

CHEMISTRY OF COAL FROM ELECTRON MICROSCOPY MEASUREMENTS

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ABSTRACT

Well established techniques of analytical electron microscopy have applications to the chemistry of coal. The techniques use one or another of several interactions which occur when electrons are incident on a specimen. Two such interactions are discussed in this paper: 1: X-ray emission spectroscopy and 2: Electron energy loss spectroscopy. Both methods are used in the study of metallic and ceramic systems. The principles of the technique are illustrated by applications to metallic and ceramic systems; initial applications to coal are then described.

INTRODUCTION

Many interactions occur when electrons are incident upon a solid. X-ray and optical photons may be emitted, electrons may back-scatter, secondary electrons may be emitted and changes in energy of transmitted electrons may occur for thin specimens. These phenomena have been utilized in the electron microprobe, the scanning electron microscope, in other electron and photon spectroscopic instruments and in the transmission electron microscope. We consider two of these spectroscopies in this paper: utilization of the characteristic x-ray lines from atoms in the solid and measurement of the loss-of-energy of the transmitted electrons when ionizing collisions are made with atoms in a thin foil.

The use of x-ray emission spectroscopy has been made extensively using the electron microprobe and the scanning electron microscope. In that case, a thick specimen is used in which the electrons are stopped in the specimen. Characteristic x-ray lines from specific atoms in the solid are counted either with a crystal detector or with an energy dispersive detector to deduce the composition of the solid. This technique has been applied extensively to metals and alloys (1-5) and also for determination of the organic sulfur content of coal (6-10). That application has been generally successful. Calibration of the system has been made using known sulfur-bearing standards. Such calibration requires that a matrix of about the composition of coal must be used since fluorescence and absorption corrections are significant. Fortunately, a single calibration constant applies to all coals without much error.

The biggest difficulty with these measurements is the relatively large volume of material from which the x-rays come. Because of electron scattering and fluorescence, the volume of measurement is about $100 \mu\text{m}^3$. Thus, homogeneity in the specimen over this volume must exist for the measurement to be reliable. For measurement of organic sulfur in coal, this has posed some problems, since one can never be sure that small sulfide particles may not

exist under the surface, unseen by examination of the surface features. Procedures have been established by a number of investigators to circumvent this problem.

This technique has been heavily exploited by mineralogist and extensive procedures have been developed to make quantitative measurement of the mineral concentrations in ores (11-14). This technique also has been used for pyrite in coal using programmed scanning of polished surfaces.

We have developed techniques of transmission electron microscopy for examination of minerals in coals (15-17) and also for examination of the concentration of organic elements in coal. Principles of these techniques are described in the next section and applications are presented for measurement of sulfur, chlorine and other organic constitutions of coal.

X-RAY EMISSION SPECTROSCOPY

Chemical analysis using emission spectroscopy is based on the measurement of characteristic $K\alpha$ or $L\alpha$ lines upon excitation with incident electrons. In transmission electron microscopy the detector is almost always an energy-dispersive detector with a resolving power of about 150 eV. This limits the detectability of adjacent elements in the periodic table, but the variety of elements present in coal is so small that no serious difficulty arises from this source. A schematic of the apparatus is sketched in Fig. 1. The spectrum displayed in the multi-channel analyzer consists of two parts, characteristic lines of the elements present and a background radiation. The background is utilized in the quantitative determination of concentration of elements present, since it can be used to deduce the volume of the specimen. A sketch of a typical spectrum for sulfur is shown in Fig. 2.

The quantitative determination of the concentration of organic elements present in the specimen depends on a method developed for biological materials by Professor T. Hall and his colleagues (18-21). The count rate for the $K\alpha$ line of sulfur is proportional to the number of sulfur atoms in the volume. Hall showed that the volume from which that radiation came could be conveniently measured by simultaneously counting the background counts -- it is known that the background (or bremsstrahlung) count rate is proportional to the total number of atoms in the volume, the radiation from each type of atom being weighted according to its atomic number. The weight percent of sulfur in the volume is proportional to the ratio of the count rate for sulfur divided by the count rate for the bremsstrahlung radiation.

$$S \text{ (wt \%)} = A C_s/C_b$$

The measurement is therefore a simple one -- the concentration of sulfur in the specimen is given by the ratio of two count rates which can be measured in a few minutes of counting time in the electron microscope.

We have developed this system and made three principal applications to coal, oil shale and amber:

1. The technique can be used to measure the average organic sulfur concentration in fuels (16). Since the organic sulfur content varies among the maceral types, it is necessary to average the measurements over a number

of independent determinations to get a good mean value. We have found that 50 measurements over random spots in a coal specimen is sufficient; Raymond has noted that only 15 measurements are needed in his SEM method, if the measurements are made over only vitrinite macerals. A plot showing measurements on four coals using our TEM method compared with standard ASTM measurements is shown in Fig. 3.

2. The TEM method is valuable to measure variation of organic sulfur content among maceral types: the general variation had been known from earlier measurements, but the TEM method shows finer variation than is possible by gross techniques.

3. We have followed the loss of organic sulfur during heating of coal. Our measurements of loss of sulfur were made for inert, oxidizing and reducing atmospheres.

OXYGEN: Determination of the oxygen content of coal by standard methods is a complex chemical analysis. In principle, the same x-ray technique we have used for sulfur might be used to determine the oxygen content directly. The main difficulty is that the $K\alpha$ x-ray line of oxygen comes at 535 eV, compared with the value of 2300 eV for sulfur. Consequently absorption problems in the detector window are much more severe for oxygen.

Even so, we have made such a measurement using window-less detector on a Philips 420 microscope. An example is given in Fig. 4. We can observe both the oxygen line and the carbon line on the same scan and thus have the possibility to compare their magnitudes to get a general notion of the relative concentration of these two elements.

In practice, the measurement is extremely difficult. The weak lines of oxygen and carbon are absorbed by the matrix. Even more, oxygen and carbon come on opposite sides of the C $K\alpha$ absorption edge: oxygen is on the high absorption side. Therefore, absorption corrections must be made even for the thinnest coal samples. Even more, surface contamination of the specimen may produce additional absorption of the two x-ray lines. Therefore, the measurement is not straightforward. Even so, using polymeric films as standards, we have made measurements on macerals of vitrinite; we are also in process of making measurements on fusinite and resinite. Clearly this technique is expensive enough that it will not be heavily used for oxygen analysis routinely. However it does offer the possibility of mapping out variations in oxygen content of coals from maceral to maceral and of measuring the spatial variation of oxygen within a given maceral.

ENERGY LOSS SPECTROSCOPY

Electrons passing through a solid make both elastic and inelastic collisions with the electrons in the material. The elastic collisions have important uses in diffraction and other features of examination of materials. However, the inelastic collisions also produce a beam of electrons containing important information. In the last twenty years, a spectroscopy termed ELECTRON-ENERGY-LOSS-SPECTROSCOPY (EELS) has come to be recognized as an important tool in study the chemistry of solids. A number of excellent review papers exist (22,23) and an enormous number of examples of application of the techniques to studies of the physics and chemistry of alloys and compounds has

been published. Consequently only a few examples will be given here to show the general characteristics of the technique and the potential for its application to the study of the chemistry of the coal and other hydrogen carbon materials.

The study of the chemistry of light elements in solids by EDAX uses rather low energy x-rays -- from perhaps 250 to 3000 eV. The x-ray detecting systems are attuned to that energy range. The energy loss spectroscopic techniques, on the other hand, use the high energy range of the incident electron beam, since the composition of the specimen is deduced from the high-energy part of the loss spectrum; i.e., the accelerating voltage of the microscope (typically 100 keV) minus the inelastic collision energies of a few hundred to a few thousand eV. This requires quite a different spectroscopy.

In practice, energy loss spectroscopy has utilized either electrostatic or magnetic means for separating the transmitted beam of electrons into energy regimes which reflect the elemental composition of the material. A typical instrumental scheme is sketched in the lower half of Fig. 1. There the transmitted electrons are separated into two groups, one a group of electrons which have traversed the specimen suffering no inelastic collisions, the other a group of electrons which have suffered an inelastic collision of energy ΔE . The increment of energy loss is typically in the range of a few hundred to a few thousand eV.

A great many studies have been made on metals, alloys and compounds. Details of these studies can be seen by the examination of the many reviews and original papers. However, we present two studies to show the power of the technique.

The first study is an examination of the alloy system V + 5%Ti + a small amount of carbon. When heat treated appropriately an extremely fine precipitate of a vanadium-titanium-carbide forms in a vanadium matrix. A micrograph of that precipitate is shown in Fig. 5. Spectra for the vanadium solid solution and for the carbide are shown in Fig. 6 superimposed on each other. The matrix of vanadium shows a strong vanadium absorption peak for the L edge at 520 eV. A small carbon edge is seen at about 285 eV. The L edge of vanadium is lost in the background at 460 eV. The same spectrum for the beam focused on the precipitate shows very clearly all three elements, the vanadium L edge the titanium L edge and the carbon K edge.

The analysis of this spectrum combined with analyses made by an x-ray emission spectrum of the same carbides and additional diffraction measurements gave the complete solution to this microstructure. The precipitate is a structure of vanadium-titanium-carbide of composition about VTi_4C_5 . This is a hexagonal carbide whose basal plane rests against the (110) plane of the vanadium matrix. The successful analysis of this material was made possible by the combined spectroscopies and diffraction techniques available in a modern analytical electron microscope (24).

A second example from our laboratory was based on an analysis of a precipitate in a crystal of titanium diboride, TiB_2 . An electron micrograph of that specimen showed a matrix containing some precipitates on well defined crystal planes (25). Energy loss spectra of both the titanium diboride matrix and the precipitate are shown in Fig. 7. The pertinent lines come at energies

of 460 eV for the L edge of Ti, 284 eV for the K edge of C and 188 eV for the K edge of B. This analysis shows that the precipitate is titanium-carbide embedded in titanium-diboride. Further diffraction analysis in the microscope showed that the carbide is an FCC structure embedded in a hexagonal matrix of the diboride. The geometry of the matching plane has also been deduced by these investigators.

Many other measurements might be cited to show the power of this effect. We have made energy loss spectra of coal and can observe the carbon and oxygen K absorption edges. An example is shown in Fig. 8. A great deal more work will be required to put this on a quantitative basis since the absorption edge for oxygen is barely visible for the short counting time used in this feasibility measurement. However, techniques are improving rapidly, and this surely means that the application is possible.

SUMMARY

Spectroscopic methods using both emission and absorption characteristics of the interaction of electrons with atoms in a solid are common in metallurgy and ceramic investigations. Each has unique characteristics and applications, but they are even more powerful when they are used in combination. Analytical electron microscopy is in its infancy for coal and oil shale, but the potential is plainly evident.

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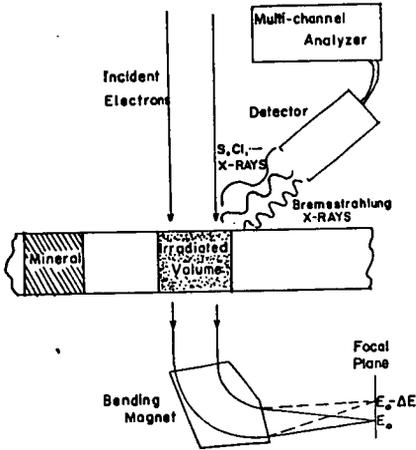


Fig. 1 Sketch of TEM with EDAX and EELS Capability.

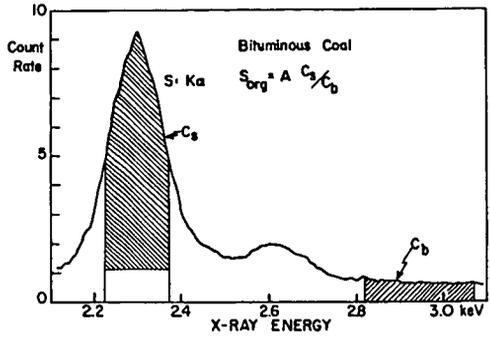


Fig. 2 EDAX Spectrum for S.

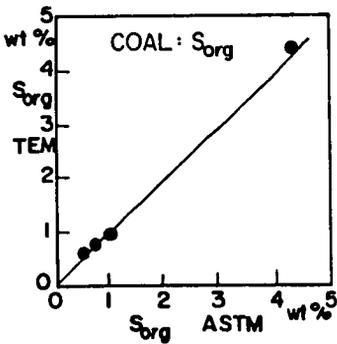


Fig. 3 Comparison of TEM and ASTM Analyses of Coal.

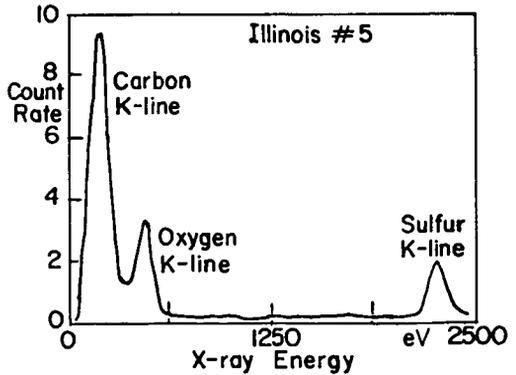


Fig. 4 Light-Element Spectrum: C and O X-ray lines.



Fig. 5 TEM Micrograph of a V-Ti-C Carbide.

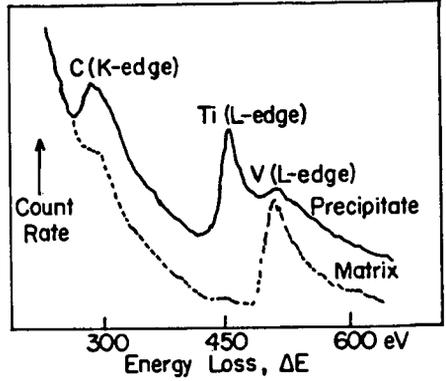


Fig. 6 EELS Spectrum of matrix and VTi_4C_5 Carbide.

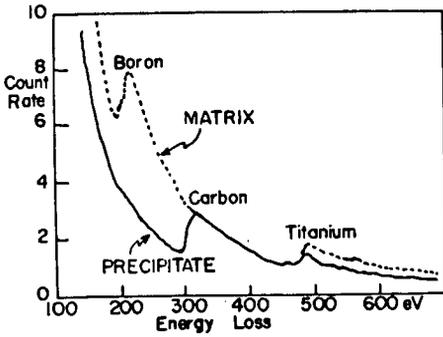


Fig. 7 EELS Spectrum for TiC in a TiB_2 matrix.

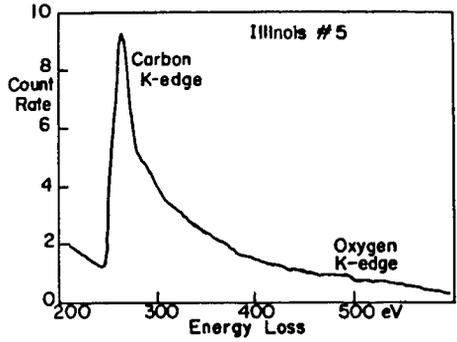


Fig. 8 Energy Loss Spectrum of a Bituminous Coal.