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Mineral matter characteristics of some American coals

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Mineral matter was separated from a number of American coals, by removing the coal substance in an oxygen plasma at low temperatures. This low temperature ashing technique was applied to some thirty-three coal samples of varying rank, twelve of which are discussed in some detail herein. The mineral matter thus obtained was analysed by x-ray diffraction, infra-red absorption, and chemical methods. By comparison with synthetic standard mineral mixtures, prepared from pure minerals, semi-quantitative data on the major mineral constituents were derived. An attempt to quantify the data for one sample was also made. Trace element analysis of the ashes was included as part of this study.

A KNOWLEDGE of the original mineral matter composition of a coal is of benefit in many aspects of coal utilization. With the development of new methods of combustion, the properties of the coal ash components will be of increasing interest to the combustion engineer, the coal consumer, and the equipment designer. It seems probable, therefore, that the source from whence this ash originates, i.e. the mineral matter, will be the focus of more detailed investigation. Already the problems of the prevention of boiler deposits and corrosion have stimulated some studies on the high temperature behaviour of coal minerals. In addition, as coal specifications become more definitive and restrictive, mineralogical composition may be an important criterion in any new standards which may evolve. Therefore, further information concerning the types of minerals in coal and their effects in all aspects of coal and coke usage would seem very desirable.

Several methods have been developed for the separation of mineral matter from coal by combustion at low temperatures. However, the low temperature ashing of coal in an oxygen plasma is perhaps the best method available for obtaining relatively unaltered mineral matter. Details of this low temperature ashing (LTA) technique have been given by Gluskoter¹, who also reports that the principal losses during ashing are the dehydration of gypsum and some loss of chlorine and organic sulphur.

Having separated the mineral matter from the coal the question then arises of how best can these multicomponent mineral mixtures be analysed. Karr *et al*² have evaluated in some detail the approach of using infra-red analysis and report considerable success with this method. Gluskoter³ was successful in separating the clay mineral fraction of some Illinois coals and used a semi-quantitative x-ray diffraction method to study the areal distribution of these minerals.

In this study, it was decided to use an approach combining x-ray diffraction and infra-red methods, supported by chemical analysis. Infra-red and x-ray diffraction analyses are essentially complementary to each other.

Infra-red analysis is extremely sensitive to short range ordering, whereas x-ray analysis is sensitive to longer range order and to a periodic arrangement of atoms in a crystalline structure. The mineral kaolinite is probably the most abundant mineral in the LTA material of bituminous coals. The high sensitivity which this mineral displays in the infra-red can, however, be a disadvantage. The sharp absorption bands of kaolinite will frequently obscure the more diffuse bands of a more poorly ordered species e.g. illite. An x-ray diffraction pattern of the same material will often tend to confirm the presence or absence of the less well ordered species.

In the study of such multicomponent mixtures, it is essential to accumulate as much information as possible concerning the individual components. A combined x-ray diffraction and infra-red study is advisable, therefore, to prevent the likelihood of overlooking a particular component in the mineral mixture.

EXPERIMENTAL

Low temperature ashing

The coal samples were ground and vacuum dried, before being ashed in Tracerlab's LTA-600 low temperature asher. In this technique, activated oxygen is obtained when commercial grade oxygen is passed through a high energy electromagnetic field produced by a radio frequency oscillator. The activated gas, which is warmed slightly, passes over the sample and oxidation takes place primarily on the surface of those particles which comprise the top of the sample. A certain amount of heat is generated in the ashing chambers due to the exothermic reaction between the activated oxygen and the coal. Approximate determinations of the temperature reached in the ashing chambers were made using Tempilstiks. This temperature was found to lie in the range 149°–163°C.

A sample weight of 1.5 g per boat and a 65 × 100 mesh particle size were utilized. Ashing was typically continued for periods up to 75 h at which time no further loss in weight was observed. At roughly six intervals during this period, the sample was weighed and redistributed in the boat in order to assure that the activated oxygen had access to all of the coal substance. The lignite sample proved to be the most difficult to ash using this technique. However satisfactory results were obtained by using a finer particle size material (150 × 200 mesh) and approximately 0.8 g per boat.

Analysis of mineral matter

The mineral matter obtained from the low temperature asher was then wetted with absolute alcohol and ground in an agate mortar until the alcohol evaporated. Grinding under alcohol is recommended, as dry grinding can destroy crystal structure⁴. Pellets for the infra-red analysis were then prepared by hand blending 0.75 mg of the preground mineral matter with 300 mg of potassium bromide powder in an agate mortar. This mixture was then pressed

in a vacuum die under a pressure of 40 ton/in²* for a period of 3 min. The pellet thus obtained was scanned on a Perkin-Elmer 621 infra-red grating spectrophotometer. When absorption bands in the 650 to 200 cm⁻¹ infra-red region were being evaluated, cesium iodide was utilized in place of potassium bromide as a matrix powder.

For the x-ray diffraction analysis, the preground mineral matter was dispersed in distilled water, sedimented onto a glass slide, and allowed to dry at room temperature. The samples were then x-rayed from 2° to 40° (2θ) using a Norelco x-ray diffractometer with nickel filtered copper radiation.

To evaluate any expandable layer clays which may be present, it is necessary to subject the samples to an additional treatment with an organic swelling agent. The samples were maintained in the vapour from an ethylene glycol bath at 60°C for a period of 1 h, and then an x-ray diffraction analysis was made. In this treatment, ethylene glycol enters montmorillonite-type structures and causes a characteristic expansion of the basal spacing to about 17Å (0.1nm), which enables a positive identification of these minerals to be made. This technique is also especially useful for studying randomly interstratified illite-montmorillonite mixed layer clays³. When further x-ray traces are made after heat treating the slides at 350°C, the mixed layer clay content, relative to the illite content, can be ascertained.

Major and trace element analyses were made on samples of coal ashed at 600°C. Determination of the major elements was achieved using an atomic absorption unit, and the analytical procedures of Suhr *et al*⁵. Alkalies were determined by flame photometry. Trace element determinations were made using a d.c. arc technique. The sample was mixed with an internal standard and graphite in the ratio of 1:1:2. The internal standard usually used was a mixture of 0.1% lutecium oxide (Lu₂O₃) plus 0.2% cadmium oxide (CdO) in sodium borate. For boron determinations, an internal standard mixture of 7% indium oxide (In₂O₃) plus 0.7% beryllium oxide (BeO) in potassium sulphate was utilized. This mixture was then burned in a Stallwood jet with an argon/oxygen atmosphere (85% argon + 15% oxygen, flow rate 6 l/min) at 15 amperes. A Jarrell Ash spectrograph was used, and photographic plates sensitive in the 2500-4800Å spectrum region were developed according to standard methods. An N.S.L. comparator-densitometer was used for intensity measurements. These measurements were converted to p.p.m. by means of an A.R.L. 'Aristo-Respectra' calculating board and working curves of p.p.m. versus relative intensity. Some minor elements were found to be present at relatively high levels; their concentrations were determined using atomic absorption methods.

RESULTS AND DISCUSSION

The twelve samples reported upon are representative of coal seams of five different States; details of the seam names and locations are included in

*1 ton/in² = 15.44 N/m²

Table 1 Identification of coals studied

<i>PSOC</i> Sample No.	Seam name	ASTM rank	Sample description	Location in seam	Locality
2	Elkhorn No. 3	HVA bituminous	dull durain with thin lenses of vitrain	15-23 in. from bottom	Deane, Kentucky
3	Elkhorn No. 3	HVA bituminous	duro-clarain	23-31 in. from bottom	Deane, Kentucky
4	Elkhorn No. 3	HVA bituminous	bright clarain	31-40 in. from bottom	Deane, Kentucky
82	Buck Mountain	anthracite	dull durain	31-39 in. from top	Zerbe, Penna.
88	Zap	lignite	—	top 18 in.	Zap, North Dakota
100	Roland	subbituminous	clarain	unknown	Gillette, Wyoming
108	Pittsburgh	HVA bituminous	duro-clarain	top 10 in.	Marianna, Penna.
109	Pittsburgh	HVA bituminous	clarain	10-35 in.	Marianna, Penna.
110	Pittsburgh	HVA bituminous	clarain brighter than PSOC-109	35-54 in.	Marianna, Penna.
111	Pittsburgh	HVA bituminous	clarain especially dull towards base	54-72 in. (base)	Marianna, Penna.
120	Tioga	HVA bituminous	duro-clarain	22-35 in. from bottom	Tioga, West Virginia
121	Tioga	HVA bituminous	bright clarain	0-22 in. from bottom	Tioga, West Virginia

Table 2 Total mineral matter in coals as determined from both low and high temperature treatment

PSOC Sample No.	% LTA		% Ash		LTA min. mat.		% Total Sulphur in coal*		% Calculated min. mat. using Parr formula		LTA min. mat. calculated min. mat.	
	Mineral matter				Ash		Sulphur in coal*		Parr formula		calculated min. mat.	
2	4.51		3.80		1.19		0.61		4.44		1.02	
3	5.04		4.47		1.13		0.62		5.17		0.97	
4	2.52		1.74		1.45		0.86		2.35		1.07	
82	11.21		9.52		1.18		0.52		10.57		1.06	
88	15.73		11.34		1.39		0.77		12.67		1.24	
100	7.03		4.06		1.73		0.52		4.67		1.51	
108	13.23		9.81		1.35		3.13		12.31		1.07	
109	6.07		5.01		1.21		0.64		5.76		1.05	
110	8.05		6.12		1.32		1.24		7.29		1.10	
111	9.08		7.19		1.26		1.59		8.64		1.05	
120	6.90		5.70		1.21		0.68		6.53		1.06	
121	3.17		2.03		1.56		1.22		2.86		1.11	

*Sulphur figures are as supplied by Commercial Testing and Engineering Co., Charleston, W. Virginia

Table 3 Mineralogical composition, % LTA mineral matter

Mineral constituents	PSOC-2	3	4	82	88	100	108	109	110	111	120	121
Kaolinite	40-50	30-40	1-10	>70	10-20	10-20	20-30	30-40	40-50	30-40	40-50	1-10
Illite	trace	trace	1-10	1-10	1-10	1-10	1-10	10-20	10-20	30-40	1-10	1-10
Chlorite	n. d.	trace	1-10	trace	trace	n. d.	n. d.	n. d.	n. d.	n. d.	1-10	1-10
Montmorillonite	n. d.	n. d.	trace	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	trace
Mixed layer illite-montmorillonite	1-10	trace	1-10	n. d.	n. d.	n. d.	1-10	n. d.	n. d.	1-10	n. d.	1-10
Gypsum	1-10	1-10	10-20	trace	30-40	40-50	n. d.	10-20	trace	1-10	10-20	20-30
Quartz	30-40	40-50	1-10	10-20	1-10	1-10	1-10	10-20	1-10	10-20	20-30	1-10
Calcite	n. d.	n. d.	n. d.	1-10	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.
Aragonite	n. d.	n. d.	n. d.	n. d.	1-10	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.
Pyrite	1-10	1-10	10-20	1-10	1-10	1-10	30-40	1-10	20-30	10-20	1-10	20-30
Siderite	n. d.	n. d.	1-10	n. d.	n. d.	n. d.	trace	trace	n. d.	n. d.	n. d.	trace
Heamatite	n. d.	n. d.	10-20	n. d.	n. d.	n. d.	10-20	n. d.	1-10	n. d.	n. d.	n. d.
Rutile	1-10	1-10	n. d.	1-10	n. d.	trace	n. d.	1-10	1-10	1-10	1-10	1-10
Thenardite	n. d.	n. d.	1-10	n. d.	1-10	1-10	n. d.	n. d.	n. d.	n. d.	n. d.	1-10

trace = <1.0% n.d. = not detected

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Table 1. All samples were lithotypes. In some cases, more than one lithotype was collected from a given coal seam. This enabled variations in the dispersion of mineralogical constituents at increasing and adjacent depths to be followed.

Mineral matter contents

Duplicate determinations of the mineral matter content in each lithotype were made. *Table 2* compares the amounts of low temperature ash with the high temperature ash (obtained upon heating to 950°C and holding for 5 h) of each of the coals and also with the mineral matter calculated from the Parr formula. In our overall survey⁶, some twenty-one high volatile coals were studied. On the average, the LTA mineral matter content was found to be 1.09 times the calculated amount. This figure is in good agreement with that (1.10) obtained by Gluskoter in his study of some Illinois bituminous coals. Although the Parr formula may not be specifically designed for use with the lower rank coals, calculations for these are also included.

Semi-quantitative mineralogical and conventional ash analyses

In *Table 3* details of the semi-quantitative mineralogical analysis are outlined, while *Table 4* contains figures for the conventional ash analysis. The first three samples (PSOC-2 to 4) are lithotypes taken from the Elkhorn No. 3 seam. Kentucky coals are noted for their relatively low ash content,

Table 4 Chemical analysis, weight % of ash

<i>Sample No.</i>	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	SO ₂
PSOC-2	59.5	26.7	4.18	3.39	2.25	0.65	0.83	0.06	1.84
PSOC-3	68.5	20.8	2.55	3.58	1.35	0.40	0.63	0.04	1.69
PSOC-4	37.0	17.8	23.25	0.53	5.60	1.18	1.79	0.22	10.86
PSOC-82	53.0	33.3	4.05	3.35	1.95	1.00	0.13	0.38	1.99
PSOC-88	23.5	13.6	5.72	0.51	18.25	5.40	8.30	0.29	21.65
PSOC-100	9.8	12.9	6.82	0.99	33.38	7.85	1.56	0.18	21.74
PSOC-108	32.3	18.5	42.23	0.81	2.80	0.34	0.61	0.38	<0.01
PSOC-109	49.5	26.8	5.30	1.11	5.50	0.90	0.94	1.18	6.68
PSOC-110	46.6	27.8	17.75	1.07	1.65	0.61	0.42	1.13	0.55
PSOC-111	54.4	23.6	11.81	1.03	3.40	0.72	0.31	2.29	1.14
PSOC-120	55.1	23.9	2.18	1.68	7.25	0.40	0.32	0.40	6.77
PSOC-121	23.5	24.9	19.55	1.12	10.50	1.43	1.46	0.67	12.22

and this is again reflected in the mineral matter content of these three lithotypes. However, PSOC-4 has a mineral matter content approximately half that of the other two samples. This can probably be attributed to the substantially higher percentage of vitrinites found in this sample, as seen in *Table 5*. That is, in comparison to other maceral types, vitrinite typically contains lower percentages of mineral matter. PSOC-4 also showed a much wider variation in mineralogical composition; and compared with the other two lithotypes, had higher proportions of gypsum, illite and pyrite and a rather low kaolinite content. Lithotypes PSOC-2 and 3 exhibit a greater similarity

Table 5 Maceral composition of selected coals

Maceral	Composition, %											
	PSOC-2	3	4	82	88	100	108	109	110	111	120	121
vitrimites	26.5	44.7	67.3	60.8	65.9	86.0	77.9	84.6	85.6	89.5	46.1	65.6
pseudo-vitrimites	4.3	—	16.8	—	—	—	—	—	—	—	4.2	7.4
semi-fusinites	3.9	9.9	0.3	24.9	6.0	1.3	3.4	1.8	1.1	1.5	10.9	2.0
fusinites	2.1	1.2	2.4	2.8	7.3	2.1	3.0	3.7	2.3	1.4	14.0	4.5
micrinites	36.5	24.0	8.6	11.5	13.5	6.4	9.2	5.1	6.5	5.1	17.7	14.7
resinites	—	—	—	—	1.4	0.7	—	—	—	—	—	—
exinites	26.6	20.4	4.5	—	5.9	3.5	6.5	4.8	4.5	3.5	7.0	5.8
alginites	—	—	—	—	—	—	—	—	—	—	0.1	—

in mineral composition and are characterized by noticeably higher kaolinite and quartz contents. In terms of macerals, these latter two lithotypes have greater percentages of micrinite and exinite in contrast to PSOC-4.

The anthracite sample (PSOC-82) has an exceptionally high kaolinite content, which is due in part to the presence of authigenic kaolinite that was observed to occur along cleats in this sample. Pennsylvania anthracites have long been recognized for their high ash fusion temperatures, and the kaolinite content of these anthracites may have an important bearing on this property. In general, the kaolinite content of the mineral matter of Pennsylvania anthracite ranges between 50 and 75%; and the more closely the composition of the mineral matter approximates to silicate of alumina, the less fusible the resulting ash is likely to be. The occurrence of the clay mineral pyrophyllite has also been reported in some Pennsylvania anthracites⁷. The presence of this mineral might be employed as an indicator of temperature conditions prevailing within particular seams during metamorphism.

The kaolinite found in the mineral matter of PSOC-82 appears to be of a well crystallized form. Evidence for this is provided from both infra-red and x-ray diffraction studies. In *Figure 1*, the O-H stretching vibrations in the frequency region 3000-4000 cm^{-1} for kaolinite are shown. Four distinct O-H stretching bands at 3690, 3665, 3650, and 3620 cm^{-1} are indicative of a well crystallized form of kaolinite. The two middle bands are the weakest, and in poorer crystalline forms frequently only one of these bands appears. The crystallinity of the kaolinite was also confirmed by examining the x-ray diffraction traces. A well crystallized form was apparent from the presence of the three prism reflections 020, 110, 111. In less crystalline material, these three peaks tend to diffuse into one broad peak on the diffraction trace.

PSOC-88 is a lithotype of North Dakota lignite and is characterized by its high calcium and sodium oxide contents, together with a high sulphur trioxide content. The sulphur trioxide is combined in lignite mineral matter as calcium sulphate and sodium sulphate or, in terms of minerals, gypsum and thenardite. However, while both of these minerals are original constituents of the lignite, it would appear that additional quantities of these minerals may be produced as a result of a chemical reaction in the oxygen plasma of the low temperature asher. Therefore, analyses of the LTA material of lower rank coals may have limited application.

Aragonite, the dimorphic form of the mineral calcite, was also detected in sample PSOC-88. Degens⁸ reports that the presence of calcium sulphate seems to increase the stability of aragonite. In addition, a strong absorption band at 1380 cm^{-1} appeared in the infra-red spectrum of the low temperature ash material (see *Figure 2*). This appeared to indicate the presence of nitrates, but again raised the possibility that this nitrate was being produced in the LTA process. However, the presence of nitrate in the original lignite was confirmed by analysing a hot water extract of a dried and preground sample. The amount of nitrate in the hot water extract was found to be 1.15% by weight, of the lignite.

Karr *et al*⁹ have investigated the occurrence of nitrate in lignites more fully and found significant amounts of sodium and alkaline earth nitrates in the

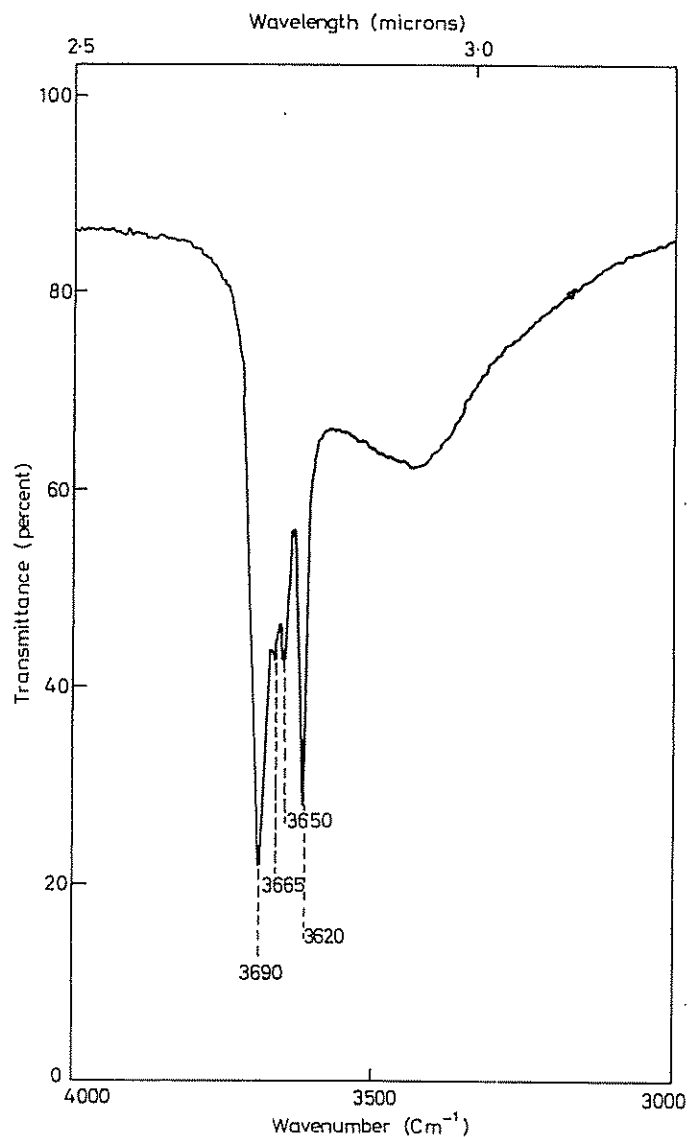


Figure 1 The O-H stretching vibrations in the kaolinite of sample PSOC-82

LTA mineral matter of Montana and North Dakota lignites. The nitrate absorption band is evident in the LTA of all of the North Dakota, Montana, and Texas lignites we have examined to date, as well as in the Wyoming sub-bituminous samples. In the coals of bituminous and anthracite rank, this band does not appear which is in agreement with previous findings⁹.

However, the question of how much nitrate is being chemically produced in the LTA process has still to be answered.

PSOC-100 is a lithotype of a Wyoming sub-bituminous coal and has a mineralogical composition fairly similar to that of PSOC-88. The nitrate absorption band was again evident in the infra-red spectrum of the mineral matter of this sample.

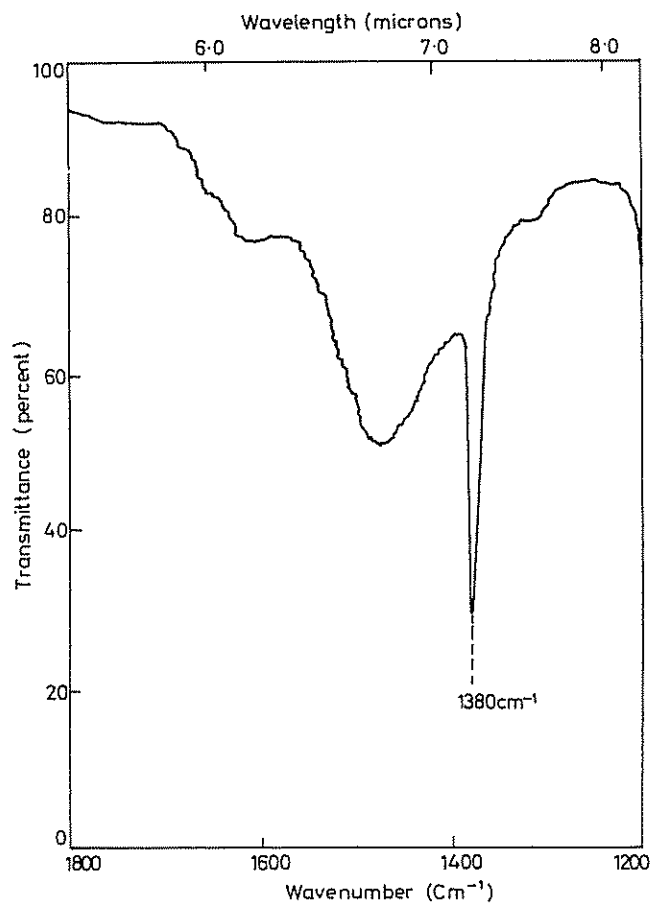


Figure 2 Strong absorption band at 1380 cm⁻¹ due to the presence of nitrate in the LTA mineral matter of sample PSOC-88

PSOC-108 to 111 are four lithotypes taken at increasing and adjacent depths from the Pittsburgh seam. The clay minerals, kaolinite and illite, appear to increase in concentration from the top to the bottom of the seam, with an exceptionally high illite content noted in PSOC-111. The distribution of gypsum in the seam is rather irregular, being absent in PSOC-108, more

than 10% in PSOC-109, a trace amount in PSOC-110, and 1 to 10% in PSOC-111. PSOC-108 and 110 have the higher iron contents, with both pyrite and hematite being detected in these lithotypes. Some similarity of mineral composition would appear to exist between PSOC-108 and 110 and PSOC-109 and 111, as seen from the data in *Table 3*. Apart from a lower vitrinite content in PSOC-108, very little variation in maceral composition is evident, as seen in *Table 5*.

Two adjoining lithotypes (PSOC-120 and 121) from a West Virginia seam show a wide variation in mineralogical composition. PSOC-121 contains less than half the mineral matter of PSOC-120 and has pyrite and gypsum as its predominant minerals. PSOC-120 has a mineral composition more typical of a bituminous coal, with kaolinite and quartz as the principal minerals. A small amount of the clay mineral, montmorillonite, was detected in the LTA material of PSOC-121. Although the presence of montmorillonite in these mineral mixtures is comparatively rare, the occurrence of randomly interstratified illite-montmorillonite mixed layer clays is much more common. They usually occur on the x-ray diffraction trace as a broad hump on the low angle side of the 10Å illite reflection. Characterization of these mixed layer clays in the heterogeneous mineral mixtures obtained from coal is difficult. If present in appreciable amounts, they can provide quite a stumbling block to any quantitative determination; and one would really have to study the clay mineral fraction of the mineral matter residues as outlined by Gluskoter³.

Quantitative mineralogical analyses

An attempt to derive some quantitative data for the major mineral constituents of the anthracite sample (PSOC-82) was also made. In the quantitative determination of the mineral constituents, kaolinite, quartz, and calcite were obtained from calibration curves prepared from pure standards of these minerals, using infra-red analytical techniques. Rutile was determined from the chemical analysis of the ash, having previously confirmed the presence of this mineral in the LTA mineral matter by means of x-ray diffraction. The high kaolinite concentration overlapped the diagnostic bands of pyrite and illite in the infra-red; and their concentrations were therefore, derived by way of the normative analysis procedure of Williams *et al*¹¹.

Having obtained the percentage composition, the next step was to ascertain if the low temperature ashing technique gives a true indication of the amount of mineral matter. This was accomplished by considering some assumed weight loss figures upon heating to 950°C for the individual minerals present and comparing the calculated ash content with that determined by standard procedures. *Table 6* summarizes the pertinent figures. Subtracting the calculated weight loss from the LTA mineral matter content for this sample (i.e. 11.21%) gives a calculated ash content of 9.68%. This is to be compared with an experimental ash content of 9.52% for sample PSOC-82. This good agreement suggests that the LTA procedure gives a useful estimate of the mineral matter present in the original coal. Obviously, it is desirable to check

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Table 6 Quantitative analysis of mineral matter in lithotype PSOC-82 and calculated loss in weight in mineral matter upon heating to 950°C

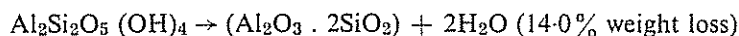
<i>Mineral constituent</i>	<i>% in mineral matter</i>	<i>Equivalent % in coal</i>	<i>Assumed losses % of mineral constituents at 950°C</i>	<i>Calculated losses % of coal at 950°C*</i>
kaolinite	72.7	8.09	14.0	1.13
quartz	11.1	1.24	0.0	0.00
illite	5.1	0.57	8.5	0.05
rutile	3.3	0.37	0.0	0.00
pyrite	5.4	0.61	33.3	0.20
calcite	2.9	0.33	44.0	0.15

*Total = 1.53

this agreement on additional coals, particularly those which do not have such a large fraction of their mineral matter present as kaolinite.

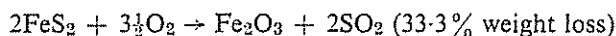
In estimating the weight losses at 950°C, an important factor to consider is that the individual mineral components are continuously changing their chemical composition and structure over various temperature ranges. Typical examples of these changes are as follows:

(a) Kaolinite is a hydrous layer lattice silicate. Water molecules are not present in the structure. The water, given off when the structure decomposes thermally, is the result of removal and reaction of OH groups originally linked to aluminum. At about 550°C, dehydration commences, resulting in a breakdown of the crystal lattice and the formation of amorphous metakaolin, which is an intimate mixture of SiO₂ and Al₂O₃. Metakaolin in turn undergoes a transformation to γ-alumina between 900 and 1050°C, with no apparent additional loss in weight. The dehydration reaction can be represented by the following equation:



(b) Illite is generally classified as a clay grade mica, which is usually not well crystallized. The illites differ from the macro-crystalline micas (e.g. muscovite) by having a lower potassium content and a higher water content. In addition, complex substitutions are known to occur in illites. Between 200 and 600°C, illite loses hydroxyl water from the lattice but still retains its essentially micaceous character. Up to 800°C, the dehydrated lattice persists with little change; but at temperatures above about 850°C, final destruction of the lattice occurs. Duplicate determinations of weight loss at 950°C were made on a sample of Fithian illite; an average value of 8.5% was obtained.

(c) Pyrite in an oxidizing atmosphere is known to undergo the following decomposition:



Decomposition commences at 370°C, and a stable complex of Fe₂O₃ and

FeSO_4 is found to exist between 440 and 600°C. Oxidation to Fe_2O_3 is complete at 780°C¹⁰.

(d) Calcite decomposes between 800 and 900°C to give lime and carbon dioxide



(e) Rutile and quartz are assumed to remain unaffected up to a temperature of 950°C.

Trace elements in mineral matter

In considering the maceral and mineral compositions of the first three lithotypes, it was found that similarities existed between samples PSOC-2 and 3 and that both of these samples differed quite markedly from PSOC-4. This difference between the lithotypes is also evident when one examines the trace element content of the three samples (see *Table 7*). Whereas the concentrations of elements in PSOC-2 and 3 are very similar, a contrast is provided when both of these samples are compared with the concentrations found in PSOC-4. Higher concentrations of the elements boron, barium, manganese, strontium, and zinc can be noted in PSOC-4. For the elements chromium, lanthanum, scandium, yttrium, and zirconium lower concentrations are recorded for this lithotype. The most striking difference occurs in the zirconium contents, where there is an eleven-fold difference. The elements, cobalt, copper, gallium, nickel, and lead show the least variation throughout the seam.

The principal feature of note in the anthracite sample (PSOC-82) is the remarkably high tin content. The distribution of tin in the Buck Mountain seam is dealt with in some detail later.

In the lower rank samples (PSOC-88 and 100), the concentrations of boron, barium, and strontium are typically high, with a barium concentration >1% being found in the lignite sample. In both samples, the barium and strontium concentrations exceed the corresponding potassium concentration, even though potassium is usually regarded as a major constituent. In addition, the sub-bituminous sample had a relatively high copper content, and in another lithotype from the same area an even higher copper content (3020 p.p.m.) was recorded. These copper values are approximately at the level of a low grade copper ore and may possibly warrant recovery.

In the four lithotypes from the Pittsburgh seam, boron shows a wide variation throughout the seam; and barium shows a higher concentration in the two lithotypes nearest the top of the seam. Strontium shows a similar distribution pattern to that of barium, as does copper. Gallium, scandium, and zirconium are the most uniformly distributed elements in the seam, with the latter two elements showing particular consistency. The highest lead and vanadium contents are associated with the ash of PSOC-108 and can probably be explained by the high pyrite concentration in this lithotype. Manganese displays a fairly regular distribution in three of the four lithotypes.

Samples PSOC-4 and PSOC-121 are comparable in that they both have

Table 7 Trace element analysis (parts per million on ash basis)

Element	PSOC-2	3	4	82	88	100	108	109	110	111	120	121
Ag	<1	<1	<1	<1	<1	50	<1	<1	<1	<1	<1	3
B	320	350	1600	68	820	1025	415	900	680	445	360	1325
Ba	1250	1160	4660	1340	13900	2600	630	630	450	450	805	450
Be	17	8	8	9	5	2	15	8	6	17	8	32
Co	25	58	65	68	16	31	100	31	56	42	85	170
Cr	315	275	105	285	23	33	200	160	180	155	135	140
Cu	645	550	595	530	58	2500	125	150	56	42	85	170
Ga	20	19	28	31	26	22	51	33	46	34	49	56
Ge	<20	<20	<20	<20	<20	100	20	<20	<20	<20	<20	<20
La	195	140	52	220	34	46	66	93	84	68	160	110
Mn	230	115	465	280	390	480	140	140	100	130	125	215
Ni	84	70	115	125	<20	41	170	103	118	107	195	610
Pb	80	54	80	86	48	50	112	53	68	75	74	560
Sc	51	40	8	51	5	9	20	23	28	23	30	22
Sn	180	150	105	4250	8	62	97	80	22	74	660	50
Sr	2370	2030	7300	340	6400	8000	1520	1270	845	430	2280	9600
V	260	235	138	230	28	145	330	180	220	165	150	260
Y	180	165	52	120	45	21	86	64	58	49	97	135
Yb	15	15	12	12	4	<2	15	7	8	6	7	13
Zn	<50	<50	210	<50	<50	96	190	84	220	80	<50	210
Zr	1250	1450	115	1200	205	130	220	230	220	215	360	230

low mineral matter contents. In terms of trace elements, some similarities are apparent. The best examples are provided by the high boron, strontium, and zinc contents that are again evident. In comparing PSOC-121 with its adjoining lithotype PSOC-120, the most marked differences are seen to occur in the boron, barium, beryllium, nickel, lead, tin, strontium, and zinc concentrations.

Table 8 Distribution of tin in ash from Buck Mountain anthracite collected at various heights

Distance from top of seam, [in.]	Sample description	% ash	% tin in ash (as SnO ₂)
0-5	Bright coal-shale lenses near top	8.0	0.11
5-7	Parting	25.4	0.40
7-19	Bright friable coal	9.7	0.05
19-22	Bony parting	34.0	0.05
22-31	Bright coal	7.9	0.03
31-39	Dull blocky coal (PSOC-82)	9.5	0.54
39-47	Bright coal	13.4	0.38

The high tin content found in sample PSOC-82 prompted further investigation. Samples from along the vertical length of the Buck Mountain seam were ashed and analyzed for tin content. Details of the seam sections and the results obtained are summarized in Table 8. Some concentration of tin is evident at the top and bottom of the seam, with the higher concentrations located in the bottom 16 in.

An additional sample of PSOC-82 was subjected to a small scale laboratory float-sink analysis, using carbon tetrachloride (s.g. = 1.60) as the medium. The sink fraction was then dried and ashed at 600°C. The ash, when subsequently analysed was found to contain 0.32% SnO₂. Although the separation analysis was not strictly quantitative, it would appear that the tin present is associated with the refuse and not with the clean coal. This is also in agreement with previous findings that elements consisting of large ions, such as tin, are associated with the inorganic rather than the organic fraction of coal.

The ash thus obtained was then put through a further float-sink test using bromoform (s.g. = 2.96) as the medium. From this test, sufficient sink material was obtained to prepare a slide for x-ray diffraction analysis. Strong peaks, were found at 26.77°, 34.04°, and 38.10° (2θ), were coincident with the (110), (101), and (200) reflections of the tin mineral cassiterite. Additional peaks, found at 33.30° and 35.81° (2θ), were due to the presence of haematite. At present, consideration is being given to the possibility of evaluating the tin content of the underclays in the neighbourhood of this seam.

CONCLUSIONS

The naturally occurring minerals, which comprise the mineral matter of coal, can be successfully separated from the coal substance by the low temperature ashing procedure. With the exception of some dehydration losses, the minerals are essentially unaltered and are in a form suitable for subsequent analysis. With conventional instrumental methods, reliable quantitative analyses of this mineral matter now appear feasible. Although quantitative data are somewhat more difficult to obtain, such information is vital in so far as the problem of predicting mineral matter behaviour during coal utilization is concerned.

Two minor elements which show a comparatively high enrichment ratio over their percentages in the earth's crust were detected in this study, i.e. copper in PSOC-100 and tin in PSOC-82. The enrichment ratios in the coal ash to the earth's crust are approximately 40 and 100, respectively. Low grade ores containing these elements at even lower percentages (0.2-0.3%) than reported here are currently being processed. Therefore, it would seem worthwhile to investigate these locations more thoroughly.

Correlation of coal seams by means of minor element distribution patterns appears difficult, mainly because of the widespread scatter in the concentration values which may occur.

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