Conf-820861--2

Presented at the 31st Annual Denver X-Ray Conference, August 2-6, 1982, Denver, CO, and submitted for publication in Vol 26, ADV IN X-RAY ANALYSIS, 1982. (Notice of acceptance for publication not received as of 9/29/82)

CONF-820861--2

DE82 906045

CHEMICAL ANALYSIS OF COAL BY ENERGY-DISPERSIVE X-RAY FLUORESCENCE UTILIZING ARTIFICIAL STANDARDS

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ABSTRACT

Accurate determinations of the elemental composition of coal by classical methods can be quite difficult and are normally very time consuming. X-ray fluorescence utilizing the powder method, however, has the ability of providing accurate and rapid analyses. Unfortunately, well characterized standards, although available, are not plentiful. In addition, the durability or stability of ground and pelletized coal samples is poor resulting in deterioration with time. As a result, artificial coal standards were prepared from certified geological materials by fusing in lithium-tetra-borate in percentages approximating expected ash contents and compositions in coal. Since the lithium-tetra-borate comprises about the same percentage of the standard as does the carbon, hydrogen, and oxygen in coal, the ground and pelletized coal sample can be assayed against the fused calibration curves by compensating for the differences in the mass absorption coefficients of the two matrices.

INTRODUCTION

Background

As a result of the world's dramatic increase in energy demands coupled with increasing cost and decreasing availability of petroleum type fossil fuels, major interest in coal as a significant substitute for oil has developed due to the extensive reserves available. Although coal is quite abundant, its utilization as a fuel can create

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problems in design and operation of boilers such as fused slag deposits, ash corrosion and erosion, combustion ash release, slagging, fouling, and excess sulfur resulting in SO_2 emissions. The nature of the coal with the resulting characteristics of the ash are, therefore, of major concern both to the designer and the operator of the system. As a consequence, accurate and rapid analysis of the elemental composition becomes imperative.

Analysis of coal by conventional methods is a lengthy process usually involving several hours for the major constituents. Complete analysis including traces, even through atomic absorption or optical emission, can consume up to five to eight hours. Although these techniques are usually excellent for most trace element determinations, they are generally poor for the quantification of major elements. X-ray fluorescence, however, can be extremely accurate for the rapid determination of the major elements and excellent to good for the trace elements through atomic number 92.

ANALYTICAL PROCEDURES

Equipment and Operating Conditions

An EG&G ORTEC 6110 Energy Dispersive X-ray Spectrometer was utilized for this analysis and operated under the instrumental parameters as listed on Table 1.

TABLE 1: Operating Parameters for Coal Analysis

Elements Determined:	Na, Mg, Al, Si, P, S, K, Ca, Ti, Mn, Fe	Sr
Anode:	Rhodium	Rhodium
Filter:	none	Rhodium
Anode Voltage:	10 kV	35 kV
Anode Current:	75 µAmps	100 µAmps
Energy Scale:	0-10 keV	0-20 keV
Atmosphere:	Vacuum	Vacuum
Counting Rate:	200 seconds	20 seconds

Standards and Sample Preparation

Several sources of coal standards exist[1-3], but as stated previously, they are generally unstable with a period of time after preparation and also do not adequately cover the range of composition and ash content experienced by some of the consumers utilizing coal as a fuel. As a result, a system utilizing durable synthetic standards which could be compared directly to the quantitative analysis of whole coal samples appeared to offer a solution to the problem of standard availability and durability.

As mentioned previously, the availability of coal standards covering the expected range of compositions and ash contents are rather limited. As a consequence, a series of artificial standards were made by fusing varying amounts of well characterized materials in an amount of $Li_2B_4O_7$ to bring the total sample (on an ignited basis) plus the lithium-tetra-borate to a total sample weight up to grams to approximate the coal. Since the whole coal which will be analyzed against the artificial standards was made up with four grams of coal plus one gram of boric acid as a binder, one additional gram of $Li_2B_4O_7$ was added to the artificial standards to make a total weight of five grams. The standards and percentages used in making these standards are illustrated on Table 2.

TABLE 2. Compositions of Artificial Standards

Standard	Composition*	$Li_2B_4O_7$ (Grams)	NH_4NO_3** (Grams)
1	5% Limestone 1c	4.8000	0.5000
2	10% Limestone 1c	4.6000	0.5000
3	7% Bauxite 697	4.7200	0.5000
4	7% Si Brick 102 + 5% Bauxite 697	4.5200	0.5000
5	2% Si Brick 102 + 1% Buaxite 697	4.8800	0.5000
6	10% Obsidian 278	4.6000	0.5000
7	15% Basalt 688	4.4000	0.5000
8	15% Cement, Blue	4.4000	0.5000
9	15% Bauxite 697 + 20% K_2SO_4	4.0000	0.5000
10	10% Cement, Blue	4.6000	0.5000
11	15% Limestone 1c + 15% K_2SO_4	4.0000	0.5000
12	5% Si Brick 102 + 2% Dolomite 88A	4.7200	0.5000
13	10% Si Brick 102 + 10% Basalt 688	4.2000	0.5000
14	7% Obsidian 278 + 6% Limestone 1c	4.8000	0.5000
15	16% Alumina Refractory 77A	4.3600	0.5000
16	8% Si Brick 102 + 1% Dolomite 88A + 8% Bauxite 697	4.3200	0.5000
17	11% Alumina Refractory 77A + 8% Si Brick 102	4.2900	0.5000
18	20% $CaSO_4$ + 5% Si Brick 102	4.0000	0.5000

* All weights are calculated for a loss-free basis.

** Oxidizing Agent.

Each individual artificial standard as listed on Table 2 was prepared by fusing those percentages based on a one-gram sample (equated to loss free) with an appropriate amount of $Li_2B_4O_7$ to bring the total sample weight up to 5.0 grams. An oxidizing agent (NH_4NO_3) was also added in the amount of 0.5 grams. The entire sample was then fused and cast in a 95% Pt - 5% Au crucible at 1100°C for ten minutes.

Sample preparation techniques for the unknown coal samples utilized the powder technique. Since particle size effects can vastly affect the intensity relationships[4,5], one coal sample was ground in a tungsten carbide rotary swing mill (5 grams sample + 1 gram boric acid binder + 100 milligrams of sodium sterate grinding aid) for one to seven minutes. The resulting powders were pelletized with a boric acid backing at 15 tons per square inch and placed in the spectrometer for intensity measurement. In addition to establishing the optimum grinding time as illustrated on Figure 1, the optimum pelletizing pressure was also determined as displayed on Figure 2. As a result, all of the unknown coal samples were ground for five minutes and pelletized at 15 tons per square inch.

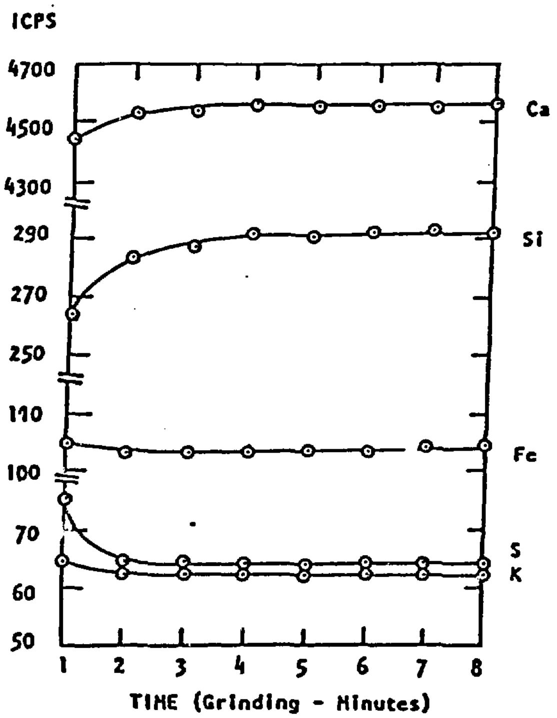

Fig. 1: Grinding Time vs Intensity

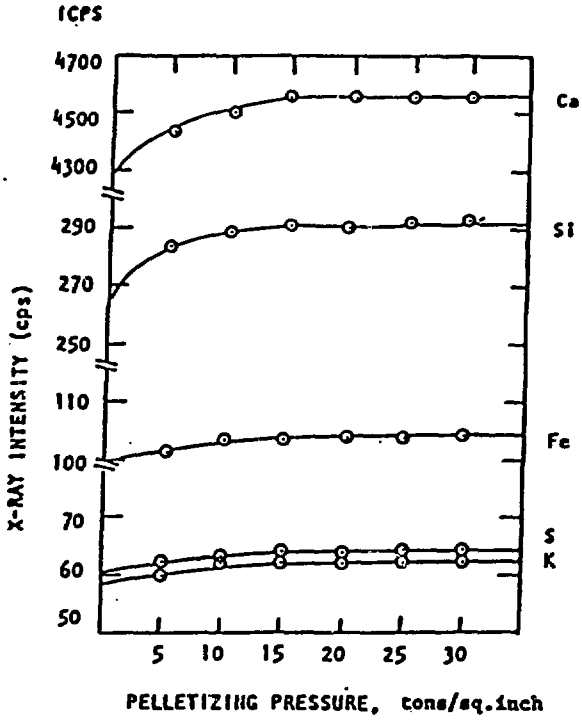

Fig. 2: Pelletizing Pressure vs Intensity

Analysis of Data

The intensity data was analyzed using the EG&G ORTEC matrix correction program, ATAC. This approach employs an exponential correction procedure for absorption and enhancement effects as a function of variations in the elemental intensities[6]. The basic equation utilized is as follows:

$$C_i = A_i + b_i I_i \exp \left(\sum_j m_{ij} I_j\right) \qquad (1)$$

$$= A_i + B_i I_i \exp \left[\sum_j m_{ij} (I_j - \bar{I}_j)\right]$$

where $B_i = b_i \exp \left(\sum_j m_{ij} \bar{I}_j\right)$

I_i = intensity of assay element i

I_j = intensity of interferring element j

$\bar{I}_j$ = average intensity of element j of all standards in calibration m = proportionality constant derived from regression analysis of the standards

C_i = concentration of assayed element i

A_i = intercept of calibration curve

The interaction coefficients are determined by a non-linear multiple least squares fit of the standards concentrations/intensity data. This requires a minimum of n+6 standards where n is the number of interferring elements. Elemental concentrations were calculated with an iterative process using equation (1) with the interaction coefficients calculated from the standards. Analysis of this material required the utilization of the interelement correction equation (1) plus a stripping routine as stated in equation (2) in order to correct for overlapping lines.

$$C_i = a+b[I_iK\alpha+I_jL\alpha - (I_jK\alpha/I_jK\alpha)(I_jK\alpha_s)] \tag{2}$$

where C_i = concentration of element i

a = x intercept of calibration curve

b = slope of calibration curve

$I_iK\alpha+I_jK\alpha$ = measured intensity of the Kα of element i + Lα of interferring element j

$I_jK\alpha/I_jL\alpha$ = intensity ratio of Kα/Lα on pure element j

$I_jK\alpha_s$ = intensity of the Kα of element j in the sample

RESULTS AND DISCUSSION

The artifically lithium-tetra-borate glass standards were analyzed in an energy dispersive x-ray spectrometer. Interelement corrections were performed through the utilization of the equation (1). The interelement corrections are evident in low Z matrices with particular emphasis being placed at the low end of the periodic table. Examination of Figure 3 clearly illustrates the necessity of interelement correction particularly involving low Z elements which are periodic neighbors. A typical example would be in the analysis of relatively low concentrations of aluminum in the presence of high and variable concentrations of silica where the mass absorption coefficient of aluminum at the silica Kα energy is in excess of 4000.

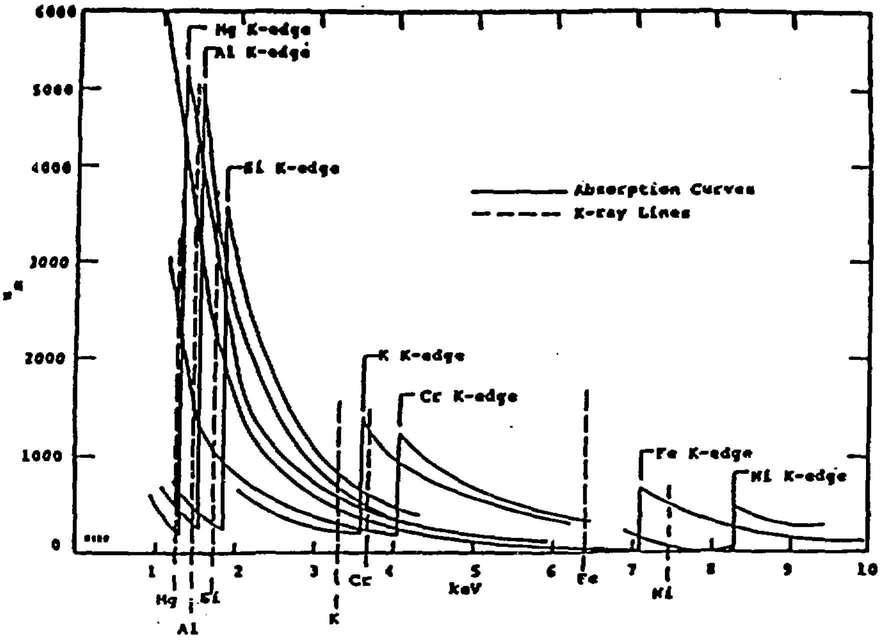

Fig. 3: Elemental Absorption Curves

Consequently, a correction must be calculated for the absorption of silica by aluminum in order to obtain reliable and meaningful results. Following this approach, the interelement corrections utilized for this analysis are illustrated on Table 3.

TABLE 3: Correction Protocol for Coal Analysis

Element Assayed	Interferring Element											
	Na	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe	Sr
Na												
Mg			b	b		b						
Al		b		b		b						
Si		b	b			b						s
P				s		b						
S				b			b	b				
K						b		b				
Ca							b				b	
Ti								b			b	
Mn									b		b	
Fe*												

Notes: b = beer's exponential equation.
s = stripping equation.
* = linear equation.

The artificial standards are made from a lithium-boron-oxygen matrix while the whole coal samples are composed essentially of a carbon-hydrogen-oxygen matrix. Since the calibrations were performed utilizing the artificial standards, a correction equating the difference in the mass absorption coefficients of the two matrices becomes necessary. Examination of Figure 4 reveals that a direct correlation of mass absorption coefficients exists between a lithium-tetra-borate matrix to that of a carbon-hydrogen-oxygen. Although natural coals vary considerably in the concentrations of carbon-hydrogen-oxygen, the variation in mass absorption coefficients from a low carbon to one of high carbon content is rather small. As a result, an average mass absorption coefficient was calculated among the low to high quality coal as illustrated on Figure 4. Equating the real coal samples to the artificial standards involves substituting a proportionality constant into equations (1) and (2) which is merely a reflection in the ratio of the differences in the mass absorption coefficients of the two matrices.

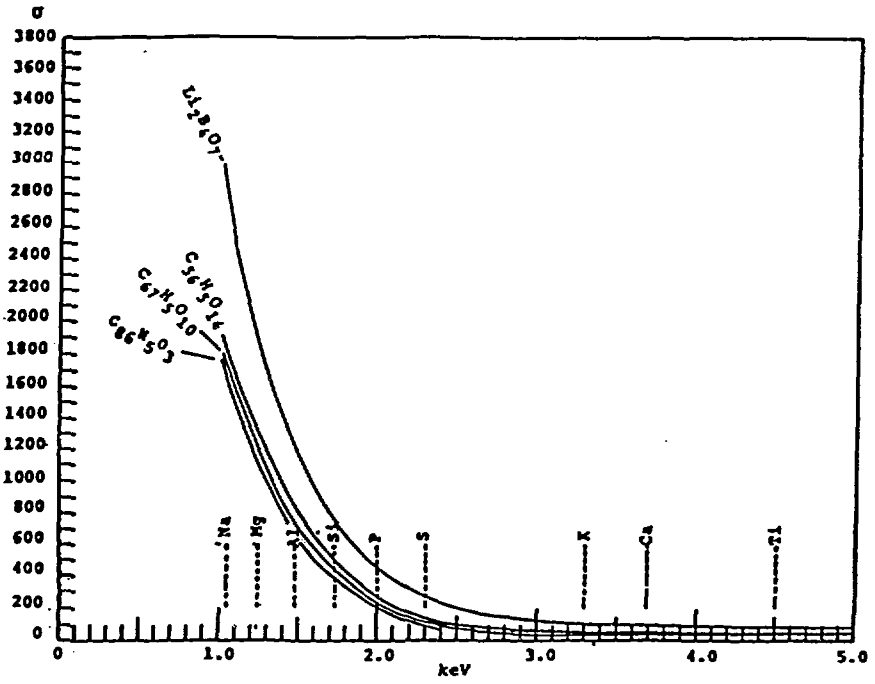

Fig. 4: Mass Absorption Coefficient of Coal

TABLE 4. Analysis of Coal (Summary)

Sample I.D.*	Composition (%)																					
	Na_2O		MgO		Al_2O_3		SiO_2		P_2O_5		S		K_2O		CaO		TiO_2		Fe_2O_3		Ash	
	List	Calc	List	Calc	List	Calc	List	Calc	List	Calc	List	Calc	List	Calc	List	Calc	List	Calc	List	Calc	List	Calc
100	-	<0.04	0.54	0.56	1.77	1.70	2.54	2.50	0.19	0.17	1.02	1.10	0.06	0.05	0.98	0.92	0.09	0.14	0.67	0.66	8.10	8.32
101	-	<0.04	0.52	0.48	4.22	4.06	11.60	11.60	0.12	0.09	0.57	0.52	0.37	0.36	1.55	1.42	0.13	0.10	0.65	0.62	20.67	20.50
102	-	0.09	0.29	0.26	4.16	3.99	11.49	11.62	0.045	0.052	4.19	4.10	0.51	0.41	1.06	0.92	0.19	0.12	3.46	3.26	22.58	22.70
103	-	0.09	0.15	0.14	2.42	2.45	6.11	6.05	0.025	0.019	3.94	3.79	0.26	0.21	0.64	0.56	0.12	0.10	2.41	2.34	12.87	12.65
104	-	0.10	0.11	0.08	1.90	1.96	4.48	4.54	0.015	0.019	4.50	4.31	0.24	0.19	0.36	0.32	0.09	0.07	3.30	2.94	10.74	10.95
105	-	0.13	0.11	0.10	2.32	2.29	4.19	4.20	0.045	0.052	1.25	1.36	0.25	0.30	0.06	0.06	0.10	0.11	0.67	0.82	7.85	8.00
106	-	0.04	-	0.03	0.50	0.48	0.54	0.55	-	0.019	0.58	0.60	0.01	<0.01	0.04	0.02	0.02	0.05	0.12	0.15	1.29	1.15
107	-	0.04	0.19	0.15	3.67	3.65	7.90	7.92	0.015	<0.019	0.49	0.53	0.36	0.42	0.03	0.03	0.17	0.19	0.52	0.61	13.05	13.20
108	-	<0.04	0.07	0.10	5.77	5.84	11.10	11.12	0.015	<0.015	0.70	0.75	0.58	0.62	0.05	0.05	0.37	0.37	0.25	0.18	18.48	18.67
109	-	<0.04	0.20	0.17	3.57	3.63	6.07	6.17	0.045	0.045	0.55	0.50	0.25	0.29	0.14	0.15	0.25	0.31	0.37	0.34	11.15	11.10
110	-	0.02	0.71	0.69	1.24	1.17	2.94	2.96	0.040	0.070	1.51	1.37	0.06	0.05	2.29	2.24	0.05	0.07	1.35	1.40	12.42	12.55
111	-	<0.04	0.42	0.47	2.03	1.92	3.58	3.80	0.14	0.14	0.91	1.04	0.01	0.01	2.26	2.25	0.14	0.14	0.45	0.39	10.60	10.50
120	0.09	0.10	0.14	0.15	2.26	2.35	6.47	6.36	0.030	0.031	3.52	3.53	0.25	0.25	0.73	0.73	0.10	0.09	2.06	2.06	13.06	13.05
121	0.06	0.03	0.16	0.18	2.60	2.67	7.26	7.22	0.036	0.040	3.47	3.33	0.36	0.34	0.60	0.67	0.13	0.10	3.31	3.44	15.01	15.15
122	0.03	0.04	0.34	0.34	1.72	1.75	4.79	4.60	0.052	0.075	0.50	0.59	0.12	0.15	1.96	2.11	0.06	0.07	0.73	0.83	11.00	10.91
123	0.05	0.08	0.10	0.12	2.05	2.10	4.78	4.83	0.027	0.022	3.45	3.55	0.24	0.22	0.35	0.39	0.10	0.08	2.79	2.84	10.99	11.06
124	0.07	0.05	0.18	0.21	2.85	2.91	7.61	7.51	0.016	0.052	1.04	1.14	0.35	0.42	0.52	0.66	0.17	0.18	1.40	1.58	13.61	13.56

*SAMPLES PLUS LISTED VALUES SUPPLIED BY AMERICAN SOCIETY TESTING MATERIALS, COMMITTEE D-5.

NOTE: LIST = CERTIFIED VALUE; CALC = VALUE CALCULATED BY REGRESSION ANALYSIS.

The results of the analysis utilizing this procedure are summarized on Table 4 in which the calculated values are compared to the listed values[7]. Ash content can be directly calculated from the composition of the coal by summing the oxide concentrations and deducting the amount of sulfur which is in excess for combination with the available calcium and magnesium with correlation of the ash content illustrated on Figure 5.

CONCLUSIONS

As illustrated by the data, energy dispersive x-ray fluorescence is a viable technique for analyzing coal for elemental composition and ash content. Since coal standards are not particularly stable with time and some compositional ranges are not adequately covered, utilization of artificial standards and calculating the variations in the two types of matrices offers a convenient method of calibration.

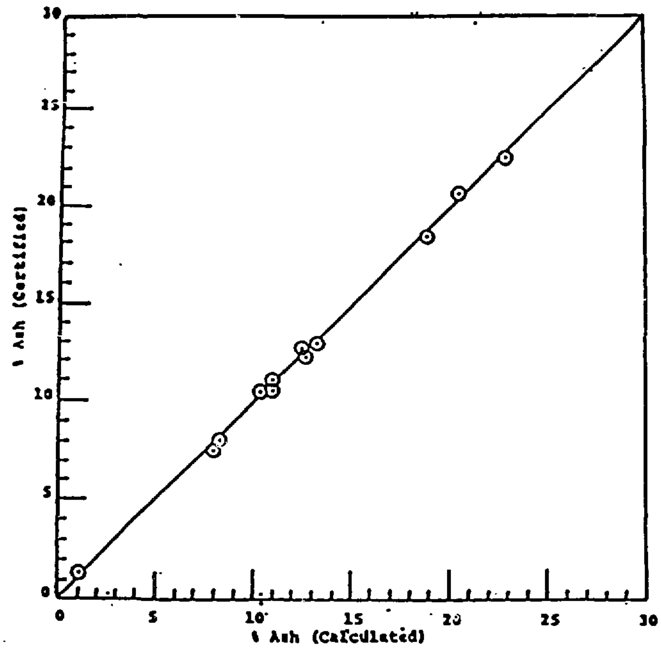

Fig. 5: Ash Content in Coal

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