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COAL ASH ANALYSIS BY X-RAY FLUORESCENCE PREPARATION AND ANALYSIS OF FUSED GLASS DISCS

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INTRODUCTION

Rapid quantitative analysis of coal ash by XRF techniques can readily be carried out using the instrumentation now available. Since coal ash samples vary considerably in mineralogical and chemical composition it would be reasonable to assume that significant particle size and absorption enhancement effects might be encountered. Consequently, a sample preparation technique which eliminates particle size effects, and dilutes matrix effects should be utilized. Fusion of a given amount of coal ash with a larger amount of an appropriate flux at high temperature to produce a "coal ash" glass disc definitely eliminates particle size effects and reduces matrix effects. However, for a high temperature fusion method to be acceptable repeatable count rates must be obtained for the major elements in coal ash when several glass discs are prepared from the same sample of ash. This paper describes such a method.

Procedures:

(1) Choice of Flux:

(a) The flux with which the coal ash is to be fused must produce strain free glass discs which are resistant to water (moisture) adsorption, and do not deteriorate on prolonged exposure to x-radiation.

Since some coal ashes contain significant quantities of sulphur the flux should contain a component which promotes oxidizing conditions in the melt, to prevent the loss of sulphur during fusion.

A flux composed of lithium tetraborate and ammonium nitrate was found to be adequate for the efficient production of coal ash glass discs, which satisfy the above requirements.

(b) Loss of Weight on Fusion of Lithium Tetraborate at 1050°C

The lithium tetraborate used in the preparation of the glass discs was obtained from K and K Laboratories, Plain View, N.Y. It was found that the lithium tetraborate loses weight upon fusion at 1050°C. This loss in weight is probably due to loss of absorbed water. The loss in weight on fusion at

1050°C for 1½ hrs. was determined for 3 separate bottles of lithium tetraborate on 3 separate days. The results are given in Table 1 below.

TABLE I

Bottle Number	Trial Number	Weight $Li_2B_4O_7$ Before Fusion at 1000°C	Weight $Li_2B_4O_7$ After Fusion at 1000°C	Loss in Weight of $Li_2B_4O_7$	% Loss on Fusion
1	Day 1	1.1250 gms	1.1135 gms	0.0115	1.02%
1	Day 2	1.1250 gms	1.1136 gms	0.0114	1.01%
1	Day 3	1.1250 gms	1.1136 gms	0.0115	1.02%
2	Dayl	1.1250 gms	1.0940 gms	0.0310	2.76%
2	Day 2	1.1250 gms	1.0933 gms	0.0317	2.82%
2	Day 3	1.1250 gms	1.0938 gms	0.0312	2.77%
3	Day 1	1.0073 gms	0.9644 gms	0.0429	4.26%
3	Day 2	5.2463 gms	5.0216 gms	0.2247	4.28%

(c) Use of Ammonium Nitrate in the Flux:

The prime reason for employing ammonium nitrate in the flux is to promote oxidizing conditions in the melt, however, the ammonium nitrate also promotes mixing of the sample and the flux as it decomposes and leaves no residue upon completion of the fusion procedure.

(2) Development of the Flux Fusion Procedure For "Coal Ash" Glass Discs

(a) Preparation of Coal Ash from -60 Mesh Coal

The air dried -60 mesh coal is isnited at 750°C for 12 hrs, in a muffle furnace under oxidizing conditions. The coal ash is then transferred to a swing mill and homogenized using freon as a wet grinding aid, for six minutes. Grinding for this period of time reduces all particles in the ash to -200 mesh. The homogenized ash is then reignited at 750°C to conant weight.

(b) Development of the Flux Fusion Procedure

Approximately 100 gms of coal ash was prepared from a -60 mesh air dried coal according to the conditions given in Section 2 (a).

Table II gives the parameters employed in the preparation of 10 separate glass discs from the coal ash.

TABLE II

Pellet Number	Weight of ash in gms	Weight * of $Li_2B_4O_7$ in gms	Weight of NH_4NO_3 in gms	Fusion Temperature ± 50°C	Fusion Time	Annealing Process	Date Prepared
1	1.000	4.5000	0.50	1050°C	1 hr.	20 min. hot plate 250°C	July 21 1978
2	1.000	4.5000	0.50	1050°C	1 hr.	20 mon. hot plate 250°C	July 24 1978
3	1.000	4.5000	0.50	1050°C	1 hr.	20 min. hot plate 250°C	July 26 1978
4	1.000	4.5000	0.50	1050°C	1 hr.	20 min. hot plate 250°C	July 26 1978
5	1.000	4.5000	0.50	1050°C	1 hr.	20 min. hot plate 250°C	July 28 1978
6	1.000	4.5000	0.50	1050°C	1½ hr.	20 min. hot plate 250°C	July 28 1978
7	1.000	4.5000	0.50	1050°C	3 hr.	20 min. hot plate 250°C	Aug. 2 1978
8	1.000	4.5000	0.50	1050°C	1½ hr.	20 min. hot plate 250°C	Aug. 3 1978
9	1.000	4.5000	0.50	1050°C	1½ hr.	20 min. hot plate 250°C	Aug. 3 1978
10	1.000	4.5000	0.50	1050°C	1½ hr.	20 min. hot plate 250°C	Aug. 3 1978

Note: * The $Li_2B_4O_7$ For all Ten Pellets Came From the Same Bottle of $Li_2B_4O_7$

(c) XRF Analysis of the "Coal Ash" Glass Discs

An ORTEC 6110 Tefa Tube excited fluorescence analyser was used to analyse all ten pellets. The analyses were carried out under vacuum using characteristic radiation plus Bremsstrahlung from a Mo anode x-ray tube operated at 10 Kev anode potential plus 100 u amp anode current, for 200 seconds.

These conditions provided excitation for the elements listed below.

Na, Mg, al, Si, P, S, K, Ca, Ti and Fe.

To obtain count rates for each of the above 10 elements, a "region of interest" centered around the K alpha line of each element was set up on the MCA of the 6110 analyser. The start and end channels for each element's region of interest is given in Appendix "C". Since the gain was set at 10 ev/channel it is possible to compute the kev equivalent for a given channel. For example to change channel 174 to its kev equivalent the following computation is employed:

$$\frac{174 \text{ channel X } 10 \text{ ev/channel}}{1000 \text{ ev/kev}} = 1.74 \text{ kev}$$

The raw count rates obtained for the 10 elements listed above on the 10 separate pellets are given in appendices C to F. The mean count rates, 95% confidence limits, and standard deviation of the count rates for each of the ten elements is given in Appendix H.

Discussion of Results

(a) Compensation for Weight Loss of Lithium Tetraborate Upon Fusion at 1050°C

It is evident from the results in Table I that any given bottle of lithium tetraborate has a fairly constant loss on fusion at 1050°C, however, it is important to note that two different bottles of lithium tetraborate might have radically different losses on fusion at 1050°C. Therefore, it is evident that in

order to obtain repeatable count rates for the major elements in coal ash when preparing "coal ash" glass discs using lithium tetraborate from different bottles it is necessary to compensate the weight of lithium tetraborate used, for the loss on fusion so that all pellets contain the same amount of tetraborate. Since it was decided that 4.500 gms ±0.0001 gms of lithium tetraborate, compensated for weight loss on fusion should be used to prepare the "coal ash" glass discs, the compensated weight of lithium tetraborate must be calculated for each separate bottle of tetraborate. The equation for calculating the compensated weight of $Li_2B_4O_7$ is given below.

$$\text{Compensated weight} = \frac{4.5000}{100 - L}$$

where L = % Loss on Fusion of lithium tetraborate

* It was found that 4.5g of $Li_2B_4O_7$ plus 1.0g of coal ash is the quantity necessary to form a disc 4-5 mm thick in a claisse fluxer mold.

(b) Detailed Procedure for the Preparation of "coal ash" glass Discs.

Taking into consideration the raw count data accumulated for the ten elements on the ten separate "coal ash" glass discs and the analysis parameters listed for each disc in Table II the following procedure is suggested for the preparation of "coal ash" glass discs by the flux fusion procedure.

(I) Into a clean dry "non wetting" platinum crucible weigh 4.5000 gms ±0.0001 gms of lithium tetraborate compensated for the loss on fusion of the tetraborate at 1050°C.

(2) Into the same crucible weigh 1.0000 gms ± 0.0001 gms of coal ash.

(3) Add approximately 0.50 gms of ammonium nitrate to the crucible and stir the contents of the crucible with a stainless steel rod.

(4) Place the crucible and contents in a muffle furnace which has been preheated to $1050^{o}C \pm 50^{o}C$.

(5) Swirl the melt in the crucible after 5 minutes and every 15 minutes thereafter until a total of $1\frac{1}{2}$ hrs. of fusion time has elapsed.

(6) Place a "non wetting" platinum mold in a vycor cruicible cover in the muffle and allow the mold to reach a temperature of $1050^{o}C \pm 50^{o}C$.

(7) Pour the melt from the crucible into the mold. Swirl the mold, and allow the mold to come to $1050^{o}C \pm 50^{o}C$.

(8) Transfer the vycor lid and mold to a hot plate at approximately $250^{o}C$. Remove the mold from the vycor lid and set it on the hot plate. Allow the mold to cool on the hot plate for 20 minutes.

(9) Remove the mold to a heat resistant surface and allow to cool for a further ten minutes.

(10 Remove the "coal ash" glass disc from the mold.

ORTEC'S XRFCALC
LINEAR OR QUADRATIC LEAST SQUARES FIT

```
DO YOU WISH TO CALCULATE CONCENTRATIONS: NO

INPUT ANALYZER RUN CONDITIONS:

DATE: 14 AUGUST 1978

MICROAMPS:      100
KILOVOLTS:      10
ENERGY SCALE:   0-10 Kev
GAIN:           10 ev/CHANNEL
FILTER:         NONE
ANODE:          MO


NUMBER OF UNKNOWNS:   10
NUMBER OF ELEMENTS:   10

SET UP BACKGROUND AND PEAK ROI'S.  WHEN FINISHED, TYPE 'GO':

INPUT ELEMENT NAMES.
```

PEAK	ELEMENT
1	NA
2	MG
3	AL
4	SI
5	P
6	S
7	K
8	CA
9	TI
10	FE

```
DO YOU WISH TO CORRECT YOUR INPUT: NO

DO YOU WISH TO INPUT ID FOR EACH SAMPLE: YES

SAMPLE ID

   1: PELLET #1
   2: PELLET #2
   3: PELLET #3
   4: PELLET #4
   5: PELLET #5
   6: PELLET #6
   7: PELLET #7
   8: PELLET #8
   9: PELLET #9
  10: PELLET #10
```

SPECTRUM ID: REGIONS OF INTEREST

SPECTRUM ROI REGIONS

REGION	START	END
1	102	108
2	122	128
3	143	155
4	166	182
5	197	205
6	222	242
7	322	340
8	360	378
9	442	460
10	630	650

*

****REPORT****

SAMPLE 1 : PELLET #1
TIME: 200 SEC

ELEMENT	INTENSITY CPS	BACKGROUND CPS
NA	2.4800	0.0000
MG	4.4250	0.0000
AL	70.9800	0.0000
SI	612.9050	0.0000
P	8.8950	0.0000
S	80.1600	0.0000
K	174.6100	0.0000
CA	185.7900	0.0000
TI	107.7050	0.0000
FE	674.7850	0.0000

SAMPLE 2 : PELLET #2
TIME: 200 SEC

ELEMENT	INTENSITY CPS	BACKGROUND CPS
NA	2.5600	0.0000
MG	4.7550	0.0000
AL	70.7950	0.0000
SI	610.7100	0.0000
P	8.6250	0.0000
S	79.4650	0.0000
K	173.8900	0.0000
CA	187.8300	0.0000
TI	106.9350	0.0000
FE	677.4200	0.0000

SAMPLE 3 : PELLET #3
TIME: 200 SEC

ELEMENT	INTENSITY CPS	BACKGROUND CPS
NA	2.7250	0.0000
MG	4.5650	0.0000
AL	71.0750	0.0000
SI	612.4000	0.0000
P	8.3750	0.0000
S	80.2550	0.0000
K	172.1850	0.0000
CA	186.3850	0.0000
TI	106.3000	0.0000
FE	677.9800	0.0000

SAMPLE 4 : PELLET #4
TIME: 200 SEC

ELEMENT	INTENSITY CPS	BACKGROUND CPS
NA	2.6900	0.0000
MG	4.5150	0.0000
AL	71.2200	0.0000
SI	611.4800	0.0000
P	8.6450	0.0000
S	80.1500	0.0000
K	173.5950	0.0000
CA	187.3600	0.0000
TI	108.8050	0.0000
FE	678.9700	0.0000

SAMPLE 5 : PELLET #5
TIME: 200 SEC

ELEMENT	INTENSITY CPS	BACKGROUND CPS
NA	2.5900	0.0000
MG	4.5750	0.0000
AL	69.6550	0.0000
SI	600.5350	0.0000
P	8.6700	0.0000
S	78.1050	0.0000
K	169.5500	0.0000
CA	183.1950	0.0000
TI	105.5000	0.0000
FE	660.3700	0.0000

SAMPLE 6 : PELLET #6
TIME: 200 SEC

ELEMENT	INTENSITY CPS	BACKGROUND CPS
NA	2.5350	0.0000
MG	4.1150	0.0000
AL	71.5300	0.0000
SI	611.6150	0.0000
P	8.5900	0.0000
S	78.8750	0.0000
K	175.4800	0.0000
CA	187.6600	0.0000
TI	106.5300	0.0000
FE	672.8600	0.0000

SAMPLE 7 : PELLET #7
TIME: 200 SEC

ELEMENT	INTENSITY CPS	BACKGROUND CPS
NA	2.6600	0.0000
MG	4.4650	0.0000
AL	71.5950	0.0000
SI	616.6850	0.0000
P	8.8700	0.0000
S	80.7550	0.0000
K	175.0850	0.0000
CA	187.9800	0.0000
TI	107.2300	0.0000
FE	677.7000	0.0000

SAMPLE 8 : PELLET #8
TIME: 200 SEC

ELEMENT	INTENSITY CPS	BACKGROUND CPS
NA	2.8300	0.0000
MG	4.5700	0.0000
AL	72.1300	0.0000
SI	613.4950	0.0000
P	8.6350	0.0000
S	79.6950	0.0000
K	172.6950	0.0000
CA	188.2400	0.0000
TI	106.9250	0.0000
FE	674.4500	0.0000

SAMPLE 9 : PELLET #9
TIME: 200 SEC

ELEMENT	INTENSITY CPS	BACKGROUND CPS
NA	2.5500	0.0000
MG	4.3850	0.0000
AL	70.6600	0.0000
SI	612.3100	0.0000
P	8.6100	0.0000
S	79.6000	0.0000
K	172.0350	0.0000
CA	184.9800	0.0000
TI	105.5700	0.0000
FE	666.4500	0.0000

SAMPLE 10 : PELLET #10
TIME: 200 SEC

ELEMENT	INTENSITY CPS	BACKGROUND CPS
NA	2.5550	0.0000
MG	4.6800	0.0000
AL	72.2700	0.0000
SI	614.1100	0.0000
P	8.7750	0.0000
S	77.8800	0.0000
K	174.0100	0.0000
CA	186.3400	0.0000
TI	109.6200	0.0000
FE	676.9350	0.0000

END OF ANALYSIS

*