

INORGANIC AND ORGANIC ANALYSIS BY INFRARED SPECTROMETRY IN COAL PROBLEMS

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SUMMARY

A group of problems are discussed. In Inorganic work the identification of mineral absorption bands in infrared spectra has been carried out by a combination of spectrometry and coal petrography. The absorption bands of the whole coal that are found to decrease significantly with the removal of mineral matter are easily identified by this means.

An important safety problem in coal mines has been substantially helped by infrared analysis of minerals. The content of rock dust found in the float dust of return airways of coal mines is important and preferably should be determined with speed. The usual procedure is to wait for dust to settle sufficiently to collect 100 mg of sample for chemical analyses. By the application of infrared spectrometry to this problem it is possible to carry out a complete analysis for rock dust content on as little as 2 mg sample. Greater speed is achieved.

In organic work, attenuated total reflectance of shock-heated coal has shown that considerable infrared fine structure is developed relative to the original coal (Spectra by Barnes Engineering Co.). The spectra obtained are, however, not representative of the whole coals. More volatile portions of the coal are found to leave the coal first as expected and to collect first on the ATR prism. Because of the very slight optical penetration of the sample by the spectral beam the spectrometer sees only the initial volatile parts of the coal. This method is therefore very good for concentration of and study of the volatile portions of the coal. A principle use of ATR at the Bureau has been in the study of spectra of sorbates added to coals.

Infrared spectral changes with acid-base interactions (charge-transfer complexes) have been studied by the ATR method. With coal as the acid (acceptor) and pyridine as the base (donor) the same changes in the pyridine spectrum are found as in other charge-transfer complexations involving pyridine.

INTRODUCTION

The application of infrared spectrometry to chemical substances represents the largest use in science of any spectral method. These applications are overwhelmingly in the field of organic chemistry. But infrared spectrometry is also used for analysis of inorganics. In addition to qualitative information it is possible to obtain quantitative information as well. As in organic infrared a straight line relationship usually exists between the concentration of each component in a mixture and the spectral absorption of that component. This paper will treat a few applications of infrared spectrometry to both organic and inorganic problems. In most cases other available spectral methods (mass spectrometry, ultraviolet-visible, nuclear magnetic resonance, electron paramagnetic resonance) are used in conjunction with infrared, but only infrared is discussed here.

INORGANIC APPLICATIONS

Inorganic materials which possess anions of oxygenated systems, namely, carbonates, chlorates, sulfates, silicates, etc., usually possess in their infrared spectra distinct, intense spectral bands. Such substances are amenable to analysis by infrared spectroscopy. One distinct difference between organic and inorganic substances is that inorganics have fewer spectral absorption bands than organics. With fewer bands to work with, analyses of complex mixtures are limited. This is one major reason why infrared analyses of inorganics have not been as popular as analyses of organics. Organic molecules produce profuse spectra because of the large number of atoms involved, and because many of these atoms are usually hydrogens which are responsible for many of the intense bands in the spectra of organic compounds. When hydrogens are present in inorganic compounds, these too show a greater profusion of spectral bands; the bicarbonates are an example.

It is interesting to note that one of the earliest and best text books on infrared, written by German spectroscopists Schaeffer and Matossi^{1/} 36 years ago, discussed the inorganic applications at length, almost to the exclusion of organic applications. It was soon after this period that the greater applicability to organic structures aroused so much activity that it practically swept aside the inorganic applications of infrared. A considerable impetus was given to infrared analysis of inorganics by Miller and Wilkins of Mellon Institute in their publication of a catalog of spectra of inorganic compounds,^{2/} and by Hunt et al. in a publication of infrared spectra of minerals.^{3/} This impetus was needed, although it did not produce any great activity in inorganic analysis until recent years--more than a decade after publication. A recurring difficulty with inorganics is that spectra of unknowns often differ significantly from the spectra of standards. This is a disturbing occurrence and makes difficult the assignment of spectra to specific structures. A list of possible reasons for spectral differences follows: (1) Infrared spectra often differ for different crystal structures of a substance. This is a factor in dealing with pure substances, and is an even bigger factor in the presence of impurities and in mixed salts. Epitaxy can produce differing crystal structures and infrared spectra. (2) Substrates can have a tremendous effect on the spectrum of an inorganic substance. Large spectral changes are well known in the case of organic materials studied *in situ* on catalysts. (3) Reaction may occur between the minute crystals of the sample and the KBr, or other halide, used for infrared pelleting.

In Bureau of Mines work infrared applications in inorganics occurred in connection with: (1) Our early work on coal spectra; unassigned bands thought to be due to ethers in bituminous coal spectra were reported in 1956 to be due to minerals, principally kaolinite;^{4/} (2) spectra of oil shales and other carbonaceous shale produced little information; (3) brief investigations of alkalinized alumina in 1963 gave limited information: the presence of sodium aluminate was indicated, which substantiated the X-ray indications of this group; the presence of sulfates (not definitely assignable) on alkalinized alumina exposed to sulfur oxides has been shown; (4) formation of inorganic carbonates in the pyrolysis of lignites and of peat at 400° C was shown; (5) recent examination of probe samples obtained in combustion experiments showed identifiable sulfates. Further work on (1) will be described.

1. Identification of Mineral Absorption Bands in Coal Spectra

The discovery of the correct assignment of certain absorption bands to minerals^{4/} came about through the observation in 1953 that the spectra of coals and their petrographic components differed considerably. As in other laboratories our suspicions were that these differences were attributable to differences in organic

structure between the coal and its petrographic constituents. But it became apparent that this could not be. A coal such as Pittsburgh seam is very largely vitrain. With only a few percent of the constituents removed from the major component, vitrain, it was not feasible that there should be differences in organic structure between coal and vitrain spectra as great as 5-fold in the intensities of some absorption bands. It eventually became evident that the constituents which were changed many fold in the isolation of vitrain were the mineral components. On comparison of these anomalous absorption bands with the spectra of the few minerals available at that time, it was found that most of the bands were assignable to kaolinite.^{4/} Thus these informative comparisons of spectra represented a very useful combination of spectral and petrographic methods.

Our published investigations on this subject were limited to the 5,000 - 650 wavenumber region.^{5,6,7/} With the advent of instruments for adequate operation below 650 cm^{-1} in the infrared (R. C. Lord has named this region the "middle infrared") it became possible to extend the study of mineral absorption bands through the combination of spectral and petrographic techniques. By a comparison of Pittsburgh coal and vitrain spectra the following bands due to minerals, principally kaolinite, have been observed in the middle infrared: 698, 543, 471, and 420 cm^{-1} . The strongest of these bands are those at 543 and 471. Both bands are attributable to kaolinite. As discussed above some of the intensity differences are extremely large and cannot possibly be attributed to differences in organic structure. For example, the strong band at 543 wave numbers in the coal is 10 times as great as the corresponding absorption intensity in the vitrain spectrum. Such radical differences can only be attributed to mineral absorption. Intensities of these absorption bands can be accurately calculated and used for quantitative determinations of minerals present.

Graphite has been examined in this region of the spectrum. Though strong absorption for graphite was detected out to 290 wave numbers no discrete absorption bands were found. Additional runs out to 100 cm^{-1} have been made by Dr. William Fateley, Mellon Institute, and no specific absorption bands occur.

2. Rock Dust in Float Dust

Infrared spectrometry has recently been applied to analysis of rock dust in float dusts from return airways of coal mines. Sample collection for the purpose of analyzing by wet chemical methods is a difficult problem usually because a considerable amount of dust, about 100 mg, must be collected. This requires more time than desirable; the element of safety is therefore involved. With the use of infrared spectrometry in such a problem only very small samples need be collected. Two mg are ample and collection is rapid.

The dust samples collected in the mine, mixtures of coal and rock dust, are prepared for infrared investigation by mixing 1 part of dust with 100 parts of potassium bromide which is pelleted by a standard technique. The infrared spectrum of the pellet is obtained. Advantageous absorption band or bands are chosen for analytical work. For quantitative analysis it is necessary to check the linearity of the concentration versus spectral absorption by preparing standard samples at various concentrations and measuring their absorption intensities at the appropriate absorption bands. After the linearity of the calibration curve is established, then unknown samples can be prepared in KBr pellets and their spectra obtained. Intensity of absorption at appropriate bands may then be applied to the calibration curve and the concentration of the desired component in the dust is obtained.

The rock dusts dealt with in this investigation were either calcite (CaCO_3) or dolomite, $\text{CaMg}(\text{CO}_3)_2$; calibration curves were obtained for each of the rock dusts plus coal. Though the rocks involved are both carbonates their absorption spectra differ slightly. This is an advantage, as each may be determined in the presence of the other if necessary. Coal also has an absorption spectrum and accordingly the coal dust collected in the mine will produce interfering absorption which must be corrected for. This is most simply done by choosing the calibration band for the carbonates if possible in regions of broad, non-specific absorption of the coal. Then from the spectrum of the mixture of coal and rock dust the absorption band of the rock dust will be superimposed on the broad background of the coal absorption. By drawing a baseline across the base of the absorption band it is possible to correct out the non-specific coal absorption.^{5,6/} The intensity of the rock dust absorption then is measured from this base line to the peak of the absorption band. In this way calibration curves were obtained.

For both calcite and dolomite two absorption bands were obtained for possible analysis. All four bands provided acceptable results, about + 10 percent of the amount present, in the desired range of about 20 to 80 percent rock dust. Results indicate that there is no preference between the two absorption bands studied for each dust. One other carbonate band, at about 7.0 microns, is available for analysis. With its greater intensity this band would be useful for analysis of traces of rock dust in coal dust. In the present problem analysis of traces is not required so the less intense, sharp bands used are preferred. It should be mentioned that only three carbonate bands are available for analysis; as stated earlier, organic materials usually have many bands that can be used. If differentiation between carbonates is required, then two bands only are available, for the strongest band at 7.0 microns is essentially identical in various carbonates.^{2,3/}

ORGANIC APPLICATIONS

1. Attenuated Total Reflectance Spectra. Shock-Carbonized Coals; Sorbates on Coal

Recent investigations on attenuated total reflectance (ATR) of coal were carried out by Bent and Ladner.^{8/} Their results demonstrated the difficulties of utilizing this technique on coals. Very close optical contact is difficult to achieve with the surface plateaus produced by conventional grinding and polishing of coal. These authors demonstrated that the method was more applicable to the spectral investigation of chloroform extracts of shock-carbonized coals.

Volatile products from shock-carbonizing of coals can be condensed directly on the ATR optical element to produce good spectra. However, this technique might be somewhat misleading; on shock carbonizing, the more volatile products and therefore the lower molecular weight products, would be expected to reach the ATR prism first. Because of the slight optical penetration of the sample by the infrared beam in the ATR technique, it is probable that only these most volatile products would be observed in the spectrum. The method is therefore very good for the concentration of and study of the volatile portions of the coal.

Spectra of the volatile products from four shock-carbonized vitrains were investigated by Barnes Engineering Company with an ATR crystal of thallium-bromide-iodide which provides 20 reflections within the crystal. The vitrains were shock-carbonized at 900° C; the volatilized material was collected on the ATR crystal and spectra were determined. Appreciable differences in the spectra of the products from three coal vitrains were observed in comparison with the spectra of the original coal vitrains; greater fine structure and new bands were produced. The fourth sample, shock-carbonized Beulah lignite vitrain showed no spectral changes other than quantitative changes. The spectral changes for the three coal

vitrains are indicated in Table 1. The formation of two doublets is interesting. The doublet at 1625-1600 in the spectra of shock-carbonized products may signify that the 1610 cm^{-1} band in coal is actually attributable to two different chemical species, as suggested by Fujii.^{9/} The doublet at 1440-1400 cm^{-1} is surprising. The origin of these bands is not known; the high temperature used undoubtedly produced considerable reaction.

Table 1.- Infrared spectral differences between ATR spectra of three coal vitrains and the corresponding shock-carbonized products.

Vitrain, coal seam	Infrared frequency, cm^{-1}			
Pittsburgh (hvab)	1610	1450	-	-
Pittsburgh, shock-carbonized	1625-1595 ^{a/}	1440-1402 ^{a/}	1250	1093
Pocahontas (lvb)	1610	1450	-	-
Pocahontas, shock-carbonized	1627-1600 ^{a/}	1443-1400 ^{a/}	1250	1093
Dorrance anthracite	1610	1450	-	-
Dorrance, shock-carbonized	1625-1595 ^{a/}	1440-1398 ^{a/}	1250	1093

^{a/} Doublets

Interest in attenuated total reflectance at the Bureau of Mines has been principally directed towards the study of sorbates on coals. Good spectra can be obtained when good optical contact is achieved. The interaction between sorbate and the substrate coal can be followed nicely by placing upon the ATR prism a slurry of coal and sorbate. Then the spectrum is scanned repeatedly as the sorbate is allowed to evaporate. If the sorbate is of low volatility a heat lamp can be used to increase the volatility.

Significant spectral changes have been observed for pyridine on coal. (see below.) Whether or not changes in the spectrum of the coal have occurred has not been ascertained because of the broadness of the coal bands and the interference of the intense, sharp, pyridine bands. Observations have also been made on benzene-coal and methanol-coal systems. No significant spectral changes have been seen for either the sorbate or the coal. Spectra of these systems can also be obtained by ordinary transmission spectral methods, but the ATR method provides better spectra, particularly for the sorbate.

2. Charge-Transfer Complexes

Charge-transfer complexes represent one type of weak acid-base interactions. The complexes are formed between electron-rich (donor) molecules and electron-poor (acceptor) molecules.^{10/} Redistribution of electron charge occurs so that the properties of the two moieties are changed; however, definite chemical reaction does not occur and the original moieties are nearly always recoverable by simple processes such as dissolution, or distillation, plus some method of separation. One of the changes experienced by both donor and acceptor molecules in a complex is a change in bond lengths, which produces changes in the vibration spectra; thus infrared spectra can indicate the formation of such complexes.

Observations of the infrared spectra of coal-pyridine systems have led to the belief that charge-complex formation occurs between pyridine (donor) and coal (acceptor). Examination of the pyridine-coal system by the ATR method (described above) provided interesting spectral changes as pyridine is allowed to evaporate. The principal spectral characteristics of the coal-pyridine system are those of pyridine itself with a background due to the coal extract. As evaporation of the pyridine progresses a new band shoulder is formed at about 1000 cm^{-1} and the neighboring band of pyridine at 990 cm^{-1} begins to disappear. As evaporation continues the pyridine band continues to decrease and finally disappears; meanwhile the new coal-pyridine band continues to shift slightly. The final location of the band is 1020 cm^{-1} ; at this point all the remaining pyridine molecules are apparently complexed with the coal extract. The interactions involved in this process are of interest. The results apparently are indicative of the formation of a charge-transfer molecular complex, as pyridine does indeed behave in this manner in the formation of charge-transfer complexes with many electron acceptors.^{10/} We have demonstrated that these same spectral changes occur as phenol is added to pyridine. It is logical to believe that the complexing of coal and pyridine involves the phenolic structures in the coal.

References

1. Schaeffer, C., and F. Matossi. "Das Ultrarote Spectrum," Springer Co., Berlin, 1930.
2. Miller, F. A., and C. H. Wilkins. Infrared Spectra and Characteristic Frequencies of Inorganic Ions. Anal. Chem., v. 24, 1952, pp. 1253-1294.
3. Hunt, J. M., M. F. Wisherd, and L. C. Bonham. Infrared Absorption Spectra of Minerals and Other Inorganic Compounds. Anal. Chem., v. 22, 1950, pp. 1478-1497.
4. Friedel, R. A., and J. A. Queiser. Infrared Analysis of Bituminous Coals and Other Carbonaceous Materials. Anal. Chem., v. 28, 1956, pp. 22-30.
5. Friedel, R. A. Infrared Spectra of Thin Sections of Coal Vitrains. Brennstoff-Chemie, v. 44, 1963, pp. 23-24.
6. Friedel, R. A. Infrared in Coal Structure Research. Ch. in "Applied Infrared Spectroscopy," ed. D. N. Kendall, Reinhold Pub. Co., New York, pp. 312-343.
7. Friedel, R. A. The Use of Infrared Spectra of Chars in Coal Structure Research. Applied Optics, v. 2, No. 11, Nov. 1963, pp. 1109-1111.
8. Bent, R., and W. R. Ladner. A Preliminary Investigation into the Use of Attenuated Total Reflectance for Obtaining the Infra-red Spectra of Coals. Fuel, v. 44, 1965, pp. 243-248.
9. Fujii, Shuya. Infrared Spectra of Coal: The Absorption Band at 1600 cm^{-1} . Fuel, v. 42, 1963, pp. 17-23.
10. Andrews, L. J., and R. M. Keefer. Molecular Complexes in Organic Chemistry. Holden-Day, Inc., 1964, San Francisco, Calif., p. 36.