4.03	-	4.20	4.16	0.97
11	Untreated activated charcoal	0.01	-	-	-	0.12	-	0.13
11	Untreated activated charcoal	0.01	-	-	-	0.12	-	0.13
23	Impregnated activated charcoal	5.76	-	-	-	9.00	-	0.99
23	Impregnated activated charcoal	6.00	-	-	-	9.12	-	1.02

* SCR = $\frac{\text{Water soluble sodium (chlorine equivalent)}}{\text{Water soluble chlorine}}$

Small quantities of coal ($\sim$500 mg) were impregnated with ^{36}Cl in 20 percent sodium chloride solution under the same vacuum conditions as described previously (section 4.5.5.1). A photograph of the apparatus used for evacuation is shown in Plate 4.9. The vacuum pump of the Nanotech Plasmaprep 100 plasma ashing unit was used to evacuate the glassware. After filtration and air drying, increments of approximately 100 mg of the radioactive samples were counted using an end-window geiger detector. These increments were then plasma ashed for 48 hours to constant weight with frequent stirring to ensure complete decarbonisation of the sample. The plasma ash was counted under the same geometry conditions as those for the coal and the percentage change in radioactivity calculated. In addition the radioactive sodium chloride solution was counted using a liquid cell geiger counter before and after impregnation of coal. The procedure was repeated on the same four coal samples to give duplicates, using the filtered radioactive solution from the first impregnation test.

The results for the first impregnation test are given in Table 4.44. The second test results have been rejected from further discussion because of loss of vacuum prior to impregnation. The results for the first test are inconsistent; of ten samples plasma ashed, five demonstrated a loss in radioactivity whilst five showed an apparent gain in radioactivity. The poor repeatability for the determination of the percentage plasma ash is attributed to inhomogeneity and insufficient air-drying of the coal samples.

The apparent increase in radioactivity of the sodium chloride solution after impregnation at first seems surprising but this can be explained by sorption of water molecules by coal under the conditions of impregnation. Attempts to relate the percentage increase in solution count rate to the BS percentage moisture holding capacity of the coals[149] were unsuccessful. The ultimate vacuum requirement for this BS test is at least two orders of magnitude lower than those used for the impregnation experiment.

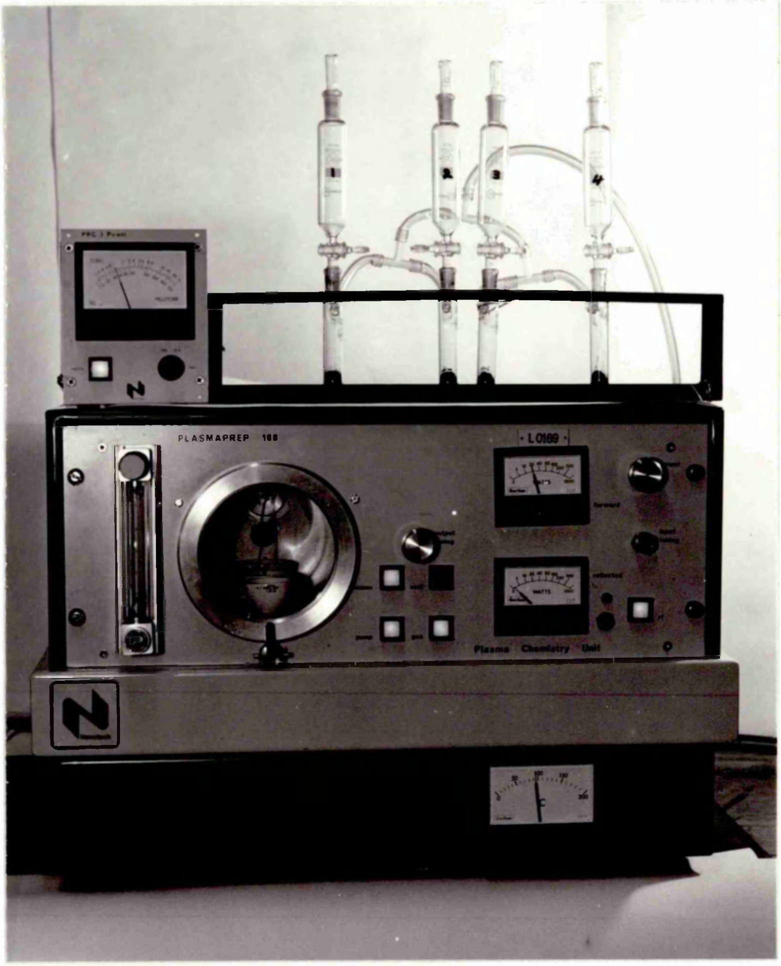
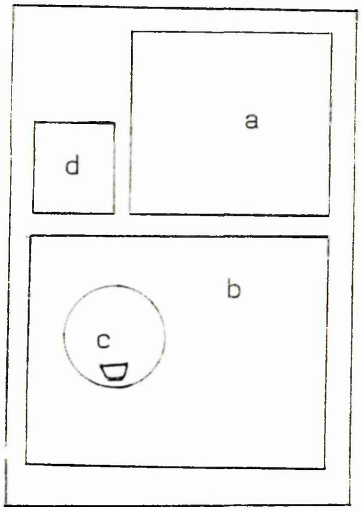


PLATE 4.9

Apparatus used to impregnate coals with radioactive chlorine (Glassware) and Nanotech Plasmaprep 100 plasma ashing unit



Key

a Pyrex impregnation glassware

b Nanotech Plasmaprep 100 instrument

c Plasma ashing chamber showing ash crucibles

d Pirani vacuum gauge

TABLE 4.44

First impregnation test - counting results before and after plasma ashing

SOLIDS

Sample No.	Coal	Plasma ash % m/m	Corrected Cpm before ashing	Corrected Cpm after ashing	Change %	Average change %
1	Thoresby Top Hard	10.25	17977	17411	- 3.2	- 6.5
		11.30	16275	14687	- 9.8	
2	Thoresby High Hazles	11.24	10141	7804	- 23.1	- 19.8
		9.93	10083	8423	- 16.5	
3	Thoresby Top Hard leached	13.93	14473	18138	+ 25.3	+ 46.8
		17.25	19192	25311	+ 32.0	
		7.16	10082	18461	+ 83.0	
4	Thoresby High Hazles leached	14.22	11073	13346	+ 20.5	+ 1.1
		11.85	8861	9693	+ 9.4	
		7.74	2867	2107	- 26.5	

SOLUTIONS

Original sodium chloride solution 25353 Cpm

	Cpm	Increase %
Filtered solution from coal sample 1	29350	15.8
Filtered solution from coal sample 2	31857	25.7
Filtered solution from coal sample 3	30828	21.6
Filtered solution from coal sample 4	28190	11.2

The problems causing inconsistency in results for counting solid radioactive coal and ash samples are two-fold; firstly the very high proportion of sodium chloride that does not react within the coal microstructure but remains on the coal surface and secondly and probably more importantly, the difference in β^- absorption by coal and coal ash matrices.

It is possible that these problems may be overcome by using a more dilute sodium chloride solution for impregnation and fusion of radioactive coal and coal ash with Eschka mixture and subsequent release of the ^{36}Cl into solution using nitric acid.

Summarising the behaviour of sodium chloride added to coal, the evidence here and in section 4.4.7 supports a hypothesis that it will retain its 'inorganic' properties as a stable crystalline solid unless it can find its way into the micropore structure of the coal. If this is accomplished by impregnation with a solution under vacuum at least 20 percent will be converted to a labile form. The proportion may be much higher, as some if not all of the balance of 80 percent exists as a superficial layer of salt left by evaporation of the water. This labile form of chlorine is not bonded to sodium or nitrogen in coal.

4.5.6 Retention of chlorine in coal as chloride by the addition of chemical fixatives

The volatile nature of chlorine present in coal is well established. The next four sections discuss the possibility of treating coal with chemical additives in order to fix the evolved chlorine as a stable inorganic chloride.

4.5.6.1 Addition of potassium carbonate

The idea that an alkali such as solid ground potassium carbonate added to coal might increase the chlorine retention in the residue after plasma ashing via reaction with hydrogen chloride was examined. Ground potassium carbonate (5 percent m/m) was added to a sample of Thoresby High Hazles coal and mixed using a spatula. This admixture was then subjected to plasma ashing for a period of 3 days to ensure complete decarbonisation of the sample. The residue was analysed for chlorine content and examined using the SEM/EDXA equipment.

The results are given in Table 4.45

A slight increase in retention of chlorine was observed, but no potassium chloride crystallites could be identified with the SEM/EDX equipment. Iapalucci et al[154] in their work on chlorine in coal combustion using a pilot plant pulverised fuel combustor-rig found an increase in chlorine retained in coal from 4.4 - 18.9 percent on addition of 1.6 percent by weight of potassium carbonate. This fundamental reaction to form a salt would be expected to occur more readily provided the coal and carbonate were intimately mixed, say in a fluidised bed environment.

4.5.6.2 Addition of calcium oxide

It seems reasonable to suggest that calcium oxide ground to $< 45\ \mu m$ and added to coal may fix some of the chlorine as calcium chloride during low temperature incineration. This was tested using samples of Thoresby Top Hard and High Hazles coals with added amounts of calcium oxide at concentrations of 5.0%, 1.0%, 0.5% and 0.1% m/m. Four 2g samples were prepared for each coal at the specified concentrations and placed in glazed porcelain crucibles. These were then heated in an air-oven at 205 ± 5°C for 16 days. A control sample without any addition of calcium oxide was also heated under the same conditions for 16 days. After this period two samples were retained, one for SEM/EDX examination and the other for Eschka chlorine determination. The third sample was subjected to further heating at 500°C for 2½ hours and the fourth to ashing at 815°C for 1½ hours.

Using the SEM/EDXA equipment crystallites of calcium chloride were identified in all samples heated at 205 ± 5°C where calcium oxide additions had been made. The amount increased as the percentage calcium oxide addition increased. An example of such a crystallite can be seen in Plate 4.10.

TABLE 4.45

Retention of chlorine in plasma ashing with potassium carbonate

Thoresby coal	Chlorine content % m/m	Chlorine retained in plasma ash based on original coal % m/m	Percentage of original chlorine retained
High Hazles	0.91	0.03	3.3
High Hazles + K_2CO_3(S)	0.89	0.09	10.1

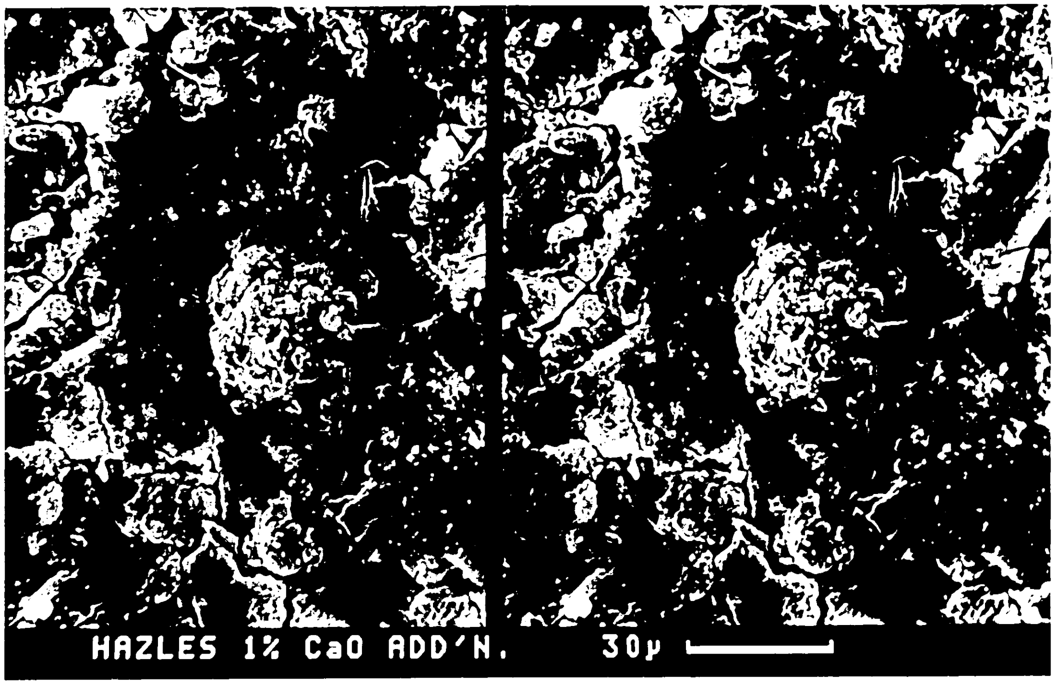


PLATE 4.10 (a)

Scanning Electron Micrograph

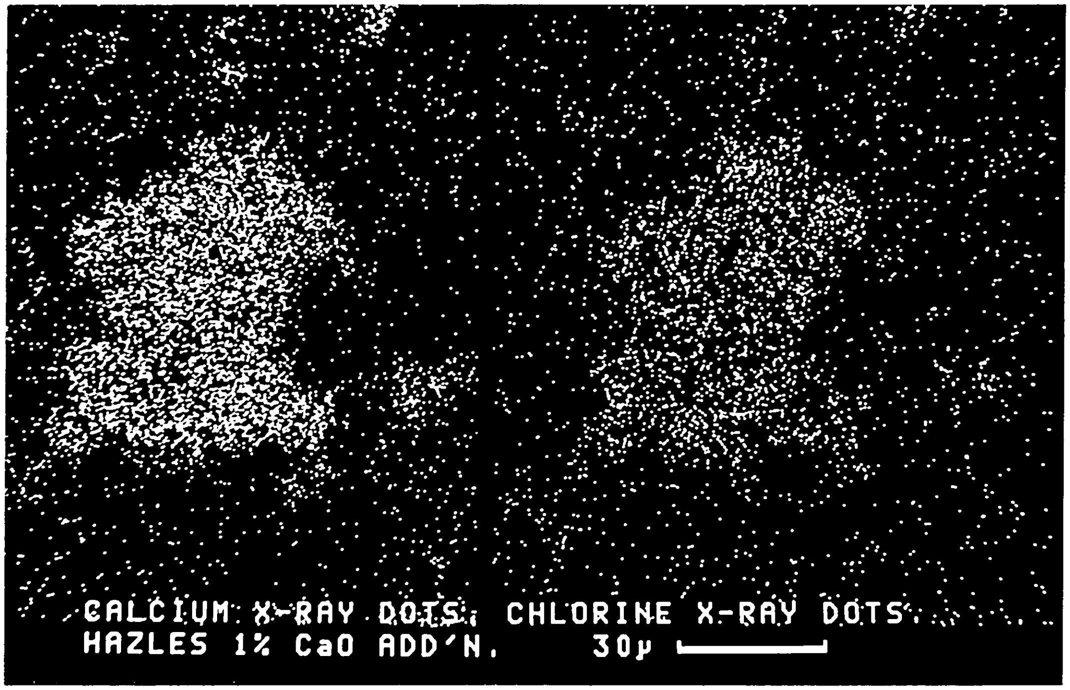


PLATE 4.10 (b)

As above showing calcium and chlorine X-ray distribution

Chlorine contents of samples heated at 205°C, 500°C and ashed at 815°C were determined by the Eschka method and the results are given in Table 4.46. These results show a chlorine retention of approximately 75% and 45% at 205 ± 5°C for 5% and 1% m/m calcium oxide additions respectively. However, concentrations of calcium oxide addition of 0.5% and 0.1% m/m gave chlorine retentions of 30% and 20% respectively. The chlorine retention for these coals without any calcium oxide addition was about 12%.

Further heating after fixation at 205 ± 5°C resulted in decomposition of the calcium chloride. Appreciable chlorine retentions were only found for the 5% calcium oxide additions after further heating at 500°C and 815°C.

Although the results show promise for the low temperature (205 ± 5°C) fixation of chlorine as calcium chloride, calcium chloride (m.pt. 772°C) is unstable at the higher temperatures likely to be encountered in practical combustion processes. High calcium concentrations would contribute to further corrosion problems by the formation of alkali-bonded deposits in boiler tubes.

4.5.6.3 Addition of iron powder

Fireside furnace corrosion can be due to the reaction with steel linings of hydrogen chloride under a reducing atmosphere.[134,135] A suggestion that iron powder mixed with coal prior to combustion may preferentially react with hydrogen chloride and so reduce corrosion was investigated.

Duplicate samples of Thoresby Top Hard and High Hazles coals were prepared with iron powder (< 212 μm) additions to give concentrations of 5%, 1%, 0.5% m/m as described in 4.5.6.2. These samples together with controls having no additions were heated in an air-oven at 205 ± 5°C for 16 days followed by Eschka determination of chlorine contents. The results are given in Table 4.47.

TABLE 4.46

Retention of chlorine in coal by the addition of calcium oxide

Coal/original total chlorine % m/m	Calcium oxide addition % m/m	Retained chlorine in coal % m/m after 16 days @ 205 ± 5°C	Percentage of original chlorine retained	Retained chlorine after heating @ 500°C for 2½ hours % m/m	Percentage of original chlorine retained @ 500°C for 2½ hours	Retained chlorine after ashing @ 815°C for 2½ hours % m/m	Percentage of original chlorine retained @ 815°C for 2½ hours
Thoresby Top Hard 0.81	5.0	0.60	74	0.45	56	0.22	27
	1.0	0.38	47	0.11	14	0.02	< 2.5
	0.5	0.23	28	< 0.02	< 2.5	0.02	< 2.5
	0.1	0.15	19	0.06	7	0.02	< 2.5
	nil	0.10	12	< 0.02	< 2.5	0.02	< 2.5
Thoresby High Hazles 0.87	5.0	0.66	76	0.58	67	0.19	22
	1.0	0.35	40	0.16	18	0.06	7
	0.5	0.29	33	0.09	10	0.02	< 2.5
	0.1	0.17	20	0.05	6	0.02	< 2.5
	nil	0.11	12	< 0.02	< 2.5	0.02	< 2.5

TABLE 4.47

Retention of chlorine in coal by addition of iron powder

Coal/original total chlorine % m/m	Iron powder addition % m/m	Retained chlorine in coal after 16 days @ 205 ± 5^{O}C % m/m	Percentage of original chlorine retained
Thoresby Top Hard 0.84	nil	0.20	24
	0.5	0.20	24
	1.0	0.22	27
	5.0	0.25	30
Thoresby High Hazles 1.02	nil	0.22	21
	0.5	0.22	21
	1.0	0.22	21
	5.0	0.23	23

The retention was increased by a maximum of 6% which clearly shows that under these conditions an insignificant amount of chlorine is 'fixed' as chloride.

This preliminary test does not match the conditions under which fireside furnace corrosion takes place in practice i.e. under reducing conditions and higher temperatures. Hence the results may be those expected under oxidising conditions, and further tests in conditions more akin to those found in practice may give encouragement.

4.5.6.4 Addition of molar calcium acetate solution

Recently reported studies using molar calcium acetate treatment of coals to fix sulphur on combustion have been reported as successful.[164] A similar treatment to fix chlorine in coal was investigated.

Samples of Thoresby Top Hard and High Hazles coals (15g) ground to <45 µm were soaked in molar calcium acetate solution for 48 hours followed by drying at 110°C for 3 hours. From this treated and homogenised sample three 1g increments of each coal were heated in the following way:

1. In an air-oven at 205 ± 5°C for 16 days.
2. In a muffle furnace at 500°C for 3 hours.
3. In a muffle furnace at 815°C for 2 hours.

Two of the 1g increments were used for Eschka chlorine determinations and the results are listed in Table 4.48. The third increment was examined for crystallites of calcium chloride using the SEM/EDX mapping facility.

The results indicate a very marginal increase in chlorine retention when the treated coals were heated at 205 ± 5°C compared with untreated coals. However, at the two higher temperatures some stability of calcium chloride is shown. The reason may be that calcium in solution has been bound to the coal surface by a cation exchange mechanism. Thus the chlorine evolved on heating is more strongly held to the coal surface by reaction with the calcium, which might have penetrated the pore structure to some extent.

TABLE 4.48

Retention of chlorine in coal by treatment with molar calcium acetate solution

	Thoresby Top Hard		Thoresby High Hazles	
Original total chlorine % m/m	0.81		0.87	
	Calcium acetate treated	Untreated	Calcium acetate treated	Untreated
Average retained chlorine after 16 days @ 205 ± 5°C % m/m	0.10	0.09	0.13	0.11
Percentage of original chlorine retained	12	11	15	12
Average retained chlorine after 3 hours @ 500°C % m/m	0.10	< 0.02	0.10	< 0.02
Percentage of original chlorine retained	12	2.5	11	< 2.5
Average retained chlorine after 2 hours @ 815°C % m/m	0.03	< 0.02	0.03	< 0.02
Percentage of original chlorine retained	4	2.5	3	< 2.5

In the case of sulphur retention in coal by calcium acetate treatment,[164] it was reported that bituminous coals needed to be mildly oxidised at 205 ± 10°C in order to ion exchange calcium[165] before soaking in ammoniated calcium acetate for 48 hours. Obviously these samples could not be preheated in a similar way as this would result in loss of chlorine. This absence of a coal oxidation pretreatment stage could be a major factor in the poor total chlorine retention found in this experiment. Examination of the residues after heating by SEM/EDXA showed many areas of calcium concentration. However chlorine was not seen to be associated with these areas, possibly due to the calcium chloride produced being of a particle size less than 1 μm.

4.6 CONCLUSIONS

The SEM/EDXA instrumental technique has been used to show the absence of metal chloride crystallites in coal, other than in trace amounts, the exception being fusain-enriched sections. The results of EDX analysis of coal powders, with and without additions of sodium chloride, has suggested that chlorine is chiefly present in coal in one bonding form.

Chlorine in coal is very labile to heat treatment, hydrogen chloride mainly being evolved at temperatures above 170°C in both air and nitrogen atmospheres. Sulphur in coal appears not be involved in this mechanism of chlorine release. The chlorine loss/time curve shows a rapid initial loss of chlorine that is characteristic of the simultaneous and independent decomposition of a mixture of materials. The loss of chlorine on heating is dependent on the particle size of the coal, increasing with decreasing particle size.

Heating coal in air to remove chlorine produces a significant loss of calorific value (CV); this loss of CV is reduced when heating occurs in nitrogen or a simulated flue gas, although the chlorine losses are similar.

There is no evidence for the release of nitrogen in the mechanism of chlorine release when coal is heated. However, traces of five organic chlorine compounds have been tentatively identified in the 205°C thermal decomposition products from coal. Plasma ashing of coal in oxygen at temperatures below 150°C removes all the chlorine. A method for the determination of 'organic' chlorine in coal has been successful in differentiating between sodium chloride and trichlorophenol but is not applicable to coal because all the chlorine is evolved on heating as hydrogen chloride without using a catalyst.

A standard test to assess the aqueous chlorine leachability of coal seams has been shown to be reproducible analytically but due to variation in proportions of lithotypes in a seam from one place to another, utility in the classification of coals is limited. However, this work confirms that chlorine can be quantitatively removed by aqueous leaching of finely ground coal but that it is not stoichiometrically associated with water soluble sodium or other alkali cations as shown by SCR and TCCR values.

Sodium chloride has been identified in roof and floor strata associated with coal seams and fusain enriched coal sections. This lends credence to the suggestion that chlorine has been deposited in coal after the rank has been established, (epigenesis) via hypersaline strata waters.

Low chlorine coals have been found to contain low water soluble sodium contents. Water soluble sodium in excess of water soluble chloride was therefore not established.

At a particle size of less than 212 µm no anion-exchange property of the chlorine to coal bond has been found.

The chlorine present in finely ground coal is insoluble in diethyl ether and is not chemically attacked by sodamide in boiling xylene, indicating that chlorine in coal is not bound covalently and does not participate in a nucleophilic substitution reaction.

A ground coal sample, after soaking in perklone, ($CCl_2 = CCl_2$) boiling point 121°C, was found to retain approximately fifty percent more chlorine after subsequent heating above the b.pt. of perklone for 24 hours, than a sample of untreated coal heated under the same conditions. This test shows that the coal substance provides some holding mechanism for the chlorinated solvent.

The different abilities of coal sections to absorb lead nitrate solution and subsequent X-ray radiographic studies, have been used to estimate values of mean pore radii and chlorine leachability of coal samples. The results obtained have been compared to results obtained using the standard leaching test for the same coals. Despite the complex nature of the pore structure in coal, the X-ray radiographic test gives a rapid guide to a coal subsections leachability and a clear picture of the macrofissuring present. Utility is however limited by the previously mentioned variation in proportions of lithotypes in a seam from one place to another.

High vacuum impregnation of coal with aqueous sodium chloride has shown that chlorine is not bonded to nitrogen in coal. The same test shows that a proportion of the added chlorine becomes unstable at low temperatures and on plasma ashing below 150°C. Water extractions of aqueous sodium chloride impregnated coal, has demonstrated that sodium remains in coal after impregnation, probably as adsorbed ions. The use of ^{36}Cl (in aqueous sodium chloride) as a radiotracer in the vacuum impregnation of coal has been unsuccessful, mainly because of the very high proportion of surface sodium chloride containing radioactive chlorine and secondly, the difference in β^- absorption by coal and coal ash matrices. It has been proven that sodium chloride retains its 'inorganic' properties as a stable crystalline solid unless it can find its way into the micropore structure of the coal. If this is accomplished by impregnation with sodium chloride solution under vacuum, then a proportion of the sodium chloride will be converted to a labile form.

Additions of chemicals to coal in order to fix the chlorine evolved at low temperatures as organic chlorides has met with mixed success. Calcium oxide is the most successful but the resulting calcium chloride is unstable at the higher temperatures likely to be found in coal combustion processes. High calcium concentrations would contribute to corrosion problems by the formation of alkali-bonded deposits in boiler tubes.

Summarising all the work, the likelihood is that chlorine is present in one form, uniformly distributed and linked ionically to the coal substance but sufficiently labile to be evolved mainly as hydrogen chloride at temperatures above about 170°C. It has no particular relationship with nitrogen, sodium or other alkali/alkaline earth metals.

At this stage, it is clear that some long-held views concerning the form in which chlorine is bound in coal have been disproved.

The accurate and precise instrumental analysis of coal is still the main aim of this study. However, this chapter clearly illustrates that knowledge of the mode of occurrence of deleterious elements is important, if coal scientists and fuel technologists are to make full use of analytical results in modern utilisation and environmental studies.

APPENDIX 4.1

SEM/EDXA of selected coals (air-dried basis)

FLORENCE ROWHURST

Element			Element % m/m	Average % m/m	BS 1016 value [149] % m/m
Cl	0.98	0.97	0.98	0.98	0.99
S	0.49	0.53	0.50	0.51	0.59
Si	0.79	0.79	0.85	0.81	1.11
Al	0.89	0.83	0.91	0.88	1.01
Fe	0.32	0.30	0.27	0.30	0.47
Ca	0.43	0.50	0.46	0.46	0.82
Mg	0.10	< 0.10	< 0.10	< 0.10	0.22
Na	0.23	0.18	0.21	0.21	0.14
K	< 0.10	< 0.10	< 0.10	< 0.10	0.02
Ti	< 0.10	< 0.10	< 0.10	< 0.10	0.03
Total	4.35	4.31	4.33	4.33	

CORTONWOOD/SILKSTONE

Cl	0.12	0.12	0.11	0.12	0.11
S	0.95	1.02	0.97	0.98	1.50
Si	0.65	0.79	0.72	0.72	1.27
Al	0.54	0.68	0.62	0.61	1.00
Fe	0.44	0.43	0.45	0.44	0.90
Ca	< 0.10	< 0.10	< 0.10	< 0.10	0.04
Mg	< 0.10	0.11	< 0.10	< 0.10	0.04
Na	< 0.10	< 0.10	< 0.10	< 0.10	0.04
K	0.10	0.15	0.13	0.13	0.17
Ti	< 0.10	< 0.10	< 0.10	< 0.10	0.03
Total	2.92	3.30	3.10	3.11	

APPENDIX 4.1 (continued)

SOUTH DURHAM 'C' SEAM

Element			Element % m/m	Average % m/m	BS 1016 value[149] % m/m
Cl	0.25	0.24	0.24	0.24	0.25
S	0.57	0.61	0.63	0.60	0.92
Si	0.35	0.34	0.37	0.35	0.39
Al	0.29	0.33	0.35	0.32	0.27
Fe	0.28	0.23	0.15	0.22	0.33
Ca	< 0.10	< 0.10	< 0.10	< 0.10	0.07
Mg	< 0.10	< 0.10	< 0.10	< 0.10	0.04
Na	< 0.10	0.18	0.14	0.11	0.06
K	< 0.10	< 0.10	< 0.10	< 0.10	0.02
Ti	< 0.10	< 0.10	< 0.10	< 0.10	0.01
Total	1.84	2.07	2.05	1.99	

CADLEY HILL (BRIGHT COAL)

Cl	0.42	0.44	0.43	0.43	0.45
S	1.33	1.34	1.34	1.34	3.02
Si	0.48	0.46	0.52	0.49	0.51
Al	0.43	0.48	0.46	0.46	0.61
Fe	0.64	0.70	0.57	0.63	1.60
Ca	0.28	0.27	0.27	0.27	0.30
Mg	< 0.10	< 0.10	< 0.10	< 0.10	0.11
Na	0.10	0.14	0.10	0.11	0.13
K	< 0.10	< 0.10	< 0.10	< 0.10	0.03
Ti	< 0.10	< 0.10	< 0.10	< 0.10	0.02
Total	3.80	3.95	3.81	3.85	

APPENDIX 4.1 (continued)

CADLEY HILL (DULL COAL)

Element			Element % m/m	Average % m/m	BS 1016 value[149] % m/m
Cl	0.37	0.37	0.37	0.37	0.39
S	1.15	1.28	1.18	1.20	2.33
Si	0.48	0.53	0.49	0.50	0.60
Al	0.40	0.48	0.45	0.44	0.51
Fe	0.46	0.51	0.38	0.45	1.04
Ca	<0.10	0.11	<0.10	<0.10	0.10
Mg	<0.10	<0.10	<0.10	<0.10	0.03
Na	0.19	0.11	0.12	0.14	0.10
K	<0.10	<0.10	<0.10	<0.10	0.02
Ti	<0.10	<0.10	<0.10	<0.10	0.02
Total	3.21	3.51	3.09	3.27	

TILMANSTONE MILYARD

Cl	0.12	0.10	0.10	0.11	0.13
S	0.86	0.82	0.88	0.85	1.50
Si	0.72	0.66	0.71	0.70	0.77
Al	0.67	0.62	0.73	0.67	0.66
Fe	0.25	0.21	0.29	0.25	0.72
Ca	0.10	<0.10	0.10	<0.10	0.13
Mg	<0.10	<0.10	<0.10	<0.10	0.04
Na	0.10	<0.10	0.17	<0.10	0.16
K	<0.10	<0.10	<0.10	<0.10	0.06
Ti	<0.10	<0.10	<0.10	<0.10	0.02
Total	2.94	2.63	3.09	2.87	

APPENDIX 4.1 (continued)

THORESBY TOP HARD

Element			Element % m/m	Average % m/m	BS 1016 value[149] % m/m
Cl	0.81	0.83	0.85	0.83	0.89
S	0.73	0.71	0.73	0.72	0.87
Si	2.43	2.53	2.60	2.52	2.67
Al	1.90	1.87	1.89	1.89	1.62
Fe	0.28	0.36	0.24	0.31	1.40
Ca	0.19	0.20	0.19	0.19	0.24
Mg	< 0.10	< 0.10	0.12	< 0.10	0.09
Na	0.34	0.20	0.40	0.31	0.33
K	0.36	0.37	0.47	0.40	0.29
Ti	0.11	< 0.10	0.11	< 0.10	0.08
Total	7.26	7.20	7.61	7.36	

THORESBY TOP HARD RESAMPLE

Cl	0.83	0.85	0.83	0.84	0.84
S	0.86	0.94	0.80	0.87	1.31
Si	0.64	0.63	0.65	0.64	0.88
Al	0.60	0.66	0.71	0.66	0.86
Fe	0.24	0.27	0.21	0.24	0.58
Ca	0.13	0.14	0.13	0.13	0.18
Mg	< 0.10	< 0.10	< 0.10	< 0.10	0.04
Na	0.24	0.27	0.32	0.28	0.29
K	< 0.10	< 0.10	< 0.10	< 0.10	0.02
Ti	< 0.10	< 0.10	< 0.10	< 0.10	0.05
Total	3.68	3.87	3.71	3.75	

APPENDIX 4.1 (continued)

THORESBY HIGH HAZLES

Element			Element % m/m	Average % m/m	BS 1016 value[149] % m/m
Cl	1.00	0.97	1.03	1.00	1.02
S	0.90	0.95	0.98	0.94	1.02
Si	0.87	0.95	0.95	0.92	0.70
Al	0.63	0.70	0.70	0.68	0.46
Fe	0.69	0.64	0.68	0.67	0.86
Ca	0.48	0.54	0.49	0.50	0.79
Mg	0.13	<0.10	0.12	<0.10	<0.02
Na	0.27	0.24	0.43	0.31	0.29
K	0.12	0.14	0.15	0.14	0.09
Ti	<0.10	<0.10	<0.10	<0.10	<0.02
Total	5.14	5.21	5.62	5.32	

LEA HALL SHALLOW

Cl	0.95	1.01	0.99	0.98	0.97
S	0.73	0.75	0.78	0.75	1.22
Si	0.29	0.27	0.27	0.28	0.44
Al	0.41	0.38	0.31	0.37	0.39
Fe	<0.10	0.13	<0.10	<0.10	0.44
Ca	0.12	0.17	0.17	0.15	0.18
Mg	<0.10	<0.10	<0.10	<0.10	0.05
Na	0.34	0.37	0.31	0.34	0.20
K	<0.10	<0.10	<0.10	<0.10	0.02
Ti	<0.10	<0.10	<0.10	<0.10	0.02
Total	3.06	3.28	3.07	3.13	

Both Mn and P <0.10% m/m in all the coals analysed

APPENDIX 4.2

Analysis of coal samples (< 212 µm) (air-dried basis)

Sample	Florence Rowhurst	Cortonwood Silkstone	South Durham 'C' Seam	Cadley Hill Bright Coal	Cadley Hill Dull Coal	Tilmanstone Milyard	Lea Hall Shallow	Babbington Blackshale	Babbington Tupton
Coal analysis % m/m									
Moisture	5.5	1.2	4.5	10.1	8.5	1.0	10.9	6.9	3.7
Ash	7.6	6.3	2.2	6.0	4.2	4.6	3.3	6.8	3.6
Sulphur	0.59	1.5	0.92	3.02	2.33	1.50	1.22	3.99	0.71
Chlorine (H T)	0.99	0.12	0.27	0.43	0.37	0.16	0.99	0.45	0.76
Chlorine (Eschka)	0.99	0.11	0.25	0.45	0.39	0.13	0.97	0.45	0.76
V M	33.5	33.2	33.1	35.0	37.5	14.7	32.9	36.2	34.7
V M (DAF)	38.6	35.9	35.5	41.7	43.0	15.6	38.3	41.9	37.4
C V (kJ/kg^{-1})	29660	33420	32620	27620	29760	34420	28960	29260	31800
C V (DAF) (kJ/kg^{-1})	34140	36120	34960	32920	32940	36450	33760	33910	34310
CO_2	1.33	0.07	0.11	0.48	0.03	0.13	0.15	N D	N D
Phosphorus	0.047	0.005	0.001	0.007	0.006	0.009	0.006	N D	N D
Swelling Index	3	8½	3½	1	1	4½	2½	4½	3½
Coke Type	F	G9	G3	B	C	F	F	N D	N D
Ash Analysis % m/m									
Al_2O_3	25.11	30.06	23.06	19.18	22.93	26.96	22.05	N D	N D
SiO_2	31.32	43.08	37.51	18.10	30.34	36.05	28.38	N D	N D
Fe_2O_3	8.78	20.51	21.58	38.18	35.43	22.40	18.92	N D	N D
TiO_2	0.60	0.74	1.13	0.50	0.86	0.72	0.92	N D	N D
Mn_3O_4	0.04	0.03	0.07	0.18	<0.02	0.07	0.05	N D	N D
CaO	15.18	0.98	4.63	7.10	3.29	4.05	7.46	N D	N D
MgO	4.87	1.15	3.12	3.08	1.05	1.30	2.37	N D	N D
Na_2O	2.49	0.75	3.61	2.86	3.25	4.74	8.38	N D	N D
K_2O	0.37	3.25	0.97	0.50	0.50	1.50	0.74	N D	N D
P_2O_5	1.47	0.17	0.20	0.26	0.48	0.48	0.44	N D	N D
SO_3	11.09	0.87	5.15	11.11	4.10	4.30	11.25	N D	N D
Silica Ratio	52.07	65.55	56.12	27.23	43.27	56.50	49.68	N D	N D

N D - Not determined

APPENDIX 4.2 (continued)

Sample	Bilsthorpe Low Main	Bilsthorpe Parkgate	Thoresby[a] Top Hard	Thoresby[b] Top Hard	Thoresby[a] Top Hard (Resampled)*	Thoresby [a] High Hazles	Thoresby[b] High Hazles	Thoresby Parkgate
Coal Analysis % m/m								
Moisture	3.4	5.1	5.0	7.5	7.8	6.7	10.0	5.4
Ash	3.3	4.3	5.6	10.8	5.4	4.5	6.8	4.4
Sulphur	2.07	1.83	1.01	0.87	1.31	1.25	1.02	1.88
Chlorine (H T)	0.73	0.69	0.80	0.86	0.83	0.92	1.01	0.73
Chlorine (Eschka)	0.74	0.69	0.80	0.89	0.84	0.93	1.02	0.73
V M.	35.8	37.5	33.6	28.9	33.0	33.7	32.1	34.4
V M (DAF)	38.4	41.4	37.6	35.4	38.0	37.9	38.6	38.1
C V (kJ/kg^{-1})	32450	30800	30480	27932	29880	30060	25900	30880
C V (DAF) (kJ/kg^{-1})	34780	34000	34100	34180	34420	33850	31120	34230
CO_2	N D	N D	N D	0.20	0.11	N D	1.07	N D
Phosphorus	N D	N D	N D	0.013	0.012	N D	0.010	N D
Swelling Index	6	4½	1	1	1	1	1	3½
Coke Type	N.D	N D	N D	C	E	N D	B	N.D
Ash Analysis % m/m								
Al_2O_3	N.D	N D	N D	28.33	29.90	N D	12.86	N D
SiO_2	N D	N D	N D	52.88	35.00	N.D	22.17	N D
Fe_2O_3	N D	N D	N D	3.32	15.40	N D	18.06	N D
TiO_2	N D	N D	N D	1.31	1.40	N D	0.35	N D
Mn_3O_4	N D	N D	N D	0.06	0.10	N D	0.24	N D
CaO	N D	N D	N D	3.05	4.60	N D	16.34	N D
MgO	N D	N D	N D	1.43	1.10	N D	0.20	N D
Na_2O	N D	N D	N D	4.08	7.20	N D	5.74	N D
K_2O	N.D	N D	N D	3.21	0.50	N D	1.62	N D
P_2O_5	N D	N D	N D	0.29	0.60	N D	0.28	N D
SO_3	N D	N D	N D	2.00	N.D	N D	23.55	N D
Silica Ratio	N D	N D	N.D	87.14	62.39	N D	39.05	N D

[a] Sample suspected to be contaminated with dust suppression water

[b] Sampled in July 1980

[c] Sampled in June 1982

APPENDIX 4.3

Analysis of Babbington Tupton ($<212\ \mu m$) coal (prepared from ¼" x 1/8" material for subsections used in leachability tests

Sub-section	A D Moisture % m/m	A D Ash % m/m	A D Sulphur % m/m	A D Chlorine % m/m	Eschka Sulphur % m/m	Eschka Chlorine % m/m	DAF Vol. Matter % m/m	BS Swelling Number	DAF Calorific Value kJ/kg^{-1}
B	6.1	3.6	0.70	0.65	0.74	0.65	37.1	1½	34340
C	7.1	5.2	0.66	0.80	0.71	0.77	37.3	2	34250
E	6.6	1.6	0.78	0.56	0.82	0.56	47.9	4	34800

A D	Air-dried basis
DAF	Dry ash-free basis
BS	British Standard

CHAPTER 5

QUANTITATIVE MULTI-ELEMENT ANALYSIS OF COAL POWDERS BY WAVELENGTH-DISPERSIVE AUTOMATED X-RAY FLUORESCENCE SPECTROMETRY

5.1 INTRODUCTION

The successful use of an energy-(or non-) dispersive technique for the analysis of coal powders using characteristic X-rays obtained by direct excitation using electrons, has been described in Chapter 3. The use of X-ray excitation to produce secondary (or fluorescent) radiation for coal analysis would be attractive for several reasons:

(i) multi-element technique;
(ii) good sensitivity down to trace levels in coal;
(iii) minimal and non-destructive sample preparation;
(iv) background is low because it is from a basically carbon matrix,
(v) the technique is highly suited for automation to give a large through-put of routine samples,

The theory of X-ray fluorescence is adequately described in suitable texts[166,167,168] but a brief introduction to XRF spectroscopic analysis is given here. Bombardment of coal by X-rays ejects electrons from the inner shells of atoms which then emit secondary X-rays (fluorescence). The wavelength of the exciting radiation must be chosen to produce fluorescent radiation (usually L to K shell transitions) of the elements of interest. The geometry to give maximum intensity requires both the target (source of excitation X-rays) and the spectrometer to be as close to the sample as possible. The energy-dispersive method previously described in Chapter 3 used a silicon (lithium) detector and an electronic analyser to measure directly each elemental X-ray by virtue of its energy. In a wavelength dispersive method the fluorescent X-rays are diffracted from a selected crystal according to the Bragg equation.[166]

$$n\lambda = 2d\sin\theta$$

where

n = an integer (usually 1-4)
θ = diffracting angle
d = lattice spacing of crystal
λ = wavelength

Alignment of the detector to the diffraction angle θ ensures that it functions as a monochromator and therefore receives only X-rays of a single wavelength i.e. a fixed channel instrument. In a sequential instrument, a polychromator alternatively measures a range of wavelengths. Rotation of the crystal and the detector on the Rowland Circle enables the Bragg angles for selected elements to be obtained in sequence. Various types of crystals and detectors are used in X-ray spectrometers.[166,167,168] Some first order lines ($n = 1$) can have the same Bragg angle as second, third and fourth order lines ($n = 2$, 3 and 4) thus creating an interference problem. The energy of a higher order line is far greater than a first order line and therefore the amplitude of the pulses it produces is greater, enabling it to be separated electronically by pulse-height discrimination. If the same order lines overlap then an alternative transition line for one of the elements must be selected.

The National Coal Board finds it necessary to analyse coal routinely for sulphur, chlorine, phosphorus and ash contents by BS methods.[149] The number of samples varies from coalfield to coalfield but typical numbers per week for the East Midlands Region which gives an analytical service to 35 collieries are: sulphur 600; chlorine 600; phosphorus 80; ash 1500. The effort required for such numbers of chemical determinations by labour-intensive methods becomes prohibitive in the face of increasing pressure on costs.

The use of an automated X-ray fluorescence method for coal analysis would give obvious benefits and the possibility has already been discussed.[169] The use of XRF for production and quality control monitoring in other fields is already well established [170, 171], and its suitability for automation accepted.[172] X-ray fluorescence in metallurgical and mineral analysis has been shown to be precise and accurate.[173]

The main problem with quantitative XRF analysis is that elemental fluorescent yield is influenced by self-absorption and by absorption or enhancement effects of the sample matrix.[166,167,168] Synthetic matrix-matched standards for coal are virtually impossible to produce.[174] The use of a 'fundamental parameters' approach to calculate theoretical correction constants[175] is complex and would require extensive chemical analysis and computation of data.

The accurate XRF analysis of powders is also influenced by particle size effects[176,177,178] and mineralogical effects.[130,166] An accurate X-ray method for the analysis of sulphur, chlorine and other elements in American brown coal has been reported by Kiss.[179] However, the concentration levels reported for sulphur and chlorine were much lower than are commonly found in coals mined in the UK. Kuhn and Henderson,[180] have reported a successful wavelength dispersive XRF system to determine 21 minor and trace elements in coal. Alternatively, some authors[181,182] have suggested the use of thin films for coal analysis using XRF techniques in order to avoid complications with matrix effects.

It was decided in this study, to investigate the use of a suite of well analysed coals and multiple regression analysis to derive XRF calibration equations for sulphur, chlorine, phosphorus and ash and evaluate their performance by analysing 'unknown' coals.

5.2 EXPERIMENTAL

5.2.1 Instrumentation

72000S, computer controlled, X-ray wavelength dispersive vacuum spectrometer with carbon, sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, potassium, calcium, titanium, manganese, iron and rhodium fixed channels. In addition, the instrument is supplied with a titanium external standard and programmable scanner with LiF and PET crystals to cover the analytical range 0.85-7.20 Ångstroms, (Applied Research Laboratories, Luton, Bedfordshire).
Hydraulic press, type HTP 40, Herzog, (Applied Research Laboratories, Luton, Bedfordshire).
High Vacuum Pump, type E2M18, (Edwards High Vacuum, Crawley, West Sussex).
Vacuum oven, type 0400, (Townson and Mercer, Runcorn, Cheshire).
Micromill, Type MS400, Retsch Spectromill, (Glen Creston, Stanmore, Middlesex).

5.2.2 Sample selection

72 commercially graded coals representing at least 2 samples from each of 35 collieries in the East Midlands Region were chosen for calibration with a further 100 coals from 6 collieries in the region being used as unknowns.[183] The analysis of the calibration coals using BS methods[149] is given in Appendix 5.1. The ranges of the main quality parameters for the coals are given in Table 5.1. These coals are mainly supplied to the domestic, industrial and power generation markets.

5.2.3 Sample preparation

The coal samples were crushed to less than 212 μm (72 BS mesh) and approximately 8g of each coal were pressed into a pellet in a 40 mm diameter steel ring at 18 tonnes per square inch for 25 seconds using a Herzog press, without a binding agent or backing material. The inherent moisture undoubtedly acts as the binding agent. The coal samples were then subjected to a vacuum of 10^{-1} Torr for a minimum of 1½ hours at room temperature in a vacuum oven, before being presented to the X-ray spectrometer. This vacuum pre-treatment removes surface moisture and volatile gases from coal which greatly increases the through-put of samples for routine operation of the spectrometer.

5.2.4 Method of calibration and analysis

The X-ray spectrometer was calibrated by regressing the X-ray intensity of the analyte against its concentration determined by BS methods.[149] The calculation then used an empirical correction procedure which minimised the influence of interfering elements on an analyte in a multi-component matrix. This multi-variable regression analysis was performed on the intensities and concentrations of the analyte and corrections for interfering elements were then made by the use of either their known concentrations or measured intensities. The method is purely mathematical and is performed by the computer (Digital PDP 1103/L 64k Bytes of read write memory and 10m Bytes of store), which controls both analysis and data processing in the spectrometer. For this reason extreme care must be exercised in interpretation of the mathematical parameters generated, if meaningful corrections and results are to be obtained.

TABLE 5.1

Range of main quality parameters for the calibration coals (air-dried basis)

	minimum % m/m	maximum % m/m	mean % m/m
Phosphorus	0.002	0.074	0.0183
Sulphur	0.75	3.28	1.73
Chlorine	0.15	0.71	0.41
Ash	2.8	24.8	12.37
Moisture	2.4	9.4	5.20
Volatile Matter	23.2	35.7	31.95
Fixed Carbon	36.9	59.8	51.7
Rank	400	800	N A

N A - Not applicable

From the mathematical models available, two were considered as simple and suitable for coal analysis; one which uses the intensity of interfering elements to compute corrections (Lucas-Tooth)[184] and one which uses the concentration of interfering elements to compute corrections (Traill-Lachance).[185,186] The latter model requires far more extensive chemical analysis of samples and computation of data.

The mathematical algorithms for these methods of correction are given below:

1) Lucas-Tooth

$$C_i = (A_o + A_1 I_i + A_2 I_i^2)\ (1 + \sum K_n I_n + \sum L_n I_n^2)$$

2) Traill-Lachance

$$C_i = (A_o + A_1 I_i + A_2 I_i^2)\ (1 + \sum K_n C_n + \sum L_n C_n^2)$$

where C_i = concentration of analyte
A_o = intercept of calibration curve
A_1 = slope of calibration curve
A_2 = second order coefficient of calibration curve
C_n = concentration of interfering elements
I_n = intensities of interfering elements
K_n, L_n = matrix correction coefficients

The model proposed by Lucas-Tooth requires the measurement and correction of background intensities for the interfering elements in the matrix if accurate corrections are to be made. Since a well analysed suite of coals was available the Traill-Lachance concentration model was evaluated extensively in this study.
The selected intefering elements which gave the best calibration curves for XRF intensity against chemical composition[149] for chlorine, sulphur, phosphorus and ash are listed below:

Element/parameter determined	Interfering elements used in regression equation for calibration
Chlorine	Carbon, aluminium, potassium and rhodium backscattered radiation
Sulphur	Iron, silicon, titanium, magnesium and calcium
Phosphorus	Silicon, rhodium backscattered radiation, potassium and aluminium
Ash (rhodium backscatter)	Silicon, potassium and carbon

The combination of interfering elements for each analyte was selected to give the smallest standard error of the estimate of the calibration curve and the smallest standard deviation of differences between XRF estimates and chemically analysed unknowns.

It should be understood that in the case of rhodium the measured X-ray radiation is backscatter from the coal surface and is therefore not fluorescence. The degree of backscatter is inversely proportional to the ash content of coal, the lower the ash content the greater the degree of backscatter. As explained in Chapter 3 the calculation of an ash content to represent the residue on combustion at 815°C[149] using X-ray analysis of the original coal is difficult because the proportion of sulphur retained in the ash is not predictable. For this reason close agreement is not to be expected.

The vacuum pre-treated coal pellets were rotated and presented to the spectrometer via a 36 sample exchanger. The whole process of analysis and data handling was automated, the input being through the VDU or printer keyboards. The X-ray excitation used a 2.7 kW rhodium tube operated at 50 kV and 40 mA at a vacuum of 10^{-1} Torr. The counting condition was set for 12 million counts of the titanium external standard which approximated to 30 seconds real-time. Spectrometer drift was adjusted each day using fused lithium metaborate bead standards which produced accurately known intensities. The intensity levels in these standards covered the normal element counting ranges found in the coals to be analysed.

5.3 RESULTS AND DISCUSSION

5.3.1 Precision of XRF analysis of pressed coal pellets

The results of 90 or 100 determinations on each of three coal pellets, using all the fixed channels available in the spectrometer, are given in Table 5.2. The instrument analysed the coal pellet for all the elements simultaneously, waited 60 seconds and then repeated the analyses. The samples examined covered a range of major, minor and trace elemental concentrations found in commercially graded coals from the East Midlands Region.

The results show a high degree of precision when using X-ray fluorescence for the analysis of the same coal pellet. The Relative Standard Deviation (RSD) for phosphorus ranged from 0.26 to 1.62; sulphur 0.15 to 0.31; chlorine 0.34 to 0.49 and rhodium backscatter 0.17 to 1.65. The poorest RSD values were found for sodium, magnesium, silicon and titanium when these elements were present in trace concentrations in coal.

In addition, for two coal samples ten pellets of each were prepared and analysed sequentially. The results given in Table 5.3 show excellent repeatability for the determinations of chlorine, sulphur, phosphorus and rhodium backscatter in the two samples examined. In the case of phosphorus this good precision is obtained even at trace level concentrations.

The results presented in Table 5.2 and 5.3 clearly show that X-ray fluorescence when applied to the elemental analysis of pressed coal powders is a very precise technique.

5.3.2 Accuracy of coal analysis by XRF compared to BS analytical methods

As explained in the introduction to this thesis, coal is analysed routinely by British Standard Methods[149] and the accuracy of any proposed new analytical technique if it is to gain credence must be assessed against the established chemical procedures. The BS methods quote repeatability and reproducibility criteria for analysis i.e precision; the former being the accepted tolerance between duplicates by the same analyst in the same laboratory, the latter being the accepted tolerance between duplicates from different laboratories. These BS tolerance values are given in Table 5.4.

TABLE 5.2

Precision of XRF analysis of pressed coal powders (air-dried basis)

Element	C	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fl	Rh
Coal A													
No. of determinations	90	90	90	90	90	90	90	90	90	90	90	90	90
Mean Value %	62.94	0.076	0.010	0.179	0.032	0.001	1.626	0.284	N D	0.056	0.006	0.896	1.97
Standard Deviation σ_{n-1}	0.141	0.0031	0.0012	0.0027	0.0028	N D	0.0024	0.0014	N D	0.0008	0.0003	0.0016	0.032
Relative Standard Deviation %	0.22	4.08	11.52	1.49	8.66	N D	0.15	0.49	N D	1.47	5.36	0.18	1.65
Coal B													
No. of determinations	100	100	100	100	100	100	100	100	100	100	100	100	100
Mean Value %	51.96	0.128	0.134	2.102	3.057	0.013	2.278	0.384	0.351	0.274	0.083	1.383	13.77
Standard Deviation σ_{n-1}	0.154	0.0032	0.0023	0.0340	0.0091	0.002	0.0054	0.0013	0.0014	0.0011	0.0007	0.0024	0.036
Relative Standard Deviation %	0.30	2.52	1.71	1.62	0.30	1.62	0.24	0.34	0.41	0.39	0.80	0.17	0.26
Coal C													
No. of determinations	90	90	90	90	90	90	90	90	90	90	90	90	90
Mean Value %	43.31	0.248	0.338	4.702	8.126	0.023	1.850	0.418	0.792	0.184	0.162	1.627	32.58
Standard Deviation σ_{n-1}	0.098	0.0041	0.0039	0.0750	0.0234	0.0006	0.0058	0.0015	0.0022	0.0009	0.0008	0.0022	0.056
Relative Standard Deviation %	0.22	1.65	1.16	1.60	0.29	0.26	0.31	0.36	0.28	0.52	0.51	0.14	0.17

N D = Not determined

TABLE 5.3

The repeatability of analysing ten different pellets for two selected coals

Coal X

Pellet No.	Chlorine % m/m	Sulphur % m/m	Phosphorus % m/m	Rhodium backscatter ash % m/m
1	0.193	2.110	0.0601	18.272
2	0.193	2.115	0.0598	18.209
3	0.193	2.109	0.0602	18.123
4	0.193	2.116	0.0594	18.155
5	0.192	2.110	0.0591	18.172
6	0.192	2.121	0.0592	18.139
7	0.193	2.109	0.0603	18.398
8	0.193	2.109	0.0597	18.170
9	0.192	2.112	0.0601	18.316
10	0.193	2.113	0.0594	18.445
Mean	0.1927	2.1124	0.05973	18.240
SD	0.000483	0.00395	0.000437	0.000483
RSD %	0.25	0.19	0.73	0.62
Chemical value[149]	0.18	2.41	0.060	19.13
Coal Y				
1	0.302	1.464	0.0041	2.867
2	0.301	1.460	0.0042	2.916
3	0.300	1.458	0.0039	2.867
4	0.299	1.457	0.0038	2.822
5	0.299	1.455	0.0035	2.852
6	0.300	1.457	0.0044	2.826
7	0.300	1.454	0.0040	2.877
8	0.299	1.456	0.0042	2.820
9	0.298	1.458	0.0037	2.844
10	0.300	1.460	0.0040	2.810
Mean	0.2998	1.4579	0.00398	2.850
SD	0.00113	0.00288	0.000266	0.0326
RSD %	0.38	0.20	6.67	1.14
Chemical value[149]	0.29	1.52	0.003	2.86

TABLE 5.4

British Standard tolerance for duplicate analyses for sulphur, chlorine, phosphorus and ash

Element/parameter	Precision of a single result (± 2σ)	Repeatability % m/m ($ts\sqrt{2}$)	Reproducibility % m/m ($ts\sqrt{2}$)
Sulphur	± 0.035	0.05	0.10
Chlorine ($<$0.4%)	± 0.014	0.02	0.02
Chlorine ($\geqslant$0.4%)	± 0.035	0.05	0.05
Phosphorus ($<$0.02%)	± 0.000135	0.002	0.005
Phosphorus ($\geqslant$0.02%)	±7% of value	10% of value	25% of value
Ash ($<$10.0%)	± 0.10	0.15	0.3
Ash (10-20.0%)	± 0.135	0.20	0.4
Ash ($>$20.0%)	± 0.17	0.25	0.5

To evaluate the accuracy of the XRF analysis procedure 99 coals were analysed for sulphur, chlorine, phosphorus and ash contents by BS methods.[149] The coals selected were from two collieries from each of the three Areas in the East Midlands Region. They were prepared and analysed using XRF as described in section 5.2.3 and 5.2.4. The results of these analyses are given in Table 5.5, with the calculated mean and standard deviations of the differences between BS and XRF methods given in Table 5.6. These elemental analysis results are discussed individually.

5.3.2.1 Chlorine

The results and calculations in Tables 5.5 and 5.6 show the accuracy of chlorine analysis by XRF to be very good. The largest Standard Deviation (SD) of the differences between BS and XRF methods is 0.022 for TY coals, with a mean SD of the differences of 0.021 for all the 99 coals. The highest mean difference between the two methods of -0.03 was found for the TL coals. This excellent agreement between chemical methods and the XRF analytical technique is further supporting evidence for the uniform distribution and mode of occurrence of chlorine in coal described in detail in Chapter 4.

5.3.2.2 Sulphur

The agreement between the two methods for the total sulphur contents for coal samples from TY, WP and PL collieries is good. These three collieries are representative of the three Areas in the East Midlands Region. The agreement for CN, TL and ON samples which are equally representative is poor and the reason for this may be the presence of different forms of sulphur in coal, already discussed in this thesis. Attempts to identify the possible difference in XRF yields between organic and pyritic sulphur have been made. For this purpose standard mixtures of accurately known sulphur contents were made up, using sulphanilic acid to represent organic sulphur, iron pyrites (less than 212 μm) for pyritic sulphur and sucrose as a carbonaceous base.

TABLE 5.5

Comparison of BS chemical determinations (Lab) with XRF determinations for sulphur, chlorine, phosphorus and ash (air-dried basis)

Sample No.	Sulphur % m/m			Chlorine % m/m			Phosphorus % m/m			Ash % m/m		
	Lab	XRF	Δ S	Lab	XRF	Δ Cl	Lab	XRF	Δ P	Lab	XRF	Δ Ash
TY 1	1.58	1.53	- .05	0.80	0.81	.01	0.014	0.018	.004	17.62	17.67	.05
TY 2	1.78	1.71	- .07	0.73	0.77	.04	0.012	0.016	.004	17.71	17.54	- .17
TY 3	1.67	1.61	- .06	0.75	0.79	.04	0.014	0.018	.004	18.73	18.62	- .11
TY 4	1.52	1.47	- .05	0.77	0.80	.03	0.012	0.017	.005	18.44	18.69	.25
TY 5	1.46	1.43	- .03	0.79	0.80	.01	0.016	0.017	.001	18.63	19.02	.39
TY 6	1.43	1.39	- .04	0.77	0.81	.04	0.018	0.020	.002	18.93	19.16	.23
TY 7	1.52	1.41	- .09	0.79	0.82	.03	0.014	0.017	.003	19.12	19.42	.30
TY 8	1.33	1.26	- .07	0.80	0.79	- .01	0.017	0.022	.005	21.47	21.89	0.42
TY 9	1.47	1.35	- .12	0.77	0.79	.02	0.016	0.019	.003	20.91	21.05	.14
TY 10	1.43	1.34	- .09	0.73	0.78	.05	0.016	0.021	.005	19.21	19.07	- .14
TY 11	1.63	1.60	- .03	0.76	0.78	.02	0.014	0.016	.002	16.05	16.35	.30
TY 12	1.40	1.34	- .06	0.79	0.82	.03	0.014	0.018	.004	19.66	19.41	- .25
TY 13	1.50	1.40	- .10	0.79	0.80	.01	0.013	0.018	.005	20.42	20.31	- .11
TY 14	1.62	1.48	- .14	0.79	0.78	- .01	0.012	0.017	.005	21.30	21.27	- .03
TY 15	1.49	1.47	- .02	0.81	0.83	.02	0.013	0.016	.003	17.59	17.70	.11
TY 16	1.58	1.54	- .04	0.83	0.81	- .02	0.012	0.015	.003	19.48	18.87	- .61
TY 17	1.56	1.46	- .10	0.80	0.80	-	0.014	0.018	.004	19.74	20.30	.56
TY 18	1.68	1.58	- .10	0.77	0.76	- .01	0.013	0.016	.003	18.27	18.14	- .13
TY 19	1.50	1.38	- .12	0.79	0.77	- .02	0.016	0.020	.004	21.20	20.68	- .52
TY 20	1.72	1.60	- .12	0.78	0.76	- .02	0.016	0.017	.001	19.85	19.05	- .80
ON 1	2.18	2.24	.06	0.73	0.70	- .03	0.005	0.005	-	8.38	8.20	- .18
ON 2	2.15	2.32	.17	0.73	0.71	- .02	0.005	0.006	.001	10.02	9.96	- .06
ON 3	2.15	2.29	.14	0.69	0.69	-	0.006	0.006	-	10.43	10.26	- .17
ON 4	2.12	2.24	.12	0.79	0.75	- .04	0.006	0.007	.001	11.28	11.05	- .23
ON 5	2.11	2.28	.17	0.73	0.71	- .02	0.006	0.006	-	10.12	9.62	- .50
ON 6	2.11	2.21	.10	0.73	0.69	- .04	0.006	0.006	-	9.54	9.03	- .51
ON 7	2.16	2.26	.10	0.68	0.66	- .02	0.007	0.006	- .001	10.60	10.12	- .48
ON 8	2.15	2.20	.05	0.74	0.72	- .02	0.006	0.008	.002	11.57	12.20	.63
ON 9	2.14	2.28	.14	0.69	0.71	.02	0.006	0.007	0.001	10.71	10.93	.22
ON 10	2.32	2.33	.01	0.73	0.71	- .02	0.006	0.007	.001	11.67	11.88	.21
ON 11	2.14	2.28	.14	0.71	0.70	- .01	0.006	0.006	-	8.77	8.90	.13
ON 12	2.20	2.36	.16	0.72	0.70	- .02	0.006	0.006	-	8.95	9.18	.23
ON 13	2.21	2.35	.14	0.71	0.70	- .01	0.006	0.006	-	9.27	9.77	.50
ON 14	2.07	2.33	.26	0.70	0.67	- .03	0.006	0.006	-	8.61	9.03	.42
ON 15	2.12	2.33	.21	0.71	0.70	- .01	0.005	0.006	.001	9.46	9.58	.12
ON 16	2.20	2.30	.10	0.73	0.72	- .01	0.006	0.007	.001	10.53	10.55	.02
ON 17	2.23	2.40	.17	0.69	0.66	- .03	0.005	0.005	-	7.90	7.80	- .10
ON 18	2.26	2.37	.11	0.70	0.68	- .02	0.005	0.005	-	8.47	8.12	- .35
ON 19	2.27	2.35	.08	0.72	0.72	-	0.005	0.005	-	8.91	9.12	.21
ON 20	2.23	2.38	.05	0.75	0.71	- .04	0.006	0.006	-	9.57	9.56	- .01

TABLE 5.5 (continued)

Sample No.	Sulphur % m/m			Chlorine % m/m			Phosphorus % m/m			Ash % m/m		
	Lab	XRF	△ S	Lab	XRF	△ Cl	Lab	XRF	△ P	Lab	XRF	△ Ash
TL 1	1.75	1.98	.23	0.39	0.36	- .03	0.005	0.003	- .002	4.11	4.23	.12
TL 2	1.73	1.93	.20	0.35	0.31	- .04	0.003	0.002	- .001	3.49	3.52	.03
TL 4	1.84	2.08	.24	0.37	0.33	- .04	0.003	0.002	- .001	3.64	3.42	- .22
TL 5	1.78	1.93	.15	0.32	0.31	- .01	0.003	0.002	- .001	3.18	3.18	-
TL 7	1.82	2.02	.20	0.35	0.32	- .03	0.003	0.002	- .001	3.84	3.84	-
TL 13	1.83	2.00	.17	0.28	0.35	- .03	0.003	0.002	- .001	3.83	3.67	- .16
TL 14	1.96	2.23	.27	0.37	0.33	- .04	0.003	0.002	- .001	3.87	3.68	- .19
TL 15	1.93	1.88	.15	0.35	0.32	- .03	0.003	0.002	- .001	3.41	3.52	.11
TL 18	1.86	2.16	.30	0.39	0.34	- .05	0.003	0.002	- .001	4.05	4.09	.04
TL 20	1.77	2.06	.29	0.36	0.32	- .04	0.005	0.004	- .001	4.39	4.40	.01
CN 1	1.54	1.92	.38	0.57	0.53	- .04	0.014	0.006	- .008	4.62	3.84	- .78
CN 3	1.50	1.90	.40	0.57	0.53	- .04	0.014	0.006	- .008	4.57	4.04	- .53
CN 6	1.41	1.85	.44	0.55	0.53	- .02	0.015	0.007	- .008	4.61	4.25	- .36
CN 7	1.49	1.85	.36	0.54	0.52	- .02	0.013	0.006	- .007	4.63	4.13	- .40
CN 8	1.63	1.99	.36	0.53	0.51	- .02	0.015	0.006	- .009	4.82	4.14	- .68
CN 9	1.57	1.93	.36	0.54	0.53	- .01	0.016	0.006	- .010	4.41	3.57	- .84
CN 12	1.60	2.08	.48	0.54	0.52	- .02	0.022	0.010	- .012	5.78	5.00	- .78
CN 14	1.40	1.76	.36	0.57	0.54	- .03	0.016	0.008	- .008	4.32	4.15	- .17
CN 16	1.49	1.70	.21	0.57	0.54	- .03	0.015	0.007	- .008	4.66	4.15	- .51
CN 19	1.42	1.68	.26	0.53	0.52	- .01	0.015	0.009	- .006	5.81	5.97	.16
WP 2	1.28	1.32	.04	0.41	0.41	-	0.023	0.019	- .004	12.99	13.07	.08
WP 4	1.09	1.10	.01	0.41	0.41	-	0.032	0.027	- .005	12.74	13.19	.45
WP 5	1.08	1.15	.07	0.45	0.44	- .01	0.023	0.021	- .002	10.45	11.03	.58
WP 6	1.33	1.36	.03	0.39	0.38	- .01	0.021	0.021	-	11.85	12.32	.47
WP 7	1.23	1.27	.04	0.40	0.41	.01	0.024	0.026	.002	12.41	12.47	.06
WP 9	1.18	1.16	- .02	0.38	0.37	- .01	0.027	0.026	- .001	11.74	11.21	- .53
WP 10	1.00	1.03	.03	0.43	0.41	- .02	0.026	0.022	- .004	9.25	9.33	.08
WP 11	1.31	1.36	.05	0.41	0.42	.01	0.025	0.022	- .003	12.50	12.48	- .02
WP 12	0.98	0.98	-	0.45	0.45	-	0.028	0.022	- .006	10.27	10.25	- .02
WP 13	1.33	1.41	.08	0.35	0.38	.03	0.025	0.021	- .004	10.68	10.55	- .13
WP 14	1.06	1.06	-	0.43	0.40	- .03	0.025	0.026	.001	12.24	12.00	- .24
WP 15	1.07	1.06	- .01	0.43	0.42	- .01	0.030	0.028	- .002	13.00	12.44	- .56
WP 16	1.22	1.25	.03	0.41	0.39	- .02	0.024	0.025	.001	13.85	13.70	- .15
WP 17	1.23	1.27	.04	0.40	0.41	.01	0.023	0.020	- .003	11.80	11.70	- .10
WP 18	1.13	1.13	-	0.39	0.40	.01	0.029	0.024	- .005	10.24	9.89	- .35
WP 19	1.39	1.49	.10	0.40	0.40	-	0.019	0.018	- .001	12.03	12.70	.67
WP 20	1.62	1.75	.13	0.38	0.38	-	0.016	0.015	- .001	12.31	12.72	.41

TABLE 5.5 (continued)

Sample	Sulphur % m/m			Chlorine % m/m			Phosphorus % m/m			Ash % m/m		
No.	Lab	XRF	Δ S	Lab	XRF	Δ Cl	Lab	XRF	Δ P	Lab	XRF	Δ Ash
PL 1	2.19	2.23	.04	0.38	0.39	.01	0.014	0.014	-	15.12	16.13	1.01
PL 2	1.98	2.02	.04	0.40	0.41	.01	0.016	0.017	.001	17.49	17.54	.05
PL 3	2.40	2.35	- .05	0.38	0.38	-	0.015	0.015	-	20.44	19.28	1.16
PL 4	2.47	2.45	- .02	0.38	0.38	-	0.014	0.013	- .001	17.11	16.88	- .23
PL 5	2.20	2.13	- .07	0.43	0.42	- .01	0.018	0.017	- .001	20.32	19.66	- .76
PL 6	2.32	2.26	- .06	0.36	0.36	-	0.015	0.016	.001	22.48	20.67	- 1.81
PL 7	2.37	2.45	.08	0.42	0.41	- .01	0.010	0.011	.001	15.05	15.04	- .01
PL 8	2.50	2.50	-	0.38	0.38	-	0.012	0.012	-	18.30	17.71	- .61
PL 9	2.50	2.58	.08	0.39	0.38	- .01	0.013	0.012	- .001	16.22	15.72	- .50
PL 10	2.11	2.28	.17	0.38	0.38	-	0.013	0.012	- .001	14.00	13.66	- .34
PL 11	2.10	2.29	.19	0.35	0.36	.01	0.016	0.016	-	17.95	17.86	- .09
PL 12	2.38	2.43	.05	0.40	0.40	-	0.009	0.012	.003	15.46	15.26	- .20
PL 13	2.27	2.28	.01	0.42	0.42	-	0.013	0.012	- .001	13.69	13.38	- .31
PL 14	2.31	2.36	.05	0.40	0.39	- .01	0.010	0.012	.002	15.34	15.38	.04
PL 15	2.20	2.24	.04	0.34	0.34	-	0.014	0.016	.002	21.44	20.27	- 1.17
PL 16	2.33	2.23	- .10	0.36	0.37	.01	0.014	0.016	.002	19.89	19.04	- .85
PL 17	2.39	2.29	- .10	0.37	0.37	-	0.013	0.015	.002	19.55	18.87	- .68
PL 18	2.09	2.15	.06	0.40	0.42	.02	0.009	0.013	.004	15.28	14.68	- .60
PL 19	2.34	2.27	- .07	0.38	0.36	- .02	0.014	0.017	.003	19.62	19.22	- .40
PL 20	2.30	2.26	- .04	0.40	0.39	- .01	0.011	0.014	.003	18.50	17.68	- .82
PL 21	2.29	2.19	- .10	0.38	0.37	- .01	0.012	0.016	.004	19.78	18.96	- .82
PL 22	2.41	2.33	- .08	0.40	0.39	- .01	0.013	0.015	.002	17.66	17.24	- .42

TABLE 5.6

Calculation of mean and standard deviation of the differences between chemical and XRF results given in Table 5.5

Colliery code			Sulphur % m/m	Chlorine % m/m	Phosphorus % m/m	Ash % m/m
TY	Number	N	20	20	20	20
	Mean	X	- .075	.013	.005	0.005
	Standard deviation of differences	σ_{n-1}	.03547	.0225	.001277	0.3559
ON	Number	N	20	20	20	20
	Mean	X	0.124	- .0205	.00035	.005
	Standard deviation of differences	σ_{n-1}	.05915	.01191	.006708	.3273
TL	Number	N	10	10	10	10
	Mean	X	.22	- .034	.0011	- .026
	Standard deviation of differences	σ_{n-1}	.05518	.01075	.0003162	.1213
CN	Number	N	10	10	10	10
	Mean	X	0.361	- 0.024	- 0.0084	- 0.489
	Standard deviation of differences	σ_{n-1}	.07838	0.01075	0.001657	0.31246
WP	Number	N	17	17	17	17
	Mean	X	0.03647	- 0.00235	- 0.00218	0.04118
	Standard deviation of differences	σ_{n-1}	0.04046	0.01437	0.00235	0.36990
PL	Number	N	22	22	22	22
	Mean	X	0.01182	- 0.00136	0.001136	- 0.38
	Standard deviation of differences	σ_{n-1}	0.08238	0.009409	0.00167	.6391
Total	Number	N	99	99	99	99
	Mean	X	0.0761	- 0.00768	- 0.000303	- 0.1223
	Standard deviation of differences	σ_{n-1}	0.1429	0.02094	0.00361	0.4556

Two ranges of samples from 0.5 to 5.0 percent by weight of sulphur were prepared, one of organic and one of pyritic sulphur. The absolute intensities measured using the XRF spectrometer, are given in Table 5.7 and plotted in figure 5.1. It can be seen from these results that the intensity of the X-ray fluorescence produced from pyritic sulphur is only approximately a quarter of that from the organic form. Whatever the reason (absorption of radiation by iron atoms being the most likely) this discrepancy probably accounts for the difficulty experienced in obtaining satisfactory accuracy in the XRF determination of sulphur in coal samples in which the relative contents of organic and pyritic sulphur are varied and unknown.

In an additional test, 0.2g of iron pyrite (355 μm - 212 μm) was ground in the micromill with 10g of sucrose for periods of 0, 5, 10, 15, 20 and 60 minutes. Each ground sample was pressed into a pellet and the absolute intensity of iron and sulphur measured using the X-ray spectrometer. The results given in Table 5.8 and plotted in Figure 5.2 show a rapid increase in XRF intensity for sulphur and iron for up to 20 minutes grinding.

The effect of grinding coal would reduce the particle size of pyrite and hence increase the XRF sulphur intensity obtained from that mineral. The fine grinding of coal does not effect the XRF intensity generated from organic sulphur. Fine grinding of coal (less than 212 μm in size) to less than 10 μm, in addition to homogenising the sample should bring the two XRF intensities from organic and pyritic sulphur in closer agreement. This would produce a more accurate calibration of XRF intensity against BS sulphur concentration. The interference corrections applied, particularly for iron, would be smaller and this should result in improved estimates of sulphur in 'unknown' coals.

TABLE 5.7

Absolute intensities for given percentages of determined sulphur occurring in two different forms determined by XRF

Percentage sulphur m/m	Absolute intensity (counts sec $^{-1}$ x 10^{3})	
	organic sulphur	pyritic sulphur
0.50	504	113
1.00	928	232
1.50	1383	354
2.00	1835	441
2.50	2187	541
3.00	2613	632
3.50	3139	758
4.00	3748	867
4.50	4086	983
5.00	4526	1109
Coefficient of correlation	0.9989	0.9991
Intercept	12.6667	8.73
Gradient of line	902	216
Standard error of estimate about the line	68.42	14.51

Figure 5.1 Absolute intensities for given percentages of sulphur occurring as organic or pyritic form in sucrose

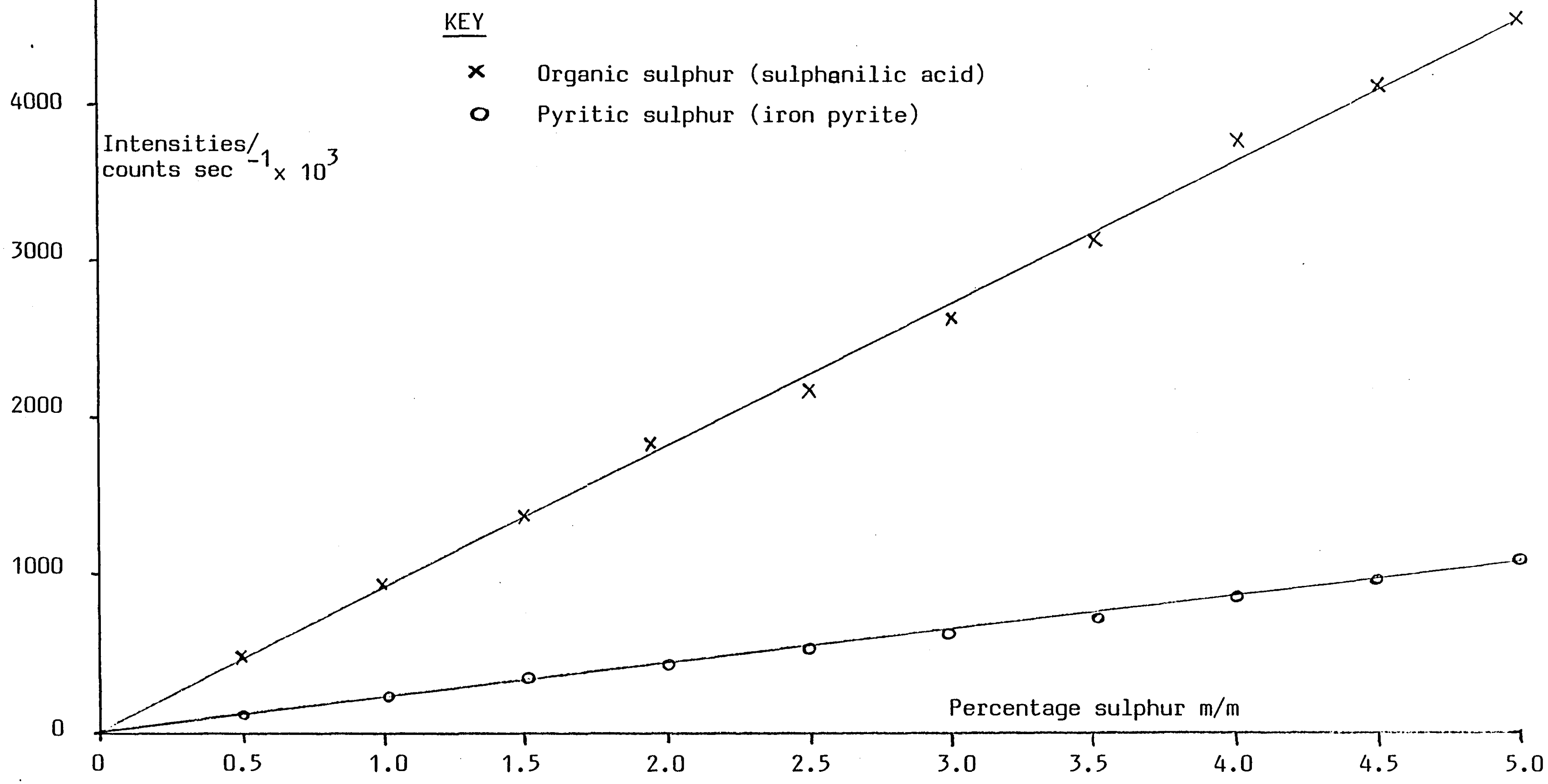
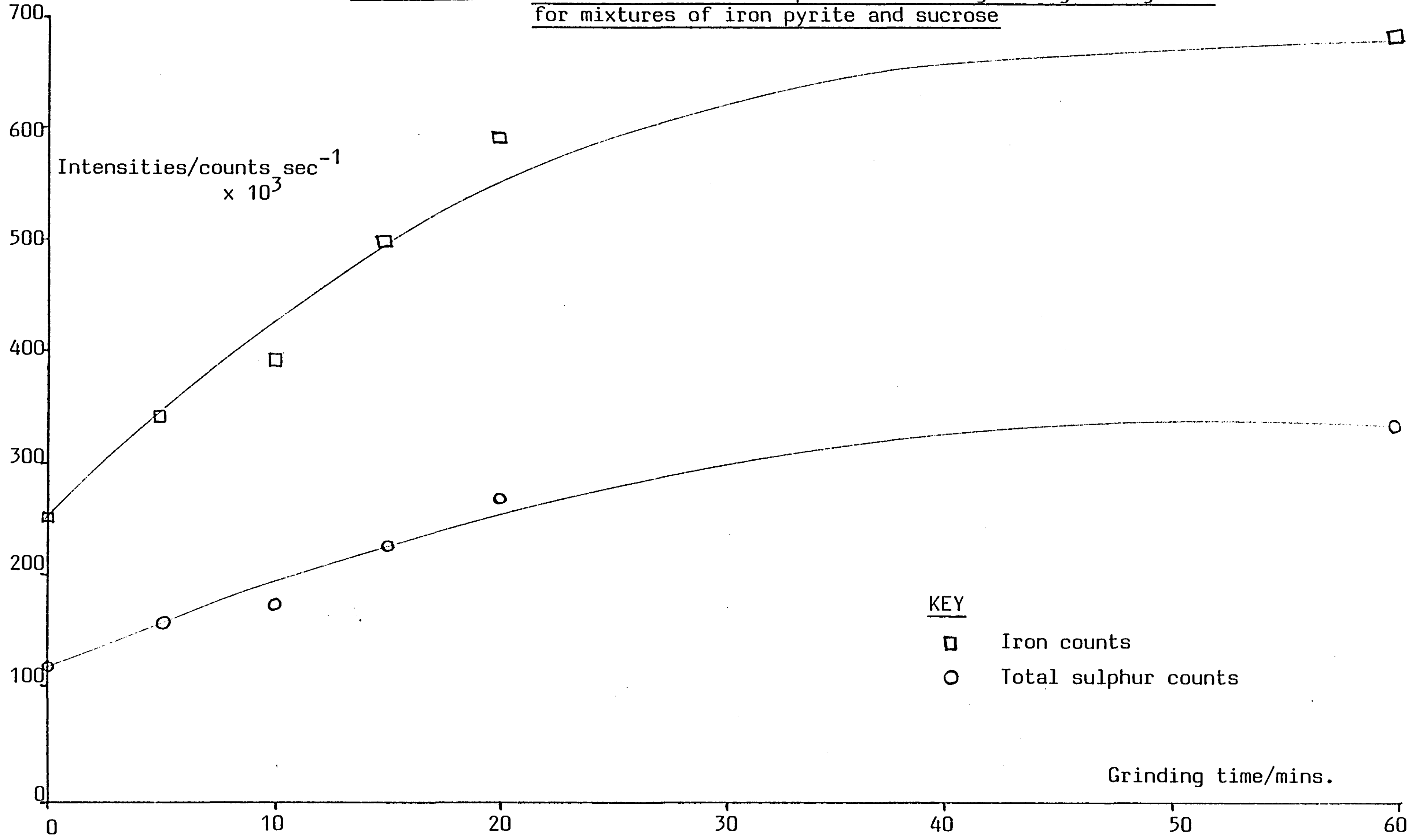


TABLE 5.8

Absolute XRF intensities for 0.2g of iron pyrite (355 µm - 212 µm) ground with 10g of sucrose for different time intervals

Time of grinding of mixture (minutes)	Absolute XRF intensity (counts sec^{-1} x 10^{3})	
	Sulphur	Iron
0	117	247
5	158	234
10	174	391
15	227	497
20	269	595
60	340	691

Figure 5.2 XRF Intensities for sulphur and iron against grinding time for mixtures of iron pyrite and sucrose



A fusion technique such as that recently described by Weber, Van Willigen and Van der Linden[187] would convert the sulphur to a single chemical form. Such sample preparation methods would remove mineralogical effects in XRF analysis but are time consuming, introduce possible volatilisation losses and defeat the object of rapid analysis directly upon coal powder.

The possibility of selecting groups of coals in respect of their area of origin or seam for calibration should not be discounted. This would facilitate the closer agreement in chemical composition of 'unknowns' and calibration coals i.e improved 'matrix matching'. Such calibrations and the fine grinding of coal should be explored to improve the accuracy of the determination of sulphur in coal by X-ray fluorescence.

5.3.2.3 Phosphorus

Excluding the CN coals which appear anomalous the results of comparing XRF analyses with chemical analyses for phosphorus given in Table 5.5 are good and the largest individual difference found between the two methods is 0.005 percent. The SD of the difference between XRF and BS methods of analysis for all the 99 coals is 0.0036. These results are considered satisfactory for routine analysis of phosphorus by XRF, although the problem with CN coals needs further investigation. It is not unreasonable to assume that a background measurement and correction for different coal matrices, might improve the accuracy of phosphorus determination by XRF and this might also be the problem with the CN coals.

5.3.2.4 Ash

The results obtained using rhodium backscattered X-ray radiation for assessment of ash, given in Tables 5.5 and 5.6 show an SD of the difference between XRF and BS methods of 0.456 for all the 99 coals. Accepting the high degree of precision of the BS estimate of ash given in Table 5.4 these results cannot be considered as satisfactory. The accuracy of the results obtained using this XRF method might be useful for on-line quality control monitoring and the NCB are investigating the use of such a simple XRF technique for this purpose. The estimation of ash or better still the mineral matter content of coal, using XRF total elemental analysis should be more accurate and a high degree of correlation using SEM/EDXA and BS ash determination has already been shown in Chapter 3. Despite the problems described in section 5.2.4. the potential usefulness of this method for ash determination directly on whole coal is clearly indicated.

5.4 CONCLUSIONS

The use of an automated wavelength dispersive XRF technique for the determination of twelve elements in pressed coal powders has been shown to be very precise. This high degree of precision is also obtained for sulphur, chlorine, phosphorus and ash determinations on ten different pressed pellets of the same coal.

The XRF method developed has also been shown to be very accurate and suitably sensitive for the analysis of chlorine and phosphorus in a range of commercially graded coals from the East Midlands Region of the NCB.

On the other hand, sulphur was only determined accurately for approximately fifty percent of the unknown samples analysed. The reason for this has been identified to be the different X-ray fluorescent yields obtained from organic and inorganic sulphur forms known to exist in coal in unknown and variable amounts. The cause of this difference is most likely the absorption of X-ray radiation by atoms of iron. An improvement in accuracy of analysis of 'unknowns' would be obtained by matching the forms of sulphur in the calibration and unknown coals more precisely and also by finer grinding of coal to homogenize these sulphur forms.

The ash determination investigated in this work attempted to relate the backscattered X-ray radiation from rhodium to the BS method of ash determination. The X-ray method although precise was not sufficiently accurate for sales quality assessment but would be acceptable for on-line washery quality control. The use of comprehensive X-ray elemental analysis of coal would require a detailed chemical analysis of the calibration coals but should give more accurate results, particularly if the X-ray intensities were related to the mineral matter composition rather than the ash determination.

The XRF analysis of coal powders has therefore been identified as a versatile and very powerful technique for routine coal analysis giving acceptable precision and accuracy.

APPENDIX 5.1

Analysis of calibration coals (air-dried basis) % m/m

Sample no.	Chlorine	Sulphur	Phosphorus	Ash	Volatile matter	Total moisture	Fixed carbon	Silicon	Iron	Titanium	Aluminium	Calcium	Magnesium	Sodium	Potassium
E01	0.36	2.20	0.027	12.19	31.78	3.36	52.70	2.711	1.240	0.064	1.837	0.169	0.079	0.144	0.349
E02	0.31	1.59	0.019	19.88	29.02	1.92	48.24	5.249	1.344	0.107	2.263	0.387	0.195	0.153	0.464
E03	0.29	1.52	0.003	2.77	35.70	2.36	59.20	0.438	0.612	0.012	0.339	0.047	0.016	0.063	0.028
E04	0.50	1.31	0.009	5.29	33.79	3.89	57.06	1.064	0.512	0.032	0.640	0.203	0.032	0.153	0.091
E05	0.54	1.74	0.014	19.24	30.01	5.59	45.16	4.558	1.172	0.115	2.540	0.440	0.139	0.258	0.497
E06	0.52	1.40	0.020	8.79	32.92	6.14	52.16	1.911	0.642	0.047	1.274	0.232	0.082	0.168	0.212
E07	0.50	1.80	0.025	17.15	30.23	4.31	48.33	4.075	1.227	0.095	2.456	0.233	0.132	0.198	0.471
E08	0.41	2.22	0.015	13.75	31.25	5.50	49.53	2.966	1.348	0.074	1.942	0.258	0.141	0.142	0.348
E09	0.45	1.02	0.032	18.22	29.90	5.38	46.52	4.654	0.859	0.102	2.383	0.395	0.165	0.180	0.380
E10	0.43	2.25	0.015	17.52	30.59	4.96	47.19	4.092	1.531	0.094	2.421	0.235	0.174	0.148	0.454
E11	0.53	2.46	0.006	6.47	34.25	5.80	53.49	1.106	1.193	0.031	0.815	0.108	0.051	0.138	0.136
E12	0.49	1.51	0.006	5.19	33.59	8.62	52.60	0.920	0.635	0.022	0.704	0.123	0.055	0.156	0.108
E13	0.43	1.79	0.010	23.25	28.77	4.28	43.70	5.630	1.598	0.129	3.238	0.362	0.252	0.190	0.624
E14	0.41	1.31	0.011	11.38	32.92	7.30	48.40	2.573	0.686	0.061	1.730	0.264	0.151	0.130	0.339
E15	0.47	1.29	0.006	3.90	35.48	8.14	52.43	0.703	0.396	0.016	0.582	0.120	0.041	0.123	0.074
E16	0.33	0.75	0.040	18.72	34.52	5.79	40.94	4.602	0.685	0.143	2.668	0.422	0.208	0.147	0.407
E17	0.51	1.23	0.023	17.62	30.73	6.13	45.53	4.140	1.023	0.090	2.423	0.399	0.225	0.199	0.553
E18	0.56	1.37	0.012	4.63	35.27	7.36	52.74	0.698	0.763	0.016	0.523	0.183	0.058	0.158	0.082
E19	0.42	1.51	0.015	17.00	30.34	4.21	48.50	4.175	1.031	0.102	2.432	0.250	0.161	0.180	0.472
E20	0.52	2.21	0.030	19.10	30.32	4.72	45.92	4.498	1.700	0.109	2.520	0.315	0.200	0.208	0.478
E21	0.17	2.02	0.015	5.93	35.41	3.00	55.71	1.154	0.888	0.031	0.796	0.091	0.043	0.062	0.121
E22	0.16	1.98	0.016	7.96	34.51	2.94	54.56	1.720	1.033	0.042	1.031	0.112	0.070	0.071	0.177
E23	0.40	1.37	0.019	5.34	33.72	5.90	55.04	1.127	0.644	0.026	0.718	0.107	0.037	0.125	0.074
E24	0.34	1.67	0.025	13.67	31.32	4.47	50.45	3.240	1.197	0.070	1.801	0.224	0.133	0.128	0.338
E25	0.22	1.55	0.017	4.84	35.05	6.41	53.69	0.957	0.814	0.016	0.459	0.191	0.038	0.063	0.031
E26	0.21	1.78	0.029	12.11	30.24	3.58	47.07	5.003	1.375	0.098	2.258	0.400	0.168	0.136	0.359
E27	0.18	2.41	0.060	19.13	30.92	2.27	47.68	4.282	1.718	0.115	2.998	0.218	0.139	0.128	0.554
E28	0.22	1.77	0.049	17.83	31.06	3.54	47.54	4.212	1.512	0.098	2.093	0.478	0.205	0.140	0.385
E29	0.26	2.23	0.026	24.71	27.82	2.28	44.59	6.052	1.802	0.126	3.262	0.389	0.209	0.193	0.648

APPENDIX 5.1 (continued)

Sample no.	Chlorine	Sulphur	Phosphorus	Ash	Volatile matter	Total moisture	Fixed carbon	Silicon	Iron	Titanium	Aluminium	Calcium	Magnesium	Sodium	Potassium
E30	0.42	1.54	0.032	18.00	30.42	3.02	48.79	4.351	1.225	0.092	2.624	0.218	0.147	0.208	0.503
E31	0.22	2.18	0.030	17.94	30.07	2.43	50.00	4.252	1.496	0.107	2.492	0.242	0.152	0.166	0.448
E32	0.32	1.94	0.016	16.82	30.29	3.50	49.51	4.174	1.368	0.102	2.226	0.212	0.168	0.175	0.452
E33	0.62	1.33	0.020	17.49	29.58	5.02	48.00	4.295	0.950	0.095	2.360	0.363	0.190	0.295	0.448
E34	0.66	1.95	0.012	14.78	30.69	5.62	48.93	3.356	1.148	0.081	2.068	0.338	0.120	0.264	0.356
E35	0.71	1.67	0.006	5.09	34.26	5.13	55.53	0.883	0.626	0.027	0.676	0.158	0.028	0.231	0.075
E36	0.29	1.51	0.012	15.78	29.96	4.27	50.10	3.899	0.962	0.095	2.287	0.220	0.134	0.179	0.452
E37	0.45	1.30	0.020	17.32	29.74	3.93	49.20	4.310	0.934	0.104	2.584	0.248	0.146	0.244	0.489
E38	0.58	1.28	0.004	5.20	33.45	7.67	53.82	0.920	0.525	0.025	0.634	0.292	0.044	0.189	0.106
E39	0.66	1.82	0.014	14.39	31.18	6.36	48.74	3.144	1.081	0.086	1.950	0.314	0.117	0.272	0.398
E40	0.50	1.51	0.008	9.94	32.01	7.02	51.27	2.090	0.784	0.054	1.365	0.294	0.084	0.198	0.280
E41	0.52	1.42	0.003	3.08	34.93	6.51	55.50	0.422	0.442	0.015	0.336	0.205	0.020	0.142	0.036
E42	0.37	2.04	0.033	21.31	28.84	3.35	46.56	5.267	1.565	0.115	2.906	0.221	0.167	0.229	0.565
E43	0.18	1.70	0.022	24.80	27.91	2.89	45.72	6.320	1.838	0.142	3.236	0.443	0.306	0.166	0.586
E44	0.22	2.00	0.026	19.42	29.49	2.98	49.58	4.250	2.152	0.093	2.205	0.708	0.222	0.122	0.435
E45	0.24	1.68	0.011	7.88	33.48	2.73	57.48	1.606	0.768	0.040	1.112	0.226	0.90	0.082	0.150
E46	0.25	1.38	0.008	4.11	35.56	2.93	59.14	0.808	0.492	0.021	0.608	0.082	0.030	0.093	0.066
E47	0.21	2.24	0.048	21.98	29.64	2.82	47.01	4.969	1.844	0.118	3.410	0.354	0.199	0.187	0.630
E48	0.46	1.48	0.020	7.22	32.40	5.28	58.17	1.220	1.432	0.039	0.892	0.134	0.061	0.152	0.111
E49	0.42	1.72	0.026	18.25	29.43	4.74	49.95	4.212	1.472	0.109	2.744	0.242	0.176	0.190	0.522
E50	0.24	1.88	0.020	8.21	33.33	7.24	55.22	1.778	1.111	0.039	0.862	0.255	0.079	0.085	0.109
E51	0.15	1.56	0.018	17.92	29.27	7.61	48.92	4.655	1.290	0.107	2.239	0.333	0.156	0.113	0.342
E52	0.62	1.88	0.010	17.72	33.45	5.37	45.92	3.906	1.356	0.117	2.524	0.494	0.155	0.263	0.448
E53	0.57	1.26	0.014	3.58	34.79	7.32	58.60	0.592	0.464	0.104	0.482	0.154	0.037	0.138	0.034
E54	0.53	1.46	0.074	5.73	32.26	5.44	59.82	0.965	0.560	0.042	0.978	0.233	0.028	0.153	0.069
E55	0.41	1.97	0.024	11.00	31.39	4.72	55.51	2.317	1.096	0.062	1.718	0.189	0.086	0.147	0.301
E56	0.36	2.26	0.028	15.94	29.76	3.69	52.55	3.611	1.493	0.086	2.439	0.200	0.125	0.154	0.463
E57	0.70	1.89	0.005	5.38	33.17	6.36	58.83	0.937	0.790	0.032	0.783	0.127	0.030	0.202	0.072
E58	0.42	1.40	0.002	4.31	34.68	4.17	59.31	0.803	0.614	0.024	0.622	0.117	0.029	0.132	0.086
E59	0.32	2.35	0.004	4.38	34.90	3.82	59.16	0.592	1.245	0.024	0.495	0.068	0.026	0.089	0.056

APPENDIX 5.1 (continued)

Sample no.	Chlorine	Sulphur	Phosphorus	Ash	Volatile matter	Total moisture	Fixed carbon	Silicon	Iron	Titanium	Aluminium	Calcium	Magnesium	Sodium	Potassium
E60	0.68	1.44	0.007	6.51	32.51	6.26	58.38	1.316	0.585	0.041	0.986	0.154	0.059	0.227	0.152
E61	0.50	2.98	0.013	15.28	32.47	6.23	49.07	3.240	1.078	0.082	2.136	0.186	0.147	0.187	0.368
E62	0.38	1.01	0.030	8.97	32.48	5.50	56.14	2.082	0.332	0.113	1.776	0.144	0.054	0.133	0.130
E63	0.50	1.23	0.008	8.08	32.62	8.56	55.49	1.606	0.714	0.044	1.132	0.242	0.104	0.162	0.228
E64	0.36	1.24	0.008	10.04	32.66	9.26	52.95	2.206	0.656	0.060	1.574	0.194	0.121	0.142	0.321
E65	0.55	2.00	0.004	4.80	35.22	5.00	57.88	0.716	0.942	0.023	0.598	0.117	0.036	0.146	0.062
E66	0.47	1.50	0.006	6.22	33.23	9.41	56.45	1.140	0.724	0.032	0.898	0.144	0.068	0.157	0.142
E67	0.35	1.30	0.006	10.16	31.41	8.76	54.43	2.174	0.770	0.058	1.568	0.228	0.135	0.117	0.312
E68	0.42	2.32	0.018	36.74	23.16	5.08	36.89	9.226	2.466	0.264	5.280	0.342	0.377	0.340	1.022
E69	0.42	0.89	0.029	4.59	33.47	8.18	58.55	0.930	0.271	0.026	0.785	0.194	0.036	0.128	0.036
E70	0.41	2.10	0.010	14.90	31.94	4.35	51.03	3.272	1.312	0.084	2.220	0.272	0.171	0.172	0.439
E71	0.45	2.32	0.006	7.72	33.08	6.22	56.50	1.470	1.116	0.040	1.106	0.130	0.065	0.129	0.166
E72	0.52	3.28	0.006	7.72	34.71	6.07	54.83	1.132	1.938	0.040	0.826	0.116	0.056	0.152	0.150
Mean $\bar{x}$	0.41	1.73	0.0183	12.37	31.95	5.20	51.70	2.832	1.086	0.072	1.721	0.243	0.116	0.163	0.304

CHAPTER 6

THE MULTI-ELEMENT ANALYSIS OF SOLUTIONS OF COAL ASH USING INDUCTIVELY COUPLED PLASMA - OPTICAL EMISSION SPECTROSCOPY

6.1 INTRODUCTION

The operational problems encountered in coal combustion and utilisation make it necessary to identify the chemical composition of coal ashes. The analyses of samples decarbonised at low temperatures are also used to provide valuable information concerning the elemental composition of coal.

Many authors have attempted to relate ash composition to the physical and chemical characteristics of coal. Bickelhaupt[188] has shown that the elemental composition of fly-ash influences its electrical resistivity and thus considerably effects the ease with which it can be collected by the electrostatic precipitators used at power stations. The chemical composition of coal ash and its relationship to high-temperature fireside corrosion and fouling of boilers have been considered by several authors.[137, 189-191] The understanding of trace element chemistry in coal combustion has been increased by analysis of both bulk and individual particles of ash.[192-194] However, without doubt the most useful application for the chemical analysis of coal and coke ashes is the assessment of fusion, softening and slagging characteristics of the ash generated in pulverised fuel combustors.[26,195-197] The NCB uses the determination of the silica ratio* described in Modern Power Station Practice[198] as one of a number of indicators of high temperature behaviour of mineral matter. This ratio is used in conjunction with the ash fusion test outlined in BS 1016[149] to assess the fusion characteristics of ash. The use of the elemental analysis of ash will become of increasing importance with the advent of modern technologies such as fluidised bed combustion.

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) is a relatively new routine analytical technique, first reported by Greenfield in 1964[199] and considered by several authors to be complementary to Atomic-Absorption Spectrometry.[200,201] A brief description of the technique is presented here but the reader is referred to more detailed reviews.[202, 203,204]

$$* \quad \text{silica ratio} = \frac{\%\ SiO_2 \times 100}{\%\ SiO_2 + \%\ Fe_2O_3 + \%\ CaO + \%\ MgO}$$

The ICP is a highly ionised, very hot gas reaching temperatures of 6000 - 10000^{o}K. It is sustained in a quartz torch by an induction coil generated by a powerful radio-frequency generator. A schematic drawing of a plasma torch showing the three separate gas flows is illustrated in Figure 6.1. The coolant gas prevents the plasma melting the torch, the plasma gas sustains the plasma and the carrier gas transports the sample aerosol into the plasma.

The discharge of a Tesla coil introduces seed electrons into the plasma argon and the oscillating magnetic field of the induction coil accelerates these electrons in an annular (toroidal) path so that they gain sufficient energy to ionise the argon, thereby producing more electrons. As the radio-frequency is continuously applied the plasma becomes self-sustaining.

The ICP-OES technique, with its high temperature and relatively long residence time of sample within the plasma, ensures almost total breakdown of the analyte species and is therefore a very efficient atom source. As the sample is confined to the narrow central channel which is externally heated by the surrounding plasma it has a relatively uniform radial temperature distribution. Thus, the plasma is said, to be 'optically thin' which minimises, 'self-absorption' and 'self-reversal' phenomena explained in Chapter 2. This characteristic results in large linear dynamic working ranges.

In the instrument used in this study the liquid sample is converted to an aerosol by the nebuliser and then passes into the spray chamber where an impact bead removes the larger droplets. The fine aerosol is transported by the carrier gas through the central tube of the torch into the plasma. In the plasma the sample is atomised and the atoms are raised to higher energy levels. These excited atoms then emit electromagnetic radiation of characteristic wavelengths which pass through the optics and slits of the spectrometer. The electromagnetic radiation is diffracted from the grating onto the secondary slit frame behind which the photomultiplier tubes are mounted. These convert the electromagnetic energy to electrical signals relative to the intensity of the elemental emission. A schematic representation of the sequential ICP spectrometer used in this study is shown in Figure 6.2

Figure 6.1 A cross section of the torch

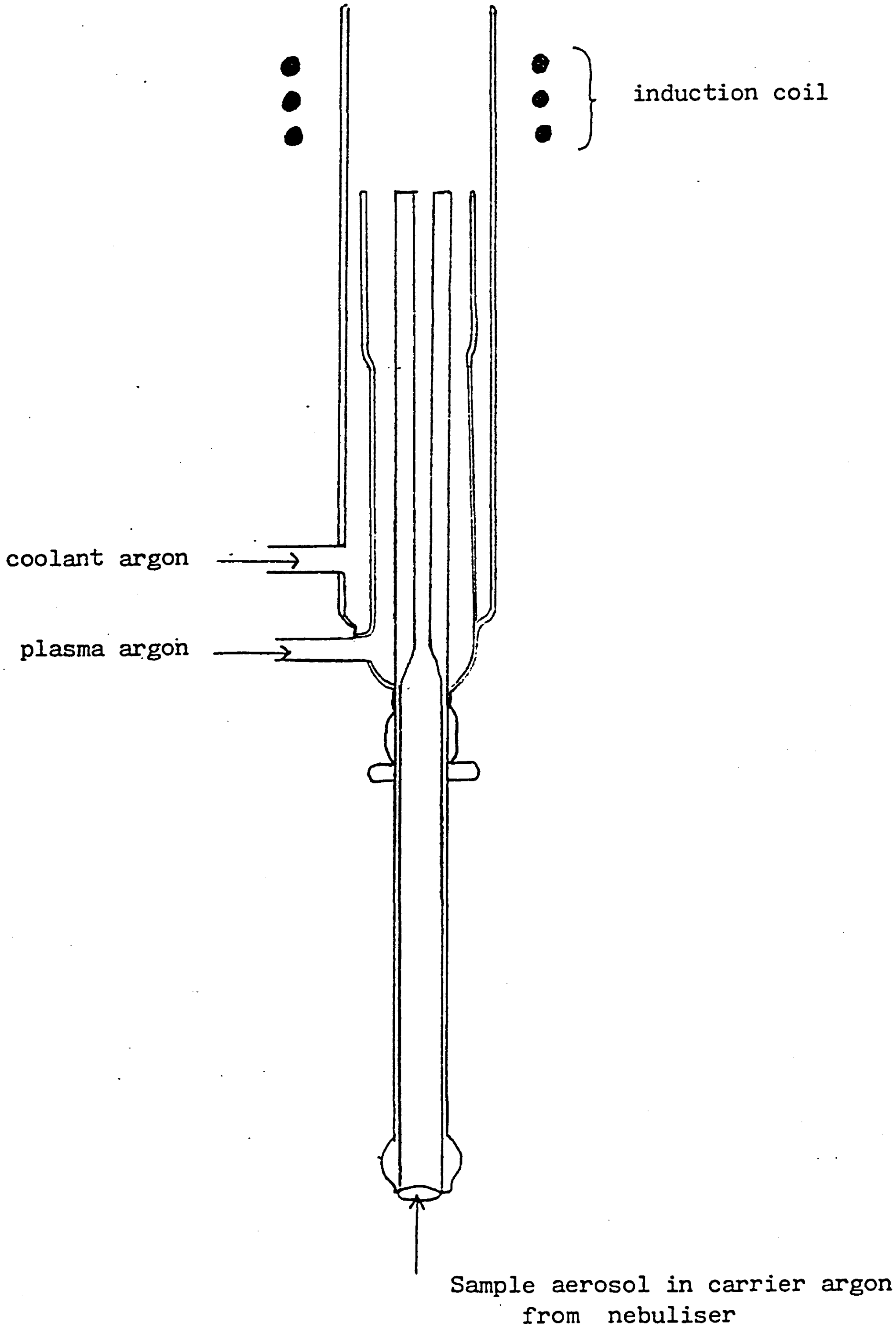
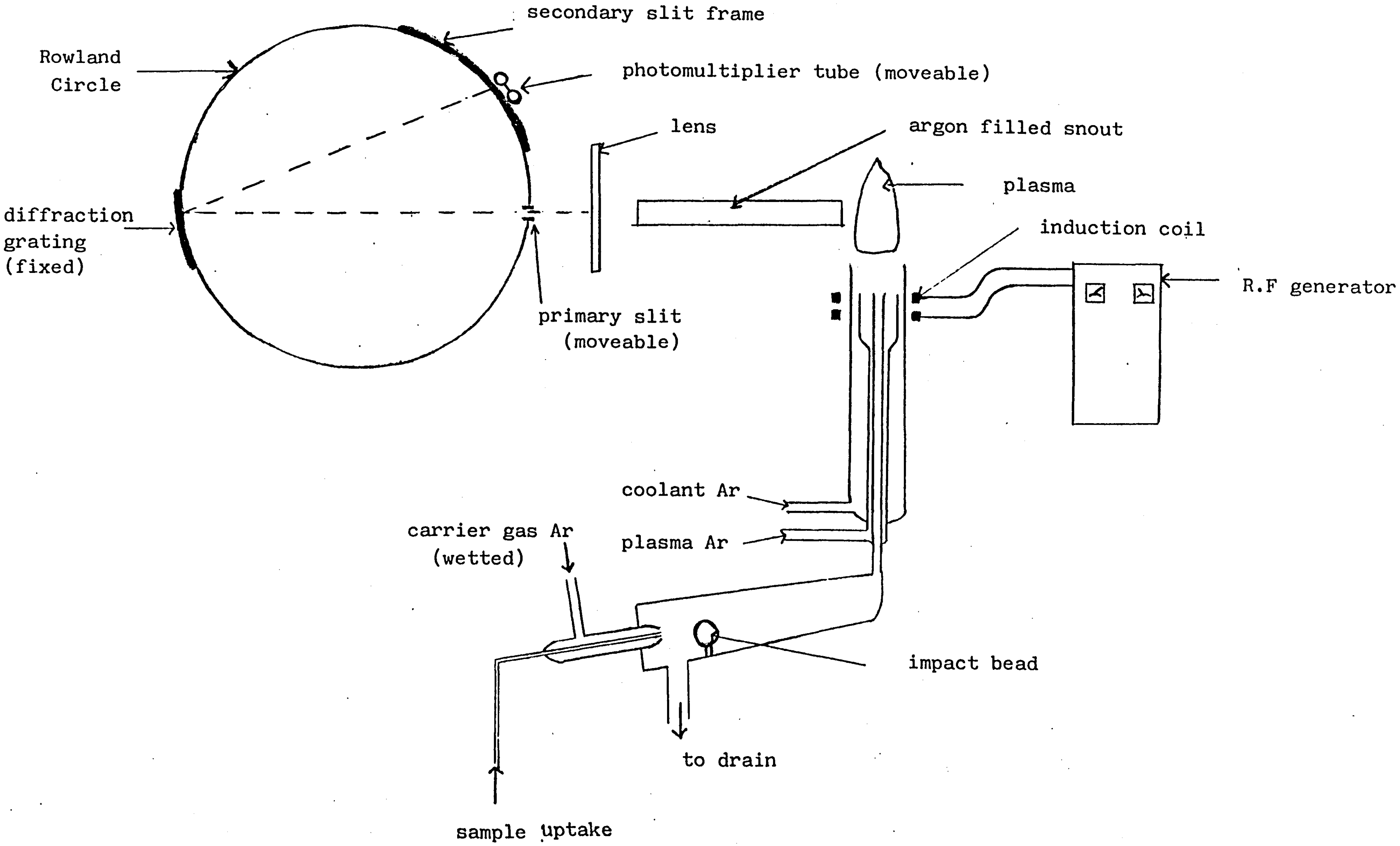


Figure 6.2 Diagram of a sequential inductively coupled plasma emission spectrometer



The ICP-OES technique has been applied successfully by Walsh for the determination of major, minor and trace elements in geological samples. The use of ICP-OES for the analysis of coal ash is relatively new, although Nadkarni[206] describes its usefulness for the comprehensive elemental analysis of coal and fly ash after digestion in a Parr bomb. Wilkinson, Ebdon and Jackson[207] have used the technique to analyse coal slurries and silicate rock powders sprayed directly into the plasma and Kin, Zerezghi and Caruso[208] for the direct injection and analysis of NBS coal fly ash.

The method outlined here describes a rapid, simple digestion procedure for the analysis of the major and minor constituents of coal ash by ICP-OES.

6.2 EXPERIMENTAL

6.2.1 Equipment

Model 3520 vacuum sequential ICP-OE spectrometer, (Applied Research Laboratories, Luton, Bedfordshire.) See Figure 6.2
100 cm^3 'Nalgene' containers (Fisons Scientific Equipment, Loughborough, Leicestershire) or 100 cm^3 teflon containers (Cowie Scientific Limited, Middlesborough, Cleveland).
Agate pestle and mortar (Gallenkamp Limited, Loughborogh, Leicestershire)
100 cm^3 'Gradplex' volumetric flasks (Fisons Scientific Equipment, Loughborough, Leicestershire).
Grade 'A' glass pipettes (Fisons Scientific Equipment, Loughborough Leicestershire)
100 cm^3 PTFE pipette (Fisons Scientific Equipment, Loughborough Leicestershire).

6.2.2 Reagents

All chemicals were obtained from BDH Chemicals, Poole, Dorset.
Hydrofluoric acid 48% v/v AnalaR grade
Boric acid solution 4% w/v AnalaR grade
Standard solutions, (silicon, aluminium, calcium, magnesium, iron, titanium, sodium, potassium and manganese), 1000 $\mu g\ ml^{-1}$ Spectrosol grade.
Sodium sulphate, Na_2SO_4 Aristar grade
Potassium dihydrogen orthophosphate, KH_2PO_4 Aristar grade
Nitric acid Sp. gravity 1.42 Aristar grade

6.2.3 Digestion of ash for Inductively Coupled Plasma Optical Emission Spectroscopy

A small sample of ash was hand-ground in a pestle and mortar so that it all passed through a 240 BS mesh sieve and then ignited at 815°C.[149] A weighed increment of this ash (50 mg ± 0.01 mg) was transferred to a 100 cm^3 teflon container, one or two drops of deionised water were added and the container swirled to ensure complete wetting of the ash. Hydrofluoric acid (2.5 cm^3) was added carefully using a PTFE pipette and the container sealed and placed in an air oven at 105-110°C for thirty minutes. The container was allowed to cool completely and boric acid solution added (65 cm^3). The boric acid complexes with the excess hydrofluoric acid to produce a fluoroborate complex. This complex attacks borosilicate glass and thus the use of polypropylene 'gradplex' flasks is recommended. The container was sealed and shaken to ensure complete dissolution of ash and precipated fluorides. The container may be returned to the oven at this stage for a further thirty minutes if dissolution was found to be incomplete. If this still does not result in dissolution, then the ash usually has not been ground as specified and the procedure should be commenced again. Experience in using this digestion method routinely for six years has shown this to be a very infrequent problem. The cooled solution was quantitatively transferred to a 100 cm^3 Gradplex volumetric flask and the nickel solution (5 cm^3 of 400 $\mu g\ ml^{-1}$ solution in 5% v/v Aristar nitric acid) added as an internal standard. The contents of the flask were finally made up to 100 cm^3 using deionised water.

6.2.4 Development of ICP-OES analytical parameters and calibration of the spectrometer

6.2.4.1 Spectral considerations

The major and minor elements and spectral lines initially examined for calibration are listed below:

Silicon	251.611 nm	atomic line
Aluminium	308.215 nm	atomic line
Calcium	317.933 nm	ionic line
Magnesium	279.553 nm	" "
Iron	259.940 nm	" "
Titanium	334.441 nm	" "
Manganese	257.610 nm	" "
Sodium	589.592 nm	atomic line
Potassium	766.490 nm	" "
Phosphorus	178.287 nm	ionic line
Sulphur	180.731 nm	" "

The spectral lines were scanned to obtain their exact wavelength position and an illustration of such a scan for titanium is given in Figure 6.3 As can be seen from this figure a titanium doublet was obtained and so an alternative line for titanium at 337.280 was located and scanned.

The spectral lines were then examined for spectral interferences by spraying separately 1000 μg ml^{-1} solutions of each of the other ten elements and noting any observed changes in intensity. An increase in intensity above the background was found at the sulphur line when 1000 μg ml^{-1} calcium solution was sprayed. The interference was attributed to the calcium 180.75 nm ionic line. A graphics plot showing this interference is given in Figure 6.4. The alternative sulphur line at 182.033 nm was examined and found to be free from interference. A blank solution and a solution with a concentration to cover the maximum anticipated, were then sprayed to enable the attenuator settings of the detector to be selected.

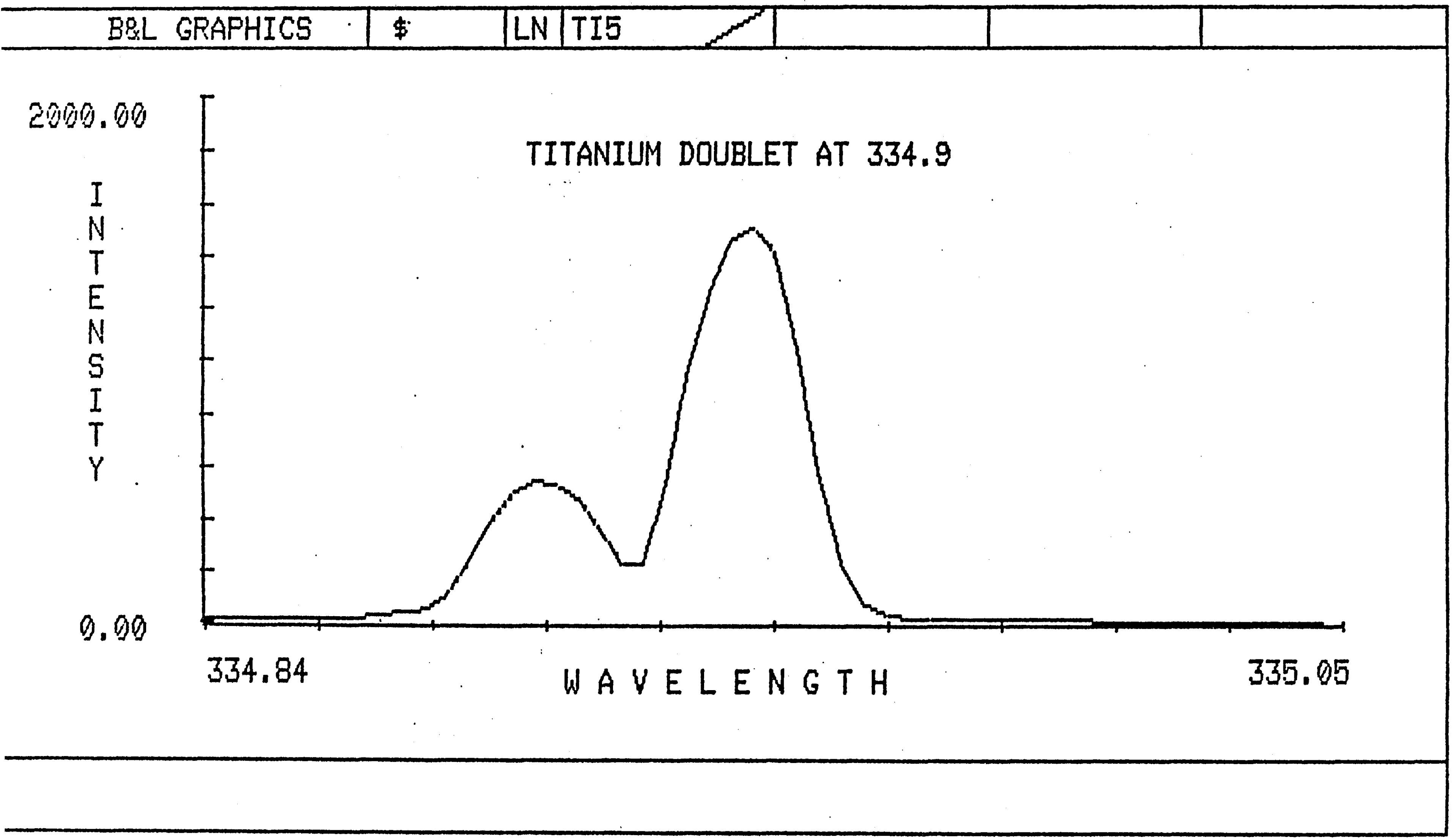
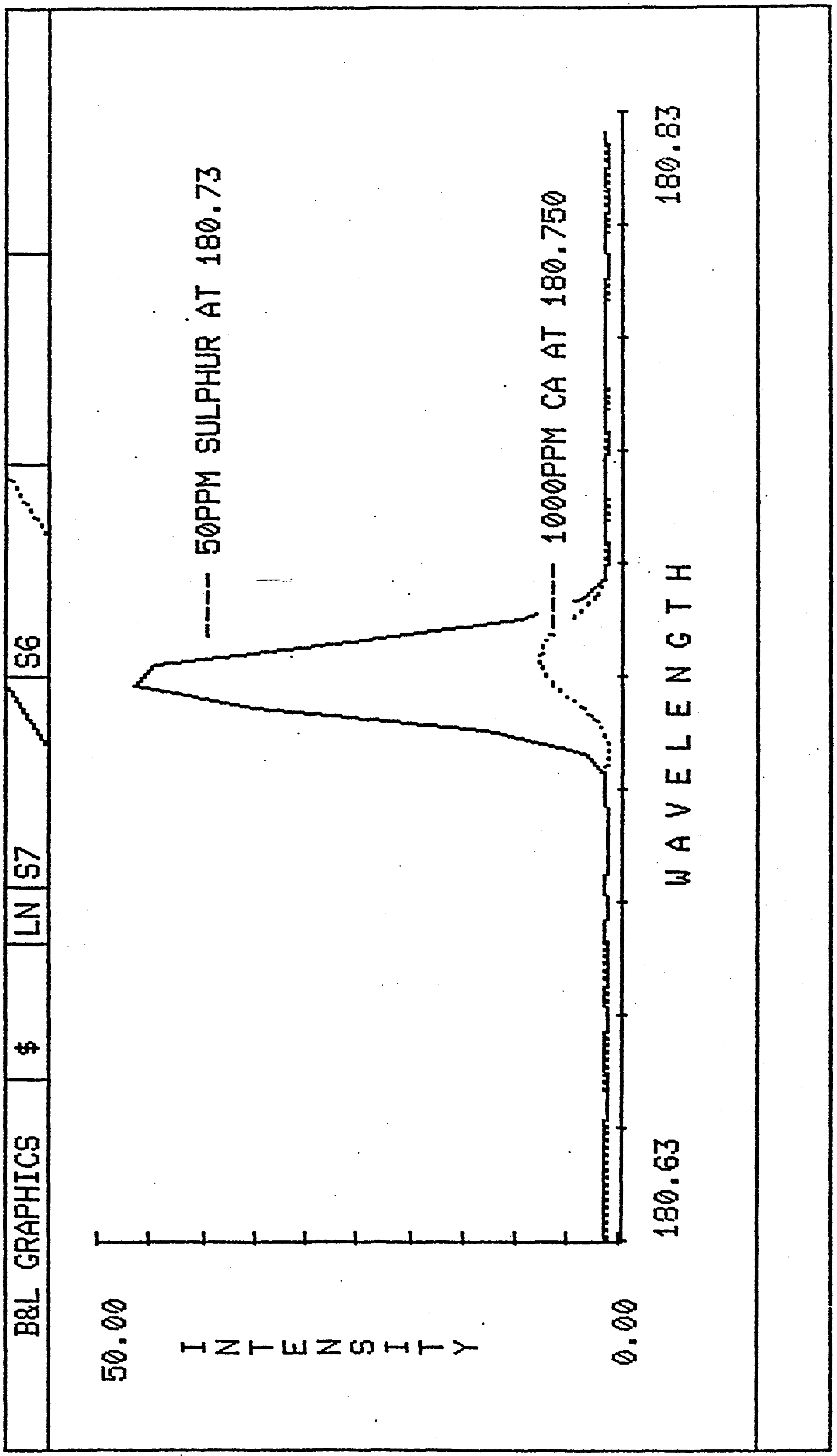

B&L GRAPHICS
$
LN
TI5
TITANIUM DOUBLET AT 334.9
2000.00
INTENSITY
0.00
334.84
WAVELENGTH
335.05

Figure 6.4 Interference of the calcium 180.75 nm line on sulphur



6.2.4.2 Calibration

The use of an aqueous calibration gave results for certified standards in poor agreement with their certified values. This is not surprising, accepting the effect of viscosity upon the absolute intensities obtained by the ICP-OES technique. The use of standards matrix-matched for hydrofluoric and boric acids gave a satisfactory calibration for all elements except aluminium. The aluminium results were found to be approximately eight percent low when compared to certified values. The most satisfactory calibration was finally obtained by taking increments of three certified reference materials, two NCB certified ash samples and 'Blast Furnace Slag' (BCS 367, Bureau of Analysed Samples Limited, Middlesborough, Cleveland) to produce calibration graphs for silicon, aluminium, iron, calcium and magnesium. The remaining six elements were calibrated using BDH spectrosol solutions matrix matched for hydrofluoric and boric acid contents. The reason for the improved calibration when using standard reference materials may be that several elements in the ash digest (particularly aluminium) precipitate as fluorides but dissolve when complexed with the boric acid solution. These elements are therefore in a different chemical form to that in the BDH spectrosol solution matrix matched for hydrofluoric and boric acid contents.

In routine operation of the instrument the sample transport system was found to be extremely temperature sensitive and so it was decided for calibration and analysis to use an internal standard to ratio element intensities. The internal standard should only occur in coal in trace amounts, not interfere with the selected elements or be interfered with itself by the elements present. It should then compensate for changes in sensitivity caused by the ICP sample transport system.

Three elements for use as an internal standard were investigated: zirconium, lanthanum and nickel. Zirconium gave problems with frequent blockage of the nebuliser and lanthanum gave erratic intensities particularly for silicon and aluminium, probably due to the complex emission spectrum of lanthanum. Nickel has the advantage that an atomic line at 232.003 nm can be used to ratio the atomic analyte lines, whilst an ionic line at 231.604 nm can be used to ratio the ionic analyte lines. For this purpose, 20 μg ml^{-1} of the spectrosol nickel solution were added to the calibration standards and samples before making up to 100 ml. The use of nickel as an internal reference standard, gave excellent results without any operational problems and was therefore evaluated in this study.

It should be noted that solutions used for ICP analysis should be free from particulate matter when using conventional nebulisers and if necessary, filtration with a Whatman 541 hardened ashless paper is recommended. The original teflon containers used were found to distort slightly in the air-oven but returned to their original shape on cooling. However, the latest vessels purchased distorted badly and were found to be thin-walled and weigh much less than the 50g of the original satisfactory ones. An alternative supply is therefore suggested in section 6.2.1 and no problems of distortion with these containers have been found.

The digestion procedure described in section 6.2.3 is improved by the addition of a few millilitres of concentrated nitric and/or hydrochloric acids for ash samples which are very high in iron, calcium or phosphorus. Such samples are in fact atypical but high calcium contents could be present in the ash from fluidised bed combustors.

6.2.5 Routine operation of the ICP spectrometer for ash analysis

At the start of the day the plasma is ignited, allowed to stabilise for approximately forty-five minutes and the spectrometer calibrated according to the manufacturer's instructions. The calibration is drift-corrected by spraying a standard at the top of the calibration range and a blank solution for each element. As a further check to ensure that no problems have occurred in the drift correction a well analysed standard ash solution is then sprayed. If the results from this standard are satisfactory $\leq$(ts$\sqrt{2}$ percent of the mean percentage*) then unknown solutions are analysed. The analysis cycle for eleven elements takes ten minutes to complete per sample and the performance of the instrument is monitored by analysis of the reference ash after every ten samples.

Sample identification and data processing instructions are input via the VDU terminal. It was found necessary to use a pre-integration time of 30 seconds and three determinations of five seconds integration for each element. The results are then displayed on the VDU or printed-out using the terminal.

The nebuliser and spray chamber are rinsed for 2 or 3 minutes with nitric acid (5% m/m) after each sample analysis. This was found to reduce dramatically nebuliser blockage which is caused by the high salt concentration (3% m/v) in the analyte solutions. It was also found that continued spraying of the analyte solution caused deposits of boric acid to build up within the inner channel of the quartz torch. This lead to poor precision and an excessive deposition of salt resulted in the plasma being extinguished.

* t = students t for 95% confidence limits
s = standard deviation calculated for the element

6.3 RESULTS AND DISCUSSION

A total of eighteen certified standard materials or standard reference samples have been analysed using the rapid ICP-OES method described. The results obtained using three separate analyses of a single sample digest are given in Table 6.1. The statistical evaluation of the differences between the ICP results and the reference values for each separate sample are given in Table 6.2, whilst the individual element comparisons are given in Table 6.3. For these statistical appraisals samples 1633(a) and 1635 have been excluded because of the large number of uncertified values used for comparison.

The results for all eleven element determinations are in excellent agreement with standard values. The best Standard Deviation (SD) of the differences was found for phosphorus pentoxide (0.0187) and the poorest for alumina (0.6932). Samples of BCS No. 315 firebrick and CA 6427E gave the best SD of the differences for the total elemental analysis (0.160), whilst the poorest SD was found for sample CA 6429E (0.502).

The precision of the method was assessed by ten replicate digestions and analyses of a well mixed typical East Midlands Regional coal ash. The digestion and analyses were carried out on different days. The day to day drift of the spectrometer is compensated by the use of a top and bottom standard for each of the calibration elements. The results of these analyses are given in Table 6.4.

Manganese oxide showed no deviation for ten determinations and the poorest Relative Standard Deviation was found for sulphur (6.4 percent). The precision of the determinations of silica, alumina and the other analyte elements is considered to be excellent and compares very favourably with British Standard Method repeatability criteria.[149] The ICP-OES method has been submitted to the British Standards Institution for acceptance.

TABLE 6.1

Comparison of ICP value with certified or reference values

Sample/Oxide		SiO_2 % m/m	Al_2O_3 % m/m	Fe_2O_3 % m/m	TiO_2 % m/m	CaO % m/m	MgO % m/m	Na_2O % m/m	K_2O % m/m	Mn_3O_4 % m/m	P_2O_5 % m/m	SO_3 % m/m	Totals
NBS 1632a (Coal)	Certified value	58.1^2	25.9^2,27.0^1	7.3	1.4^1	1.5	0.8^1	0.5	2.3	0.1	0.3^2	-	-
	ICP determinations	58.0	26.6	7.3	1.1	1.7	0.8	0.5	2.5	< 0.1	0.3	1.0	99.8
		58.3	26.5	7.1	1.0	1.7	0.8	0.5	2.5	< 0.1	0.2	0.9	99.5
		58.1	26.5	7.4	1.1	1.7	0.8	0.5	2.6	< 0.1	0.3	1.2	100.2
	Mean ICP figure	58.1	26.5	7.3	1.1	1.7	0.8	0.5	2.5	< 0.1	0.3	1.0	99.8
NBS 1633a (Ash)	Certified value	48.8	26.5^1	13.4	1.3^1	1.6	0.8	0.2	2.3	< 0.1	-	-	-
	ICP determinations	49.3	28.2	13.0	1.3	1.7	0.8	0.2	2.3	< 0.1	0.4	0.3	97.5
		49.3	28.3	13.5	1.4	1.7	0.8	0.2	2.2	< 0.1	0.4	0.3	98.1
		49.0	28.4	13.5	1.4	1.7	0.8	0.2	2.3	< 0.1	0.4	0.3	98.0
	Mean ICP figure	49.2	28.3	13.3	1.4	1.7	0.8	0.2	2.3	< 0.1	0.4	0.3	97.9
NBS 1635 (Coal)	Certified value	29.0^2	12.8^1	7.2	0.7^1	16.6^2	3.4^2	6.8^1	0.2^2	0.1	-	-	-
	ICP determinations	33.8	13.3	7.1	0.7	17.0	3.5	6.3	0.4	0.1	1.1	15.0	98.3
		34.0	13.1	7.1	0.7	17.0	3.4	6.4	0.5	0.1	1.2	14.9	98.4
		33.9	13.3	7.1	0.7	17.1	3.5	6.6	0.5	0.1	1.2	15.2	99.2
	Mean ICP figure	33.9	13.2	7.1	0.7	17.0	3.5	6.4	0.5	0.1	1.2	15.0	98.6
BCS No.315 (Firebrick)	Certified value	51.2	42.4	3.0	1.2	0.3	0.6	0.1	0.5	< 0.1	-	-	-
	ICP determinations	51.1	42.3	3.0	1.2	0.5	0.6	0.1	0.5	< 0.1	< 0.1	< 0.1	99.3
		51.0	43.0	3.0	1.2	0.5	0.6	0.1	0.4	< 0.1	< 0.1	< 0.1	99.8
		51.6	42.3	3.1	1.2	0.5	0.6	0.1	0.5	< 0.1	< 0.1	< 0.1	99.9
	Mean ICP figure	51.2	42.5	3.0	1.2	0.5	0.6	0.1	0.5	< 0.1	< 0.1	< 0.1	99.6
BCS No.372 (Portland Cement)	Certified value	21.3	5.4	2.5	0.3	65.8	1.3	0.2	0.6	0.1	-	2.4	-
	ICP determinations	21.8	5.4	2.5	0.3	66.0	1.4	0.1	0.5	0.1	0.2	2.3	100.6
		21.5	5.7	2.5	0.3	65.3	1.3	0.1	0.7	0.1	0.2	2.2	99.9
		21.3	5.6	2.5	0.3	65.9	1.3	0.3	0.6	0.1	0.2	1.9	100.0
	Mean ICP figure	21.5	5.6	2.5	0.3	65.7	1.3	0.2	0.6	0.1	0.2	2.1	100.1
776-1 (Firebrick Std)	Certified value	62.8	29.3	1.4	1.6	0.3	0.5	0.5	2.9	-	-	-	-
	ICP determinations	63.2	30.4	1.4	1.5	0.4	0.5	0.5	3.0	< 0.1	0.1	0.9	101.9
		62.6	29.9	1.5	1.5	0.4	0.5	0.4	3.0	< 0.1	0.1	0.8	100.7
		63.7	30.0	1.4	1.5	0.4	0.5	0.4	3.1	< 0.1	0.1	0.7	101.9
	Mean ICP figure	63.2	30.1	1.5	1.5	0.4	0.5	0.4	3.0	< 0.1	0.1	0.8	101.5

TABLE 6.1 (continued)

Sample/Oxide		SiO_2 % m/m	Al_2O_3 % m/m	Fe_2O_3 % m/m	TiO_2 % m/m	CaO % m/m	MgO % m/m	Na_2O % m/m	K_2O % m/m	Mn_3O_4 % m/m	P_2O_5 % m/m	SO_3 % m/m	Totals
AEH III (Ash)	Reference value	49.0	16.8	10.7	0.7	8.6	3.3	1.0	2.0	-	-	5.4	-
	ICP determinations	50.0	17.0	10.8	0.6	8.9	3.5	0.9	2.0	0.1	0.5	5.5	99.8
		49.5	16.6	10.7	0.6	8.9	3.4	0.9	1.9	0.1	0.5	5.3	98.4
		49.9	16.8	10.8	0.6	8.9	3.4	0.9	2.0	0.1	0.4	5.2	99.0
	Mean ICP figure	49.8	16.8	10.8	0.6	8.9	3.4	0.9	2.0	0.1	0.5	5.3	99.1
CA6466E (Ash)	Reference value	57.6	26.5	7.2	1.0	0.9	1.2	0.3	3.4	0.1	0.2	-	-
	ICP determinations	59.0	27.1	7.2	1.0	0.8	1.4	0.3	3.4	0.1	0.2	0.2	100.7
		58.3	26.7	7.2	1.0	0.8	1.4	0.2	3.4	0.1	0.2	0.1	99.4
		59.0	26.8	7.3	1.0	0.8	1.4	0.3	3.4	0.1	0.2	0.1	100.4
	Mean ICP figure	58.8	26.9	7.2	1.0	0.8	1.4	0.3	3.4	0.1	0.2	0.1	100.2
CA6656E (Ash)	Reference value	41.8	21.1	16.4	-	6.5	2.4	2.1	2.1	-	-	-	-
	ICP determinations	42.4	20.3	16.4	1.1	6.6	2.7	2.0	2.1	0.1	0.4	5.9	100.0
		41.7	19.8	16.5	1.0	6.6	2.7	2.0	2.1	0.1	0.4	5.7	98.6
		42.4	20.2	16.7	1.0	6.7	2.7	2.0	2.2	0.1	0.3	5.6	99.9
	Mean ICP figure	42.2	20.1	16.5	1.0	6.6	2.7	2.0	2.1	0.1	0.4	5.7	99.4
CA6427E (Ash)	Reference value	46.7	35.3	7.2	1.0	3.0	1.4	1.0	1.9	-	-	-	-
	ICP determinations	46.0	34.9	7.0	1.0	3.1	1.5	0.9	2.0	< 0.1	1.5	1.4	99.3
		45.7	34.6	7.1	1.0	3.1	1.4	0.9	2.0	0.1	1.5	1.2	98.6
		46.5	34.8	7.1	1.0	3.1	1.4	0.9	2.1	0.1	1.5	1.3	99.8
	Mean ICP figure	46.1	34.8	7.1	1.0	3.1	1.4	0.9	2.0	0.1	1.5	1.3	99.3
CA6428E (Ash)	Reference value	46.9	23.7	25.1	1.3	1.2	0.5	0.4	0.8	-	-	-	-
	ICP determinations	46.5	24.9	24.8	1.1	1.2	0.5	0.4	0.8	< 0.1	0.4	0.1	100.7
		46.0	24.7	24.9	1.1	1.2	0.5	0.4	0.8	< 0.1	0.4	< 0.1	100.0
		46.2	24.6	25.1	1.1	1.2	0.5	0.4	0.9	< 0.1	0.4	< 0.1	100.4
	Mean ICP figure	46.2	24.7	24.9	1.1	1.2	0.5	0.4	0.8	< 0.1	0.4	< 0.1	100.2
CA6429E (Ash)	Reference value	53.7	29.3	9.1	1.5	1.2	0.9	0.6	2.2	-	-	-	-
	ICP determinations	54.1	31.0	8.8	1.3	1.1	0.9	0.5	2.4	< 0.1	0.3	< 0.1	100.4
		53.6	30.7	8.8	1.3	1.1	0.9	0.5	2.3	< 0.1	0.3	< 0.1	99.5
		54.3	30.4	8.9	1.3	1.2	0.9	0.6	2.7	< 0.1	0.4	< 0.1	100.7
	Mean ICP figure	54.0	30.7	8.8	1.3	1.1	0.9	0.5	2.5	-	0.3	< 0.1	100.1

TABLE 6.1 (continued)

Sample/Oxide		SiO_2 % m/m	Al_2O_3 % m/m	Fe_2O_3 % m/m	TiO_2 % m/m	CaO % m/m	MgO % m/m	Na_2O % m/m	K_2O % m/m	Mn_3O_4 % m/m	P_2O_5 % m/m	SO_3 % m/m	Totals
YRL 4094 (Ash)	Reference value	42.5[3],43.0	37.2[3],37.6	4.4	1.2	4.0	1.2	1.7	1.1	< 0.1	3.0	1.1	-
	ICP determinations	42.6	36.9	4.2	1.1	3.9	1.2	1.6	1.2	< 0.1	3.1	0.7	96.5
		42.1	36.9	4.2	1.1	4.0	1.2	1.8	1.0	< 0.1	2.9	0.8	96.0
		41.8	35.8	4.2	1.1	3.9	1.1	1.8	1.3	< 0.1	3.2	0.8	95.0
	Mean ICP figure	42.2	36.5	4.2	1.1	3.9	1.2	1.7	1.2	< 0.1	3.1	0.8	95.8
YRL 4092 (Ash)	Reference value	53.0[3],53.3	34.6[3],34.0	5.8	1.6	0.8	0.7	0.2	2.4	< 0.1	0.4	0.2	-
	ICP determinations	52.1	34.3	5.6	1.6	0.7	0.8	0.1	2.2	< 0.1	0.4	< 0.1	97.8
		52.3	34.0	5.5	1.6	0.7	0.7	0.1	2.5	< 0.1	0.4	< 0.1	97.8
		51.9	34.1	5.6	1.5	0.7	0.7	0.3	2.4	< 0.1	0.5	< 0.1	97.7
	Mean ICP figure	52.1	34.1	5.6	1.6	0.7	0.7	0.2	2.4	< 0.1	0.4	< 0.1	97.8
YRL 3463 (Ash)	Reference value	35.2[3], 34.6	23.0[3],23.5	17.6	0.8	9.4	1.4	1.8	1.6	0.1	0.6	8.0	-
	ICP determinations	34.2	23.2	16.9	0.8	9.4	1.3	1.7	1.3	0.1	0.6	8.1	97.6
		34.5	23.2	17.5	0.8	9.4	1.3	1.8	1.6	0.1	0.5	7.8	98.5
		34.8	23.4	17.3	0.8	9.4	1.3	1.9	1.5	0.1	0.7	7.4	98.6
	Mean ICP figure	34.5	23.3	17.2	0.8	9.4	1.3	1.8	1.5	0.1	0.6	7.7	98.2
E48X (Ash)	Reference value	36.2	23.4	28.4	0.9	2.6	1.4	2.8	1.8	0.2	0.6	1.7	100.0
	ICP determinations	36.3	22.7	28.9	0.7	2.4	1.4	2.6	1.9	0.2	0.6	1.9	99.8
		36.8	22.7	28.6	0.7	2.5	1.4	2.6	2.0	0.2	0.6	1.8	99.9
		36.6	22.8	29.1	0.7	2.5	1.4	2.6	2.1	0.2	0.6	1.9	100.5
	Mean ICP figure	36.6	22.7	28.9	0.7	2.5	1.4	2.6	2.0	0.2	0.6	1.9	100.1
E64X (Ash)	Reference value	47.0	29.6	9.4	1.0	2.7	2.0	1.9	3.9	0.1	0.2	1.6	99.4
	ICP determinations	47.3	29.2	9.5	0.9	2.6	2.1	1.7	4.0	0.1	0.2	1.6	99.3
		47.3	29.0	9.5	0.9	2.6	2.1	1.6	4.0	0.1	0.2	1.5	98.8
	Mean ICP figure	47.3	29.1	9.5	0.9	2.6	2.1	1.7	4.0	0.1	0.2	1.6	99.1
AEH II (Ash)	Reference value	49.4	27.5	10.7	1.1	2.4	1.8	1.0	2.5	-	-	2.0	-
	ICP determinations	50.6	28.2	10.5	1.0	2.5	1.9	0.8	2.6	0.1	0.3	2.0	100.5
		50.1	27.8	10.4	1.0	2.5	1.9	0.8	2.6	0.1	0.3	2.0	99.5
		50.5	28.1	10.5	1.0	2.5	1.9	0.8	2.6	0.1	0.3	1.9	100.2
	Mean ICP figure	50.4	28.0	10.5	1.0	2.5	1.9	0.8	2.6	0.1	0.3	2.0	100.1

1 NBS uncertified value

2 E S, Gladney, Analytica Chimica Acta, 118, 1980, 385

3 East Midlands Regional Laboratory values by atomic absorption for alumina and colorimetric for silica using the HF digestion procedure.

TABLE 6.2

Comparison of ICP values for individual samples with reference values

	NBS 1632a	BCS No.315 Fire-brick	BCS No.372 Portland cement	YRL 4094	YRL 4092	YRL 3463	E48X	E64X	AEH II	AEH III	776-1 Firebrick standard	CA 6466E	CA 6656E	CA 6427E	CA 6428E	CA 6429E
Correlation Coefficient	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Gradient of regression line	0.9979	1.000	0.999	0.9841	0.9837	0.9921	1.0086	1.0013	1.0209	1.0149	1.0091	1.0202	1.0008	0.9859	0.9939	1.0147
Intercept	0.0340	0.0353	0.0051	0.0444	0.0081	0.0374	0.0691	0.0344	0.0841	-0.0618	0.0493	0.0292	0.0393	0.0347	0.0640	0.0186
Standard deviation about regression line	0.1284	0.0803	0.1496	0.1778	0.1632	0.1583	0.3288	0.2281	0.1677	0.1331	0.2383	0.1016	0.5047	0.0799	0.4980	0.5019
95% confidence limits	±0.256	±0.160	±0.299	±0.354	±0.326	±0.316	±0.658	±0.446	±0.336	±0.2662	±0.476	±0.202	±1.010	±0.160	±0.996	±1.004

TABLE 6.3

Statistical evaluation of ICP ash analysis for each element expressed as the oxide

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	Mn_3O_4	P_2O_5	SO_3
Correlation Coefficient	0.998	0.997	1.000	0.971	1.000	0.995	0.996	0.996		1.000	0.998
Gradient of regression line	1.0077	0.9919	1.0070	0.9244	0.9983	1.0969	0.9359	1.0338	?	1.0417	0.9755
Intercept	-0.2646	0.2658	-0.1100	-0.0035	0.0367	-0.0852	-0.0072	0.0077		-0.0247	-0.0438
Standard deviation about regression line	0.6497	0.6932	0.2249	0.0820	0.1361	0.0858	0.0697	0.0963		0.0187	0.1828
95% confidence limits	±1.2994	±1.3864	±0.4498	±0.1640	±0.2722	±0.1716	±0.1394	±0.1926		±0.0274	±0.3656

? insufficient variation for a statistical calculation

TABLE 6.4

Analysis of a typical coal ash to estimate precision of method

	Separate digests	% m/m									Mean	Range	σ	95% confidence limits	RSD/ %
	1	2	3	4	5	6	7	8	9	10					
SiO_2	54.01	52.93	52.82	53.38	53.39	53.75	53.32	53.34	52.80	53.52	53.33	52.80-54.01	0.392	53.33±0.78	0.74
Al_2O_3	26.28	26.03	25.76	25.96	25.96	26.18	25.84	25.92	25.67	26.28	25.99	25.67-26.28	0.208	25.99±0.42	0.80
Fe_2O_3	9.69	9.81	9.67	9.70	9.54	9.53	9.74	9.60	9.69	9.56	9.65	9.53-9.81	0.092	9.65±0.18	0.95
TiO_2	0.85	0.83	0.83	0.79	0.77	0.75	0.84	0.79	0.82	0.85	0.81	0.75-0.85	0.035	0.81±0.07	4.32
CaO	2.24	2.29	2.29	2.29	2.25	2.24	2.31	2.27	2.29	2.24	2.27	2.24-2.31	0.026	2.27±0.05	1.14
MgO	1.69	1.67	1.66	1.68	1.68	1.68	1.65	1.68	1.66	1.64	1.67	1.64-1.69	0.016	1.67±0.03	0.96
Na_2O	1.06	1.04	1.05	1.07	1.03	1.03	1.05	1.04	1.05	1.06	1.05	1.03-1.07	0.013	1.05±0.03	1.24
K_2O	3.09	3.04	3.02	3.07	3.13	3.20	3.08	3.11	2.97	3.11	3.08	2.97-3.20	0.063	3.08±0.13	2.05
Mn_3O_4	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	-	ND	0.09±0.00	ND
P_2O_5	0.37	0.35	0.38	0.38	0.37	0.37	0.39	0.37	0.39	0.34	0.37	0.34-0.39	0.016	0.37±0.03	4.32
SO_3	1.34	1.30	1.29	1.47	1.24	1.27	1.18	1.31	1.20	1.34	1.29	1.18-1.47	0.082	1.29±0.16	6.36

ND = Not determined

The effect of a digestion time on completeness of solution and stability of the digest has been investigated by the analysis of a high sulphate ash, digested for periods varying between 10 minutes to 18 hours. The results are given in Table 6.5. All the elements, except sulphur are stable for up to eighteen hours digestion time. Sulphur may be lost in digestion, if periods in excess of two hours are used. Iron is the only element not completely digested in ten minutes and therefore the digestion time of thirty minutes used in Section 6.2.3 is considered as most suitable.

The method is ideally suited to cover the concentration levels normally found in coal ashes with adequate sensitivity for the accurate analysis of the minor elements (0.1 percent m/m). In routine operation it has been found that thirty ash analyses can be completed in a working day with the same accuracy as BS procedures but with at least a fivefold increase in throughput. The method should be suitable for extension to trace element determinations in coal ash and this is to be investigated.

6.4 CONCLUSIONS

The ICP-OES method has been shown to be both accurate and precise for the determination of eleven major and minor elements in coal ash. The method gives at least a fivefold increase in sample throughput over current BS procedures without loss in accuracy or precision. The use of nickel as an internal reference standard precludes the analysis of samples containing major or minor levels of nickel. The digestion and analysis procedure described should be suitable for the determination of trace elements (except nickel) in coal ashes. The method has been submitted to the British Standards Institution for acceptance as an improved analytical technique for the analysis of the major and minor constituents of coal and coke ashes.

TABLE 6.5

Results of analysis of ash solutions after different digestion times

Length of time in air oven at 105°C	Elemental oxide % m/m										
	Fe_2O_3	SO_3	SiO_2	Al_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	Mn_3O_4	P_2O_5
10 minutes	16.9	11.8	28.0	19.5	0.6	10.2	1.1	7.0	1.0	0.1	0.3
20 minutes	19.4	11.8	27.9	19.5	0.6	10.3	1.1	7.0	1.0	0.1	0.3
30 minutes	19.0	11.4	28.3	19.5	0.6	10.2	1.2	6.9	1.1	0.1	0.3
1 hour	19.3	11.3	28.0	19.5	0.6	10.2	1.1	6.9	1.1	0.1	0.3
2 hours	19.0	11.8	28.2	19.4	0.7	10.2	1.1	7.0	1.1	0.1	0.3
18 hours	19.3	9.2	28.5	19.7	0.7	10.1	1.1	7.0	1.1	0.1	0.3

The constraints applied to coal analysis laboratories in terms of staff and costs continue to increase. The analysis of coal is a branch of analytical chemistry which suffers from labour-intensive 'wet' chemical procedures. The British Standard Institution methods for coal analysis are geared to universally applicable, simple and inexpensive methods. The introduction of new instrumental methods requiring high initial capital outlay has not been received with much enthusiasm. Such methods of analysis require large sample throughputs before they become cost effective. Other reasons for this lack of enthusiasm have been that the new methods proposed to date have lacked either sensitivity, precision or accuracy, or are totally unsuited for routine analysis of large numbers of samples. The work reported here demonstrates that with a high initial capital outlay the gap between the instrumental analytical chemist and traditional coal scientist can be bridged.

The aim of this study has been to identify promising new analytical methodologies that can be used by coal analysis laboratories for the determination of minor and trace elements in coal and coal ash. To reduce operational time and expense, the techniques selected for study were ones which require minimal sample preparation.

The methods considered to have the requisite sensitivity, speed of analysis with acceptable precision and accuracy and very often incorporating multi-element capabilities are:

(i) atomic-absorption spectrometry using electrothermal atomisation and coal slurries;
(ii) scanning electron microscopy and energy-dispersive X-ray multi-element analysis of coal powders;
(iii) quantitative multi-element analysis of coal powders by wavelength dispersive automated X-ray fluroescence spectrometry;
(iv) multi-element optical emission spectrometry of solutions of coal ash using an inductively coupled plasma.

Each of these techniques is described and evaluated in separate chapters in this thesis. An appraisal of their usefulness for coal analysis is given in the conclusions at the end of each chapter.

The atomic-absorption spectrometric electrothermal atomisation technique for the direct analysis of coal slurries is shown to be very successful for the determination of arsenic in trace amounts. The method developed has been submitted to the British Standards Institution for acceptance. The problems encountered with background correction systems when using solid-sampling and electrothermal atomisation are critically discussed. The background problems are high-lighted when the proposed methodology is applied for the determination of selenium in coal. However, providing that accurate background corrections are made and matrix modifications to the coal are employed carefully, the method should have a wide application for accurate trace element analysis.

A scanning electron microscopy and energy-dispersive X-ray analysis technique for the determination of minor elements in coal is shown to be rapid and precise. Its accuracy for the particularly deleterious element chlorine is in very good agreement with British Standard methods. The analyses of eight other minor elements are in reasonable agreement with results using conventional ashing, digestion and flame atomic-absorption techniques. The determination of sulphur is not in such good agreement and this is attributed to the different mineralogical forms of this element present in coal.

The use of an automated wavelength-dispersive X-ray fluorescent technique for the direct analysis of pressed pellets of coal powders also gives inaccurate results for sulphur. The reason is identified to be different X-ray fluorescent yields obtained from organic and inorganic sulphur forms known to exist in coal in unpredictable and variable amounts. The precision and accuracy for the determination of chlorine and phosphorus when compared to British Standard methods are excellent. Its use is suggested for the on-line monitoring of the mineral composition of coal (which can be related to ash content).

The XRF technique is identified as a versatile and precise method for routine coal analysis. It is possible that the inaccuracies obtained in the XRF determination of sulphur may be overcome by more careful selection of the calibration coals to give a higher degree of 'matrix matching' and/or fine grinding of coal. The prospects of this technique for rapid, accurate and precise simultaneous multi-element analysis of coal powders is clearly illustrated in this study.

Inductively coupled plasma optical emission spectroscopy is the most recently developed technique evaluated. A rapid method using this technique is outlined for the determination of eleven minor elements present in a solution of coal ash. The method has also been submitted for acceptance by the British Standards Institution. The procedure described is versatile, should be widely acceptable and easily extended for trace elemental analysis of coal or coke ashes.

Although not the main aim of the thesis, an understanding of the effects of minor and trace elements in coal combustion or utilisation is necessary and the mode of occurrence of these elements is very often important, when strategies for their control or removal are to be postulated. Chapter 4 of this thesis is devoted to studies into the mode of occurrence of a particularly deleterious element, chlorine found in coal. The importance of such studies, if coal scientists and fuel technologists are to make use of the analytical results in utilisation and environmental fields, are illustrated by the work reported in this chapter. It is clear that some long-held views concerning the form in which chlorine is bound in coal are disproved. The likelihood is that chlorine is present in one form, uniformly distributed and linked ionically to the coal substance but sufficiently labile to be evolved as hydrogen chloride at low temperatures. It has no particular relationship with the nitrogen, sodium or other alkali/alkaline earth metals present in coal.

All the techniques evaluated can be expected to make a significant contribution to the analytical work of coal laboratories requiring to analyse accurately large numbers of samples. None of the methods can be regarded as able to perform all the trace and minor element determinations required and they should therefore be regarded as complementary in achieving the aim of rapid, precise and accurate analysis of coal.

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COURSES OF STUDY AND SCIENTIFIC MEETINGS ATTENDED

(i) Lectures from the CNNA MSc course in 'Instrumental Chemical Analysis', Sheffield City Polytechnic, on Atomic Spectroscopy and Metal Analysis.

(ii) Sheffield City Polytechnic and Sheffield University Analytical Colloquium and Sheffield Modern Methods of Analysis Group joint meeting, Sheffield, November 1979 'The determination of mercury by cold-vapour atomic fluorescence spectrometry using an improved argon-sheathed atom cell'.

(iii) CamScan, Cambridge, October 1979, Scanning Electron Microscopy training course.

(iv) Link Systems, High Wycombe, November 1979, Energy-Dispersive X-ray analysis training course.

(v) RSC, North East region meeting, Chesterfield, January 1980, 'Coal as a chemical feedstock'.

(vi) RSC, North East region meeting, Chesterfield, January 1980, 'Coke oven effluents in relation to EEC legislation'.

(vii) Chemical Society, Analytical Division, Annual Reports on Analytical Atomic Spectroscopy, Sheffield, March 1980. 'The preparation of sample solutions for atomic spectroscopy'.

(viii) Sheffield City Polytechnic and Sheffield University Analytical Colloquium, Sheffield, May 1980, 'A novel gas chromatographic detector for mine-air analysis'.

(ix) Micro 80 International Symposia and Exhibition, August, 1980.

(x) RSC, North East region, Analytical Division, Sheffield, December 1980, 'Industrial Hygiene Monitoring'.

(xi) Perkin-Elmer Equipment Exhibition and Lecture, April 1981, Nottingham, 'Heated graphite atomisation atomic-absorption and inductively coupled plasma optical emission spectroscopy'.

(xii) Sheffield City Polytechnic and Sheffield University Analytical Colloquium, Sheffield, May 1981, 'Direct analysis of metal alloy chippings using electrothermal atomisation atomic-absorption spectroscopy'.

(xiii) RSC, North East region, Analytical Division meeting, December 1981, 'Coal Analysis'.

(xiv) RSC, Atomic Spectroscopy Group and Institute of Physics, Sheffield, July 1982, 'First Biennial National Atomic Spectroscopy Symposium'.

(xv) Evaluation of ICP instrumentation, visits to Instrumentation Laboratories, Perkin-Elmer and Applied Research Laboratories, September 1982.

(xvi) Applied Research Laboratories Symposium, Harrogate, November 1982, Applications of inductively coupled plasma optical emission spectroscopy and X-ray fluorescence spectroscopy.

(xvii) RSC, Analytical Division, Loughborough, January 1983, 'Applications of inductively coupled plasma optical emission spectroscopy'.

(xviii) RSC and Health and Safety Executive, London, February 1983, 'Environmental Analysis'.

(xix) Perkin-Elmer, Beaconsfield, March 1983, 'Zeeman background correction system'.

(xx) UMIST, Manchester, March 1983, 'Inductively Coupled Plasma Workshop'.

(xxi) Perkin-Elmer, demonstration of 5500 instrument, Wath-on-Dearne, March 1983, 'ICP and HGA'.

(xxii) Chemical Society, Analytical Division, Annual Reports on Analytical Atomic Spectroscopy, Sheffield, April 1983, 'The analysis of materials with complex matrices'.

(xxiii) SCI, London, April 1983, 'Analytical Methods for Coal Analysis'.

(xxiv) Applied Research Laboratories, May 1983, X-ray fluorescence spectroscopy training course, Lausanne, Switzerland.

(xxv) Applied Research Laboratories, October 1983, Inductively Coupled Plasma Optical Emission Spectroscopy software training course, Luton.

(xxvi) Link Systems, High Wycombe, November 1983, ZAF/PB Energy-Dispersive X-ray analysis software course.

(xxvii) RSC, Analytical Division, North East Region meeting, November 1983, 'Inductively Coupled Plasma Optical Emission Spectroscopy'.

PAPERS PUBLISHED AND PRESENTED

(i) Co-author with Dr. L. Ebdon.
'Direct determination of arsenic in coal by atomic-absorption spectroscopy using solid sampling and electrothermal atomisation.'
Analyst, August 1982, 107, 942.

(ii) Co-author with Dr. L. Ebdon and J.W.F. Hill
'Scanning electron microscopy and energy-dispersive X-ray analysis of coal powders.'
Submitted for publication.

(iii) Joint meeting of Sheffield City Polytechnic and Sheffield University Analytical Colloquium, Sheffield, May 1981.
'The determination of arsenic in coal using solid-sampling and electrothermal atomisation atomic-absorption spectroscopy.'

(iv) North East Region, Analytical Division, RSC, 'Coal Analysis' meeting, Sheffield, December 1981,
'The determination of minor elements in coal using scanning electron microscopy and energy-dispersive X-ray analysis.'
(Invited lecture)

(v) RSC, Analytical Division, Annual Reports on Analytical Atomic Spectroscopy. Sheffield, April 1983.
'The determination of arsenic and selenium in coal by atomic-absorption spectrometry using solid-sampling and electrothermal atomisation.'
(Invited lecture).

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