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L. Janke

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DETERMINATION OF MAJOR AND MINOR ELEMENTS IN FUSED COAL ASH SAMPLES AND RELATED MATERIALS WITH ENERGY DISPERSIVE X-RAY SPECTROMETRY

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Louis Janke

CANMET, Energy Research Laboratories
Department of Energy, Mines and Resources
Ottawa, Ontario Canada

ABSTRACT

The rapid quantitative determination of the major and minor elements in coal ash is essential to the efficient utilization of coal in industrial processes such as power generation, industrial heating and the production of coke for the steel industry. Present day state of the art energy dispersive spectrometers are well suited to this purpose as they can be used for the simultaneous determination of a large number of analytes at a much lower cost per analyte than other instrumental methods such as neutron activation analysis. Employing a fusion procedure for sample preparation coal ashes, furnace deposits, and other related materials covering wide analyte concentration ranges can be reliably analysed using digital computation of absorption factors to compensate for interelement effects. An in depth presentation of the advantages and limitations of a fusion procedure for sample preparation and the acceptability of the digital computation of interelement effects to determine ash composition are discussed in this paper.

INTRODUCTION

Chemical analysis of coal ash and related materials may be carried out by conventional wet methods or instrumental methods such as atomic absorption, neutron activation analysis or x-ray fluorescence analysis. Conventional wet methods and atomic absorption analysis are rather time consuming and also coal ashes can present serious analysis problems when employing these procedures (1).

Both neutron activation analysis and x-ray fluorescence analysis offer considerable time savings although neutron activation instruments tend to cost a good deal more than present day state of the art x-ray spectrometers. Hence, x-ray fluorescence spectrometry can serve as a rapid and economical instrumental method for the qualitative and quantitative determination of the chemical elements in coal ash and related materials.

In x-ray fluorescence analysis samples are irradiated with a beam of x-rays from an x-ray tube causing each element in the specimen to emit an x-ray line having a wavelength or energy characteristic of that element (this is the basis for qualitative analysis) and an intensity related to the concentration of element (this is the basis for quantitative analysis). In general x-ray spectrometers may be divided into two types; wavelength dispersive and energy dispersive. In a wavelength dispersive spectrometer the x-ray lines emitted by the chemical elements in a sample are dispersed or separated by means of a diffracting crystal on the basis of their respective wavelengths and detected individually. In an energy dispersive spectrometer the x-ray lines emitted by the chemical elements in a sample are detected collectively and then dispersed or separated by electronic means on the basis of their respective energies. The focus of this paper will be on the use of energy dispersive x-ray spectrometry for the quantitative determination of major and minor elements in coal ash and related materials.

Energy dispersive x-ray fluorescence instruments will yield highly reliable analytical results provided that sample preparation techniques and treatment of the x-ray data obtained either minimize or eliminate the problems associated with x-ray analysis. The problems associated with x-ray analysis are generally lumped under the catch all phrase of matrix effects which can be further subdivided into particle size and interelement effects both of which can influence the intensity of the x-ray lines emitted by the chemical elements present in a sample (3). Evaluation of these two problems indicates that a fusion procedure for sample preparation to eliminate particle size effects and mathematical manipulation of x-ray data to compensate for interelement effects produces the most acceptable analytical results for coal ash and related materials (2).

ELIMINATION OF PARTICLE SIZE EFFECTS BY FUSION

Particle size effects are essentially a function of sample mineralogy and must be minimized or eliminated in order to obtain x-ray intensities which will yield meaningful analytical results (3,4). Coal ashes are by nature mineralogically heterogeneous since the coals from which they are derived may contain a wide variety of minerals and in most cases coal ashes contain substantial amount of low Z elements such as aluminum and silicon (5,6). If a material is mineralogically heterogeneous and contains significant quantities of elements with Z less than 16 then the material must be ground to a submicron particle size in order to obtain acceptable x-ray intensities for those elements with Z less than 16 since the x-ray intensities for these elements can pass through very fine particles only (4,7). Grinding any substance to sizes approaching a micron is extremely difficult and is controlled by the physical properties of the minerals present in the sample. Furthermore, contamination by the grinding elements is unavoidable (4). Therefore it would seen virtually impossible to minimize particle size effects to an insignificant level by grinding coal ashes.

However, if coal ashes are fused with a glass forming substance such as $Li_2B_4O_7$ the mineralogy of the sample is destroyed and particle size effects are eliminated with the result that glass pellets with highly reproducible intensities are produced as indicated by the data in Table 1.

Although fusion of coal ashes with a flux such as $Li_2B_4O_7$ to produce glass pellets is simple in concept, the actual preparation procedure must be strictly controlled in order to obtain homogeneous pellets. The method employed by CANMET is given in detail for reference purposes.

Preparation of Fusion Pellets

A. Preparation of "ash

All samples are air dried, ground to pass a No. 60 sieve and ignited at 750°C for 12 h, in a muffle furnace under oxidizing conditions.

The resulting ash is ground in an agate mortar to pass No. 200 sieve. The minus No. 200 sieve ash is then reignited to constant weight and prepared according to the fusion procedure described below.

B. Fusion procedure

1. Equipment and materials

(a) Hotplate capable of maintaining a temperature of 250°C ±25°C.
(b) Muffle furnace capable of maintaining a temperature of 1050°C ±50°C.
(c) 95% Pt/5% Au non wetting crucibles of at least 25 mL capacity plus 95% Pt/5% Au flanged molds.
(d) Lithium tetraborate flux.

2. Recommended procedure

(a) Into a clean dry preweighed non wetting platinum crucible weigh 1.0000 g of ash.
(b) Add approximately 2.5000 g of $Li_2B_4O_7$ flux, mix and cover with 2.0000 g of $Li_2B_4O_7$ to give 4.5000 g of $Li_2B_4O_7$ compensated for loss on fusion.
(c) Place crucible and contents into a muffle which has been preheated to 1050°C ±50°C.
(d) Swirl the melt every 15 minutes for a total of 1 1/4 h fusion time.
(e) Remove the crucible and melt. Weigh to determine the loss on fusion of the sample. Place the crucible and contents back in the muffle.
(f) Place a mold in the furnace and allow it to reach 1050°C ±50°C.
(g) Pour the melt from the crucible into the mold. Swirl the mold and allow the mold and melt to reach 1050°C.
(h) Transfer the mold and melt to a hotplate maintained at 250°C ±25°C and allow the pellit to anneal on the hotplate for 10 minutes.
(i) Remove the mold to a heat resistant surface and allow the pellet to cool to room temperature.
(j) Remove the glass pellet from the mold.

Several comments on the procedure are relevant at this point. An agate mortar is used to grind all samples as this results in essentially no contamination of the samples. A large wide door muffle 14" x 8" x 12" deep is employed for melting the sample/flux mixtures as a large number of ashes can be processed in a batch, and temperature parameters are very easy to control.

The lithium tetraborate itself presents a special problem. When lithium tetraborate is fused at high temperatures certain volatiles are expelled resulting in a weight loss (8,9). This loss in weight has been found to be virtually constant for a given lot of $Li_2B_4O_7$ but can vary considerably between different lots as indicated in Table 2.

Therefore, in order to produce glass pellets from different lots of $Li_2B_4O_7$ which will contain the same amount of $Li_2B_4O_7$ it is necessary to compensate the weight of the flux used in the fusion procedure for the loss on fusion just described. The compensated weight of $Li_2B_4O_7$ flux to be used for the fusion procedure is given by:

$$\text{Compensated weight} = \frac{450 \times 1}{100 - \text{LOF}}$$

The sample and lithium tetraborate must be weighed and mixed exactly as described because even when "non wetting" platinum crucibles are used some coal ashes will "hang up" on the sides of the crucibles. By following the steps exactly as specified any sample hanging up on the sides is "washed" into the bottom of the crucible. Swirling the melt promotes fusion of the sample and ensures a homogeneous melt. The total elapsed fusion time of 1 1/4 h is critical especially for ashes derived from furnace deposit samples as these substances are often multiphase containing fine powdery material as well as hard silica sphericals. To achieve complete fusion of the silica granules a minimum of 1 h fusion time is required. The crucible and contents are weighed before and after fusion since the ashes are prepared at 750°C and in some cases further heating results in the loss of such volatile substances as sulphur trioxide from the ash and this information is required for accurate analytical results. Steps (f) to (i) of the fusion procedure must be strictly observed as the actual pouring of the melt and annealing of the pellet may result in enrichment or depletion of certain elements at the surface of the pellet which is to be exposed to x-rays unless the precautions stipulated in the method are exercised (4,10). By employing the procedure described above it is possible to obtain a homogeneous solid solution of coal ash dissolved in lithium tetraborate in which particle size effects have been eliminated.

Analysis of fused coal ash samples by energy dispersive x-ray fluorescence

Once a coal ash has been fused to form a homogeneous glass pellet it may be presented to the x-ray spectrometer for analysis. As mentioned earlier the pellet to be analysed is irradiated with x-rays and the chemical elements present in the ash emit x-ray lines having energies characteristic of the element and intensities related to the concentration of the element. The x-ray lines emitted by the elements are processed by the spectrometer to yield a spectrum such as the one in Figure 1.

The element line intensities which are represented by the height of the peaks in the spectrum are converted to counts per second and then mathematically manipulated to obtain the concentration of each element in the coal ash sample.

At this point the second problem associated with matrix effects, the interelement effect is encountered. Interelement effects are a function of the elemental composition of the sample only and may be subdivided into absorption effects and enhancement effects. Absorption effects occur when the x-ray line of a given element is reduced in intensity by the other elements in a sample. Enhancement effects occur when the x-ray line of a given element is increased in intensity by the other elements in a sample. In fused pellets the interelement effects are predominantly due to absorption with enhancement effects being negligible. Absorption effects can be mathematically compensated for by use of a fundamental equation derived from physics which is

$$I_L = KC_A F(A) \qquad (1)$$

Where

I_L	is	Background corrected element line intensity
K	is	Physical constant
C_A	is	Weight fraction of element A in the sample
F(A)	is	Absorption factor of the flux and the elements in the sample for element A

In coal ash glass pellets F(A) the absorption factor of the flux and the elements in coal ash for a given element A is essentially dependent on the range of concentration of element A normally encountered in coal ash. If the concentration range of element A is greater than 10% then F(A) will have a highly variable effect on the intensity of element A and absorption effects must be taken into consideration. This situation occurs for aluminum, silicon, sulphur, calcium and iron in coal ashes. If the range of concentration of element A is 10% or less than F(A) will have an insignificant effect on the intensity of element A and absorption effects may be ignored. This situation occurs for magnesium, phosphorus, potassium and titanium in coal ash. In fact for these elements equation (1) may be rewritten as:

$$C_A = K_1 I_L , \quad K_1 = \frac{1}{KF(A)} \qquad (2)$$

Equation (2) implies that the concentration of magnesium, phosphorus, potassium and titanium in fused coal ash glass pellet samples may be directly derived from their intensities as measured by the x-ray spectrometer. However, as stated previously, I_L is the background corrected or more simply "net" element line intensity. Unfortunately, the intensities measured by an x-ray spectrometer include background generated by scatter of tube x-rays and by various contributions from other elements in the sample. Consequently, before acceptable concentration values for any element in coal ash can be derived from intensity data the "raw" element line intensities measured by the x-ray spectrometer must be converted to "net" intensities by removal of the background. Once this process has been carried out it should be possible to calculate the concentration of magnesium, phosphorus, potassium and titanium directly from their "net" line intensities, whereas for aluminum, silicon, sulphur, calcium and iron absorption corrections will also be required.

The computation of background corrected intensities from raw intensities obtained from an energy dispersive x-ray spectrometer can be difficult due to the complex nature of the background generated under a given element line.

In a fused pellet the main background under an element line consists of background counts contributed by the scatter of tube x-rays from the $Li_2B_4O_7$ flux in the pellet and background counts contributed by peak overlap or peak tailing from other elements in the sample.

The background counts contributed by the scatter of tube x-rays from the $Li_2B_4O_7$ flux to a given element's x-ray line may be determined from a pellet made of pure $Li_2B_4O_7$. The background counts contributed to a given element's x-ray line by peak overlap and/or peak tailing from other elements in the sample may be measured from pure pellets of each of these elements. The background counts contributed by peak overlap and/or peak tailing from an element "B" to each of the other x-ray lines in a sample is directly proportional to the intensity of element "B" and therefore may be mathematically calculated (11).

The analysis of phosphorus in coal ash glass pellets although essentially unaffected by absorption effects is especially difficult with an energy dispersive spectrometer as there is considerable background contributed by the flux, peak tailing from sulphur and peak overlap from silicon and the calcium escape peak which is an electronic contribution generated by the lithium drifted silicon detector used in most energy dispersive systems, when calcium is present in a sample.

Figure 2 illustrates a plot of phosphorus (as P205) concentrations in various coal ash samples calculated from raw (background uncorrected) intensities and from net (background corrected) intensities arrived at by mathematically removing the background contributions mentioned earlier against accepted phosphorus (as P205) concentrations in the coal ashes. The removal of background counts from under the phosphorus x-ray line produces acceptable analytical results without the need for further corrections.

Unfortunately, for aluminum, silicon, sulphur, calcium and iron concentration values cannot be determined directly from their background corrected intensities as absorption effects must be taken into consideration for these constituents. For these elements equation (1) may be rewritten as

$$C'_A = K_2 I_L \quad (3)$$

where

$$K_2 = 1/K$$

$$C'_A = C_A\,F(A)$$

C'_A may be referred to as the "apparent" concentration of element A in the coal ash or more simply the concentration of element A that the x-ray spectrometer "thinks" it sees. Therefore, using equation (3) it is possible to calculate the "apparent" concentration of elements requiring absorption correction from the background corrected intensity of these elements. From these "apparent" concentrations an absorption factor for each element requiring absorption corrections may be calculated using the equation

$$F(A) = \frac{M_A}{(\theta + \sum mi\ Ci)} \qquad (4)$$

where

F(A)	is the absorption factor
mi	is the mass absorption coefficient of element i for element A
Ci	is the weight fraction of element i in the sample
Θ	is the absorption factor of the $Li_2B_4O_7$ flux for element A
M_A	constant characteristic of element A

In equation (4) mi the mass absorption coefficient is a fundamental physical property of an element which measures the ability of the element to absorb a given x-ray line. This mi is different for each element for a specified x-ray line and different for each x-ray line for a specified element, and may be obtained from published tables (12).

Once the absorption factors have been calculated for all elements requiring absorption corrections a first estimate of "actual" concentrations for these elements may be established using the equation

$$C_A = \frac{C'_A}{F(A)} \qquad (5)$$

Employing these first estimates of "actual" concentrations another F(A) is calculated and a second estimate of "actual" concentrations is calculated again using equation 5. This process is repeated until the change in the calculated "actual" concentrations for all elements requiring absorption corrections is less than some preset value (e.g. 0.10%).

Iron in coal ash glass pellets suffers especially severe absorption effects. Figure 3 illustrates a plot of iron (as Fe_2O_3) concentrations in various coal ash samples calculated from net intensities without absorption corrections and from net intensities with absorption corrections against accepted iron (as Fe_2O_3) concentrations. Without absorption corrections the calculated values deviate markedly from the accepted values especially for high concentrations of iron whereas with absorption corrections the agreement with accepted values is excellent.

Tables 3 and 4 give the analytical results for MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, K_2O, TiO_2 and Fe_2O_3 as determined by energy dispersive x-ray fluorescence by the methods described in this paper as well as the "list" results determined by a variety of chemical and instrumental methods for a series of "reference" samples covering wide concentration ranges. In general the agreement of the XRF values with the list values is excellent, and well within the specified limits of reproducibility set out by ASTM in D 2795 and D 3682 (1,2).

SUMMARY

Energy dispersive x-ray spectrometry is a rapid analytical tool which may be successfully applied to the analysis of wide concentration ranges of major and minor elements in coal ash. Matrix effects in the form of particle size effects are eliminated by fusion of the ash samples with $Li_2B_4O_7$ flux and interelement effects are minimized by the digital computation of absorption factors from published mass absorption coefficient data. The analytical results obtained are well within the limits set by ASTM.

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