

# ANALYSIS USING INFRARED SPECTROSCOPIC METHODS

ROBERT A. OETJEN

*Department of Physics, The Ohio State University, Columbus 10*

## REQUIREMENTS OF A PHYSICAL-ANALYTICAL METHOD

The essential requirements in any analysis based on a physical method is that there must be some physical property of the substance being analyzed that is unique. Thus, for example, if one has a mixture of two substances, the density of each of which is known, the composition of the mixture can be determined by measuring its density. Or, the physical property may be the index of refraction. If the indices of refraction of the components of a mixture and the index of refraction of the mixture are known, it may be possible to determine the composition of the mixture. In this case, mixtures of more than two components may be analyzed if the indices are known for more than one wavelength. These physical properties are satisfactory for an analysis of a mixture of substances whose identities are

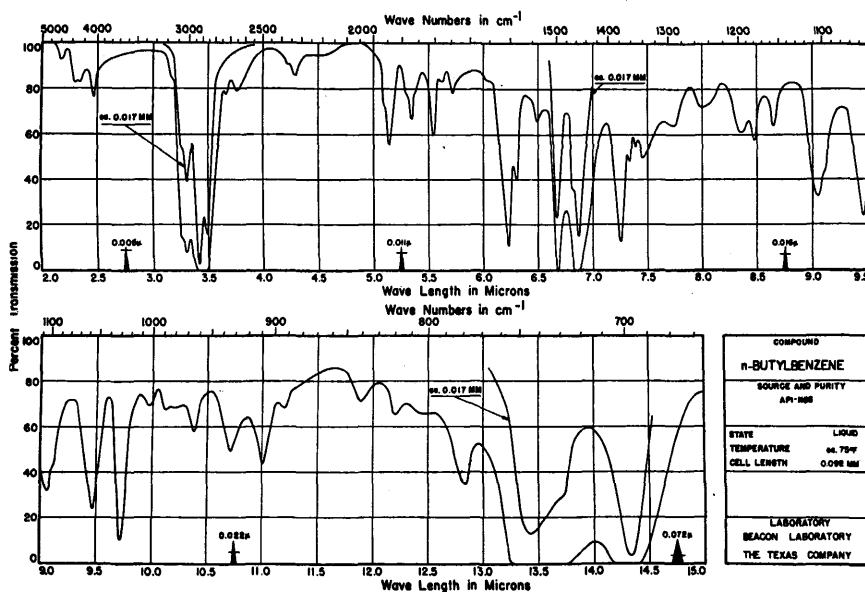


FIGURE 1. Infrared Spectrogram of n-butylbenzene. (Courtesy The Texas Company.)

known. If many components are involved or if the exact nature of the components is not known, the analysis becomes more complicated. One must depend either upon the determination of several physical properties or upon a physical property which has several values associated with it for each constituent of the sample being analyzed. Because ultraviolet, visible, infrared, or x-ray data or the mass spectrum have many numbers associated with a given substance, these are properties which may permit analysis of a complex mixture by using only one such property. The use of two or more such methods will extend the field of usefulness still further. Although the following discussion refers directly to the use of the infrared spectrum as a means of analysis, much of it would be equally applicable to other methods.

Figure 1 is a spectrogram<sup>1</sup> of a typical hydrocarbon, n-butylbenzene, in which it may be seen that in the wavelength interval between 2 microns, i.e., 20,000 Angstroms, and 15 microns, there is a large number of absorptions. (Absorptions are represented by valleys in the curves). A spectrogram for any other compound, even one so similar as iso-butylbenzene, would be quite different, in that there would be absorptions at different places in the spectrum. Some of the absorptions occurring at the same wavelengths would have different intensities in the two spectrograms. This illustrates that infrared spectroscopic data satisfy the requirement that many values characterize the substance in question. Thus the frequent reference to infrared spectra as fingerprints of molecules is justified.

#### ORIGIN OF INFRARED SPECTRA

What is it about the molecules that gives rise to the different infrared spectra? Basically, these spectra result from the fact that the molecules are vibrating and rotating. A molecule is characterized by many energy levels. Figure 2 is an oversimplified diagram of energy levels for a hypothetical molecule. The longest

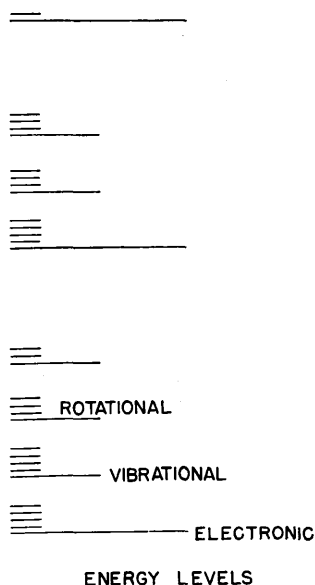


FIGURE 2. Simplified energy level diagram for a hypothetical molecule. Longest, intermediate and shortest lines correspond respectively to energy levels for different electronic, vibrational and rotational states.

lines, representing electronic energy levels, are farthest apart; vibrational energy levels are closer together; and rotational energy levels are separated by the smallest interval of all of these. If electromagnetic energy falls upon a molecule under proper conditions, it may absorb some of that energy and be raised to a higher energy level. Thus for example if a photon having the proper amount of energy hits the molecule, the molecule may change electronic states. Or if the energy is somewhat less, it may change vibrational states. If a still smaller amount of energy characterizes the photon, it may give rise to a change in rotational levels. Frequently the absorption of energy may result in changes of states of all three types. The energy  $\Delta E$ , transferred in such a change is related to the frequency  $\nu$  through the relation:

$$\Delta E = h \nu \text{ (sec}^{-1}\text{)}$$

<sup>1</sup>Spectrograms of this type are to be found in the Catalog of Infrared Spectrograms compiled by the American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology under the direction of Dr. F. D. Rossini.

where  $h$  is the Planck constant. The frequency is related to the wavelength  $\lambda$  by

$$\nu \text{ (sec}^{-1}\text{)} = \frac{c}{\lambda \text{ (cm)}}$$

where  $c$  is the velocity of light expressed in cm/sec. The reciprocal of the wavelength, i.e., the number of waves per cm, is commonly referred to as the "wave number" and is designated by  $\nu'$ . Then:

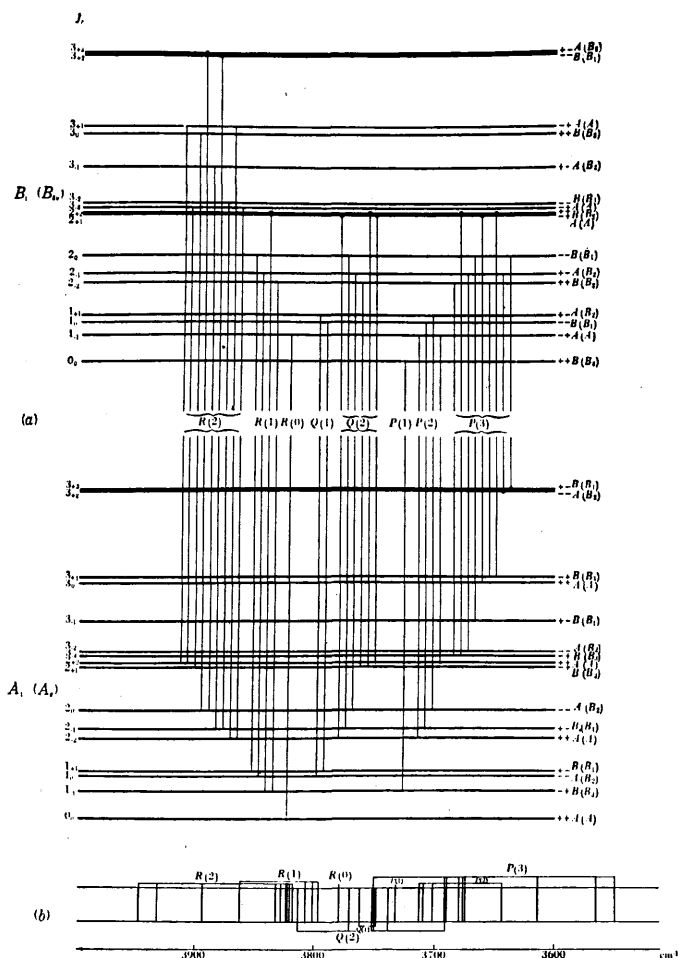


FIGURE 3. Energy level diagram for one band of water vapor. (Courtesy G. Herzberg and D. Van Nostrand Co., Inc.)

$$\frac{\nu \text{ (sec}^{-1}\text{)}}{c} = \frac{1}{\lambda} = \nu' \text{ (cm}^{-1}\text{)}$$

and

$$\Delta E = \frac{h c}{\lambda \text{ (cm)}} = h c \nu' \text{ (cm}^{-1}\text{)}$$

Thus the change in energy is inversely proportional to the wavelength or directly proportional to the frequency or wave number. The chief thing to note is that since the electronic transitions involve large amounts of energy, the frequency of the radiation is large and the wavelength is short. Thus this type of transition leads to absorptions in the visible or ultraviolet portion of the spectrum. Changes in vibrational levels involve somewhat less energy and give rise to absorptions in the infrared region in which we are interested. Changes in rotational level involve still longer wavelengths and are associated with absorptions in what is known as the far infrared spectral region, i.e., radiation whose wavelengths are 25 microns or longer.

The presence of different atoms in a molecule, or a different spatial arrangement of the same atoms results in a different vibrating-rotating system. All such systems represent problems which may be solved by the methods of mechanics. Actually these problems are so complicated that theoretical physicists have largely confined their efforts to attempts to relate the wavelength of absorption with the frequency and the normal mode of vibration of only the simplest molecules (Wu, 1939; Herzberg, 1945, 1950). Fortunately for the analyst, it is no more difficult to obtain experimental data from a complex molecule than from a simple diatomic

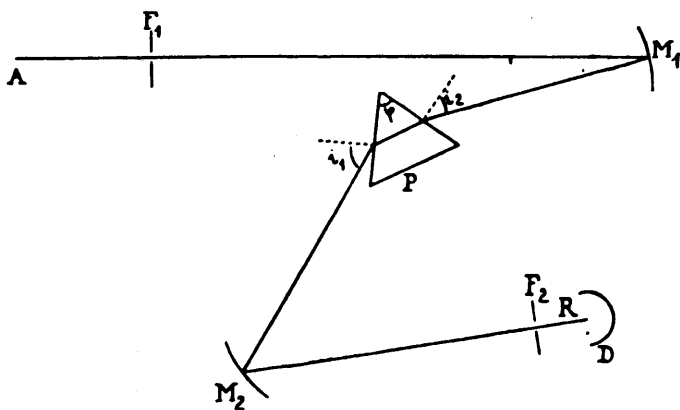


FIGURE 4. Simplified diagram of a spectrometer. A is the source,  $F_1$  is the entrance slit,  $M_1$  is a collimating mirror; P is a dispersing device (a prism here).  $M_2$  is a focussing mirror.  $F_2$  is an exit slit. R and D are the components of the radiation detector.

molecule. If a photon approaches a molecule and if the energy of the photon is equal to the difference in energy states of the molecule, there is a finite probability that that molecule will absorb that photon. Having many molecules in a beam of light, some of them are constantly absorbing radiations of all wavelengths corresponding to energy level separations for which transitions are permitted. Figure 3 is a diagram showing a few of the energy levels and permitted transitions for one of the bands of the water molecule. This illustrates that these transitions are numerous and that the spectra become complicated.

#### INSTRUMENTATION

The next question of interest is how one ascertains these differences in the spectra of various compounds. Figure 4 is a simplified diagram of a spectrometer used to obtain such spectra. A is a source of radiation;  $F_1$  is an entrance slit;  $M_1$  is a mirror which collimates the radiation. The parallel rays of radiation traverse the dispersing device represented by the prism P. The mirror  $M_2$  focuses

the radiation on the exit slit  $F_2$  after which it reaches the detector R. The source, the prism, and the detector will be considered briefly.

*Source.* In obtaining infrared absorption spectra, it is most convenient to use an incandescent body which emits radiation of all wavelengths in the regions to be investigated. Most of the sources used have emission characteristics approaching those of a black body. Figure 5 contains the familiar series of curves of black body sources radiating at different temperatures. This illustrates the fact that such sources, although continuous, do not have uniform intensity throughout the spectral region. It is further to be noted that although the curves extend only to about 6 microns at the long wave end, even at this relatively short wavelength

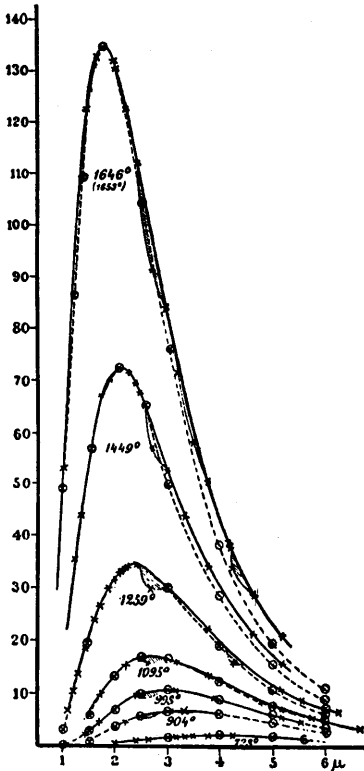


FIGURE 5. A family of black body curves, showing the relative amounts of radiation emitted as a function of wavelength. The number associated with each curve is the absolute temperature.

there is a considerable decrease in intensity. The Rayleigh-Jeans law which applies well at longer wavelengths for sources at these temperatures indicates that the intensity falls off inversely as the fourth power of the wavelength. Hence at 15 or 25 microns, there is relatively little power available. This puts a limitation on the range of wavelengths which may be examined readily. However techniques have been developed so that there is no great difficulty in determining absorption characteristics at wavelengths as long as 25 microns. The Nernst glower and the Globar are the two most commonly used sources of radiation. They both operate in the temperature range of 1000 to 1500 degrees Kelvin.

*Dispersing device.* The next component considered is the dispersing device. In figure 4, a prism is shown. Gratings are sometimes used for this purpose. The three requirements upon a prism are that it be transparent to radiation of the region being investigated, that it be characterized by relatively high dispersion, and that the material be available in form suitable for making a prism. If the

index of refraction is plotted against wavelength, it is seen that the highest dispersion is obtained in the wavelength region just shorter than that at which the material becomes opaque. Table 1 lists the wavelengths below which materials transmit radiation, hence indicates the region in which that material is the best for making a prism. The only comment that needs to be made with respect to this table is that the material labelled KRS-5 is a mixture of thallium bromide and thallium iodide.

TABLE I  
*Wavelengths below which materials transmit radiation*

Material	Wavelength
Glass	2.5 microns
Quartz	4.0 "
LiF	5.5 "
CaF <sub>2</sub>	12.0 "
NaCl	15.0 "
KBr	25.0 "
KRS-5	45.0 "

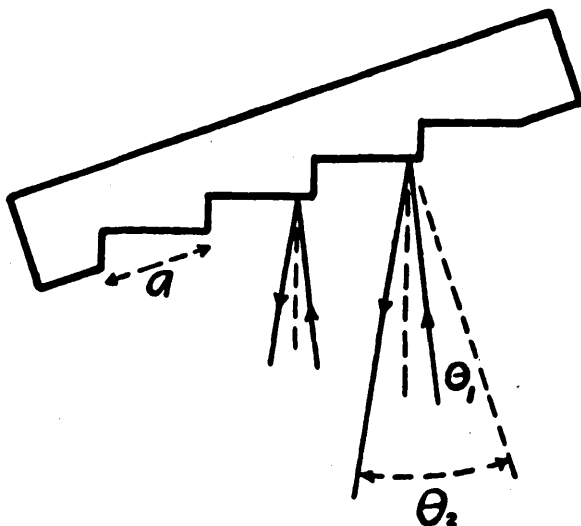


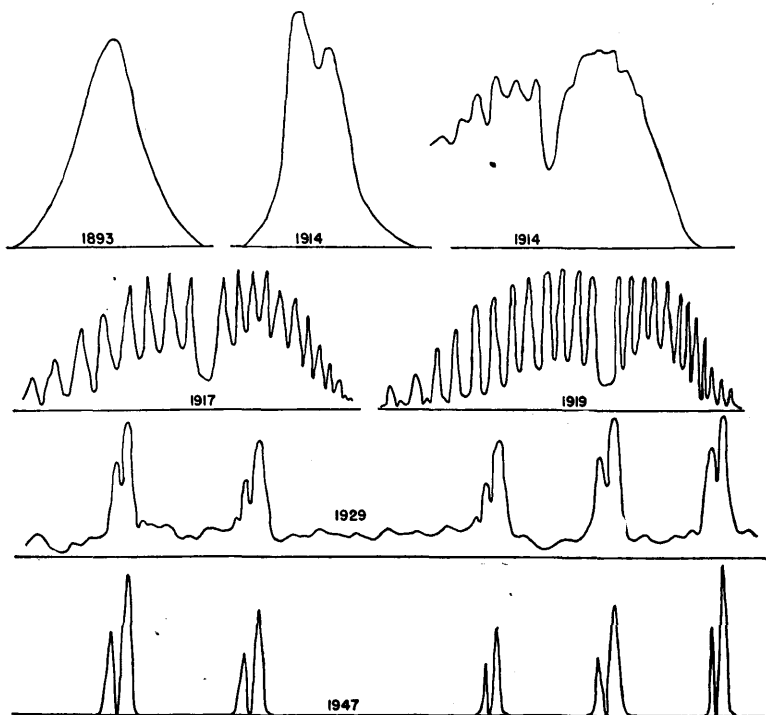
FIGURE 6. Diagram of the face of an echelette grating.

The other type of dispersing device commonly used is a grating. Because relatively coarse gratings are required in infrared spectroscopy, it is common to use an echelette grating (Wood, 1910). The shape of the grooves in an echelette grating is shown in figure 6. The grooves are step-shaped, with the result that the radiation may be concentrated in a given direction. This is important because it means that it is possible to obtain most of the radiation of a given wavelength in one order. It should be emphasized, however, that the radiation of other orders and different wavelengths will be reflected in the same direction in accord with the usual grating formula:

$$n \lambda = d(\sin i + \sin \theta)$$

where  $n$  is the order,  $d$  is the spacing between the rulings on the grating,  $i$  is the angle of incidence and  $\theta$  is the angle of diffraction. Hence there is still a problem

of filtering that is sometimes a difficult one to solve in grating spectroscopy. Gratings rather than prisms are ordinarily used when the highest dispersion is required. The result is that the presence of spectral lines which are closer together may be observed. To the analyst, this means that a larger number of physical quantities characteristic of that substance is available. Hence there is a greater possibility that this tool may be used as a means of identifying the substance in question. It is true that today most infrared analyses are being conducted on prism spectrographs. This is not to suggest that such will always be the case. Perhaps not many years hence grating spectrometers will be used extensively for analytical purposes. Figure 7 illustrates graphically what may be achieved through



#### HYDROGEN CHLORIDE VAPOR SPECTROGRAMS

FIGURE 7. The 3.5 micron HCl vapor band examined using the highest resolving power available at the date under each curve. Absorption is plotted upward in these curves.

the use of higher resolution. This happens to be a historical display of the best resolving power available at different dates. A portion of the 3 micron hydrogen chloride band is shown. In 1893 it was known that there was a single absorption in this band, absorption being indicated upward in this figure. By 1947 the band had been separated into many pairs of lines, a few of which are shown at the bottom of the diagram.

*Detector.* The other component of the instrument of some interest is the detector. Devices used for detection of the presence of infrared radiation may be arranged in three classes. Most widely used is the thermocouple or thermopile. This is not the laboratory type of twisted iron and constantan wires, but is rather a delicate, extremely sensitive device which nevertheless operates on exactly the

same principle as the heavier ones. The second type of detector is a bolometer which is a sensitive resistance thermometer, sometimes put in a modified Wheatstone bridge. A third type of detector is a gas thermometer. Like the other detectors this is of minute dimensions and has several special features associated with it, with the result that it, too, is capable of showing the presence of small amounts of radiation. The minimum power which may be measured by any of these devices ranges from a microwatt downward.

*General remarks.* So little has been said about the instrumentation as a whole that the impression may be conveyed that it is simple. Such is not the case. The desire to obtain data rapidly and in a most useful form has served as a stimulant for instrument designers to build into spectrographs the ability to subtract the absorption due to solvents and to record data as percent transmission. This is all done automatically and quickly on some spectroscopic instruments available commercially.<sup>2</sup> As a result of these engineering developments, instead of being a very simple optical instrument, the infrared spectrograph has become an electronic instrument with the optical components housed in one of the smaller boxes comprising the instrumentation.

The samples may be examined in a form of a solid, a liquid, or a gas. If it is a solid, such as a thin film of plastic or rubber, it is only necessary to support it in the radiation beam. Otherwise it may be necessary to make a mull or solution or to otherwise prepare it for use. If it is a liquid, the liquid is ordinarily inserted between a pair of transparent plates, such as sodium chloride, potassium bromide, or silver chloride with an appropriate spacer. If the sample is a gas, it is merely necessary to have a tube, closed with appropriate windows on the ends, which will hold enough of the sample to obtain the desired absorption.

#### QUALITATIVE ANALYSIS

All of the foregoing is introductory to the matter of analysis. Now that the absorption spectrogram can be obtained, what can be done with it? That is, how does one interpret the spectrogram of the unknown substances? The investigator should have some idea of what is contained therein. Even if he does not, the chances are that the spectrogram will give some clues to the experienced observer. For example, absorptions between 3.2 and 3.5 microns suggest the presence of C-H bonds. Absorptions in the 6 micron region may be indicative of double bonds such as C=C or C=O carbonyl groups. Furthermore, the exact wavelength of the absorption will assist in identifying the type of carbonyl group if that is indicated. This is the type of interpretation that is useful in a qualitative analysis. Ultimately the analyst will hope to compare this spectrogram with a spectrogram of a pure substance and find the two to be identical. This means that it is necessary to know the spectrogram of the pure compound if a complete analysis is required. This is no more unreasonable than demanding that the exact index of refraction of a substance be known if one wishes to use the refractive index method for analysis.

#### QUANTITATIVE ANALYSIS

In undertaking quantitative analyses, there should be available the spectrograms of the pure components as well as that of the mixture whose composition is to be determined. If there exists a particular wavelength at which only one component absorbs, determination of the magnitude of the absorption at that wavelength will be a measure of the concentration of that component. Such ideal situations rarely occur. Ordinarily, all components absorb radiation of all wavelengths to some extent. This necessitates an inquiry into the laws governing the absorption

<sup>2</sup>Literature describing infrared spectrophotometers available commercially may be obtained from: Baird Associates, Cambridge, Mass.; Beckman Instruments, Inc., S. Pasadena, California; and Perkin-Elmer Corporation, Glenbrook, Conn.



of radiation. While this is not so simple a matter as may at first appear, with the result that there are still some ambiguities about these laws, it is frequently the case that the exponential law, variously referred to as the Lambert-Beer-Bouguert law is applicable (discussed by Dr. Timma in the preceding article). As a result of the working of this law, the amount of a substance is proportional to the optical density which is defined as the logarithm of the reciprocal of the radiation transmitted by the sample. Furthermore, if there are several substances present, in the simplest cases the optical densities at a given wavelength are additive. The proportionality constants, which are different at each wavelength for each substance, may be, at least in principle, determined from the spectrograms of the pure substance.

In the quantitative analysis of a multi-component mixture, there results a series of simultaneous linear equations. Thus if one is analyzing a mixture for four possible components, it becomes necessary to make the analysis at four different wavelengths. These wavelengths are ordinarily chosen as those at which the absorption of the supposed constituents are most uniquely characteristic of that component. Putting constant obtained from the spectrogram of the known constituents into the equations, one may solve for the concentrations of these four constituents. The solution of four simultaneous equations is not always simple. Furthermore, if one is attempting to obtain solutions to six or eight or ten or twelve simultaneous equations, normal methods of solutions learned in college algebra are not practical. These, however, may be solved by iterative methods (Crout, 1941). Or, better yet, there are available electronic computers (Morgan and Crawford, 1944; Berry et al., 1946) which may be used to solve such simultaneous equations by setting up electrical circuits which are analogous to the equations involved.

To summarize, the method of analysis involves comparison, on a qualitative or quantitative basis, of the spectrogram of the sample being analyzed with spectrograms of substances presumed to be constituents of the sample.

#### EXAMPLES OF ANALYSES

What kind of analyses can be made using infrared spectroscopic methods? Probably the best answer to this can be obtained by referring to articles by Barnes and Gore (1949), and Gore (1950, 1951) which survey the uses of infrared spectroscopy. Each of these articles covers the developments for a one-year period. In each article there are between three and four hundred references to the literature. This shows somewhat of the scope of the application of the method. A few examples will be discussed briefly which will indicate types of analyses that can be made.

An interesting application was made by Coy, Sabo, and Keeler (1949) at the Squibb Laboratories at New Brunswick, New Jersey. Methods were developed for determining the potency of aged penicillin salts. It had been determined that a particular absorption band is present in the penicillin salt but not in any degradation products. Therefore, by making an analysis at one particular wavelength, it was possible to tell how much of the salt was still biologically active. Comparison with biological tests showed excellent agreement.

Another example, not altogether different from the foregoing, relates to the question of whether lubricating oils are from a Pennsylvania crude base. It has been found by Fred and Putscher (1949) that all Pennsylvania crude oils have an absorption band at 10.3 microns. With minor exceptions, others do not. In particular, certain Texas crudes which have color and other physical properties resembling the Pennsylvania crudes have no absorption at this band. Therefore, if one wishes to assure himself that he is obtaining Pennsylvania oil, or that he is not obtaining Pennsylvania oil, depending upon his desires, his car should be equipped with an infrared spectrograph. It is thought that this 10.3 micron

band may be due to an olefin with an internal unsubstituted double bond, since many olefinic compounds with such double bonds also have absorptions there.

Methods have been developed for quantitative analysis of alpha, beta, gamma, delta, and epsilon isomers of 1, 2, 3, 4, 5, 6-hexachlorocyclohexane (Daasch, 1947). The gamma isomer of this particular compound is an excellent insecticide. In order to satisfy governmental regulations pertaining to the purity of this substance, it was necessary to know the exact concentration of the gamma isomer. Techniques were developed for determining the presence of the isomers to less than 0.1 % of the total sample.

A similar problem solved by Anderson and Zerwekh (1949) involved the development of a method for the determination of the amounts of contaminating hydrocarbons in concentrates of n-heptane.

A liquid analysis, not involving concentrates, is described by Perry (1951). In this investigation, mixtures of five C<sub>10</sub> aromatics were analyzed. Synthetic mixtures showed that the accuracy of the method averaged about plus or minus 0.5% of the total sample. This is typical of liquid analyses using these techniques.

#### SUMMARY

Molecules that have different structure vibrate and rotate differently, hence have different infrared absorption spectrograms. Apparatus is available for detecting these differences. This satisfies the requirements for a method of chemical analysis based on differences in a physical property of the substances. That the method is satisfactory has been demonstrated in hundreds of applications.

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