MULTI-ELEMENTAL ANALYSIS OF ARGONNE PREMIUM COAL SAMPLES BY SIMULTANEOUS PROTON-INDUCED GAMMA-RAY/X-RAY EMISSION SPECTROMETRY

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INTRODUCTION

Although the Argonne Premium whole coal samples are widely used by the coal research community,[1] relatively little work has been done on determining the trace element composition of these materials. Of the more than 340 references in the Users Handbook for these reference materials,[2] only three papers report trace-element concentration data. Instrumental neutron activation analysis (INAA)[3], inductively coupled argon plasma-atomic emission spectrometry (ICAP-AES)[4] and X-ray fluorescence spectrometry (XRF)[5] have been applied to the Argonne Premium coal samples. The INAA measurements were performed on the whole coals while the XRF and ICAP-AES measurements utilized ashed samples.

We have used external beam proton-induced gamma-ray and X-ray emission (PIGE/PIXE) analysis to determine the concentration of 28 minor and trace elements in 8 Argonne Premium whole coal samples. Briefly, PIGE and PIXE are rapid, nondestructive multielemental analysis techniques that can be *instrumentally* applied to coal, fly ash, and coal derived materials. Because PIGE and PIXE can be applied to whole coal, they can, like INAA, be used to measure elements that might be volatilized during ashing. The other chief advantage of these two ion beam analysis techniques is that they are free of the chemical interference effects that arise in the elemental analysis of such complex matrices by more traditional methods such as ICAP-AES and GF-AAS. In principle, PIXE is capable of determining the concentration of all elements from sodium through uranium with relatively uniform sensitivity . In practice, up to 20 elements are commonly determined per irradiation at fractional mass sensitivities of 1.0 to 10.0 ppm. Unlike PIXE, the sensitivity of PIGE varies greatly from element to element. It does, however, provide concentration information for the light elements lithium, fluorine, sodium and aluminum in these samples.

EXPERIMENTAL PROCEDURE

Sample Preparation. The samples were oven dried for 24 hours at 105 °C and prepared by pelletizing *c.a.* 200 mg of the coal (-100 mesh) in a 13 mm stainless steel die at 90 Mpa. Single and multielemental graphite standards were used in the thick-target PIXE analysis. High purity graphite powder (-100 mesh) was spiked with single ($CaCl_2$ and KCl) and NIST multielement SRM spectrometric solutions (SRM 3172 and 3174) and dried at 105° for 24 hours. The spiked graphite was then mixed in a methacrylate vial on a mixer mill for 30 minutes and pressed into a 13-mm diameter pellet.

Thick-Target PIGE/PIXE Analyses. The measurements were performed at the University of Kentucky 7.5 MV Van de Graaff accelerator.[6] The γ-rays were detected with a

HpGe detector with a full-width-half-maximum (FWHM) resolution of 1.87 keV at 1274 keV which was placed 3.0 cm from the target at an angle of 90° relative to the beam direction. The X-rays were detected with a Si(Li) detector with a FWHM resolution of 165 eV at 5.90 keV that was placed 5.4 cm from the target at an angle of 45°. A 700 μm thick mylar filter and a 10 μm thick Cr critical absorber were placed in front of the Si(Li) detector to reduced the bremsstrahlung background and the intensity of Fe X-rays. A total of five irradiations were performed; the critical absorber was removed during two of the irradiations in order to determine the concentration of Cr. All irradiations were performed at 2.5 MeV (on target) with an external proton beam in helium using on-demand beam pulsing. The beam, normal to the target surface, was rastered over the sample at 1 Hz irradiating a spot of 5 mm by 7 mm. The proton beam current, on the extraction foil, ranged from 50 to 100 nA and the irradiation times ranged from 10 to 15 min. per sample. Rather than adjust the beam current to maintain a constant count rate, a pulser was used to correct for the dead time in the PIGE spectra. In this case, the dead time in the PIGE spectra was less than 3% for all coal samples. The accuracy of the measurements was determined by analyzing three NIST coal SRM's (1632a, 1632b, 1635).

RESULTS and DISCUSSION

PIGE Analysis. A typical PIGE spectrum of an Argonne Premium coal sample is shown in Figure 1. The nuclear reactions utilized in the PIGE measurements were $^{7}Li(p,p_1)^{7}Li$, Eγ = 478 keV; $^{19}F(p,p_2)^{19}F$, Eγ = 197 keV; $^{23}Na(p,p_1)^{23}Na$, Eγ = 439 keV; and $^{27}Al(p,p_2)^{27}Al$, Eγ = 1013 keV. The concentrations of Li, F, Na and Al were determined by comparison of the normalized γ-ray yields with those obtained from either the NIST 1632a or NIST 1635 coal SRM's. In the comparative method, the concentration of an element (C) is determined by:

$$C = C_{std} \cdot (Y \cdot S)/(Y_{std} \cdot S_{std})$$

where Y is the normalized γ-ray, S is the stopping power of the proton beam (at 2.5 MeV), and C_{std} is the concentration of the element in the standard. NIST 1632a was used as the reference standard for Li and Na in all samples. The Argonne samples with a F concentration of less than 100 ppm and an Al concentration of less than 1 wt. percent were compared to NIST 1635. The PIGE results given in Table I are the average values obtained from 7 irradiations of each Argonne sample. The errors are reported as the standard error of the mean.

The sensitivities for these four light elements in whole coal samples are: Li, 5 ppm; F, 5 ppm; Na, 10 ppm; and Al, 200 ppm. These limits of detection (LOD) are based upon a minimum observable peak area of $3\sqrt{bkg}$ where bkg is the background over 1 FWHM about the γ-ray peak's centroid. The relative standard deviation, based upon counting statistics, for a single measurement ranged from 2% to 20%.

The Na concentration values given in Table I agree well with the values determined both by INAA[3] and ICAP-AES[4] and the Al values are in good agreement with those obtained by ICAP-AES.[4] In the case of Li, the PIGE values for two of the Argonne coals (POC and UT) agree with the FAAS results of Doughten and Gillison.[4] For the remaining six samples, the PIGE results are consistently lower than the FAAS values. Similarly, the F values given in Table I for the ND, POC, and UT samples are in good agreement with the ISE results of Doughten and Gillison.[4] Our results for the remaining five samples are, again, considerably lower than the ISE values.

PIXE Analysis. A typical PIXE spectrum of an Argonne Premium coal sample is shown in Figure 2. A comparison of our thick-target PIXE results with the literature values for the NIST SRM's[7] are given in Table II. With the exception of Cr, Ge, and Th, the values obtained by PIXE in this study agree, within the error bars reported, with the literature values for the NIST SRM's.

The results of the PIXE analysis for 24 minor and trace elements in the Argonne premium coal samples are given in Table I. The errors are the standard error of the mean from the 7 irradiations. In the majority of cases, the PIXE results agree, within the error bars reported, with the values obtained by INAA[3] and ICAP-AES.[4]

CONCLUSION

The concentrations of 28 minor and trace elements in 8 Argonne premium coal samples have been determined by simultaneous PIXE/PIGE analysis. In general, the PIXE/PIGE results agree with the values obtained by INAA[3] and ICAP-AES.[4] However, additional analyses are needed to resolve the discrepancy between the Li and F concentration values reported in this work and by Doughten and Gillison.[4] From previous work on the determination of F in similar reference materials,[8] we would suggest that a series of pyrohydrolysis measurements could resolve the differences observed for fluorine.

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Table Ia. Concentrations of elements (μg/g) in 8 Argonne premium coal samples by PIGE/PIXE.

Element	WV	ND	POC	UT	PITT	IL	UF	WY
Li	36 ± 2	**	5 ± 1	5 ± 1	26 ± 3	21 ± 4	26 ± 8	17± 2
Na	340 ± 30	5600 ± 500	760 ± 30	1300 ± 170	320 ± 30	1000 ± 55	355 ± 30	1110 ± 90
Al*	2.96 ± 0.12	0.44 ± 0.05	0.53 ± 0.01	0.39 ± 0.03	0.89 ± 0.06	1.14 ± 0.07	1.58 ± 0.09	0.80 ± 0.03
F	130 ± 30	35 ± 6	20 ± 4	56 ± 7	90 ± 40	86 ± 7	86 ± 12	56 ± 9
K	4700 ± 460	320 ± 80	225 ± 90	264 ± 40	1090 ± 30	2330 ± 50	2300 ± 250	230 ± 65
Ca*	0.05 ± 0.01	1.44 ±0.05	0.42 ± 0.01	0.43 ± 0.02	0.21 ± 0.02	0.88 ± 0.06	0.35 ± 0.01	1.13 ± 0.07
Ti	2860 ± 270	202 ± 6	360 ± 20	217 ± 4	550 ± 30	610 ± 20	620 ± 50	610 ± 50
Cr	37 ± 2	4 ± 1	8 ± 2	7 ± 1	18 ± 1	36 ± 4	23 ± 3	7 ± 1
Mn	12 ± 2	85 ± 9	12 ± 1	5 ± 1	20 ± 4	87 ± 7	27 ± 6	23 ± 5
Fe*	0.39 ± 0.06	0.05 ± 0.03	0.57 ± 0.02	0.28 ± 0.02	1.11 ± 0.01	2.01 ± 0.01	1.35 ± 0.1	0.38 ± 0.01
Co	9.4 ± 3.7	**	3.2 ± 1.4	1.3 ± 0.3	1.5 ± 0.7	**	**	1.0 ± 0.6
Ni	14 ± 3	3.3 ± 0.1	4.1 ± 0.7	5.1 ± 0.1	4.7 ± 0.8	15 ± 3	9.4 ± 1.2	3.5 ± 2.1
Cu	20 ± 4	4.2 ± 1.1	12 ± 1	5.4 ± 0.4	5.1 ± 1.6	7.7 ± 1.1	12 ± 1	15 ± 5
Zn	12 ± 1	5.7 ± 2.5	4.3 ± 1.3	6.8 ± 2.1	9.7 ± 2.1	130 ± 20	18 ± 3	23 ± 7

* Concentrations in weight percent.
** Below detection limit.

Table Ib. Concentrations of elements (μg/g) in 8 Argonne premium coal samples by PIGE/PIXE.

Element	WV	ND	POC	UT	PITT	IL	UF	WY
Ga	10 ± 1	**	2.1 ± 0.1	1.5 ± 0.2	3.8 ± 0.6	3.9 ± 0.6	4.3 ± 0.1	3.5 ± 0.5
Ge	1.3 ± 0.8	**	0.8 ± 0.7	**	1.1 ± 0.5	7.0 ± 0.4	4.0 ± 1.3	3.5 ± 0.8
As	6.9 ± 0.4	3.3 ± 0.1	6.9 ± 0.4	1.2 ± 0.8	4.5 ± 0.4	3.2 ± 1.4	11 ± 1	3.5 ± 0.4
Se	8.0 ± 0.9	2.2 ± 1.2	2.1 ± 0.5	1.9 ± 0.6	2.2 ± 1.0	3.1 ± 0.4	1.4 ± 0.5	1.2 ± 0.1
Br	13 ± 2	0.9 ± 0.4	40 ± 3	1.6 ± 0.4	12 ± 1.5	4.6 ± 0.5	50 ± 2	2.1 ± 1.1
Rb	34 ± 4	0.9 ± 0.2	6.1 ± 1.3	0.7 ± 0.2	6.7 ± 0.2	16 ± 2	17 ± 3	9.6 ± 1.2
Sr	65 ± 5	650 ± 50	100 ± 2	72 ± 4	68 ± 7	28 ± 1	53 ± 1	240 ± 50
Y	12 ± 1	2.4 ± 1.3	5.8 ± 0.7	2.1 ± 0.5	3.4 ± 0.5	3.7 ± 0.7	11 ± 1	4.3 ± 1.0
Zr	72 ± 9	16 ± 5	12 ± 2	24 ± 2	19 ± 3	16 ± 2	16 ± 1	20 ± 3
Mo	**	**	3.3 ± 1.8	**	**	5.7 ± 0.8	1.5 ± 0.2	2.1 ± 0.4
Ba	140 ± 40	480 ± 60	130 ± 50	32 ± 7	37 ± 6	**	88 ± 11	270 ± 31
Pb	3.6 ± 0.6	0.2 ± 0.1	1.3 ± 0.7	1.9 ± 0.6	3 ± 0.9	2.5 ± 0.8	1.5 ± 0.4	1.4 ± 0.5
Th	4.4 ± 1.0	**	**	0.9 ± 0.2	1.3 ± 0.9	**	2.4 ± 0.5	2.0 ± 0.9
U	1.7 ± 0.7	**	**	**	1.2 ± 0.4	1.7 ± 0.4	2.9 ± 0.8	1.4 ± 0.8

** below detection limit.

Table II. Concentrations of elements (μg/g) in NIST coal standards by PIGE/PIXE.

Element	NIST 1632b	NIST 1632a	NIST 1635
K	716 ± 14	4310 ± 310	101 ± 50
	[748 ± 28]	[4110 ± 60]	[96 ± 16]
Ca*	0.22 ± 0.01	0.25 ± 0.02	0.55 ± 0.06
	[0.20 ± 0.01]	[0.24 ± 0.02]	[0.54 ± 0.03]
Ti	436 ± 7	1707 ± 11	187 ± 11
	[454 ± 17]	[1750]	[202 ± 6]
Cr	11 ± 2	28 ± 3	4 ± 1
	[11]	[34.3 ± 1.5]	[2.5 ± 0.3]
Mn	8 ± 3	24 ± 5	23 ± 7
	[12.4 ± 1.0]	[28 ± 2]	[21.4 ± 1.5]
Fe*	0.74 ± 0.02	1.10 ± 0.03	0.23 ± 0.02
	[0.76 ± 0.05]	[1.11 ± 0.02]	[0.24 ± 0.05]
Cu	5.1 ± 0.8	14 ± 2	4.8 ± 2.3
	[6.3 ± 0.3]	[15.9 ± 1]	[3.6 ± 0.3]
Zn	14 ± 2	26 ± 1	6.0 ± 1.4
	[11.9 ± 0.8]	[28 ± 2]	[4.7 ± 0.5]
Ga	2.6 ± 0.2	8.8 ± 0.9	1.4 ± 0.5
	---	[8.49]	[1.05]
Ge	2.7 ± 0.2	3.3 ± 0.1	1.1 ± 0.6
	---	[2.5]	[0.5]
As	3.8 ± 1.1	9.3 ± 1.6	**
	[3.7 ± 0.1]	[9.3 ± 1.0]	[0.4 ± 0.2]
Se	1.7 ± 1.1	2.4 ± 0.5	0.8 ± 0.5
	[1.3 ± 0.1]	[2.6 ± 0.7]	[0.9 ± 0.3]
Br	18 ± 1	41 ± 1	1.4 ± 0.6
	[17]	[41 ± 2]	[1.4 ± 0.4]
Rb	**	32 ± 8	0.8 ± 0.1
	[5.1 ± 1.1]	[30 ± 2]	[0.9 ± 0.1]
Sr	98 ± 2	77 ± 3	139 ± 14
	[102]	[85 ± 6]	[121 ± 19]
Zr	13 ± 1	52 ± 5	17 ± 4
	---	[53 ± 5]	[16 ± 2]
Ba	60 ± 6	140 ± 50	45 ± 16
	[67.5 ± 2.1]	[120 ± 15]	[73 ± 5]
Th	**	3.7 ± 0.1	1.4 ± 0.7
	[1.3 ± 0.1]	[4.5 ± 0.1]	[0.6 ± 0.1]
U	**	1.2 ± 0.3	1.1 ± 0.5
	[0.4 ± 0.1]	[1.3 ± 0.1]	[0.2 ± 0.1]

[ ] NIST compilation value[7] *Concentrations in weight percent **Below detection limit.

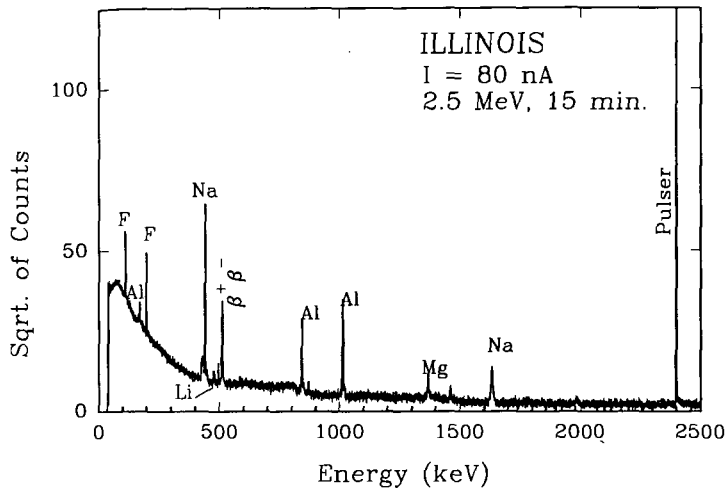

Figure 1. PIGE spectrum of an Argonne premium coal sample.

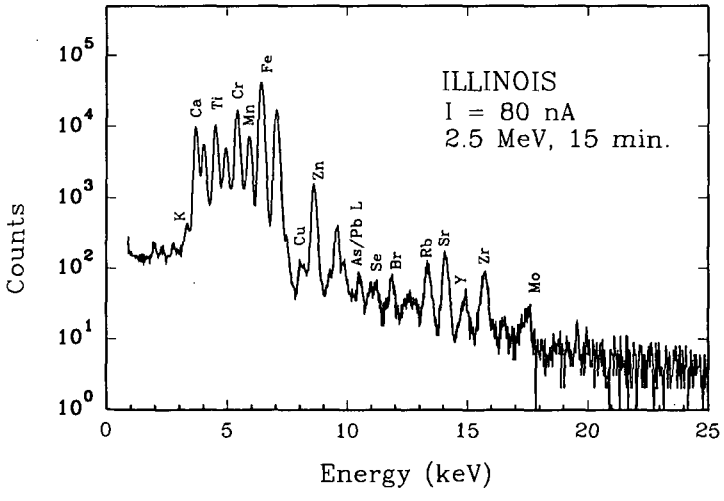

Figure 2. PIXE spectrum of an Argonne premium coal sample with 700 μm mylar and 10 μm Cr filters