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The Determination of 28 Elements in Whole Coal by Direct-Current Arc Spectrography

by

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Introduction

The combustion of coals as a source of energy for thermal and electrical power generation is a well-established technology that has been, and continues to be, in use throughout the world. The chemical products, both volatile and residual, of coal combustion sometimes are considered as potential materials resources, but most frequently, simply become pollutants of the biosphere. In addition to such concerns over the possible fates in the environment of the many inorganic elements in the combustion process, there are other quite valid interests in the concentrations and distributions of these elements for use in research on coal origins, in constructing trace element models of coal strata, in synfuel processes, or in the production of chemicals from coal. The potential number of samples and of chemically diverse elements to be determined in investigations stemming from these interests requires analytical methods having multiple-element analysis capability, such as that offered by atomic emission spectrography (Mills, et al., 1981).

The majority of existing chemical and instrumental analysis methods are for coal ash that comes from oxidizing pulverized coal at 500° C (ASTM, 1979). A significant number of elements having probable organic association as organic acid salts, porphyrins, organometallics, or other forms, may be volatilized during these common ashing procedures. Ag, B, Be, Br, Cl, Ga, Ge, I, Mo, Ni, P, S, Sc, Se, Sr, Ti, U, and W now are identified as elements that are at least partially associated with organic phases in coals (Finkelman, 1980; Ruch, et al., 1974; Gluskoter, et al., 1977). Volatilization losses of these elements during ashing procedures obviously can be detrimental to the accuracy of analysis, and the normally considered benefit of 'enrichment' of elements by ashing totally lost. The advantages of analysis directly on whole coals are apparent in terms of circumventing long ashing intervals, volatilization losses, and additional exposures of samples to possible contamination.

Until now, the only widely-used multiple-element analysis techniques for whole coals have been instrumental neutron activation analysis and spark source mass spectrography. Neither technique is particularly suitable for rapid, inexpensive analyses of large quantities of samples. Single element determinations by X-ray fluorescence spectrometry (S, Cl, Br, Se), spectrophotometry (As, Sb), specific ion electrode (F), and electrothermal atomization atomic absorption spectrometry (Hg, As, Sb, Se) are in common use (Simon and Huffman, 1971). Progress is being made in the analysis of coal ashes and whole coals, including coal microlithotypes, by energy-dispersive x-ray fluorescence spectrometry

(Benson, et al.,m 1980; Johnson, et al., 1980). Recently, Langmuhr and Aadalen (1980) succeeded in directly determining Cu, Ni, and V in powdered samples of coal and petroleum coke by graphite furnace atomic absorption spectrometry. The need for greater analytical capacity is quite apparent. This communication details two newly-developed atomic emission spectrographic methods that enable accurate multiple-element determinations of 28 elements in pulverized whole coal samples. The methods have proved to be particularly useful for the analysis of coal microlithotypes, such as vitrites. The simplicity, efficiency, and low cost of these methods are expected to be attractive to those involved in the characterization of coals.

Approach

A principal difficulty encountered in attempts to directly arc pulverized coal samples centers on the rapid evolution of gases that occurs immediately following initiation of the arc and the subsequent burning of the organic phases that remain in a cup-shaped electrode (anode). The evolved gases can, and usually do, blow material from the anode, thus creating uncontrolled losses of previously weighed sample material, and the erratic flaming of the organic phase can produce unwanted spectral bands from carbon-centered free radicals. These events constitute very irreproducible processes that control the transport of material from the hot anode cup into the arc discharge column. Such severe problems related to the arcing process have been solved for the sample types discussed herein by mixing the powdered coal with an appropriate buffer to control both sample transport into and excitation conditions in the arc column and to greatly diminish the possibility for flaming of the hot coal dissociation products. With these very important aspects of arcing well controlled for coal samples, the methodology for d.c. arc spectrographic analysis becomes quite conventional.

Method

A. The Sample

In general, samples pulverized to approximately -100 mesh are received from the grinding laboratory operated by the Branch (Branch of Analytical Chemistry). Most small, unground samples of coals, such as hand-picked vitrites, are pulverized in the spectrographic laboratory by a hand-grinding process in an agate mortar. This grinding procedure requires that the agate mortar and pestle be cleaned well to avoid contamination of samples and that simple precautions be taken to avoid losses of sample from the mortar.

A procedure for cleaning the surfaces of an agate mortar and pestle consists of the following steps: 1) Soak the grinding surfaces of the mortar and pestle in dilute (1:1) nitric acid for approximately 20 minutes. Pour off this dilute acid solution and rinse the mortar and pestle with distilled water. 2) Grind clean beach (quartz) sand in the mortar until the sand is a fine powder. Discard the pulverized sand. 3) Wash the mortar surface with a laboratory detergent, using a stiff-bristle brush to thoroughly scrub the surface. 4) Thoroughly rinse the grinding surfaces of both the mortar and pestle with distilled water, and allow both to dry in a clean area of the laboratory. Drying is sometimes accelerated by a final rinse of the grinding surfaces with ethanol. This complete cleaning procedure is done only once, at the beginning of a series of similar coal samples, and then, between samples in the series, only step 2 is used.

Grinding of Sample

Crush whole coal fragments ($\leq$10 g, total) in an agate mortar that has a circular plastic cover (plexiglass*) to prevent loss of particles spattered during the grinding process. The agate pestle fits through a circular aperture in the center of the plastic cover. Grind each coal sample to approximately -100 mesh. Then, place the pulverized sample into a clean glass bottle, cover the bottle with a watch glass, and place the covered bottle in a drying oven maintained at 110° C. After drying the sample in the oven overnight, remove the sample, in its container, and place it in a desiccator (desiccant: drierite*), where it should be kept until the next stage of preparation.

Preparation of Sample

Place 100 mg of the dry, pulverized coal sample into a clean agate mortar. To this coal powder, add 100 mg of pure Li_2CO_3 (maximal impurities 10 ppm) and 50 mg of pure graphite powder (-200 mesh). Thoroughly mix and grind these materials to obtain a final homogeneous mixture. For samples that have especially high concentrations of analyte elements, a higher weight ratio of Li_2CO_3 to sample may be necessary. However, this weight ratio should not exceed 10, which generally is considered to be a cut-off point for successful hand mixing of pulverized solids. Transfer 25 mg of this mixture, as weighed on a torsion or electronic balance, into the appropriate graphite electrode (Table I), and firmly tamp the mixture into the electrode cup with a nippled tamper (See Dorrzapf (1973) for a description of an Al tamper). Just prior to arcing these electrodes, dry the filled electrodes in an oven at 110° C for 4 hours. A convenient holder for these electrodes consists of a 9 x 15 cm aluminum block into which a rectangular array of 45 holes (6.4 mm diameter and 18 mm depth) had been drilled. This drying step removes water and other readily volatilized components that usually cause loss of sample material from the anode just after initiation of the arc discharge.

Preparation of Standards

Calibration standards consist of homogeneous mixtures of oxides and carbonates of the analyte elements in a Li_2CO_3 matrix. Dilutions of commercially available standards, 43 elements in Li_2CO_3 (Spex Industries*, Metuchen, New Jersey), provide calibration standards for the concentration range from 1 ppm to 1000 ppm for each element of interest. Dilute individual standards on a weight-weight basis with high purity Li_2CO_3 ($<$10 ppm total impurities), while being

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* Names of products and of companies are included for information purposes only and no endorsement of them is made by the U.S. Geological Survey.

careful to avoid strictly serial dilutions that produce undesirable additive errors in the concentrations of elements at the lower concentration levels. Do all mixing for these dilutions by thoroughly grinding together the necessary materials in a clean agate mortar.

Reference standards are prepared from National Bureau of Standards (NBS) coals numbered 1632, 1632a, and 1635, which can be diluted with lithium carbonate in the same fashion as the samples. Drying and handling of the NBS standards should follow the procedure used for samples.

Arcing of Samples and Standards

All samples and standards are arced in an argon-oxygen, or argon, laminar stream that is concentric to the anode and is introduced through an alumina nozzle arrangement known as a Helz jet (Helz, 1964). Both the arcing conditions and the atmosphere were chosen to give complete volatilization of analyte elements from an anode cup into the arc column and to effectively excite those atomic energy levels giving the spectral lines listed in Table II, without causing high spectral background. In the case of the volatile elements (Group II, Table II), the objective is to vaporize and excite these elements over a relatively long interval while distilling insignificant amounts of matrix elements into the arc column. The present method is one adapted from that of Annell for volatile elements in silicate and carbonate rocks (Annell, 1967). For elements in chemical forms that exhibit low volatility (Group I, Table II), total vaporization of each sample into the arc column is necessary for an accurate determination.

Complete details on the spectrographic equipment and the conditions for arcing samples and for making the necessary spectrographic measurements are given in Table I. Maintaining a 4-mm gap between the tips of the electrodes is essential to the achievement of the accuracy and precision that this approach is capable of producing.

Table I. Spectrographic Equipment and Operating Conditions.

Subject	Group I Elements (Involatile)	Group II Elements (Volatile)
Sample	100 mg pulverized whole coal mixed with 100 mg Li_2CO_3 powder (American Potash) and 50 mg graphite powder (-200 mesh, Ultra Carbon*). 25 mg of mixture tamped into anode cup.	100 mg pulverized whole coal mixed with 100 mg Li_2CO_3 powder (American Potash) and 100 mg graphite powder (-200 mesh, Ultra Carbon*). 50 mg of mixture tamped into anode cup.
Spectrograph	Ebert mounting, 3.4 m focal length, 0.5 nm/mm reciprocal linear dispersion in first order, grating: 600 grooves/mm, blazed for 300 nm.	Eagle mounting, 3 m focal length, 0.55 nm/mm reciprocal linear dispersion in first order, grating: 590 groves/mm, blazed for 300 nm.
Slit	25 µm x 2 mm for spectra from standards and samples. 25 µm x 4 mm for spectra from iron arc.	25 µm x 2.5 mm for spectra from standards and samples. 25 µm x 5 mm for spectra from iron arc.
Wavelength Range	240 - 360 nm, first order.	250 - 340 nm, second order.
Illumination	Arc image focused on collimator mirror by a 450 mm focal length cylindrical quartz lens located at the entrance slit.	Arc image focused on grating by a 450 mm focal length cylindrical quartz lens located near the entrance slit.
Filters	Neutral density, 35% T plus 75% T, for exposures of samples and standards. Two-step neutral density filter, 40% T: 100% T, for iron arc exposures used in calibration of the photographic emulsion.	None for exposures of samples and standards. Two-step neutral density filter, 50% T: 100% T, for iron arc exposures used in calibration of the photographic emulsion.
Electrodes	Cathode: 3.2 mm (0.125 inch) diameter x 3.8 cm (1.5 inches) long graphite rod (Ultra Carbon* no. 5001). Anode: 3.6 mm (0.14 inch) diameter, thin-walled graphite electrode (Ultra Carbon* no. 1590).	Cathode: Same as for Group I. Anode: 5.7 mm (0.225 inch) diameter graphite electrode (Ultra Carbon* no. 3170).

Continued

Table I. Spectrographic Equipment and Operating Conditions. (Continued)

Subject	Group I Elements (Involatile)	Group II Elements (Volatile)
Excitation	Arc Current: Stepped arc current, 5 A d.c. for 10 s, 15 A d.c. for 95 s, across constant 4 mm arc gap. Voltage source of 300 V, open circuit. Electrode supporting the sample is the anode.	Arc Current: Stepped arc current, 8 A d.c. for 10 s, 25 A for 110 s, across constant 4 mm arc gap. Voltage source of 300 V, open circuit. Electrode supporting the sample is the anode.
	Atmosphere: 80% Ar, 20% O_2; 6.6 L/min through Helz jet (Helz, 1964).	Atmosphere: Ar, 6.6 L/min through Helz jet (Helz, 1964).
Photography	Eastman-Kodak* III-0 emulsion on 101 x 254 mm (4 x 10 inch) glass substrate. Emulsion processed in Kodak D-19 developer for 3 min (20°C), short stop solution for 30 s, and fixer for 10 min. Then, the plate was washed in tap water for 10 to 20 min, allowed to drain, and dried with warm air for 5 min.	Same as for Group I elements.
Microphotometry	All microphotometry was done by conventional methods, such as those described by ASTM (ASTM, 1971).	Same as for Group I Elements.

Table II. Elements, Spectral Lines, and Determination Limits.

Group I[a]	Wavelength[b],nm	Spectrum[b]	Determination Limits, %[c]		
Al	265.248	I	0.01	-	2.0
	266.039	I	0.01	-	2.0
B	249.773	I	0.005	-	0.1
Ba	455.403	II	0.002	-	0.05
Ca	315.887	II	0.01	-	0.3
	422.673	I	0.005	-	0.01
Co	345.350	I	0.0002	-	0.05
Cr	302.156	I	0.002	-	0.2
	425.435	I	0.0002	-	0.02
Cu	327.396	I	0.0002	-	0.02
Fe	259.837	II	0.05	-	2.0
	302.107	I	0.002	-	1.0
Mg	277.983	I	0.01	-	0.2
	285.213	I	0.0002	-	0.02
Mn	279.482	I	0.0002	-	0.1
	279.827	I	0.0002	-	0.2
Mo	317.035	I	0.0005	-	0.2
Nb	316.340	II	0.002	-	0.1
Ni	305.082	I	0.002	-	0.1
	341.476	I	0.0002	-	0.05
	349.296	I	0.01	-	0.2
Si	251.920	I	0.2	-	3.0
Ti	308.940	II	0.002	-	0.2
	316.257	II	0.005	-	0.2
V	318.341	I	0.0005	-	0.1
Zr	327.926	II	0.001	-	0.2
Group II[a]					
Ag	338.289	I	0.0002	-	0.02
As	278.020	I	0.02	-	0.2
Bi	306.772	I	0.0002	-	0.005
Cd	326.106	I	0.0002	-	0.1
Ga	294.364	I	0.0002	-	0.05
Ge	265.118	I	0.0005	-	0.05
	303.906	I	0.0005	-	0.005
Hg	253.652	I	0.002	-	0.1
Pb	283.306	I	0.0002	-	0.01
Sn	317.505	I	0.0002	-	0.02
Tl	276.787	I	0.0002	-	0.02
Zn	334.502	I	0.001	-	0.05

a. Group I and Group II refer to the involatile and volatile groups of elements, respectively.

b. Wavelength and spectrum are from the NBS Wavelength Tables (Meggers et al., 1975).

c. Lower and upper limits for each element are in units of weight percent, that is (g element / g sample) X 100.

Accuracy and Precision

In general, one can correctly expect the accuracy of analysis by d.c. arc spectrography to be directly related to successful element-by-element calibrations of an instrument with standard materials that closely resemble the materials to be analyzed. However, in this instance, the effective matrix of the "arced sample" has been substantially modified through the use of a lithium carbonate buffer. This modification of the sample matrix makes the "arced sample" resemble the lithium carbonate matrix of the Spex* calibration standards. The quantity of lithium carbonate, relative to that of the sample in any given "arced sample", is sufficient to control the fusion, vaporization, transport, and excitation processes. Thus, a situation is created in which the effective sample always arced is lithium carbonate. The validity of this approach is supported by the correlation plot of Figure 1, showing the trend in measured analyte concentration with the analyte concentration published by NBS for the Pennsylvania bituminous seam coal, NBS standard reference material number 1632a. Log-log axes have been used in Figure 1 to enable a single correlation plot that covers several magnitudes of concentration, that is, from low ppm values for the elements Co, Ga, Pb, etc. to percent concentration values for Fe, Al, and Si. The concentration ranges for the fifteen elements used in this illustration, plus other elements capable of being determined by the d.c. arc spectrographic methods described in the present work, are summarized in Table II. The reference, or accepted, concentrations used in this plot are values that are certified by NBS (*) (National Bureau of Standards, 1978), published as information only (uncertified) concentrations by NBS (x) (NBS, 1978), or published by Failey (Failey, 1979) as concentrations determined by prompt gamma neutron activation analysis(+). Elements exhibiting the largest deviations from the unity-slope line of Figure 1 are Al, Ca, Mn, and Si. Experience in the analyses of other coals, vitrinites, exinites, and inertinites indicates that the deviations for these four elements are random, rather than systematic. Measurement errors for our spectrographic method are typically ±20%, and the precision of the method is ±10% for concentrations well above (X5) the determination limits.

Application of Method

Our experiences with this spectrographic method have focused on the analysis of coal microlithotypes (organic constituents), expecially a series of vitrites from a length of a single drill-core sample of coal. Vitrites and vitrinites appear to be end products from humic acids and humic substances which have high sorptive capacities for trace elements, particlarly in the initial phases of coalification. This drill core is from the I and J coal beds of the Ferron Sandstone member of the Mancos Shale, Emery County, Utah, for which Ryer (1981) has developed a depositional model. The existence of this model has made cores from these coal beds particularly attractive for petrographic study. The core was taken from the most landward of the drill-core series which followed a landward-to-seaward transect across the edge of the swamp in which material of the I and J coal beds accumulated. The drill core extends 1.37 m through the J coal (drill core depth interval 39.11 to 40.48 m), through an intervening shale layer of bentonite (40.57 to 40.75 m), and finally, through the I coal (40.75 to 47.30 m). Variations in the concentrations of Al, Si, Ca, and Fe in vitrinites

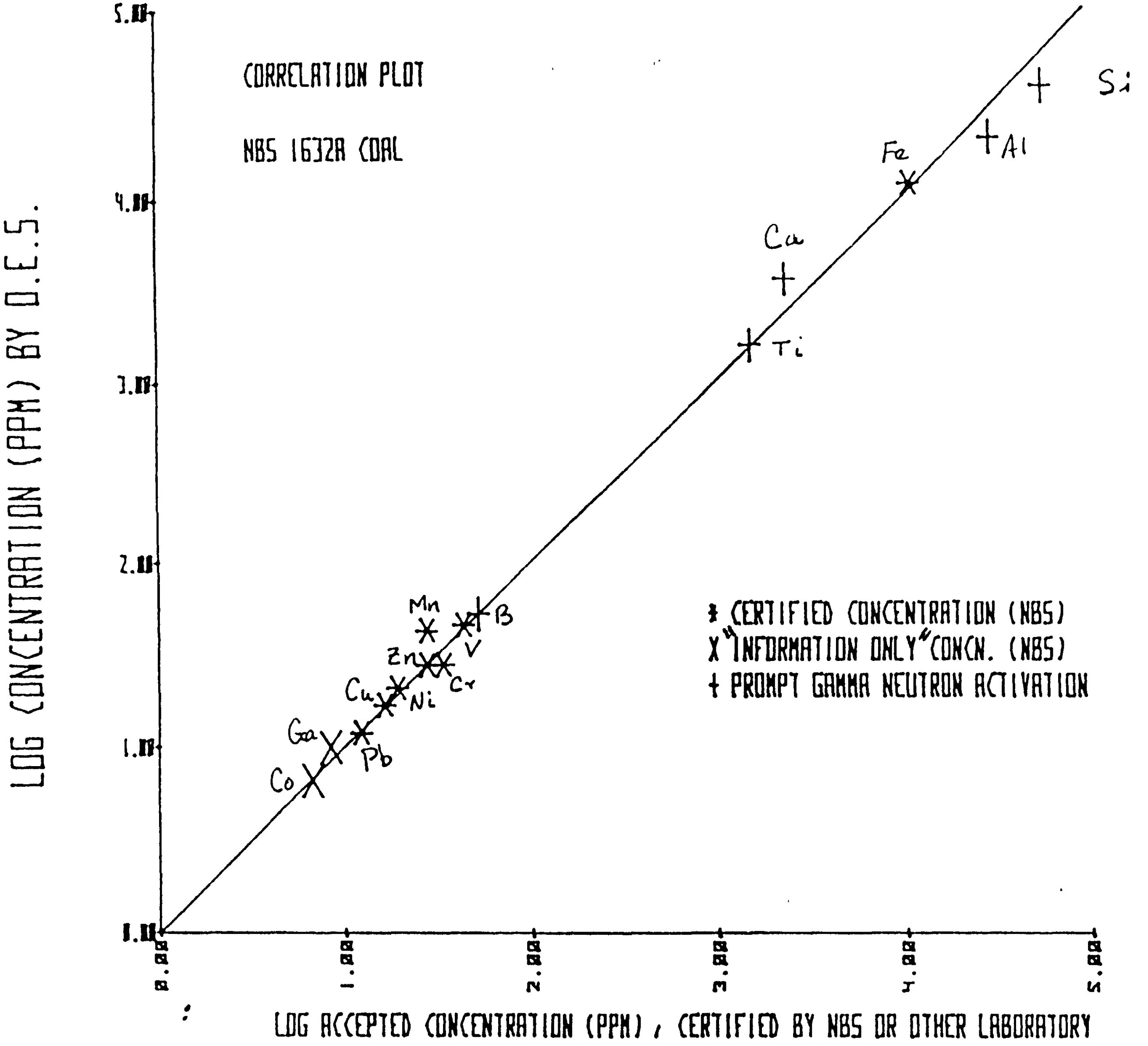

Figure 1. Correlation Plot for Fifteen Elements Determined in NBS 1632A Bituminous Coal Standard by D.C. Arc Spectrography.

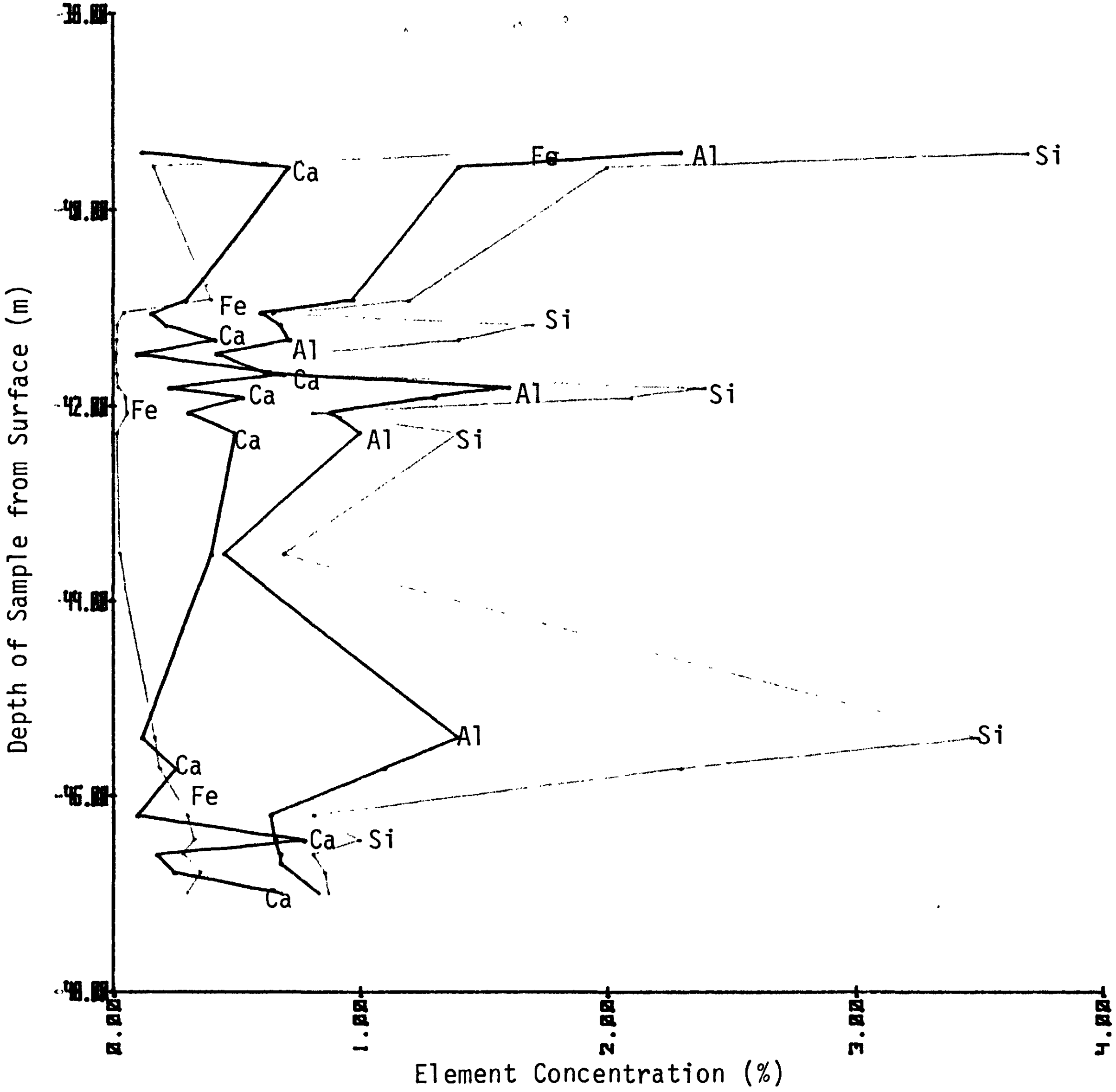

Figure 2. Variations in the Concentrations of Four Elements in Vitrinites as a Function of Depth for a Single Drill Core.

from 20 different segments of this core, as determined by our d.c. arc spectrographic method, are illustrated in Figure 2. The significance of some variations in elemental concentrations with location in the drill core have been described for a larger group of 23 elements that included Al, Si, Fe, and Ca by Minkin et al. (1982) and by Chen et al. (1984), particularly for their measurements with a proton microprobe and from 8.391 keV and 16.284 keV synchrotron radiation, respectively. For the present purpose of illustrating the capabilities of the d.c. arc spectrographic technique, it is adequate to note that the variations in the concentrations for Al, Si, Fe, and Ca, shown in Figure 2, and the variations for all other elements for which concentrations were measured both by d.c. arc spectrography (Table II), and by proton microprobe and synchrotron radiation showed satisfactory agreement in a comparison of results. Importantly, two vitrain "standard samples", H2-42-P1 and EC77CL1, that were used as reference materials for proton microprobe (Minkin et al., 1982), and to a lesser degree for synchrotron radiation (Chen et al., 1984), were largely charcterized by the d.c. arc spectrographic method described herein. The spatial correlations of Al and Si appear to be clay-related, whereas the Fe distribution shows a general trend of increasing concentration from top to bottom, with accumulation areas occurring at three separate intervals (42.09-43.52 m, 44.30-82 m, and 45.77-46.72 m). Chen et al., (1984) have suggested that this variation in Fe concentration with depth potentially can be used as a criterion in coal facies analysis. Concentrations of Ca and Fe in the vitrinite from Upper Freeport coal have been observed to vary in a parallel fashion (Minkin et al., 1982), but here, these two elements demonstrate only a very approximate correlation. Interpretation of these data in the light of possible processes that can produce the measured trends in concentration is beyond the scope of this discussion. However, the capabilities and usefulness of the described direct-current arc spectrographic method to provide useful concentration data for studies of coals have been established.

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