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NUCLEAR METHODS IN COAL RESEARCH

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ABSTRACT

Nuclear methods, particularly neutron activation analysis (NAA) provide useful information about elemental constituents in coal and fly ash, but often other techniques are required to supplement NAA data. Spark source mass spectrometry and atomic absorption have been studied as methods for determination of certain elements in coal that are not easily measured by NAA. In work concerned with the chemical speciation of elements in fly ash, a number of analytical techniques have been used; these include NAA, chemical etching and separation, optical and electron microscopy and x-ray diffraction.

INTRODUCTION

Coal is to become increasingly important in energy production in this country. Nuclear methods of analysis are making significant contributions to our understanding of coal composition, coal combustion, and the structure and composition of fly ash. Neutron activation analysis (NAA) is the most useful and universally applied nuclear analytical technique, but the complex chemical problems associated with coal utilization are not going to be solved by application of NAA or any other single technique. Rather, instead, the analytical chemist must be knowledgeable in many aspects of his discipline and should be able to choose from a battery of methods those that can best help solve his problem.

This paper presents examples of two such multi-disciplinary approaches: (1) comparison of several analytical methods for trace elements in coal difficult to determine by NAA and (2) use of old fashioned wet chemistry, optical and scanning microscopy, and chemical inference for the elucidation of the chemical speciation of elements in fly ash.

STATISTICAL STUDY OF METHODS FOR SOME DIFFICULT ELEMENTS

In the course of a 15-month study of trace elements in coal from three different steam plants (1), we decided to make some comparisons between several analytical techniques that might be used for elements not easily determined by NAA.

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DISCLAIMER

Isotope dilution spark source mass spectrometry (IDSSMS) was compared with instrumental neutron activation analysis (INAA) for determination of Ba, Cr, Sr, and As. For IDSSMS a known weight of a mixture of stable isotopes to be used as tracers was added to a sample of ground coal. The stable isotopes plus sample were homogenized and then fired in the RF arc of the spark source mass spectrometer. The intensities of the lines of the isotopes present were measured, and the concentrations of these elements in the coal were obtained by comparing the intensities of the lines from the known added enriched stable isotopes to those of lines from the sought elements. An underlying assumption in this method is that sample and spike both volatilize in an identical manner.

Mercury was determined by flameless atomic absorption (AA). Arsenic was determined by an arc emission, atomic absorption method described in (3).

In a second series of special comparisons, AA was compared with IDSSMS for determining Zn, Cu and Pb. These data were not combined with the other since the comparisons were not run over the full 15 months.

Table I summarizes the results of a statistical comparison of the values obtained on coal samples by these methods. As can be seen from the significance probabilities, the agreement between INAA and IDSSMS is

TABLE I

Comparison of INAA with IDSSMS for Determination of Ba, Cr, and Sr, and with He Arc Emission for Determination of As

Procedure	N	$\bar{X}$ μg/g	σ	X_{min} μg/g	X_{max} μg/g	t	Significance Probabilities*
				Ba			
INAA	42	155.6	42.3	94	232	3.19	0.01
IDSSMS	42	132.3	46.0	40	220		
				Cr			
INAA	45	29.54	6.6	21	59	2.61	0.011
IDSSMS	45	24.91	10.6	7	48		
				Sr			
INAA	43	115.7	31.7	46	185	0.097	0.923
IDSSMS	45	114.9	37.6	44	230		
				As			
INAA	31	29.66	11.8	12.4	58	5.61	0.001
He Arc	31	36.24	13.3	16.2	65		

*Probability that the t value is due to chance alone. Values $\leq$.01 are taken as indicating a significant difference in the calculated means of the analytical results for a given element.

marginal for Ba and Cr but excellent for Sr. Barium is determined by activation through measurement of the 166 keV gamma-ray of 86-minute ^{139}Ba after a 20-minute decay. The Compton background is large due to the presence of other short-lived activities, and this could be a cause for error in the INAA method. Chromium is determined by measuring the 320 keV gamma-ray from 27.8 day ^{51}Cr after a long decay. No obvious explanation can be found for why this INAA value should be high. A possible cause for low values in IDSSMS is failure to volatilize spike and sample element at the same rate. Both the IDSSMS and INAA laboratories run the NBS coal standard (SRM #1632) and agreement between the laboratories for both Ba and Cr is usually within a few percent.

The INAA values for arsenic are all consistently lower than the He arc values, and although we have no explanation for this, we believe the AA values to be more reliable.

Table II gives results obtained on a 6-month trial comparison of AA versus IDSSMS for three elements. The purpose of this test was to see if AA could be used to reduce some of the sample load on the mass spectrometer. Here the significance probabilities show that the methods do give comparable results. Thus, it appears that the simpler and less expensive AA technique can replace IDSSMS for determinations of Cu, Zn, and Pb.

TABLE II
Comparison of AA and IDSSMS for Determination of Cu, Zn, and Pb in Coal

Procedure	N	$\bar{X}$ μg/g	σ	X_{min} μg/g	X_{max} g/g	t	Significance Probabilities*
				Cu			
AA	23	21.77	1.73	17.3	25.0	1.18	0.25
IDSSMS	23	20.2	6.03	12	42		
				Zn			
AA	23	24.90	7.87	14.2	40	0.34	0.74
IDSSMS	23	24.09	8.46	10	40		
				Pb			
AA	23	13.22	4.67	8.2	30	1.33	0.19
IDSSMS	23	11.43	4.44	5.0	21		

*(See Table IV for explanation)

RESEARCH METHODS FOR STUDY OF THE CHEMICAL SPECIATION OF FLY ASH

At the Third International Conference on Nuclear Methods in Environmental and Energy Research (1977), this author stated, "Of these (problems) probably the most urgent, difficult and important is the development of speciation techniques". Since that time very little information has appeared on chemical speciation of trace elements in fly ash. In our group at ORNL Lester Hulett and co-workers have taken an indirect approach to this problem. There is no "magic spectroscopy" with which one can unambiguously detect elements such as Cr, Ni, As, Pb, at the 100 ppm level and directly determine their chemical state. Therefore, Hulett used classical methods of chemical inference, taking the solids apart by physical (size fractionation and magnetic separation) and chemical (HF etching) methods. NAA was the primary tool then used to analyze these fractions. It is our thesis, based on chemical inference, that chemical species of trace elements in fly ash are largely determined by the matrix in which the elements are dissolved.

Fly ash from four TVA power plants was studied in these experiments, complete details of which are given in reference 4. These four plants used different firing conditions and different coals but results from all four were essentially the same. Ash was separated according to size and magnetic character. Most of the work reported here was done on four nonmagnetic 100-200 μm fractions and their 100-200 μm magnetic counterparts. One sample of nonmagnetic ash size <37 μm was also studied, and results agreed qualitatively with those obtained on the larger size samples. We, therefore, think our conclusions are applicable to all sizes of particles.

Seen before etching under the optical microscope the particles were qualitatively the same for all four ashes. We categorized them into four types:

1. Spheres and spherical shards--some were transparent and translucent, some were white-opaque, having solid cores, some were of the hollow cenosphere types.

2. White opaque oblong shapes--these had the general appearance of miniature pebbles.

3. Nonfused quartz sand particles--these particles had sharp edges and fracture surfaces. X-ray diffraction confirmed that they were quartz.

4. Carbon-cinder particles--these are very high in carbon and sulfur. Type-4 particles constitute a rather large weight percentage of the 100-200 μm size fraction for all four ashes.

The effect of etching was also qualitatively the same for the four different specimens studied. Concentrated HF consumed almost all the mineral components, leaving only the type-4 particles. In this manner we accounted for the carbonaceous material, so we could estimate the total aluminosilicate content of the four specimens.

Particles were etched with a 1% HF solution for 16-20 hours. The material removed by the etch is believed to be primarily glass; the noncarbonaceous residue is mostly crystalline mullite. Type-3 and 4 particles were relatively unaffected by the 1% HF etch. A large number of the type-1 and type-2 particles retained their overall shapes through the etching process, even though large percentages of their masses had been removed. We isolated collections of type-1 and type-2 particles for x-ray diffraction and scanning electron microscopy energy dispersive x-ray fluorescence (SEM-EDX) analysis. For all four ashes we found that the etched type-1 and type-2 particles produced very strong diffraction patterns corresponding to mullite. Some patterns also had weaker lines corresponding to quartz. The SEM-EDX spectra showed, for all four ashes, that the Si:Al ratio was reduced to a value corresponding to mullite compositions. It is also significant that the hardness of the etched type-1 and type-2 particles was much less than for the unetched. The etched particles were easily crushed; the glass phase which cemented the mullite crystals together and gave the particles their strength was removed by the etching. Most of the nonetched particles resisted crushing. It is beyond the scope of this paper to discuss the morphology of these particles, but it is interesting to see the changes wrought in one of them by etching. Figure 1 shows an etched type-1 particle that contains a clustering of mullite crystals having the needle-form habit (acicular form). Etching has changed the Al:Si ratio in this particle from about 1:2 to 3:1, which is the ratio in mullite.

Glass and crystal phases of the nonmagnetic matrices were isolated from each other for separate elemental analyses. The dilute HF etching procedure was used for dissolving the glass phases, leaving mullite-quartz and C residues. The mullite quartz phases were then removed from the C with 48% HF. Aliquots of these extracts were evaporated to dryness in specially designed capsules and submitted for NAA. Portions of the remaining solutions were analyzed by atomic absorption. Element distributions between glass and mullite-quartz phases for Bull Run fly ash are listed in columns 1-2 of Table III. Weighted averages of columns 1-2 are entered in column 3, labeled "Mass Balance." These were calculated by multiplying the concentrations in columns 1 and 2 by the respective weight fractions of glass and mullite-quartz and summing. The mass balance data of column 3 of Table III can be compared with the total analysis data of columns 4 and 5. The data of column 4, labeled "Total Aluminosilicate" were obtained by extracting samples with 48% HF, in which all mineral matter was dissolved, leaving C behind. The concentrations of column 5 were measured by activation analysis only of combined aluminosilicate plus C.

Table III shows that the mullite-quartz phase is relatively pure and free of most of the trace elements. All of the alkali and rare earth elements are clearly more concentrated in the glass phases. All of the alkaline earth elements are also more concentrated in the glass phases with the exception of Mg. We think the Mg concentrations for the crystalline phases are too high. They do not agree with analyses of individual crystallites by SEM-EDX, in which no Mg was found. This discrepancy was probably caused by the extraction of Mg from C during the 48% HF dissolution of the quartz-mullite phase. We, therefore, make the generalization that the mullite-quartz phase is free of all +1 and +2 valent elements. This means that the majority of trace elements in the aluminosilicate matrix of fly ash are concentrated in the glass phases.

There are certain trace elements having +3 and +4 valences that are notable for their high concentrations in the mullite-quartz phases: Ti, V, Cr, Fe, Ga, and Zr. Vanadium is about equally distributed in the glass and crystalline phases while Cr and Ga are predominantly contained in the crystalline. All of these elements have ionic radii small enough to allow isomorphic substitution in the mullite lattice. Therefore we have the following inference about the chemical species of certain of the trace elements:

> Trace elements contained in the mullite matrix of fly ash are in the form of isomorphic substitutions:

TABLE III

BULL RUN FLY ASH: ELEMENT DISTRIBUTIONS IN ALUMINOSILICATE PHASES
CONCENTRATIONS IN μg/g

	Glass Phase	Mullite-Quartz	Mass Balance	Total Alumina-silicate	Alumino-Silicate Plus carbon
Al	86262	203532	135513	143356	150700
Fe	19582	3358	12849	12644	13100
Si*	343000	287000	------	------	------
Na	1711	256	1107	1004	1000
K	25057	5274	16847	16333	17100
Rb	532	12	316	62	93
Cs	0	0	0.3	3	8
Mg	10418	15498	12526	12689	13900
Ca	------	0	------	-----	1800
Sr	798	174	539	889	180
Ba	319	69	215	163	365
Sc	31	7	21	20	18
Ti	10874	4626	8281	8378	8480
V	176	127	155	166	171
Cr*	169	311	227	255	225
Mn	87	9	55	56	53
Co	25	2	16	16	14
Ni*	174	78	134	172	------
Cu*	144	17	91	144	------
Zn*	209	17	129	155	------
Ga	0	12	8	0	7
As	42	2	26	25	24
Se	54	7	35	26	3
Mo	0	3	1	0	20
Cd*	0.32	0.27	0.3	0.5	------
Hf	6	3	5	4	6
Ta	3	1	2	2	2
W	4	1	3	3	4
Hg	8	1	5	3	0
Pb*	35	2	21	12	------
La	61	0	36	18	82
Ce	119	6	72	18	135
Eu	2	0	1	0	3
Tb	5	0	3	0	2
Dy	10	0	6	0	9
Yb	4	0	2	0.4	0
Th	5	0	3	2	21
U	13	1	8	4	9

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*Asterisk indicates that atomic absorption spectroscopy was used. All others were determined by neutron activation spectroscopy. Silicon concentration calculated by difference.

$$3(Al_{2.x}O_3).2(Si_{1-y}O_2).M_x^{+3}.M_y^{+4}$$

$$M^{+3} = V, Cr, Fe, Ga$$

$$M^{+4} = Ti, Zr.$$

There are no quantitative data on Zr because they were not credible. We did, however, examine the mullite-quartz phase qualitatively by x-ray fluorescence and found large concentrations of Zr. We have not been able to completely physically isolate the magnetic component of fly ash. The magnetic portions consisted of "strongly magnetic" and "weakly magnetic" fractions. We have been able to isolate the nonmagnetic matrix from the magnetic, but not vice versa. It appears, however, that the nonmagnetic and strongly magnetic fractions are appreciably different in kind with respect to trace element distributions. The first two columns of Table IV compare distributions of elements for the aluminosilicate matrix to magnetic matrix for Bull Run. The first-row transition elements tend to be more concentrated in the strongly magnetic fractions. This suggests that the chemical species of some of the trace elements may be as substitutions in spinels. There is, however, an appreciable concentration of alkali, alkaline earth, and rare earth elements in the magnetic material that is unexplainable, except to presume that they are dissolved in aluminosilicate material that is sintered to or occluded in the magnetic phase.

An attempt was made to isolate the magnetic phases by dissolving them in 12 *M* HCl over a steam bath for a period of about three weeks, but the magnetic material was only partially dissolved. Aliquots of the 12 *M* HCl solutions were evaporated in specially constructed capsules and analyzed by neutron activation analysis. Remaining portions of the liquid extract were analyzed by atomic absorption spectroscopy. Results are listed in column 3 of Table IV. The differences between the magnetic and aluminosilicate phases are now much more apparent. The most significant features of the magnetic phases are as follows:

1. Al and Fe were extracted in about the same mole ratios.

2. All alkaline earth elements are absent in the extracted magnetic phase. Presumably the Na, K, and Cs that were extracted were in the form of carbonates or other soluble surface species.

3. Except for Ce and La, all of the rare earth elements are absent from the magnetic phase.

4. The first-row transition elements V, Cr, Mn, Co, Ni, Cu, and Zn are concentrated in the magnetic phase by factors as high as 10-50.

Concentrations listed in the third columns of Table IV were calculated by assuming stoichiometric equivalents of O for Al and Fe. The results of this work indicate that the magnetic component of fly ash is not magnetite, Fe_3O_4, as is commonly reported, but an aluminum-substituted ferrite. Further work is needed to support this interpretation. Presently our evidence is as follows: Al was extracted in high concentrations, along with Fe, for all four specimens. One might argue that Al was extracted as Al_2O_3, but x-ray diffraction studies of the unextracted material showed no peaks corresponding to Al_2O_3. The diffraction peaks that were found indicated a compound with spinel structure, but the lattice parameter was significantly smaller than that of Fe_3O_4. Assuming

TABLE IV

BULL RUN FLY ASH: COMPARISON OF ELEMENT DISTRIBUTIONS IN ALUMINOSILICATE AND MAGNETIC PHASES CONCENTRATIONS IN μg/g

	Total Alumino-silicate	Magnetic Physically extracted	Magnetic (HCl extract)
Al	143356	76300	86641
Fe	12644	385000	605344
Na	1044	501	2078
K	16333	8200	3587
Rb	62	180	229
Cs	3	3	0
Mg	12689	8500	0
Ca	1800	1700	0
Sr	889	150	0
Ba	163	208	0
Sc	20	17	15
Ti	8378	3480	0
V	166	165	150
Cr*	255	273	1374
Mn*	56	501	1038
Co	16	172	251
Ni*	172	----	2270
Cu*	144	----	496
Zn*	155	----	382
Ga	0	15	0
As	25	50	0
Se	26	28	38
Mo	0	79	0
Cd*	0.5	----	1.2
In	0	0.2	0
Sb	0	4	0
Hf	4	3	0
Ta	2	1	0
W	3	4	0
Hg	3	0	0
Pb*	12	----	5.1
La	18	37	14
Ce	18	66	141
Eu	0	1	1
Tb	0	1	0
Dy	0	5	0
Yb	0.4	0	0
Th	2	11	5
U	4	7	4

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*Asterisk indicates atomic absorption analysis that all of the HCl-extracted Al and Fe were associated with each other as ferrite materials, we calculate compositions varying from $Fe_{1.68}Al_{1.22}O_4$ to $Fe_{2.27}Al_{0.73}O_4$. We could not find lattice constants for ferrites having Al concentrations this high, but we did find a constant (5) for the compound $Fe_{2.78}Al_{0.22}O_4$. Mossbauer spectra (6) of some of these magnetic fractions were taken. They were considerably different from that of pure magnetite. It is well known that magnetitite and ferrites can accept the transition metal ions V, Cr, Mn, Co, Ni, Cu, and Zn as isomorphic substitutions of the type:

$$Fe_{3-x}M_xO_4.$$

Possibly this accounts for their chemical states and is an explanation of why they are so heavily concentrated in the magnetic phase.

CONCLUSION

We have used NAA in conjunction with other analytical techniques to study trace elements in coal and fly ash. IDSSMS and AA were shown to give satisfactory results for elements not easily determined by NAA. Etching studies of fly ash support our thesis that chemical species of trace elements are defined to a large extent by the matrix in which they are dissolved.

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