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Identification of Surface Functional Groups on Active Carbon by Infrared Internal Reflection Spectrophotometric

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PREVIOUS EFFORTS (*1-3*) to obtain infrared spectra for carbon black, activated carbon, and coal have involved transmission measurements on prepared KBr pellets or Nujol mulls. Although some information regarding structure of the bulk materials has been gained in this manner, such techniques have proved rather unsatisfactory for identification of the surfaces of carbon materials because of invariably poor resolution. Ergun (*4*) has shown that the extinction coefficient of graphite in the infrared spectral range is very high, approaching that of a metal. The average extinction coefficient, k, is about 0.66 in the visible region, and little variation is observed through the short wavelength region of the infrared (*4*). Common organic compounds or functional groups exhibit extinction coefficients approximately two orders of magnitude smaller than that of graphite, and therefore transmit sufficient radiation to give infrared spectra of reasonable contrast. From the present spectral studies of active carbon, it appears that the bulk extinction coefficient of this material is approximately that of graphite. On this basis it is reasonable to conclude that light cannot be transmitted through particles of carbon unless they are extremely thin, in fact, light of 5-μ wavelength will decay to 1% of its initial value after passing through 3.7 μ of graphite. Thus, infrared light incident upon most microcrystals of active carbon will be totally absorbed, unless it hits at a sufficiently grazing angle to allow the light to be reflected from the particle.

In view of the magnitude of the extinction coefficient for active carbon it would appear that the attempts reported in the literature to obtain transmission spectra of this material in KBr or Nujol have actually involved measurement of a complicated type of mixed transmission and reflection spectrum. This type of spectrum results from a combination of forward scattered radiation and radiation which misses the particles entirely, as illustrated in Figure 1, as well as radiation which
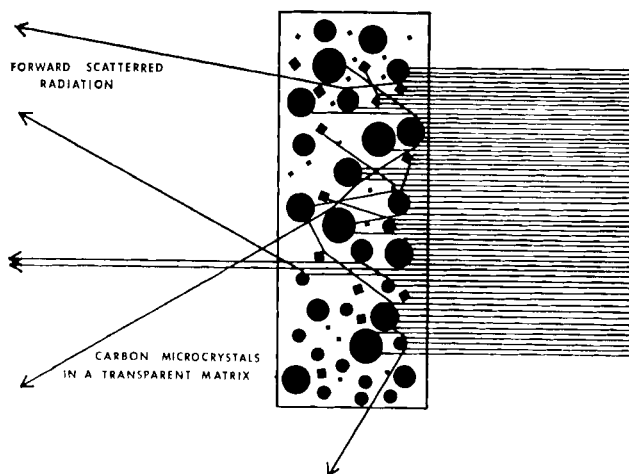

Figure 1. Schematic diagram of the forward scattering process obtained when strongly absorbing carbon particles are included in KBr or Nujol, and infrared light is transmitted through the matrix

passes through extremely small particles. The resulting spectrum might be best referred to as a "diffuse reflectance" spectrum. This approach to examining the surface of a material such as active carbon is complicated by the fact that light losses due to scattering are inversely proportional to the fourth power of the wavelength, producing huge scattering losses at shorter wavelengths.

Internal reflection spectrometric (IRS) (*5*) techniques allow all of the incident light to interact with the sample, without losses due to scattering (*6*). Thus it is possible to obtain spectra of high contrast and resolution with which to examine the nature of surface structures of active carbon. The general theory behind the use of IRS has been discussed by Harrick (*6, 7*). The present study has involved the use of IRS to

(1) V. A. Garten, D. E. Weiss, and J. B. Willis, *Aust. J. Chem.*, **10**, 295 (1957).
(2) J. K. Brown, *J. Chem. Soc. (London)*, **1955**, 744.
(3) R. A. Friedel and J. A. Queiser, ANAL. CHEM., **28**, 22 (1956).
(4) S. Ergun, in "Chemistry and Physics of Carbon," Vol. 3, Philip L. Walker, Ed., Marcel Dekker, Inc., New York, 1968, pp 45-119.

(5) J. Fahrenfort, *Spectrochim. Acta*, **17**, 698 (1961).
(6) N. J. Harrick and N. H. Riederman, *Spectrochim. Acta*, **21**, 2135 (1965).
(7) N. J. Harrick, "Internal Reflection Spectroscopy," Interscience, New York, 1967.
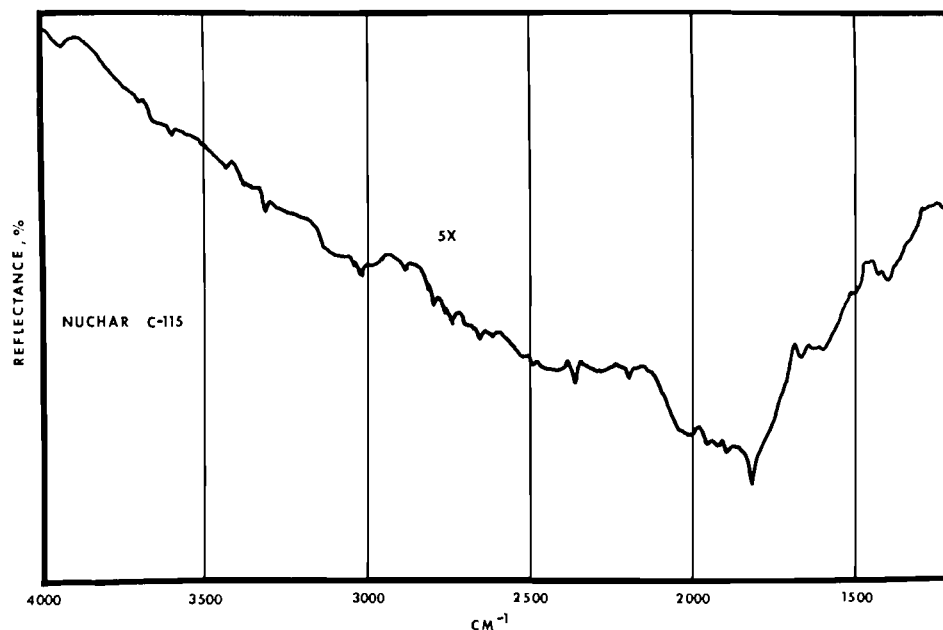
Figure 2. IRS spectrum of Nuchar C-115 (5× scale expansion)

measure spectra of active carbon, and in particular to obtain spectrometric evidence of the nature of functional groups on the active carbon surfaces. The experimental details necessary to obtain such information are presented here along with the results of some preliminary studies on the effects of adsorption of p-nitrophenol on the spectra of activated carbon.

EXPERIMENTAL

A Perkin-Elmer 621 infrared spectrophotometer is employed along with a Wilks Model 12 IRS attachment (Wilks Scientific Corp., South Norwalk, Conn.). It is necessary to purge the 621 for two to four hours with dry, CO_2-free air because it is difficult to ensure equal path lengths in both the reference and sample beams with the Wilks Model 12 in place. Atmospheric absorptions will otherwise interfere with the sample absorptions in the 20× scale expansion mode employed. The Wilks Model 12 attachment is used in the double beam mode with 45° germanium crystals 2 mm in thickness, 52.5 mm in length, which provide 25 reflections in each beam. Scrupulous attention must also be paid to the cleanliness of the surfaces of these crystals. They must be freshly polished and employed in no other application than that for which they are intended. *Germanium absorbs many organic compounds, forms a set of surface oxides, and is generally very susceptible to fouling.* While solid active carbon without any labile compounds associated does not pose a problem, absorbed organic molecules, such as the p-nitrophenol used in the preliminary studies reported herein, are readily transferred to the germanium surface in sufficient quantity to pose an interference at high levels of signal amplification. Polishing with jeweler's rouge between each run is the minimum cleaning required. Because germanium is relatively inert to organic solvents, as well as to mild acids and bases, chemical cleaning is preferable to that provided by mechanical abrasion alone. Spectrometrically pure graphite (from Ultra Carbon Corp., Bay City, Michigan) is used as the reference material. It is assumed that this material effectively cancels most absorptions due to the graphite-like bulk structure of active carbon. An overall advantage in using a graphite reference is that it nearly balances out the very high bulk extinction coefficient of the sample. The magnitude of the signal expected to result from absorption of light by a functional group on the carbon surface can be estimated as follows. The complex refractive index of an absorbing medium is given by

$$\hat{n} = n + ik$$

where k is the extinction coefficient and n is the observed refractive index (8). The energy lost to the absorbing medium in attenuated total internal reflection is given by

$$\int_0^\infty P_x dx = \int_0^\infty \frac{nk\langle E_x^2\rangle}{\lambda} dx = \frac{nk\langle E_0^2\rangle dp}{\lambda} \tag{1}$$

where P_x is the power absorbed per unit volume at a distance x into the medium, $\langle E_x^2\rangle$ the time average of the square of the amplitude of the electric vector at x, and dp is the depth of penetration (7, 9) into the absorbing medium. Calculation of dp according to Hansen (9), assuming that the carbon is covered with a 50 Å thick layer of organic molecules gives:

$$\frac{\text{Energy absorbed with organic layer}}{\text{Energy absorbed by pure graphite}}$$

$$= \frac{n_{org}k_{org}(50\text{ Å}) + n_{GR}k_{GR}dp}{n_{GR}k_{GR}dp}$$

$$\cong 1.0004 \tag{2}$$

After 25 reflections, the ratio is $(1.0004)^{25} \cong 1.01$. The change in reflectance is about 1%. For this reason, it is necessary to use the maximum scale expansion of the instrument (20×) in order to detect this small signal on top of the large bulk absorption. It is not possible to use a different IRS crystal material due to the high refractive index (2.2- of the carbon (4, 7, 10), as well as the desirability for obtain) ing spectra out to 10 μ.

The graphite reference had a 1-μ particle size, and the carbon samples were ground and passed through a 325-mesh screen. The carbon was washed with triply distilled water, and that portion which would decant off after a reasonable settling time was discarded. The range of particle sizes thus selected was about 10–40 μ. The particle size was dictated by experimental considerations; the surface coverage on the IRS crystal is determined by packing considerations, and it was necessary to analyze the solutions in the p-nitrophenol adsorption studies by colorimetric methods.

Because of some difference in the extinction coefficients

(8) J. A. Stratton, "Electromagnetic Theory," McGraw-Hill Book Co., New York, 1941, p 490.
(9) W. N. Hansen, *J. Opt. Soc. Amer.*, **58**, 380 (1968).
(10) Wilks Scientific Corporation, South Norwalk, Conn., "Internal Reflection Spectroscopy," Vol. 1, 1965.
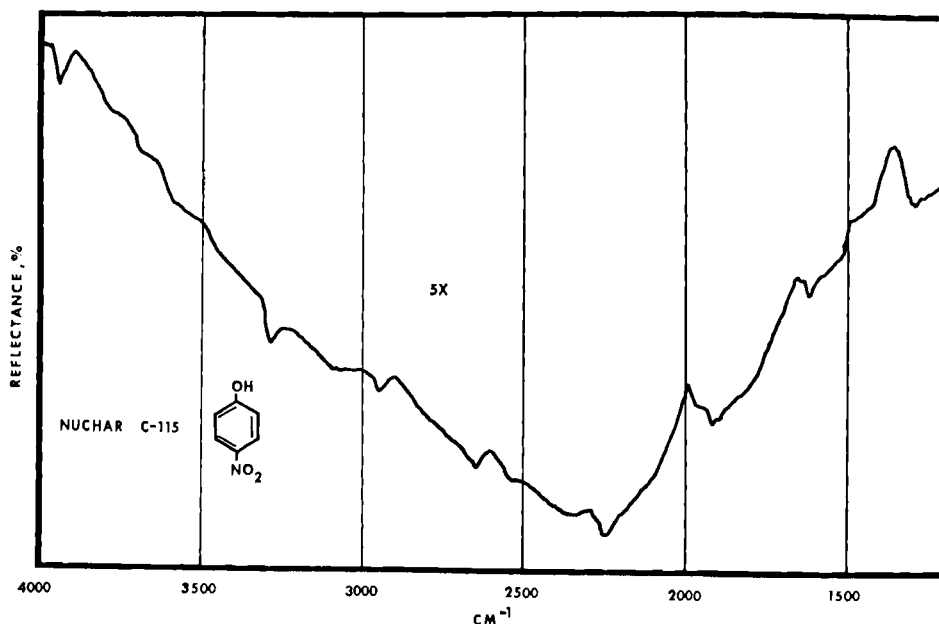
Figure 3. The IRS spectrum of Nuchar C-115 after adsorption of 1.6 mequiv p-nitrophenol from pH 2 solution (5 × scale expansion)

for graphite and active carbon, and because the evanescent wave (7) depth of penetration increases with wavelength, the spectra exhibit a well-defined sloping base line. The spectra reported here have been corrected for the base line.

RESULTS AND DISCUSSION

As an example, the results of a study on a sample of Nuchar C-115, a lignin based carbon obtained from West Virginia Pulp and Paper Co., are reported here. Spectra were obtained from: (*i*) the sized, washed, and dried (to constant weight at 200 °C) original material, (*ii*) a portion of (*i*) which was used for obtaining an adsorption isotherm of p-nitrophenol and subsequently dried at 200 °C, and (*iii*) a portion of (*i*) which was subjected only to the pH 2 solution of HCl used in (*ii*) to stabilize the neutral species of p-nitrophenol. The original sample was also subjected to elemental analysis (Spang Microanalytical Laboratory, Ann Arbor, Mich.) and found to contain 92.1% carbon, 1.3% hydrogen, 0% nitrogen, and 1.1% sulfur, with an ash content of 0%. The amount of oxygen present was determined in this laboratory by triton activation, giving 12.2% oxygen (*11*). (The higher value for the oxygen content is probably due to tightly bound H_2O_2.)

Figures 2 and 3 show 5× scale expansion spectra of both samples. Some of the absorption peaks observed in these spectra correspond to those observed in the diffuse reflectance spectra of Garten and Weiss (*1*), Brown (*2*), and Friedel and Quieser (*3*). Because internal reflection spectra, in the case of particulate matter significantly larger than the depth of penetration of the evanescent wave, are representative of surface structures, this supports the contention that the spectra obtained by previous workers are actually from diffuse reflectance, containing a large amount of forward scattered light, rather than transmission alone.

The absorption at 3300 cm⁻¹ can be seen in both samples (*i*) and (*ii*), and the size of the band in sample (*ii*) shows some increase over that in (*i*). These results support assignment of this

(11) J. S. Mattson and H. B. Mark, Jr., Department of Chemistry, University of Michigan, Ann Arbor, Mich., unpublished results, 1968.
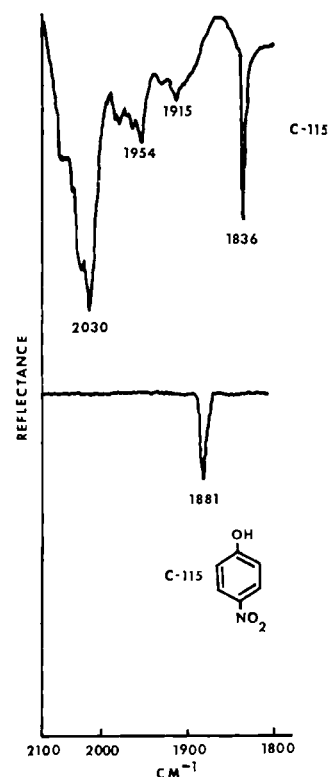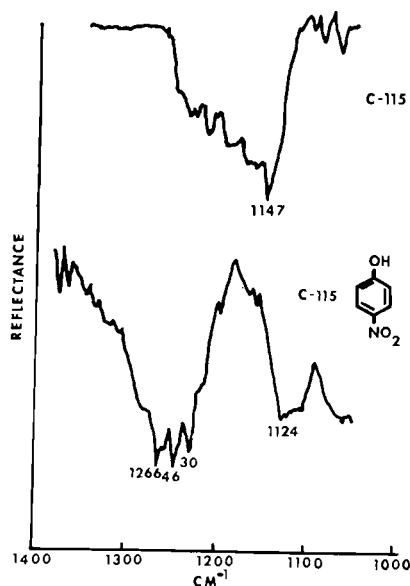
Figure 4. 2100-1800 cm⁻¹ region, top spectrum of Nuchar C-115 before treatment, bottom spectrum obtained after adsorption of p-nitrophenol (20 × scale expansion)

band to phenolic —OH, but upon thorough drying of sample (*ii*) (not shown), this band is observed to disappear. Although the latter fact suggests that the absorption is caused by tightly bound water, this would require the presence of some chemical mechanism which disposes of the —OH hydrogen on the p-nitrophenol upon adsorption. This phenomenon is presently under study.

Broad bands at 2050–1800 cm⁻¹ in Figure 2, 1250–1150 cm⁻¹ are not present after adsorption of p-nitrophenol, nor do they

Figure 5. **1400-1050 cm⁻¹ region, top spectrum of Nuchar C-115 before treatment, bottom spectrum obtained after adsorption of p-nitrophenol (20× scale expansion)**
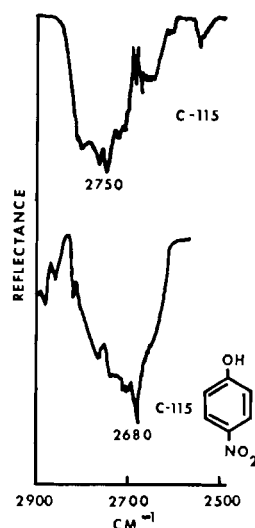

Figure 6. **2700 cm⁻¹ absorption band due to C—H in close proximity to carbonyl group; note band is not affected by adsorption of p-nitrophenol (20× scale expansion)**
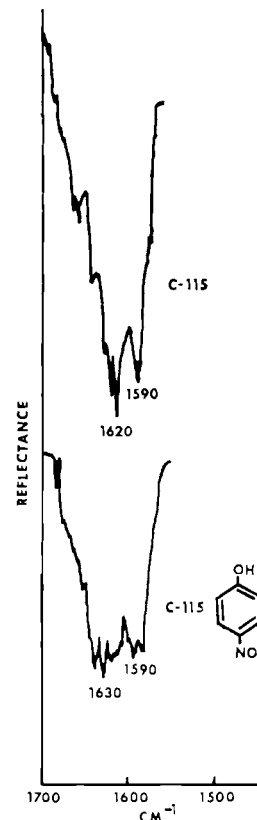

Figure 7. **1600 cm⁻¹ band due to vinyl-like C—C absorption; note that absorption band is unaffected by adsorption of p-nitrophenol (20× scale expansion)**

show up in the spectrum of the sample (*iii*) which was exposed only to the pH 2 HCl solution. The loss of the first band is shown in Figure 4, and of the latter in Figure 5. The appearance of the two bands together before exposure to acid, and their disappearance after adsorption suggest either an interaction with the acid or with the p-nitrophenol. Investigation of sample (*iii*) showed that the higher energy band was eliminated by acid treatment. Acid hydrolysis of a lactone group would produce the spectral change observed. The fate of the lower band escaped detection because of experimental difficulties. It is conceivable that the lower band represents the C—O—C of an ester, and the higher band the C=O of the same ester. The position of this carbonyl absorption is high (2030 cm⁻¹), and represents a 600-cal/mole shift over the energy of an ordinary lactone carbonyl group (1820 cm⁻¹).

Figure 6 shows the detail around 2700 cm⁻¹, attributable to a C—H bond shifted to lower energy than normal, quite probably as a result of its proximity to the carbonyl groups observed. This peak is unaffected by the adsorption of either acid or p-nitrophenol. Figure 7 shows the strong peak occurring at 1600 cm⁻¹. In previous investigations (*1*), this has been attributed to ring vibrations of the graphite-like bulk structure, but in light of what has been presented here, it is more likely that it represents a vinyl-like C=C functional group. The strong peak at 1836 cm⁻¹ in sample (*i*) is observed to shift to 1865 cm⁻¹ in (*iii*) (not shown), and to shift to 1881 cm⁻¹ in the p-nitrophenol isotherm sample (Figure 4). This band is attributed to another type of carbonyl C=O group, but the overall functional group cannot be readily identified because all of the C=O groups on the surface studied exhibit unusual vibrational energies. The three peaks observed in Figure 5 after adsorption are caused by ring vibrations in the p-nitrophenol, and the C—O of the phenolic O—H on the p-nitrophenol causes broadening of the 1250 cm⁻¹ peak in that group.

A detailed study of the spectra of a variety of different activated carbons and carbon blacks and the effects of various adsorbates on their surface structure is in progress. It is

hoped that these studies will indicate which (if any) functional groups are involved in chemisorption processes and will shed light on the nature of the bonding involved. Correlations of the surface composition of functional groups and effectiveness in adsorption processes with the preparation conditions are being studied. A subsequent paper will report the results of these studies in detail.

ACKNOWLEDGMENT

ERRATA

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The word Spectrophotometric was substituted for Spectrophotometry in the title. On p. 356, lines 15 and 18 under "EXPERIMENTAL," the words "absorbs" and "absorbed" were substituted for "adsorbs" and "adsorbed". On p. 357, line 16 under "Results and Discussion," "H_2O_2" was substituted for "H_2O."