

USE OF SEM WITH WAVELENGTH-DISPERSIVE SPECTROMETRY FOR ORGANIC OXYGEN IN COAL

G. A. Norton, K. A. Younkin, W. E. Straszheim, and R. Markuszewski

Ames Laboratory, Iowa State University, Ames, Iowa 50011

ABSTRACT

Scanning electron microscopy (SEM) and wavelength-dispersive spectrometry (WDS) were used to determine organic oxygen in four geographically diverse coals and in amber. Subsequent to the previously reported feasibility study, analytical modifications and refinements in sample handling and preparation were made. In addition, the precision of the SEM-WDS analyses was examined. SEM-WDS results were comparable to values obtained by neutron activation and by the indirect ASTM procedure for one coal, while significant discrepancies were observed for the other coals and the amber. Preliminary results suggest that the discrepancies may be caused by the electron beam, which possibly volatilizes oxygen-containing compounds in some of the samples analyzed by this SEM technique. Results also indicated that additional work is required to reduce matrix correction factors.

INTRODUCTION

Organic oxygen in coal is an important measure of coal quality, and thus it is determined as an integral part of routine coal analyses. A variety of techniques, including oxidative, reductive, and radiochemical methods, have been employed for directly determining the oxygen content of coal. The oxidative procedures, which generally use gaseous oxygen as the oxidizing medium (1), are cumbersome and incorporate potentially large relative analytical errors. In general these methods are not widely used.

In the reductive methods, coal is pyrolyzed, and oxygen in the pyrolysis products is then reduced with hydrogen or carbon. When hydrogen is used, oxygen in the pyrolysis products is catalytically converted to water, which is then taken as a measure of the oxygen content of the coal (1). Disadvantages of this method include relatively complex apparatus and possible catalyst poisoning by sulfur and chlorine in the coal. Methods employing carbon as a reducing agent, such as the classic Unterzaucher method (2), are relatively common. These methods generally involve reducing oxygen in the coal pyrolysis products to CO, which is then oxidized and determined as CO₂. Although satisfactory results can be obtained by such pyrolysis methods, they are usually slow and tedious.

Fast-neutron activation analysis (FNAA), which has been used relatively recently for oxygen in coal (3,4), is based on irradiating the coal with 14-MeV neutrons and measuring the radiation of the ¹⁶N produced from the oxygen. However, this technique requires a suitable nuclear reactor and specialized equipment for radiochemical analysis.

A general drawback to the above methods is that all or part of the inorganic oxygen is included in the determination. Therefore, corrections for the inorganic oxygen must be made, or else the coals must be demineralized prior to analysis.

Because of difficulties and/or errors associated with these techniques, ASTM Method 3176, the Standard Method for Ultimate Analysis of Coal and Coke (5), specifies that the organic oxygen content be determined by difference from the ultimate analysis, using the equation:

$$\%O_{org} = 100 - (\%C + \%H + \%N + \%S + \%ash) \quad 1)$$

This indirect determination, however, is also plagued by potential analytical errors. In addition to cumulative errors associated with the other five constituents in the ultimate analysis, the nature of the mineral matter is significantly changed during ashing. Furthermore, the ASTM procedure is designed for unaltered coals and may not be applicable to chemically treated coals. Clearly, the need remains for a fast, simple, direct, versatile, and accurate method for determining the organic oxygen content of coal.

Electron beam microanalytical techniques provide possible alternatives for determining directly the organic oxygen content of coal. Such techniques have been used previously for the direct determination of organic sulfur in coal (6-8). In one of those studies, the organic oxygen content of various coal macerals was also determined (8).

In previous work at Ames Laboratory, the feasibility was explored of using scanning electron microscopy (SEM) with wavelength- and energy-dispersive spectrometry (WDS and EDS, respectively) for the direct determination of organic oxygen in coal (9). X-ray analysis techniques were emphasized, while sample preparation and handling were not carefully monitored or controlled. Because of encouraging results with the SEM technique, additional exploratory work was performed in this study.

EXPERIMENTAL

Samples

The four coals in this study were Illinois No. 6 (Captain Mine, Percy, Illinois), Pittsburgh No. 8 (Grafton Mine, Churchville, West Virginia), Dietz No. 1 and 2 (Decker Mine, Decker, Montana, and Charming Creek (Charming Creek Mine, Buller Coalfield, New Zealand). These coals were ground to -200 mesh, dried at 100-110°C for two hours under vacuum and stored under argon in a freezer. Sample pellets were prepared by mixing the coal with ultra-high molecular weight polyethylene powder, pouring the mixture into a hot press, and heating to 140°C for about five minutes under 4200 psi pressure in a nearly air-tight chamber. The pellets were ground with silicon carbide sandpaper and lapping oil and polished with a diamond paste and oil. The pellets were then cleaned in a mixture of hexanes (Skelly-B), coated with approximately 50A of carbon, and stored under nitrogen at 5°C prior to analysis.

In addition to the coals, a sample of amber from an unspecified source from the Baltic Sea region in Poland was analyzed. It was thought that the amber could serve as a model compound for certain coal macerals, particularly resinite. This sample was ground to -60 mesh and was then prepared for analysis in the same manner as the coals.

Conventional Analyses

Ultimate analyses were performed with a Perkin-Elmer Model 240 CHN Analyzer and a Fisher Model 470 Total Sulfur Analyzer. Ash was determined by conventional ASTM procedures and the organic oxygen was then calculated by difference as shown in Eq. 1. Data for total oxygen in coal were obtained by FNAAs at the University of California at Irvine. These analyses were for different sample splits than the ones used for the ASTM and SEM analyses and were performed on "as-received" rather than on dried coals. After correcting the total oxygen values to a dry basis per ASTM standard D-3176 (5), which includes the correction to account for oxygen in moisture, the organic oxygen was estimated by assuming 50% of the mineral matter to be oxygen (10). The FNAAs and

ASTM organic oxygen values were converted to a mineral matter-free basis by using a modified Parr formula (11) to estimate the mineral matter content of each coal.

Thermogravimetric Analyses (TGA)

TGA was performed on the coals and the amber with a DuPont Model 1090 thermogravimetric analyzer. The samples were heated from room temperature to about 800°C at a rate of 10°C per minute under a nitrogen atmosphere.

SEM-WDS Analyses

A JEOL (Japan Electron Optics Laboratory) Model JSM-U3 scanning electron microscope was used in conjunction with a Microspec WDX-2A spectrometry system to quantify oxygen in the samples. Energy-dispersive spectrometry (EDS) was performed with a KEVEX Si(Li) detector and a Tracor Northern Model TN-2000 energy-dispersive x-ray analyzer. Since the low energy oxygen x-rays are absorbed by the beryllium window in our EDS detector, oxygen had to be measured by WDS.

For the coals, x-rays were collected in the spot mode using typical analysis conditions of 15 kV accelerating voltage, 30 nA beam current, and a 25° x-ray take-off angle. For the amber, a 20 x 20 μm square raster was used with an accelerating voltage of 10 kV. Samples were first screened visually at 5000x in the SEM to avoid mineral inclusions. EDS was then used to monitor the particles for Al, Si, Ca, and Fe. Since oxygen was determined by WDS only when significant levels of these elements were absent, the oxygen had to be associated with the organic matrix. Two points within each of 12 particles were analyzed for each coal. This sampling approach, used previously to determine organic sulfur in coal, was found to give statistically acceptable results (7). Due to analytical difficulties, only one point for each of 7 particles was analyzed for the amber.

Because organic sulfur and small amounts of Al, Si, Ca, and Fe were sometimes present in the analyzed particles, EDS was used to collect spectra for a set of standards containing these elements prior to analyzing the coal. Quartz (SiO₂) was used for Si, aluminum metal for Al, apatite (Ca₅(PO₄)₃ OH) for Ca, and pyrite (FeS₂) for the Fe and S. Quartz was also used for the oxygen standard since a suitable organic oxygen standard for the SEM technique has not yet been found. Although boric acid, citric acid, urea, and acetanilide were tested as possible organic oxygen standards, they could not withstand the high beam currents. Other materials could be investigated for use as organic oxygen standards.

After collecting the spectra from the sixth and twelfth coal particles, additional spectra from a standard were collected to monitor the beam current. Each coal was analyzed twice by the SEM technique. For the second SEM-WDS analysis, the same pellet was used, but a new surface was exposed and analyzed. Sample pellets of amber were only analyzed once.

For each coal, the wavelength of the maximum oxygen intensity was measured for 10 sampled points. The values were averaged, and organic oxygen was determined by collecting oxygen intensities at the average wavelength for a given coal. For the amber, the average wavelength from 6 sampled points was used.

Energy-dispersive spectra and oxygen x-rays obtained by WDS were each collected for 30 seconds. The total oxygen intensity was transferred to the EDS unit for data reduction. The Tracor Northern program "Super ML", a multiple least-squares fitting program, was used to reference the sample spectra against the standards. The organic oxygen concentrations were calculated from the observed oxygen intensities using the Tracor Northern "ZAF" correction program to correct for the

atomic number, absorption, and fluorescence effects in the coal matrix.

The theoretical detection limit for oxygen for the equipment used in this study was determined using Ziebold's equation (12):

$$C_{d.l.} \geq 3.29a / (n\tau P \cdot P/B)^{0.5} \quad 2)$$

where $C_{d.l.}$ is the minimum detectable limit, " τ " is the time of each measurement, " n " is the number of repetitions of each measurement, " P " is the pure element counting rate, " P/B " is the peak to background ratio of the pure element, and " a " relates composition and intensity of the element of interest by:

$$a = c (1 - k) / (1 - c)k \quad 3)$$

where " c " is the concentration and " k " is the measured intensity ratio. For typical operating conditions, $C_{d.l.}$ was about 1%, which is well below the oxygen concentration in the samples used for this study.

RESULTS AND DISCUSSION

The organic oxygen values from the ASTM ultimate analyses, shown in Table 1, were converted to a mineral matter-free basis and incorporated into Table 2 for comparison of the ASTM results with the FNAA and SEM results. The error limits of the SEM analyses shown in Figure 2 were calculated directly from the analytical statistics and represent 95% confidence limits (i.e., $\pm 2\sigma$). The error limits for the ASTM values were calculated by summing the reproducibility limits for the C, H, N, S, and ash analyses. For the FNAA values, error limits were calculated from counting statistics and represent 95% confidence limits. As can be seen in Table 2, the SEM-WDS organic oxygen values were comparable to those obtained by the ASTM and FNAA techniques for the Pittsburgh coal, while significant discrepancies were generally noted for the remaining coals and the amber. Although the SEM oxygen value for the amber was fairly close to the ASTM value, SEM analysis of this sample was unsatisfactory due to poor contrast between the amber and mounting material as well as other analytical problems. Reproducibility was best for the Dietz coal and was worst for the Illinois coal. The low, yet consistent SEM-WDS values for the Dietz coal suggest a systematic error in the SEM-WDS procedure.

The discrepancies between the SEM values and those obtained by the FNAA and ASTM procedures may reflect errors in the SEM technique it-

Table 1. ASTM Analyses of Samples Used in This SEM-WDS Study for Organic Oxygen^a

| | Charming Creek Coal | Dietz Coal | Illinois Coal | Pittsburgh Coal | Baltic Amber |
|------------------|------------------------|---------------|------------------|--------------------|-----------------|
| Moisture | 0.71 | 2.47 | 1.24 | 1.07 | 0.85 |
| C | 78.48 | 70.07 | 65.39 | 76.01 | 79.89 |
| H ^b | 5.12 | 4.41 | 4.11 | 4.86 | 10.69 |
| S _{tot} | 5.63 | 0.48 | 4.56 | 3.20 | 0.46 |
| N | 1.31 | 0.91 | 1.11 | 1.15 | 0.98 |
| Ash | 1.23 | 5.25 | 13.97 | 6.93 | 0.19 |
| O (By Diff.) | 8.23 | 18.87 | 10.85 | 7.83 | 7.79 |

^aValues are in % and, except for moisture, are reported on a dry basis.

^bCorrected for hydrogen in the moisture.

Table 2. Organic Oxygen Values Determined by ASTM, FNAF, and SEM-WDS^a

| Sample | ASTM | FNAF | SEM-WDS | |
|---------------------|------------|------------|------------|------------|
| | | | Analysis 1 | Analysis 2 |
| Charming Creek Coal | 8.35±0.72 | not detd. | 4.97±0.62 | 5.99±0.90 |
| Dietz Coal | 20.06±0.72 | 19.85±0.16 | 8.43±1.10 | 8.67±1.58 |
| Illinois Coal | 13.04±1.02 | 10.51±0.24 | 8.38±1.00 | 11.94±1.54 |
| Pittsburgh Coal | 8.56±1.02 | 8.21±0.12 | 9.71±0.56 | 8.34±0.62 |
| Baltic Amber | 7.89±0.67 | not detd. | 5.9±1.2 | not detd. |

^aValues are in % on a dry, mineral matter-free basis.

self. These errors may involve differences in oxygen peak shape and/or location, volatilization of oxygen-containing species during analysis, or potential errors in the matrix correction routine.

Peak shape and location can possibly be affected by the distribution of oxygen functional groups in the coal, since differences in bonding energy will change slightly the energy of the emitted x-rays, particularly for light elements. If these effects are significant for the samples analyzed in this study, then determining the oxygen at a single wavelength for a given sample could introduce significant errors into the determination. Integration of peak areas may be required for accurate analyses. Oxygen peak shapes and locations for the coals and quartz are shown in Figure 1. An oxygen curve was not obtained for the amber. Although additional work is required for confirmation, the peak shapes appear to be significantly different between samples. Also, it can be seen that variations of only 0.050A in the peak location could result in variations in the measured intensity by as much as 20%.

To study the possibility of sample volatilization, oxygen counts were collected for successive five-second intervals under different operating conditions for the Dietz and Illinois coals. Twelve measurements were collected on each of several particles for both coals, with a one-second break in between each interval. When relatively high energy fluxes were used, oxygen counts for both coals decreased by 18-36% over a 72-second period. However, the Illinois coal was able to withstand a higher beam current without experiencing a decrease in the oxygen count. Results of thermogravimetric analyses, shown in Figure 2, indicate that the Dietz coal is more volatile than the other coals. Thus, it is probably more susceptible to loss of oxygen during SEM analysis. In view of this, the Dietz coal was reanalyzed using milder operating conditions. Under the modified analytical conditions, the oxygen content was about 15%, as opposed to the values of 8-9% reported in Table 2. This adds additional support to the sample volatilization hypothesis. No similar experiments were performed on the amber.

The "ZAF" matrix correction routine is a third possible source of error. Using typical operating conditions, absorption factors for oxygen in coal were between 7 and 9, which are of particular concern since the oxygen standard (SiO₂) is not similar to the coal matrix. The absorption corrections can be minimized by altering operational parameters. Also, in lieu of a different oxygen standard, using other correction routines could minimize errors associated with the matrix corrections.

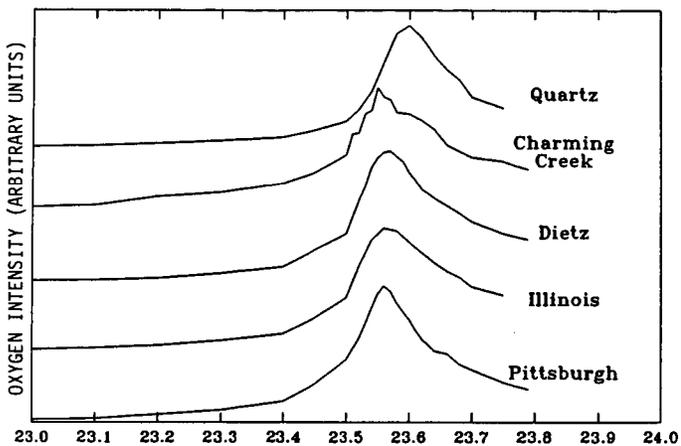


FIGURE 1. Oxygen peak shapes for quartz and coals used in this study.

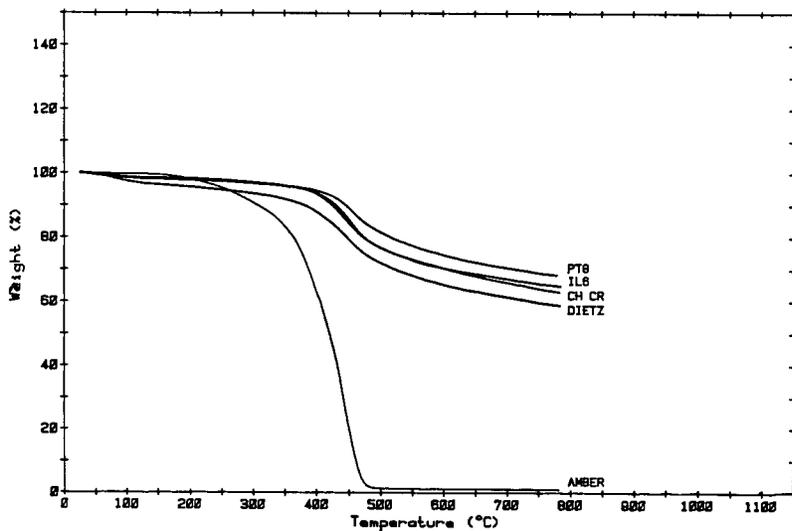


FIGURE 2. TGA analyses of coals and amber.

CONCLUSIONS

Although some encouraging results were obtained with the SEM-WDS technique, additional work is required to optimize analytical conditions to perform quantitative oxygen determinations. Maintaining sample integrity will need to be considered when selecting optimum x-ray acquisition parameters. Additional work is also required to further ascertain analytical precision and to further establish statistical parameters. The validity of the sampling approach, which has been shown to be acceptable for determining organic sulfur in coal, should be evaluated further to test its applicability to organic oxygen determinations. The theoretical detection limit of about 1% for oxygen is low enough for the technique to be applicable to a wide variety of coal and coal products. Difficulties with analysis of the amber indicate that alternate sample mounting techniques should be available for analyzing different sample types.

ACKNOWLEDGEMENTS

Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract W-7405-Eng-82. This work was supported by the Assistant Secretary for Fossil Energy, Division of Direct Coal Utilization, through the Pittsburgh Energy Technology Center. Special thanks to Surender Kaushik, who performed the thermogravimetric analyses.

REFERENCES

1. Ode, W.H. in Chemistry of Coal Utilization, Supplementary Volume (Ed. H.H. Lowry), John Wiley and Sons, Inc., New York, NY, 1963, pp. 219-220.
2. Unterzaucher, J. Ber. Deut. Chem. Ges. 1940, 73, 391.
3. Mahajan, O.P. Fuel 1985, 64, 973.
4. Hamrin, C.E., Jr., Johannes, A.H., James, W.D., Jr., Sun, G.H., and Ehmann, W.D. Fuel 1979, 58, 48.
5. Annual Book of ASTM Standards, Part 26: Gaseous Fuels; Coal and Coke; Atmospheric Analysis, ASTM, Philadelphia, PA, 1982.
6. Maijgren, B., Hubner, W., Norrgard, K., and Sundvall, S. B. Fuel 1983, 62, 1076.
7. Straszheim, W.E., Greer, R.T., and Markuszewski, R. Fuel 1983, 62, 1070.
8. Friel, J.J. and Mitchell, G.D. in Microbeam Analysis (Ed. R.H. Geiss), San Francisco Press, San Francisco, CA, 1981, pp. 148-150.
9. Norton, G.A., Straszheim, W.E., Younkin, K.A., and Markuszewski, R. Am. Chem. Soc. Div. Fuel Chem. Preprints, 1986, 31(1), 130.
10. Kinson, K. and Belcher, C.B. Fuel 1975, 54, 205.
11. Given, P.H. and Yarzab, R.F. in Analytical Methods for Coal and Coal Products, Vol. 2 (Ed. C. Karr, Jr.), Academic Press, New York, NY, 1978, pp. 3-41.
12. Goldstein, J.I., Newbury, D.E., Echlin, P., Joy, D.C., Fiori, C., and Lifshin, E. Scanning Electron Microscopy and X-ray Microanalysis, Plenum Press, New York, NY, 1984, p. 434.