

DIRECT DETERMINATION OF ORGANIC OXYGEN IN COAL USING SCANNING ELECTRON
MICROSCOPY WITH WAVELENGTH-DISPERSIVE X-RAY ANALYSIS

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ABSTRACT

Illinois No. 6, Pittsburgh No. 8, and Dietz No. 1 and 2 coals were analyzed directly for organic oxygen content by using scanning electron microscopy and wavelength-dispersive x-ray analysis. The technique is a modified extension of a method previously developed for the direct determination of organic sulfur in coal. To assure statistical validity, 12 particles were analyzed for each coal at two different points per particle. Mean organic oxygen values were obtained, as well as inter- and intra-particle variations in the oxygen content. The mean values for organic oxygen obtained by this technique agreed favorably with values calculated from previously obtained data by prompt neutron activation analysis and by the indirect ASTM method.

INTRODUCTION

The organic oxygen content of coal is an important parameter in coal characterization and utilization and is a part of routine coal analyses. It must be known in order to perform some of the process calculations for coal combustion and various coal conversion technologies such as liquefaction and gasification (1). The organic oxygen content of coal is generally determined by ASTM Method 3176, the Standard Method for Ultimate Analysis of Coal and Coke (2). In this method, oxygen is the only element comprising the organic coal matrix which is not determined directly. Rather, it is determined by difference from the ultimate analysis, using the equation:

$$\%O = 100 - (\%C + \%H + \%N + \%S + \% \text{ ash}) \quad \text{Eq. 1}$$

Thus, the accuracy of this indirect oxygen determination suffers from cumulative errors inherent in the analytical methods used for each of the other elements. In addition, it is dependent on the ash content which is obtained by heating the coal at about 700°C for one hour; but since the ash produced at these temperatures is not directly relatable to the original mineral matter in the coal, another source of error is thereby introduced into the oxygen determination.

Furthermore, if the coal has been subjected to chemical treatment which alters the ash-forming mineral matter, the definition of "ash" used in Eq. 1 becomes a problem.

Although various methods for determining oxygen in coal directly have been employed, including neutron activation analysis (NAA) and oxidative or reductive techniques, analyses by these methods include all or some of the inorganic oxygen. Therefore, coal demineralization or corrections for inorganic oxygen must be performed in order to obtain the organic oxygen content.

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In this study, the feasibility was explored for using a scanning electron microscope (SEM) in conjunction with energy- and wavelength-dispersive x-ray analysis (EDX and WDX, respectively) to determine the organic oxygen content of coal directly. The technique is similar to methods used previously for the direct determination of organic sulfur levels in coals (3-8). In one such technique, a transmission electron microscope was used to quantify the sulfur content of the organic coal matrix (3). Other studies used an electron microprobe to determine organic sulfur in coal (4, 5). In one of those studies, the organic oxygen content of various macerals in a Kentucky No. 3 coal also was determined (5). By knowing the petrographic composition of the coal and the average organic oxygen content of each maceral examined, a weighted average was used to obtain an oxygen concentration for the organic matrix as a whole. The organic oxygen concentration thus obtained was in good agreement with the concentration obtained by the indirect ASTM procedure.

A third method used scanning electron microscopy coupled with energy-dispersive x-ray analysis (SEM-EDX) to obtain organic sulfur levels in raw and chemically desulfurized coals (6-8). In two of the studies using the SEM-EDX technique, mineral portions of the coal were avoided by locating organic maceral components of coal using 5000x magnification with the SEM and by monitoring the levels of Fe, Ca, Al, and Si (6, 7). Sulfur values which were obtained only for those areas where the other elements were not detected were assumed to be associated with the organic portion of the coal. Analyses were usually performed on 12 vitrinite particles by examining at least two points (with volumes of 2-3 microns in diameter) per particle. This was sufficient to obtain data with a precision of $\pm 10\%$ (relative) for organic sulfur levels. The results were comparable to those obtained by the common indirect ASTM method.

In our study, a similar SEM technique was used to determine organic oxygen levels in coal along with inter- and intra-particle variations. Organic oxygen values obtained by this technique were compared to values obtained by the indirect ASTM procedure and by neutron activation analysis.

EXPERIMENTAL

Channel samples of Illinois No. 6 (Captain Mine, Percy, Illinois), Pittsburgh No. 8 (Grafton Mine, Churchville, West Virginia), and Dietz No. 1 and No. 2 (Decker Mine, Decker, Montana) coals were powdered, dried, and subsequently mounted in one-inch pellets of epoxy. After polishing the mounted samples to a smooth cross section with silicon carbide sandpaper and alumina, they were coated with approximately 50 Å of carbon by evaporation in order to provide a conductive surface.

A JEOL (Japan Electron Optics Laboratory) model JSM-U3 scanning electron microscope (SEM) was used in conjunction with a Microspec WDX-2A wavelength-dispersive x-ray analysis system to perform quantitative oxygen determinations on the coals. Oxygen was determined by wavelength-dispersive x-ray analysis (WDX) because it could not be detected by the EDX system, being an element of low atomic number.

Samples were examined in the SEM with an accelerating voltage of 15 kV and a current of about 30 nA with an x-ray take off angle of 25°. The SEM was allowed to stabilize for 15 to 30 minutes after sample changes before collecting x-ray intensities. X-ray data were collected from square sample areas of 20 μm on a side. A square raster was used for the analyses instead of the traditional spot mode due to the high beam currents used. Prior to analysis, mineral portions of the coal were avoided by examining the sample visually at a magnification of 5000x in the SEM. Energy-dispersive x-ray analysis (EDX) was then performed with a KEVEX Si(Li)

detector and a Tracor Northern Model TN-2000 energy-dispersive x-ray analysis system to monitor the particles for Al, Ca, Fe, and Si. The absence of these elements ensured that mineral inclusions were excluded from the sampled areas. Since oxygen was determined by WDX only when significant levels of the elements screened by EDX were absent, the oxygen was assumed to be associated with the organic matrix.

Because organic sulfur and small amounts of Al, Si, Ca, and Fe were present in the analyzed particles, EDX spectra for a set of standards containing these elements were collected prior to analyzing the coal. Silica (SiO₂) was chosen for the oxygen standard since organic compounds which were tested did not hold up well under the electron beam. Organic compounds which were tested for use as a standard included urea, acetanilide, and citric acid. After analyzing a coal for organic oxygen content, one of the inorganic standards for the other elements was run for a second time to make sure that no significant drift in beam current occurred.

In this study, no attempt was made to distinguish between different maceral types. Two points within each of 12 particles were analyzed for each coal. EDX spectra and total oxygen counts obtained by WDX were each collected for 30 seconds. The total oxygen intensity was then transferred to the EDX unit for data reduction. The Tracor Northern program Super ML was used to reference the coal spectra against the standards, while the Tracor Northern ZAF correction program was used to correct for atomic number, absorption, and fluorescence matrix effects. In addition to mean organic oxygen concentrations, inter- and intra-particle variations in oxygen content were obtained.

RESULTS AND DISCUSSION

Average organic oxygen concentrations obtained by SEM-WDX on each of the coals are shown in Table 1. For comparative purposes, data obtained previously by neutron activation analysis (NAA) and by the indirect ASTM procedure are also included.

Table 1. Organic Oxygen Content of Illinois, Pittsburgh, and Dietz Coals.¹

Analytical Procedure	Coal		
	Illinois #6	Pittsburgh #8	Dietz #1 & 2
SEM-WDX	11.94	11.55	16.67
ASTM	9.44	8.07	20.67
NAA ²	10.67	7.85	22.70

¹ Values are in % on a dry mineral matter free basis.

² Organic oxygen content was obtained from total oxygen values by estimating the inorganic oxygen concentration and subtracting from total oxygen, as discussed in text.

The SEM values represent averages for the 24 sampled areas for each coal; ASTM and NAA data represent averages of duplicate determinations. Only total oxygen values were available in the original NAA data. For comparison on the same basis, the raw data obtained by NAA were used to estimate organic oxygen concentrations (shown in Table 1) by subtracting inorganic oxygen levels from the total oxygen levels. For these calculations, the inorganic oxygen values were estimated by first using a modified Parr formula (9) to approximate the mineral matter content

based on the known ash and pyritic sulfur contents for each coal. This formula is:

$$\%MM = 1.13 (\% \text{ ash}) + 0.47 (\% \text{ pyritic sulfur}) \quad \text{Eq. 2}$$

The amount of inorganic oxygen was then estimated using the equation

$$\%O_{\text{Inorg}} = 0.5 (\% \text{ MM}) \quad \text{Eq. 3}$$

This equation has been reported to give good inorganic oxygen estimations for well-known coals with relatively low ash contents (10). Thus, organic oxygen levels were obtained by calculating the difference in levels of total and inorganic oxygen. The mineral matter content of each coal, as calculated using the modified Parr formula, was used to convert the NAA and ASTM values to a mineral matter-free basis. The SEM-WDX data required no corrections for mineral matter because mineral inclusions were avoided during those analyses.

In view of the analytical uncertainties in each of the techniques, the SEM-WDX values agreed favorably with the values obtained by NAA and ASTM procedures. For the Pittsburgh No. 8 and Illinois No. 6 coals, there was a significant lapse in time between the SEM-WDX analyses and the determinations made by NAA and ASTM procedures. The coals were used frequently over this time period and often had been in contact with air. Thus, it is likely that some oxidation would have occurred during this time and that the somewhat elevated SEM-WDX data for these two coals reflect this oxidation.

For the Dietz coal, the SEM-WDX value is significantly lower than the values obtained by the other methods. This may be somehow connected with the fact that the Dietz coal is subbituminous, as opposed to the bituminous ranking of the other coals. More study is needed to resolve this discrepancy.

Also, although the same coals were used for the analyses by SEM-WDX, NAA, and the ASTM procedure, analyses by SEM-WDX were performed on different sample splits than the ones used for analysis by the other techniques. Coal composition between various splits from standard riffing procedures is generally comparable, but variations in chemical composition may still occur as a result of sample inhomogeneity and difficulties involved with obtaining representative samples of coal.

Thus, discrepancies between analytical data obtained by the various techniques may reflect actual differences in composition in addition to possible errors associated with the analytical methods. Future work will include more rigid monitoring of the various sample variables than was done in this preliminary study.

Statistical parameters for the SEM-WDX data are shown in Table 2. Details on the statistical parameters employed have been described previously (6, 7). These analyses enabled estimates for deviations from the sample mean within the particles (intra-particle deviations) and deviations from the sample mean between different particles (inter-particle deviations) to be calculated.

It is interesting to note that for each coal, intra-particle variations were larger than inter-particle variations. For the Illinois coal, analysis of variance gave a negative number for the inter-particle variation. Therefore, a value of zero is reported. Between coals, the inter-particle variations were less consistent than the intra-particle variations. This implies that some coals may require more extensive analyses due to a less uniform distribution of organic oxygen. One factor which could be important is the maceral distribution for a given coal.

Table 2. Statistics for Organic Oxygen Levels Obtained by SEM-WDX.

Coal	Org. O ^a (%)	S \bar{x} ^b	S _a ^c	S _p ^d
Illinois No. 6	11.94	0.37	1.43	0.00 ^e
Pittsburgh No. 8	11.55	0.24	0.97	0.45
Dietz No. 1 & 2	16.67	0.44	1.40	1.16

^a Values are on a dry mineral matter free basis.

^b S \bar{x} is the standard deviation in the sample mean.

^c S_a is the standard deviation within particles.

^d S_p is the standard deviation between particles.

^e Value of zero reported since analysis of variance gave a negative number.

Since the organic oxygen content can vary considerably between different macerals (5, 11), the maceral composition and distribution could have a large effect on the intra- and inter-particle variations.

The SEM-WDX technique may be particularly useful for determining organic oxygen in chemically cleaned coals, especially since ASTM procedures sometimes give questionable ash results for such coals (12), thereby throwing a large error into the ASTM organic oxygen determination.

CONCLUSIONS

Examination of the SEM-WDX results indicates that this technique has good potential for the direct determination of organic oxygen in coal. Analysis of inter- and intra-particle variations provides useful information on the distribution of organic oxygen in the coal. Because mineral phases are excluded from the analysis, a sample with a representative ash content is not nearly as important for this procedure as it is for NAA and ASTM procedures where ash corrections are necessary. However, since the SEM-WDX technique is surface-sensitive, extra care must be taken to keep the coal from oxidizing. Because of the numerous operating parameters involved in the analyses by SEM-WDX, the procedural details of this technique require optimization. In addition, applicability to a broad spectrum of raw coals and to chemically cleaned coals needs to be shown.

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