

A SURVEY OF EMISSION X-RAY ANALYSIS OF COAL

J. K. Kuhn and L. R. Henderson

Illinois State Geological Survey
Urbana, IL 61801

Measurement of emitted X-rays is finding widespread acceptance as an analytical tool for determining minor and trace elements in coal and coal-related materials. Because the method requires a short time for analysis and can determine concentrations ranging from a few parts per million up to 100% in a single sample, it is a desirable alternative to many other techniques (1).

Following the development of the method of Rose et al. (2), accurate analyses of coal ash have been routinely performed for several years. Methods for X-ray analysis of whole coal, however, despite earlier work by Sweatman et al. (3), have developed more slowly (4,5,6,7). Recent improvements in equipment, especially innovations in detectors and excitation sources, have brought about renewed interest in the technique.

Two types of spectroscopic systems are now available. One is the wave-length dispersive unit which uses crystals with various lattice spacings to diffract and separate the X-rays emitted from excited samples. A goniometer is then used in conjunction with either a gas-flow or a scintillation detector to measure the angle and intensity of the emitted radiation. The second type of system consists of a solid state detector, either lithium-drifted silicon or intrinsic germanium, connected to a multichannel analyzer. A typical detector, with resolution of 140ev to 160ev, produces pulses whose amplitudes can be separated and quantified for most X-rays. These systems, therefore, are capable of simultaneous multi-elemental analyses over a wide range of energies.

The X-ray tube, both with and without filters, is a common excitation source, but a number of other kinds of sources are useful. In systems where portability is desirable, isotope sources are commonly used with solid state detectors. These sources give nearly mono-chromatic exciting radiation which means that background corrections are smaller for effects due to scattered radiation and background. Decay of isotopes limits their useful life, but sources such as americium 241 (used with secondary targets) can provide reasonably stable excitation for many years. Excitation by electron probe, ion probe, scanning electron microscopy, etc., is now widely used for X-ray analysis. Energetic protons, also used to induce X-ray emission, have the additional advantage of producing gamma radiation, which increases the number of elements that can be determined (8).

Regardless of the type of spectrometer or the exciting source used, a number of other problems must be solved before accurate analysis of coal and its related products can be obtained. Foremost among these is the problem of adequate standards. At present only two certified standards are available, one for trace elements in coal and one for trace elements in fly ash. This means that each laboratory must produce its own set of standards. Mathematical correction procedures may be applied instead but they are unsatisfactory when there are large variations in matrix. The second major problem is the acquisition of representative samples for analysis. Coal itself, is perhaps the simplest material to sample but still presents problems due to inhomogeneity. Variations within the coal seam or feed stock may limit precision to 5% (9), and the presence of discrete mineral particles may result in even greater errors (10). Coal-related materials - e.g. chars, ashes, residues, and products from liquefaction and gasification processes - vary greatly depending upon temperature,

physical location in the system, processing time, and other factors. These materials may range from nearly totally inorganic minerals to wholly organic liquids; occasionally a very viscous slurry that is almost impossible to homogenize is encountered.

The great variability of these materials causes not only sampling difficulties but also significant analytical problems. X-ray analysis is highly dependent upon matrix variations, which are normally handled in one of three ways. One solution is to prepare a sufficient number of standards so that every conceivable matrix can be very closely matched. Though this is not impossible, it is usually impractical for most laboratories.

A second method of handling the matrix problem is to prepare analytical samples in such a way as to make the variations almost insignificant. This may be done by dilution with an inert material (11), by addition of a heavy adsorber (2), or by preparation of a sample thin enough that all X-rays generated in the material will escape (6,8). The first two techniques tend to raise the limit of detection of the trace elements in the original sample. Even though the third technique requires great care to prepare a uniform, representative sample, it is being used quite successfully by a number of laboratories.

The third method of correcting for matrix effects employs mathematical procedures. These procedures may be divided into three groups. The first includes various methods for empirically measuring the mass absorption coefficient of the material for the radiations of interest. These methods have been reviewed extensively by Lubecke (12) and Sparks et al. (7). In the second group of procedures, Compton scatter is used to estimate mass absorption coefficients (13,14,15,16,17). In the last group of techniques, all corrections are made mathematically from a knowledge of fundamental parameters (18). This method requires observation of the intensities of the radiation from all of the major elements in the sample.

Although any one of the matrix correction procedures listed above may work for a particular analytical problem, a combination of two or even all three is justified in a laboratory with a wide variety of sample types. All these procedures require the use of a satisfactory background correction. Since the background is due not only to the mass absorption coefficient and to elemental concentrations of the sample but also to the exciting source, the detector, and the analyzing system, it may well be the limiting factor in the precision of analysis, especially for trace elements in most materials. A good discussion of these problems is presented in a recent review by Russ (19).

The coal analyst must be familiar with all of these problems inherent in X-ray procedures. Most of them can be handled satisfactorily with computer programs. When samples are properly prepared, the analyst can handle types ranging from liquids to solids and from almost pure organic materials to totally inorganic minerals. Such samples can be analyzed 'as is' as long as the surface presented to the spectrometer is uniform, representative, and exhibits no particle-size effects. This may require the use of samples with particles of less than -325 mesh down to a few microns in size especially for the determination of elements of low atomic weight.

Precision for modern X-ray systems is approximately 5% to 25% overall, for trace elements, depending upon the optimization of the spectrograph for the elements of interest. For major and minor elements, depending upon the system used, precision may well be less than 1%. The elements with lower atomic numbers, i.e., Na thru Ca, can not be analyzed as precisely as the heavier elements, especially with energy-dispersive systems.

The limit of detection by X-ray analysis, with presently available commercial equipment, ranges, for coal samples, from 100 for sodium to .5 to 4 PPM for the elements iron through cerium (10). For those elements of heavier atomic weight where the L series X-rays are used for analysis, the limit of detection is approximately 10.

While precision and limit of detection do not necessarily indicate accuracy, with good standards and good programs for matrix corrections the results of X-ray analysis compare favorably with results by other methods of analysis. Its simplicity and ease of operation make it the method of choice where a large number of samples are to be investigated for many elements.

REFERENCES

- (1) Kuhn, J. K., Harfst, W. F., Shimp, N. F., "X-Ray Fluorescence Analysis of Whole Coal," *Advances in Chemistry* 141, 66-73 (1975).
- (2) Sweatman, T. R., Norrish, K., Durie, R. A., CSIRO Misc. Rept. 177, 30 pp. (1963).
- (3) Rose, H. J., Alder, I., Flanagan, F. J., U.S. Geological Survey Prof. Papers 450-B, 80-82 (1962).
- (4) Berman, M., Ergun, S., Bureau Mines Rept. Invest. 7124, 20 pp. (1968).
- (5) Kuhn, J. K., "Trace Elements in Whole Coal Determined by X-Ray Fluorescence," *Norelco Reporter* 20, 3 (1973).
- (6) Giauque, R. D., Jaklevic, J. M., "Rapid Quantitative Analysis by X-Ray Spectroscopy," *Advances in X-Ray Analysis* 15, pp. 164-174 (1971).
- (7) Sparks, C. J., Ogle, J. C., "Quantitative Trace Element Analysis With X-Ray Fluorescence," First Annual N.S.F. Trace Contaminants Conf., ORNL Conf. 730802 pp. 421-439 (1973).
- (8) Blokhim, M. A., "Methods of Spectrochemical Research," Trans. from Russian by F. L. Curzon, Pergamon Press, pp. 344-346 (1965).
- (9) ASTM Standards, Annual Book, Part 26, pp. 269-283 (1976).
- (10) Ruch, R. R., Gluskoter, H. J., Shimp, N. F., Ill. Geol. Survey, Environmental Geology Note No. 61, 43 p. (1973).
- (11) Claisse, F., "Accurate X-Ray Fluorescence Analysis Without Internal Standard," *Norelco Reporter* 3, 3 (1957).
- (12) Lubecki, A., "Theoretical Discussion of Methods of Elimination of Matrix Effects in Non-Dispersive X-Ray Analysis," *J. Radioanal. Chem.* 2, 3-18 (1969).
- (13) Reynolds, R. C., "Matrix Corrections in Trace Element Analysis by X-Ray Fluorescence: Estimation of the Mass Absorption Coefficient by Compton Scatter," *Amer. Mineral.* 48, 1133-1143 (1963).

- (14) Reynolds, R. C., "Estimation of Mass Absorption Coefficient by Compton Scattering: Improvements and Extensions of the Method," Amer. Mineral. 52, 1493-1502 (1967).
- (15) Walker, D., "Behavior of X-Ray Mass Absorption Coefficients Near Absorption Edges: Reynolds Method Revisited," Amer. Mineral. 58, 1069-1072 (1973).
- (16) Victoreen, J., "The Absorption of Incident Quanta by Atoms as Defined by the Mass Photoelectric Absorption Coefficient and the Mass Scattering Coefficients," J. Applied Physics. 19, 855-860 (1948).
- (17) Victoreen, J., "The Calculation of X-Ray Mass Absorption Coefficients," J. Applied Physics 19, 1141-1147 (1949).
- (18) Criss, J. W., Birks, L. S., "Calculation Methods for Fluorescent X-Ray Spectrometry," Anal. Chem. 40, 1080-1086 (1968).
- (19) Russ, J. C., "Processing of Energy-Dispersive X-Ray Spectra," X-Ray Spectrometry 6, 1 (1977).