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Overview of analytical methods for inorganic constituents in coal

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Abstract

Environmental legislation has had significant impact on coal utilization, especially coal combustion for power generation, in limiting emissions of potentially hazardous materials to the environment. For the most part, such emissions derive from the inorganic constituents in coal. However, as such legislation becomes ever more encompassing, it has increased the need to understand better the behavior of the inorganic species in coal processing to ensure, in part, that such legislation is not unduly burdensome. Consequently, it has led to significant development of new models for the behavior of inorganics in coal combustion and a complementary enhancement of many analytical methods for determining inorganics in coal.

In this paper, analytical methods for inorganics in coal are reviewed on three fronts: (i) methods for determining elemental concentrations; (ii) methods for determining the mineralogy of coals; and (iii) methods for determining modes of occurrence (speciation) of trace elements in coal. The concept of association with respect to mineral–maceral and mineral–mineral occurrences is also discussed. Where possible, comparison of different analysis methods has been made by reference to data on well-characterized suites of coals, such as the Argonne premium coal samples.

Incremental enhancements will continue to be made in analytical methods for elemental concentrations; however, major improvements are needed in the other two areas. There is a great need to verify and corroborate by direct speciation methods, the many inferences made by indirect methods regarding trace element speciation. Also, improvements in the measurement of mineral association and its integration into the coal mineral analysis by means of the computer-controlled scanning electron microscopy (CCSEM) would be a significant advance. Accurate determinations of both association and coal mineralogy would lead to significant and much-needed refinements of models for the behavior of inorganics in both coal cleaning processes and coal combustion.

Keywords: Analysis; Ash; Association; Coal; Inorganics; Mineralogy; Mode of occurrence; Trace elements

1. Introduction

The passage of the 1970 Clean Air Act, the 1990 Clean Air Act Amendments (CAAA), and, most recently, the National Ambient Air Quality Standards (NAAQS) in the USA and of similar legislation in other countries has increased the need and technical challenges to use coal in as an efficient and environmentally friendly manner as possible to meet the energy demands of the world. Most technical and environmental problems associated with coal utilization arise because of the mostly non-combustible, inorganic components in coal. But, because coal consists of two major solid components that are intimately associated, a complete, economically feasible separation of this undesirable inorganic fraction from the

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desirable organic fraction can never be achieved and even a well-cleaned coal will contain a significant fraction of inorganics. Consequently, the presence of inorganics in coal utilization *cannot be avoided* and the resolution or minimization of many coal-utilization environmental problems requires that the behavior of the inorganic components during utilization be well understood. However, typically, it is not enough to determine just elemental concentrations in order to understand how a particular inorganic component will behave. Increasingly, it has become recognized (Raask, 1985; Swaine, 1990; Finkelman, 1994) that the mode of occurrence and the association of an element are often as important as its concentration in determining its behavior during coal cleaning, coal combustion, and other coal utilization processes.

Owing to the huge tonnages of coal consumed for electrical power generation, the power generation industry is a key target for reduction of both inorganic and organic emissions to the atmosphere and has become subject to increasingly stringent environmental regulations. Indeed, one of the major achievements of the Clean Air Act has been a significant reduction in emissions of SO_x from coal combustion for power generation. More recently, other components in coal have come under scrutiny in order to comply with regulations proposed in the 1990 CAAA and the NAAQS. Even elements that exist in coal only at sub-ppm levels are under consideration for mandated controls (Davidson, 1996; U.S. EPA, 1998). Such targeting has resulted in much research aimed at understanding the behavior and minimizing the environmental impact of specific inorganic components during coal utilization. Furthermore, increasingly sophisticated analytical methods have been applied to characterize these components in coal. Such methods and their application to understanding the behavior of specific inorganic components during coal utilization, especially combustion, will be the main theme of this review paper.

As indicated in Fig. 1, methods for analysis of inorganic components in coal can be divided into the following categories: (i) methods that measure elemental concentrations in the coal (or ash); (ii) methods that determine mineralogical components; and (iii) methods that determine elemental modes of occurrence. Each of these three types of analysis provides different information about inorganic components in coal and to understand fully the behavior of a specific entity in coal utilization may require data from each type of analysis. Inorganic components in coal will be broadly defined for the purposes of this review. For, although many elements in coal exist in both organic and inorganic forms, it is usually not possible to separate such forms for analysis purposes. However, topical areas such as analysis of heteroatoms, which can be better considered as part of the analysis of the organic components in coal, will not be included.

For the purposes of this 50th Issue review, we will emphasize work described since the inception of the International Journal of Coal Geology. Earlier work is quite comprehensively covered in the three-volume set, entitled "Analytical Methods for Coal and Coal Products" (Karr, 1978, 1979) and the monographs on "Coal and Coal Products: Analytical Characterization Techniques" (Fuller, 1982) and on "Trace Elements in Fuel" (Babu, 1975). Mention should also be made here of other key resources, including "Trace Elements in Coal" by Swaine (1990), "Elemental Analysis of Coal and Its By-Products" edited by Vourvopoulos

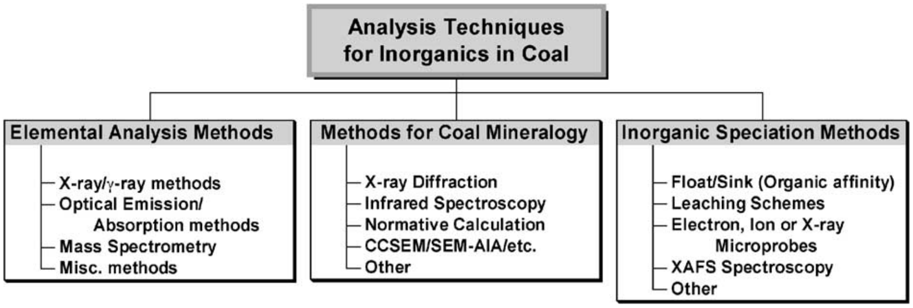


Fig. 1. Subdivision of analytical techniques for inorganics in coal.

(1992), various IEA publications on trace elements (Smith, 1987; Clarke and Sloss, 1992; Davidson, 1996, 2000), a series of papers in a special issue of Energy and Fuels on research with coals from the Argonne Premium Coal Sample Bank (APCSB) (Vorres, 1990, 1993), the Illinois State Geological Survey Circular 499 (Gluskoter et al., 1977), US Geological Survey Bulletins 1823 (Golightly and Simon, 1989) and 2144 (Palmer, 1997), and the US Geological Survey Coal Quality Database, (version 1.3, Bragg et al., 1994; version 2.0, Bragg et al., 1998).

Outlines of many standard methods of analysis of inorganic species can be found in Volume 05.06 of the Annual Book of American Society for Testing and Materials (ASTM) Standards (ASTM, 2000) and in similar volumes published by other national testing societies. Although they are mostly outside the scope of this review, it should be noted that many other methods for determining specific entities in coal that could be considered to be in the inorganic realm, including wt.% ash in coal (Standard D 3174, ASTM, 2000), forms-of-sulfur analysis (Standard D 2492, ASTM, 2000), total sulfur in coal (Standards D 1757, D 3177, D 4239, ASTM, 2000), total chlorine in coal (Standards D 2361, D 4208, ASTM, 2000) and SO_3 in ash from coal (Standard D 5016, ASTM, 2000), can also be found in such volumes. The complexities of some of these analyses have been discussed in some detail by Given and Yarzab (1978).

2. Analytical methods for elemental concentrations

There are many methods available for determining the concentrations of major and trace inorganic elements in coal. Such methods vary from those that are applicable to just one element in a particular matrix to instrumental techniques that are, in principle, capable of determining all elements in the periodic table in any matrix. We can divide elemental analysis techniques into four broad groups (Fig. 2).

- Instrumental X-ray/γ-ray techniques: these techniques are usually capable of determining many elements simultaneously and depend on the generation, detection and measurement of characteristic X-rays and/or γ-rays for element determination.
- Optical absorption/emission techniques: these techniques are also capable of determining many elements simultaneously, but depend on the generation, detection and measurement of characteristic atomic transitions in the visible and near-visible regions of the electromagnetic spectrum for elemental determination.
- Mass spectrometric methods: these techniques are also capable of determining most elements in the periodic table simultaneously, but depend on total volatilization of the sample and its introduction in such form into a mass spectrometer so that the atomic mass can be used to discriminate quantitatively among the different elements (and isotopes).

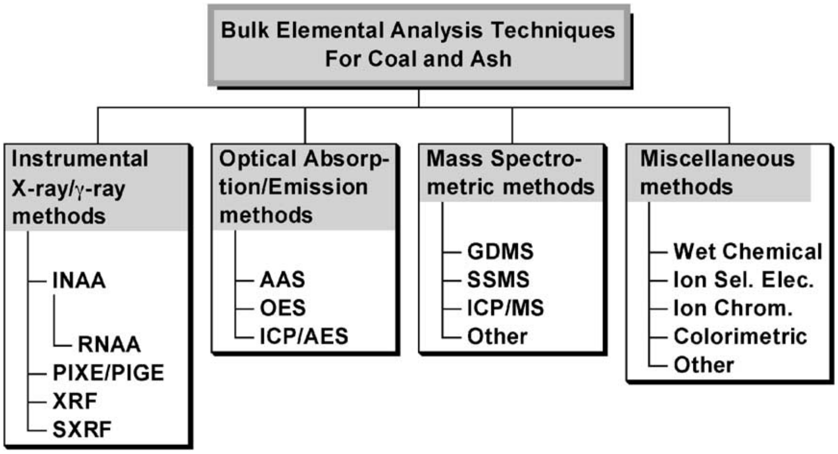


Fig. 2. Classification of bulk elemental analysis methods for coal.

- Miscellaneous techniques: such techniques generally determine one or a few elements that, for one reason or another, cannot be adequately determined by other more general methods; such techniques include wet chemical and various electroanalytical methods.

In this section, individual techniques belonging to each of these groups will be briefly described and discussed. Emphasis in the discussion will be given to summarizing the relative advantages and disadvantages of the techniques. Where possible, comparison of the techniques is made on the same group of coals, *viz*. coal samples from the Argonne Premium Coal Sample Bank (APCSB) (Vorres, 1990, 1993). In addition, emphasis will be given to determinations of the more critical trace elements, such as the 15 trace elements (As, Cd, Cr, Hg, Ni, Pb, Se, Be, Co, Mn, Sb, F, Cl, Th and U) defined as hazardous air pollutants (HAPs) in Title III of the 1990 CAAA, (U.S. Congress, 1990). This list of elements includes all eight of the elements of "prime environmental interest" defined by Swaine (1990) and also most of the 14 others listed by him "that could be of environmental interest".

Many of the analytical techniques to be discussed here are also discussed in detail in overviews by researchers at the US Geological Survey, Reston, (Golightly and Simon, 1989; Palmer, 1997) and, with emphasis on trace elements, by Swaine (1985, 1990). These sources should be consulted regarding further details of the techniques and their applications described herein. However, before describing the techniques, some discussion is presented of whether the elemental analyses should be performed on the coal itself or ash.

2.1. Whether to analyze ash or coal?

The elemental analysis methods described in this section can be performed on the whole coal directly or may be done on high-temperature ash (HTA), prepared by controlled combustion at a temperature between 400 and 800 °C, or on low-temperature ash (LTA), prepared by oxidizing away the carbonaceous matter under an oxygen plasma at temperatures that normally do not exceed 200 °C (Gluskoter, 1965; Shirazi and Lindqvist, 1993; Kizil'shtein and Shpitsgluz, 1994). Whereas an HTA can be prepared in a few hours or overnight, an LTA will often take many days to reach constant weight. For the purpose of determining major elemental concentrations (typically Si, Al, Ti, Ca, Fe, Mg, K, Na, and P), it does not make much difference whether HTA or LTA is used, although typically there is slight, but significant difference in the wt.% ash determined by these different methods due to transformations of the minerals at higher temperatures, which result in the loss of volatile species, such as H_2O, CO_2 and sulfur as SO_x, and which is counterbalanced by formation of sulfates such as $CaSO_4$ (e.g., see discussion by Given and Yarzab, 1978). Such transformations are the basis of the derivation of wt.% mineral matter in coal from the wt.% HTA using either the Parr formula or the KMC formula (Given and Yarzab, 1978). Mineral transformations and other sources of error that may occur during LTA are discussed by Jenkins and Walker (1978) and Pike et al. (1989).

There are, however, significant trade-offs to consider between performing the analysis on the coal or on either the HTA or LTA, especially for analysis of trace elements. Generally, working directly on the coal allows a quicker and simpler sample preparation and one that is least likely to result in loss of volatile elements, such as As, Se, Hg, B, halogens, etc. However, whether working with ash or coal, most techniques yield their best results on samples that are finely pulverized and well homogenized. Such preparation should never be circumvented. Ashing has the advantage that it can concentrate an element by a factor of typically 5–10 and thereby significantly improve the sensitivity and precision of the determination of a trace element. However, the matrix corrections required by some techniques (e.g., XRF) are also significantly larger for ash than for coal, which can somewhat offset the advantage. Furthermore, even at a preferred lower temperature of around 500 °C rather than the ASTM recommended temperature of 750 °C (Standard D-3174, ASTM, 2000), high-temperature ashing will cause easily volatilized trace elements to be released from the sample and completely lost from the analysis. Sample preparation by low-temperature ashing (Gluskoter, 1965; Shirazi and Lindqvist, 1993; Kizil'shtein and Shpitsgluz, 1994) offers a good compromise between working on coal or HTA for trace element determinations, but unfortunately is less routinely practiced. A notable exception was the landmark study carried out at the Illinois State Geological Survey (Gluskoter et al., 1977) on trace elements in 172 US coals. A considerable portion of the analytical work in that study was performed on LTA.

One further advantage that ashing usually ensures is much easier dissolution of the inorganics. For certain techniques, notably AAS, ICP/AES and ICP/MS, the performance and quantitative precision are significantly better if the elements are introduced into these instruments in solution or liquid form, rather than in solid form. Hence, ashing is often considered a necessary step in preparing suitable analytes for these techniques. However, more recently, direct coal digestion has been explored as a means of preparing suitable liquids for these techniques, while at the same time avoiding both LTA and HTA. Such digestion methods enable a solution of coal and its components to be obtained that is suitable for analysis by techniques such as AAS, ICP/AES or ICP/MS. Methods for direct digestion of coal include microwave-oven acid digestion (Fadda et al., 1995; Laban and Atkin, 1999; Ikavalko et al., 1999), and a two-step acid digestion in a PFA bomb (Querol et al., 1996, 2001). These coal digestion methods have been shown to yield analytical results that agree well with data for standard reference coals obtained by more conventional methods (Ikavalko et al., 1999; Querol et al., 2001).

2.2. Instrumental X-ray/γ-ray techniques

Instrumental neutron activation analysis (INAA) and X-ray fluorescence (XRF) became accepted for elemental analysis of coal in the late 1960s and early 1970s. Subsequently, in the 1980s, two related techniques, synchrotron XRF (SXRF) and particle-induced X-ray/γ-ray emission (PIXE/PIGE), were also developed and applied for elemental analysis of coal. The physics involved in these methods and the differences among them are succinctly discussed by Paradellis (1992). Other techniques that might be included in this group, such as electron microprobe analysis and other related focused-beam techniques, will be discussed in the section on determination of mode of occurrence (q.v. Section 4.2.2).

2.2.1. Instrumental neutron activation analysis (INAA)

Detailed descriptions of INAA and its application to elemental analysis of fossil fuels can be found in the literature (Frost et al., 1975; Sheibley, 1975; Abel and Rancitelli, 1975; Weaver, 1978; Steinnes, 1979). The most common method of INAA involves the generation of low-energy thermal neutrons, also known as “slow” neutrons. The main principle underlying INAA is the fact that irradiation of a material by thermal neutrons causes stable isotopes of an element in a material to absorb neutrons and become radioactive isotopes, which can then emit γ-rays that can be used for elemental determination. In the general case (Paradellis, 1992):

$$^{A}X_{Z} + n \rightarrow {}^{A+1}X_{Z} + \gamma - \text{ray} \qquad (1)$$

The radioactive isotopes, $^{A+1}X_{Z}$, then decay with the emission of characteristic γ-rays that can be measured instrumentally by means of a high-resolution, energy-dispersive detector, typically a Li-doped germanium or silicon detector. Both the γ-ray energy and the half-life of the decay process can be used to identify the element (isotope) in question, while the intensity of the emitted γ-ray is used for determination of the element’s concentration.

Data reduction in INAA involves comparison of the γ-ray spectrum obtained from the coal with that from a standard material of established elemental composition. Originally, metals and chemical standards were used for this calibration because matrix effects in INAA are not very critical and appropriate reference materials were not available. Nowadays, especially with the availability of the National Institute of Standards and Technology (NIST) standard reference materials (SRMs) for coal and coal ash, it has become common practice to use more appropriate standards, such as NIST SRMs 1623a and 1633a, for calibrating the INAA method (e.g., Palmer and Baedecker, 1989; Palmer, 1990; Palmer and Lyons, 1996).

Major advantages of INAA are: (i) ashing of the coal does not provide significant benefit and therefore sample preparation and the potential for contamination are minimized; (ii) up to 40 elements can be determined simultaneously; (iii) it is capable of determining some elements at sub-ppm concentrations; and (iv) the adjustment for matrix effects is generally much less critical than for the other techniques in this group. Major disadvantages of the technique are: (i) for best precision, a neutron reactor should be used as the source of the thermal neutron flux, which of course is a serious limitation on the availability of the technique; (ii) some elements, notably B, Be, Cd, Cu, F, Hg, Mo, Ni, Pb and Tl, are not easily analyzed by INAA because their cross-sections for thermal neutron capture are low and hence, these elements have relatively large detection limits; and (iii) the technique tends to have a long turnaround time because it is typical practice to perform γ-ray counting immediately after irradiation and then again some weeks or months later so that interferences from short-lived radioactive species are eliminated and better precision can be obtained on longer-lived species. Despite these limitations, it is likely that INAA has been the most widely used method for obtaining concentration data on trace elements in coal and other fossil fuel materials (Bettinelli et al., 1992). Recent INAA studies on coals include investigation of US coals (Palmer, 1990; Senior et al., 2000), of European coals (Bettinelli et al., 1992), of Nigerian coals (Ogugbuaja and James, 1995), and of whole coal and mineral separates in US and German coals (Palmer and Lyons, 1996).

There are a number of variations on the standard INAA method that have been developed in order to circumvent some of the disadvantages of INAA with thermal neutrons or to enhance analytical precision for a particular element. For example, the use of higher energy epithermal neutrons can improve the sensitivity of INAA by enhancing the formation of a desired radionuclide relative to interference from other nuclides (Rowe and Steinnes, 1977; Steinnes, 1979). INAA using high-energy fast neutrons that are generated in a Cockroft–Walton accelerator offers other advantages over INAA using thermal neutrons (Volborth, 1979). The accelerator used to generate fast neutrons costs much less than the reactor needed for generation of thermal neutrons and, furthermore, unlike the thermal flux, the fast neutron flux can be switched on and off. More importantly, various light elements in coal, such as O, N, Si, etc., which cannot be determined with thermal neutrons, can be determined accurately using fast neutrons (Volborth, 1979).

Radiochemical neutron activation analysis (RNAA), in which a radiochemical separation is performed after the neutron irradiation is done, is effective in enhancing the precision of a determination of an element present in low concentrations by avoiding or minimizing elemental interferences. Frost et al. (1975) describe various RNAA methods for a number of different elements in coal, including the HAPs elements Hg, Se, As, Sb, and Cd and Perritt and Swaine (1976) also developed a RNAA method for Hg and Se in coal and fly-ash. More recently, Blanchard and Robertson (1997) list different RNAA methods that have been developed for Hg and describe a new method based on detection of the longer-lived ^{203}Hg isotope rather than short-lived ^{197}Hg isotope used in previous RNAA methods. They were able to use this other isotope of mercury by eliminating the interference from ^{75}Se using a gold amalgamation separation method.

In his INAA studies of trace elements in the APCSB coals, Palmer (1990, 1997) included NIST SRMs in the irradiation to serve as standards for the data reduction. Data for 29 elements in the APCSB coals were presented in triplicate, from which one may obtain an indication of the breadth and precision that can be obtained with INAA in modern-day practice. Table 1 presents a summary of the analyses for the whole coal samples. The original paper (Palmer, 1990) should be consulted for details and discussion of the experimental precision, but the experimental precisions (95% confidence limits) for most determinations were less than 10%, even for elements at the sub-ppm level. For some elements, however, the experimental precision did not change systematically with concentration. For example, determinations of zinc in certain of the APCSB bituminous coals had much larger errors than those for the two western US low-rank coals of relatively low zinc contents. It is apparent that there are other factors that affect the precision of the Zn determination by INAA than just counting statistics.

2.2.2. X-ray fluorescence (XRF) analysis

XRF methods have been used for chemical analysis of major elements in geological materials, including coals and other fossil fuels, for many years (e.g., Kiss, 1966; Kuhn et al., 1975; Gluskoter et al., 1977). Subsequently, XRF techniques have been extended to determinations of trace elements in coal as well (e.g., Kuhn et al., 1975; Prather et al., 1979; Evans et al., 1990) and also to liquids derived from coal (Stergarsek et al., 1989; Wertz et al., 1993).

The basic principle of XRF is to bathe the coal or ash sample in the broad white radiation spectrum obtained from a standard laboratory X-ray tube. Typically an X-ray tube with a Cr or W target is used

Table 1
Element concentrations in APCSB Coals by INAA

	UF	WY	IL	PITT	POC	UT	WV	ND
Na	340	1150	1020	340	780	1460	400	5300
K	2700	300	2000	1100	300	200	5100	290
Sc	4.1	1.7	2.6	2.6	1.8	0.8	7.6	0.85
Cr	20.3	6	33	15	9	5	36	2.2
Fe	17,800	3700	26,700	13,500	5100	3200	4000	5500
Co	5.3	1.7	4.4	2.6	4.1	1.0	7.8	0.8
Ni	14	5	21	10	9	4	15	<6
Zn	20	11	220	9	6	6	14	5.7
As	17	3.6	4.7	8.4	10.3	0.5	6	2.6
Se	2	1.6	4	1.5	2.5	1.1	5.5	0.6
Br	66	2.9	6.7	15.6	50	1.1	16.9	1.4
Rb	20	<5	16	8	<6	1.0	30	0.9
Sr	50	250	40	60	110	70	64	600
Sb	0.5	0.2	0.9	0.23	0.5	0.11	0.5	0.15
Cs	1.5	0.17	1.14	0.7	0.26	0.13	1.9	0.09
Ba	60	310	94	50	200	40	130	680
La	10.1	5.4	6.1	6.2	6.8	3.3	21.5	2.8
Ce	18	9.4	12.6	11.3	12	4.8	36	4.4
Nd	8	<13	9	<12	<18	2.5	12	2.3
Sm	2.0	1.0	1.2	1.1	1.2	0.5	3.5	0.4
Eu	0.40	0.20	0.23	0.22	0.23	0.10	0.70	0.08
Tb	0.26	0.12	0.14	0.13	0.17	0.06	0.40	0.06
Yb	0.9	0.4	0.5	0.47	0.56	0.2	1.6	0.3
Lu	0.22	0.10	0.14	0.12	0.14	0.03	0.20	0.04
Hf	0.66	0.60	0.55	0.50	0.44	0.48	1.8	0.34
Ta	0.22	0.15	0.19	0.17	0.12	0.06	0.64	0.09
W	1.1	0.4	1.5	0.8	0.8	0.4	1.7	0.4
Th	2.7	1.6	2	1.5	1.2	0.62	6.4	1.1
U	0.83	0.54	4.3	0.4	0.5	0.7	1.6	0.5

In ppmw whole coal basis (modified from Table 3 in Palmer, 1990).

Sample abbreviations (Vorres, 1990): UF—Upper Freeport seam (medium volatile bituminous), PA; WY—Wyodak–Anderson seam (subbituminous), WY; IL—Illinois #6 seam (high volatile B bituminous), IL; PITT—Pittsburgh seam (high volatile A bituminous), PA; POC—Pocahontas #3 seam (low volatile bituminous), VA; UT—Blind Canyon seam (high volatile B bituminous), UT; WV—Stockton–Lewiston seam (high volatile A bituminous), WV; and ND—Beulah–Zap seam (lignite), ND.

for XRF of fossil fuels because these elements are usually of low abundance. The absorption of the radiation by individual elements is generally by means of excitation of a 1s electron (K-edge) absorption process or a 2s or 2p electron (L-edge) absorption process for higher atomic number elements. These excited, predominantly atomic states immediately decay to the ground state by emission of lower energy X-rays associated with the filling of the vacant 1s, 2s or 2p electron level by a bound electron from a higher shell (usually K or L emission lines for K absorption processes and L, M or N emission lines for L absorption processes). These fluorescent X-rays occur at characteristic energies for each element and typically are determined individually and sequentially in a wavelength-dispersive (WDXRF) detector, especially if precision and accuracy are of paramount importance. However, if speed and throughput are more critical, then energy-dispersive (EDXRF) spectrometers, in which the elements are measured simultaneously, can be used for quantitative XRF analysis. For low Z elements (from Na to Cl), the K and L emission lines tend to be easily absorbed by air or even helium; hence, for accurate work in this part of the periodic table, a vacuum XRF spectrometer is highly desirable. Although computerization and the development of better instrumentation for both WDXRF and EDXRF techniques have improved their sensitivity and speed, actual XRF procedures on coal and coal ash have changed little over the last 20 years. Such procedures are well described in the literature (Prather et al., 1979; Willis, 1988; Johnson et al., 1989; Evans et al., 1990; Standard D-4326, ASTM, 2000).

The major advantages of XRF are: (i) it is a versatile and relatively common laboratory instrument and therefore is widely available; (ii) modern instruments are often fully automated for unattended operation with up to 50 samples; (iii) sample preparation is relatively easy and usually involves no more than pulverization and pelletization; (iv) it covers the concentration range from <1 ppm to 100 wt.%. The main disadvantages appear to be: (i) its sensitivity to trace elements is comparatively low and hence detection limits and the precision and accuracy of the technique are not as good as for other methods; (ii) matrix corrections, although generally predictable, are needed for the best precision; and (iii) the escape depth for the fluorescent radiation is variable from less than 5 μm to as much as 200 μm, depending on the energy of the radiation. Willis (1988) provides an excellent discussion of the relative advantages and disadvantages of XRF and PIXE analysis methods.

Both EDXRF and WDXRF have been performed on whole coal samples with some success (Kuhn et al., 1975; Prather et al., 1979; Evans et al., 1990), but problems associated with coarse mineral grains (Kuhn et al., 1975) and, until recently, the scarcity of well-characterized standard reference materials for whole coals (Evans et al., 1990) would appear to limit the precision of the method. However, it remains a simple analysis to perform and many coals can be screened in the time it takes to low-temperature ash a few coals (Kuhn et al., 1975). Generally, working on the ash provides a significant improvement in precision (except, of course, for those elements subject to volatilization) because of the 5- to 10-fold enrichment in concentration that ashing affords. In addition, by using the lithium tetraborate ($Li_2B_4O_7$) fusion method (Johnson et al., 1989) relatively homogeneous glassy materials can be prepared from coal ash for XRF analysis. Such homogenization is especially important for precise determinations of the major elements.

One recent development that has significantly lowered detection limits for determining trace elements by EDXRF is the use of polarized incident radiation (Heckel et al., 1991; Spears et al., 1999). Such radiation reduces background fluorescence radiation thereby increasing the signal/noise ratio and, as Spears et al. (1999) have recently demonstrated, polarized EDXRF has sensitivity to sub-ppm levels for many important trace elements in coal. Another variation on EDXRF that permits enhanced sensitivity for trace elements in materials is total-reflectance X-ray fluorescence (TXRF) (Knochel, 1990; Aiginger, 1991; Hein et al., 1992). Although this technique does not yet seem to have been applied to coal samples, it has been applied to other fossil fuels (Schirmacher et al., 1993; Pasti et al., 1996) and would appear well suited for the analysis of small ash samples collected on filters (e.g., Theisen and Niessner, 1999), such as those samples that are now being generated for investigation of fine airborne particulate matter from combustion of coal and other fossil fuels.

Although EDXRF has benefited significantly from these recent developments, as well as from new detector technology and computerization, and is the superior method in terms of equipment cost, speed of analysis, and throughput, WDXRF is still typically the superior method in terms of precision for many elements. Consequently, then, it is often necessary to apply both EDXRF and WDXRF methods to determine a wide range of major and trace element concentrations in coal as a compromise between precision and the time taken for the analysis.

One such detailed study using both WDXRF and EDXRF techniques was reported by Johnson et al. (1989) and Evans et al. (1990) on the major and trace element contents of the APCSB coals. Both methods, WDXRF for major elements and EDXRF for trace elements, were performed on coal ash prepared at 525 °C and then fused and pelletized by the $Li_2B_4O_7$ method. WDXRF was also performed on whole coal samples to determine P and Cl. In this study, the accuracy of the WDXRF determinations was estimated to be between ±2% and ±5% for the major elements and no worse than ±5% for the EDXRF determinations of trace elements. For P and Cl, the two elements determined by WDXRF on whole coal samples, the uncertainties were estimated to be ±10%. Results from this study (Johnson et al., 1989; Evans et al., 1990) are summarized for the eight APCSB coal samples in Table 2.

Other recent studies involving XRF investigation of trace elements in coal or ash include Spears et al. (1999) on English coals, Vijayan et al. (1997) on Indian fly-ash, and Akyuz et al. (1996) on ash from Turkish power

Table 2
Element concentrations in APCSB Coals by XRF (modified from Tables 1–3 in Evans et al., 1990)

	UF	WY	IL	PITT	POC	UT	WV	ND	Method
Major oxides in wt.% ash basis									
Na_2O	0.3	1.5	1.0	0.5	1.9	3.8	0.1	7.1	WD-Ash
MgO	1.0	5.0	0.9	0.6	2.1	1.4	0.7	7.3	WD-Ash
Al_2O_3	21.6	15.0	14.1	20.2	19.6	15.2	30.8	9.0	WD-Ash
SiO_2	42.3	31.3	40.2	45.6	32.5	41.5	54.0	17.3	WD-Ash
P_2O_5	0.1	0.7	0.1	0.2	0.1	0.1	0.1	0.4	WD-Ash
SO_3	1.0	8.2	3.8	2.0	6.3	8.3	0.7	20.5	WD-Ash
K_2O	2.5	0.4	1.5	1.5	0.7	0.6	2.9	0.4	WD-Ash
CaO	4.2	18.5	7.8	3.1	11.7	12.2	0.4	22.6	WD-Ash
TiO_2	1.0	1.0	0.7	1.1	1.2	0.8	2.1	0.3	WD-Ash
MnO	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	WD-Ash
Fe_2O_3	20.5	5.5	23.9	22.4	14.1	9.0	2.8	6.7	WD-Ash
	94.5	87.0	93.9	97.2	90.1	92.9	94.6	91.6	
Trace elements, in wt.% coal basis									
P	<0.01	0.06	<0.01	0.02	<0.01	<0.01	<0.01	0.04	WD-Coal
Cl	0.15	<0.01	0.05	0.06	0.16	<0.01	0.04	<0.01	WD-Coal
Trace elements, in ppmw ash basis									
Cr	193	97	268	195	232		236	28	ED-Ash
Ni	102	47	110	102	133		87	20	ED-Ash
Cu	152	151	59	67	237		122	35	ED-Ash
Zn	161	125	824	91	90		60	57	ED-Ash
Rb	157	41	91	97	44		225		ED-Ash
Sr	450	3070	185	740	2100		400	6700	ED-Ash
Y	77	42	25	53	130		109		ED-Ash
Zr	202	267	137	223	318		415	63	ED-Ash
Nb	19	12	12	21	16		43	<10	ED-Ash
Ba	385	3200	460	390	3400		565	4900	ED-Ash
La	61	<30	<30	40	40		90		ED-Ash
Ce	126	50	45	97	140		155		ED-Ash

plants. Parus et al. (2000) have recently developed XRF to determine the carbon contents of coal and ash samples. Suarez-Fernandez et al. (2001) have examined the potential of using a radioisotope source for XRF investigation of elements in coal.

2.2.3. Synchrotron X-ray fluorescence (SXRF)

Synchrotron X-ray fluorescence (SXRF) is basically a variation of the conventional XRF method described above, except that it employs a synchrotron as the source of the X-ray white radiation rather than an X-ray tube. This specialized source is both the main advantage and disadvantage of this technique. Such sources of X-rays are significantly more intense; it is estimated, for example, that the X-radiation intensity at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, New York, is as much as six orders of magnitude brighter than that from a standard X-ray tube in a conventional laboratory. The much higher flux of X-rays emitted by the synchrotron source should enable considerably more precise determinations of elements to be made with significantly lower detection limits than standard XRF methods. Hence, more elements should be amenable for analysis by SXRF than by conventional XRF. However, synchrotron sources are not readily available for routine analysis. Of the four major synchrotron sources presently in operation in the USA for materials research, only four or five beam-lines (out of more than 100) have been developed for XRF experimentation. This restricted availability limits its usefulness as a routine analytical method. In fact, most of the applications (Chen et al., 1984; White et al., 1989; Jones and Gordon, 1989; Spears, 1991) indicate that SXRF will be more useful in fossil fuel trace element analysis with respect to determinations of trace element association and modes of occurrence (q.v. Section 4.2.2) rather than for bulk analysis of coal.

SXRF can also be done in the total-reflectance mode and the combination of the intense synchrotron X-ray source (Streli, 1995; Gorgl et al., 1997; Pianetta et al., 2000) and the very high sensitivity for heavy metals afforded by the TRXRF experiment should enable extremely low detection limits to be attained for trace elements in small volume, high area ash samples, such as filter samples.

2.2.4. PIXE/PIGE spectrometry

In comparison to XRF and SXRF, PIXE/PIGE spectrometry uses much more energetic radiation (particles accelerated up to several MeV) to induce X-ray and γ-ray emission processes in elements. It is a relatively rapid technique capable of determining up to 75 elements simultaneously. Generally, protons are used to induce emission, but other charged particles (ions) can be used. Like the neutron reactor needed for INAA, a specialized source such as a particle accelerator or a Van de Graaff generator is needed to produce the energetic ion particle beam. Unlike neutrons, proton particles have a very limited penetration depth in materials and, until the late 1980s, corrections for the significant attenuation effects in thick samples, involving both the depth of penetration of the proton beam and the fluorescence yields of the induced X-rays or γ-rays, were considered to be too large and fraught with uncertainty that accurate results could not be obtained for elemental abundances in thick samples. As a result, PIXE/PIGE techniques were originally developed for very thin samples, for which the attenuation corrections are neither so large nor so critical. The technique is more sensitive to trace element species than conventional XRF (although polarized EDXRF is at least as sensitive) and is well suited to very small samples, especially those deposited in thin layers (Boni et al., 1990). For example, the first reports of PIXE/PIGE analyses of US coals were carried out with <2 mg of coal, pulverized to less than 20 μm, spread on a thin plastic substrate (Simms et al., 1977; Kullerud et al., 1979). Willis (1988) presents a valuable comparison of XRF and PIXE techniques and points out where one should be preferred over the other for trace element analysis of coals and other geological materials. In Willis' opinion, one of the most serious limitations of PIXE compared to XRF is the small volume of sample excited by the particle beam. Not only is the penetration depth small (<50 μm), but the spread or coverage area of the typical proton beam is also rather small (<0.25 cm^2). However, such factors become advantageous when discussing various microscope or microprobe instruments based on instrumental analysis techniques, and the proton microprobe, which uses PIXE for elemental analysis (Caridi et al., 1993), may be significantly more sensitive to trace elements than an X-ray microscope that uses SXRF.

For thick samples, recent work indicates that the matrix correction problems, which, in the past, were a significant impediment to accurate results, have now been largely overcome (Teesdale et al., 1988; Burnett et al., 1988; Pineda and Peisach, 1988). A PIXE/PIGE study conducted on the APCSB coals (Wong and Robertson, 1992) was carried out on thick pellets of coal using both element-doped graphite standards and NIST SRM coals as reference standards (Wong and Robertson, 1992, 1993). Agreement between the PIXE/PIGE and other instrumental elemental determinations for both the NIST SRMs and the APCSB coals is within experimental errors for most elements. Data for the PIXE/PIGE analyses of the APCSB coals (Wong and Robertson, 1992) are shown in Table 3.

PIXE/PIGE techniques can also be carried out on ash materials derived from coal or from power plants (Boni et al., 1990; Bellotto et al., 1990; Valkovic et al., 1992; Bellagamba et al., 1993; Xinfu et al., 1993; Vijayan et al., 1997) and related environmental samples, especially airborne aerosols and particulate matter, collected on filters (Braga Marcazzan et al., 1987; Maenhaut et al., 1993; Huggins et al., 2000c). In various studies (Braga Marcazzan et al., 1987; Fazinic et al., 1992), PIGE techniques have been explored for application to light elements, such as Li–P. Fluorine, in particular, appears to be an element that is well suited to PIGE analysis (Savidou and Paradellis, 1990; Caridi et al., 1992; Wong et al., 1992, 1994).

The main advantages of PIXE/PIGE appear to be: (i) it is well suited for very small samples, such as material collected in thin layers (e.g., fly-ash collected on filters), surface layers, etc.; (ii) it is capable of

Table 3
Element concentrations in APCSB Coals by PIGE/PIXE

	UF	WY	IL	PITT	POC	UT	WV	ND
Li	26	17	21	26	5	5	36	<dl
Na	355	1100	1000	320	760	1300	340	5600
Al	15,800	8000	11,400	8900	5300	3900	29,600	4400
F	86	56	86	90	20	56	130	35
K	2300	230	2300	1100	230	260	4700	320
Ca	3500	11,300	8800	2100	4200	4300	500	14,400
Ti	620	610	610	550	360	220	2900	200
Cr	23	7	36	18	8	7	37	4
Mn	27	23	90	20	12	5	12	90
Fe	13,500	3800	20,100	11,100	5700	2800	3900	500[a]
Co	<dl	1	<dl	1.5	3	1.3	9	<dl
Ni	9	4	15	4.7	4	5.1	14	3.3
Cu	12	15	8	5	12	5.4	20	4
Zn	18	23	130	10	4	7	12	6
Ga	4.3	3.5	4	4	2	1.5	10	<dl
Ge	4	3.5	7	1	1	<dl	1.3	<dl
As	11	3.5	3	4.5	7	1	7	3.3
Se	1.4	1.2	3.1	2	2	2	8	2
Br	50	2	4.6	12	40	1.6	13	1
Rb	17	10	16	6.7	6	0.7	34	1
Sr	53	240	28	70	100	72	65	650
Y	11	4.3	4	3.4	6	2	12	2.4
Zr	16	20	16	19	12	24	70	16
Mo	1.5	2	6	<dl	3	<dl	<dl	<dl
Ba	90	270	<dl	40	130	32	140	500
Pb	1.5	1.4	2.5	3	1.3	2	4	0.2
Th	2.4	2	<dl	1.3	<dl	1	4	<dl
U	3	1.5	1.7	1.2	<dl	<dl	2	<dl

In ppmw coal basis (modified from Tables 1a and b in Wong and Robertson, 1992).

[a] Obviously erroneous value, perhaps mis-written in original.

determining most elements in the periodic table; and (iii) it is relatively rapid. The main disadvantages appear to be: (i) its availability is dependent on devices for generating the particle beam that are generally not commercially available; (ii) the small volume of excitation raises questions of sample representativeness and homogeneity; and (iii) matrix corrections tend to be large, especially for thick samples. It is also clear that the development of PIXE/PIGE techniques is less mature in comparison to INAA and XRF techniques and future developments may yet enhance this technique significantly.

2.3. Optical absorption/emission techniques

These techniques were the first multi-element techniques applied to trace element determinations in fossil fuels (see, for example, Brown and Swaine, 1964). Although emission techniques predate absorption techniques by a few years, there has been a resurgence in the older method recently due to the development of a much improved excitation source, namely the inductively coupled plasma (ICP). ICP techniques will be addressed separately.

2.3.1. Optical emission spectroscopy (OES)

Also known as atomic emission spectroscopy (AES) (Swaine, 1990), OES techniques depend on the measurement of atomic emission processes in the visible and near-visible (infrared and ultra-violet) regions of the electromagnetic spectrum. Swaine (1990) presents an excellent review of the development of this technique as applied to fossil fuel materials. The stability of the excitation process has always been a source of problems with this technique and a variety of excitation methods have been tried, including direct current (DC) arc in an open atmosphere, DC arc in controlled atmosphere, alternating current (AC) spark, ruby laser, shock tube, etc., before the inductively coupled plasma (ICP) excitation method became the method of choice. Of the older excitation methods, most work was done with the DC arc excitation method, in which a relatively small amount of sample (10–20 mg) is mixed with powdered graphite (20–40 mg) and held in the anode cup of the electrode pair that forms the arc. A current of 15–20 A at a voltage of 250–325 V ignites the arc across a 0.5±0.1 cm gap between electrodes and the arc is maintained for as long as 2.5 min, during which time the emitted radiation is dispersed and the different characteristic energy lines are detected at different wavelengths.

Detection of the emitted radiation has evolved from photographic methods to the more sensitive direct reading spectrometric methods, which were introduced in the late 1960s. The sensitivity of the technique for a given element depends largely on how well the emission line used for the determination of the element appears in the photograph or spectrometer, and interferences among elements can be a problem for some elements. The merits of both detection methods are discussed by Dreher and Schleicher (1975) and spectral interferences are discussed by Swaine (1990). OES techniques, now usually referred to as “semi-quantitative DC arc spectrographic analysis” are still in use today because the technique is quick, readily available,

Table 4
Element concentrations in APCSB coals by DC Arc Spectrography (modified from Tables 3–5 in Skeen et al., 1990)

	UF	WY	IL	PITT	POC	UT	WV	ND
Major oxides, in wt.% ash basis								
Na_2O	0.5	2.1	1.2	0.5	3.3	2.1	0.3	*
MgO	1.8	7.1	1.2	1.3	3.3	1.5	0.8	9.0
Al_2O_3	33.3	11.8	23.7	43.3	25.7	13.3	38.0	4.7
SiO_2	49.3	33.3	47.7	62.3	38.7	40.0	55.0	13.3
P_2O_5	<0.16	0.7	<0.16	<0.16	<0.16	<0.16	<0.2	0.3
SO_3	nd	nd	nd	nd	nd	nd	nd	nd
K_2O	2.7	0.5	1.9	1.7	0.8	0.5	2.2	0.5
CaO	6.6	19.3	13.7	6.2	15.3	8.7	0.6	20.7
TiO_2	0.7	0.7	0.7	1.1	0.9	0.7	1.5	0.3
MnO	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.1
Fe_2O_3	16.7	4.6	21.0	29.3	13.3	7.4	3.0	5.9
	111.5	80.1	111.1	145.7	101.2	74.1	101.4	54.6
All elements, in ppmw ash basis								
Be	10	1.7	6	13	13	4.3	16	2.9
B	220	820	730	560	330	>1000	290	700
Na	3300	15,700	9200	3930	24,300	15,700	1870	**
Mg	10,900	42,000	7130	7100	19,700	8800	4970	54,000
Al	173,000	62,000	123,000	230,000	133,000	69,700	200,000	27,300
Si	230,000	157,000	223,000	290,000	180,000	183,000	267,000	63,000
P	<700	3130	<700	<700	<700	<700	750	1040
K	22,000	3870	16,000	14,000	6700	3800	18,300	3870
Ca	47,300	147,000	100,000	44,300	111,000	62,000	4000	140,000
Sc	15	16	16	20	25	15	33	9.5
Ti	4070	4200	4100	6200	5300	4100	9200	1900
V	120	105	150	140	130	80	160	40
Cr	140	70	230	210	160	105	200	25
Mn	410	390	670	390	460	130	100	1100
Fe	116,000	32,000	147,000	203,000	93,700	52,000	20,700	39,000
Co	26	15	23	29	48	14	32	6
Ni	100	60	130	140	120	90	110	20
Cu	130	150	70	70	360	65	80	55
Ga	45	30	30	50	45	25	60	20
Ge	27	<5	55	13	9	<5	6	<5
As	220	<100	<100	180	280	<220	<220	<220
Sr	470	2650	250	1000	2100	1900	360	6600
Y	35	35	30	33	86	40	47	25
Zr	80	200	90	130	220	250	160	130
Nb	12	17	15	20	20	11	18	6
Mo	11	8	32	9	40	11	7	8.5
Ru	<2	<2	<2	<2	<2	<1	<1	<1
Rh	<2	<2	<2	<2	<2	<1.5	<1.5	<1.5
Pd	<1	<1	<1	<1	<1	<1	<1	<1
Ag	1.5	0.8	2.4	1	1.8	10	2.4	<0.1
Cd	<30	<30	<30	<30	<30	<20	<20	<20
In	<10	<10	<10	<10	<10	<7	<7	<7
Sn	12	10	15	14	1500	8	10	6
Sb	<70	<70	<70	<70	<70	<35	<35	<35
Ba	300	3770	375	560	330	775	680	6130
La	50	70	60	63	140	64	70	40
Ce	65	80	<200	<200	230	150	130	<65
Pr	<100	<100	<100	<100	<100	9	8	7

Table 4 (*continued*)

	UF	WY	IL	PITT	POC	UT	WV	ND
All elements, in ppmw ash basis								
Nd	50	<70	<70	45	115	<150	95	<150
Sm	<10	<10	<10	<10	15	8	6	4
Eu	<2	<2	<2	<2	<2	2	3	<0.7
Ho	<7	<7	<7	<7	<7	<1.5	2	<1.5
Yb	6	3.5	4	6	8.5	4.7	8	2.2
Pb	80	40	85	80	200	40	80	26
Bi	<10	<10	<10	13	13	<22	<22	<22

* Analysis compromised by unresolved interference.

and inexpensive in comparison to most other trace element methods. Further experimental details are given in the literature (Dreher and Schleicher, 1975; Swaine, 1990; Skeen et al., 1990).

There have been attempts to use variations of the OES technique for coal directly, without ashing (e.g., Fletcher and Golightly, 1985; Fletcher and Skeen, 1997), but the vast majority of work has been done on coal ash. Such techniques are performed on high-temperature ash, usually prepared from coal by controlled combustion in air at a temperature between 450 and 750 °C. Hence, volatile elements such as the halogens, Hg, Se, etc., cannot be determined by this technique. However, as Swaine (1990) points out, these elements are usually below the detection limit of the DC arc technique anyway. The technique is generally considered to be semi-quantitative and precision is typically quoted as ±30%, but for many elements in coal ash, the precision is often better than this (Swaine, 1990). Comparison with analytical standards must be used for the most precise results.

The major advantages of OES methods are: (i) their speed and low cost; and (ii) the common availability of such techniques. The major disadvantages are: (i) their precision is not as good as other trace element techniques and they are often described as being only semi-quantitative; (ii) such techniques are rarely done directly on coal, but on high-temperature ash samples prepared from coals. In the future, it is anticipated that such techniques will primarily be used to screen large numbers of samples before applying more accurate (and expensive) methods.

Automated semi-quantitative DC-arc spectrographic analyses have been reported for the eight APCSB coals (Skeen et al., 1990; Dorrzapf et al., 1989). Data for 62 elements were reported for these coals. The determinations were done on ash prepared from the APCSB coals and NIST SRM coals were used as standards. The data from this analysis method are summarized in Table 4.

2.3.2. Inductively coupled plasma atomic emission spectrometry (ICP/AES)

ICP/AES is the technique that is largely superseding other OES techniques because of the superior properties of an ICP as an excitation source (Swaine, 1990). In this method, excitation is achieved by a high-temperature (>5000 K) plasma formed from an electrode-less discharge in argon. This plasma is maintained by inductive coupling of the plasma to a radio-frequency electromagnetic field. Solutions for analysis are injected as aerosols at the bottom of the plasma and emissions from elements in the solution are excited by transit through the hot plasma. Modern spectrometers for ICP/AES can either be operated in sequential mode, in which each element is determined individually and consecutively, or they can be operated in a multi-element mode, in which up to 20 elements can be determined simultaneously by means of individual detectors. Both the detection limits and precision for the determination of trace elements in coal ash by ICP/AES are superior to those for other OES techniques.

For coal ash, complete solubilization is usually possible by means of fusion with lithium tetraborate, or similar fluxing material, and/or acid digestion. Instead of solutions, suspended solids or slurries, or even pulverized solids can be introduced into the plasma; however, the precision and reproducibility of the elemental determinations are generally not as good as from a solution. Slurry atomization, in which an aqueous suspension of coal is sprayed (Ebdon and

Wilkinson, 1987) or directly injected (Riley et al., 1992) into an ICP/AES, and direct introduction of pulverized coal into the ICP/AES (Ng et al., 1984) have been attempted as possible methods to avoid the drawbacks associated with ashing and dissolution. Generally, such techniques for solid samples work better with direct-current plasma (DCP) methods, because the DCP torch can tolerate solids better (McCurdy et al., 1985). More recently, research has indicated that direct coal digestion methods appear to have significant potential for use with ICP/AES and thereby avoid the need for LTA or HTA (Querol et al., 1996, 2001).

The latest developments with ICP and trace element analysis of coal appear to be moving in the direction of combining ICP with mass spectrometry (ICP/MS); this combination is discussed below in the section on mass spectrometric methods (Section 2.4.2).

The main advantages of ICP/AES are similar to those listed above for other OES methods: (i) it is a relatively rapid and inexpensive method, well suited to a large throughput of samples, yet with better precision than older OES techniques; (ii) operation of an ICP/AES spectrometer is now well automated for multi-sample operation; and (iii) the technique is widely available, both in research and commercial analytical laboratories. The main disadvantages are also similar to those for older OES techniques: (i) analysis is best done on solutions of coal ash or on acid-digested coal rather than on coal directly; and (ii) the plasma can take as long as 1.5–2.0 h to stabilize before reproducible results can be obtained.

Selected elements in the APCSB coals have been determined by a combination of ICP/AES, AAS, and ISE techniques (Doughten and Gillison, 1990). Various major and trace elements in coal ash were determined in triplicate by ICP/AES on a coal-ash solution derived by first ashing the APCSB coals at a maximum temperature of 525 °C and then dissolving the resulting ash in a combination of nitric, perchloric, hydrofluoric and hydrochloric acids. NIST SRM coals were used as comparison reference materials. Data for ICP/AES, AAS and ISE (for F) determinations of Li, Be, F, V, Cr, Mn, Co, Ni, Cu, Zn, Sr, Y, Cd, Ba, Hg, and Pb in the APCSB coals are shown in Table 5. The reproducibility for the elements determined by ICP/AES is generally within ±5% of the mean (Doughten and Gillison, 1990).

2.3.3. *Atomic absorption spectrometry (AAS)*

AAS techniques were developed for chemical analysis in the 1950s, when it was shown that most elements that give free atoms in flames could be detected by their characteristic resonant absorption.

Table 5
Element concentrations in APCSB coals by AAS, ICP/AES and ISE methods

	UF	WY	IL	PITT	POC	UT	WV	ND	Method[a]
ppmw coal basis									
Li	15	4.1	7.8	8.6	5.8	5.1	29	2.7	FAAS
Be	1.5	0.25	0.76	0.77	0.8	0.13	1.9	0.18	
F	310	230	270	210	110	70	170	50	ISE
V	26	14	32	15	11	4	44	3.5	
Cr	20	6.2	31	14	9	4.9	40	2.5	
Mn	41	20	77	17	16	4	15	80	
Co	5	1.6	4.3	2.5	3.8	0.8	1.8	<1	FAAS
Ni	15	4.9	18	8.5	6.7	3.4	16	1.3	
Cu	19	12	10	5.5	12	3.9	19	4.7	
Zn	20	10	175	7.8	4	6.2	13	5	
Sr	60	147	29	64	85	60	48	500	
Y	9.3	3.8	4.2	4.2	6.4	2.1	10.7	1.9	
Cd	0.07	0.09	0.6	0.06	0.08	0.06	0.08	0.05	GFAAS
Ba	55	15	80	41	16	31	125	425	
Hg	0.01	<0.005	<0.005	<0.005	<0.005	<0.005	0.005	<0.005	CVAAS
Pb	7.5	3	6.5	2.9	2.5	1.6	12	1.5	GFAAS

In ppmw coal basis (modified from Tables 5 and 8 in Doughten and Gillison, 1990).

[a] By ICP/AES if not otherwise indicated.

To promote the resonant absorption processes, the flame is placed directly in the path of radiation from a strong stable light source in order to excite transitions of valence electrons in elements in the flame. This arrangement effectively removes light at the wavelengths of these absorption processes from the continuum of light transmitted through the flame. These resonant absorption lines (strictly, absences) are then separated by means of a monochromator and detected by a photomultiplier. This signal is then amplified and measured spectrophotometrically or, more commonly today, electronically. Four distinct AAS methods exist, depending on the method of excitation (Swaine, 1990): flame AAS (FAAS); electrothermal or graphite-furnace AAS (EAAS or GFAAS); hydride AAS (HAAS); and cold-vapor AAS (CVAAS). Pollock (1975) describes various wet chemical and preparation procedures for these AAS and other techniques.

In FAAS, the sample in solution is atomized into a flame, usually an air-acetylene torch. FAAS is sensitive for many elements and is the simplest of the different variations of AAS. Electrothermal heating, which led to the development of graphite furnaces for AAS, is an especially attractive method for trace elements, as it has the best sensitivity of all four variations. Variations of electrothermal AAS have been developed for a number of specific elements, such as Mn and Ag (Bhattacharyya, 1994; Bhattacharyya et al., 1996), and for determining trace metals in coal slurries (Silva et al., 1999). Hydride methods for AAS depend on the reduction of dissolved compounds by sodium borohydride ($NaBH_4$) to form gaseous hydrides that are then atomized in a flame. Hydride AAS methods are generally useful for those elements in fossil fuels that form stable covalent hydrides, such as As, Bi, Pb, Sb, Sn, and Te. Cold-vapor AAS (CVAAS) is especially useful for the determination of Hg as other AAS methods do not determine this element reliably. This technique for Hg involves separation of mercury from the coal by combustion and/or oxidizing acid digestion into the Hg^{2+} state in solution (Aruscavage and Moore, 1989; Doughten and Gillison, 1990). The mercury is then reduced to metallic Hg by stannous chloride, and captured in a silver or gold amalgamation process (Kalb, 1975). The Hg is then released from the amalgamated silver or gold and determined in a CVAAS cell. Various different methods of mercury liberation have been attempted (Swaine, 1990; Aruscavage and Moore, 1989; Doughten and Gillison, 1990; Kalb, 1975).

A related method that is in use in some laboratories as an alternative to hydride AAS and CVAAS for determination of As, Hg and Se is atomic fluorescence spectroscopy (Swaine, 1990; Querol et al., 2001). Amalgamation of Hg on gold followed by flameless AAS has also been developed as an alternative to the CVAAS determination of Hg (Swaine, 1990).

AAS methods generally require that the sample be totally in solution and many different methods have been devised and tried to ensure that coal ash is totally dissolved (Swaine, 1990). However, efforts have been made to introduce coal directly into a graphite furnace, and aqueous suspensions of finely ground coal, in particular, have been tried with limited success (O’Reilly and Hicks, 1979). Very recently, Ikavalko et al. (1999) have successfully developed microwave-assisted acid digestion of coal as a means of introducing solubilized coal directly into the AA spectrometer. Standard solutions for each element to be determined are a necessity for development of in-house calibration curves for the most precise determinations; however, the use of reference standard materials, such as NIST SRMs, is generally not necessary as matrix effects are negligible.

The major advantages of AAS methods appear to be: (i) the relative simplicity, availability, and speed of the technique; (ii) it is suitable for major and trace element species; (iii) the detection limits and precision for some trace element determinations by GFAAS can be as low as ppt (parts per trillion); (iv) sufficient variations exist so that many elements in the periodic table can be determined by this technique. The major disadvantage appears to be that the technique is much better done on liquid rather than solid samples.

Data for a number of elements in APCSB coals by AAS techniques have been reported by Doughten and Gillison (1990). Both FAAS and GFAAS techniques were used in this study and experimental details for both techniques were described. FAAS was used for determinations of Li and Co, whereas GFAAS was used for Pb and Cd; data for these elements and the other elements determined by ICP/AES are shown in Table 5. In the same study, Hg was determined by the cold-vapor AAS procedures described in more detail elsewhere (Aruscavage and Moore, 1989; Doughten and Gillison, 1990).

2.4. Mass spectrometric (MS) methods

Mass-spectrometric methods tend to differ mainly in the mechanism for ion generation as the ion detection and measurement is similar for each MS method. Generally, any mass spectrometer with a reasonable mass resolution can be used as an elemental detector and most modern MS instruments exceed the minimum requirements. MS techniques have a long history of application to fossil fuels, commencing with spark-source (SSMS) mass spectrometric methods in the 1960s, and appear poised for a renaissance as a result of recent improvements in technology and other developments. This is currently a rather active area of research in chemical analysis and MS detection is being investigated and appended to many different volatilization methods for elemental analysis. For fossil fuel analysis, ICP/MS appears to be the most promising new technique; however, there are other promising new mass-spectroscopic techniques, such as ion-beam MS techniques, e.g. Secondary Ion Mass Spectrometry (Martin et al., 1985; Hickmott and Baldridge, 1991), SIMS, and Accelerator Mass Spectrometry (Allen, 1988), AMS, both of which have not been applied extensively to fossil fuels.

2.4.1. Older mass spectrometry methods

The spark generation mechanism for generating ions for spark-source mass spectrometry (SSMS) is well described in the literature (Sharkey et al., 1975; Carter et al., 1975, 1978). In this method, the spark is produced by ignition between two conductors in a vacuum with a pulsed high frequency potential of 50 kV. During this process, the electrode substance is evaporated and ionized. The ions are then accelerated by a constant potential of 25 kV through source slits into an electrostatic field that functions as an energy filter. The ions then enter the magnetic field of the mass spectrometer and are deflected in an arc, the curvature of which is determined by the mass-to-charge ratio of the ion species. At the focus plane of the different arcs is a photographic plate, or more commonly today, an array of electron multipliers that measure the ion spectrum as a function of mass. From the mass spectrum, the amount of the element (isotopes) present in the sample can be estimated. The electrode materials for SSMS are prepared by mixing the pulverized coal or ash with a conductor such as silver or graphite powder. The 1:1 mixture by weight is pressed into polyethylene slugs to form the electrode.

An alternative ionization method, especially useful for liquid fossil fuels, is simply to invoke thermal emission of ions in the spectrometer vacuum. This method, thermal emission mass spectrometry (TEMS), has also been applied to coals (Carter et al., 1975, 1978). A more recent variation of the ionization method is glow discharge (Luo and Huneke, 1992), which gives rise to the technique of glow-discharge mass spectrometry (GDMS). In GDMS, the conducting solid sample serves as a cathode for a DC glow discharge in about 1 Torr of argon. Atoms sputtered from the surface of the cathode/sample diffuse into the argon plasma and a fraction of these liberated atoms are then ionized by Penning ionization processes upon collision with excited argon atoms and electrons in the plasma. These ions are then accelerated into the mass spectrometer for analysis.

A different approach to the determination of trace elements is to apply isotope dilution (Hintenberger, 1956) to SSMS (IDSSMS) or TEMS (IDTEMS). In this technique, an enriched isotope, usually of low abundance in the original coal or ash, is mixed with the sample in a known amount and the isotopic ratio for the element of interest is then determined, from which the abundance of the element can be calculated upon comparison with a sample unspiked in the enriched isotope. Although this method is limited to elements that have two or more naturally occurring or long-lived isotopes, it affords a very sensitive and precise determination in comparison to SSMS and TEMS alone.

Although SSMS and related MS techniques are applicable to all elements in the periodic table, and with detection limits of 0.02 ppm or better for some elements (Swaine, 1990), the technique is generally regarded as semi-quantitative with experimental errors that are typically as large as ±50% for elements in coal without standards. The more recent technique of GDMS is both more sensitive and precise, with detection levels for many elements in the sub-ppb range and accuracies on the order of ±20%, even for standardless application. These MS techniques are therefore very well suited for semi-quantitative survey studies. Towards this end, both the sample preparation time and analysis time are not demanding and sample throughput can be high. It appears that with effort

GDMS could become a reasonably quantitative method for rapid analysis of trace elements in coal ash; however, more research is needed on direct use of coal in GDMS, as low-rank coals, in particular, appear to give rise to significant problems (Luo and Huneke, 1992).

2.4.2. Inductively coupled plasma/mass spectrometry (ICP/MS)

Just as ICP sources are enhancing the precision and accuracy of atomic emission spectroscopy, the same sources are creating similar improvements in MS techniques. The excellent properties of the ICP as an atomic vaporization process (viz. stability, very high temperature, etc.) also make it an excellent source of ions for use in a MS. Positive, single-charged ions dominate in the plasma as negative ions, multiple-charged ions, and molecular ions are generally of very low abundance. Furthermore, the energy of the ions created in the plasma is in the range of 2–20 eV, which is optimum for separation in a quadrupole MS. A detailed description of one ICP/MS instrument that uses solutions of ash prepared in air at 500 °C for the elemental analysis of coal is presented by Conrad and Krofcheck (1992). It was demonstrated that, except for Se of the 16 elements investigated, ashing at 500 °C was as effective at retaining elements as the much slower and more technically demanding closed oxygen bomb ashing method. The product of the ashing was then subjected to an acid solubilization treatment and the resulting solution injected into the ICP. Bettinelli and Baroni (1995) describe a similar ICP-MS method for analysis of coal fly ash.

The ICP/MS method of analysis for ash offers a number of benefits that are not duplicated readily by any other single technique. It is rapid; only a few minutes are needed to obtain quantitative results for virtually all elements in the periodic table. It is sensitive; detection limits for many elements are in the ppt range. It is highly selective; isotopic interferences are relatively few, and all elements, except In, have at least one isotope of unique mass. It is easy to calibrate; stock solutions of various elemental abundance levels can be used to generate calibration data or SRMs such as NIST coals or ash can be used. The major disadvantages to this method is that the analyte signal is very susceptible to variation in the plasma nebulizer flow and the radio-frequency power applied to the plasma, and great care must be taken to avoid systematic errors from these sources. Instrumental drift can also be a problem as the instrument “warms up” over the first hour or two of operation.

As for other MS techniques used for trace-element analysis, an important question to be addressed is whether or not such techniques can be developed for direct measurements on the coal rather than ash, so that the problem of loss of volatile elements during ashing may be avoided. One attempt to address this problem involves combining laser ablation (LA) processes on coal with an ICP/MS system (Lichte, 1992). In this process, a pulsed Nd/YAG laser operated at the primary wavelength of 1068 nm was used for the laser ablation. Samples of coal for the LA process were prepared from finely ground coal pressed to form a pellet. The ablation process was found to work best with the laser operating in the pulsed Q-switched mode, rather than the free-running mode. In the Q-switched mode, the laser power is dissipated over 5 ns, rather than over typically 140–160 ns in the free-running mode. This operational difference results in a 10^5-fold increase in power density for the Q-switched mode, which promotes ion/electron sputtering process in the sample. The LA process forms very fine particles that are then swept by an argon stream into the ICP, where they are vaporized and ionized for the MS determination. Separate mass integrations were used for major and trace constituents to keep the determinations within the linear range of the detector. The parameters controlling the laser pulsing, pulse frequency and power dissipation, were also optimized for the analysis. Recommended standards for this variation of ICP/MS are the NIST SRM coals or similar well-analyzed coals as the matrix effects will be most closely similar to coal.

More recent variations of the ICP-MS method on whole coal have been described by Fadda et al. (1995), Booth et al. (1999), Rodushkin et al. (2000) and Querol et al. (2001). These methods vary mostly from that described by Lichte (1992) in the means used to prepare the coal for its introduction into the ICP. Fadda et al. (1995) used microwave oven acid digestion, whereas Rodushkin et al. (2000) used both solution nebulization and laser ablation, and Querol et al. (2001) used a two-step acid digestion in a PFA-bomb.

Up to 67 elements, ranging from lithium to uranium, and including such major elements as carbon, can be analyzed by ICP/MS (Conrad and Krofcheck, 1992). Detection limits for many trace elements are in the range of 5–100 ng/g. Accuracy and precision appear to be limited principally by sample homogenization as typically less than 5 mg of coal is consumed in the analysis (Lachas et al., 1999). However, the precision, typically of the order of ±20% for a single scan, can be improved by combining multiple determinations as a single determination generally takes less than a minute. Results obtained for the eight APCSB coals by Meier (1997) are summarized in Table 6.

Table 6
Element concentrations in APCSB coals by ICP/MS

	UF	WY	IL	PITT	POC	UT	WV	ND
Ga	40	22	22	36	34	22	48	12
Ge	32	4.3	52	14	5.4	4.9	8.6	3.9
As	120	29	24	83	185	–	34	8
Rb	163	21	97	88	40	22	185	15
Nb	18	16	14	18	21	12	31	8.3
Mo	19	6.1	39	8.0	51	9.2	6.5	4.4
Ag	3.4	2.8	3.8	3.3	4.3	3.3	6.4	1.6
Cd	1.2	1.4	4.9	1.2	1.1	1.7	0.3	0.5
Sn	7.1	3.8	4.4	6.2	7.0	3.6	9.0	3.9
Sb	3.6	1.9	4.9	2.2	5.6	1.9	2.9	1.6
Cs	14	2.4	8.6	8.7	4.2	3.1	12	1.1
La	60	47	34	51	107	54	90	22
Ce	125	95	75	112	215	100	190	43
Pr	15	11	8.5	12	25	12	21	4.5
Nd	55	42	32	47	96	46	77	16
Sm	11	8.3	6.2	9.0	19	8.2	14.4	2.7
Eu	2.5	2.0	1.2	1.9	4.0	1.8	3.2	0.57
Gd	11	7.9	5.6	7.8	19	8.1	12	3.1
Tb	1.7	1.2	0.83	1.2	3.1	1.2	2.0	0.52
Dy	11	8.2	5.6	8.5	21	7.4	14	3.6
Ho	2.2	1.5	1.0	1.6	4.0	1.4	2.6	0.72
Er	5.9	4.2	3.0	4.1	11	4.0	6.9	2.2
Tm	1.1	0.76	0.54	0.77	1.8	0.68	1.3	–
Yb	6.0	4.5	3.2	4.7	11	4.3	8.0	2.4
Hf	6.2	8.0	4.8	6.7	11	12	12	4.4
Ta	1.4	1.4	1.1	1.4	2.2	1.2	3.2	8.7
W	9.4	5.4	12	9.3	21	11	??	3.8
Tl	8.9	0.85	10	6.1	4.4	0.64	2.7	–
Pb	56	19	52	41	32	32	63	15
Bi	0.87	0.63	0.50	1.3	0.97	0.77	1.2	–
U	8.6	7.4	40	6.2	12	18	11	4.7

In ppmw ash basis (modified from Tables 1 and 2 in Meier, 1997). Values shown are averages of triplicate determinations. For determination of the rare-earth elements (La–Yb), Hf, Ta, and W, the samples were ashed and dissolved by sinter method; for the remaining elements, the samples were ashed and dissolved by an acid digestion method.

The ICP/MS variations described above appear to constitute a powerful new technique for quantitative trace element determinations in fossil fuels. The technique, although at the expensive end for laboratory equipment as a whole, is well suited to a laboratory environment, as no large specialized source of radiation is needed.

2.4.3. Secondary ion mass spectroscometry

The ion-beam MS technique of secondary ion mass spectrometry (SIMS) has also been applied to coal (Martin et al., 1985; Hickmott and Baldridge, 1991); however, this technique is designed to be a surface technique and may find more use for forms-of-occurrence studies and geochemical applications than for bulk analysis. A preliminary study of heterogeneous sulfur isotopic ratios in iron sulfide minerals performed by SIMS with an ion microprobe indicates the potential of this technique (Hickmott and Baldridge, 1991). Similar isotopic studies on coals or coal components (minerals, macerals) may be very useful for placing constraints on the origin of coals and coalification processes.

2.5. Miscellaneous methods

For certain of the HAP trace elements, notably the halogens, none of the techniques discussed above is sufficiently sensitive for an accurate determination and/or the element is highly volatile so that it cannot be trapped efficiently by ashing and, hence, can only be determined on a whole coal basis. For these elements, various individualized analytical methods have been developed. These methods include electroanalytical methods, such as ion-selective electrode and ion chromatography, and chemical analysis methods. For completeness, also included in this section are spectrophotometric or colorimetric methods, which were among the first techniques developed for analysis of trace elements in coal, but which have now been largely superseded by instrumental methods.

2.5.1. Ion-selective electrode (ISE)

Such methods are generally applied to those elements that form stable anions in aqueous solutions, e.g. F^-, Cl^-, where an anion selective electrode can be used to determine the concentration of the desired anionic species. Procedures for fluoride determination, starting from coal ash, have been described (Kirschenbaum, 1989; Doughten and Gillison, 1990; Standard method D-3761, ASTM, 2000). Generally, pretreatment techniques are used to separate and/or concentrate the anionic species of interest prior to the determination. Such methods include alkali fusion (Kirschenbaum, 1989), oxygen bomb digestion (Standard method D-3761, ASTM, 2000), and pyrohydrolysis (Godbeer and Swaine, 1987). It is felt (Godbeer and Swaine, 1987; Swaine, 1990; Wong et al., 1992) that pyrohydrolysis consistently gives higher (and truer) results for fluorine than the other two methods of preparation. Standard solutions of fluoride are used to prepare calibration curves with the ISE prior to the measurement of fluoride in the sample solution.

2.5.2. Ion chromatography (IC)

The field of ion chromatography was established by efforts to couple a conductivity detector to separations performed on an ion-exchange chromatographic column and this technique has become the method of choice for the determination of anions in a wide range of samples (Cox et al., 1992). As alternatives to conductivity detectors, amperometric and indirect photometric detectors have also been used with IC. For determinations of anionic species in coal, the major problem is to ensure complete extraction of all the anionic species from the coal, and total coal digestion methods are generally preferred. Fluorine, chlorine, and sulfur can be readily determined by IC methods after oxygen bomb digestion (Cox et al., 1992) and other additional species, namely bromine, phosphorus, and nitrogen, may also be determined by this method (Rigin, 1987).

An interesting variation of IC methods, high performance gradient ion chromatography (HPIC), has been reported for the determination of the rare-earth elements (REEs) in geological materials, including coal (Ridley et al., 1992; Watkins et al., 1995). In this technique, the REEs are separated as trivalent cations in oxalate and diglycolate anionic complexes on a chromatographic column (Dionex CS-5). Microwave digestion of whole coal samples in PTFE pressure vessels was performed to ensure the coal was completely solubilized. With use of SRMs, the determinations have detection limits and precisions that compare well with alternative methods for determination of REEs in coal (Ridley et al., 1992; Watkins et al., 1995).

Swaine (1990, pp. 71, 72) lists a number of other related methods that have been described for one or more elements in coal. Such methods include polarography, anodic stripping voltammetry, fluorimetry and other chromatographic methods.

2.5.3. Chemical methods

More modern methods of analysis are superseding the traditional wet chemical methods (Standard D-2795, ASTM, 2000) of determining major inorganic elements (typically Si, Al, Ti, Ca, Fe, Mg, K, Na, and P). Both X-ray fluorescence and atomic absorption methods for these major elements in coal ash are now listed as ASTM approved methods (Standard methods D-4326 and D-3682, respectively, ASTM, 2000).

Various colorimetric or spectrophotometric methods for trace elements, such as Cl, As, F, B, Ge, Hg, Be, Ga, Mn, P, Ti, etc., are briefly described by Swaine (1990). The determination of each of these elements depends on the formation of an individual, uniquely colored, coordination complex in solution, the absorbance of which can be measured spectrophotometrically and related to the concentration of the element in the solution, and hence, to its concentration in the ash and/or coal. The skills of the chemist are needed here to ensure: (i) that all of the element of interest is present in solution, and (ii) that there are no interferences in the spectrophotometric determination. These methods have, for the most part, been superseded by the multi-element instrumental methods listed above.

2.6. Evaluation of different methods

In this section, the relative merits of the different techniques are compared. This discussion is divided into sections for the major elements and for trace elements.

2.6.1. Major inorganic elements

The major ash-forming elements (Na, Mg, Al, Si, K, Ca, Ti, Fe) and some of the more significant trace elements (P, Cl, Mn) in coal can be determined by a number of methods. However, the best technique for such analyses currently appears to be X-ray fluorescence (XRF) by energy-dispersive (ED) methods on

Table 7
Comparison of instrumental determinations of selected trace elements in the APCSB coals, ppmw of whole coal

Element	INAA	XRF	PIXE/ PIGE	AAS, ISE ICP/AES	OES	ICP/ MS
A. Upper Freeport, PA, coal (13.03 wt.% ash)						
Be	n.d.	n.d.	n.d.	1.5	1.3	n.d.
F	n.d.	n.d.	86	31	n.d.	n.d.
Cl	n.d.	1467	n.d.	n.d.	n.d.	n.d.
Cr	20	25	23	20	19	n.d.
Mn	n.d.	n.d.	27	41	53	n.d.
Co	5.3	n.d.	9.4	5	3.4	n.d.
Ni	14	13	9.4	15	13	n.d.
Zn	20	20	18	20	n.d.	n.d.
As	17	n.d.	11	n.d.	29	16
Se	1.9	n.d.	1.4	n.d.	n.d.	n.d.
Cd	n.d.	n.d.	n.d.	0.07	<dl	0.16
Sb	0.53	n.d.	n.d.	n.d.	<dl	0.47
Ba	61	50	88	55	39	n.d.
Hg	n.d.	n.d.	n.d.	0.01	n.d.	n.d.
Pb	n.d.	n.d.	1.5	7.4	10	7.3
B. Wyodak–Anderson, WY, coal (6.3 wt.% ash)						
Be	n.d.	n.d.	n.d.	0.25	0.1	n.d.
F	n.d.	n.d.	56	23	n.d.	n.d.
Cl	n.d.	<dl	n.d.	n.d.	n.d.	n.d.
Cr	6.1	6	7	6.2	4.3	n.d.
Mn	n.d.	n.d.	23	20	26	n.d.
Co	1.7	n.d.	1	1.6	1	n.d.
Ni	4.9	3	3.5	5	3.1	n.d.
Zn	11	7	23	10	n.d.	n.d.
As	3.6	n.d.	3.5	n.d.	<dl	1.8
Se	1.6	n.d.	1.2	n.d.	n.d.	n.d
Cd	n.d.	n.d.	n.d.	0.09	<dl	0.09
Sb	0.19	n.d.	n.d.	n.d.	<dl	0.12
Ba	310	202	270	15	238	n.d
Hg	n.d.	n.d.	n.d.	<dl	n.d.	n.d
Pb	n.d.	n.d.	1.4	3	2.5	1.2
C. Illinois #6, IL, coal (14.25 wt.% ash)						
Be	n.d.	n.d.	n.d.	0.8	0.8	n.d.
F	n.d.	n.d.	86	27	n.d.	n.d.
Cl	n.d.	533	n.d.	n.d.	n.d.	n.d.
Cr	33	38	36	31	33	n.d.
Mn	n.d.	n.d.	87	77	95	n.d.
Co	4.4	n.d.	<dl	4.3	3.3	n.d.
Ni	21	15	15	18	19	n.d.
Zn	220	117	130	176	n.d.	n.d.
As	4.7	n.d.	3.2	n.d.	<dl	3.4
Se	4.3	n.d.	3.1	n.d.	n.d.	n.d.
Cd	n.d.	n.d.	n.d.	0.06	<dl	0.7
Sb	<dl	n.d.	n.d.	n.d.	<dl	0.7
Ba	94	66	n.d.	81	53	n.d.
Hg	n.d.	n.d.	n.d.	<dl	n.d.	n.d.
Pb	n.d.	n.d.	2.5	6.5	12	7.4

Table 7 (*continued*)

Element	INAA	XRF	PIXE/ PIGE	AAS, ISE ICP/AES	OES	ICP/ MS
D. Pittsburgh, PA, coal (9.1 wt.% ash)						
Be	n.d.	n.d.	n.d.	0.7	1.1	n.d.
F	n.d.	n.d.	90	21	n.d.	n.d.
Cl	n.d.	633	n.d.	n.d.	n.d.	n.d.
Cr	14	6	18	14	19	n.d.
Mn	n.d.	n.d.	20	17	35	n.d.
Co	2.6	n.d.	1.5	2.5	2.6	n.d.
Ni	10	3	4.7	8.5	13	n.d.
Zn	9	8.2	9.7	7.8	n.d.	n.d.
As	8.4	n.d.	4.5	n.d.	16	7.6
Se	1.5	n.d.	2.2	n.d	n.d.	n.d.
Cd	n.d.	n.d.	n.d.	0.06	<dl	0.11
Sb	<dl	n.d.	n.d.	n.d.	<dl	0.20
Ba	47	35	37	41	38	n.d.
Hg	n.d.	n.d.	n.d.	<dl	<dl	n.d.
Pb	n.d.	n.d.	3	2.9	7.2	3.8
E. Pocahontas #3, VA, coal (4.74 wt.% ash)						
Be	n.d.	n.d.	n.d.	0.8	0.6	n.d.
F	n.d.	n.d.	20	11	n.d.	n.d.
Cl	n.d.	1600	n.d.	n.d.	n.d.	n.d.
Cr	9.1	11	8	9.2	7.9	n.d.
Mn	n.d.	n.d.	12	16	21	n.d.
Co	4.1	n.d.	3.2	3.8	2.2	n.d.
Ni	8.6	6.8	4.1	6.7	5.8	n.d.
Zn	6.4	4.3	4.3	3.9	n.d.	n.d.
As	10	n.d.	6.9	n.d.	13	8.8
Se	2.5	n.d.	2.1	n.d.	n.d.	n.d.
Cd	n.d.	n.d.	n.d.	0.07	<dl	0.05
Sb	<dl	n.d.	n.d.	n.d.	<dl	0.27
Ba	198	162	130	16	191	n.d.
Hg	n.d.	n.d.	n.d.	<dl	n.d.	n.d.
Pb	n.d.	n.d.	1.3	2.4	9.5	1.5
F. Blind Canyon, UT, (4.49 wt.% ash)						
Be	n.d.	n.d.	n.d.	0.1	0.2	n.d.
F	n.d.	n.d.	86	70	n.d.	n.d.
Cl	n.d.	<dl	n.d.	n.d.	n.d.	n.d.
Cr	5.3	<dl	7	4.8	4.7	n.d.
Mn	n.d.	n.d.	5	4	6	n.d.
Co	1	n.d.	1.3	0.8	0.6	n.d.
Ni	3.7	<dl	5.1	3.4	3.9	n.d.
Zn	6	<dl	7	6	n.d.	n.d.
As	0.5	n.d.	1.2	n.d.	<dl	<dl
Se	1.1	n.d.	1.9	n.d.	n.d.	n.d.
Cd	n.d.	n.d.	n.d.	0.06	<dl	0.08
Sb	<dl	n.d.	n.d.	n.d.	<dl	0.09
Ba	40	<dl	32	31	35	n.d.
Hg	n.d.	n.d.	n.d.	<dl	n.d.	n.d.
Pb	n.d.	n.d.	1.9	1.6	1.9	1.4

(*continued on next page*)

Table 7 (*continued*)

Element	INAA	XRF	PIXE/ PIGE	AAS, ISE ICP/AES	OES	ICP/ MS
G. Stockton–Lewiston, WV, coal (19.36 wt.% ash)						
Be	n.d.	n.d.	n.d.	1.9	3	n.d.
F	n.d.	n.d.	130	170	n.d.	n.d.
Cl	n.d.	433	n.d.	n.d.	n.d.	n.d.
Cr	36	46	37	40	39	n.d.
Mn	n.d.	n.d.	12	n.d.	20	n.d.
Co	7.8	n.d.	9.4	8.1	6.3	n.d.
Ni	15	17	14	16	21	n.d.
Zn	14	12	12	13	n.d.	n.d.
As	6.2	n.d.	6.9	n.d.	<dl	6.6
Se	5.5	n.d.	8	n.d.	n.d.	n.d.
Cd	n.d.	n.d.	n.d.	0.06	<dl	0.06
Sb	<dl	n.d.	n.d.	0.08	<dl	0.56
Ba	130	109	140	123	132	n.d.
Hg	n.d.	n.d.	n.d.	0.05	n.d.	n.d.
Pb	n.d.	n.d.	3.6	12	16	2.9
H. Beulah–Zap, ND, lignite (6.59 wt.% ash)						
Be	n.d.	n.d.	n.d.	0.2	0.2	n.d.
F	n.d.	n.d.	35	50	n.d.	n.d.
Cl	n.d.	<dl	n.d.	n.d.	n.d.	n.d.
Cr	2.2	1.8	4	2.5	1.7	n.d.
Mn	n.d.	n.d.	85	80	72	n.d.
Co	0.8	n.d.	<dl	<dl	1.2	n.d.
Ni	<dl	1.3	3.3	1.3	1.2	n.d.
Zn	5.7	3.7	5.7	4.7	n.d.	n.d.
As	2.6	n.d.	3.3	n.d.	<dl	0.9
Se	0.6	n.d.	2.2	n.d.	n.d.	n.d.
Cd	n.d.	n.d.	n.d.	0.05	<dl	0.03
Sb	<dl	n.d.	n.d.	n.d.	<dl	0.11
Ba	680	320	480	423	404	n.d.
Hg	n.d.	n.d.	n.d	<dl	<dl	n.d.
Pb	n.d.	n.d.	0.2	1.5	1.8	1.0

high-temperature ash (HTA). Although EDXRF may not be quite as precise as the wavelength-dispersive (WD) method, the errors due to counting statistics of the two methods are probably not the major sources of error in either technique, so that there is little to be gained by utilizing WDXRF rather than EDXRF. However, the convenience, lower cost, and throughput rate of EDXRF are significant advantages. Furthermore, the recent development of polarized EDXRF offers additional improvement in the technique, especially for extending the XRF technique to trace elements or for carrying out the analyses on whole coal samples.

It is important for XRF methods, however, that sample preparation, pulverization, and homogenization procedures, including fusion of the ash with lithium tetraborate, be carefully employed to ensure the best results. Except for chlorine, none of the major or more significant trace elements is likely to be significantly volatilized from bituminous and higher-rank coals during ashing. However, for lower-rank coals, which contain significant amounts of major elements (Ca, Na, etc.) bound by carboxyl and other organic functional groups to macerals, the ashing procedures may have to be modified to minimize loss of such dispersed inorganics.

2.6.2. Comparison of methods applied to trace elements in the APCSB coals

As documented in Tables 1–6 in this review and elsewhere (Palmer and Klizas, 1997; Palmer, 1997), a number of techniques have been applied to the determination of trace elements in the coal samples from the Argonne Premium Coal Sample Bank (APCSB) program (Vorres, 1990, 1993). For comparative purposes, values for the 15 HAP elements have been extracted from these tables and listed in Table 7 for each APCSB coal individually. For those analyses presented on an ash basis rather than on a whole coal basis, the data have been converted to a whole coal basis by multiplication of the ash-based data by the fraction of ash in the coal (Vorres, 1990, 1993). As can be seen from Table 7, no single instrumental technique appears capable of determining all of the HAPs.

In the survey summarized in Table 7, the PIXE/PIGE method is the single technique that provides data on the largest number of HAPs (10 of 15) directly on the coal, but it is followed closely by INAA (8 of 15). However, neither technique is sensitive enough to determine Hg or Cd, when performed in the normal manner, and Be cannot be determined by either method. The combination of AAS, ISE, and ICP/AES provides data on 11 of 15 HAPs, but it is necessary to prepare ash from the coal or use specialized techniques for these analyses. However, these methods do determine the three or four elements not determined by the instrumental methods, INAA and PIXE/PIGE, on the coals. Hence, the combination of either INAA or PIXE/PIGE methods on the coal *and* the AAS/ISE/ICP group of methods would provide complete coverage of the 15 HAPs, assuming chlorine to be also determined by ISE.

The comparison of values obtained for the HAPs shown in Table 7 shows some good agreements among the different techniques for some HAPs (e.g., Cr, Co, Mn, Ni, Zn) in most instances, but rather large differences for different determinations of other trace elements. Even those techniques that were calibrated with respect to the same NIST standard reference samples (PIXE/PIGE, OES) show surprisingly large differences for elements such as Pb and F.

For fluorine, the determination by PIGE is always significantly higher than that by ICP/AES determinations. As discussed elsewhere (Godbeer and Swaine, 1987; Swaine, 1990; Wong and Robertson, 1992; Wong et al., 1992), the method of release of fluorine from the coal is thought to be critical for its determination. It has been demonstrated convincingly by Wong et al. (1992) that the pyrohydrolysis method provides better results than other methods of fluorine release.

Although good agreement is found for all methods of determination of Ba for six of the APCSB coals, determinations of Ba by ICP/AES for the Wyodak and Pocahontas coals are clearly significantly lower (by a factor of 10–20 times) compared with data from other determinations. This difference was noted by the analysts who performed the ICP/AES determination (Doughten and Gillison, 1990) and was attributed to possible differences in mode of occurrence of barium in the Wyodak and Pocahontas coals compared to the other six coals that resulted in greatly different behavior for the element during ashing or dissolution preparative techniques for the ICP/AES analysis.

Arsenic appears to be overestimated by OES techniques compared to INAA and PIXE methods, which by and large show reasonable agreement. However, the detection limit for arsenic by these other two techniques is much smaller than for OES and, hence, the imprecision of the OES determination is likely to be significantly larger for this technique. For other elements, e.g. Pb, the reasons for significant differences between determinations of the same element in the same coal by different techniques are not so easy to deduce.

2.6.3. Best analytical technique for HAP trace elements

From the above assessment of the available methods for HAP trace elements (HAPs) in coal, there does not appear to be one instrumental analytical technique that is applicable to all the HAP elements in fossil fuels. The reason for this is that the 15 HAPs elements differ significantly in abundance level, forms-of-occurrence, volatility during ashing, and chemical (e.g., electronegativity, position in periodic table) and geochemical (e.g., chalcophilicity, most stable valence state) properties. Of all techniques discussed here, the SSMS and GDMS techniques are least sensitive to such differences and can determine most HAPs, but their accuracy and precision are definitely inferior to other less widely applicable methods. PIXE/PIGE and INAA methods generally determine elements more precisely than SSMS or GDMS, but have less complete coverage of the HAPs, including such significant exceptions as mercury, cadmium, and beryllium that neither technique can adequately determine.

If the sample to be analyzed is an ash or slag, then analytical techniques such as ICP-AES, ICP-MS, AAS, etc., can readily determine most of the HAPs, as long as the sample can be dissolved completely. It appears that dissolution techniques are available that can liberate the elements quantitatively from ash and form a solution for analysis in almost all situations. However, as discussed above for Ba (Section 2.6.2), such dissolution techniques may not apply to all forms of an element.

However, it is clear that no one technique is sufficiently general or precise to be universally applicable to all HAP trace elements in all fossil fuel matrices. For complete coverage of all the HAPs in solid fossil fuel matrices, it is recommended that the combination of either PIXE/PIGE, INAA or polarized EDXRF directly on the solid fossil fuel and ICP/MS or ICP/AES, along with specialized AAS methods on digested coal or on solutions of the ash prepared by ashing at temperatures of not more than 500 °C would provide coverage of all HAP elements. IC or ISE methods would also have to be done to determine the two halogen elements. The chart shown in Table 8 indicates how the 15 HAPs are best covered by these methods. Similar findings have been indicated by Swaine (1990) and Palmer and Klizas (1997). It is recommended that a comprehensive determination of all HAPs be done by a combination of techniques that include methods than can be applied directly to the solid fossil fuel and methods that require ashing. The overlap of determinations for specific elements, e.g. Ba, Cr, Co, Mn, Zn, would then provide a useful

Table 8
Recommended methods of analysis for HAPs elements (based on data in Tables 1–6)[a]

Element	INAA	PIXE/PIGE (or pol. EDXRF)	ICP/AES	ICP/MS	AAS[b]
Sb	×			×	HAAS
As	×	×		×	HAAS
Ba	×	×	×		×
Be			×		×
Cd				×	GFAAS
Cl[c]					
Cr	×	×	×		×
Co	×	×	×		×
F[d]		×			
Pb		×	×	×	GFAAS
Mn	×	×	×		×
Hg	RNAA[e]				CVAAS
Ni	×	×	×		×
Se	×	×			HAAS
Th	×		×		
U	×			×	
Zn	×	×	×		×

[a] The conclusions presented in this table are based entirely on the referenced studies that gave rise to Tables 1–6. It is probable that additional elements could be determined adequately by a given technique, but were not included in the reference study.

[b] X=Standard FAAS techniques; other specialized methods indicated: HAAS—hydride AAS; GFAAS—graphite furnace AAS; CVAAS—cold vapor AAS.

[c] WDXRF, or ion chromatography, or ion selective electrode.

[d] Ion selective electrode or ion chromatography after pyrohydrolysis.

[e] INAA followed by radio-chemical separation.

cross-check on the validity of the ashing/dissolution methods.

3. Determination of coal mineralogies

The determination of the mineralogy of a coal provides valuable information about the inorganics in coal that cannot be obtained from a chemical analysis alone. In particular, geologists, interested in following the origin and depositional history of coal-forming peats and transformations of such peats into coal (coalification), can gain much information from the mineralogical and geochemical assemblages present in coal (e.g., Harvey and Ruch, 1986; Rimmer and Davis, 1986). In addition, researchers interested in how critical elements behave during utilization processes, such as combustion and cleaning, need to know what minerals are present in the coal, what their size distributions might be, and how such minerals control or interact with critical elements during utilization. In order to do this, the researcher needs to obtain as complete a mineralogical description of the coal as possible.

However, it is not nearly as easy to determine the mineralogy of coal as of other geological materials. Traditional petrographic methods such as optical mineralogy and X-ray diffraction are made considerably more difficult because of the intimate admixture of inorganic matter and macerals in coal. There is, therefore, significant interest in the development of new methods that will allow the mineral matter in a coal to be determined accurately and reliably. Furthermore, such methods should preferably be done without separation of the mineral matter from the coal so that association of minerals with macerals and of minerals with other minerals might also be determined.

In their review of analysis methods of mineral matter in coal, Jenkins and Walker (1978) list four distinct methods of determining the mineral matter in coal: (i) X-ray diffraction (XRD); (ii) infrared spectroscopy; (iii) chemical analysis (normative calculation); and (iv) optical and scanning electron microscopy (SEM) methods. Since that review was published, however, no new methods for determining mineral matter in coal have been developed and, except for SEM and, to a lesser extent, XRD techniques, there has been little in the way of new developments in these four methods. Consequently, in this section, the discussion will primarily center on developments in XRD and SEM methodology for the determination of mineral matter in coal. However, in order to be complete, the other methods will also be briefly described.

3.1. X-ray diffraction (XRD)

There has been much use of XRD for examination of the mineral matter in coals. The technique can be performed both qualitatively and, with significant care, reasonably quantitatively. Usually, to ensure best results, it is recommended (Jenkins and Walker, 1978) to work on low-temperature ash (LTA). Even then, there may be problems associated with mineral transformations and incomplete ashing (Pike et al., 1989) during the low-temperature ashing and with preferred orientation of clay minerals (Renton, 1986). Experimental and preparative procedures for obtaining semi-quantitative to quantitative determinations of major minerals in LTA of coal using X-ray powder diffractometry are well described in the literature (Rao and Gluskoter, 1973; Klug and Alexander, 1974; Jenkins and Walker, 1978; Russell and Rimmer, 1979; Renton, 1986; Pike et al., 1989; Spears and Martinez-Tarazona, 1993). Generally, such determinations are made based on a calibration procedure that involves use of an internal standard, such as calcium fluoride, CaF_2, and comparison of the height or area ratios of diffraction peaks from minerals in the coal relative to those of CaF_2 against a calibration curve based on the same peak-height or peak-area ratios for mixtures of CaF_2 and specific minerals (e.g., quartz, pyrite, kaolinite, etc.) of known composition. Under optimum circumstances, errors of estimation based on conventional XRD of between ±5% and 10% can be achieved, although individual minerals may be estimated more precisely using specialized methods. Such methods have included the estimation of pyrite in Spanish coals (Querol et al., 1993) and of quartz in Indian coals (Acharya, 1992). Although such conventional powder diffraction methods are still widely used, the more powerful Rietveld method is becoming more commonplace for the analysis of phases in LTA (Bellotto and Cristiani, 1991) and in HTA (Winburn et al., 2000), and of minerals in fossil fuels (Mandile and Hutton, 1995; Dale et al., 1997).

It is of course possible to perform XRD directly on the coal, and, as Wertz (1990) and others have shown, the XRD pattern reflects both the crystalline components and the amorphous carbon forms present in the coal. The latter give rise to typically three very broad peaks of diminishing intensity and increasing width at positions of approximately 25, 40, and 75–80 $°2\theta$ using copper K_α radiation. Superimposed on this undulating background are much sharper peaks arising from the mineral matter associated with the coal. This undulating background has to be subtracted in order to quantify the minerals based on peak heights or areas (e.g., Wertz, 1990). Although XRD on the coal is significantly more rapid by avoiding the LTA step, the errors due to the undulating background and weaker diffraction-peak intensities make it significantly less precise than working on the LTA. More recently, Mandile and Hutton (1995) have described the development of Rietveld XRD analysis methods for improved determination of mineral and organic phases in organic-rich rocks, including coals. Dale et al. (1997) have also described a similar Rietveld-based method for XRD analysis of minerals in coal. Such methods hold significant promise for achieving a reasonably quantitative and precise mineralogical analysis directly on the coal without the need for ashing.

High-temperature ash or coal combustion byproducts (fly-ash, bottom ash, etc.) can also be investigated by XRD techniques; however, the non-crystalline or glass phases formed during combustion do not contribute to the X-ray diffraction pattern, except as broad, low-intensity peaks in the background. Such components can be estimated approximately as the remaining quantity once all the percentage estimates of individual crystalline phases have been summed. Or alternatively, more sophisticated analysis can be attempted, such as that described by Behr-Andres et al. (1993), which involves both XRD and SEM/EDX methods. Again, Rietvald XRD techniques are being applied to such analyses (Dale et al., 1997; Winburn et al., 2000) and appear to offer superior precision than conventional XRD techniques.

3.2. Infra-red spectroscopy

Jenkins and Walker (1978) considered infrared (IR) spectroscopy to be the most promising new method for determinations of major minerals in coal. However, the technique has not achieved this promise and appears to be rarely used for this purpose at the current time. Infrared spectroscopic methods can be carried out directly on the coal, but there is significant overlap of certain bands arising from the organic functional groups in macerals with those arising from the minerals in coal, which seriously complicates the analysis of the inorganic species. Therefore, for the most precise work, the infrared spectroscopic analysis is normally carried out on LTA (Painter et al., 1978a).

The quantitative determination of minerals in coal using conventional IR techniques was first demonstrated by Estep et al. (1968). Subsequently Painter et al. (1978a,b, 1981) further developed the method and also applied the more powerful technique of Fourier transform infrared (FTIR) spectroscopy to measure the spectrum of LTA. By means of least-squares fitting and other spectral analysis methods, reasonably quantitative estimates of the six or seven major minerals present in a coal or LTA can be obtained from the FTIR spectrum (Jenkins and Walker, 1978; Painter et al., 1978b, 1981). However, since the establishment and demonstration of the method in the early 1980s, there do not appear to be any further significant developments of infrared spectroscopy for quantifying coal mineralogies and few examples of its application.

Although not used to quantify minerals in coal or ash, infrared emission spectroscopy has been developed by Vassallo et al. (1992) to study minerals in coal at temperatures similar to those encountered during coal combustion. Such studies are very useful for understanding mineral transformations and deposit formation during pulverized coal combustion. One major advantage that such infrared studies have over XRD studies is that the infrared technique is capable of analyzing amorphous materials that are not amenable to analysis by XRD techniques and hence the glassy phases formed during combustion can be directly investigated.

3.3. Normative calculation

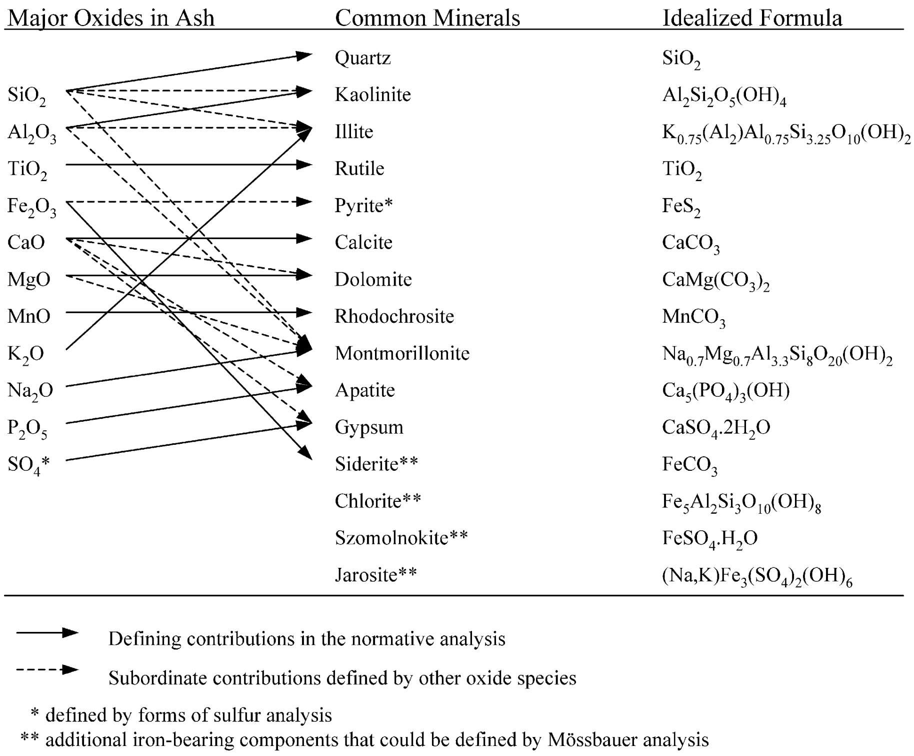
There have been a number of proposed methods to infer coal mineralogies based on variations and extensions of the well-established procedure in igneous petrology of normative analysis, in which the mineralogy of an igneous rock is estimated from its chemical analysis. Such methods, devised initially by Cross et al. (1902), have merit for specific igneous rock types in which a relatively small set of well-defined mineral species of usually predictable composition are formed under conditions at or close to chemical equilibrium. In normative methods, the mineralogy of a rock or coal is calculated according to a rigid sequence of rules that assigns specific chemical oxides or fractions of such oxides to minerals that are assumed to exist in the coal. For example, a composition can be assumed for illite, say $K_{0.75}(Al_2)Al_{0.75}Si_{3.25}O_{10}(OH)_2$; hence, by assigning all the K_2O from the chemical analysis to illite, the molar contributions of Al_2O_3 and SiO_2 to illite can also be estimated. Then any remaining Al_2O_3 can be assigned to kaolinite according to the formula, $Al_2Si_2O_5(OH)_4$, and any remaining SiO_2, after its contributions to both illite and kaolinite have been subtracted, would be attributed to the mineral quartz, SiO_2. A hypothetical mineralogical analysis can be calculated in this manner from the major oxides in an ash analysis; however, it incorporates many assumptions about the chemical compositions of the minerals.

A possible normative scheme for coal of bituminous rank is shown in Fig. 3. The number of minerals that can be estimated is limited by the amount of information that is used in the normative scheme. A basic set of data consisting of the relative concentrations of the 10 major oxides in coal ash and the forms of sulfur analysis (D 2492, ASTM, 2000) for pyritic and sulfate sulfur permits 12 minerals to be estimated in the normative scheme. Note that the relative fraction of each mineral is effectively defined by one piece of analytical data from the chemical analysis or forms of sulfur analysis. Information from other techniques could be added. For instance, the distribution of iron among various iron bearing minerals as determined by Mössbauer spectroscopy would permit as many as another three minerals to be included in the scheme. Examples of published normative calculations of mineral matter in coals include Reidenouer et al. (1967), Bland et al. (1976), Lee et al. (1978), and Kizil'shtein et al. (1995).

The main problem with normative calculation for determining the mineralogy of coals is that it is based on an idealized set of minerals. In reality, many of the minerals in coal, especially the clay minerals, have variable and wide ranging compositions that cannot be represented by simplified formulae such as those shown in Fig. 3 for illite and montmorillonite. Furthermore, many elements present in low rank coals (lignites, subbituminous coals, brown coals, etc.) do not exist as true minerals but rather are bound to the maceral matrix by means of oxygen bearing functional groups (e.g., carboxyl and phenol functionalities). Such non-mineral occurrences are clearly outside the realm of normative calculation. Normative analysis would appear to be best suited to higher rank coals and for comparison and discrimination of coals of similar geological origin, such as might be found in problems of seam recognition (Bland et al., 1976) and paleoenvironmental reconstruction (Reidenouer et al., 1967).

3.4. Computer-controlled scanning electron microscopy (CCSEM)

Scanning electron microscopy (SEM) has often been used qualitatively and occasionally semi-quanti-



Common Minerals	Idealized Formula
Quartz	SiO_2
Kaolinite	$Al_2Si_2O_5(OH)_4$
Illite	$K_{0.75}(Al_2)Al_{0.75}Si_{3.25}O_{10}(OH)_2$
Rutile	TiO_2
Pyrite*	FeS_2
Calcite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$
Rhodochrosite	$MnCO_3$
Montmorillonite	$Na_{0.7}Mg_{0.7}Al_{3.3}Si_8O_{20}(OH)_2$
Apatite	$Ca_5(PO_4)_3(OH)$
Gypsum	$CaSO_4.2H_2O$
Siderite**	$FeCO_3$
Chlorite**	$Fe_5Al_2Si_3O_{10}(OH)_8$
Szomolnokite**	$FeSO_4.H_2O$
Jarosite**	$(Na,K)Fe_3(SO_4)_2(OH)_6$

* defined by forms of sulfur analysis

** additional iron-bearing components that could be defined by Mössbauer analysis

Fig. 3. A normative scheme for bituminous coal (after Lee et al., 1978).

tatively to examine mineral matter in coal. The great potential of SEM for recognizing mineral occurrences and semi-quantitatively determining their relative abundances in coal, even for many trace elements, can be clearly seen in the detailed studies carried out by Finkelman (1981, 1988). However, in addition, it is equally recognized that such studies, if they are to be quantitative, cannot be done by manual techniques because of the time needed to evaluate each mineral grain and the probable lack of objectivity of the operator. For these reasons, faster SEM-based methods, in which the judgment of the operator has been essentially eliminated, have been developed for the quantitative determination of the mineral matter in coal. To eliminate the operator, the SEM is placed under computer control; hence, the various SEM-based methods that have been developed for quantifying coal mineralogy can be grouped under the heading of computer-controlled scanning electron microscopy (CCSEM). Such techniques have also been referred to as SEM automated image analysis (SEM-AIA).

In comparison to bulk XRD and FTIR methods of coal mineral analysis, CCSEM methods are more informative, not only because they supply information on a larger number of minerals, but also because they supply information on particle-size distributions (psd) of individual mineral species. Such psd information is of relevance to our understanding and modeling (e.g., Charon et al., 1990; Sarofim and Helble, 1994) of the behavior of mineral matter during pulverized coal combustion. In addition, CCSEM methods are capable of supplying information on mineral/maceral and mineral/mineral associations; such information is also highly relevant for modeling pulverized coal combustion and the formation of ash and slag deposits, as well as other coal utilization problems, notably coal cleaning.

3.4.1. Development of CCSEM techniques for coal mineralogy

The first successful attempt to develop a CCSEM technique for coal mineralogy was the work by E.W.

White and co-workers (Lebiedzik et al., 1973) at the Pennsylvania State University. This innovative work was the benchmark for most of the subsequent developments in CCSEM applied to coal mineralogy through to the current day. The technique developed by White and co-workers incorporated four concepts: (i) the method was carried out on the polished surface of an epoxy-mounted, pulverized and homogenized coal sample; (ii) it located mineral grains in the coal and determined their cross-sectional area in the polished section of coal on the basis of their contrast in the back-scattered electron image; (iii) it determined 7 major inorganic elements (Al, Si, S, K, Ca, Ti, Fe) in mineral grains by energy-dispersive X-ray (EDX) analysis and used the relative X-ray intensities of these elements to identify individual mineral grains; and (iv) compositional and size data from as many as 2000 mineral particles were integrated to determine the coal mineralogy. These four steps are present in most current CCSEM methods.

Based in part on the work at Penn State and in part on other innovations in computer-control of SEMs, R.J. Lee and co-workers at US Steel Corporation then developed an SEM-AIA system to address a number of different applications within the steel industry (Lee and Kelly, 1980), including the determination of coal mineral matter. Their coal mineral analysis method is described in preliminary form (Lee et al., 1978) and a revised final version (Huggins et al., 1980, 1982). The major difference between the Penn State and US Steel methods was that the latter method incorporated the measurement of minerals for a specific size-range only at an optimum magnification. By performing such measurements at different magnifications, a much more robust and quantitative analysis was achieved than by measuring mineral grains of all sizes at a single magnification. Other minor improvements, such as extending the EDX analysis to include 4 more elements (Na, Mg, P, Cl) and thereby permit more minerals to be recognized, were also incorporated. Further, it was recognized that the coal minerals analysis by CCSEM had some ambiguities with respect to the iron minerals, especially for oxidized coals. This deficiency was rectified by combining the CCSEM information with data from ^{57}Fe Mössbauer spectroscopy (Huggins and Huffman, 1979) on the distribution of iron among the various iron-bearing minerals in the coal (Huggins et al., 1982). Such combined CCSEM and Mössbauer methods were also extended to low-rank coals (Huffman and Huggins, 1984). It was recognized that the CCSEM coal minerals analysis only determined the discrete mineral matter in such coals; the highly dispersed inorganics (e.g., Ca and Na) in the coal were generally omitted from the analysis (Huffman and Huggins, 1984; Straszheim et al., 1988).

Similar CCSEM instruments for coal minerals analysis have subsequently been described by Straszheim et al. (1986), Birk (1989), Jones et al. (1992), Yu et al. (1994) and Wigley and Williamson (1994, 1998). Although the general operation of these instruments is quite similar, differences exist in detector response to the 11 or so elements included in the analysis because of variation in detector type (thick window vs. thin window vs. windowless). As a result, each instrument has a somewhat different scheme for defining different minerals from the EDX analysis. In addition, older versions of CCSEM would use a single spot analysis located at the center of the mineral particle. More recent instruments can now incorporate more sophisticated algorithms for obtaining a more representative analysis by stepping the beam over the area of the particle (e.g., Wigley and Williamson, 1998). For these reasons, it was recognized that the inter-laboratory variation of such instruments should be investigated and two such studies have been reported (Casuccio et al., 1990; Galbreath et al., 1996). Both of these studies consisted of a comparison of the data obtained by different CCSEM instruments on the same coals. Although much of the variation within a single laboratory's repeat determinations could be accounted for by counting statistics, significant variation was found among the data from the different groups that could not be attributed simply to counting statistic errors alone. Such differences were largely attributable to differences in the definitions of minerals used by the different groups and the difficulty of distinguishing kaolinite from the background. Also, the bias in the measurement of pyrite, previously noted by Huggins et al. (1980) and Straszheim et al. (1986), was confirmed by Galbreath et al. (1996). An independent review of CCSEM methods, undertaken by Skorupska and Carpenter (1993), concluded that CCSEM techniques have much promise, but that standardization of aspects of the technique, notably in sample preparation and mineral classification, remains to be achieved.

There have also been a number of developed SEM-based methods that are somewhat further removed in concept from the CCSEM method for determining coal mineralogies, but have been or can be used for similar purposes. Such methods include that described by Moza and Austin (1983) for analysis of individual coal particles, the QEM*SEM method developed at CSIRO (Gottlieb et al., 1992), and the SEM Point Count (SEM-PC) method developed at EERC (Jones et al., 1992; Folkedahl et al., 1994) that is similar to the standard petrographic technique of point counting. Most of these methods are aimed at understanding combustion behavior of coal mineral matter.

A novel instrument, similar in concept to the CCSEM method, but combining automated image analysis with an electron microprobe rather than an SEM, has been described by Shirazi et al. (1994). As a result of the much higher generation of X-rays produced from samples under the electron beam in a microprobe compared to that in an SEM, the atomic number contrast of different minerals is significantly better in the microprobe. For example, it is possible to discriminate between marcasite and pyrite, despite the fact that they have identical average atomic number, because of the difference in specific gravity of the two minerals that results in them exhibiting discernibly different contrast levels in the back-scattered electron image.

3.4.2. CCSEM techniques for determination of mineral association

It is increasingly recognized that how minerals are associated with the macerals and with other minerals in coal particles is an important concept in understanding their behavior during coal preparation, coal combustion and other utilization processes. Mineral grains in pulverized coal run the gamut from being completely liberated from the macerals to being completely enclosed by the macerals and all degrees in between. Such different occurrences of a particular mineral will behave differently in pulverized coal combustion because of their association or lack of association with the carbonaceous material. In addition, the minerals are not distributed randomly in coal. Some minerals tend to occur as isolated grains in the coal, whereas other minerals occur together in mineral-rich inclusions within the carbonaceous matrix or in mineral partings. The association of one mineral type with another can significantly influence how they behave during coal combustion. For example, an intimate association of a basic mineral grain and a clay mineral grain will result in significant partial melting during combustion, whereas a similar association of two clay minerals or two basic minerals will not. Quantitative measures of both mineral/maceral association and mineral/mineral association would contribute greatly to our understanding and modeling of coal combustion processes and related deposit formation, the liberation of mineral matter in coal preparation, and other coal utilization problems.

CCSEM techniques for addressing the problem of the determination of mineral/maceral association were first described by Straszheim and Markuszewski (1990a,b, 1992). Their method involved measurement of both the coal particles and mineral grains in cross-section using a two-step back-scattered electron image threshold to delineate firstly the coal particles from the mounting medium and secondly the mineral grains from both the coal particles and the mounting medium. As a result, the amount and nature of the mineral matter associated with each mineral grain was determined. Data on the degree of association of mineral matter and macerals were then derived and compared to results from float-sink and flotation tests. The measurement of association was successful for understanding float-sink test results, but less so for the flotation data.

Using a similar experimental strategy to that employed by Straszheim and Markuszewski (1992), Yu et al. (1994), Wigley et al. (1997), and Wigley and Williamson (1998) also determined mineral/maceral association and applied the results to combustion problems. The same investigators also attempted to determine mineral/mineral associations (Yu et al., 1994; Wigley and Williamson, 1998) and were able to make some qualitative conclusions regarding the relative mineral association of various major minerals. For example, Wigley and Williamson (1998) indicated that the CCSEM method of measuring association in cross-section "strongly underestimates" mineral–mineral association.

3.4.3. Mineral matter determinations of the Argonne premium coal samples

Some results have been presented on determinations of specific minerals in the Argonne premium coal samples. Wertz (1990) and Harvey (2001) have presented some XRD results for pyrite, calcite and quartz, while Shah et al. (1990) have presented CCSEM data for the major discrete minerals in six of the eight coals. In addition, these last authors also presented Mössbauer data for iron-bearing minerals in all eight APCSB coals, from which mineralogical data for pyrite have been calculated. These mineral determinations are summarized in Table 9. As shown in Table 9 and also Fig. 4, the agreement among the various methods for wt.% pyrite in coal is satisfactory, except perhaps for the Illinois #6 coal. Agreement for quartz between the XRD and CCSEM methods, however, is less satisfactory as large differences are seen for the Upper Freeport (UF), Illinois #6 (IL), and Utah (UT) APCSB coals. But when total silicates (quartz+clays+mixed silicates) are compared between the two methods, a better agreement is obtained. It is probable then that some of the quartz in the IL and UT coals is not being identified as such in the CCSEM method because it is associated with the clay minerals and is contributing significantly to the mixed silicates category. Fig. 5 compares the distribution of the Si/Al ratio in aluminosilicate-rich particles for the IL and WV coals. As can be seen from this figure, the IL coal has a significant tail from quartz into the mixed region, suggesting that quartz in this coal may indeed have a significant association with clay minerals. More specific resolution of mixed mineral classes in the CCSEM method may yet be possible to resolve such differences.

3.5. *Current status of coal mineralogy determinations*

There appear to be only two methods that are currently in use for determining mineral matter in coal: viz., XRD and CCSEM methods. Both of these methods have their merits and drawbacks. XRD methods are limited to supplying information on no more than about the six most abundant minerals in coal, and, for best results, they should be performed on low-temperature ash, although the Rietveld method of analysis appears capable of obtaining a reasonably quantitative analysis directly on the coal. CCSEM methods, on the other hand, are best performed on polished sections of pulverized and homogenized coal, and will supply information on significantly more minerals than XRD methods. CCSEM methods

Table 9
Comparison of mineralogical determinations on APCSB coals

(a) Data from APCS Handbook (Harvey, 2001)

Minerals	UF	WY	IL	PITT	POC	UT	WV	ND
Wt.% of LTA	15.3	8.7	18.1	10.9	5.5	5.3	21.6	8.7
Wt.% of coal								
Quartz	1.5	2.0	3.4	1.7	0.3	0.8	2.6	0.6
Pyrite	3.4	0.1	5.5	2.4	0.1	0.5	0.3	0.3
Calcite	1.0	0.4	1.9	0.5	1.7	1.3	0.3	1.7
Clays (by diff.)	9.4	6.2	7.3	6.3	3.4	2.7	18.4	6.1

(b) Data from X-ray diffraction (modified from Table 4, Wertz, 1990)

Minerals	UF	WY	IL	PITT	POC	UT	WV	ND
Wt.% of coal								
Quartz	1.5	0.6	3.3	1.6	0.3	1.0	2.3	0.3
Pyrite	3.5	0.1	5.0	2.5	0.1	0.4	0.3	0.2
Calcite	3.4	n.d.	1.7	0.5	0.9	1.1	n.d.	n.d

(c) Data from CCSEM (modified from Table 2, Shah et al., 1990)[a]

Minerals	UF	IL	PITT	POC	UT	WV
Wt.% coal basis						
Quartz	0.8	1.6	1.3	0.22	0.21	2.2
Kaolinite	1.4	0.6	0.9	0.55	0.50	3.2
Illite	5.4	2.3	2.1	0.45	1.9	10.4
K-feldspar	–	<0.1	–	<0.05	–	–
Chlorite	0.15	–	–	0.22	–	–
Montmorillonite	–	<0.1	<0.1	<0.05	0.05	–
Misc. silicates	2.6	4.2	2.8	1.9	2.2	5.4
Pyrite	3.8	4.9	2.7	0.22	0.16	0.2
Misc. sulf.	0.3	0.2	0.1	0.05	<0.05	<0.2
Siderite	–	<0.1	–	<0.05	<0.05	<0.2
Calcite	–	1.5	0.1	0.40	0.10	–
Ankerite	–	–	–	<0.05	–	–
Misc. carb.	0.15	0.2	<0.1	0.3	0.05	<0.2
Ti-rich	–	0.2	0.1	<0.05	–	0.2
Al-rich	–	–	–	0.15	–	–
Other	0.6	1.1	0.8	1.1	0.15	0.2

(d) Mössbauer data (modified from Table 4, Shah et al., 1990)

	UF	WY	IL	PITT	POC	UT	WV	ND
%Fe in								
Pyrite	94	74	97	99	20	72	53	100
Clay	6		3	1	33		32	
Siderite		26			46	28	15	
Wt.% pyritic S[b]	1.60	0.13	2.14	1.26	0.11	0.25	0.20	0.22
Wt.% pyrite (coal)[c]	3.00	0.24	4.01	2.36	0.21	0.47	0.37	0.41

[a] Calculated from wt.% of mineral matter×wt.% LTA (Table 8).

[b] Wt.% coal basis, after method described by Huggins and Huffman (1979).

[c] Wt.% coal basis, calculated from value for pyritic sulfur.

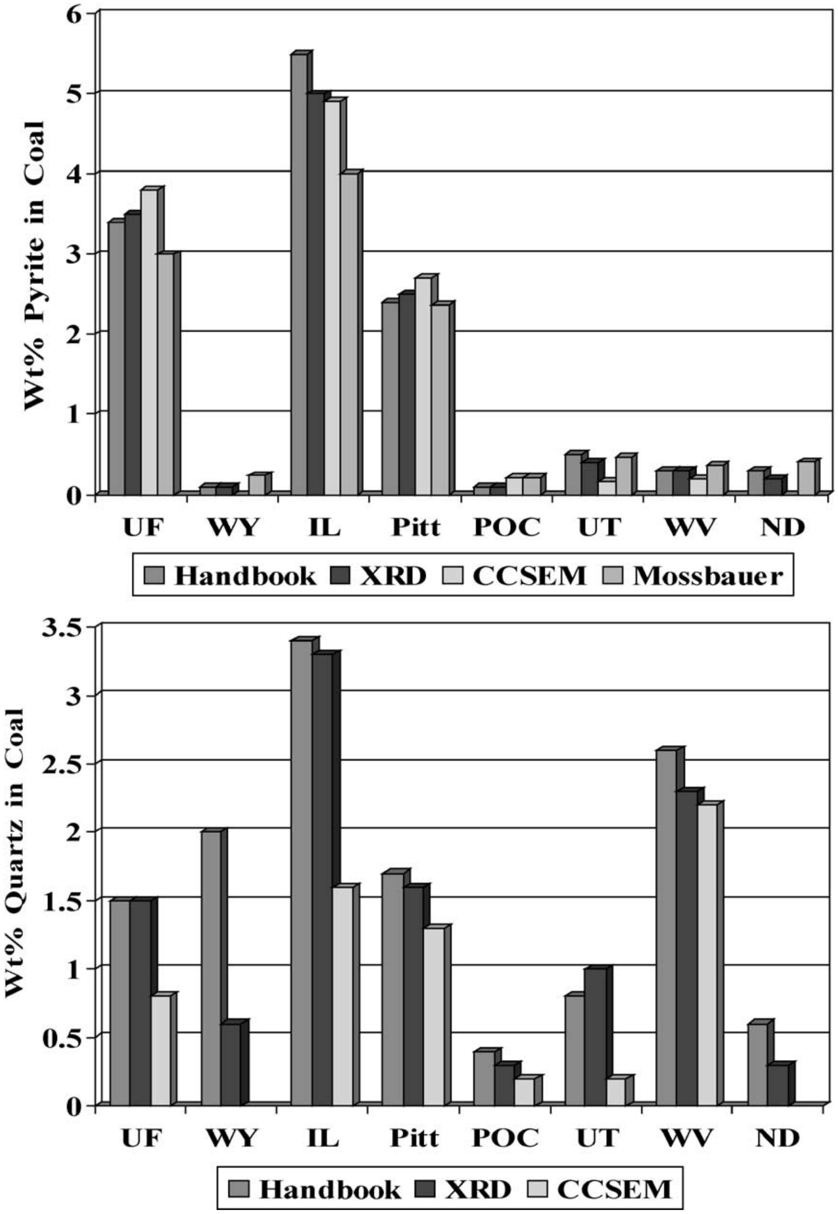


Fig. 4. Comparison of determinations of wt.% pyrite and quartz in Argonne premium coal samples as determined by X-ray diffraction, CCSEM, and Mössbauer spectroscopy.

can, in theory, also supply information about mineral–maceral and mineral–mineral association. However, mineral–mineral association can also mask contributions to individual mineral categories in the CCSEM mineralogical analysis by assigning minerals to mixed categories. Neither XRD nor CCSEM methods can provide information on dispersed inorganics in macerals, although such measurements should be possible in the CCSEM, especially one equipped with a windowless or ultrathin window X-ray detector or in a hybrid instrument such as that described by Shirazi et al. (1994).

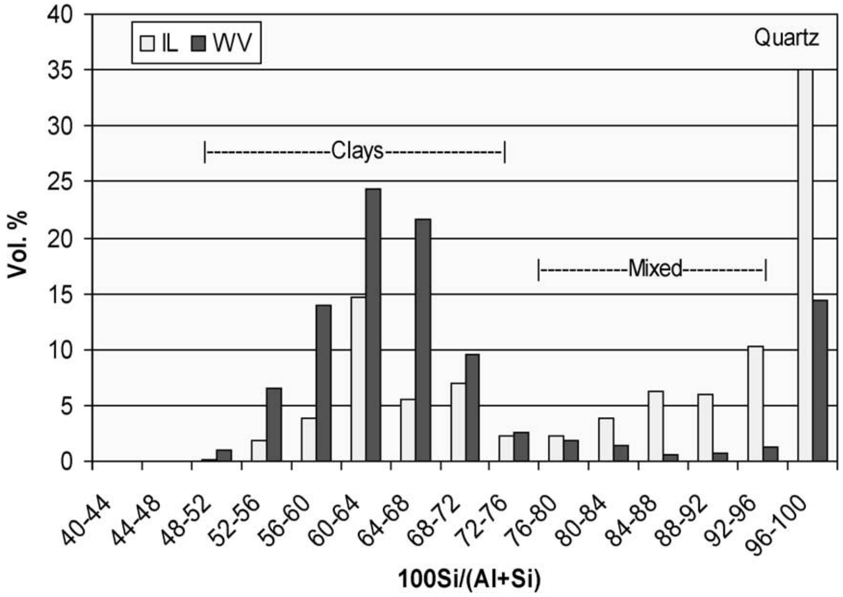


Fig. 5. Distribution of Si/(Si+Al) ratio in aluminosilicate particles in the IL and WV APCSB coals. Note the significant tail away from quartz for the IL coal in the mixed region, suggesting that there is a significant association of quartz and clays.

On a conceptual basis, it would appear that the CCSEM method for coal minerals analysis could yet be enhanced to resolve these deficiencies and at the same time provide a more robust analysis of coal mineral matter and its associations in coal. This would be a very worthwhile PhD project for an enterprising student, as a useful, practical measurement of coal mineral matter, its mineral–maceral associations and mineral–mineral associations would be invaluable for resolving many complex questions in coal combustion and cleaning.

4. Determination of modes of occurrence of trace elements

4.1. Introduction

Concentration is not the only factor of importance that needs to be considered in assessments of the behavior of trace elements in coal utilization and of related environmental concerns. A second factor of equal and, in some situations, perhaps, of more importance that should also be included in such assessments is information on *how* the trace elements occur in coal or ash. The mode or form of occurrence (i.e., whether the element forms a specific mineral, whether it is dispersed within a particular host mineral or in the coal macerals, with which fraction of the coal the element is associated, in which oxidation state the element occurs in the coal, etc.) may control, to a large extent, the potential hazard posed by the element to human health and the environment. To date, such information has been largely ignored in proposed environmental regulation regarding trace elements.

Various indirect methods have been tried for the determination of trace-element modes of occurrence in coal. The concept of organic affinities, defined by how a trace element partitions among float and sink gravity fractions, has been used to classify trace element occurrences in coal (Zubovic, 1966; Gluskoter et al., 1977) with some success. More recent variations on these procedures have been presented by Spears and Martinez-Tarazona (1993) and Querol et al. (2001). However, questions regarding the association of the element (e.g., whether an element is present in solid solution in a major mineral or forms its own mineral) are usually not answered by this indirect method.

More recently, attention has shifted away from float-sink methods to leaching methods as the prime indirect method of determining elemental modes of occurrence. However, as pointed out by Davidson (2000), there is no one preferred sequential leaching scheme, but rather a large variation in practice, that makes it difficult to compare data from different leaching methods, even on the same coal. Further, leaching schemes are based on an *assumed* limited set of elemental occurrences. There is no provision in such tests for unanticipated occurrences. Consequently, there remains considerable uncertainty regarding the validity of the data obtained in such tests, unless they are verified by direct observational methods.

Various electron and ion probe techniques have been used to examine trace element modes of occurrence directly on coal. Finkelman and Stanton (1978) and Finkelman (1981, 1982, 1988) used scanning electron microscopic observations and micro-X-ray diffraction techniques to investigate directly the occurrence and association of many trace elements in the Upper Freeport coal and other coals. Similar studies have also been made using the electron microprobe, the proton microprobe, the synchrotron X-ray microscope, the laser microprobe mass analyzer, and various types of ion microprobes. However, such observational microscopic techniques are very time-consuming, even for semi-quantitative information, and tend to favor the occurrences of trace elements in discrete mineral forms rather than the dispersed occurrences of the element in macerals in the coal.

A quite different direct approach is to establish spectral “fingerprints” for various standard occurrences of an element and then employ the same spectroscopic technique to measure the spectra from the element in a coal or coal fraction. Hence, by comparing the spectrum from the coal with spectra in the database of standards and employing spectra deconvolution or simulation methods where needed, it is possible to determine the major modes of occurrence of an element in a particular coal. One spectroscopic technique that has been extensively employed for investigating the forms of occurrence of trace elements in coal and ash is X-ray absorption fine structure (XAFS) spectroscopy.

Either of the direct microscopic or spectroscopic methods or both can be combined with indirect methods of determining modes of occurrence, such as float-sink methods (Huggins et al., 1997, 2000a) or sequential leaching methods (Kolker et al., 2000a; Huggins et al., 2000b) and the net result is better understanding of both the modes of occurrence of the elements and of the assumptions inherent in the indirect methods.

4.2. Specific methods for forms of occurrence determination

4.2.1. Indirect methods

The concept of the organic affinity of an element is so basic and experimentally simple that it is still of value today (e.g., Querol et al., 2001). Organic affinities are estimated from the partitioning of trace elements among different float/sink fractions. By performing float/sink tests at different specific gravities and then determining the trace element contents in the different fractions, the organic affinity of the element can be determined. The higher the organic affinity the more the element reports to light specific gravity fractions, and hence, the more it is associated with the organic fraction of the coal. This method, originally proposed by Zubovic (1966), was exhaustively used in the major trace element study performed by Gluskoter et al. (1977). These classic studies showed that the organic affinity of many elements varied significantly from coal to coal.

The major problem with determinations of the effective organic affinity is that there is no compelling reason to expect a specific form of an element to be present in or absent from a particular float-sink fraction. This is because the separation is based on the specific gravity of coal particles, which normally consist of varying amounts of macerals and minerals and only very rarely, if at all, of a single coal component, either mineral or maceral. As a result, the efficiency of float/sink processes with respect to a given trace element *in a specific form* may vary greatly from coal to coal, merely as a consequence of how the host mineral or maceral distributes between the float/sink fractions. These different pieces of information cannot be separated. Hence, different values of organic affinity for a given element among different coals have little or no significance. In addition, the knowledge that the effective organic affinity for a trace element in a coal is low still does not provide any insight into whether the trace element is dispersed in a major mineral or forms its own mineral.

Despite these limitations, however, the concept of organic affinity may still be a useful parameter in the absence of other information. Furthermore, the more float/sink fractions into which the coal is divided, the better will be the insight obtained from such analysis. For example, Querol et al. (2001), separate coals into more than 10 individual fractions by combining heavy liquid separations with centrifugation and fine grinding and for many coals obtain a light fraction with less than 1% ash and a heavy fraction with more than 80% sulfide minerals.

Leaching methods have a major advantage over float-sink methods in that specific elemental forms are anticipated to be either present or absent in different fractions depending on their solubility behavior in the various reagents used for the different leaching stages. A number of sequential leaching methods have also been proposed for understanding elemental modes of occurrence and basically each laboratory has their own leaching scheme. Davidson (2000) compares methods and data from sequential leaching schemes developed at the US Geological Survey (Finkelman et al., 1990; Palmer et al., 1993), at the University of Sheffield, UK (Cavender and Spears, 1995) and at CSIRO, Lucas Heights, Australia. These three schemes are compared and contrasted in Fig. 6. In all three schemes, the idea is to leach specific groups of inorganics or minerals progressively from the coal. After each stage of the leaching scheme, a multi-element chemical analysis is performed on the residue and/or the leachate to

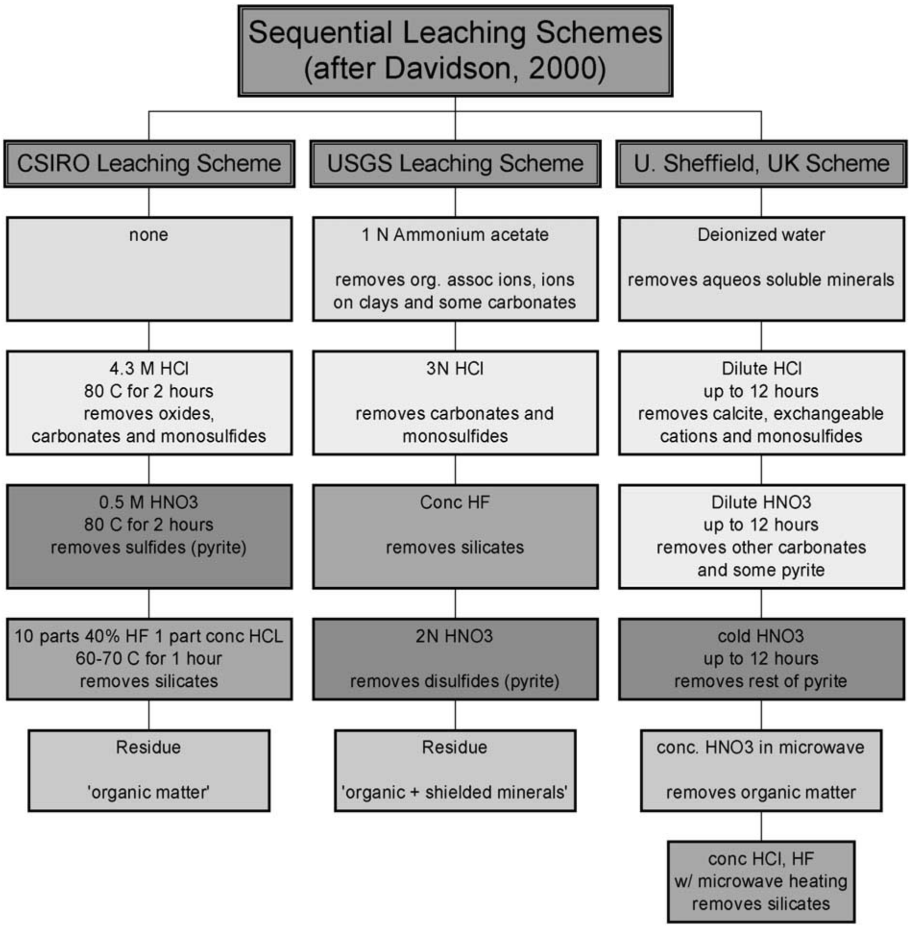


Fig. 6. Comparison of sequential leaching schemes used in the IEA speciation study (after Davidson, 2000).

determine the amounts of trace elements removed by that particular leaching reagent. The different fractions of an element removed by the various leaching reagents are then assumed to have occurred in the coal in different forms, as indicated in Fig. 6.

The main problem with sequential leaching protocols is that the classification is principally based on the *expectation* of how certain minerals will behave in a suite of increasingly stronger reagents and there is little accommodation of any variation in leaching behavior due to variations in composition, grain-size, association, etc. For example, "carbonate minerals" are expected to dissolve in HCl, but depending on the strength of the solution, the solution temperature, the grain-sizes of the carbonate minerals, and the time of exposure of the coal to the leachant, such procedures may be effective for calcite, but less effective or even ineffective for other, less-common carbonates, such as siderite, magnesite, rhodochroisite, or dolomite. Querol et al. (2001) list a number of other specific deficiencies of leaching methods. It must also be re-emphasized that leaching protocols will never identify an unusual or unexpected elemental occurrence.

Both sequential leaching and float/sink separations have difficulty dealing with fine mineral matter that is highly dispersed and encapsulated in macerals by organic matter. For float/sink methods, the highly dispersed nature of such fine mineral matter generally causes them to be associated with the lightest specific-gravity fractions; consequently, such inorganic components are typically referred to as "organically associated". For leaching methods, the encapsulation of inorganics by organic matter can make them impregnable to attack by the leaching agents and hence such inorganics are always incorrectly assigned. There are ways to avoid this complication. For example, the leaching protocol developed by Cavender and Spears (1995) includes an organic digestion step (Fig. 6), in which the inorganics associated with the organic matter are liberated. However, the position of this step so late in their leaching scheme must be questioned, as it really does not provide much extra information. It would seem that such a step ought to come first in any sequential leaching scheme, but the problem then is that that the reagent used to chemically oxidize the organic matter is so strong that it will consume much of the mineral matter as well. An alternative approach might be to conduct sequential leaching schemes on low-temperature ash, in which all the encapsulating organic matter has been oxidized away. Such an approach does not appear to have been explored significantly.

In order to establish trace element occurrences better, various approaches have been attempted that combine two indirect methods. For example, Finkelman et al. (1990) employed sequential leaching complemented by data on element volatility from sequential combustion (ashing) tests at different temperatures. Querol et al. (2001) used results from both sequential leaching and float-sink separation. However, the results obtained by these indirect techniques, even when combined, still often remain inconclusive and they need to be complemented and confirmed by data from more direct methods.

4.2.2. Direct microscopic methods

A scanning electron microscope (SEM), equipped with an energy-dispersive X-ray (EDX) detector and a back-scattered electron (BSE) detector, can be used to determine trace element occurrences in polished or fracture surfaces of coal specimens. The reason why the SEM is capable of finding many trace element occurrences is because the brightness of the back-scattered electron image (BSEI) is determined in large part by the average atomic number of the material under the electron beam. As a result, phases rich in heavy trace elements appear much brighter than normal silicate and sulfide minerals in the coal and can be readily located for standard EDX analysis in the SEM.

The main advantage of the SEM-EDX technique is that information is obtained on the chemical association of the trace element, from which the mineral occurrence can often be deduced. On occasion, the individual mineral grain containing the trace element can sometimes be removed and subjected to micro-X-ray diffraction to confirm its mineralogical identity. Although significant information regarding the forms of occurrence of many trace elements has been obtained by this method (Finkelman and Stanton, 1978; Finkelman, 1981, 1982, 1988; Kolker et al., 2000a), even to the point of semi-quantitative estimates of different forms-of-occurrence for given elements, the method is very time-consuming and demanding of the microscopist.

Although SEM-EDX is an excellent method of locating and measuring *discrete* trace-element mineral occurrences, in which the trace element is a major component, it is not nearly as powerful for determining trace element occurrences that are *dispersed* at low abundance levels, either in major minerals or in macerals in the coal. In addition, the lower the atomic number of the trace element, the more difficult it becomes to locate, regardless of whether it is present in discrete or dispersed form. Hence, this technique is likely to be biased towards the discrete and exotic forms of occurrence of heavy trace elements, unless the investigator is extremely systematic in his sampling.

Electron microprobe (Minkin et al., 1979; Ruppert et al., 1992) and synchrotron-based X-ray microscopic methods (White et al., 1989; Jones and Gordon, 1989) are similar in scope to SEM methods, but have significantly lower detection limits for most elements compared to SEM-EDX methods and are, therefore, more capable of detecting the dispersed occurrences of trace elements in minerals. In particular, such methods have been used to examine trace element occurrences associated with pyrite (White et al., 1989; Ruppert et al., 1992). X-ray mapping techniques, in which maps or area scans of elemental X-ray intensities are obtained in the SEM or microprobe from polished sections of coal, could also be developed to determine element occurrences and associations. However, such mapping techniques could probably only be done with trace element species of fairly high abundance (>1000 ppm). For example, chlorine was shown to have an organic association in the Upper Freeport coal (Minkin et al., 1979) on the basis of such observations.

There are a number of other microscope-like techniques that have also been used to investigate trace element occurrences in coal and ash. Such methods include the proton microprobe using PIXE for elemental analysis (Minkin et al., 1982; Hickmott and Baldridge, 1991; Caridi et al., 1993), the ion microprobe mass analyzer (IMMA) (Finkelman et al., 1984), the laser microprobe mass analyzer (LAMMA) (Lyons et al., 1987; Morelli et al., 1988), laser ablation microprobe-inductively coupled plasma-mass spectrometry (LAMP-ICP-MS) (Chenery et al., 1995), and the sensitive high-resolution ion microprobe (SHRIMP) (Kolker et al., 2000b), the latter three of which use mass spectrometric techniques for elemental determinations. The latest version of the SHRIMP instrument employs reverse geometry (SHRIMP-RG), in which the electrostatic sector is downstream of the magnetic sector in the mass spectrometer (Kolker et al., 2000b). This arrangement provides superior mass resolution over earlier forward-geometry instruments. All of these microscope/microprobe techniques have been employed in detailed survey studies of trace elements in coal or ash aimed principally at investigating specific trace element occurrences in major components (vitrinite, pyrite, clays) in coals or in aluminosilicate phases in ash. It is anticipated that such studies will continue to provide a wealth of information about trace element occurrences.

4.2.3. XAFS spectroscopy

XAFS spectroscopy appears to be the only spectroscopic method, currently available, that is capable of obtaining significant information on trace element forms of occurrence in fossil fuels and related materials. Unlike the microscopic methods described above, the XAFS spectrum derived from a given element is a weighted average of all forms of occurrence of the element in the coal or coal fraction, regardless of whether the element forms a discrete mineral or is dispersed in major minerals or macerals. Indeed, if there is a bias with this technique, it is likely to be towards dispersed forms-of-occurrence rather than discrete mineral occurrences of a trace element, as has been demonstrated for the major element, sulfur (Huggins et al., 1992). Further, in addition to being a direct probe of an element's mode of occurrence in coal or ash, the technique is also nondestructive.

XAFS spectroscopy for trace element speciation is best performed at a major synchrotron source of intense X-ray radiation. In the USA, there are three such sources: the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, NY, the Stanford Synchrotron Radiation Laboratory (SSRL) at Stanford University, CA, and the Advanced Photon Source (APS) at Argonne National Laboratory, IL. Only at these X-ray sources and at comparable facilities elsewhere in the world are the X-ray fluxes sufficiently intense that useful spectral signals can be obtained from ppm levels of trace elements in coal and ash. As is normally done with dilute species in XAFS spectroscopy, the spectra are recorded in fluorescent mode, in which the X-rays fluoresced by the sample in response to the X-ray absorption process are measured as a function of energy. Hence, the XAFS spectrum for a specific element consists of a measurement of the variation in X-ray absorption by the sample as a function of energy in the vicinity of one of the characteristic absorption edges of the element in question. XAFS spectroscopy can therefore be "tuned" to a specific element in a coal or ash in order to obtain detailed information relevant to the local bonding and structure of the element, from which the form of occurrence may be deduced.

The earliest XAFS investigations on elements in coal were either carried out with non-typical samples of unusually high concentrations of the trace element (Maylotte et al., 1981; Huggins et al., 1989) or with trace elements of generally higher abundance (>100 ppm), but of less critical concern, such as Ti, Mn and Sr (Sandstrom et al., 1982; Wong et al., 1983; Huggins et al., 1989). However, more recent work (Huggins et al., 1993; Huggins and Huffman, 1996a,b) using detection techniques optimized for trace element investigations has shown that useful information can be obtained from a number of critical trace elements (As, Cr, Se, Zn, etc.) in coal down at least to the 5 ppm level. For XAFS spectroscopy, there is no real advantage of working on LTA or HTA instead of coal, because the carbon-rich matrix is relatively transparent to X-rays, except for those of lower energy from the lightest elements.

Various techniques can be implemented at the synchrotron to enhance the XAFS signal/noise ratio of trace elements. These include: (i) the use of wiggler and undulator insertion devices into the synchrotron ring to increase the white radiation X-ray intensity for the XAFS beam-line; (ii) the use of a multi-element solid-state germanium detector (Cramer et al., 1988), in which each Ge detector element effectively collects an individual spectrum that can be added to those from the other detector elements; (iii) use of pulse-height analysis (PHA) methods to limit the detected radiation to that fluoresced by the element of interest only; (iv) the use of filters and Soller slits (Stern and Heald, 1979); and (v) multiple scanning and addition of individual spectra. The net result of combining all these factors means that XAFS spectroscopy may be sensitive to as little as 1 ppm of an element, and that useful information can be obtained from as little as 5 ppm of the element (Huggins et al., 1993; Huggins and Huffman, 1996b).

The major advantages of XAFS spectroscopy are as follows: (i) it is specific for the element of interest; the few spectral interferences that exist can usually be avoided by means of PHA windowing; (ii) the technique is both direct and non-destructive; and (iii) sample preparation is simple and usually involves only pulverization and mixing to ensure a representative sampling of the solid material under the X-ray beam. The major disadvantages are: (i) that the technique can only be performed at a synchrotron source and, consequently, the availability of the method is limited; and (ii) only a single spectrum is obtained that is a weighted average of the spectra of the different forms of occurrence of the element in the coal or ash. This latter disadvantage can be circumvented by analysis of different fractions of the coal, such as float-sink separates (Huggins et al., 1997) or leaching fractions (Huggins et al., 2000b), as well as by spectral deconvolution and simulation techniques.

The information obtained from XAFS spectroscopy usually includes (i) identification of the major oxidation state or states of the absorbing trace element as it is present in the sample; (ii) identification of the principal nearest-neighbor elements surrounding the absorbing trace element; and (iii) the coordination number of at least the first such coordination sphere. This basic information, coupled with comparison of XAFS spectra of standard compounds with XAFS spectra of the trace element, is often sufficient to identify the major form or forms-of-occurrence of the trace element in the fossil fuel or ash. Quite fine distinctions can be drawn using this technique as a probe of the trace element environment in coal. For example, it has proved possible to discriminate readily between arsenic as arsenopyrite (FeAsS) and arsenic in solid solution in pyrite (FeS_2) for coals in which the arsenic abundance is less than 10 ppm (Huggins and Huffman, 1996a).

In theory, XAFS spectroscopy is applicable to virtually all elements in the periodic table. In practice, however, the technique is currently limited experimentally to trace elements with atomic numbers above 20 that occur in coal in excess of about 5 ppm. This abundance limit may soon be reduced significantly due to the development of improved X-ray fluorescence detectors with up to 100 detection elements and construction of new synchrotron beam-lines of significantly higher X-ray flux (up to ~ 10^3 times) than those that are currently available. As a result, XAFS techniques should eventually be applicable to almost all critical trace elements in fossil fuels and should help resolve many of the uncertainties that exist regarding the forms-of-occurrences of trace elements and their behavior in combustion and power generation.

4.3. Comparison of speciation methods

XAFS spectroscopy was also used to investigate element speciation in the four coals studied in the round-robin investigation summarized by Davidson (2000). Four fractions of each coal were prepared by a combination of Denver cell flotation and heavy-liquid separation. The fractions were then subjected to analysis using PIXE and XAFS spectroscopies for elemental concentration and forms of occurrence identification, respectively. In this way, different forms of an element are revealed and by measuring the concentration of the elements in the different fractions, as well as the weight fractions of the different fractions, semi-quantitative to quantitative estimates of the different forms-of-occurrence were then made. Results from the round-robin study are shown for As, Cr and Zn in Table 10b along with results from a density fractionation study conducted by Querol et al. (CSIC, Spain) and summarized by Davidson (2000). These data can be compared to the corresponding data obtained by sequential leaching methods listed in Table 10a.

It is difficult to compare the results from the XAFS speciation analysis with those from less direct methods as the definitions of the groupings are different. Nevertheless, there is reasonable agreement among the methods on a number of points.

- Most of the chromium in each coal appears to be distributed between an organic association and an association of Cr with silicates and all methods agree that the latter form is the dominant form of chromium in the UK coal (Gascoigne Wood). The XAFS data identifies the silicate association as Cr-bearing illite for the US and UK coals and the organic association for the US coal is tentatively identified as a poorly crystallized (small particle) chromium oxyhydroxide. The chromium forms in the Australian coal were not identified, but were noted to be different from those in the other two coals.
- For arsenic, if it is assumed that the ‘carbonate’ fractions from the leaching methods represent oxidation products of arsenical pyrite, as has been recently shown by Kolker et al. (2000a) and Huggins et al. (2000b), then all methods agree that much, if not all, of the arsenic in the US and UK coals and about half of the arsenic in the Wyee coal is originally associated with pyrite. The remaining fraction of arsenic in the Wyee coal is less clearly identified and may be associated with silicates or an organic As^{3+} form, as suggested by the XAFS data.
- The agreement for zinc is less good. Whereas all methods agree that the US coal has most of its zinc in sulfide form, either associated with pyrite or as sphalerite (ZnS), the agreement is less good for the UK coal, for which two groups indicate a strong silicate association, two other groups a sulfide association, and the fifth group shows a relatively even distribution over all classes. For the Wyee coal, there is very little agreement at all for zinc among the different techniques.
- As summarized by Davidson (2000), agreement among the methods for other element speciation varied from reasonable (Mn, Cu, Cd, Se, and Hg) to poor (Co, Ni, Be, Sb), with the remainder intermediate (Se, Pb).

It would appear that both the indirect methods and the direct method of XAFS spectroscopy could benefit significantly from better suites of standards for certain elements. But the problem of how to simulate some of the occurrences in coal is not easy. For example, it is becoming clear that the organic chromium occurrence, tentatively identified as small-particle CrOOH, which was observed in the IEA US coal and in other US bituminous coals (Huggins et al., 2000a), must involve shielding of the chromium form by the organic matrix because any Cr^{3+} oxyhydroxide would be expected to be soluble in one or other of the reagents used. Such an occurrence would be difficult to duplicate in a synthetic standard. Further, the possible oxidation of minerals, especially pyrite, in the coal must not be overlooked as a mechanism of altering mineral occurrences and shifting the element from one class to another in the leaching schemes. However, what would appear to benefit both the indirect and direct methods most would be for them to be done on the same fractions. A recent study by Huggins et al. (2000b), in which XAFS spectroscopy was performed

Table 10

a: Comparison of speciation results for three sequential leaching schemes for Cr, Zn and As in three IEA Round Robin Coals (after Davidson, 2000)

	Illinois #6, USA			Gascoigne Wood, UK			Wyee, Australia		
	CSIRO	USGS	U. Shef	CSIRO	USGS	U. Shef	CSIRO	USGS	U. Shef
Cr									
‘Organic’	50	65	46	<5	40	10	68	60	5
‘Silicate’	40	35	26	80	50	86	<5	35	66
‘Carbonate’	5		7	15	5	4	29	5	29
‘Pyrite’	<5		22	<5	5	<1	<5		1
Zn									
‘Organic’	<5	20	4	<5	15	6	<5	0	4
‘Silicate’	<5	10	19	<5	25	67	<5	30	56
‘Carbonate’[a]	100	25	18	85	35	12	100	30	23
‘Pyrite’	<5	45	60	10	25	14	<5	40	16
As									
‘Organic’	12	40	0	<5	25	0	<5	25	–
‘Silicate’	12	10	7	18	10	34	38	20	–
‘Carbonate’	18	10	8	20	10	41	11	20	–
‘Pyrite’	58	40	85	54	55	25	44	35	–

b: Comparison of speciation results for Cr, Zn and As in three IEA round robin coals from a density fractionation scheme (CSIC, Spain) and XAFS analysis (modified from Davidson, 2000)

	Illinois #6, USA		Gascoigne Wood, UK		Wyee, Australia	
	CSIC	XAFS	CSIC	XAFS	CSIC	XAFS
Cr						
‘Organic’	40	85		<20	50	80
‘Silicate’	60	15	90	>80	50	20
‘Carbonate’						
‘Pyrite’						
‘Other’		<5 chromite	10 hvy min.	<5 chlorite		
Zn						
‘Organic’		25		<5		80
‘Silicate’			30	>90	40	20
‘Carbonate’						
‘Pyrite’	100[b]		70[b]		60[b]	
‘Other’		75 ZnS				<5
As						
‘Organic’	12	<10	10		10	35
‘Silicate’	10		10		30	
‘Carbonate’						
‘Pyrite’[c]	78	95	80	100	60	65

[a] It should be noted that, as indicated in Fig. 6, the four mineral classes are defined ‘operationally’ (‘labels of convenience’ Davidson, 2000) and somewhat differently in each leaching scheme. For example, although the CSIRO leaching scheme has 100% of the zinc reporting to the ‘carbonate’ class, the likely actual mineral form of Zn that is being leached by HCl is the sulfide, sphalerite, ZnS.

[b] Associated with the pyrite group fraction, but likely present as sphalerite, ZnS.

[c] For As, ‘pyrite’ includes both As substituting for S in pyrite and As in arsenate from oxidation products derived from pyrite.

directly on the residues from a sequential leaching scheme, showed clearly how different forms of As were associated with different stages in the leaching scheme. Detailed combined studies of this type would clearly benefit the elucidation of element speciation in coal and at the same time would provide the leaching methods with better-defined classes.

5. Conclusions

Environmental issues associated with coal utilization, especially the release of particulate matter and HAPs to the atmosphere from coal combustion, are placing increased emphasis on accurate and reliable analytical methods for inorganics in coal. At the current time, it would appear that elemental concentrations can be reliably determined using techniques such as X-ray fluorescence for the major inorganics in coal and a combination of various methods (e.g., INAA, PIXE/PIGE or polarized XRF combined with ICP/MS or ICP/AES and AAS methods) for the 15 or so trace elements listed as HAPs in the 1990 Amendments to the Clean Air Act. Mineralogical determinations can be best done by the Rietveld method of X-ray diffraction. CCSEM methods, which appear capable of determining both the mineralogy and mineral association, have the potential to supply significantly more information than XRD methods. However, it would appear that there is still some significant further developmental work that needs to be done to integrate these two aspects of the method. Such improvements in CCSEM methods would find immediate application in models of both coal combustion and coal cleaning and would greatly contribute to enhancing fundamental understanding of the behavior of inorganics in these processes. Finally, various methods for determining the mode of occurrence of trace elements in coal were reviewed. There appears to be a significant need here for the combined application of both direct and indirect methods for elemental speciation. Data based solely on inferences from indirect methods are fraught with uncertainty because such methods are based on unverified assumptions. Use of electron or ion probe methods to obtain information on the elemental associations of the trace element will help resolve such uncertainties. Similarly, although XAFS spectroscopy can be used to determine elemental modes of occurrence directly, it would appear to be more powerful when combined with leaching or other indirect speciation methods, because it can also test the assumptions and help resolve the uncertainties inherent in the indirect methods.

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This review is a reflection of the interests of the author, who recognizes it as being rather incomplete. Certainly there are numerous other techniques that might have been included in this review, including various surface analysis methods, notably X-ray photoelectron spectroscopy, major element speciation methods, such as Mössbauer spectroscopy and XAFS spectroscopy, and methods specific for certain coal types, such as low-rank coals that contain many inorganics dispersed throughout the macerals for which a variety of unique analysis methods exist. Such methods are not included here and the author regrets their omission.

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