

INFRARED ANALYSIS OF CLAYS AND RELATED MINERALS

BY PAUL G. NAHIN*

Introduction. The identification of clay minerals either in pure form or admixture with other minerals is not always easy. In some few instances it is sufficient to use only one of the many methods now available. Usually, however, the composition of the mineral sample is complex and requires the use of two or more supplementary analytical techniques for establishing the nature of the minerals and their relative amounts. The petrographic microscope, chemical analysis, dye adsorption, determination of cation-exchange capacity, differential thermal analysis, X-ray diffraction, and the electron microscope provide us with a battery of tools which, employed as a team, is adequate for the solution of most problems of mineral analysis. Recently, a promising new method of analysis has been developed (Hunt 1950; Keller and Pickett 1949, 1950; Nahin et al. (1951) based on the absorption of infrared radiation by minerals. The purpose of the following discussion is to survey the available information in this field, to make some brief correlations among the spectra, and to outline a few problems which, if clarified, might increase the value of the method.

The infrared spectrum comprises the portion of the electromagnetic spectrum lying between the long-wavelength edge of the visible and the short end of the radio-microwave spectrum. Roughly, the infrared region is sometimes divided into two sections: the near-infrared from 0.75 to 25 microns and the far-infrared from 25 to 1000 microns. The spectra obtained in the near-infrared arise from the resonance absorption of monochromatic radiations of wavelengths corresponding exactly to those vibrational frequencies of specific atoms or groups of atoms involved in a change of dipole moment of the molecule. Absorption of radiation in the far-infrared reflects the presence of complex molecular rotational or massive lattice vibrational energy levels, for which no data are available for mineral systems. The region of the infrared spectrum which has proved, thus far, to be of greatest interest for most types of molecules including minerals lies in the fundamental vibrational region from 2 to 16 microns. For detailed discussions of the origin of spectra the reader is referred to text books on spectroscopy (Barnes et al. 1944; Harrison et al. 1948; Mellon 1950).

Most infrared spectra being reported in the literature are now obtained with commercially available instruments having resolving powers of the order of a few hundredths of a micron at all wavelengths. The essential elements of all these instruments, in one or another arrangement, are shown schematically in figure 1 for a single beam. The radiation from an infrared glower is focused on the sample; the transmitted portion of the beam is collimated and monochromatized by a prism and mirror optics and measured by a thermal detector. A light chopper, CH, with a frequency usually of 10 cycles per second is included to minimize the effect of false radiation within the instrument. The spectrum is constructed either manually or automatically from determination of the ratios of the transmitted to incident intensities as a function of the wavelength.

* Research Division, Brea Research Center, Union Oil Company of California, Brea, California.

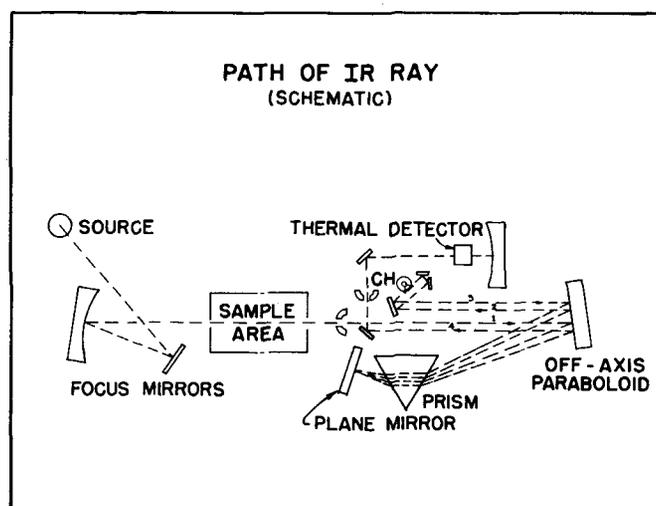


FIGURE 1.

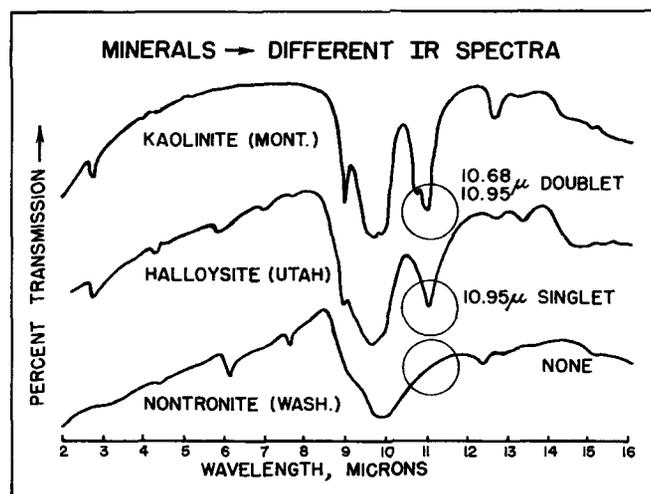


FIGURE 2.

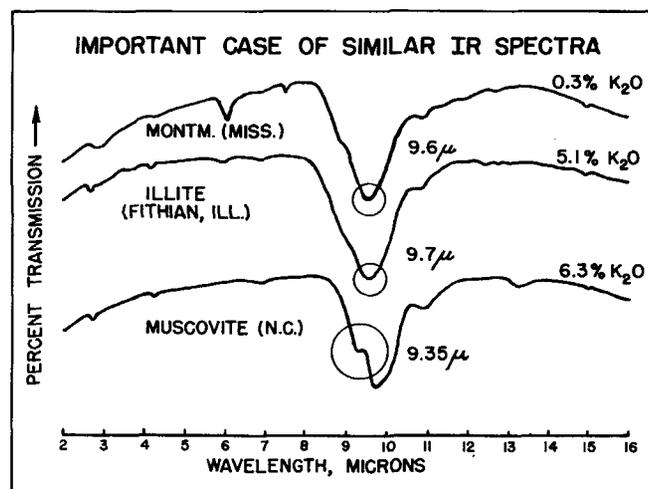


FIGURE 3.

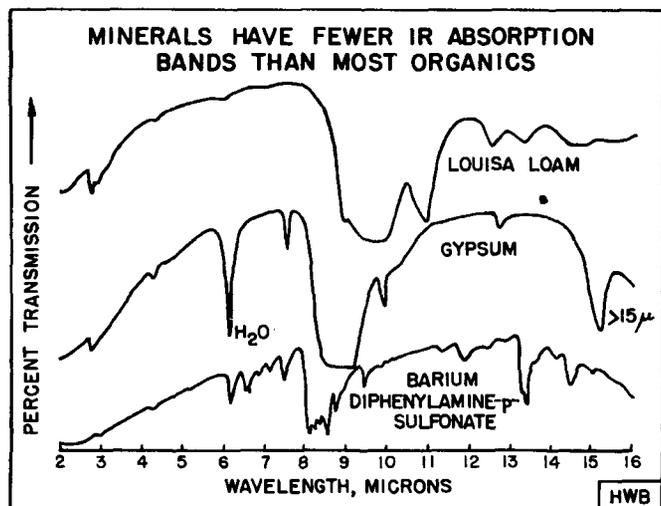


FIGURE 4.

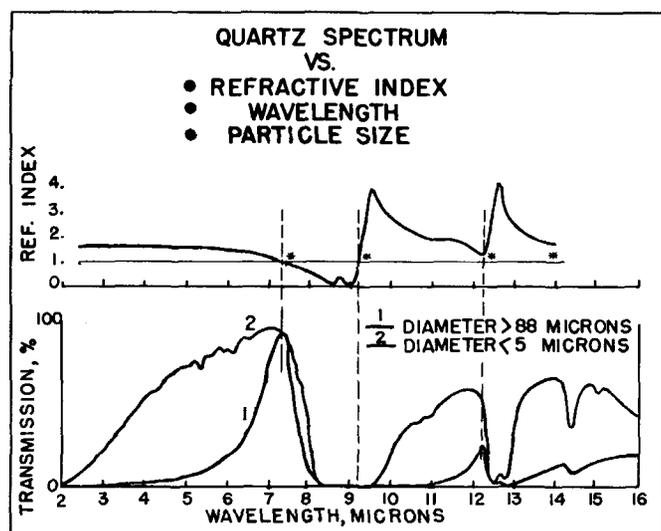


FIGURE 5.

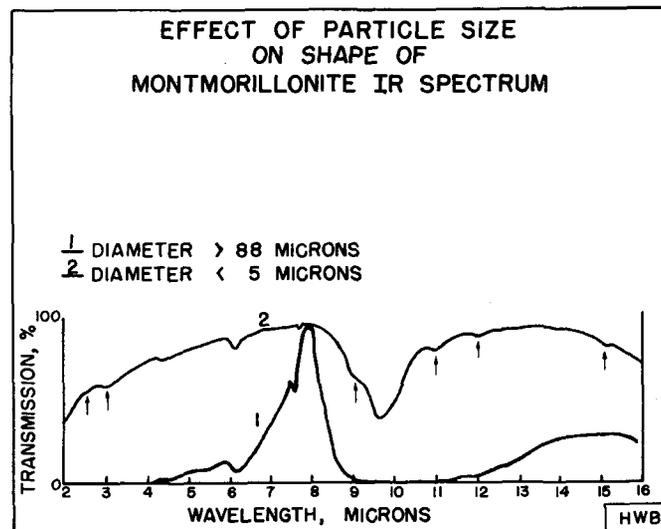


FIGURE 6.

Gross Features of Mineral Spectra. As is true for other classes of compounds, the infrared spectrum is a "molecular fingerprint" and can be used to differentiate the various minerals including the clays. An example of this specificity is shown in figure 2. Here, there is no difficulty in noting that the spectra of the two-layer minerals kaolinite and halloysite and the three-layer mineral nontronite are obviously different as emphasized by the indicated absorptions in the 10 to 11 micron region. This example is one of many which establish the basis for infrared spectroscopy as a clay identification method: *different minerals produce different infrared absorption spectra.* However, not all combinations of clay mineral spectra are as obviously unique as that of figure 2. An important array of similar spectra is shown in figure 3. Here, montmorillonite, illite, and muscovite are compared in the 9 to 10 micron region. All three appear generally similar visually except that muscovite has a pronounced absorption at 9.35 microns. Usually, montmorillonite and illite are difficult to distinguish, although it has been stated (Hunt et al. 1950) this may be done on the basis of the peak position of the strongest band, 9.6 microns in montmorillonite and 9.7 microns in illite. The potassia contents are included in figure 3 to underscore the value of supplementary data for clay identifications.

Another characteristic of mineral spectra is that generally they have fewer infrared absorption bands than have most organic compounds. This is shown in figure 4 for the cases of a loam, an inorganic compound and an organic salt. Many organic compounds do not absorb strongly (Hunt and Turner 1953) beyond 15 microns as do some of the feldspars, barite, ilmenite, and other minerals (Hunt et al. 1950).

In addition to the various instrumental performance factors, the shape of the spectral curve is intimately associated with the refractive index and particle size of the sample. Since the dispersion curve of quartz for the ordinary ray from 1 micron to 14 microns is known (Henry, 1948) it is possible to exhibit this dependence (fig. 5), using the particle size data of Hunt, Wisherd and Bonham (1950). Figure 5 shows that the transmission is greatest at wavelengths corresponding to refractive indices near unity except at about 9.2 microns where the absorption can be ascribed to an assigned (Plyler, 1929) fundamental mode of vibration. The effect of reducing the particle size to below 5 microns can be seen in the increased transmission and degree of resolution attained throughout most of the spectrum. Experience has shown that the best spectra are obtained with samples having a narrow particle size distribution (Lecomte, 1951; Nahin et al., 1951) with maximum particle diameter not greater than, and preferably less than, the shortest wavelength used. Figure 6 provides verification of the particle size requirement for montmorillonite. The arrows indicate significant absorptions either absent or almost indiscernible in the coarse powder spectrum.

Preparation of Samples. As is clear from the preceding discussion, satisfaction of the particle size requirement is crucial for obtaining definitive spectra of minerals. In some of the earlier work on infrared spectra of minerals the sample was triturated in refined mineral oil (nujol), spread on a salt plate and inserted in the

sample cell of the spectrometer. Even with suspension in the nujol of properly sized particles, the technique is unsatisfactory both from the standpoint of stability of the suspension and from the necessity for subtracting its absorption spectrum to obtain the mineral spectrum. The techniques used by Hunt and his associates at Carter Oil Company and those employed by Union Oil Company are representative of present practice and are here described briefly.

In the Carter method (Hunt and Turner, 1953) a 5- to 10-gram sample is ground to smaller than 250 mesh and jet-pulverized in a "Micronizer" to a particle size less than 5 microns. Approximately 10 to 20 milligrams of the powder is placed on a sodium chloride window, made into a paste with a few drops of isopropyl alcohol, smoothed with a microscope slide and dried in air. After obtaining the spectrogram, the film weight and other data descriptive of sample thickness and extent of coverage are determined.

The Union method (Nahin et al., 1951) differs somewhat from the Carter method. The clay sample, suspended in distilled water, is fractionated with a Sharples supercentrifuge to yield a colloid fraction of particle size in the range of 0.1 to 1.0 micron diameter as checked by electron micrographs. The fine fraction is suspended in 0.001N aqueous ammonia, deposited drop by drop on a single crystal silver chloride (Harshaw Chemical Co.) cell window to cover completely the area traversed by the beam. The cell window and suspension are dried in a vacuum oven at 50°C and scanned in a Beckman IR-2T infrared spectrophotometer. The sample weight is determined by calibration of the dilute clay suspension and by weighing of the dried film.

Recently, the two new techniques of lamination and impregnation for the mounting of solid samples have been described (Sands and Turner, 1952). Although they have not yet been applied to minerals, the authors recommend these methods as potentially valuable for the study of inorganic and non-plastic materials. In the lamination technique the sample pellet is placed between two sheets of mica or silver chloride. The laminate is inserted between two stainless steel aluminum or chromium foil protected platens in a hydraulic press, heated to plastic temperature and sheeted out under pressure to a total thickness of about 0.004 inch. The impregnation technique is used when lamination is not feasible. The sample pellet is placed on a polyethylene sheet, pressed between foil protected platens, rolled into a ball, and sheeted out on the press; the process is repeated until homogeneity is attained.

Discussion of Particular Absorption Bands. A sufficiently large number of infrared spectra of solids is now available so that by a process of elimination certain recurring frequencies within series of reasonably homologous minerals can be inferred to represent particular atomic groupings. In this sense, the absorptions in the ranges of 2.7 to 3.2 microns, 6.0 to 6.2 microns (and sometimes the weak absorption at about 7.55 microns (Hunt et al., 1950)) are assigned to hydroxyl and hydrate water respectively. A careful study (Buswell, Krebs, and Rodebush, 1937; Buswell and Dudenbostel, 1941) of the dehydration behavior of a series of montmorillonite salts demonstrated that the characteristic absorp-

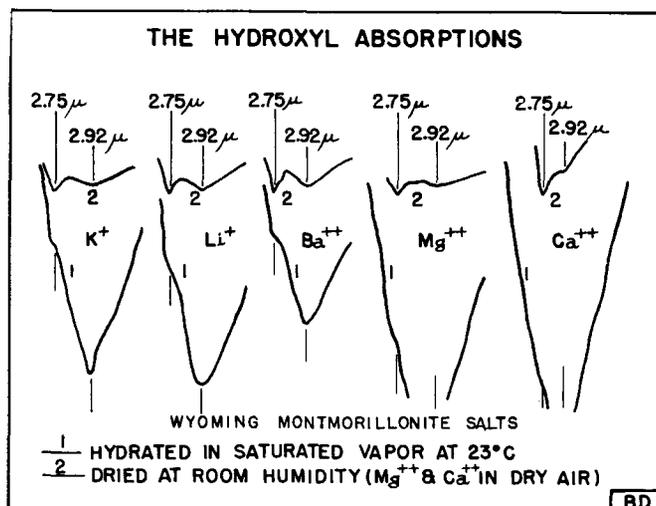


FIGURE 7.

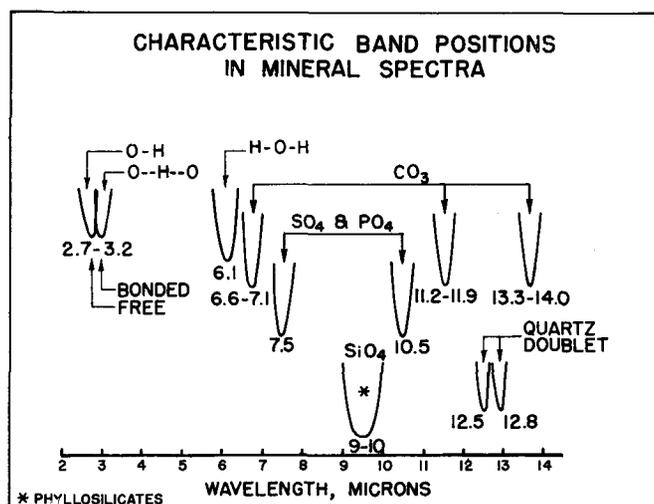


FIGURE 8.

tion at 2.75 microns represents the presence of essential or lattice hydroxyl of structure sometimes called "unbonded" or free hydroxyl because of its crystallographic similarity to the hydroxyl of the strong alkali metal bases (Wells, 1945). The absorption at 2.92 microns is ascribed to hydrogen bonded hydroxyl, perhaps mainly hydroxyl of the clay surface. Figure 7 illustrates the relationship between these absorptions and the hydration states of some montmorillonite salts. The curves for the sodium, ammonium and hydrogen analogues are also consistent with this assignment. The hydration water assignment is made from the infrared spectrum of water as well as by direct correlation with the spectra of the hydrated and dehydrated forms of simple inorganic crystals.

Keller, Spotts and Biggs (1952) have just published a thorough study of silicate spectra. Their work indicates that the phyllosilicates or sheet-silicates, of which the clays are representatives, are characterized by one main absorption band centered between 9.0 and 10.0 microns. This position is assigned to the SiO_4 group. Quartz has a well defined spectrum with major absorptions at 8.6

and 9.20 microns and a diagnostically useful doublet at 12.50 and 12.84 microns. These positions, together with the principal absorptions for carbonates, sulfates and phosphates, are shown in figure 8. For the carbonates it has been demonstrated (Hunt and Turner, 1953) that the 11.2 to 11.9 micron region is diagnostic, the absorption here being shifted to longer wavelengths with increasing atomic weight of the cation. Conclusive distinction between absorptions due to silica tetrahedra and aluminum octahedra has not been made although Adler (1950) has suggested a number of frequencies which may apply in the case of montmorillonite and a few related minerals.

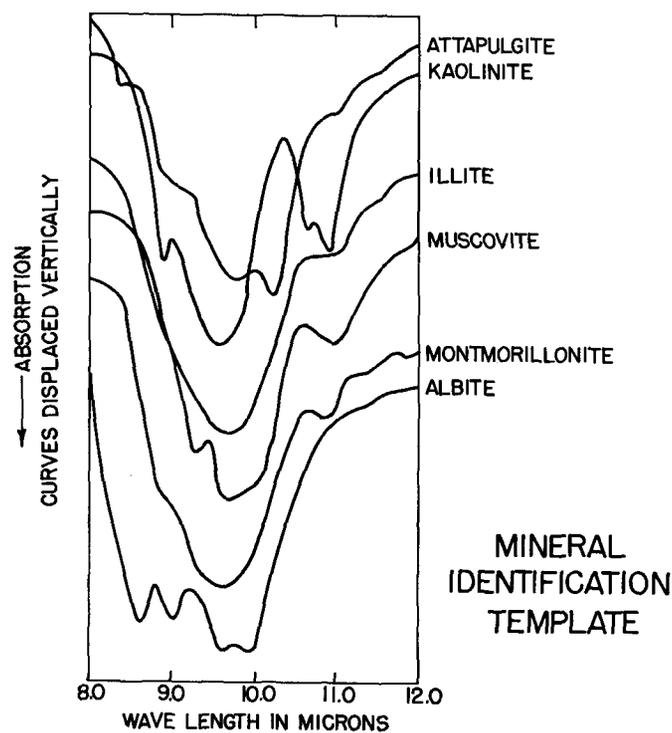


FIGURE 9.

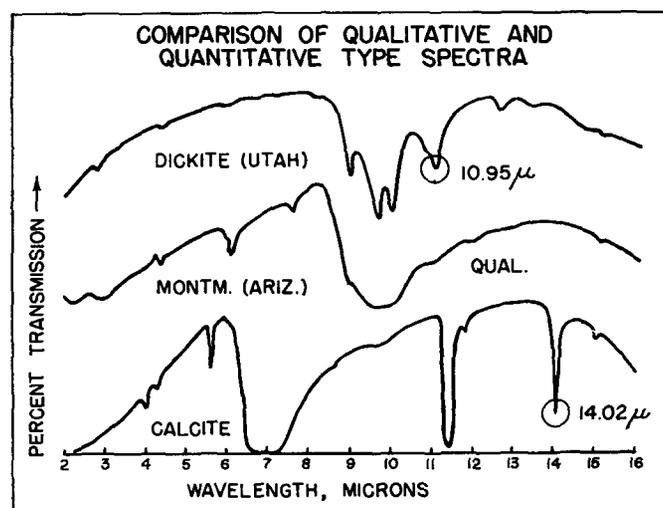


FIGURE 10.

Qualitative and Quantitative Analysis. Nearly all of the published work on infrared analysis of minerals is concerned with the recording and qualitative interpretation of the spectra. The one exception is the paper of Hunt and Turner (1953) which presents quantitative data obtained in the analysis of both synthetic rock mixtures and natural sediments. For the largest available library of clay infrared spectra, the reader is referred to Preliminary Report No. 8 of API Project 49 (Hunt et al. 1950). Rapid identification can sometimes be made by superposing a template of mineral curves on the spectrum of the unknown. Figure 9 (Hunt and Turner 1953) is an example of such a device, representing a condensed array of the major absorptions of some of the most frequently encountered clays and related minerals.

The qualitative and quantitative analysis of mineral mixtures from their infrared spectra depends on the independent appearance of the major diagnostic absorptions of each constituent provided that the peak positions are sufficiently resolved and non-interfering. According to Hunt,¹ kaolinite is determined quantitatively from measurement of the 10.95-micron band; illite and montmorillonite can often be distinguished qualitatively but they have not yet yielded to quantitative analysis. The method of Hunt and Turner (1953) for quantitative analysis is to construct working curves from spectra of the pure minerals by plotting the optical densities of selected absorptions against different film weights in milligrams per square centimeter. From the optical densities of the corresponding absorptions in the spectrogram of the unknown mixture, the percentage of each mineral can be determined to within about 5 to 10 percent of the amount present.

Applications of Infrared Mineral Analysis. From the literature only a few practical applications are known, all having some connection with oil production. The Carter group (Hunt, Wisherd, and Bonham, 1950; Hunt and Turner 1953) has exhibited spectra of a Wisconsin reef limestone, a limy oil shale and a limy shale from the Uinta Basin in Utah, a mahogany shale from the same source, three natural sediments from Utah, Oklahoma and Texas, a quantitative analysis of four inter-reef limestones, and an analysis of drilling mud penetration into a Mississippi sandstone core. The Union group (Nahin et al. 1951) has published spectral curves of the fractionated clays extracted from California cores taken in the Gatchell zone of Northeast Coalinga field and in the Stevens zone of Paloma field.

Needed Research. It is evident from the preceding survey that much remains to be done before this method of mineral analysis, particularly as applied to the clay minerals, can be said to have gotten off to more than just a good beginning. Perhaps a listing of some of the problems which must be answered to obtain an understanding of clay-mineral infrared-absorption spectra may challenge the interest of other academic and industrial workers in the field of clay mineralogy. It is with this hope that the following suggestions are offered.

1. The spectra of quantitatively described surface-homoionic and surface-heteroionic clays should be obtained for all of the clay mineral types. Better and

¹ Private communication.

Table 1. Infrared spectra of clays and structurally related minerals.^a
Positions of absorption band centers.
Wave-length range, microns

	Reference ^b	2-3μ	4μ	5μ	6μ	7μ	8μ	9μ	10μ	11μ	12μ	13μ	14μ	15μ	Remarks
I. Kaolin group															
Kaolinite	H3	2.73m			6.1w	7.55w	8.03s	9.65s, 9.90s	10.68m, 10.95s		12.50m, 12.65m	13.3w	14.5m		Pair of doublets in 9-11μ region similar to kaolinite except at 8.15μ
Dixite	H30	2.73-2.83m			6.1w	7.55w	8.15m, 8.93s	9.65s, 9.90s	10.68s, 10.95s		12.55m	13.3w	14.5w		
Nacrite	A1							9.60, 9.88	10.73, 10.96		12.50	13.2			Like dixite but for 10.73μ peak
Anaxite	N1	2.7					8.9	9.6, 9.90	10.7		12.6	13.2			Similar to kaolinite
Hallysinite	H30	2.73m			6.0w, 6.1w	7.0w, 7.55w	8.90s	9.65s, 9.9s	10.95s		12.5w	13.3w	14.6w		Differs from kaolinite in no 10.68μ band, weak absorption at 12.5μ
Allophane	A1	3.0			6.2				10.2						Broad center at 10.2μ
II. Montmorillonite group															
Montmorillonite	H3	2.8-3.2m			6.15m	7.55w	8.95m	9.6s	10.95m	11.4m, 11.85m	12.75w	13.3w			Like illite
Nontronite	H30	2.8-3.1m			6.1m	7.55w		9.0m, 9.8s	10.95m		12.8m	13.3w			Prominent 9.8μ and 12.25μ bands 9.9μ may be distinctive
Hectorite	Al, B3, H30	2.9w			6.1	7.3m		9.9	10.95m		12.23m	13.3w	14.05m	15.0m	Like montmorillonite, may differ at 9.6-9.7μ
Illite	H3	2.8-3.2m			6.0w, 6.1w	7.0w, 7.55w	8.95m	9.7s	10.95m		12.05w	13.3w			Characteristic spectrum
Attapulgite	H30	2.8-3.2m			6.0m, 6.15m	7.55w	8.4w, 8.9m	9.7m	10.15s	11.0m					
III. Related minerals															
Pyrophyllite	H30	2.73m		5.3w			8.3m, 8.6m, 8.90s	9.32s, 9.50s, 9.8s	10.55m, 10.95m	11.52w, 11.97m	12.3w, 12.50m, 12.80m	13.2w	14.4w		Sharp spectrum in 11.5-13.0μ region
Talc	H3							9.8s					14.9m	15.1w	Has only two clearly defined bands
Muscovite	H3	2.78m						9.35s, 9.7s		11.0m		13.35m	14.8w		Characteristic strong band at 9.35μ
Biotite	H3								10.0s, 10.3s				14.3m		Easily distinguished from muscovite
Gibbsite	A1	2.3, 2.5, 3.5			6.9	7.3		9.78	10.30			13.8			Major bands at 9.78μ and 10.30μ
Brucite	K2	2.3, 2.7, 3.5			6.9	7.3	8.7					13.8			No sharp absorptions
α-Quartz	H3			5.1w, 5.6, 5.35w, 5.38w	6.2w		8.60s	9.2s	10.95w		12.52m, 12.82m		11.42m		Four main bands: 8.60, 9.2, 12.52, 12.82μ
Opal	H3	3.0w		5.38w	6.1w		8.2m	9.2m	10.5m		12.55m				Distinctly different from quartz

^a The data for which relative intensities of the absorption bands are indicated were taken from the papers of Hunt (1950) and Hunt, Wisshard, and Bonham (1950). The symbols have the following meanings:

s = less than 25 percent transmission with a film density of 0.6 mg/sq cm
 m = between 25 and 75 percent transmission with a film density of 0.6 mg/sq cm
 w = more than 75 percent transmission with a film density of 0.6 mg/sq cm
 μ = micron.

^b Key to references: A1, Adler 1950; B3, Bay and Stevens 1950; H3, Hunt, Wisshard and Bonham 1950; H30, Hunt 1950; K2, Keller and Pickett 1950; N1, Nahin et al. 1951.

easier methods of homoionization of a clay surface are needed. Perhaps the use of synthetic, organic ion-exchange resins may be an answer (Wicklender 1951; Lewis 1953).

2. The complex relationships among the clay structures and their spectra are almost completely unknown, although Adler and the Hunt and Keller groups have made a good beginning.

Can specific absorptions be correlated with tetrahedrally bonded ions (Si^{4+} and Al^{3+} in montmorillonite and beidellite) and others with octahedrally positioned ions to give us another measure of structural distinction between the two- and three-layer clays?

The manner in which the spectra reflect isomorphous replacement within the lattice might be advantageously studied by comparison of highly resolved and surface-homoionized samples of reasonably homologous series such as pyrophyllite, nontronite, saueonite (Ross 1946), hectorite, saponite (Ross and Hendricks 1945), and talc in which the essential octahedral positions are occupied by Al^{3+} , Fe^{3+} , Zn^{2+} , Mg^{2+} , Li^+ , Mg^{2+} , Mg^{2+} , respectively. Of course, the degree of tetrahedral proxying of Al^{3+} for Si^{4+} will have to be taken into account both in selection of suitable samples and in interpretation of the spectra.

It appears that the infrared spectra may prove useful for classifying the nature of the bonds in minerals in terms of percent covalent or ionic character. Pauling (1948), Gruner (1950), and Keller, Spotts and Biggs (1952) have called attention to the covalent character of mineral bonds. Keller and co-workers make the point that wholly ionic-bonded minerals do not absorb appreciably in the infrared, indicating thereby that the significant infrared absorption by minerals is evidence for some covalent bonding.

What is the effect of the exchange cation upon the positions of the major infrared absorptions of the clay minerals? Do we find a shift toward longer wavelengths with increasing atomic weight as in the case of carbonates (Adler 1950; Hunt and Turner 1953) and non-clay silicates (Keller, Spotts, and Biggs 1952)?

Since the absorption spectra are presumed to be functions of the geometrical configurations not only of individual atomic groupings but also of the massive lattice, what aspects of the infrared spectra of kaolinite, dickite, nacrite, anauxite, hydrated halloysite, and metahalloysite reflect the order of stacking in the *c*-axis direction? Does allophane show up as the silica-alumina analogue of zero order?

Closely related to the preceding suggestion would be a study of the effect of sample orientation upon the spectra; e.g., compare the spectra of kaolinite laminae parallel to and perpendicular to the incident radiation.

What is the relation between the degree of hydrogen bonding and the exact location of the hydroxyl absorption in the interval 2.7-3.2 microns? Does deuteration of hydrated clays produce sufficient separation of the lattice hydroxyl and bonded-hydroxyl absorptions to permit estimating the relative amount of each form present?

If the presumption is correct that the characteristic absorption at 2.75 microns represents unbonded hydroxyl of structure then upon calcining the clays at various temperatures up to 800° C. there should exist a

1:1 correspondence between its appearance in the infrared spectrum and the intensity of the diagnostic lines in the X-ray diffraction pattern of any given clay.

Is the calcination temperature dependence of the retention of fluorine-proxied hydroxyl in hectorite similar to that of the OH-montmorillonites?

The spectral differences among the various natural hydrated and non-hydrated halloysites as well as the artificially produced complexes such as "glycerol halloysite," etc., should be examined in detail and attempts made to correlate the spectra with their unusual morphologies as revealed by electron micrographs (Bates et al. 1950). Perhaps this will lead to a better understanding of the structural changes accompanying the irreversible dehydration of halloysite.

3. The infrared absorption spectra of organo-clays should be investigated. The interest here lies in determining the spectral effects of adsorption (as well as of real exchange in the case of organic cations) of organic molecules on clay surface. Thus, studies of the magnitudes of the bathochromic and hypsochromic shifts (toward longer and shorter wave-lengths, respectively) induced by the different clay surfaces should be made. It is conceivable that the resultant data might enable a larger number of different minerals in a rock mixture to yield to quantitative analysis through measurement of the degree of spectral shift of one or more of the prominent bands present in the organo part of the clay in a region of the spectrum which is normally featureless in the unclad clay. Along these lines, the work of Yaroslavskii and Terenin (1949) on the infrared absorption spectra of adsorbed molecules and of Vedeneva (1947) on changes in the ultra-violet spectra of dyes when adsorbed on clay minerals is of interest. The latter found that different samples of bentonite gave malachite green maxima differing by as much as 60 millimicrons. An important conclusion from this work is that intensification of the ionic bond between clay and dye causes a bathochromic effect, and intensification of the dipole bond a hypsochromic effect.

4. An important contribution would be the development of better techniques for quantitative mineral analysis, particularly of montmorillonite in the presence of illite, kaolinite, feldspar, quartz, and carbonate.

5. The spectral range of study should be enlarged from the presently used 2 to 16 microns to from 0.75 to 25 microns. It is realized that this involves a difficult instrumentation problem, but the rewards for finding additional fundamental frequencies could well be important for raising the level of clay mineral analysis.

6. Finally, as an important aspect of the interpretation problem, it is urged that many more spectra of widely diverse but carefully described clays and sediments be obtained in order to expand the available library of reference curves.

Conclusion. It is concluded that the infrared absorption spectra of clays and related minerals are, at present, of limited usefulness for the purpose of qualitative and quantitative analysis of complex and unknown mineral mixtures. However, the value of the method will undoubtedly become greater as more is learned concerning the variations of the spectra with structure and chemical composition. In the petroleum industry, the infrared

spectra of minerals have served as an important supplement to the data provided by X-ray diffraction, electron microscopy, and the other well-known methods for examining minerals.

Acknowledgment. The author is grateful to Dr. John M. Hunt and the Carter Oil Company for permission to use unpublished data; to Professor W. D. Keller for his promptness in making available the results of his most recent studies; to Professor Ralph E. Grim for gifts of clay mineral standards; to Mr. James S. Brown of Union Oil Company of California for obtaining a number of the clay mineral spectra; and to Union Oil Company of California for permission to publish this survey.

DISCUSSION

A. M. Soldate:

What is meant by the phrase "tailored surfaces," and "homoionic and heteroionic surfaces"?

P. G. Nahin:

By a "tailored surface" I mean a surface of known composition, prepared in the laboratory according to specifications of the experimenter; a homoionic surface is one on which every exchange site is occupied by a single element, as in a Na-montmorillonite; heteroionic surface is one on which the exchange sites are occupied by two or more elements, as in a Ca-Mg-montmorillonite. My purpose in mentioning such surfaces is to urge that studies be made with clays of known and desired surface composition rather than with clays just as they come in nature.

R. L. Stone:

Dr. Nahin, do you know of any study relating to the effect of particle orientation on infra-red absorption?

P. G. Nahin:

No, but I think that such a study would be very desirable; kaolinite may be the simplest system to begin with in such a study.

Adolf Pabst:

The effect of orientation on absorption was examined extensively by physicists in many countries long ago. The matter has been summarized by Schäfer and Matossi (1930).

P. G. Nahin:

I believe that these deal with relatively large oriented crystals and not with powdered samples, the particle size of which are smaller than the smallest wave length used. The question of the effect on absorption of such oriented particles is still unanswered.

SELECTED REFERENCES

- Adler, H. H., 1950, Infrared investigations of clay and related minerals: Am. Petroleum Inst. Proj. 49, Prelim. Rept. 8, pp. 1-72, New York, Columbia University.
- Barnes, R. B., Gore, R. C., Liddel, U., and Williams, V. Z., 1944, Infrared spectroscopy, industrial applications and bibliography: New York, Reinhold Pub. Corp., p. 11.
- Bates, T. F., Hildebrand, F. A., and Swineford, A., 1950, Morphology and structure of endellite and halloysite: Am. Mineralogist, v. 35, pp. 463-484.
- Bray, E. E., and Stevens, N. P., 1950, The preparation of clay samples for infrared absorption measurement: Am. Petroleum Inst., Prelim. Rept. 8, pp. 73-104, New York, Columbia University.
- Buswell, A. M., Krebs, K., and Rodebush, W. H., 1937, Infra-red studies. III. Adsorption bands of hydrogels between 2.5 and 3.5 μ : Am. Chem. Soc. Jour., v. 59, pp. 2603-05.
- Buswell, A. M., and Dudenhostel, B. F., 1941, Spectroscopic studies of base exchange materials: Am. Chem. Soc. Jour., v. 63, pp. 2554-58.
- Gruner, J. W., 1950, An attempt to arrange silicates in the order of reaction energies at relatively low temperatures: Am. Mineralogist, v. 35, pp. 138-148.
- Harrison, G. R., Lord, R. C., and Loofbourow, J. R., 1948, Practical spectroscopy: p. 261, Prentice-Hall, Inc.
- Henry, R. L., 1948, The transmission of powder films in the infra-red: Optical Soc. America Jour., v. 38, pp. 775-789.
- Hunt, J. M., 1950, Infrared spectra of clay minerals: Am. Petroleum Inst. Proj. 49 Prelim. Rept. 8, pp. 105-121, New York, Columbia University.
- Hunt, J. M., Wisherd, M. P., and Bonham, L. C., 1950, Infra-red absorption spectra of minerals and other inorganic compounds: Anal. Chemistry, v. 22, pp. 1478-1497.
- Hunt, J. M., and Turner, D. S., 1953, The determination of the mineral constituents of rocks by infra-red spectroscopy: Anal. Chemistry, vol. 25, pp. 1169-1174.
- Keller, W. D., and Pickett, E. E., 1949, Absorption of infrared radiation by powdered silicate minerals: Am. Mineralogist, v. 34, pp. 855-864.
- Keller, W. D., and Pickett, E. E., 1950, The absorption of infrared radiation by clay minerals: Am. Jour. Sci., v. 248, pp. 264-273.
- Keller, W. D., Spotts, J. H., and Biggs, D. L., 1952, Infra-red spectra of some rock-forming minerals: Am. Jour. Sci., v. 250, pp. 453-471.
- Lecomte, J., 1951, Jour. Physics Radium, v. 12, pp. 827-828.
- Lewis, D. R., 1953, Replacement of cations of clay by ion exchange resins: Ind. Eng. Chemistry, v. 45, pp. 1782-1783.
- Mellon, M. G., editor, 1950, Analytical absorption spectroscopy: p. 440, New York, John Wiley & Sons, Inc.
- Nahin, P. G., Merrill, W. C., Grenall, A., and Crog, R. S., 1951, Mineralogic studies of California oil-bearing formations. I. Identification of clays: Jour. Petroleum Technology (Am. Inst. Min. Met. Eng. Petroleum Trans.), v. 192, pp. 151-158.
- Pauling, L. C., 1948, Nature of the chemical bond, 2d ed., p. 240, Cornell University Press.
- Plyler, E. K., 1929, Combination frequencies of the infra-red bands of quartz: Physical Review, v. 33, pp. 48-51.
- Ross, C. S., 1946, Sauconite—a clay mineral of the montmorillonite group: Am. Mineralogist, v. 31, pp. 411-424.
- Ross, C. S., and Hendricks, S. B., 1945, Minerals of the montmorillonite group, their origin and relation to soils and clays: U. S. Geol. Survey Prof. Paper 205-B, pp. 23-79.
- Sands, J. D., and Turner, G. S., 1952, New development in solid phase infrared spectroscopy: Anal. Chemistry, v. 24, pp. 791-793.
- Schäfer, C., and Matossi, F., 1930, Das ultrarote Spektrum Springer, Berlin, 400 pp.
- Vedeneeva, N. E., 1947, Izmeneniya spektrov krasitelei pri adsorbtsii na mineralakh glin (Changes in the spectra of dyes when adsorbed on clay minerals): Zhurnal Fizicheskoi Khimi: (Jour. Phys. Chemistry) (U. S. S. R.), v. 21, pp. 881-891.
- Wells, A. F., 1945, Structural inorganic chemistry: p. 104, Oxford University Press.
- Wicklander, L., 1951, Saturation of colloids and soils by means of exchange resins: Ann. Royal Agri. Coll. Sweden, v. 18, pp. 154-162.
- Yaroslavskii, N. G., and Terenin, A. N., 1949, Infrakrasnye spektry pogloshcheniya adsorbirovannykh molekul (Infra-red adsorption spectra of adsorbed molecules): Doklady Akad. Nauk SSSR (Reports of the Academy of Science of the U. S. S. R.), v. 66, pp. 885-888.