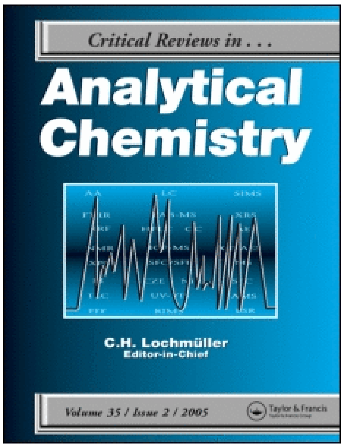

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MODERN METHODS IN BITUMINOUS COAL ANALYSIS: TRACE ELEMENTS

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> The work of and the demands on the analytical chemist are growing more exacting every day, and we cannot afford to lose the analytical viewpoint.
>
> G. E. F. Lundell, 1933[1]

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I. INTRODUCTION

The analysis of coals and related materials for trace elements is still demanding and the best results depend on constant efforts by analytical chemists. Any suggestion that more sophisticated instruments remove the need for analytical chemists is a myth. Indeed, there is a danger that the *figures* produced by such instruments may be taken unquestionably for *results*. In order to obtain valid results for trace elements in coals, it is necessary to know something about the nature of coal so that the various methods of analysis can be used validly. For the proper operation of an instrumental method, the chemist must know the theoretical background, the optimum operating conditions, and the kind of know-how that comes only with experience.

A proper approach to the analysis of trace elements in coals should be based on an appreciation of the heterogeneous nature of coal, of the mode of occurrence of the trace elements, and of the concentrations that are commonly found in coals for which information is available.

As expected for a naturally occurring material formed under varying conditions over a long period, coal contains most of the elements in the Periodic Classification. Data have been published for the concentrations of carbon, hydrogen, nitrogen, oxygen, sulfur, 7 major inorganic elements, and 66 trace elements in coals from various parts of the world. For the sake of this review, elements usually found at less than about 0.1% will be regarded as trace elements. Also, the review is restricted to bituminous coals, i.e., to coals with greater than 77% carbon on a dry ash-free basis. In practice, the same methods of analysis can be used for anthracite, subbituminous coal, lignite, and brown coal, albeit with some modifications.

Attention must be paid to sampling in the mine and from dumps, trucks, rail wagons, and ships. The preparation of subsamples for analysis, the avoidance of contamination, and finally the choice of methods are of paramount importance. Each of these aspects will be considered.

The upsurge of interest in trace elements in coal has accompanied the increased use of coal over the past decade. Trace elements should be taken into account during coal mining, preparation, and storage and during the usage of coal for coke making, power production, and liquefaction. For example, the quality of steel may be impaired by small amounts of phosphorus and arsenic which could be introduced in metallurgical coke. The current interest in environmental matters has increased the need for information on the fate of trace elements during the combustion of coal in power stations.[2] In this connection, trace elements may be divided into two groups, namely, those of prime environmental interest (arsenic, cadmium, chromium, fluorine, lead, mercury, nickel and selenium) and those that could be of environmental interest (antimony, beryllium, boron, chlorine, cobalt, copper, manganese, molybdenum, thallium, thorium, tin, uranium, vanadium, and zinc).[3] Several of these elements should also be considered during the planning for the rehabilitation of areas after coal mining, where trace elements in the overburden, which becomes topsoil, may limit the growth of vegetation, favoring either deficiency or excess conditions.[4] Some trace elements are useful in ascertaining the degree of marine influence on coal during the early stages of coalification [5,6] and attempts have been made to use trace element contents for correlating coal seams.[7]

II. BACKGROUND INFORMATION RELEVANT TO THE ANALYSIS OF COALS FOR TRACE ELEMENTS

In order to analyze coals for trace elements, it is useful to have some information on their mode of occurrence, on contents (based on published work), and on major elements. Although only bituminous coals are being considered, the general approach applies to anthracites, subbituminous coals, lignites, and brown coals; relevant differences will be noted.

A. Mode of Occurrence

"In general, trace elements are associated with both the coaly matter and the mineral matter in coal. This is not surprising in view of the origin of coal, i.e. from plant matter, and the diagenetic processes operating during coalification."[8] During coal formation, fine particles from the atmosphere, e.g., volcanic dust, reached the swamp and were available for incorporation into the coal and dirt bands.

In the U.S., coal is taken to be an easily combustible rock with more than 50% by weight of combustible material. However, a more useful approach is to designate samples with an ash yield, under standard conditions, of less than 35% as coal, while those with higher ash yields may be designated dirt bands. Dirt bands are usually thin strata, e.g., of carbonaceous shale, which are intercalated with the coal in seams. Although it is not known exactly how trace elements are present in the organic matter (coal), it is likely that at least some will be associated with phenolic (-OH), imino (-N=), and mercapto (-SH) groups. During the early stages of coalification, many trace elements would probably have been present as complexes with humic acids in decaying plant matter. As coalification proceeded, there would have been changes in the ability of the organic matter to form complexes and perhaps some competition with bisulfide ions, as has been suggested for marine conditions.[9] Trace elements may be associated with the mineral matter as discrete minerals,[10] e.g., sphalerite (ZnS), galena (PbS), barite ($BaSO_4$), as replacement cations, e.g., manganese in siderite ($FeCO_3$),[11] or associated

Table 1
THE INORGANIC OCCURRENCE OF SOME TRACE ELEMENTS IN BITUMINOUS COALS, MAINLY FROM U.S.[12]

Element	Occurrence
Antimony	Probably as a sulfide
Arsenic	In solid solution in pyrite
Beryllium	Mainly organically associated
Boron	Mainly organically associated; some in illite
Cadmium	In sphalerite (ZnS)
Chlorine	Mainly organically associated
Chromium	In clays
Cobalt	Associated with sulfides
Copper	As chalcopyrite ($CuFeS_2$)
Fluorine	Probably in apatite, clays, and other minerals
Lead	As galena (PbS)
Manganese	In siderite ($FeCO_3$)
Mercury	In solid solution in pyrite
Molybdenum	Probably associated with sulfides
Nickel	May be with sulfides or clays
Phosphorus	As apatite
Selenium	Organically associated and in pyrite
Thallium	In sulfides
Thorium	In rare earth phosphate minerals
Tin	Probably as oxide or sulfide
Titanium	As Ti oxides and in clays
Uranium	Organically associated and in zircon
Vanadium	In clays
Zinc	As sphalerite (ZnS)

with clays, either as replacement cations or adsorbed. As a result of an extensive study of trace elements in coals from the U.S. and a few from overseas,[12] Finkelman proposed the actual and probable mode of occurrence for several trace elements in bituminous coals (Table 1). Results for Australian coals are in general agreement with those in Table 1, with a few minor additions, e.g., manganese was also found in calcite ($CaCO_3$),[11] the nickel sulfide, millerite (NiS)[13] was found in a New South Wales coal, and vanadium is regarded as probably organically associated.[14] There are reports that arsenic may occur as arsenopyrite,[14] and that chlorine may occur in inorganic forms, e.g., NaCl.[14] Zircon has been found in Australian coals,[10] and thallium was associated with sulfide inclusions, mainly pyrite, in Russian coals.[15]

The mode of occurrence of trace elements in anthracites, subbituminous coals, and lignites differs only slightly from bituminous coals, although gypsum may occur more often in subbituminous coals and lignites. Quartz, kaolinite, and pyrite (marcasite) are found in Victorian brown coals,[16] but calcium, magnesium, most of the sodium, and some of the iron and aluminum are organically combined, the cations replacing hydrogen ions of carboxylic acid groups.[17] Similar occurrences of these elements may also be found in some lignites. Carbonate minerals are not present in acidic brown coals and lignites.[18]

It is clear that coal is a heterogeneous mixture of organic matter and mineral matter, the latter varying from submicrometer size inclusions in the organic matrix[19,20] to millimeter size particles. Trace elements are associated with the organic matter and with the mineral matter in various forms. Some knowledge of the mineralogy of particular coals is useful prior to sampling and analyzing for trace elements.

Table 2
TRACE ELEMENT CONTENTS IN BITUMINOUS COALS: VALUES GIVEN AS PPM IN DRY COAL

Element	U.S.[27]	Australia[8,28,29]	South Africa[30]	U.K.[31,32]	Poland[33]	West Germany[34]
Ag	0.005—0.5	<0.2—1		<0.7		0.2—1.2
As	<1—170	<0.1—55	0.9—8.2	2—73	0—40	1.5—50
B	<0.6—160	1.5—300		<20—160	10—50	9—91
Ba	4—570	<40—1000	86—474	30—350		45—350
Be	0.2—14	<0.4—8		0.4—3	0.5—10	0.9—3.5
Cd	<0.004—9	0.05—0.20		<0.3—3.4	0—4	<1.3—10
Cl	130—2400	<100—1000		200—9100		
Co	0.8—90	<0.6—30	3.3—14	2—20	3—50	7—30
Cr	2—84	<1.5—30	12—63	3—45	0.6—12	4—80
Cu	3—160	2.5—40	4.2—16	12—50	8—150	10—60
F	<13—1900	15—500		27—202	50—400	20—370
Ga	0.7—35	1—20	7.1—18	1.5—		
Ge	<0.07—36	<0.3—30	0.7—10	<3—8		
Hg	0.01—1.8	0.026—0.40		<0.2—0.7		<0.7—1.4
La	<1—58		<4—50	2—38		
Li	1.1—370	12—28			5—50	
Mn	1—1400	2.5—900	0—180	11—250		
Mo	<0.1—16	<0.3—6	<1—2.7	<1—4.3		6—30
Ni	1.4—130	0.8—70	6.9—32	8—35	6—30	15—95
P	1—1200	30—4000	40—1270			40—1240
Pb	<1—62	1.5—60	1.9—25	8—63	4—150	20—270
Sb	<0.1—7.4	<0.1—1.7	<2	1—10		0.4—2
Sc	0.6—27	<0.3—30	4.8—13	1.3—8		
Se	<0.6—20	0.21—2.5	<0.4—0.9	1—4		0.6—5.5
Sn	<0.3—3	<0.9—15	<1—11	<3		
Sr	4—920	<20—∼1000	49—514	15—280		15—265
Th	<3—26	<0.2—8	4.0—21	0.7—6.7		
Ti	70—4800	400—4000		100—1500		
Tl	<0.3—13	<0.2		<3		<4
U	<0.1—15	0.4—5	3.0—7.3	0.5—2.3	0—1	<1—1.3
V	2—120	4—90	17—43	8—150	5—180	31—179
Y	<1—41	1—25	14—30			
Zn	1—1600	12—73	3.2—16	30—200	5—300	17—210
Zr	1—170	6—400	47—356	4—30		

B. Contents

Although there are reports of the presence of some trace elements in coal ash from about the middle of the 19th century, the main impetus came from extensive studies by Goldschmidt[21,22] and his co-workers dating from about 1930. Detailed information on the contents of several trace elements in a wide range of bituminous coals has been published for coals from the U.S.[23-27] and Australia.[8,28] Some results are also available for coals from other countries. Data for 34 trace elements in bituminous coals from U.S.,[27] Australia,[8,28,29] South Africa,[30] U.K.,[31,32] Poland,[33] and West Germany[34] are given in Table 2. Occasional values outside these ranges have been reported; e.g., zinc and cadmium tend to be relatively high in some coals from the Illinois Basin, U.S.[26] Some elements vary over wide ranges, while others have fairly similar ranges which warrant the calculation of reasonably realistic mean contents, e.g., nickel has a mean content of 15 ppm Ni in bituminous coals.[35] Perhaps a more useful approach is to consider the data for 90% of values, in other words, for the common ranges. These have been estimated for the 22 trace elements of environmental interest, using data for about 600 samples from Pennsylvania, Ohio, Maryland, West Virginia, Virginia, and

Table 3
TRACE ELEMENT CONTENTS IN BITUMINOUS COALS: RANGES FOR 90% OF VALUES (GIVEN AS PPM IN DRY COAL)

Element	U.S.[27]	Australia[3,28]
As	1—70	0.2—10
B	1—130	4—200
Be	0.7—5.6	<0.4—5
Cd	0.02—1.2	0.06—0.15
Cl	240—1700	<100—400
Co	1.5—25	<0.6—20
Cr	3.7—47	<1.5—20
Cu	5—47	6—30
F	<20—340	20—190
Hg	0.01—1.3	0.03—0.20
Mn	2.2—110	4—600
Mo	0.30—10	0.3—4
Ni	3.6—75	3—50
Pb	1.5—44	2—40
Sb	0.2—4.1	<0.1—1.3
Se	0.8—12	0.25—1.6
Sn	<0.3—1.8	<0.9—7
Th	<3—9	<0.2—6
Tl	<0.3—2.2	<0.2
U	<0.2—7.1	0.4—3.8
V	4.1—77	10—60
Zn	2.4—170	13—46

Indiana,[27] and for about 600 samples from New South Wales and Queensland, Australia[3,28] (Table 3). As expected, the ranges are narrower and often very similar, e.g., beryllium, cobalt, copper, nickel, lead, thorium, and vanadium. Coals from the U.S. tend to be higher than those from Australia for arsenic, cadmium, chlorine, mercury, selenium, thallium, and zinc, but these are generalizations that do not necessarily apply to all coals from the U.S. These ranges should be good guides for most coals, always realizing that there are exceptions and that a few coals exceed even the upper limits for arsenic, barium, cadmium, chlorine, copper, manganese, lead, selenium, thorium, uranium, and zinc given in Table 2.[25,26,28]

There are also data for other trace elements, mainly those of more academic interest. Of the lanthanides (rare earths), coals from U.K.,[31] U.S.,[27] and Australia[36,37] may have up to 100 ppm cerium, while 10 of the others are usually less than a few ppm. Data for coals from U.S.,[26,27] U.K.,[31] South Africa,[30] and Australia[36,37] indicate the following ranges (in ppm) for rubidium (<1 to 60), cesium (<0.1 to 8), hafnium (<0.1 to 5), tungsten (<0.2 to 8), bromine (0.6 to 155), iodine (<0.3 to 22), niobium (<0.09 to 18), gold (<0.002 to 0.01), and indium (0.009 to 0.63). There are only a few scattered data for bismuth, iridium, osmium, platinum, palladium, rhodium, rhenium, ruthenium, tantalum, and tellurium, indicating that these elements are unlikely to be present in concentrations greater than 1 ppm or even 0.1 ppm. For example, Australian coals had 0.09 to 0.33 ppm tantalum,[36] and U.K. coals had <0.002 to 0.011 ppm iridium.[31] Most coals from U.S. had <0.005 ppm platinum,[38] although some coals from western Kentucky had up to 0.21 ppm platinum.[39] Palladium (<0.001 ppm) and rhodium (<0.0005 ppm) were not detected in coals from U.S.[38]

In general, the contents of trace elements in anthracites, subbituminous coals, lignites, and brown coals should be similar to those given in Table 2.[25] The low ash

Table 4
MAJOR ELEMENT COMPOSITION (% W/W) OF ASH FROM BITUMINOUS COALS

	U.S.[27]		Australia[11,42,43]		
	Range	Mean	Range	Common range	Mean
SiO_2	9.5—78	44	14—85	45—63	57
Al_2O_3	4.9—42	25	13—43	22—37	29
Fe_2O_3	1.1—81	17	0.4—51	0.5—15	6.5
CaO	0.2—20	2.1	<0.01—28	0.09—5	2.2
MgO	0.1—3.0	0.8	<0.01—8	0.03—3	1.0
Na_2O	<0.05—2.4	0.46	<0.01—3	0.03—1.5	0.65
K_2O	0.06—5.4	1.9	0.2—6	0.2—2	1.1
SO_3	0.07—16	2.4	<0.01—11	0.2—3	0.95
Ash yield	2—46	12	4—36	6—25	14

(commonly <3%) brown coals from Victoria, Australia, are lower in most trace elements than bituminous coals,[40] the exceptions being mercury, selenium, and zinc which have similar contents to Australian bituminous coals. There are unusual local occurrences of coals with higher than expected contents of some elements. An example is lignite from some parts of the western U.S., where uranium is found up to about 0.1%.[41]

Although some coals may be relatively high in certain trace elements, in general, the ranges of values are similar for coals, shales, and soils.[4] However, there is a tendency for some coals to have more selenium than shales. If comparisons are made between coal ash, shale, soil, and the crust of the earth, then some trace elements will be in the highest concentrations in coal ash. For example, for coals from New South Wales, Australia, the concentrations of boron, germanium, molybdenum, phosphorus, lead, strontium, and zirconium tend to be higher in the ash than in the crust of the earth.[28]

Since the determination of many trace elements is carried out on ash, estimates of the amounts of trace elements likely to be in a coal ash can be made from the data in Tables 2 and 3 using a multiplication factor based on the ash yield of the coal, say, from about 3 to 25%. In general, it is clear that trace elements occur in concentrations ranging from less than 1 ppm to more than 100 ppm, depending on the element and on the particular coal to be analyzed.

C. Major Elements

Those elements that occur in coals usually above about 0.1% are regarded as the major constituents. These are mostly stated as oxides in ash, mainly because their practical significance rests on their behavior during combustion, when they form deposits, fly ash and the like, as distinct from the coal which forms gases. However, it is important to know something about the major elements because they form the matrix in which trace elements are to be determined.

Results for several hundred coal ash samples from coals from U.S.[27] and Australia[11,42,43] are summarized in Table 4. Most coals yield ashes high in silicon and aluminum, fairly high in iron, together with lesser amounts of calcium, magnesium, sodium, and potassium. Some of the sulfur from the organic matter and pyrite in the coal is fixed in the ash. The ash yield varies from a few to about 46% in U.S. coals and from about 6 to 25% in most Australian coals (Table 4), the means being about 12 and 14%, respectively.

The major elements in most coals occur in clays (kaolinite, illite, montmorillonite, mixed layer clays), carbonate minerals (calcite, dolomite, ankerite, siderite), sulfide minerals (pyrite), quartz, micas, and feldspars.[10,44] These minerals are either intimately admixed with the coal or in cracks and cavities. However, they may remain in the coal sample used for analysis especially if the coal is directly from the mine and has not undergone any form of beneficiation to remove some of the mineral matter.

Anthracites tend to have slightly more aluminum and slightly less iron than bituminous coals, while subbituminous coals and lignites tend to have more calcium, magnesium, and sodium, but less iron, than bituminous coals.[25] Subbituminous coals and lignite have more sulfate in the ash than the higher rank coals.[25]

As noted earlier, some trace elements are associated with the minerals in coal and the determination of trace elements usually has to be carried out in the presence of the major elements. In other words, analysis must take into account several percent of silicon, aluminum, and iron and up to a few percent (or more) of calcium, magnesium, sodium, and potassium.

III. SAMPLING IN FIELD AND LABORATORY

"Unless the complete history of any sample is known with certainty, the analyst is well advised not to spend his time in analyzing it."

Thiers, 1957[45]

Good analysis depends on the initial sampling and on the preparation of the laboratory sample. Because many trace elements are in low concentrations (around the ppm level), great care must be taken to minimize contamination (see Section IV.A). Coal is heterogeneous, and hence it "presents one of the most difficult challenges in the world of sampling".[46] However, good sampling can be achieved, as proved by replicate analyses carried out in several laboratories.

A. Sampling in the Field

It is desirable to know the origin of the sample (mine, seam, location in seam), the nature of the sample (channel, pillar, hand-picked), if the sample can be regarded as representative, the state of the coal (fresh, weathered), the date of sampling, and relevant comments from the geologist, especially concerning dirt bands or discrete mineral matter (inclusions). If core samples are used, information should be provided about the drilling fluids. It is important to minimize oxidation, which affects some properties of coal, e.g., moisture and pyritic sulfur. Undue oxidation may produce acid conditions from the oxidation of pyritic sulfur, especially in the framboidal form, thereby dissolving some trace elements which may be translocated within the sample.[4] Suitable guidelines have been published.[47,48]

Samples of coal have also to be taken from stockpiles, railway wagons, trucks, barges, and ships, where the total amounts may vary from about 20 to 100,000 t. This may be done manually or mechanically. Sampling may be done *in situ*, intermittently or continuously, the latter being preferred with large bulk samples, where mechanical samplers can be used for coal on conveyor belts.[46] Useful information is available in the form of standard methods.[48-51] Although sampling theory is useful, there is no replacement for experience and much experience has gone into the formulation of standard methods. Since good sampling is a *sine qua non* for good analysis, sampling should at least be planned and supervised by an analytical chemist who will ensure the validity of the sample and the avoidance of obvious contamination, i.e., the preservation of constant composition.

B. Preparation of the Sample for Analysis

The preparation of the laboratory sample from the bulk or gross sample must ensure that the composition of the original coal remains unchanged. The first treatment is to reduce lumps to fine material. The final sieve size recommended in various methods is -250 μm (ASTM[52]) -200 μm (SABS, South Africa[51]), −180 μm (U.S. Geological Survey [47]), -75 μm (CSIRO, Australia[53]), -200 μm (SAA, Australia[48]), and −150 μm or finer depending on the analysis to be carried out (Illinois State Geological Survey[26]). In a well-mixed sample, the sampling reproducibility increases with the number of grains, i.e., with a decrease in grain size. In practice it is rarely necessary to grind finer than about 75 to 100 μm. It has been suggested that a 5-mg subsample of coal ground to −75 μm could be used for microanalysis of coal.[54] The laboratory samples should be stored properly in order to reduce oxidation. If steel crushers or presses are used, it is advisable to make the face plates of manganese steel (low in chromium and other alloying elements); most coals are high enough in manganese to tolerate a few ppm contamination. At CSIRO, Australia,[53] lumps of coal are reduced to a few millimeters in size in a tungsten carbide jaw crusher or press, then ground in a tungsten carbide or agate ring grinder to −75-μm particle size. Nylon sieves may be used, but are time consuming. Hence, it is preferable to find out experimentally the time needed to grind the required weight of coal to the required mesh size, and thereafter omit the sieving. It may be necessary to air dry coal before carrying out any size reduction.

Several trace elements in coal are determined in ash mainly because the carbon is removed and because of the concentration achieved. Temperatures reported vary from about 150 to 1050°C,[28] but modern practice favors 450,[55] 500,[26] or 525°C.[47] The low temperature plasma ashing technique (about 150°C) is good, but very slow (several days). Provided that the coal is ashed in thin layers in a shallow dish under oxidizng conditions and that the time of ashing is not prolonged, then dry ashing of a coal is suitable for several trace elements. Porcelain dishes are not recommended, but quartz or high-silica crucibles[56] or pure aluminum dishes[55] are suitable at a temperature of 450 or 500°C. The ash is suitable for analysis by optical emission spectroscopy (OES), atomic absorption spectrometry (AAS), and X-ray fluorescence spectrometry (XRF). There has been much discussion on possible losses of trace elements during ashing. It is clear that very volatile elements, i.e., chlorine, bromine, iodine, mercury, and fluorine, are volatilized significantly even under low temperature conditions (150°C),[57] while selenium is retained at 150°C.[57] There are differences of opinion about arsenic and antimony. When available, neutron activation analysis on whole coal is good. However, arsenic may also be determined on low temperature ash[57] and arsenic and antimony may be determined on ash made by heating coal mixed with nickel nitrate and magnesium nitrate at 500°C.[58,59]

The dissolution of ash, and of coal for some elements, requires attack by chemical reagents in order to ensure that the elements to be determined are in a form suitable for analysis by, say, AAS. There is useful information on decomposition in open and closed systems by fusion and by sintering,[60,61] and on container materials and a wide range of dissolution techniques, including oxidation procedures.[62]

Another approach, especially for volatile elements, is to burn the coal sample in a bomb, similar to that used for the determination of specific energy, with oxygen under pressure, say, 2000 kPa, and finally to wash out the contents of the bomb with water.[63]

Whole coal, ground to a suitable size, may be used directly for neutron activation analysis (NAA), XRF, and for wet chemical analysis (mainly for mercury and fluorine). The trend towards the use of whole coal directly is commendable, but the use of ash for many elements should not be undervalued. It has been stated that dry ashing lost favor but this "appears to be largely undeserved, at least for biological material".[45] The same comment applies to coal, especially where less costly methods have to be used, e.g., OES and AAS. Two recent developments involve the use of whole coal directly with AAS. One uses the injection of powdered coal slurries into the flame,[64] and the other uses direct heating of a solid coal sample in an electrothermal graphite furnace integrated with an atomic absorption spectrometer.[65]

The various methods of preparing coal for analysis have been reviewed and relevant details given.[66]

IV. ANALYSIS

"The determination of trace inorganic elements in coal is one of the most difficult problems facing the analytical chemist."

Guidoboni, 1973[67]

The analysis of coal for trace elements is difficult, but proper attention to details certainly enables good results to be obtained. Prior to about 1960, the main methods used were wet chemical and OES (mainly semiquantitative). Since then, the addition of AAS, XRF, and NAA has extended the range of elements that can be determined, especially at sub-ppm levels. In general, comprehensive surveys of trace elements in coals utilize several methods so that the most appropriate method is available for each element, especially at low concentrations. For example, the U.S. Geological Survey[68] and the Illinois State Geological Survey[26] used INAA, XRF, AAS, OES, and chemical methods to obtain data for the 34 trace elements in Table 2 and several others, while the data (Table 2) from Australia was obtained by using OES, AAS, NAA, and chemical methods. However, it must not be assumed that older methods are necessarily less precise than modern instrumental methods which are generally more costly. It is often advantageous to use a multielement method, i.e., one that enables the determination of several elements on the one sample. The selection of the most suitable method depends on the judgment of the analytical chemist, sometimes limited by the availability of certain instruments. Before discussing the methods in detail, two important matters will be dealt with, namely, contamination and reference standards.

A. Contamination

"Contamination is one of the major problems hampering analyses at the trace (1 to 100 μg/g) and ultratrace (<1 μg/g) level."[69] Care must be taken at every stage of sampling and during the preparation of the sample for analysis. This means the proper choice of implements, storage in suitable containers, and the avoidance of contamination during handling (ashing, chemical treatments, preparation for instrumental analysis). Checks must be made on materials used for dishes and on chemical reagents. The storage and filtration of very dilute solutions of cations may give rise to losses by adsorption.[70] Another source, of what can be termed negative contamination, is losses by volatilization, e.g., during size reduction or treatment with acids, especially hydrochloric acid. An unexpected source of contamination was found during the ashing of coal in high-silica crucibles; the coal ash removed some arsenic from the surface of the crucible.[58]

In order to correct for the contamination, it is necessary to carry out the determination, either omitting the sample or using a pure sample, i.e., one free of the elements in question. This provides a "blank" value which can be subtracted from the actual determination to correct for contamination. The validity of the "blank" depends on its constancy, which depends on controlling the various contamination factors and on the competence of the analytical chemist in using the methods. Successful trace element analysis cannot be achieved unless correction can be made for contamination. In some methods, the limits of detection for certain elements may be unattainable in practice because the "blank" is of the same order of magnitude. It is important that the "blank" be precise, so that a meaningful correction can be made, especially at low concentrations.

B. Reference Standards

The attainment of good precision is not necessarily synonymous with accuracy. Accurate data for trace elements in coals are required for some industrial purposes and for geochemical studies. Such data usually rely on the availability of good reference standards. The need for such standards for coal and related materials became apparent to all in 1974, when the results of a round-robin study of samples of coal, fly ash, residual oil, and gasoline were published.[71] It has been stated that these results "were shocking, as they were often order-of-magnitude ranges of values reported for given elements in particular standards".[72] There was clearly an urgent need for good reference standards for coal and related materials. Initially, the National Bureau of Standards, Washington, D.C., had prepared a standard for trace elements in coal (NBS SRM 1632) and another one for coal fly ash (NBS SRM 1633). These were followed by standards for subbituminous coal (NBS SRM 1635) and replacements of the earlier ones which had sold out (SRM 1632a, SRM 1633a). A careful study by four laboratories using instrumental neutron activation (INAA) methods produced good agreement between their results and those of the NBS for SRM 1632 and SRM 1633.[72] The NBS standards are designated as Standard Reference Materials (SRM) and are issued with a statement giving "certified values" and "values for information only". The number of trace elements, for which values are given, varies from 18 to 23. However, there are also data for other elements in these standard samples, e.g., data for 51 elements in SRM 1632a and for 43 elements in SRM 1635.[73] Much effort has been expended in the analysis of these and other standard samples and there are different ways of compiling the data and of assessing its usefulness.[74] Probably the most useful practical approach has been put forward by Gladney and Burns[74] who use the term "consensus value" to refer to the composition which is deduced from published data for ranges and mean values of many standards. It is stressed that "the responsibility for the end use of these data lies with the individual investigator".[74] Gladney and Burns' approach is commendable and their compilations[75,76] of data for standard materials, including coal and fly ash, should be consulted by anyone who plans to analyze coals for trace elements. Although these standard samples have been regarded as homogeneous for subsamples of the order of a few hundred milligrams, an investigation of the precision of beryllium showed that results for 0.3- to 2.0-mg subsamples of SRM 1632 had a precision of better than ±10% of the amount present (1.52 ppm Be).[77] Reference standards are necessary for establishing valid relationships between results from different methods. In this connection, the concept of traceability is relevant. This "implies that each level in a hierarchical tier of measurement systems should be able to relate and trace its measurement results back to the next higher level in the tier."[78] In practice, it is also desirable to have laboratory or in-house standards which have been compared with reference standards. Relevant methods for setting up such standards and the criteria for establishing certified values for the NBS Standard Reference Materials have been published.[78] Three carefully prepared samples of South African coals have been analyzed recently in an international round-robin,[79] and they should be available soon for use as reference standards. These samples have ash yields of about 10, 29, and 35% and the trace element contents cover useful ranges for most elements.

There is a continuing need for good coal reference standards, so that methods can give results related to common bases, thereby increasing the accuracy of the results and making comparisons more meaningful.

C. Methods

Useful factual reviews of methods of analysis for trace elements in coals are published biennially in *Analytical Chemistry* (under "Solid and Gaseous Fuels", in the April issue) and elsewhere.[80] Comments will be made here on the main methods used. In general, the trend has been towards multielement methods.

1. Chemical

Apart from chlorine, fluorine, and phosphorus, nowadays trace elements are not usually determined by chemical methods, i.e., noninstrumental methods. However, prior to about 1930, sundry determinations of some trace elements in coal were carried out by spectrophotometric and other chemical means. The interest in coal as a possible source of germanium was the reason for so many determinations being made from 1934 to 1959 on coals from several countries.[28] A spectrophotometric method of analysis was commonly used in which the germanium was measured as a complex with phenylfluorone.[81]

Determinations of phosphorus, manganese, and titanium are often done as part of the analysis of coal ash for major elements, the measurements being done spectrophotometrically.[82] The standard method for chlorine involves oxidation, e.g., by heating coal with Eschka mixture (1:2 anhydrous sodium carbonate plus magnesium oxide) and determining the extracted chloride by Volhard titration or potentiometrically.[83]

Arsenic may be determined spectrophotometrically (molybdenum blue coloration) after oxidizing the coal either by wet digestion or by heating in a stream of oxygen (coal mixed with 1:1 magnesium oxide plus potassium permanganate).[84] However, this method is not suitable for determining arsenic at the 1 ppm or lower levels which are found with some coals (Table 2). Phosphorus is generally determined spectrophotometrically using the yellow molybdovanadophosphate complex or the molybdenum blue complex. At the concentrations commonly found in coals, spectrophotometric methods are suitable for chlorine and phosphorus.

The determination of fluorine in coal with up to 25% ash yield is usually carried out by the oxygen bomb-ion selective electrode method.[85,86] However, current investigations of Australian coals are showing that there is a tendency for this method to give slightly lower results for some coals than a pyrohydrolysis method.[87] At this stage it would seem to be warranted to assume that the bomb method does not release all the fluorine from the coal.[88] Hence, it has been suggested that the ASTM method (oxygen bomb) should be withdrawn.[87] Boron is sometimes determined spectrophotometrically by the carminic acid complex, after ashing the coal with sodium carbonate and extracting with water and sulfuric acid.[89]

2. Optical Emission Spectroscopy (OES)

Initially, most of the data for trace elements in coals were from optical emission analyses, often done spectrographically (semiquantitative)[28,90] and sometimes spectrometrically (quantitative).[26] Although the U.S. National Bureau of Standards does not accept OES as a reference method,[74] there is still a place for these methods (semiquantitative and quantitative) for determining trace elements in coal. For example, the ranges of concentrations for about 30 trace elements in representative Australian bituminous coals were established about 20 years ago by analyzing several hundred samples from most seams by optical emission spectrographic methods (semiquantitative).[28] Recent quantitative determinations by other methods have shown little, if any, deviations from these ranges.[36] Optical emission techniques are still used by the U.S. Geological Survey[27] and by the Illinois State Geological Survey[26,91] for determining some trace elements in coal. All these OES methods used coal ash, often prepared at about 800°C. Although this temperature is suitable for several elements, it is probably better to ash at 450 to 500°C. Details have been given of semiquantitative OES techniques[28,92,93] that are still relevant for ashes prepared from most coals except brown coals and some low-ash lignites. In order to minimize spluttering during arcing, it is advisable to dry the coal ash, graphite powder, and spectroscopic buffers in an air oven at about 110°C prior to mixing and filling electrodes, and to keep the filled electrodes in the oven until they are to be arced.[55] A steady discharge during direct current excitation with the sample in graphite as anode is aided by having a carbon cathode, thereby increasing the arc temperature.[94] In general, these methods are still most useful for gaining ball-park values for a wide range of elements in coals, and it could be argued that there is merit in having a large number of semiquantitative results rather than a few quantitative results. Semiquantitative information is also useful before carrying out quantitative determinations.

An improved excitation source, i.e., the inductively coupled plasma, is being used in an emission spectrometric method (ICPAES) which is applicable to trace elements in coal. Tests on coals from U.S.[95] gave good results for 12 trace elements in solutions made by dissolving coal ash in a mixture of aqua regia plus hydrofluoric acid in a Parr acid-digestion bomb, with a final addition of boric acid to react with insoluble fluorides and to mask excess fluoride, thereby allowing the use of a glass nebulizer system. The Parr bomb is similar to the original design of Bernas.[96] For ICPAES, the trace elements are generally in solution, which is usually prepared from ash. The high temperatures reached in the plasma may enable solids to be atomized directly,[97] e.g., perhaps a slurry could be used,[98] although this could cause trace element variations in the plasma. Among the factors that should be taken into account when using ICPAES are restricting the total solids content to about 1% in solution, running the plasma long enough for stabilization, say about 1.5 hr, and strict control of the flow rate of argon (sample and coolant) and of the power into the plasma. The introduction of the sample solution into the plasma is important and depends on a properly designed nebulizer and flow system. Improvements in the efficiency of transferring the sample to the plasma, currently only a few percent, would improve the sensitivity. Another approach is the use of the direct current argon plasma and a spectrometer with a high dispersion echelle grating. This technique was used with solutions prepared by fusing coal ash with lithium metaborate, followed by dissolution in 4% nitric acid, and adequate results were obtained for barium, chromium, copper, strontium, vanadium, and zirconium.[99]

There is still a place for spectrographic analysis (semiquantitative) of coal ash, mainly to establish the ranges of values and thereby to check for coals with trace element contents outside these ranges. These estimates also provide useful information prior to setting up the more exotic methods, e.g., ICPAES, NAA, and SSMS (spark source mass spectrometry). Modern developments of ICPAES are establishing this method for trace elements in coal, currently using solutions prepared from coal ash, but possibly in the future using coal slurries. It was stated in 1980 that "a similar atmosphere prevails at symposia on the inductively coupled plasma"[100] as there was with AAS during the period of 1962 to 1969, described as "one of explosive growth."[100] Hence, it is reasonable to regard ICPAES as not yet matching the maturity of AAS, but further research should bridge the gap.

3. Atomic Absorption Spectrometry (AAS)

There is a good review of the applications of AAS and other atomic spectroscopic methods for analyzing coal and related materials.[66] The use of AAS for trace elements in coal dates from the early 1960s[101,102] and it is now widely accepted as a good, relatively cheap method which is amenable to a high throughput of samples, although it does not have the simultaneous multielement capability of ICPAES, NAA, or SSMS.

However, the potential for simultaneous multielement AAS has been investigated using a continuum source and a dedicated microcomputer,[103] and this would be most useful even for a limited number of trace elements in coal, say 6. An imprimatur for AAS was given recently, namely, "the best analytical method has the best selectivity and precision coupled with high sensitivity, permitting the determination of a large number of species. The instrument required should be cheap to buy and easy and inexpensive to operate. Such an ideal method does not exist, but AAS has characteristics pointing in this direction."[104]

The two main atomic absorption methods, using solutions, are flame atomic absorption and furnace atomic absorption, the latter being the more sensitive. Several approaches have been used for preparing solutions from coal ash, preferably made at 450 to 500°C, although 800°C is suitable for some elements. In the ASTM Standard Test Method[56] for determining beryllium, chromium, copper, manganese, nickel, lead, vanadium, and zinc in coal ash, the 500°C ash is treated with aqua regia and hydrofluoric acid in a plastic bottle (e.g., polypropylene[88]) with a screw top at steam-bath temperature. The trace elements are determined by flame atomic absorption procedures. Solutions may also be obtained by fusing coal ash with lithium metaborate followed by dissolution in nitric acid[105] or by treating coal plus nitric acid in a Parr oxygen bomb which may be fitted with a quartz liner to minimize contamination.[106] Brown coals may be digested with nitric acid, followed by hydrogen peroxide to give solutions suitable for flame AAS.[107] For some elements that form gaseous hydrides, e.g., arsenic, antimony, and selenium, the hydrides may be formed and passed into the flame of an AAS[108] or into a heated quartz tube. A special method is used for mercury, namely, flameless cold vapor AAS.[109] Electrodeless discharge lamps are brighter than hollow cathode lamps and are particularly effective for the more volatile elements. Their increased stability leads to improvements in sensitivity.

The increased sensitivity for many elements with graphite-furnace AAS, compared with flame AAS and, indeed, with most other methods, makes this an attractive method for determining those trace elements that are often at very low concentrations in coals, e.g., arsenic,[58] antimony,[58] cadmium,[110] and selenium. A comprehensive review of the analysis of atmospheric particulates by graphite-furnace AAS[111] is relevant to coal, in particular those aspects concerning interference effects and detection limits. Progress has been made with the use of direct analysis using powdered coal.[65,112] It is essential to control the analytical conditions in order to minimize interferences from the coaly matter.[65] It has been shown[65] that 1 to 5 mg of powdered coal ground to −75 μm can be analyzed directly by graphite-furnace AAS to give results with a precision better than about ±10% of the amount present (often around 1 ppm).[87] Although there is some loss in sensitivity, coal slurries have been used to introduce powdered coal into the flame for AAS.[64] Attention to sample preparation, especially the grinding, is important. This approach merits further investigation, as it may be useful for getting trace element results of sufficient precision for some purposes and quickly.

It has been pointed out that modern instrumentation for AAS using microprocessors should not be accepted uncritically, e.g., single-point calibration is poor practice.[100] As O'Keefe stated: "If all the customer wants is a number, sell him a random number generator. If he wants the correct number, show him how to get it."[113] A recent statement summarizes the status of AAS well: "while one still looks over one's shoulder at the ICP, the basic simplicity of AA and hence, low cost, coupled with the power of electrothermal atomization are yet to be matched by the ICP."[114]

Although AAS requires a solution to be prepared from the coal or ash and elements are usually determined singly, it is still a very sensitive method, especially the graphite-furnace technique. For laboratories that do not have NAA, XRF, or SSMS facilities, AAS is probably the most-used method and less costly than the other approaches.

4. Neutron Activation Analysis (NAA)

During the past decade there has been much work done on the development of NAA methods suitable for whole coal and related materials.[72,115-123] Instrumental NAA (INAA) has high precision and accuracy, low detection limits for most trace elements, and the minimum handling of samples keeps contamination low. Access to a nuclear reactor is required in order to achieve the high neutron flux commensurate with high sensitivity (ranging from 10 to 100 fg to 1 to 10 ng[124]). Data on 30 to 40 trace elements in coal can be obtained. Pure metals or chemical compounds may be used as standards, but nowadays it would seem preferable to use well-certified reference standards,[125,126] thereby improving the accuracy of the results.[126] INAA was used to determine the trace element contents of the NBS reference standards (coal SRM 1632 and fly ash SRM 1633) by four laboratories in the U.S.[72] There was good agreement between the results from these laboratories and those from the NBS for most trace elements, thereby establishing the viability of INAA as a precise and accurate method. Further confirmation was obtained by analyses in another U.S. laboratory of SRM 1632a (coal) by INAA for 32 trace elements,[127] the results agreeing well with published results.[73]

There are good accounts of NAA and its use for coal analysis.[116,123,124] At each of the three main stages in INAA, i.e., irradiation, counting, and computerized data acquisition, care must be taken to avoid errors. However, research over the years has overcome most of these, but it is clear that all NAA methods require special facilities and experience. Nowadays, improvements in gamma-ray detectors, e.g., the use of lithium-drifted germanium Ge(Li) crystals instead of the NaI(Tl) detectors, have made it possible to determine 30 to 40 trace elements in coal simultaneously, the counting statistics being generally ±5% or less.[123] For low concentrations of some trace elements, e.g., mercury, arsenic, cadmium, and selenium, radiochemical separation techniques have been used with NAA, but the advent of the Ge(Li) detector has removed the need for radiochemical separation of most trace elements in coal.

Some measure of the role of NAA in the analysis of coal for trace elements is given by a summary of the methods used for the three coal and two fly ash NBS SRMs; between 61 and 100% of results published before 1980 were obtained by NAA methods.[128] However, because of the cost and specialized nature of NAA, it has not been used much outside research laboratories. It is best suited for large numbers of samples, where the throughput lowers the cost per sample. As with most, if not all, methods there are some trace elements not amenable to NAA, e.g., beryllium, boron, cadmium, and fluorine, while copper, lead, mercury, and thallium are not always determined. Special methods have been developed for boron and cadmium (neutron-capture prompt gamma-ray activation analysis[73]) and for fluorine. A special technique involving NAA and a separation procedure has been developed for low concentrations of selenium, arsenic, zinc, cadmium, and mercury in coal and other organic materials.[129] There is no doubt that NAA methods are most useful for the determination of about 30 trace elements in coal simultaneously. Under proper conditions the results should be more than precise and accurate enough for most purposes.

5. X-Ray Fluorescence Spectrometry (XRF)

X-ray fluorescence may be used directly with coal or coal ash. For trace element determinations, it is better to use whole coal, thereby avoiding possible losses during ashing (e.g., Cl, Br, I, Se). The limits of detection for several elements, including some of environmental interest, are around 1 ppm.[30,130] XRF was used to determine major elements and chlorine in Victorian brown coal,[131] and in U.S. coals, mainly from the Illinois Basin.[24,132] Results for the U.S. (Illinois) coals showed that the method was also very good for 10 trace elements. Sample preparation consisted of grinding whole coal with 10% of a binding material and then pressing into a disk at 275 MPa (40,000 psi).

The disk was dried in a vacuum oven to avoid losses by volatilization, and the trace elements were measured by XRF again in a vacuum so that there was no scattering of X-rays due to adsorption of water on the surface of the disk.[24] Precision can be improved by grinding the coal to −45 μm, but in practice -75 μm is sufficient using 1 to 2 g of whole coal.[24] Refinements have extended XRF to cover about 55 trace elements in coal.[130] Again the ground coal (-75 μm) was mixed with a binder and 6 g of the mixture was briquetted. Due to the lack of suitable standard materials, several synthetic standards were prepared from spectrographically pure compounds and briquetting graphite. Great care is needed in the preparation of these standards[133] which are vital to the success of the method. Using the recommended instrumental procedure with a sequential spectrometer, including matrix absorption corrections for variations in ash yield and sulfur content, good results were obtained for three coal SRMs.[130] Results for Australian coals[134] showed that the ranges of values agreed well with those determined by other methods.[8]

A thorough investigation of trace elements in South African coals has shown that "the quality of the data depends critically on the accuracy of the mass absorption coefficients and the accuracy with which the background and line overlap corrections can be calculated".[135] Some problems with obtaining accurate corrections for very low-ash coals, where the mass absorption coefficients are very low, say less than about 1.3 for MoKα radiation, are being sorted out.[136] Results for trace elements in South African coals determined by an XRF spectrometric method agree well with those determined by INAA.[137]

The above discussion has dealt only with wavelength-dispersive XRF (diffraction by crystals to separate X-rays from excited samples, then dispersion by goniometer and measurement by detector), but energy-dispersive XRF can also be used (solid-state detector in conjunction with a multichannel analyzer). The main differences are the better precision with wavelength-dispersive XRF, and the lower cost of energy-dispersive XRF.[65] For some purposes, energy-dispersive XRF may be useful, as has been shown[138] for some samples of coal fly ash and rocks and for coals from British Columbia, where the data was useful in correlating seams from different locations.[139] Another use of energy-dispersive XRF was with trace elements on cation-exchange resin filters.[140] The coal sample was treated with mixed acids to dissolve the sample completely, diluted, and filtered to concentrate the trace elements on the filter. Care must be taken to avoid overloading the resin. For five trace elements that were determined the precision was within ±10%.

Another X-ray method (PIXE) involves excitation by protons to yield X-rays characteristic of most trace elements. The coal sample is ground very fine (at least to −20 μm) and 3 mg is placed on thin plastic which is the target for a proton beam.[141] Limits of detection vary from 1 to 2 ppm up to about 10 ppm, e.g., one Indiana coal had 4.7 ± 1 ppm As, 1.5 ± 0.25 ppm Se, and 2.8 ± 0.7 ppm U.[142] PIXE is a rapid, simultaneous, multielement method which can be used for trace elements in coal, but the cost of the equipment is very high. A modification of PIXE using a fine beam (PIXE microprobe) has been used to determine the concentrations of trace elements associated with the organic constituents in coal (vitrinite, exinite, inertinite).[143] However, this method, like transmission electron microscopy and scanning electron microscopy, is best suited for investigating minerals in coal and the distribution of trace elements in microsections of coal, rather than for bulk analysis.

XRF, particularly in the wavelength-dispersive form, is a good method for determining several trace elements in coals. The instrument must be kept in optimum condition, as with other instrumental methods, and synthetic calibration standards must be properly prepared.[144] There is a standard for determining the precision of wavelength-dispersive XRF spectrometers.[145] Methods using several background corrections are not readily applicable to multichannel spectrometers, but ways of overcoming this limitation and of even using no background measurements are being investigated.[146] One cannot expect one method to be suitable for determining all trace elements in coal or, indeed, all those of environmental interest. In the case of XRF, cadmium, mercury, and thallium are below the limits of detection for most coals and fluorine ($C_L = 50$ ppm) and antimony ($C_L = 1$ ppm) are only marginally useful, but some others of geochemical, but not of environmental, significance (e.g., rare earths) are useful. Boron and beryllium, being of low atomic numbers, are not detected.

6. Spark Source Mass Spectrometry (SSMS)

Recent developments in mass spectrometry using spark source or thermal ionization techniques have increased its usefulness for determining trace elements in coal and related materials. For high precision work, say, around ±1%, thermal ionization is preferable, but for the analysis of coal for a large number of elements simultaneously, the spark source technique is normally used.[147,148] Basic information on SSMS indicates that more than 30 elements can be determined simultaneously with detection limits down to about 0.02 ppm or better with good precision and accuracy, say about ±10%, for sample weights of 5 to 10 mg. There are good reviews of SSMS[149,150] giving useful basic information on the analytical capability of the method, the detection limits, precision, accuracy, and instrumentation factors. The versatility of the method has been increased and the time of analysis decreased by the use of electrical detector systems, instead of photoplates, and by computerized data handling. Details have been given[151] for the determination of trace elements in coals by SSMS, either semiquantitatively or quantitatively. Although an early semiquantitative method used an electrode made from raw coal plus graphite (1:1),[152] coal ash mixed with pure graphite is normally briquetted to form a suitable electrode for the spark source.

Improvements in precision and accuracy can be achieved by using isotope dilution SSMS. Although solutions are usually used, a dry powder technique has been used with coal. A mixture of stable isotopes (spikes) in pure graphite or silver powder is added to ground coal ash and equilibrated chemically or thermally. It is assumed that the isotopes from the spike and the sample behave identically in the ion source of the mass spectrometer. Although formerly thermal ionization was preferred, spark source may be used also.

There is no doubt that SSMS is a very sensitive method for trace elements which may be determined semiquantitatively or quantitatively with acceptable precision and accuracy. However, the instrumentation is costly, and the proper operation requires a specialist staff, a proviso that applies also to some other instrumental methods. It has been stated that "high accuracy and low detection limits are in every case only achievable by painstaking measurements".[149]

7. Other Methods

The methods that have been discussed above are those that have been used to analyze relatively large numbers of samples for several trace elements, often simultaneously. For example, all the data in Table 2 were obtained by OES, AAS, NAA, XRF, and chemical methods (usually only for fluorine, chlorine, and phosphorus). Sometimes, other methods were used for some trace elements, but these were not versatile enough for multielement determinations and will not be considered in detail. Among other methods are polarography, anodic stripping voltametry, electron microscopy (scanning with XRF attachment), electrochemistry, and gas chromatography coupled with MS. Where a laboratory is set up for such methods, it may then be convenient to use them for analyzing coals for certain trace elements.

D. Results

The statement of results is the product of much work and the value of the results depends on the quality of sampling and analysis. Hence, the statement of the results should be made on the basis of good sampling and good analysis and information should be given to permit the user to assess the value of the results for his purposes. If semiquantitative results are sufficient for a particular purpose, then this should be made clear in the statement of results, in order to avoid a seeming increase in accuracy when the results are used for another purpose or transcribed. In general, trace element contents are given as parts per million (ppm), which is in modern parlance $\mu g\ g^{-1}$, expressed as the element, not as the oxide or other compound. For most purposes, it is sufficient to refer to air-dried coal or to dry coal (105 to 110°C) or sometimes even to as-received coal. If an element has not been detected, then a value of zero should not be assigned, but rather a value of less than the limit of detection.

The analytical chemist usually determines the precision of his method, i.e., the measure of the reproducibility of the method. By analyzing a sample a suitable number of times, a range of values is obtained and the deviation from the mean can be ascertained and this is the extent of the random errors. However, it is also desirable to know the accuracy of results, i.e., the closeness to the true value. Accuracy is a measure of the systematic and random errors which are inherent in any determination. Accurate results should be the aim, especially when results have to be compared with data from elsewhere. The attainment of accuracy depends on the availability of good standard reference materials and relevant information for coal is given in Section IV.B. Basic information on precision and accuracy shows how results may be stated realistically.[153,154] There are several ways of improving analytical quality assurance[155] (a measure of the validity of analytical work), e.g., by stating the precision and accuracy claimed and by giving basic information on sampling and method of analysis.

Some idea of the precision that can be attained under what may be termed ideal conditions can be seen in the certified values for the two bituminous coal standard samples, NBS SRM 1632 and 1632a (Table 5). These coal samples have been analyzed in other laboratories and examples of their results are also given. In general, the agreements are satisfactory, and the precisions for a particular element are similar. Although the precision may be better than ±10% of the value for some elements, this would seem to be difficult to surpass for most elements.

It is important to state results in a way that is meaningful for the user, rather than just for other chemists. Various statistical operations may be carried out on the data in order to obtain the standard deviation, the relative standard deviation, the coefficient of variation, or other measure of precision or accuracy. However, trace element contents in coal may be stated simply as a range of values, for particular seams, locations, geological areas (e.g., a coal basin) or geographical areas. This enables the user to ascertain the variability of results for various trace elements and the presence of abnormal, especially high, results. Examples of the usefulness of ranges can be seen in Table 2, where it is clear that cadmium is lower in Australian coals than in those from other continents, while thallium is rarely above a few ppm in any coals. A useful approach is to give the range for about 90% of values (Table 3). Sometimes mean values are useful for comparing results and the mean for 90% of values is a way of avoiding the bias from the too low and too high values. An estimate of the most probable concentration (mode) can be calculated and is designated as the geometric mean (GM). Variations from GM can be calculated to give the geometric deviation (GD — antilog of standard deviation of logarithms of concentration). Since the data for trace elements in coals have a common tendency to show positively skewed frequency distributions, the use of the GM and GD is a valid means of normalizing the data, as is done by the U.S. Geological Survey.[25,27] Results that are given as zero, surely a meaningless value,

Table 5
REPORTED VALUES FOR NBS COAL STANDARD REFERENCE MATERIAL (AS PPM IN DRIED COAL)

	SRM 1632		SRM 1632a	
Element	NBS[•]	Steinnes[122]	NBS[•]	Germani et al.[73]
As	5.9 ± 0.6	6.3 ± 0.2	9.3 ± 1.0	10.2 ± 0.5
B				53 ± 2
Be	(1.5)			
Cd	0.19 ± 0.03		0.17 ± 0.02	0.21 ± 0.03
Cl		844 ± 37		790 ± 20
Co	(6)	5.70 ± 0.12	(6.8)	6.5 ± 0.2
Cr	20.2 ± 0.5	20.8 ± 0.8	34.4 ± 1.5	34 ± 2
Cu	18 ± 2	15.0 ± 1.2	16.5 ± 1.0	
Hg	0.12 ± 0.02		0.13 ± 0.03	
Mn	40 ± 3	41 ± 4	28 ± 2	32 ± 3
Mo		3.1 ± 0.1		
Ni	15 ± 1	16	19.4 ± 1.0	26 ± 4
Pb	30 ± 9		12.4 ± 0.6	15 ± 4
Sb			(0.6)	0.60 ± 0.09
Se	2.9 ± 0.3	3.0 ± 0.3	2.6 ± 0.7	2.6 ± 0.3
Th	(3.0)	3.12 ± 0.10	4.5 ± 0.1	4.8 ± 0.2
Tl	0.59 ± 0.03			
U	1.4 ± 0.1	1.46 ± 0.02	1.28 ± 0.02	1.2 ± 0.1
V	35 ± 3	35.0 ± 2.9	44 ± 3	44 ± 3
Zn	37 ± 4	39 ± 6	28 ± 2	31 ± 6

[•] Values in parentheses are "for information only".

or better as less than the limit of detection, must be taken into account when calculating mean values. Sometimes it is sufficient to treat such values as half the limit of detection, but it is preferable to use procedures that have been developed to minimize bias in estimating mean values.[156] Properly calculated mean values (GM or arithmetic mean for 90% of values) are a useful way of comparing trace element contents.

In general, for trace elements in a heterogeneous material like coal, an accuracy of ±10% of the amount present is surely acceptable, especially at ppm and sub-ppm levels. The precision may well be better than this. It is sobering to consider what may be termed the "Horwitz trumpet",[157] which is a plot of the coefficient of variation against concentration for the range 10^{-1} to 10^{-12}; at the ppm level the coefficient of variation is about ±15% increasing to about ±45% at the ppb level. However, not all trace element determinations have such poor precision. The advice of G. Ampt many years ago is still apposite: "Be as accurate as you may; define the accuracy you have achieved; your conclusion will need no further support."[155]

V. COMMENTS ON METHODS FOR SPECIFIC ELEMENTS

Some detailed comments on the 22 trace elements of environmental interest will be given as an aid to choosing a suitable method for a few or several elements. An overall assessment of methods is given in Table 6 where X means suitable for most coals, O means unsuitable or limited by sensitivity or interference, and a blank means unsuitable. These suggestions are based mainly on multielement methods, but, if necessary, for a particular element chemical methods are available and sometimes special techniques may be used, as shown under Others. Comments for ICPAES are similar to those for OES. For each of the methods it is often possible to improve sensitivity or

Table 6

SUITABLE METHODS FOR DETERMINING TRACE ELEMENTS IN BITUMINOUS COALS

Trace element	OES	AAS	INAA	XRF	SSMS	CHEM	Others
As	O	X	X	X	X•	X	
B	X				X	X	X Prompt gamma-ray INAA
Be	X	X			X		X Fluorimetry
Cd	O	X		O	X		X Anodic stripping voltametry
Cl			X	X		X	
Co	X	X	X	X	X•		
Cr	X	X	X	X	X•		
Cu	X	X	O	X	X		
F					X		
Hg		X	O		X		
Mn	X	X	X	X	X		
Mo	X	X	O	X	X		
Ni	X	X	O	X	X•		
Pb	X	X		X	X		
Sb	O	X	X	O	X		
Se		X	X	O	X		
Sn	X	X	X	X	X		
Th			X	X	X		
Tl	X	X			X		
U			X	X	X		X Fluorimetry
V	X	X	X	X	X		
Zn	X	X	X	X	X		

Note: X, suitable for most coals; O, unsuitable or limited by sensitivity or interference; blank, unsuitable.

• Possible interference from molecular ions.[149]

correct for interferences by using special techniques. No method will cope with all the elements simultaneously, although SSMS almost does this.

In the discussion of methods for specific trace elements, pertinent comments will be made on suitable methods, based mainly on published data. For example, SSMS was not used to obtain any of the results given in Table 2 and hence it will not be regarded as a primary or specially recommended method, although it may well be such in a laboratory where it is used widely.

A. Arsenic

Arsenic in coal may be determined by OES, AAS, INAA, XRF, SSMS, and by chemical methods, the main need being to cover the range 0.1 to 10 ppm, although some coals have higher contents (more than 150 ppm). Perhaps the most satisfactory methods are AAS, INAA, and XRF. For most coals OES methods are not sensitive enough for As. It has been found with AAS that the As line at 193.7 nm is affected by spectral interference from aluminum probably Al^{2+} and Al^{+} ions which absorb at this wavelength.[158] However, arsenic can be determined by graphite-furnace AAS using the resonance line at 197.2 nm.[158] Arsenic has also been determined by hydride generation-AAS.[98] Some standard methods use a spectrophotometric determination based on the molybdenum blue coloration.[84] However, this method tends to give unreliable results at concentrations around a few ppm[58] and is unsatisfactory at less than 1 ppm As.

B. Boron

The most suitable method for determining boron in coal is probably OES (on ash), while ICPAES is also useful. Other methods are SSMS, prompt gamma-ray INAA,[159] and a spectrophotometric technique using a carminic acid complex.[89] In order to compensate for matrix effects in OES (direct current arc), a graphite-lithium fluoride buffer has been used together with germanium dioxide, the germanium being a good internal standard for boron, as shown by their almost parallel evolution curves (line intensity vs. time).[160] It is also advisable to correct for interference from SiO band emission in the 250-nm region. Another OES method uses high voltage spark emission from a briquette made from a mixture of coal ash, graphite powder, copper oxide (internal standard), and cellulose powder. Correction is made for interferences from SiO and from iron.[134]

There are conflicting reports on the volatility of boron during the ashing of coal. However, bituminous coals ashed in covered crucibles at 500 to 700°C should give ashes which retain the boron from the whole coal.[57] It is advisable to check the retention of boron for particular coals and ashing conditions. The determination of boron in whole coal may be carried out by burning the coal in an oxygen bomb, similar to that used for determining the specific energy of coal, dissolving the residue, and determining the boron by ICPAES.[63]

C. Beryllium

Beryllium may be determined in coal ash by OES, AAS, SSMS, and fluorimetric methods. An early survey of beryllium in 1385 coals from the U.S. was carried out spectrochemically on coal ash using the lines at 234.9 nm (for concentrations around 1 ppm) and 313.1 nm (for concentrations above 10 ppm in ash).[161] Graphite-furnace AAS was used to determine beryllium in the standard coal SRM 1632, using 0.3 to 2 mg of coal, the result being 1.52 ± 0.11 ppm Be.[77] This shows that good precision can be achieved with low sample weight, and it is also evidence of very good homogeneity of the sample. There is a standard method[56] for beryllium in coal. The sample of whole coal (-150 μm) is ashed at 500°C, and approximately 0.2 g of ash is treated with aqua regia and hydrofluoric acid in a plastic bottle (with a screw cap) on a steam bath. Saturated boric acid solution is added to complex fluoride. Finally, the determination is carried out by an AAS procedure using a nitrous oxide-acetylene flame and background correction on the beryllium line at 234.9 nm. The repeatability (results of two determinations under exactly the same conditions in one laboratory) should be 0.2 ppm for the range 0.5 to 5 ppm Be, and the reproducibility (means of 2 determinations carried out in different laboratories) should be 0.5 ppm. A similar approach is being considered for endorsement as an International Organization for Standardization (ISO) standard method.

D. Cadmium

Cadmium can be determined satisfactorily in coal ash by AAS and SSMS, but OES and XRF are limited to higher concentrations than the usual few ppm or less found in coals. The high sensitivity of anodic-stripping voltametry would cope with sub-ppm concentrations found in some coals. However, the most suitable method is graphite-furnace AAS,[24] using a solution made from coal ash (450°C) treated with aqua regia then hydrofluoric acid in a Teflon® capsule in a bomb at 110°C. This method has been used to determine cadmium in Australian coals with 0.01 to 0.20 ppm Cd with good accuracy and precision.[110]

E. Chlorine

The usual method of determining chlorine in coal is a chemical one, although INAA and XRF are also suitable. The American National Standard method[83] is similar to that endorsed by the British Standards Institution and by the Standards Association of Australia. This method involves heating a sample of coal with Eschka mixture (1:2

anhydrous sodium carbonate plus magnesium oxide) either in an oxidizing atmosphere or in a bomb with oxygen and ammonium carbonate solution. The chloride extracted from the residue or already in solution in ammonium carbonate is determined by a modified Volhard titrimetric method or by potentiometric titration. The limit of detection is about 100 ppm Cl, but this is sufficient for most coals, although the mean for Australian coals is about 150 ppm Cl.[8] A variation of this standard method involves burning a sample of coal in oxygen at 1350°C, absorbing the gases in neutral hydrogen peroxide, neutralizing the solution with sodium borate, and determining the chloride by titrating sodium hydroxide formed by adding mercuric oxycyanide. Another method uses combustion of coal in an oxygen bomb followed by washing out the bomb with water and finally determining chloride with an ion-selective electrode.[63] The determination of chloride ions by an ion chromatographic method, which has been used for geological[162] and other samples, would surely be applicable to the bomb washings from the burning of coal, the high sensitivity being an advantage if low concentrations (less than 50 ppm) were of interest.

F. Cobalt

Cobalt can be determined satisfactorily in coal by OES, AAS, INAA, XRF, and SSMS. The sensitivity of flame AAS is not sufficient for coals with low concentrations (around 1 ppm), but these coals would be amenable to graphite-furnace AAS. Most of the data for cobalt in Table 2 were obtained by OES, INAA, or XRF.

G. Chromium

Chromium can be determined well by OES, AAS, INAA, XRF, or SSMS. Most of the data in Table 2 were obtained by OES, INAA, or XRF. However, the American National Standard method is flame AAS.[56] Whole coal (−150 μm) is ashed at 500°C and the resulting ash is treated with aqua regia and hydrofluoric acid in a sealed plastic bottle on a steam bath. After the addition of saturated boric acid solution to complex fluoride, chromium is determined by AAS using a nitrous oxide-acetylene flame and the line at 357.9 nm with background correction. The repeatability is 3 ppm Cr for the range 5 to 50 ppm and the reproducibility for the same range is 5 ppm. For very low concentrations, say around 1 ppm Cr, it may be advisable to use a graphite-furnace AAS method, thereby gaining sensitivity and precision.

H. Copper

Suitable methods for determining copper in coal are OES, AAS, XRF, and SSMS. Most of the data for copper in Table 2 was obtained by OES, AAS, and XRF. The American National Standard method is flame AAS.[56] Ash prepared from whole coal (−150 μm) at 500°C is treated as outlined for chromium (Section V.G) and copper is determined in the solution by AAS using the line at 324.8 nm with background correction in an air-acetylene flame. The repeatability is 2 ppm Cu for the range 5 to 50 ppm and the reproducibility for the same range is 3 ppm. This method can be used for most coals.

I. Fluorine

Fluorine is not easy to determine in coal and it is not amenable to the multielement methods OES, INAA, and XRF or to AAS. It can be done by SSMS, but the usual method is chemical. Early work on fluorine in coal was based on either combustion in a bomb or fusion with sodium carbonate, the released fluorine being estimated colorimetrically by a bleaching effect on a zirconium-alizarin complex or a thorium-alizarin complex,[163] the latter being a more stable reagent than the former. An improvement[164] was the measurement of the blue color formed by fluoride ions with the complex formed by alizarin complexan and cerous nitrate.[165]

There is an American National Standard method[86] which is based on a method developed at the Illinois Geological Survey.[85] This involves burning coal in an oxygen bomb with a dilute base (1*N* NaOH), the resulting solution being buffered and the fluoride determined by ion-selective electrode. The repeatability is 15 ppm F (calculated for results in the range 25 to 100 ppm) and the reproducibility is also 15 ppm. This method has been tested on coals with up to 25% ash yield. Another approach is to fuse the coal with sodium carbonate, care being taken to avoid losses of volatile fluorine compounds. At present, there are several investigations of a pyrohydrolysis method which is based on techniques used to determine fluorine in rocks, iron ores, and the like. Whole coal (−75 μm) is mixed with a catalyst, and heated in a stream of oxygen at about 1000°C and then in a stream of oxygen plus steam to release all the fluorine into the gaseous phase. The gases are passed into an alkaline solution and the fluoride is determined by an ion-selective electrode. Fluoride may also be determined by an ion chromatographic technique.[162] The heating has been carried out in a tube furnace and also in an induction furnace.[166] After an investigation of fluorine in coals with ash yields in the range 1.6 to 33.2% using three methods, i.e., alkaline fusion, oxygen bomb combustion, and pyrohydrolysis in a tube furnace, it was concluded that pyrohydrolysis was to be preferred because of its simplicity, speed, and precision.[87] There was a tendency for the oxygen bomb combustion method (ASTM) to give lower results than the pyrohydrolysis method.[87] It seems to be warranted to assume that this means that all the fluorine in the coal is not released in the bomb method. Perhaps there is a loss of fluorine as an aerosol after the pressure is released in the bomb. On the other hand, there is a possibility that fluorine in coal in a form other than fluorapatite may not be released during combustion in the bomb, whereas it could be released at the higher temperature of the pyrohydrolysis. The current investigations of Australian coals should give answers to these questions.

It is clear that the determination of fluorine in coal is still not settled, at least if results are to be better than ±10 or 15% relative at about the 100 ppm F level. At this stage, it would be unwise to displace the bomb combustion method (ASTM), although further research may show that the pyrohydrolysis method is to be preferred. The lack of other suitable comparative methods and of standard coal samples with stated fluorine values make the task even more difficult.

J. Mercury

Mercury in coal is very volatile and is lost even during low temperature ashing (so-called oxygen plasma technique) and hence the determination must be carried out on whole coal. Care must be taken to avoid contamination during sampling and analysis, keeping in mind that many coals have <1 ppm Hg. Although mercury can be well determined by special NAA methods and by SSMS, it is usually determined by an AAS method. Surveys of mercury in Illinois coals[24] and in Australian coals[167] were carried out by special NAA methods. To avoid losses the coal samples were ground by hand and air dried before irradiation. After chemical separation, counting was carried out by gamma-ray spectrometry. In each case the lowest value was 0.03 ppm Hg and the precision was very good.

Currently, most mercury determinations in coal are done by a flameless cold-vapor AAS method, using the line at 253.7 nm. There are several variations of this approach,[168] one being the American National Standard method,[109] which uses combustion of the coal sample in an oxygen bomb containing dilute nitric acid to absorb the mercury. The bomb washings are heated with potassium permanganate solution, then hydroxylamine hydrochloride solution, and reduction is then carried out with stannous chloride solution, the evolved mercury being measured by a flameless cold-vapor AAS method. For the range 0.05 to 0.20 ppm Hg, the repeatability should be 0.019 ppm and the reproducibility 0.031 ppm. A good alternative method has been developed,[168] after an investigation of several approaches, including oxygen bomb combustion for releasing mercury from coal. This method uses high temperature combustion at 1350°C in a tube furnace, similar to that used in the determination of carbon and hydrogen in coal.[169] After treatment of the effluent gases and reduction by stannous chloride solution under carefully controlled conditions, the mercury was determined by cold-vapor AAS. Another approach[170] is to free the mercury from coal by nonoxidative pyrolysis in nitrogen at 800°C and finally to determine mercury by atomic fluorescence spectrometry (AFS) with a gas-shielded atom cell. Although better sensitivity was achieved by AFS, the widely used cold-vapor AAS method is satisfactory.

The determination of mercury in coal, usually in concentrations of less than 1 ppm Hg, depends on special care in avoiding contamination during sampling and analysis and to attention to detail in the procedures prior to determining the mercury by flameless cold-vapor AAS. Although bomb combustion has been used successfully to release mercury from coal, there are advantages in using high temperature combustion (1350°C or somewhat lower) to release mercury from coal. It has been recommended that subsamples for mercury determinations should be taken as soon as the laboratory analysis sample is opened in the laboratory,[87] thereby minimizing contamination and volatilization.

K. Manganese

Manganese is readily determined in coal by OES, AAS, INAA, XRF, and SSMS. The American National Standard method[56] uses AAS with an air-acetylene flame and the line at 279.5 nm with background correction. Coal ashed at 500°C is treated as outlined under chromium (Section V.G). The repeatability is 3 ppm Mn for the range 10 to 300 ppm and the reproducibility is 6 ppm for values less than 50 and 20 ppm for the range 50 to 500 ppm. This method is suitable for most coals.

L. Molybdenum

Molybdenum can be determined in coals by OES, AAS, XRF, and SSMS, but the sensitivity of XRF limits this method to concentrations above 1 to 2 ppm Mo. It is usually necessary to use graphite-furnace AAS because of the limitations of sensitivity with flame AAS. Most of the published data for coals from the U.S. and Australia were obtained by OES methods. Iron interference on the molybdenum line at 317.0 nm was not found using DC arc excitation of samples of coal ash with up to about 20% Fe_2O_3.[171]

M. Nickel

Nickel has been determined in coal by OES, AAS, XRF, SSMS, and by special NAA methods. Most Ni data in Table 2 was obtained by OES, AAS, and XRF. Although the range of values for most coals from several countries is from 1 to 70, the mean is close to 15 ppm Ni.[35] The American National Standard method uses AAS with an air-acetylene flame and the line at 232.0 nm with background correction.[56] Coal ashed at 500°C is treated as outlined for chromium (Section V.G). The repeatability is 1 ppm for values <5 ppm Ni and 3 for the range 5 to 30 ppm. The reproducibility is 3 for values less than 5 ppm and 9 for the range 9 to 30 ppm. For concentrations at the ppm level, it may be advisable to use graphite-furnace AAS.

N. Lead

Although lead in coal may be determined by OES, AAS, XRF, and SSMS, most published data was obtained by OES, AAS, and in recent times, by XRF, the latter method using whole coal directly. The American National Standard method[56] uses

AAS with an air-acetylene flame and the line at 283.3 nm with background correction. Coal ashed at 500°C is treated in the same way as for the determination of chromium (Section V.G). The repeatability for the range 10 to 100 ppm Pb is 2 ppm and the reproducibility is 9 ppm. For concentrations up to about 10 ppm a graphite-furnace AAS method is needed. Because acidity decreases the absorbance, attention should be given to keeping excess acid, especially nitric acid, to a minimum.[172]

O. Antimony

Antimony may be determined in coal by AAS, INAA, and SSMS. The high sensitivity of INAA is advantageous, but a graphite-furnace AAS method has been developed for antimony concentrations down to 0.1 ppm Sb in Australian coals.[58] A method with the same sensitivity has been developed based on acid extraction of whole coal, followed by removal of antimony from a sulfuric acid-iodide solution into toluene, and finally determination by a graphite-furnace AAS method.[173] Since antimony forms a hydride that is gaseous at ordinary temperatures, it should be possible to use the hydride-AAS approach for determining antimony in coal.[108] As a result of a study of SRM 1632 (coal) by four laboratories using NAA methods, it was found that there were variations in the concentrations of antimony in several samples.[174] This was not an interference effect, but may be due to some inhomogeneity in the samples.

P. Selenium

The best published data for selenium in coal have been obtained by NAA, usually after radiochemical separation. For example, a radiochemical-separation NAA method was used to determine selenium in Australian coals,[167] most values being in the range 0.25 to 1.6 ppm Se (Table 3).

Modern XRF methods have improved the limit of detection for selenium to 0.4 ppm Se,[130,135] which will make XRF suitable for most coals. An example is the analysis of 14 South African coals which had <0.4 to 0.9 ppm Se with only three samples having <0.4 ppm.[30] Graphite-furnace AAS, after treatment of coal with acids and removal of selenium as iodide into toluene, has been used to analyze U.S. coals with selenium contents of a few ppm.[173] A specialized technique, using gas chromatography with a microwave emission spectrometric detection system, was used to determine selenium in coal, after chelating Se^{IV} with 5-nitro-*o*-phenylenediamine and extraction of the piaselenol complex into toluene.[175]

Selenium has been determined in coal by hydride generation-AAS. It was found that detection limits were improved by using an electrodeless discharge lamp instead of a hollow-cathode lamp and by taking the peak area rather than the peak height as a measure of the absorbance.[108] Another hydride technique achieved lower detection limits with AFS than with AAS.[98]

The determination of selenium in coal by graphite-furnace or by hydride-AAS requires careful treatments of the sample, always keeping in mind the volatility of many selenium compounds, especially during heating. The minimum handling of samples in NAA and XRF methods is advantageous for volatile elements.

Q. Tin

Tin may be determined by OES, AAS, INAA, XRF, and SSMS methods, although most of the data in Table 2 was obtained by OES.[8,27,28] Many coals have less than about 2 ppm Sn and special efforts to refine the determination of such low concentrations are scarcely justified. It should be easily determined by graphite-furnace AAS after dissolution of coal ash, and a hydride-AAS method has been reported.[108]

R. Thorium

Thorium can be determined in coal by INAA, XRF, and SSMS. The data in Table 2 for coals from the U.S., Australia, and the U.K. was obtained by INAA and those for South Africa by XRF. In the absence of OES and AAS methods, INAA or XRF would be suitable, depending on the availability of the necessary facilities.

S. Thallium

Most coals have <1 ppm thallium, the usual methods of analysis being OES, AAS, and SSMS, with detection limits of about 0.3 ppm Tl. Coal ash (450 or 500°C) is used. Flame AAS is not sensitive enough, but graphite-furnace AAS should be suitable for most coals. A very sensitive method[176] for determining thallium in rocks (down to 0.005 ppm Tl) should be adaptable to coal ash. The thallium is extracted as thallium iodide into amyl acetate and determined by graphite-furnace AAS. However, there is little incentive to develop more sensitive methods, when the main interest, at least environmentally, is to ascertain if there are any coals with high concentrations of thallium, and this would be detected readily by current methods.

T. Uranium

Uranium can be determined in coal by INAA, XRF, and SSMS methods, the first two methods being those used to obtain the data in Table 2. Fluorimetric methods have been used for determining uranium in rocks, but the quenching effects of certain elements, including manganese, reduce the sensitivity, and would probably make the method difficult for coal. Coals are mostly in the range 0.1 to about 10 ppm U, although there are areas where higher concentrations are found, e.g., in some lignite from parts of the western U.S.[41] It has been reported recently that 99% of the values for uranium in 230 samples of coal "from many different countries" are in the range 0 to 6 ppm (presumably as U).[177] A similar conclusion could be made from the data in Tables 2 and 3. Determinations by INAA and XRF are carried out on whole coal. There is no need to ash coal, as the limits of detection by INAA (about 0.2 ppm[27]) and XRF (1 ppm U[130]) are sufficient for most coals.

U. Vanadium

Vanadium can be determined in coal by OES, AAS, INAA, XRF, and SSMS. There is an American National Standard method[56] which uses AAS with a nitrous oxide-acetylene flame and the line at 318.0 nm with background correction. Coal ashed at 500°C is treated in the same way as for the determination of chromium (Section V.G). The repeatability is 5 ppm V for the range 10 to 100 ppm and the reproducibility is 9 ppm for the range 10 to 50 ppm and 20 ppm for the range 50 to 100 ppm. Useful data can be obtained by any of the above methods, but the attainment of good precision and accuracy requires extra efforts, which are probably not justified. In a test for accuracy the American Standard method gave 45.7 ± 4 ppm compared with the NBS-certified value of 35 ± 3 ppm.[56]

V. Zinc

Zinc can be determined in coal by OES, AAS, INAA, XRF, and SSMS. There is an American National Standard method[56] which uses AAS with an air-acetylene flame and the line at 213.9 nm with background correction. Coal ashed at 500°C is treated in the same way as for the determination of chromium (Section V.G). The repeatability is 3 ppm for values <50 ppm and 8 ppm for the range 50 to 100 ppm. The reproducibility is 4 ppm for values <50 ppm and 17 ppm for the range 50 to 100 ppm. Good results can be obtained by any of the above methods.

VI. CONCLUDING REMARKS

Since coal is a heterogeneous mixture of organic-rich material and mineral matter, great care must be taken with sampling in the mine and from stockpiles and the like, as well as with making the subsample for laboratory analysis. Trace elements are associated with the organic-rich material and with the mineral matter. The contents of trace elements in coal vary greatly from sub-ppm (e.g., cadmium, antimony, mercury, selenium, and thallium in many coals) to a range of about 1 to 30 ppm (e.g., chromium, copper, nickel, and zinc in many coals) and even to hundreds of ppm (e.g., manganese, phosphorus, and titanium in most coals). These trace elements are present in a matrix of major elements, principally silicon, aluminum, iron, and calcium. Hence, the analysis for trace elements must take into account a wide range of variables.

There is a tendency to favor multielement techniques, namely, OES, NAA, and XRF, but no one of these can cover all the trace elements of environmental interest (Table 6). The most versatile method is probably SSMS, but the instrumentation is costly and the technique is very specialized. Since SSMS does not use whole coal, there is the limitation that volatile elements cannot be determined. The instrumentation for NAA is also expensive. However, AAS — flame and graphite-furnace — is moderately priced and widely used. There is no doubt that the proper application of each of these methods requires experience and they can only be used routinely under expert guidance.

Trace elements other than those listed in Table 2 can also be determined by one or other of the above-mentioned methods. For example, the rare earths are readily determined by SSMS, NAA, and XRF. Some elements present at the ppb level, e.g., gold, can be determined by NAA. An advantage of a multielement method is that it is not much more trouble to determine 40 elements than 10, although the precision may not be uniform. The criteria for an ideal analytical method include good sensitivity for many elements, specificity plus simultaneous determinations, a minimum of matrix effects and interferences, low cost, simplicity of operation, automation, nondestruction of sample, good precision, and independence of operator error.[69] Of course, no such ideal method exists and compromises must be made to achieve the determination of as many elements as realistically possible. If cost and the availability of instruments are relevant factors, then AAS must emerge as the method of choice. Recent developments in XRF are making this an acceptable method for several trace elements.[30,130] It should be stated again that NAA and probably SSMS are good methods for coal, provided that the necessary experience is available. Also, developments in ICPAES and PIXE are making these methods useful for coal.

In some cases, semiquantitative results may suffice, and OES can provide these readily. For example, in a study of coal supplied to five power stations in New South Wales, Australia, the following values were found: 10 to 20 ppm Cu, 20 to 60 ppm B, 0.4 to 2 ppm Mo, 3 to 8 ppm Pb, and 40 to 70 ppm V.[37] The refinement of these values by more quantitative methods would not be justified, unless the data were part of a quantitative assessment. However, in another study of 29 samples of coal from one seam, it was found that the results for lead showed little variation, namely, 9.3 to 14.1 with a mean of 11.8 ppm Pb.[88] In this case, the determinations were carried out by quantitative AAS, otherwise the variations would not have been detected.

The statement of results should indicate the precision, preferably as a percentage of the amount present. A realistic approach is to aim at $\chi \pm 10\%$ relative, which is surely good at the ppm level. If accuracy is justified, then proper standards must be used. The American National Standard method for beryllium, chromium, copper, manganese, nickel, lead, vanadium, and zinc[56] does not always have a repeatability as good as ±10%, but for most cases this method (AAS) is sufficient.

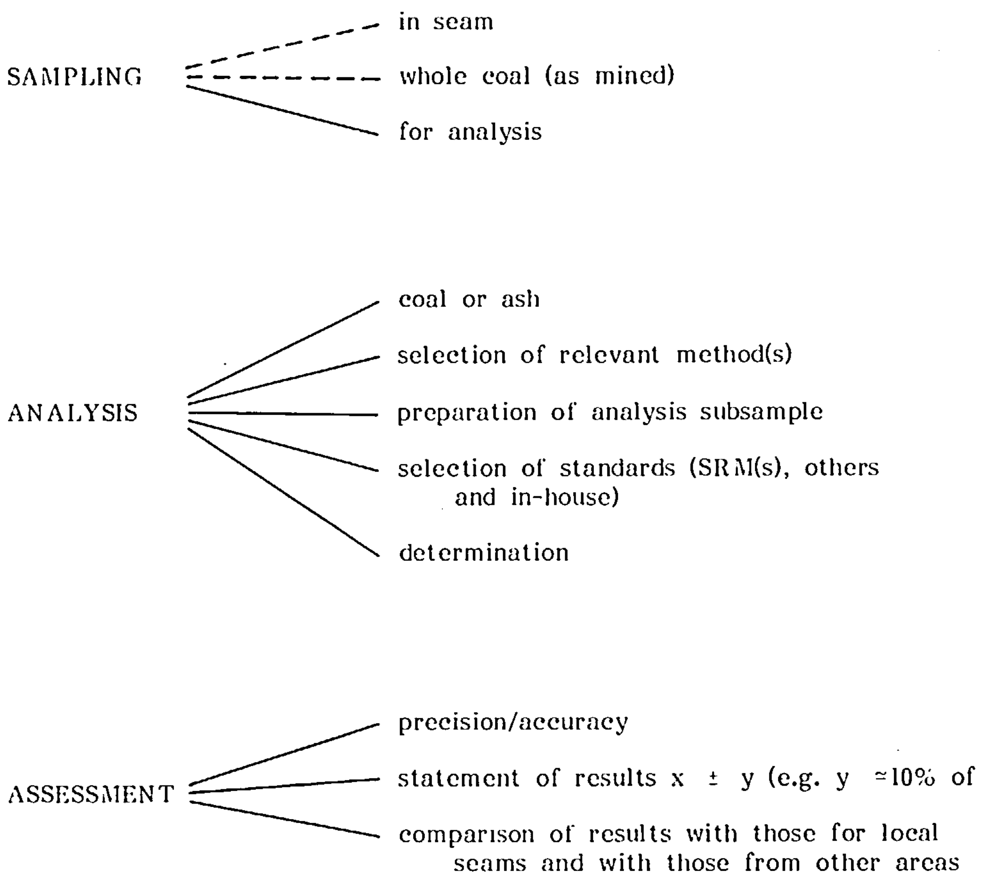

FIGURE 1. The role of the analytical chemist in obtaining meaningful data for trace elements in coal.

Finally, the role of the analytical chemist must be stressed. The attainment of meaningful results for trace elements in coal and, indeed, in general, means that the analytical chemist must be involved at all stages, i.e., sampling, analysis, and assessment (Figure 1). The only exception could be the sampling of the seam and of the whole coal as mined. It must be stressed that the total variance of a determination is the sum of the variances from sampling, preparation, and analysis, and hence, a reason for the total involvement of the analytical chemist. The mere existence of sophisticated equipment and standard methods does not obviate the need for competent analytical chemists. As Abbey has stated very aptly, "The reliability of a result depends more on *who* produced it than on *how* it was done."[178]

This review has aimed to provide enough relevant information from personal experience and from published sources to enable scientists to choose suitable methods either for their own use or for analyses done by others. Proper attention to the several matters discussed will improve data for trace elements in coal.

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