

Visible and Near Infrared Absorption Coefficients of Kaolinite and Related Clays

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Abstract

Estimates of the optical absorption coefficients for kaolinite, halloysite, and dickite were made by application of diffuse reflectance spectroscopy in the spectral region from 0.4 to 2.4 μm . Values on the order of 10 cm^{-1} were obtained in the 1.4 and 2.2 μm bands. A very weak band at 0.95 μm was found, with an absorption coefficient less than 1 cm^{-1} , due to higher order overtones of the fundamental vibration modes. A semiquantitative comparison between the values of the absorption coefficients in the 1.4 μm band and the 2.7 μm band in these clays is presented, based on KBr pellet spectra. This comparison indicates that the absorption coefficient may reach 10^2 or 10^3 cm^{-1} in the 2.7 μm region.

Introduction

The kaolinite clays are common soil minerals which often occur in atmospheric dust. Infrared analysis of dust samples by Hoidale and Blanco (1969), and by Sakabe *et al* (1965), indicate that kaolinite type clays may make up a significant fraction of the mineral content of the atmospheric aerosol. Because of this laboratory's interest in the effect of the atmospheric aerosol on the propagation of light, it is necessary to know the absorption coefficient of such minerals. Clay minerals, by their very nature, are always composed of aggregates of fine particles, a situation which makes conventional transmission spectroscopy and application of the Bouguer-Lambert law difficult, because of the intense scattering of light in the sample. For this reason only qualitative information about the absorption spectra of such minerals is available (Hunt and Salisbury, 1970; Lindberg and Snyder, 1972). Although such spectra are very useful in studies of the structure of minerals, more quantitative absorption information is needed to assess the effect of clay particles on the propagation of light. This work is intended to provide a quantitative estimate of the absorption coefficient of kaolinite clays by application of a method based on the Kubelka-Munk theory of diffuse reflectance.

Measurement Method

The method used was recently developed by Lindberg and Snyder (1973). A thin (50-100 μm)

layer of powdered clay is collected on a membrane filter, and the diffuse reflectance of the clay-filter combination is measured with both a white and a black background. The reflectance of the clean filter on both backgrounds is measured in advance. From these four reflectance measurements, and the thickness of the sample layer measured with a micrometer microscope, the Kubelka-Munk absorption coefficient is calculated. Details of this calculation are given in the reference above.

Clay samples were ground in a mortar and pestle, and sieved through a 200 mesh screen (hole size 74 μm) into a chamber from which a vacuum pump was pulling air. The layer of clay was collected on a 10-micrometer pore size teflon membrane filter at the input to the vacuum pump.

The Kubelka-Munk absorption coefficient is defined as the fraction of incident light absorbed per unit path length in an infinitesimally thin layer of the sample. Since it is a property of the bulk powder, it is not precisely equivalent to the more familiar Bouguer-Lambert law absorption coefficient, but it is closely related to it. Discussions of this point are available in Kortum (1969), Mudgett and Richards (1971), and Brinkworth (1972).

As an illustrative example of the relationship between the absorption coefficient determined by the reflectance method used here and that determined by direct transmission spectroscopy, both were applied to a sample of pyrope-almandine garnet, a material available in optically clean monocrystals.

Two thin wafers with different thickness were cut and polished from such a crystal. By placing the thinner one in the reference beam of a Beckman DK-2A spectrophotometer, and the thicker one in the sample beam, one can obtain the absorption coefficient k from the expression

$$k = \frac{A}{d \text{ Log } e}$$

where A is the absorbance reading, and d is the difference in thickness of the two garnet wafers. The Kubelka-Munk absorption coefficient for a finely ground powder of this same garnet was determined by the reflectance method described above. Both of these absorption coefficients are shown in Figure 1.

These two absorption coefficients are in reasonable agreement. For wavelengths shorter than about 0.4 micrometers, the diffuse transmittance of the membrane filter used here becomes too low, and the reflectance measurement technique is not satisfactory. The Kubelka-Munk theory assumes that the filter and dust layer scatter light isotropically, a condition only approximately met in practice. The degree of deviation from isotropic scattering is not large for the sample or the filter, but it is probably somewhat wavelength dependent, which is why the agreement is better at some wavelengths than others. However, Figure 1 shows that the reflectance method does give a reasonable estimate of the optical absorption coefficient of the powdered material.

All the reflectance measurements were made on a Cary Model 14 spectrophotometer equipped with an accessory 25 cm integrating sphere, as described by Hedelman and Mitchell (1968). The reference standard used was highly refined BaSO_4 . Its reflectance values were obtained from Grum and Luckey (1968).

In the Cary 14 spectrophotometer, the slit width varies with wavelength in a manner depending on the spectral character of the source lamp, characteristics of the detector, and efficiency of the integrating sphere. The resulting monochromator-spectral bandwidth variations are from 10^{-3} micrometers in the visible to 9×10^{-3} micrometers at the long wavelength end of the spectral interval. Comments on resulting resolution will be made later in the paper.

Results and Discussion

The four samples of kaolin clays investigated in this report were obtained from Ward's Natural

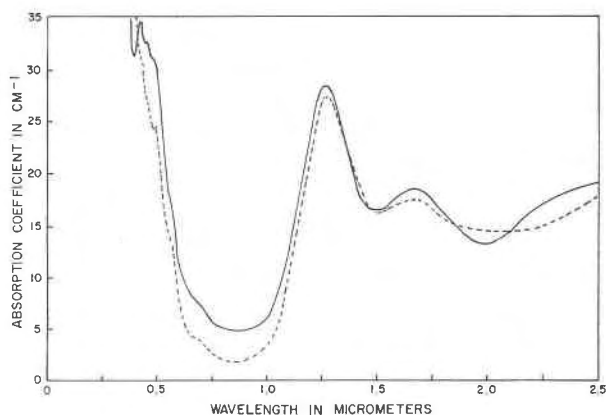


FIG. 1. Absorption coefficient for a sample of pyrope-almandine garnet, determined by transmission spectroscopy of polished monocrystal plates (solid line), and by the diffuse reflectance method used in this report, applied to the same crystal after it was ground to a fine powder (dotted line).

Science Establishment. The supplier states that they were collected in 1955 by Dr. Ralph J. Holmes, of Columbia University, from sites as close as possible to those of the samples used in the American Petroleum Institute (API) study of reference clay minerals (Adler *et al.*, 1950), and that they have been checked against the original API reference specimen by X-ray diffraction and differential thermal analysis. The four samples were kaolinite #9, kaolinite #17, halloysite #13, and dickite #16. In this laboratory the identities were checked by both X-ray diffraction and infrared potassium bromide pellet spectroscopy. One sample, labeled dickite #17, was found to resemble kaolinite more than dickite. Adler *et al.* (1950) state that differential thermal analysis showed the original API sample of "dickite #17" to be kaolinite. The new infrared spectra reported here are also consistent with this result, so in this report the "dickite #17" sample is referred to as kaolinite #17.

For each of these samples, the Kubelka-Munk absorption coefficient is shown for wavelengths from 0.4 to about 2.4 micrometers (Fig. 2-5). Absorption bands are shown, corresponding to the overtones and combination tones of fundamental vibrational modes, which cause the reflectance minima seen in the diffuse reflectance spectra reported by earlier workers (Hunt and Salisbury (1970), Lindberg and Snyder (1972)). The absorption coefficient varies from a fraction of one cm^{-1} to 10 or 15 cm^{-1} in wavelength regions cor-

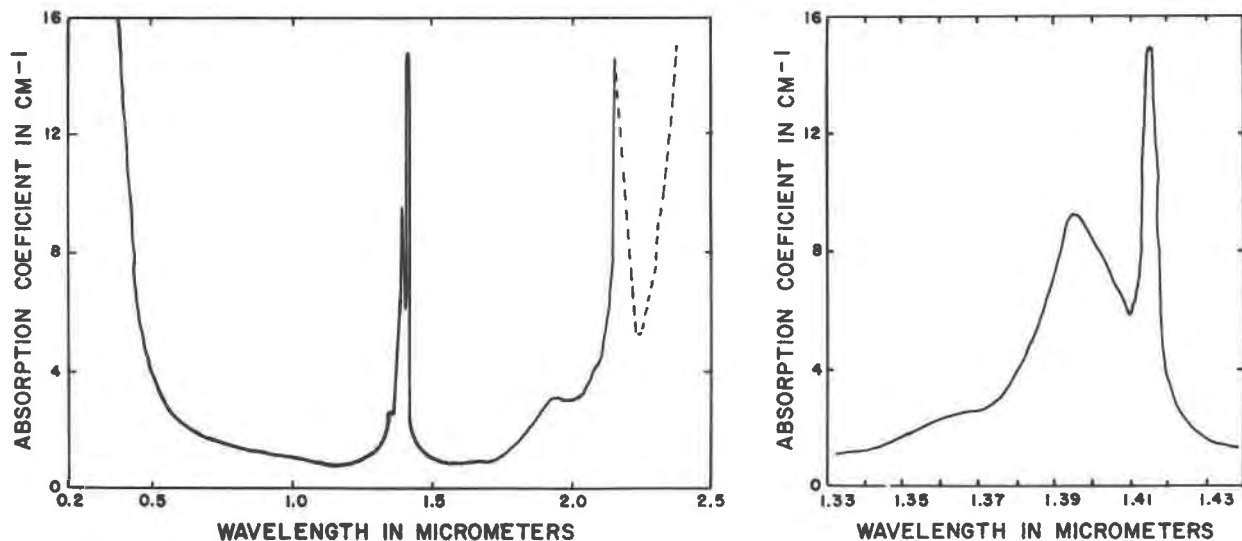


FIG. 2. Absorption coefficient of kaolinite #9 from Mesa Alta, New Mexico, as determined from diffuse reflectance measurements on a powdered sample.

responding to absorption bands of water. Because of low signal-to-noise ratio, the bands at 2.2 micrometers may not be completely resolved, which is why the data are presented as a dotted line in this region.

The 1.4 band shows considerable structure in all of these samples. For clarity this region is presented with an expanded abscissa in each figure. The detail in this region is sufficient to see differences between the three types of kaolin clays. Wavelengths of significant absorption maxima are

listed in Table 1. Note that the spectra for kaolinite #9 and kaolinite #17 are very similar.

The spectral bandwidth of the spectrophotometer in this wavelength interval was 0.0065 micrometers. This appeared to be sufficiently narrow to resolve all the features shown with the exception of the sharp line near 1.415 micrometers. In the case of the two kaolinite samples, this line's intensity was slightly dependent on instrument slit width, and therefore may not be completely resolved.

At 1.9 micrometers all the samples showed a

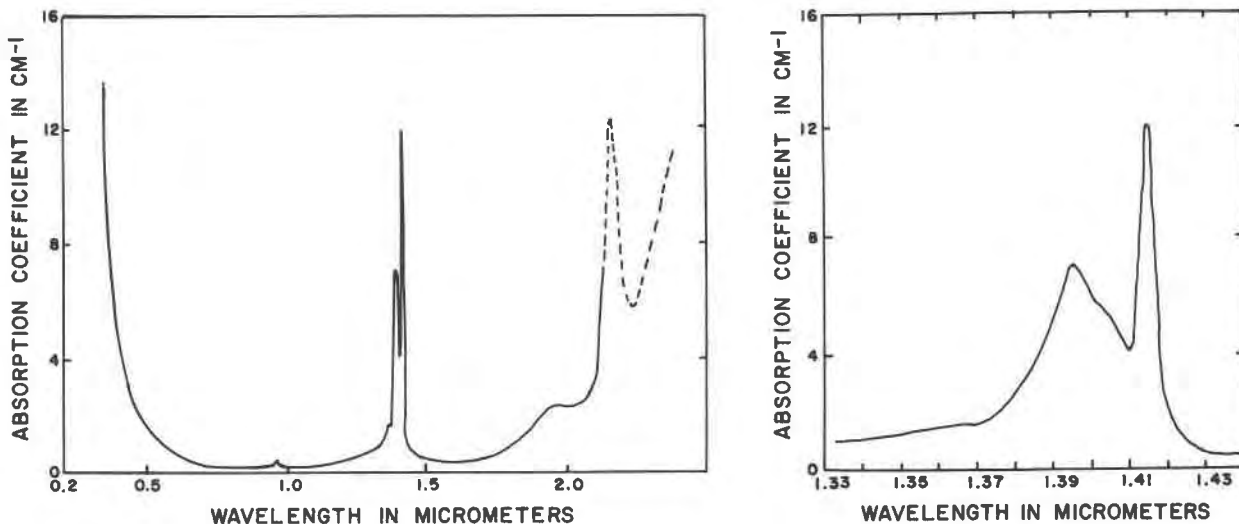


FIG. 3. Absorption coefficient of kaolinite #17 from Lewistown, Montana, as determined from diffuse reflectance measurements on a powdered sample.

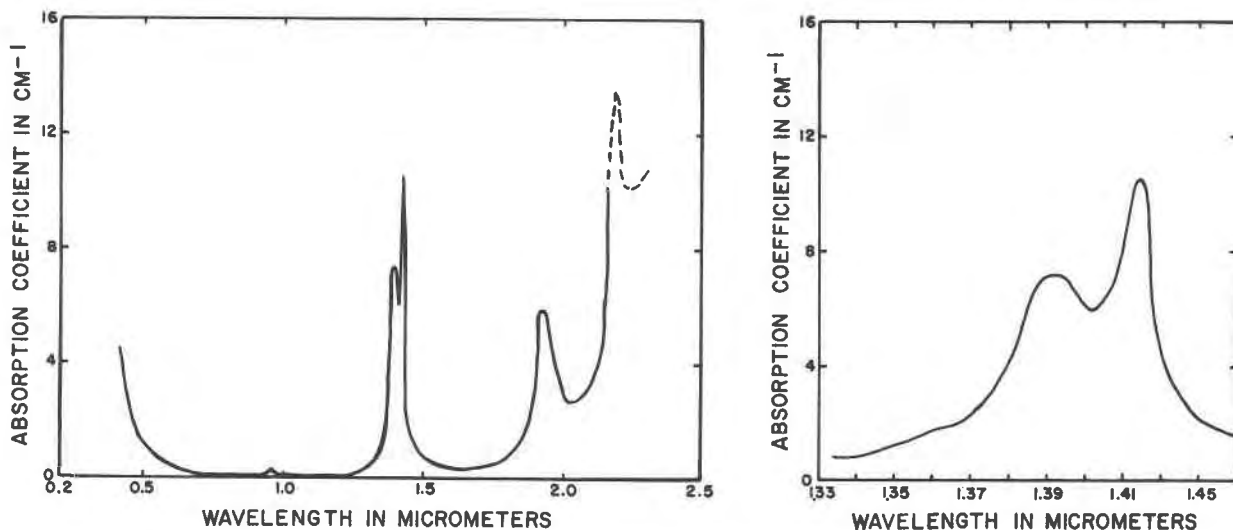


FIG. 4. Absorption coefficient for a sample of halloysite #13 from Eureka, Utah, as determined from diffuse reflectance measurements.

slight absorption due to the presence of molecular water. This was significantly greater in the halloysite #13 spectra.

At 0.95 micrometers all the samples showed a very weak absorption band. The contribution to the absorption coefficient due to this band is on the order of a few tenths cm^{-1} , and therefore does not show well in Figures 2-5. This band was examined in detail by conventional diffuse reflectance spectroscopy, and spectral structure was seen that looked qualitatively similar to that seen in the 1.4 band of the corresponding minerals. Like the 1.4 band, the 0.95 band is thought to arise from overtones and combination tones of the fundamental

O-H stretching vibrations, these wavelengths being included in Table 1 for each of the four samples.

Visual comparison of the bulk samples of these four kaolin clay minerals permits qualitative comparisons concerning their colors. Halloysite #13 appears practically white; dickite #16 is nearly white, but perceptibly less so than halloysite #13; kaolinite #17 appears "darker"; and kaolinite #9 is the "darkest" of all, having what would be called a very pale yellow color. These qualitative observations are consistent with the absorption coefficient data presented in Figures 2-5. The material with the lowest absorption coefficient will have the brighter appearance. The pale yellow color of the

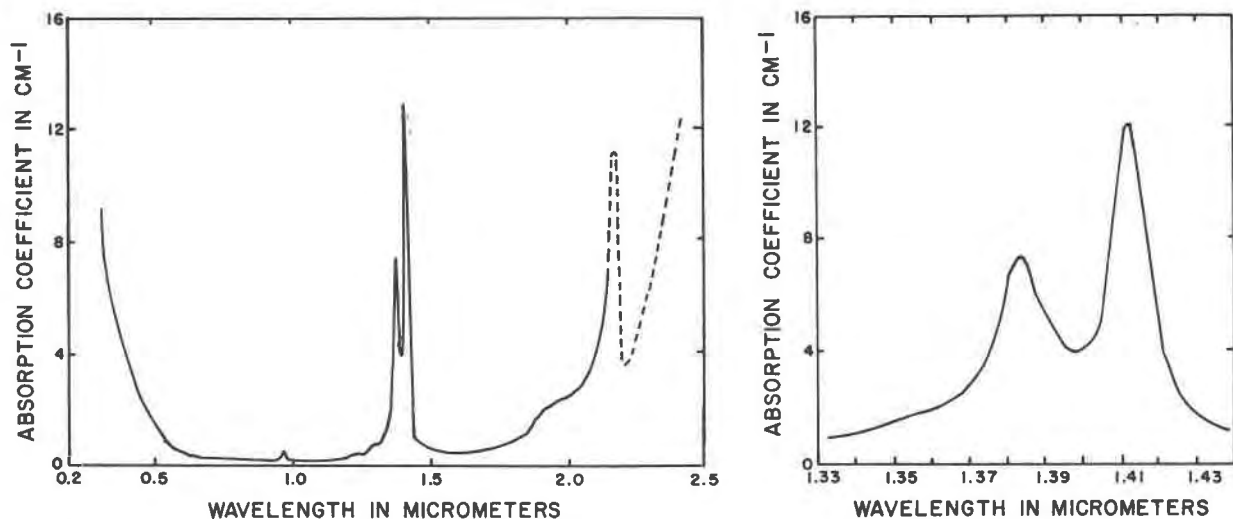


FIG. 5. Absorption coefficient of a sample of dickite #16 from St. George, Utah, as determined from diffuse reflectance measurements

TABLE 1. Wavelengths of Absorption Coefficient Maxima for the 0.95 and 1.40 μm Bands in Kaolin Clays*

Kaolinite #9	Kaolinite #17	Halloysite #13	Dickite #16
—	0.915	0.915	0.915
0.954	0.955	0.950	0.946
0.967	0.967	0.966	0.966
1.360	1.360	1.358	1.355
1.396	1.395	1.390	1.384
1.415	1.415	1.413	1.413

*In each of the two bands of wavelengths, in μm , shown above, the long wavelength line was the strongest and sharpest of the three. The shortest wavelength line was extremely weak and wider. The intermediate wavelength line was intermediate in intensity as well.

These wavelengths were obtained from measurements of the diffuse reflectance of powdered samples of each clay.

kaolinite samples arises because absorption is significantly greater in the shorter wavelength part of the visible spectrum.

The potassium bromide (KBr) pellet spectra reported by Adler *et al* (1950) and Wolff (1963) show that kaolin clays have strong absorption bands in the 2.7 μm spectral region. The technique used for measuring absorption coefficient in this report was not applicable beyond about 2.4 μm because of limitations in the spectrophotometer. The KBr technique does not permit a quantitative calculation of absorption coefficient, since total extinction (the sum of scattering and absorption) is all that is really measured. However, it is possible to compare band strengths in a KBr pellet, if the bands are not too far apart in wavelength. Therefore it was decided to use the pellet technique to examine these clay minerals in the region from about 0.5 to 3.5 μm , and to attempt a semiquantitative estimate of the strength of the 2.7 band by comparison to the bands at shorter wavelengths.

The use of KBr pellets is usually confined to wavelengths longer than about 2.5 μm , because scattering effects predominate at shorter wavelengths. One uses about 1 mg of sample in a 200 mg KBr pellet to obtain a useful infrared spectra. Such a spectra will show the 2.7 μm bands in kaolin clays very well, if properly prepared, but will not show the much weaker overtone bands at shorter wavelengths. Therefore it is necessary to use pellets containing much more of the clay sample to bring out these shorter wavelength features. This is very difficult but can be done, especially if thicker KBr pellets are used. Figure 6 shows spectra of three pellets containing halloysite #13. Curve A is for a pellet containing 1 mg of sample and 600 mg of KBr so as to yield a good spectrum in the 2.5

to 40 μm region, where this technique is normally used. Curve B is for a similar pellet with 5 mg of sample, and Curve C represents the effect of 30 mg of the same clay.

Figure 4 shows that the maximum absorption coefficient in the 1.4 μm band of halloysite is on the order of 10 cm^{-1} . Examination of Figure 6 shows that the 1.4 μm band in the 30 mg sample does not show up nearly as strongly as the 2.7 μm band in the 1 mg sample. It therefore seems reasonable to infer that the maximum absorption coefficient for this clay sample in the 2.7 μm spectral region may be as much as two orders of magnitude higher than at 1.4 μm —that is, on the order of 10^2 or 10^3 cm^{-1} . This is what one would expect, since the 2.7 band arises from fundamental O-H vibrations. A similar result was obtained for the other three kaolin clays.

Concluding Remarks

Estimates of the Kubelka-Munk absorption coefficient, a quantity closely related to the Bouguer-Lambert absorption coefficient, for several kaolin clays in the visible and near-infrared spectral region indicate that the absorption coefficient of these clays in atmospheric dust can be very low, on the order of 1 cm^{-1} in regions where absorption bands do not occur. But at 1.4 and 2.2 micrometers, the absorption is on the order of 10 cm^{-1} . In the near ultraviolet it rises rapidly with decreasing wavelength to values in excess of 10 cm^{-1} . At 2.7 μm

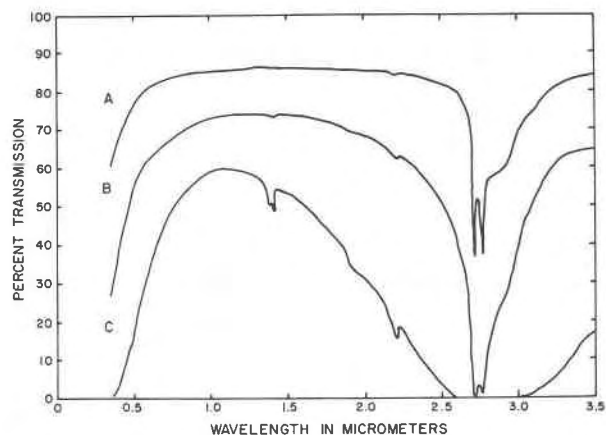


FIG. 6. Transmission spectra of pressed pellets consisting of 600 mg of KBr and 1 mg (curve A), 5 mg (curve B), and 30 mg (curve C) samples of halloysite #13. The transmission was measured with a 600 mg pure KBr pellet in the reference beam of the spectrophotometer.

the absorption coefficient may reach values on the order of 10^3 cm^{-1} . The 1.9 band, due to the H-O-H bending mode of molecular water, is variable in these clays, changing in intensity from about 1 to 10 cm^{-1} or more, depending on the hydration state of the sample, as one would expect.

Acknowledgment

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