

THE APPLICABILITY OF STANDARD TEST METHODS  
TO THE ANALYSIS OF COAL SAMPLES FOR COAL RESEARCH

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INTRODUCTION

Standard test methods for routine coal analysis in the United States include those of the American Society for Testing and Materials (ASTM) and, with limited application, those of the International Organization of Standardization (ISO). The former consist of national standards used in the United States and Canada, while the latter have been developed by ISO member nations for international trade. While these methods are used throughout the coal industry and in commerce to establish coal quality, they may not be applicable in the analysis of coal samples for research purposes. One problem area is the chemical analysis of coal. This becomes particularly evident when using ASTM methods which were primarily designed for the analysis of bituminous coal to analyze lignitic and subbituminous coals. Here, researchers and analysts find themselves trying to fit a square peg in a round hole.

In this paper some of the difficulties that have been observed in our analysis of research coal samples for major, minor, and trace elements are emphasized, and suggestions for eliminating these problems are presented.

DISCUSSION

Moisture in the Analysis Sample

Determining the moisture in the analysis by weight loss at 104-110°C presents several problems, especially if the current ASTM method D3173 (1) is used. In our experience, the ASTM method is unsuitable for low-rank coals because it does not use an inert gas as the purge gas and recommends too short a drying period. Oxidation -- gain in weight as the sample reacts with oxygen in the air -- can take place, and not all of the 104-110°C moisture is removed during the recommended one-hour drying time. In addition, with certain low-rank coals, decarboxylation during the drying period can result in weight loss. At present, our use of moisture data is primarily for calculation of sulfur, ash, and trace element data to moisture-free bases, so a modified ASTM method similar to the ISO method 331 (2) is used. The coal sample is heated in an oven at 104-110°C for three hours. The oven is purged with dry, purified, and preheated nitrogen.

Ash in the Analysis Sample

The ash in coal is the noncombustible residue that remains when coal is burned. In the ASTM method D3174 (3), the coal sample is placed in a cold furnace and heated gradually so the temperature reaches 450 to 500°C in one hour and 700 to 750°C at the end of the second hour. The ISO method 1171 (4) recommends a 815°C final temperature. In both methods the sample is ignited at the appropriate final temperature to constant weight.

For our research samples, we have selected a procedure in which the coal samples are placed in a cold muffle furnace; the temperature is incremented at the rate of 100°C per hour until the final temperature is attained. Although slower, this procedure prevents ignition of the coal, which can result in the physical loss of material. In addition, this slower rate minimizes sulfur retention in the ash.

#### Ash Analysis - Major and Minor Ash Elements

The analysis of coal ash for major and minor elements is important for determining the ash chemistry. The current ASTM method D3682 (5) requires fusion of the sample with lithium tetraborate followed by analysis by atomic absorption spectrophotometry (AAS). Presently the list of routinely determined ash elements includes Si, Al, Fe, Ti, Ca, Mg, Na, K, P, and S. For our research samples a more complete ash characterization is necessary so that elements such as Sr, Ba, Mn, and Zn are also determined. In addition, methods utilizing mixed-flux fusions are being evaluated to eliminate the need to use one flux (lithium metaborate) for highly siliceous ashes and another flux (lithium tetraborate) for ashes containing high contents of iron oxides. These aspects are being addressed because of the extreme variability in the ash chemistry encountered when analyzing lignite ash versus bituminous coal ash.

Although AAS is the technique utilized in the ASTM standard method, the determination of additional elements, coupled with the need to reduce analysis turnaround time, has prompted the evaluation of multielement sequential and/or simultaneous determination systems such as inductively coupled plasma-atomic emission spectrometry (ICP-AES) for coal ash analysis.

#### Ash Analysis - Trace Elements in Coal Ash

The determination of trace elements in coal ash is relatively straightforward and will be indicative of the trace element content of the coal if the particular trace element is not volatilized during ashing. The current ASTM method D3683 (6) utilizes a 500°C ash for the determinations of Be, Cu, Cr, Mn, Ni, Pb, V, and Zn by flame atomic absorption spectrophotometry. While flame AAS is satisfactory for most of the trace elements mentioned, many coal ashes contain levels of Pb and V that are just above the flame AAS detection limits; hence, quantification for those elements is difficult. Flameless AAS is being evaluated as an alternative for the Pb determination and ICP-AES is being evaluated for the V determination as well as for the other trace elements listed above.

#### Analysis of Coal for Major, Minor, and Trace Elements

As mentioned previously, if the inorganic components present in the coal are not volatilized during ashing of the coal, and the ash content is known, these elements can be determined in the ash and calculated to a coal basis. Unfortunately, the literature reports situations where selected elements in coal, such as sodium, lead, and cadmium, are volatilized during ashing (7,8,9). Situations such as these cast doubt on the universal applicability of elemental analysis methods for coal that require muffle furnace ashing.

Wet ashing techniques include the use of mixtures of perchloric and other acids for the dissolution of coal. While wet ashing minimizes the risk of volatilization of the major, minor, and trace elements, most coal analysis laboratories avoid the use of perchloric acid. Other approaches of coal sample preparation for analysis such as microwave oven digestion and slurry techniques exhibit contamination problems and/or low recoveries for many elements.

We recommend the use of nitric-perchloric acid digestions (10) and oxygen bomb combustions (11) in the preparation of coal samples for spectrochemical analysis. These procedures eliminate any ambiguity associated with potential elemental losses by volatilization during the sample preparation.

#### CONCLUSIONS

In analyzing coal research samples for their chemical composition, it is apparent that certain current standard test methods require modification or they are not applicable. Coal research, and possibly most new uses of coal, will require higher standards of quality control and accuracy than are currently quoted in many of the existing standard test methods. These factors will become increasingly more important when economic decisions must be made based on the validity, i.e., accuracy, of coal analysis data.

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