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AN ESCA EXAMINATION OF COAL AND COAL ASH SURFACES

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ABSTRACT

Four North American coals and their ashes were examined using the direct, surface sensitive technique of X-ray photoelectron spectroscopy (ESCA). Two U.S. National Bureau of Standards reference coals (SRM 1632a, SRM 1635) and one ash (SRM 1633a) were used for instrument calibration. These results verified the semi-quantitative nature of ESCA and its previously determined element detection level of $\approx 10^{-9}$ gm cm⁻² of surface (≈ 0.1 bulk wt %). ESCA detected elements present in the coal and/or ash in different chemical environments, for example sulphur as the sulphide or sulphate and carbon as graphite, carbonyl, carboxyl or hydrocarbon. The results of this preliminary study indicate ESCA is useful to elucidate element siting within coal; information difficult to determine by analytical techniques that require sample destruction prior to analysis. Several raw coals contained fluorine and chlorine near the percent level. It was found that fluorine and sulphur were also highly concentrated on several coal ash surfaces possibly indicating surface sorption reactions during combustion. Application of ESCA in coal geochemistry is indicated by this study. ESCA has the potential to measure elements at the minor and possibly trace level and confirm element siting within coal and coal ash. In addition it may be possible to identify coal from different deposits by their unique broad scan ESCA spectra fingerprint.

Keywords: coal, coal ash, surface chemical analysis, X-ray photoelectron spectroscopy (XPS), ESCA.

INTRODUCTION

An increasingly larger percentage of the world's energy requirements are being derived from coal. It has been estimated that electric utilities in the United States will increase their consumption of coal to ≈ 850 million tonnes per year by 1985, an increase by nearly 100% in one decade (1). Globally, coal combustion surpassed the 3 billion tonne mark in 1975 (2). This increased use of coal poses serious technological and environmental implications. Many components of the biomass are scavengers of trace metals in the environment (3). Coal reflects this phenomenon with carbon fuels to a large degree, perhaps as a function of the environment of its deposition where its precursors acted as a "carbon filter" for continental

waters during their migration to the oceans, a process enhanced by the high permeability of coal beds during diagenesis. Contaminants, and hence environmental risks, increase as the coal quality decreases. Low-grade deposits, e.g. peat and lignite, are geochemically more "dirty" compared to anthracite; this quality is a function of time, temperature and pressure during the coalification process.

In this study, several North American coals and their ashes were examined by X-ray photoelectron spectroscopy (ESCA). This novel analytical technique is surface sensitive, direct and non-destructive. In a concomitant study, spark source mass spectroscopy (SSMS) was employed for a "bulk" semi-quantitative survey of 60 elements (4). Electron spectroscopy for chemical analysis (ESCA) is a relatively new analytical technique which can probe, qualitatively to semi-quantitatively, the first 1-5 nm thickness of the outer layer of a sample. All elements except hydrogen can be monitored with an ultimate sensitivity approaching 10^{-9} g cm⁻² of surface. Often, it is also possible to confirm chemical environment (oxidation state and coordination number) of an element from chemical shift information. Extensive reviews of ESCA theory, instrumentation and application are available (5-8). ESCA analysis of coal for the specific elements carbon, oxygen and sulphur, and also the monitoring of pyrite oxidation in coals have been published recently (8-10). Coal fly ash has also been examined by ESCA and other related spectroscopic techniques (14,15). These studies indicate volatile elements are enriched at the ash surfaces during or closely following coal combustion, probably due to condensation or adsorption from the flue gases.

EXPERIMENTAL

The nomenclature adopted in this paper follows that used in the SSMS study. Three samples of bituminous coal from Cretaceous formations were used (No. 1, 5, 8) and one North Dakota lignitic coal (No. 10). United States National Bureau of Standards (USNBS) raw coals No. 1632a, No. 1635 and coal ash No. 1633a (14,15) were used for calibration purposes. ESCA spectra were recorded using a McPherson 36 spectrometer equipped with an aluminum anode. The instrument was optimized for high electron count rates by using wide slits, optimum baffle settings (60/40) and a relatively high X-ray power (200 W).

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The spectrometer's binding energy scale was calibrated using gold (Au 4f_{7/2}; E_b = 84.0 eV). The raw coals were crushed to ~ 1 cm sized pieces and hand-sorted to yield samples possessing relatively flat surfaces. These samples were then fashioned to fit the instrument sample holder; the coal surface analysed was not handled, polished or cut during this sizing step.

Ground samples of raw coal (~ 100 mesh) and their ashes were also analysed, held on the sample probe by double sided sticky tape. To exclude the possibility of recording contaminants associated with the tape, a very thick layer of powdered coal or ash was placed over the entire exposed tape area. The tape was also analysed separately and found free from trace elements that would enhance the coal or ash results.

Broad scan spectra, covering the energy range 0-1000 eV, were initially recorded to give a qualitative surface chemical composition. The 50-250 eV sections of these broad scans were re-analysed at enhanced resolution and are referred to henceforth as wide-scan spectra.

Greater resolution spectra, narrow-scans, of individual peaks were then recorded. The times of acquisition for broad-scan, wide-scan and narrow-scan spectra are ~ 2 h (10 scan), 1 h (10 scan) and 5 min (2 scan), respectively. The electron (peak) intensities, and hence the absolute detection limits are dependent on this acquisition time. Dwell time for all spectra was 2 s; acquisition energy increments were 1 eV, 0.4 eV and 0.2 eV, respectively, for broad, wide and narrow scans.

Narrow-scan spectra of carbon (C 1s), oxygen (O 1s), and fluorine (F 1s) were recorded for all samples; calcium (Ca 2p), titanium (Ti 2p), magnesium (KLL Auger and Mg 2s), sulphur (S 2p, S 2s), iron (Fe 2p) and barium (Ba 3d) narrow scans were run based on the broad-scan fingerprint. The carbon (C 1s) spectra were deconvoluted using an iterative-type programme written by Bancroft et al. (16).

Electrons possessing a particular binding energy, i.e. peak position, originate from a particular electronic orbital of an atomic species. Thus each ESCA peak can be assigned to a specific element. The number of electrons counted having a specific energy, i.e. the peak intensity, is thus directly related to the surface concentration of the specific elements.

DISCUSSION

General

ESCA analysis of the NBS reference coals and coal ash indicated the instrument detection level for particular elements and compared the precision of this method with bulk chemical techniques. The surface composition of each sample (coal or ash) was then determined from the ESCA spectra using the following procedures.

It is possible to equate ESCA peak intensities to elemental surface composition using an equation of the form:

$$\frac{n_1}{n_2} = K \frac{I_1}{I_2}$$

where: n_1, n_2 element concentrations; I_1, I_2 ESCA peak intensities of these two elements; and K , a function of the spectrometer and the elements examined. Details of the function K and this calculation are given in recent publications (6,17). Ratios of surface element concentrations are thus readily obtained for each sample.

ESCA analysis of these samples published earlier required NBS standards as instrument calibrants (18). In that study the oxygen and carbon components were not included in the resulting compositions. Since that work was completed a more satisfactory method of handling the ESCA data has been determined. For example, there is now no need to equate one XPS atomic ratio (n_2) to a weight percent determined by a bulk analytical technique such as XRF. In the present paper, the ESCA peak intensities for each broad scan spectrum have been normalized to that spectrum's Si 2s peak intensity except in one case where no silicon signal was detected (raw coal No. 10). In that sample, the Al 2s peak was used instead. The NBS standard analysis (Tables 1 and 2) indicate the semi-quantitative nature of the ESCA method. It is probable the surface composition of the NBS standard samples differ with the certified bulk chemical analysis. The results (Tables 1 and 2) for the "surface" versus "bulk" analysis however agree surprisingly well except for the elements iron, sulphur and fluorine.

The surface detection level is $\approx 10^{-9}$ g cm⁻², assuming the depth of analysis is 5 nm, this sensitivity translates into a bulk detection limit of ≈ 1000 ppm (0.1 wt %). Thus, only elements concentrated $> 0.1\%$ will be detected by ESCA. Ashing effectively concentrates the residual mineral fraction in the raw coal by an order of magnitude, i.e. combustion reduces coal weight by $\approx 90\%$. ESCA analysis of the ash is thus more informative, although combustion does release volatile elements sited within the organic fraction of the raw coal and possibly alters the surface of the residuals. In addition to major element surface analysis, the ESCA technique fingerprints the coal or coal ash samples; note that each ESCA broad-scan spectrum is unique for each deposit. Duplicate analysis of each coal indicated good reproducibility and supported this uniqueness. Further studies within each deposit, laterally along seams, and between different seams is, however, required for verification of the unique fingerprint.

The ESCA technique has given interesting results concerning the chemistry of the four coals and their ashes, which are not measured by bulk chemical analysis. These findings are discussed separately later.

Raw Coal

Coal is highly heterogeneous owing to the influence of the variable bio-geological processes occurring during and after initial deposition of the organic debris. Fine-grained detrital minerals, e.g. quartz, alumina-silicates (clays, feldspars, etc.), and chemical precipitates (iron oxides, gypsum, etc.), are trapped and incorporated into the organic debris in aqueous environments (19). During diagenesis,

TABLE 1 - ESCA Chemical Analysis of Raw Coal Surfaces

Element (wt %)	Raw Coal Samples ^a											
	NBS Standards				North American Coals ^c							
	1632a		1635		8		10		1		5	
± 15%	ESCA	bulk ^b	ESCA	bulk ^b	ESCA	bulk	ESCA	bulk	ESCA	bulk	ESCA	bulk
Si	7.7	5.8	1.3	0.52	2.7	1.0	N.D.	2.0	10.5	6.0	1.0	1.0
Al	5.20	3.1	0.8	0.30	7.4	1.0	1.2	2.0	10.6	2.0	2.5	2.0
Fe	N.D. ^d	1.1	N.D.	0.22	N.D.	0.50	0.9	1.0	N.D.	2.0	0.4	0.1
Ca	N.D.	0.24	1.5	0.54	2.4	0.30	N.D.	0.5	N.D.	5.0	1.7	2.0
Ti	N.D.	0.15	N.D.	0.02	N.D.	0.1	0.9	0.3	N.D.	0.1	N.D.	0.5
S	N.D.	1.59	0.8	0.32	N.D.	2.0	3.1	3.0	N.D.	2.0	N.D.	3.0
F	1.25	N.A. ^e	1.4	N.A.	3.8	N.A.	N.D.	N.A.	N.D.	N.A.	1.9	N.A.
Cl	N.D.	0.08	N.D.	0.003	0.9	N.A.	1.5	N.A.	0.8	N.A.	1.1	N.A.
N	1.2	1.27	1.5	1.0	1.4	N.A.	N.D.	N.A.	0.3	N.A.	2.0	N.A.
C ^f	59.3	{ 86.7	73.8	{ 97.1	60.0	{ 95.1	71.8	{ 91.2	48.1	{ 82.9	74.0	{ 91.4
O ^g	25.3		18.9		21.4		20.6		29.7		15.3	

^a Surface concentrations are calculated from equation 1 using ESCA peak intensity ratios normalized to Si 2s except Sample No. 10, where Al 2s had to be used. Note the surface compositions have been calculated on a hydrogen free basis as hydrogen cannot be detected by ESCA.

^b Accepted values from US NBS certificate of analysis (14) and/or reference (15).

^c Bulk analysis by XRF and/or SSMS (4); note carbon and oxygen (a combined value) are determined by difference.

^d N.D. not detected. ^e N.A. not analyzed.

^f Carbon content measured by ESCA includes a small sorbed portion (hydrocarbons) derived from the UHV system.

^g Oxygen content measured includes a small portion of adsorbed oxygen due to handling in air prior to analysis.

reducing conditions enhance the growth of sulphide minerals, e.g. pyrite. Increasing pressure and temperature alter the H/C and O/C ratios producing an increasingly carbon-rich coal (20). Thus the organic and mineral fractions may vary significantly between deposits, between stratigraphic units within deposits and even within individual coal beds. Broad-scan ESCA spectra of the raw coals (NBS standards and unknowns) are shown in Figure 1a. The two largest peaks are due to carbon (C 1s) and oxygen (O 1s). Several other peaks are evident corresponding to the mineral components (Al, Si, Ca, S). The wide-scan spectra, Figure 1b, reveal these peaks more clearly. Large fluorine (F 1s) and chlorine (Cl 2p) peaks are observed in several of these samples (Figures 1 and 2). The chlorine and fluorine may either be bonded organically or be sited inorganically within minerals such as clays, fluorite, etc., or both. The O 1s and C 1s peak intensities include a relatively small contamination component from exposure to the air prior to analysis, and from hydrocarbons originating from the ultra high vacuum (UHV) system. This contaminant layer has only a slight effect on overall sample compositions, however, note the ESCA carbon and oxygen contents for the NBS raw coals agree well with bulk analysis (Table 1). Note the large variations in spectra count rates per scan for these coals (Figure 1). Elemental surface analysis was then determined from the spectra of Figure 1 using equation 1. The calculated compo-

sition for the raw coals are shown in Table 1. One raw coal, No. 10, contains iron and titanium above the detection level as well as high sulphur. The position of this sulphur peak indicated it is present in this sample in the reduced state (S²⁻) probably as pyrite. Iron was also measured in coal No. 5 however no sulphur was detected indicating the iron probably exists in clays or as the oxide.

Coal sample No. 8, having the largest fluorine content is also unique because of its complex carbon content. The computed narrow-scan carbon (C 1s) spectra (Figure 3) indicate that sample No. 8 contains a carbon species not present in the other coals examined. The C 1s peaks at ~ 285, ~ 287, and ~ 289 eV represent carbon bonded as hydrocarbon, carbonyl and carboxyl, respectively (21-23). The fourth peak at ~ 284 eV, only seen in sample No. 8, is indicative of carbon in the form of graphite (23). Graphite carbon (C 1s) on the McPherson 36 spectrometer is found at a binding energy of 284.3 ± 0.2 eV referenced to gold (Au 4f_{7/2}, E_b = 84.0 eV) (24). The carbon spectra of the ashed sample shows similar results. The large hydrocarbon C 1s signal at ~ 285 eV is due principally to the coal's hydrocarbon fraction, however a small, variable hydrocarbon contamination contribution from the ESCA vacuum system enhances this signal. The elemental surface analyses (Table 1) indicate only fair agreement between the ESCA analyses and the bulk analyses. Analysis of the ashed coal was more

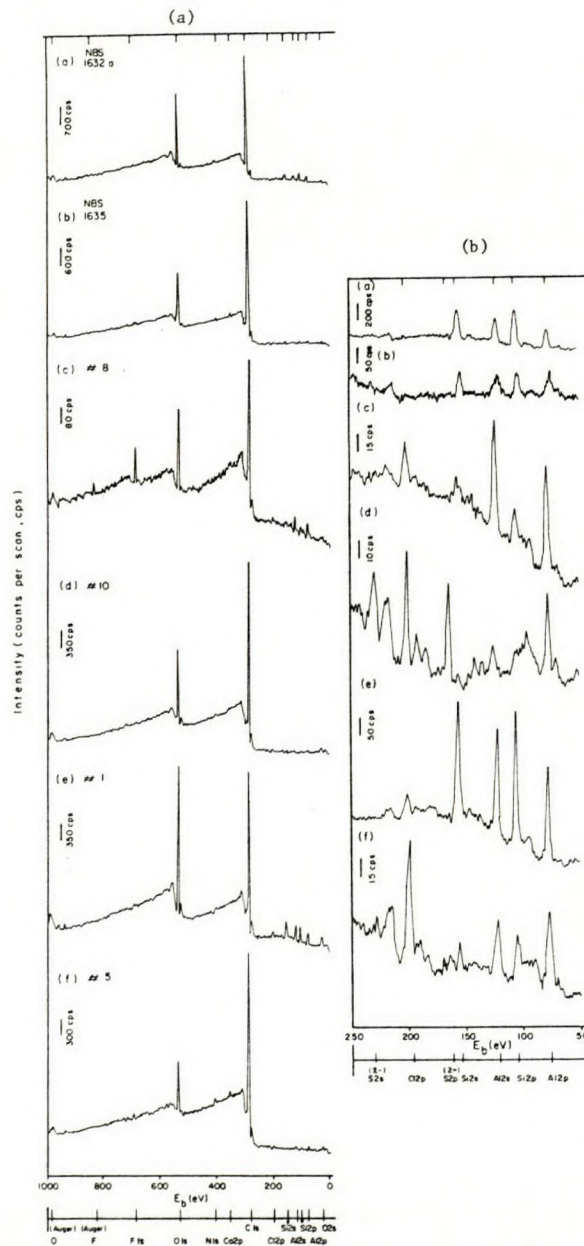


Figure 1: ESCA spectra of two National Bureau of Standards (SRM) coals and four North American coal samples; (a) Broad-scan spectra (10 scans) and (b) wide-scan spectra (10 scans). See text for details.

informative.

Ashed Coal

The four North American coals were ashed in a muffle furnace at 600°C for 6 h. Complete broad-scan and wide-scan spectra are shown in Figure 4a and 4b, respectively. The surface composition of the ashes were calculated from broad scan spectra, Figure 4, and equation 1; again each peak in the spectrum was normalized to Si 2s. There is an increased number of elements observed by ESCA in the ashed coals. The surface analysis of NBS 1633a reference ash agrees quite well with the bulk for oxygen, carbon and reasonably well for Si, Al, Ca and Ti. The results indicate the surface is depleted however in Fe and enriched in S and F.

The total surface carbon content of the NBS ash is ≈ 14 wt %. This value is thus a reasonable upper limit to UHV hydrocarbon contamination. This surface layer of hydrocarbons will be relatively constant for samples physically and chemically similar and analyzed in the instrument for essentially equal times. Thus the larger carbon contents of the in-house ashed coals indicate incomplete combustion of the coals (600°C for 6 h) and/or preferential surface deposition of carbonaceous material has been deposited on the ash surfaces. The NBS ash sample is significantly lower in surface carbon indicating it underwent more complete combustion. Ash No. 8 contains ≈ 67 wt % carbon, the narrow scan spectrum, (Figure 3), indicates much of this carbon is in the graphite form ($E_b \approx 284$ eV); note graphite is not combustible at the ashing temperature used here. Note that with the other three coals the hydrocarbon species ($E_b \approx 285$ eV) burned off, leaving behind or generating more oxygen species ($E_b \approx 287$ eV).

The majority of the oxygen measured on the ash surfaces is associated with minerals, as oxides, silicates and sulphates. The oxygen content determined by ESCA agrees with that required to chemically balance the metals and sulphur present. For example, ≈ 41 wt % oxygen is required to balance the elements Si, Al, Fe, Ti and Ca (oxides) and S (sulphate) in the NBS 1633a ash, in good agreement with that observed ≈ 46 wt %. The remaining $\approx 5\%$ is adsorbed oxygen and/or oxygen associated with carbonaceous residue coating the ash after combustion.

Ashed coals Nos. 10 and 1 contain appreciable iron, sulphur, magnesium, silicon and aluminum. Sodium is also abundant in ash No. 10. Note the high titanium content of ashes No. 1 and 5. The surface chemical analyses, Table 2, agree reasonably well with analyses by SSMS (4). The preferential surface concentration of sulphur and fluorine is apparent. Ash No. 8 contains appreciable sulphur equally distributed as sulphate (S^{6+}) and sulphide (S^{2-}). This sulphur content may originate from iron sulphide (pyrite, etc.) whose outer surface has been oxidized to iron sulphate. The iron content of the ash surfaces are substantially lower than measured by bulk analytical methods. This may be caused by a masking effect; as pyrite grains become coated by a thick oxidation shell of sulphate generated during combustion. The volatile element fluorine is probably associated with minerals such as fluorite

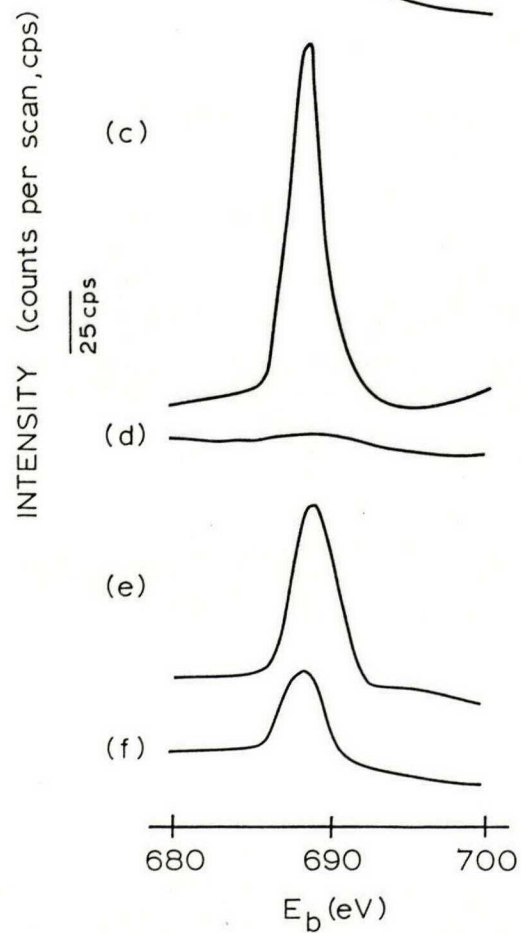


Figure 2: Narrow-span ESCA spectra (10 scans) of fluorine (F 1s) covering the 680-700 eV energy region of the broad scans shown in Figure 1a.

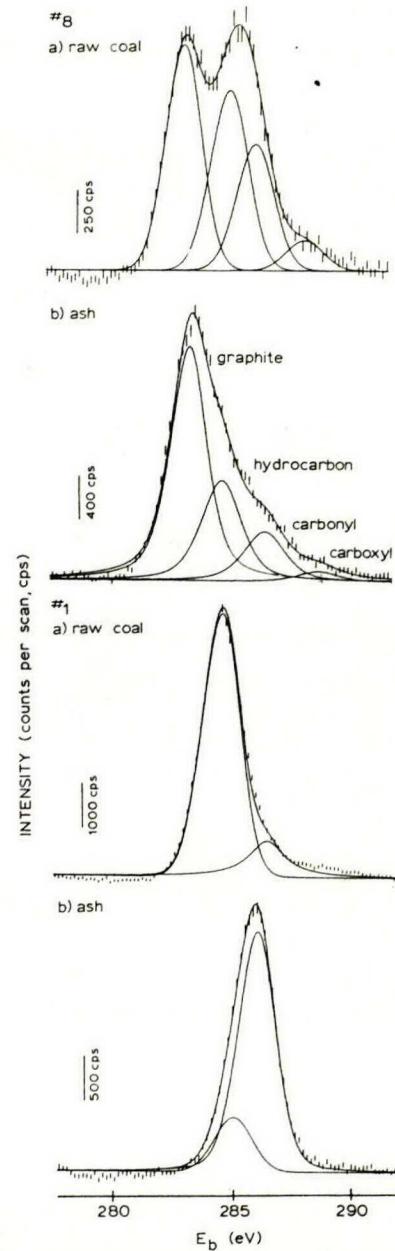


Figure 3: Narrow scan spectra (2 scans) of carbon (C 1s) covering the 278-298 eV energy region of the broad scans of Figures 1 and 4. Note the ESCA spectra of raw coals No. 1, 5, 10 were essentially identical in appearance (2 peaks) as were their ashes and, therefore, only sample No. 1 results are shown here.

TABLE 2 ESCA Chemical Analysis of Coal Ash Surfaces

Element (wt %) ± 15%	Ashed Samples ^a									
	NBS Standard		North American Coal Ash ^c							
	1633a		8		10		1		5	
	ESCA	bulk ^b	ESCA	bulk	ESCA	bulk	ESCA	bulk	ESCA	bulk
Si	16.9	22.8	2.8	3.0	5.1	10.0	10.9	10.0	21.5	25.0
Al	10.0	(14.0)	6.4	3.0	11.3	9.0	8.2	7.0	10.0	10.0
Fe	2.7	9.4	1.1	0.1	4.2	10.0	1.4	6.1	N.D.	1.0
Ca	2.2	1.1	2.9	0.1	5.1	4.0	5.8	10.0	0.9	0.5
Ti	1.3	(0.8)	0.6	0.03	0.6	0.3	1.5	0.1	2.5	1.0
S ^d	4.2	[≥0.05]	$\left\{ \begin{array}{l} 1.6 \\ 1.6 \end{array} \right.$	N.D.	3.74	N.D.	1.87	N.D.	N.D.	N.D.
F	2.0	[=0.05]	1.0	0.05	N.D.	0.05	0.9	0.05	N.D.	N.D.
Ba	N.D.	(0.15)	1.5	0.6	N.D.	0.3	0.8	0.2	N.D.	0.06
Mg	N.D.	0.50	N.D.	N.D.	6.7	10.0	0.9	5.0	N.D.	0.10
Na	N.D.	N.A.	N.D.	N.A.	3.2	N.A.	N.D.	N	N.D.	N.A.
C ^e	14.1	{ 51.14	66.5	{ 93.12	34.4	{ 56.35	40.5	{ 61.55	31.4	{ 62.34
O ^f	46.6		14.0		25.7		27.3		33.7	

^a Surface concentrations are calculated from equation 1 using XPS peak intensity ratios normalized to Si 2s.

^b Accepted values from US NBS certificate of analysis (14); values in brackets listed but not certified, values in square brackets determined in concomitant SSMS study (4).

^c Analysis by XRF and/or SSMS (4).

^d Sulphur is present as the sulphate species (S⁶⁺) except for ashed sample No. 8 where sulphide (S²⁻) was also detected.

^e As per Table 1; note some of this carbon is probably carbonaceous surface sited residue deposited during the coal ashing step.

^f As per Table 1; some of this oxygen will be from oxygen species such as CO, CO₂ etc., associated with the carbonaceous coating (see e).

(CaF₂), clays etc. In ash No. 8 there is the possibility that sulphur-carbon bonding exists, perhaps associated with the graphite component. Fluorine on the ash surfaces is more likely adsorbed during combustion of the coal and/or be associated with resistate mineral matter. Fluorine contamination of the sample surfaces through handling or from the spectrometer is unlikely. Elevated levels were also detected using spark source mass spectroscopy and the fluorine levels varied significantly between consecutive sample analysis by XPS and SSMS. Coal No. 8, No. 10 and their ashes contain low silicon but appreciable aluminum. It is therefore possible that this aluminum is bonded organically, as has been previously postulated (1) and/or exists as the oxide Al₂O₃. The presence of appreciable calcium and fluorine in coal ash No. 1 and 8 possibly indicates the presence of mineral fluorite (CaF₂). Coal ash No. 5 contains only oxygen, carbon, aluminum, silicon, titanium and calcium in excess of the detection limits (≈ 0.1%). The ratio of Si/Al is much greater than unity indicating the presence of quartz rather than clay minerals.

The ESCA surface findings agree semi-quantitatively with the NBS reference bulk ash values for silicon, aluminum, calcium, iron, titanium, carbon and oxygen.

The surface contents of sulphur and fluorine, however, greatly exceed those found in the fly ash bulk analysis indicating their preferential surface concentration on ash particles. Note that the ashed samples do not contain detectable chlorine and nitrogen although high levels are measured in the raw coal. Combustion liberates the nitrogen and chlorine indicating some/all is organically bound.

CONCLUSIONS

The results of this preliminary study indicate ESCA is a useful spectroscopic technique for fingerprinting coal deposits. It can be applied semi-quantitatively for major elements in coal and ash if appropriate reference standard samples are available. Ashing raw coal improves the detection limits by an order of magnitude, however, volatiles (F, Cl, S, etc.) may be lost. In-situ analysis of raw coals by ESCA, although less sensitive, measures volatiles lost during sample preparation and analysis by other analytical techniques. ESCA is excellent for monitoring surface concentrated species, e.g. F and Cl, on fly ash and has detected elements in different chemical environments, e.g. sulphur as S²⁻ and S⁶⁺ and carbon as graphite, hydrocarbon or oxy-carbons.

The absolute detection limit of $\approx 10^{-9}$ g cm $^{-2}$ ($\approx 0.1\%$ bulk), determined in previous work, is verified in this study using the NBS coal reference standards. Several interesting results not possible to determine by non-surface techniques were revealed using ESCA for these coals and ashes; for example, the unique nature of coal No. 8, the high S and F levels

on ashes and the association of Cl, F, and Al with the mineral and possible the organic fractions of coal are indicated.

An estimate of the minerals present in the coal and ash is made directly and non-destructively using ESCA. For example ashed coal No. 5 contains appreciable quartz but little clays (alumina-silicates). ESCA spectra produced in future coal studies at greater resolution and longer acquisition times may detect additional elements and improve the present knowledge of coal element siting.

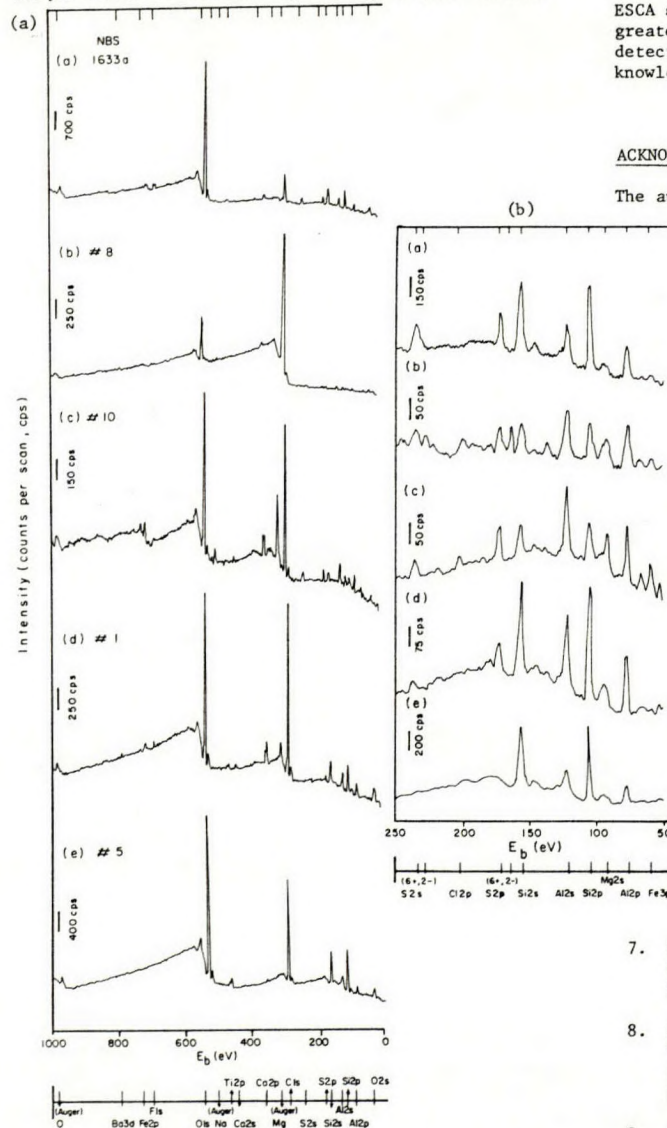


Figure 4: ESCA spectra of the National Bureau of Standards (SRM) coal ash and four North American coal ashed samples; (a) broad-scan spectra (10 scans) and (b) wide-scan spectra (10 scans). See text for details.

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