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Infrared Absorption Spectra

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A RECENT REVIEW of the applications of infrared absorption spectrophotometry to problems in fat and oil chemistry (50) revealed that during the four-year period from 1950 through 1954 more than 100 papers dealing with this subject had appeared in the technical literature. The report showed that application of infrared absorption techniques is widespread, reaching just about all phases of the fat and oil industry.

The purpose of this paper is to discuss the characteristics of infrared absorption, to show how this branch of spectroscopy can be of considerable use in fat and oil chemistry, and to illustrate with specific examples some of its successful applications.

Figure 1, listing the various branches of spectroscopy in 15 subdivisions based on radiations in various portions of the electromagnetic spectrum and the use to which these radiations are put, provides a definition of "infrared absorption spectroscopy"—a study of the absorption by any specific material, of radiation in that portion of the electromagnetic spectrum between about 1 and 100 μ. A consideration of the energy relations of radiations in this wavelength range of the electromagnetic spectrum with the aid of the fundamental equation of Bohr,

$$\triangle E = h\,c/\lambda$$

(E = energy, h = Planck's constant, c = speed of light, and λ = wavelength), shows that they are related to energy level changes of about 1 kcal. (1 kcal. is equivalent to 30 μ.) Thus infrared absorption spectroscopy is intermediate in the three orders of magnitude of energy level changes, *ca.* 100 kcal., 1 kcal., and 0.01 kcal. Energy level changes of this intermediate value are changes in vibrational levels (Figure 2). Hence infrared absorption spectroscopy is vibrational spectra. Figure 2 illustrates that vibrational changes do not occur without accompanying changes in rotational levels. Hence absorption or emission of molecules in the infrared will, like electronic spectra, appear as bands consisting of many lines so close together in wavelength that, with the commercial spectrophotometers used in chemical spectroscopy, they will not be resolved. Infrared absorption spectra is thus vibrational (or strictly vibrational-rotational) band spectra involving intermediate values

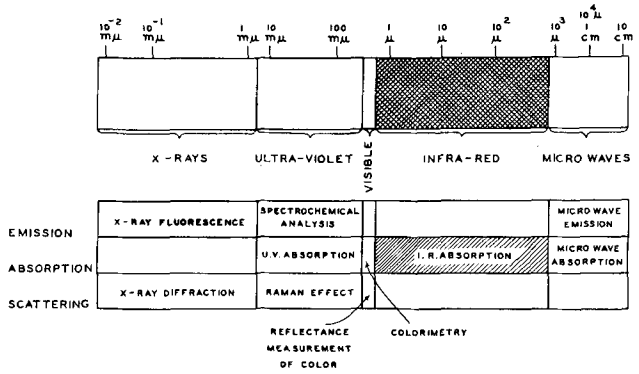

FIG. 1. Divisions of Chemical Spectroscopy.

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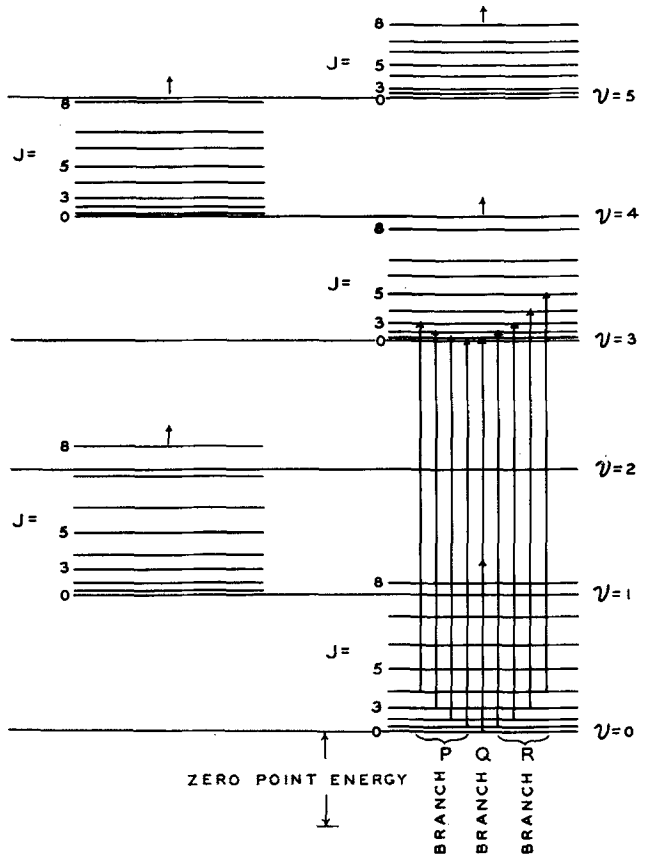


FIG. 2. Energy Level Table—Vibrational-Rotational Transitions.

of energy level changes. Examination of these bands, with instruments which have sufficient resolution to permit measurements of individual lines of the band structure, reveals that they often exhibit a central transparent region (as if a line were missing) with a series of lines going off to both short and long wavelength sides of this center. Selection rules limit changes in the rotational quantum number J to $\triangle J = \pm 1$ or 0. When $\triangle J = +1$, the total energy change in the vibrational-rotational transition will be greater than when $\triangle J = 0$; and when $\triangle J = -1$, it will be less than when $\triangle J = 0$. As energy change is related, by the Bohr equation, to the reciprocal of the wavelength, the greater energy changes, when $\triangle J$ is $+1$, will result in radiations of shorter wavelengths and when $\triangle J = -1$ will result in radiations of longer wavelengths. Those lines in the band arising from transitions in which $\triangle J = +1$, which are to the shorter wavelength side of the band, are called the R branch. Lines to the longer wavelength are called the P branch. The central single line which arises when $\triangle J = 0$, which is frequently missing, is called the Q branch.

The position in wavenumber (σ) of a rotational line in a vibrational-rotational band can be approximated (for a diatomic molecule) from the expression: $\sigma = \sigma_{vib.} \pm 2JB$; where $\sigma_{vib.}$ is the wavenumber for a pure vibrational transition, J is the rotational quantum number which takes on successive values 1, 2, 3, . . . , and B is a constant. When selection rules limit $\triangle J$ to ± 1, it can be seen from this expression that there can be no line corresponding to pure vibration. The Q branch will be missing. Such a band, with the central line missing, is called a parallel band from the fact that in a linear molecule when the dipole moment is parallel to the molecular line $\triangle J = 0$ is forbidden and a band with a blank center is observed. If $\triangle J = 0$ as well as ± 1 is permitted, a third or Q branch will appear where $\sigma = \sigma_{vib.}$ at the same frequency as that of the pure vibration. This Q branch will thus be at the center of the band. Bands which have all three, P, Q, and R, branches are called perpendicular bands, for in certain vibrations of linear molecules the dipole moment changes in a direction perpendicular to the molecular line, selection rules allow $\triangle J = 0$, and a central line appears in the band spectra. The 3.0 μ band of HCl vapor is a parallel band with the central gap. The 3.3 μ band of benzene vapor is an illustration of a perpendicular band with P, Q, and R branches. Transitions which give rise to P, Q, and R branches are illustrated for an overtone band in Figure 2. Consideration of the P, Q, and R branches are sometimes helpful in making assignments of individual infrared absorption bands.

A molecule having N atoms has 3N kinds of motion. Three of these are simple translations, and three are rotations about the three axes of inertia. The remaining $3N - 6$ kinds of motion are vibrational, and each is associated with a fundamental vibrational frequency which theoretically can give rise to an absorption band in the infrared portion of the electromagnetic spectrum. If the molecule is linear, there are only two modes of rotation and therefore $3N - 5$ vibrational frequencies.

It may thus be assumed that the number of infrared absorption bands is always readily computed exactly, for a known molecule, simply as $3N - 6$ (or $3N - 5$ for a linear molecule). Actually infrared absorption spectra is not this simple. Several factors contribute to make the actual number of observed bands considerably more or considerably less than $3N - 6$ and the resulting spectra considerably more complex. Among factors which decrease the number of absorption bands are these. a) The band is beyond the range of the measured spectrum; b) the band is too weak to be observed under the conditions of the particular measurements; c) the band is not observed because of degeneracy; and d) the band is forbidden by reasons of symmetry. These last two terms require some further explanation.

Two normal vibrations may take place at the same frequency. Obviously such vibrations will give rise to only a single observable absorption band. Such vibrations are called doubly-degenerate. In Figure 3 several types of vibrations are illustrated with the names frequently applied to each type. Figure 3-E illustrates double degeneracy. The deformation may be either in the plane of the paper or perpendicular to it. Both of these deformation vibrations will take place at the same frequency, and will give rise to only a single absorption band, *i.e.*, they are doubly-degenerate.

To be so-called "infrared active" a molecular vibration must be accompanied by a change in dipole moment. Hence molecules which have no dipole moment will not be expected to exhibit infrared absorption bands unless at the normal vibrations a variable moment occurs. A symmetrical molecule which has no permanent dipole moment will therefore not exhibit an infrared absorption band associ-

ated with a normal vibration which does not induce an electric dipole moment. Even in molecules which have a permanent electric dipole moment, not all the 3N — 6 normal vibration frequencies need result in absorption bands since in some instances a normal

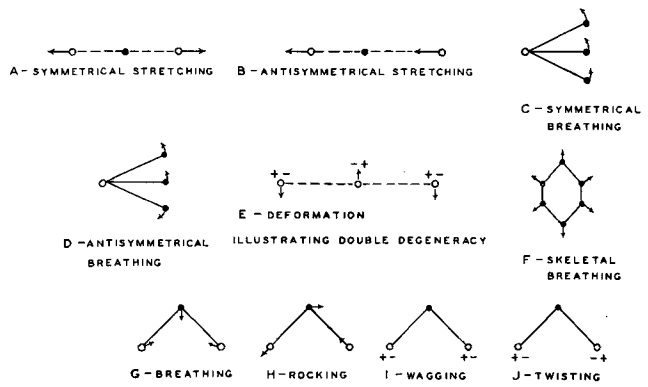


FIG. 3. Types of Molecular Vibrations which Give Rise to Infrared Absorption Bands.

vibration may induce no electric dipole moment, as is illustrated by the inactive torsional vibration of CH_3CCl_3.

Factors which increase the number of observed bands are appearance of: a) overtone bands, b) 3N — 6 modes of vibration give rise to fundamental frequencies, and the absorption bands resulting from difference bands, and c) combination bands. The them are the fundamental bands. These bands are usually, but not always, the most intense in the spectra. Overtone, combination, and difference bands can be found which may greatly complicate the observed absorption spectra.

If all the 3N — 6 fundamental vibrations were harmonic and all molecules considered only in the vapor state, all vibrational energy levels may be equidistant and all changes in vibrational levels, $\triangle v$, would be limited to ± 1 (or to 0). Actually neither of these assumptions is entirely valid, and the selection rules must be altered. The chief consequence of this is to allow $\triangle v$ to be ± 2 or more, permitting the appearance of overtone bands and combination or difference bands. The weak, but frequently observed, band at 2.24 μ has been assigned as a combination band of the 3.24 μ (3085 cm^{-1}) C-H fundamental stretching vibration and the 7.25 μ band (1380 cm^{-1}) arising from a CH_3, methyl group, bending — 3085 + 1380 = 4465 cm^{-1} = 2.24 μ. A weak band at 5.5 μ has been assigned as an overtone of a fundamental C-H deformation, at about 11 μ, of the $=CH_2$ group — 11 μ = 909 cm^{-1}; 909 × 2 = 1818 cm^{-1} = 5.50 μ. A band at 6.95 μ, 1440 cm^{-1}, is assigned to a difference between the fundamental bands at 3.24 μ = 3085 cm^{-1} (C-H fundamental stretching) and at 6.10 μ = 1640 cm^{-1} (C=C valency fundamental) — 3085 — 1640 = 1445 cm^{-1} = 6.95 μ.

Empirical Approach

While infrared absorption bands arise as a result of changes in vibrational levels of a molecule, a specific absorption is associated with some vibrating part of the molecule, influenced by the "molecular environment" of the molecule as a whole. Thus infrared absorption bands can usually be "assigned" to vibrations of parts of molecules which chemists call "functional groups." Julius (35) was probably the first to show that the infrared spectra of all compounds containing a specific group exhibited the same absorption maxima. He showed, for example, that the infrared spectra of compounds containing the methyl group always exhibit a band with maximum at 3.45 μ. Such empirical correlation of vibrating groups with specifically observed absorption maxima suggested the possibility of chemical identification and even of quantitative determinations. They are today the basis for analytical applications of infrared absorption spectra. The number of such correlations which have been studied and reported has been continually increasing. The review previously referred to (50) contains a table listing one hundred absorption bands employed in the application of infrared spectroscopy to fatty acid chemistry and the functional groups with which each can be correlated.

Correlations of this type are usually found in the infrared region between about 2 and 8 to 9 μ, and this region has become known as the "group frequency"

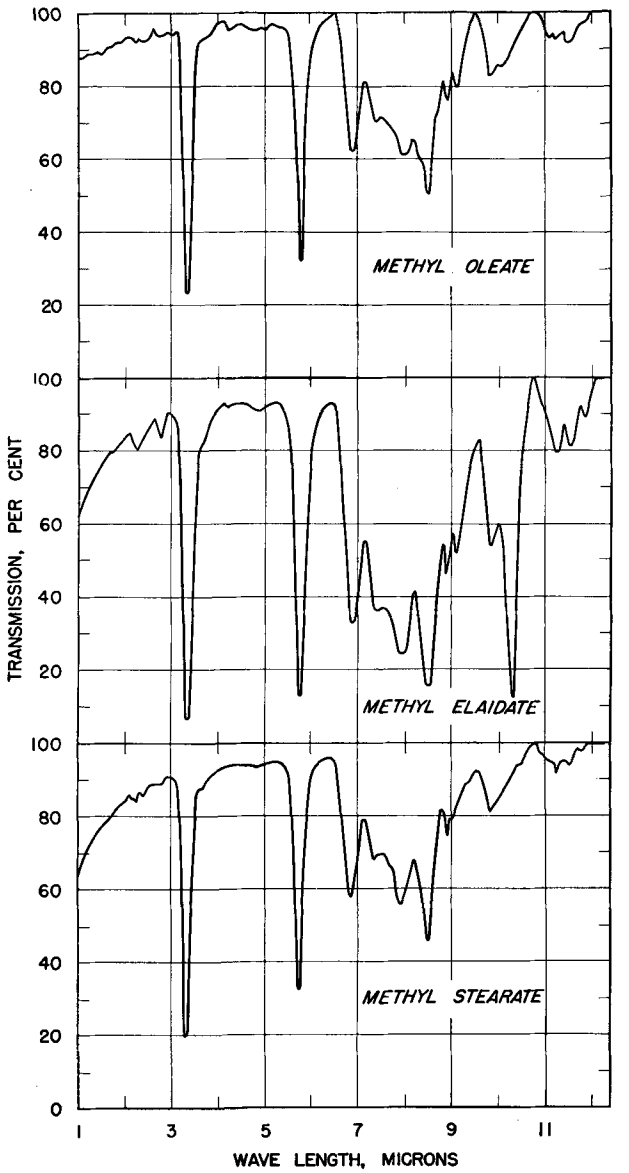


FIG. 4. Infrared Spectra of Methyl Oleate—Methyl Elaidate and Methyl Stearate.

region of the infrared spectra. Above about 10 μ to 25 μ or even out to about 40 μ the infrared region is called the "fingerprint" region for reasons which will appear later.

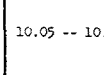
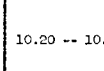
Measurements in the "group frequency" region can be used to establish the presence (or absence) of specific groups in attempts to identify unknown substances or to confirm (or obtain initial clues to) molecular structures. Absorptivities calculated for bands assigned to specific groups can be used in the equations derived from the Bouguer-Beer laws for quantitative analysis of single components or multicomponents in a manner exactly analogous to the use of these expressions in ultraviolet spectroscopy. The identification and the intensities of bands correlated to specific groups can also be used to follow the course of chemical reactions or to determine the rates of these reactions.

Specific Applications to Fat and Oil Chemistry: Determination of Trans-Acids

In the survey of the uses of ultraviolet absorption spectroscopy in fat and oil chemistry it was seen that while several successful applications have been made, one, the determination of polyunsaturated nonconjugated fatty acids by means of alkali isomerization, has received by far the greatest interest and attention. Similarly, in infrared absorption spectroscopy, a single application has created a great demand for use of the infrared spectrophotometer. This is the determination of *trans*-unsaturated acids and related compounds in the presence of their *cis*-unsaturated isomers and of saturated acids. This all started with the observation of Rasmussen, Brattain, and Zucco (57) that a strong band at 10.3 μ in the spectra of unsaturated compounds appears to be due to a *trans* C = C group (see Figure 4). The band has since been shown to arise from a C—H deformation about a *trans* C=C in the group RHC=CHR, *i.e.*, an internally unsaturated group (59), the type usually encountered in fatty acid chemistry. Shreve and his coworkers (60) developed a method for the quantitative determination of internal, isolated *trans*-bond concentration in saturated and monounsaturated octadecenoic acids and related compounds based on quantitative measurements of this 10.3 μ band in the spectra of elaidic acid. They found an absorptivity of about 0.4 in carbon disulfide solution. Paschke, Jackson, and Wheeler (52) showed that this absorptivity is about the same in the absorption spectra of pure methyl *cis*-9, *trans*-12-linoleate and that the absorptivity of this band in the spectra of pure methyl linoleaidate (*trans*-9, *trans*-12) was very nearly twice this value. These data strongly indicate that the absorptivities of the isolated *trans*-band at 10.3 μ are additive in nonconjugated compounds and that the method of Shreve *et al.* can be extended to the analysis of polyunsaturated nonconjugated olefinic acids and related compounds. Bickford and his coworkers (11) found that the absorptivity at 10.3 μ in the spectra of α-eleostearic acid (*cis*-9, *trans*-11, *trans*-13-octadecatrienoic) is exactly twice that reported for elaidic acid, and in the spectra of β-eleostearic acid (*trans*-9, *trans*-11, *trans*-13-octadecatrienoic) it is three times that of elaidic acid. These data strongly indicate that the intensities of the C—H deformation about the C = C group are additive in conjugated as well as nonconjugated compounds.

TABLE I

C—H Deformations About the C=C, Ethylenic, Group in the 10–15 μ Region

No.	Wavelength position of observed absorption band	Vibrating group giving rise to observed absorption band
	microns	
1.	10.05 -- 10.15	
2.	10.20 -- 10.36	 (trans)
2a.	10.34	Isolated trans
2b.	10.17	Cis, trans-conjugated
2c.	10.12	Trans, trans-conjugated
2d.	10.11	Cis, cis, trans-conjugated
2e.	10.09	Cis, trans, trans-conjugated
2f.	10.06	Trans, trans, trans-conjugated
3.	10.90 -- 11.05	
4.	11.17 -- 11.30	
5.	11.90 -- 12.50	
6.	13.0 > 15.0	 (cis)
6a.	10.95	Isolated cis
6b.	?	Cis, cis-conjugated
6c.	10.53	Cis, trans-conjugated

The use of the band at about 10 microns in the infrared absorption spectra is not limited to the detection and determination of isolated *trans*-double bonds although this is the only determination which has been described in detail. As shown in Table I, an early use of this assignment was to determine whether the C=C was an internal or a terminal group, and if terminal whether an isopropenyl, isopropylidene, etc. Similarly, as also shown in Table I, various conjugated combinations give rise to band maxima at specific wavelengths. Most of these correlations have been reported by Jackson *et al.* (34) and confirmed by Ahlers and coworkers (3). Ahlers *et al.* account for the position of maxima in the spectra of conjugated acids containing *trans*-bonds as a hypsochromic shift from the position of the isolated *trans*-band, small but significant and consistent with the effect of conjugation on the C—H deformation frequency of the system. O'Connor (50) extended this to include a similar, somewhat greater hypsochromic effect in *cis*-conjugated systems (Table I). All of these positions have been confirmed experimentally, except for the *cis, cis*-conjugation which was postulated to be at about 10.7 μ (50). Unfortunately, quantitative data and purified standards for measurements on available commercial instruments are lacking for development of precise quantitative methods. However infrared absorption spectra are capable of: a) providing a means for detection and determination of isolated *trans*-bonds, b) differentiating between terminal and internal C=C groups, c) detecting qualitatively and determining quantitatively the different

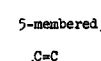
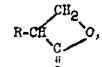
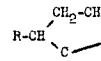
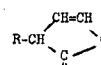
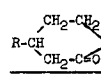
types of terminal C=C groups, and d) of qualitatively identifying and quantitatively determining diene and triene conjugated systems of various *cis-* and *trans*-bonds.

A summary of the actual practical uses of this method for determining isolated *trans*-bonds (which, as mentioned before, is the only determination for which a precise quantitative method has as yet been published) could easily be the subject of an entire paper, and space will permit only the briefest mention of some of them here. The quantitative method was shown to be more rapid, more specific, and more accurate than the chemical lead salt-alcohol method of determining *trans*-octadecenoic acid (33, 67). It has been used to establish the presence of *trans*-acids, esters, or glycerides in natural products including freshly rendered edible beef fat and edible oleo oil and oleostearin obtained from it (66); to confirm the *cis-trans* configuration of naturally occurring acids as the *α-* and *β*-eleostearic acids in tung oil (11, 53), punicic acid in pomegranate seed oil (6) and in snake gourd and Indian gourd oils (4); and to verify the absence of *trans*-acids in fatty acids isolated from fresh water algae (54).

The infrared absorption method for isolated *trans*-bonds has been used in a number of detailed studies

TABLE II

Absorption Bands in the Regions at About 3 μ and at About 6 μ Which Have Been Used in Applying Infrared Absorption Spectra to Autoxidation and Related Investigations

No.	Wavelength position of observed absorption band	Vibrating group giving rise to observed absorption band
	microns	
		A. About 3 μ
1.	2.75 -- 2.80	Free -O-H.
2.	2.82 -- 2.90	Bonded -O-H...O of single-bridged dimer.
3.	2.95 -- 3.25	Bonded H...O-H...O- of double-bridged polymer or cyclic -O- H -O- dimer.
4.	3.00 -- 3.05	R≡C-H
5.	3.22 -- 3.25	R_2=C-H_2
6.	3.28 -- 3.32	R_2=C-HR
7.	3.40 -- 3.45	R-C-H_3
8.	3.42 -- 3.50	R_2-C-H_2
9.	3.45 -- 3.48	R_3-CH
10.	3.50 -- 3.70	R-C(=O)-H
11.	3.70	C-H and bonded O-H...O combination band
		B. About 6 μ
		1. Aldehydes
12.	5.75 -- 5.80	RC(=O)H, saturated
13.	5.83 -- 5.90	PhC(=O)H, aryl
14.	5.85 -- 5.95	R-CH=CH-C(=O)H, α,β-unsaturated
		2. Ketones
15.	5.80 -- 5.85	$RCH_2C(=O)CH_2R$, saturated
16.	5.90 -- 5.95	Ph-C(=O)-CH_3, aryl-alkyl
17.	6.00 -- 6.02	Ph-C(=O)-Ph, diaryl
18.	6.00 -- 6.05	R-CH=CH-C(=O)-R, α,β-unsaturated
19.	5.63	 C=O, 4-membered, saturated ring
20.	5.73	 C=O, 5-membered, saturated ring
21.	5.81	 C=O, 6-membered, saturated ring, or  5-membered, α,β-unsaturated ring.
22.	5.95	 C=O, 6- (or 7-) membered, α,β-unsaturated ring
23.	5.90 -- 6.00	O=Ph=O, quinone, 2 C=O's on 1 ring
24.	6.05 -- 6.10	O=Ph-Ph=O, quinone, 2 C=O's on 2 rings
		3. Acids
25.	5.68	R-C(=O)-OH, saturated monomer
26.	5.80 -- 5.88	R-C(=O)-OH...O=C-R, saturated dimer
27.	5.90 -- 5.92	R-C=C-C(=O)-OH, α,β-unsaturated
28.	5.90 -- 5.95	Ph-C(=O)-OH, aryl
29.	6.00 -- 6.05	Chelated hydroxy-acids, some dicarboxylic acids.
		4. Esters
30.	5.65	H_2-C=C-C(=O)-OCH_3, vinyl ester
31.	5.75	R-C(=O)-OCH_3, saturated
32.	5.80 -- 5.82	R-C=C-C(=O)-OCH_3, α,β-unsaturated, or R-COOPh, aryl
		5. Lactones
33.	5.50	 β, or 4-membered saturated ring
34.	5.65	 γ, or 5-membered saturated ring
35.	5.72	 γ, or 5-membered α,β-unsaturated ring
36.	5.75	 ε, or 6-membered saturated ring

of both hydrogenation and autoxidation of vegetable and drying oils and similar products. Several workers have used infrared absorption to show that hydrogenation is accompanied by a *cis*- to *trans*-change in some of the double bonds of the unsaturated fatty acids (9, 41, 42, 58, 63, 72). Feuge and coworkers (21, 22) made a quantitative study of the hydrogenation of methyl oleate and triolein and of methyl linoleate and cottonseed oil, showing that the rate of formation of *trans*-isomers is increased by increasing the temperature, increasing the catalyst concentration, and decreasing the degree of dispersion of hydrogen during the hydrogenation.

Knight, Eddy, and Swern (38) and Swern and coworkers (65) have shown that autoxidation of methyl oleate results in the formation of hydroperoxides with *trans*-configurations regardless of whether autoxidation is conducted in the dark or in the presence of ultraviolet radiation. Several investigations have lead to the conclusions that autoxidation of methyl linoleate results in *cis, trans*-hydroperoxides if the autoxidation occurs at 0° but *trans, trans*-hydroperoxides if at room temperature or above (13, 29, 37, 55, 56).

Applications to Autoxidation, Rancidity, and Drying Properties

While a large portion of the attention which has been given to infrared absorption spectroscopy by fatty acid chemists has centered around studies of *cis*- and *trans*-isomerization by means of the bands at about 10.0 μ, applications using this tool have not been limited to such *cis, trans*-configurations. Several papers have reported investigations of the autoxidation of vegetable and drying oils by means of infrared absorption spectroscopy, and this technique has been applied to the related studies of the mechanism of reactions and identifications of products formed during rancidity of vegetable oils and the drying process of drying oils.

A method which can identify and quantitatively follow the fate of such groups as hydroxyl, hydroperoxido, epoxy, carboxy, carbonyl, etc., affords many possible means to increase our knowledge of these complicated mechanisms. Even with the number of applications reported recently, only scant advantage has as yet been taken of these new opportunities.

Morris (47) reviewed the recent studies on the mechanisms of fat oxidation and its relation to rancidity and included a discussion of the applications of infrared spectra to this problem. Gamble and Barnett (26) were probably the first to use infrared spectra to investigate the drying mechanism of oils, and a recent paper by Crecelius, Kagarise, and Alexander (17) credits infrared spectroscopy, along with ultraviolet, with considerably stepping up progress toward an understanding of drying oil oxidation mechanisms. In their excellent review entitled "Studies of the Mechanisms of Drying Oil Oxidation" they discuss in detail the interpretations of infrared spectra and changes in infrared spectra during drying.

Applications of infrared absorption spectroscopy to autoxidation, rancidity, and drying properties involve principally examinations of the changes in spectral properties about the 3.0, 6.0, and the 10.0 μ bands.

In Table II are listed some of the absorption bands with wavelength positions of maxima and correlations with vibrating groups which give rise to them, which have been of particular interest in examinations of autoxidation by means of infrared spectral changes in the 3 and the 6 μ regions. Bands which have been investigated in the 10 μ region are included in Table I.

The 3 μ Region

Lemon, Kirby, and Knapp (43) found that, in the early stages of autoxidation at temperatures from 22 to 100°, fractionated products of methyl esters of peanut oil fatty acids develop a band in the 3 μ region. This band was attributed to the —O—O—H, hydroperoxide, group. Later two bands at longer wavelengths appear, believed to be due to decomposition of the hydroperoxide to other compounds containing —O—H groups. Increasing the temperature increased the rate of both hydroperoxide formation and decomposition. The presence of iron stearate catalyzed only the decomposition.

Dugan, Beadle, and Henick (20) studied the infrared spectra of autoxidized methyl linoleate, using lithium fluoride optics to obtain higher resolution. Two bands were observed, both increasing with increased peroxide value, one sharp and distinct at 2.88 μ, the other broad with maximum about 2.92 μ. Reduction of the oxidized samples with KI reagent resulted in the disappearance of the band with maximum at 2.92 μ and appearance of a new band with maximum at 2.86 μ. The band with maximum at 2.92 μ was attributed to the —O—O—H group associated by hydrogen bonding. The bands at 2.86 and 2.88 μ were attributed to —O—H stretching vibrations. This conclusion is different from that of Shreve *et al.* (62), who considered the hydroperoxide and the hydroxyl stretching vibrations to be identical. However only under conditions of highest resolution would the differences reported by Dugan *et al.* be observed.

Adams and Auxier (1) reported changes in the infrared spectra in this region for synthetic oil as a function of drying time. The intensity of the hydroperoxide group, as followed by a band with maximum at 2.8 μ, increased while a band with maximum at 3.27 μ decreased. This latter band was attributed to a C—H stretching on a carbon atom adjacent to a double bond. The results thus indicate increase in hydroperoxide and decrease in unsaturation during drying. Similar results were found by Adams, Auxier, and Wilson (2) in their studies of the infrared absorption of dipentaerythritol esters of oleic, linoleic, and linolenic acids.

Several other investigators have used bands at about 3.0 μ to study autoxidation reactions including work reported by Honn, Bezman, and Daubert (32), McKay, Levitin, and Jones (44), Smith, Freeman, and Jack (64), and by Nicholls and Hoffman (48). The conclusions which can be reached from these studies at the present time and some of the problems which remain to be solved can be briefly summarized:

The appearance of bands at about 2.93 μ indicates formation of hydroperoxides. Appearance of additional bands at about this wavelength probably indicates alcoholic hydroxyl groups arising from further decomposition products during the oxidation. A specific method for differentiating between the hydroperoxide and alcoholic groups is still needed. Studies with higher resolution than those as yet reported are probably required for this work.

The disappearance of the band at 3.2 μ indicates the replacement of hydrogen on a double bond with some other radical, probably indicating polymerization. It is not unequivocally established whether a 3.2 μ position for a C—H

stretching indicates a C—H on an unsaturated carbon atom, RCH=CHR, or on a carbon α to a double bond, an α-methylenic group. Probably additional study, particularly with instruments capable of higher resolution, will resolve this question.

The 6 μ Region

Chang and Kummerow (16) used infrared spectra to detect the ketonic carbonyl group at 5.83 μ in the presence of the ester carbonyl group at 5.75 μ, thereby settling a controversial point by proving that oxidation polymers of ethyl linoleate are linked through carbon to oxygen bonds rather than carbon to carbon bonds.

The course of autoxidation of milk fat was followed by observations of changes in the infrared spectra of the volatile components by A. S. Henick (30). An off-flavor, off-odor sample of milk was steam-distilled *in vacuo,* and the infrared spectra of the distilled fractions were examined in CS_2 solution. The spectra of fresh milk exhibited only two bands in this region at 5.80 and 5.75 μ. Upon storage the 5.80 μ band remains unchanged, but the 5.75 μ band shifts to 5.70 μ. With longer storage new peaks appear at 5.86 and 5.91 μ, and still longer storage results in a band with maximum at 6.10 μ which increases in intensity as the storage period is increased. Infrared spectrophotometry was found to be more sensitive to changes than a qualified taste panel and considerably more sensitive than peroxide value determinations.

There is some difficulty in resolving the various C=O vibrations at about 6 μ. Dugan, Beadle, and Henick (20), even with their lithium fluoride, report that absorption arising from keto and aldehyde carbonyl appeared only as indefinite shoulders on the strong bands due to ester carbonyl. In spite of this difficulty, infrared absorption spectroscopy has made considerable contributions to the understanding of autoxidation reaction by the interpretations of additional bands which appear about the 5.72 μ ester C=O stretching and which indicate the formation of aldehydes, ketones, or acids.

The 10 μ Region

Most interpretations of infrared absorption spectra at about 10 μ involve *cis, trans*-differentiations already described. Wheeler, reporting on the thermal polymerization of esters of isomeric linoleic and linolenic acids (71), made considerable use of absorption in this region to explain dimer and trimer formation. *Cis, trans*-conjugated isomers were found to polymerize about six times as rapidly as nonconjugated compounds, and *trans, trans*-conjugated isomers five times as rapidly as the *cis, trans*-conjugated isomers. Linolenates react in a similar manner, but the rate of polymerization is much more rapid than for the corresponding dienes.

Smith, Freeman, and Jack (64) obtained infrared absorption curves of monoethenoid methyl ester fractions of milk fat in the range C_{10} to C_{20} and compared them to available spectra of pure saturated and unsaturated esters of long chain fatty acids. A band at 10.36 μ indicated *trans*-bond formation, estimated from 14 to 27% in the various monoethenoid methyl esters. Spectra of the C_{18} to C_{20} fractions indicated conjugation entirely of the *cis, trans*-configuration. The C_{10} fraction exhibited infrared evidence for terminal bonds between the 9 and 10 carbon atoms.

Use of the bands at about 10 μ can be briefly summarized by saying that the detection and determination of isolated *trans*-bonds, and the identification of various *cis, trans*-isomerizations has proven of considerable value in autoxidation studies.

Applications to Glycerides, Lipides, and Phospholipides and to Oil-Styrene Copolymerization

Kuhrt and coworkers (39, 40) identified the monoglycerides isolated from lard and bread and the monoglycerides from triglycerides in the intestinal tract of humans by means of infrared spectra. O'Connor, DuPré, and Feuge (51) compared the infrared spectra of mono-, di-, and triglycerides. They found three regions of the spectra in particular which might be useful in the development of analytical procedures: a) the O—H stretching region at about 3.0 μ, which can be used to confirm the absence of mono- or diglycerides in the preparation of triglycerides by the complete absence of the characteristic O—H stretching vibration band; b) the region of C—O stretching at about 9 μ where monoglycerides exhibit a characteristic band at 9.5 μ, diglycerides exhibit a band with maximum at 9.6 μ, and triglycerides exhibit no bands. (Bands with maxima at 9.5 and 9.6 μ were assigned to C—O stretching of α-substituted secondary alcoholic groups. The difference in wavelength position of the maxima is accounted for by the difference in the α-substituent groups. These bands probably permit the quantitative determination of mono-, di, and triglycerides in admixtures by means of the multicomponent spectrophotometric method); c) the region of C—H bending about *trans* C=C groups, above 10 μ where triglycerides of mixed long and short chain fatty acids, *i.e.,* acetoolein, dibutyroolein, etc., exhibit a band with maximum at 10.4 μ. [The intensity of this band must be considered in applying the method of Shreve *et al.* (60) to determine the concentration of *trans*-isomers in such triglycerides by including in the "background" correction, values obtained from the spectra of the appropriate pure triglycerides.]

Several studies have been made of the spectral properties of lipides and phospholipides. Baer (7) presented the spectra of three synthetic L-α-lecithins (dimyristoyl, dipalmitoyl, and distearoyl), which constitute a homologous series of pure phospholipides. The infrared spectra of α-cephalins of the L-series were studied by Baer, Maurukas, and Russell (8), who reported the spectra of distearoyl-, dipalmitoyl-, and dimyristoyl-cephalin. The infrared spectra of lipoproteins isolated from human blood serum were compared with similar spectra of reference compounds including vegetable oil, ovalbumin, cholesteryl, egg lecithin, etc., by Freeman, Lindgren, Ng, and Nichols (24). Considerable use of infrared spectra is described by Marinetti and Stotz (45, 46) in their studies of the structure of phospholipides. The infrared spectra of dipalmitoleyl-L-α-glyceryl-phosphorylcholine from yeast was compared to that of its hydrogenation product, dipalmitoyl-L-α-lecithin, and to the spectra of palmitoleic acid by Hanahan and Jayko (27).

From the data compiled by these workers several applications of infrared absorption spectra to the structural problems and analysis of lipides and phospholipides can be suggested.

a) Lipide content can be determined by estimation of the intensity of the C=O ester carbonyl band.

b) Unesterified cholesterol can be determined by the band at 9.5 μ.

c) Protein content can be estimated by consideration of the ratio of the intensities of the absorption bands at 5.8 and 6.1 μ.

d) A P—O—C stretching vibration gives rise to a band with maxima at 10.3 μ. Hence this band is found in both saturated and unsaturated phospholipides. Consequently *trans*-bonds in these compounds cannot be determined by measurement at this wavelength only. A method has been suggested involving measurement at 10.3 μ for the combined P—O—C stretching and the *trans* C=C group, followed by hydrogenation and remeasurement of the band. Decrease in the intensity can be correlated with *trans*-unsaturated absorption.

e) Glycerophospholipides can be determined in admixture with sphingolipides by the multicomponent spectrophotometric method by measurement of bands at 5.76–5.78 μ (glycerophospholipides) and at 6.1 μ (sphingolipides).

Infrared spectra have proven very useful in oil-styrene copolymer studies. Oil content in the oil-styrene copolymer can be determined by use of the strong ester C=O band at about 5.8 μ, a region where polystyrene is relatively transparent. Styrene can be detected and probably determined quantitatively by use of the benzenoid nuclei "breathing" bands at 13.2 and 14.3 μ (12). The effect of several different fatty acids on the polymerization of styrene was investigated by Harrison and Tolberg (28). They established a multicomponent system for analysis of the benzoate, fatty ester, and polystyrene. Bezman and Browning (10) used the 5.8 μ band to measure quantitatively the oil content of copolymers made in aqueous emulsions of styrene with linseed oils. They showed that untreated, nonconjugated oil does not form polymers but that copolymerization does occur in treated, *i.e.,* blown, thermally polymerized, or oxidized oils containing conjugated linkages. They conclude that "in systems as complex as natural drying oils this" (*i.e.,* infrared spectra) "may indeed be the only reliable method for determining reaction of oil and the changes in chemical groups."

Elucidation of Molecular Structure

One of the principal uses of infrared absorption spectra has been to aid in studies of the elucidation of molecular structure. In the field of fats and oils several fascinating examples of this use of infrared spectra have been reported. A description of the stepwise application of infrared absorption spectra to a problem of establishing the structure of an entirely unknown molecule is, even in outline form, too lengthy to be attempted here. The work of Paschke and his group (53) and of Bickford and his coworkers (11) on the structure of α- and β-eleostearic acids and of Marinetti and Stotz (45, 46) on the structure of phospholipides, by means of infrared absorption spectra, have been referred to earlier. To the reader interested in details of the method employed, the work of Celmer and Solomons (15) on the proof of the structure of mycomycin and isomycomycin, which appeared in a series of four papers in the Journal of the American Chemical Society, is recommended.

In a search for the hypotensive principle of tung oil Davis, Conroy, and Shakespeare (19) used infrared absorption to prove that a crystalline unsaturated hydroxylated monocarboxylic acid was 9,14-dihydroxy-10,12-octadecadienoic acid. The structure of lactobacillic acid was established by Hofmann, Lucas, and Sax (31) and of sterculic acid by Nunn (49), largely by use of infrared absorption spectra. Khan (36) used infrared absorption to show that stearolic acid had an internal triple bond, and Freeman (23) and Cason, Freeman, and Sumrell (14) describe a detailed proof of the structure of a C_{27} phthenoic acid based mainly on infrared absorption data. Other uses of infrared absorption spectra for problems of these types have been reported by Walborsky, Davis, and Howton (70), Friedberg, Marshall, and Newman (25), and by Crombie (18).

Miscellaneous Applications of Infrared Absorption Spectra

As we attempt to pick out results of specific workers to illustrate the wide applications of infrared absorption spectroscopy, the efforts of many other investigators cannot even be mentioned. We will content ourselves with mention of only three or four more applications which seem particularly pertinent.

Shreve *et al.* (61, 62) showed in a detailed study of the infrared absorption spectra of epoxy and hydroperoxide compounds that in the spectra of the former a band with a maximum at 11.2 μ is exhibited if the oxirane ring is derived from an internal monounsaturated compound having the *trans*-configuration at the double bond while the corresponding *cis*-configuration gives rise to a weak band at 12.0 μ only.

Thomas (68) showed that even when the two groups are present in the same molecule as in ω-hydroxypalmitic acid, it is possible to determine quantitatively, by means of infrared absorption spectroscopy, the concentration of the alcoholic —OH and the carboxyl COOH groups. Ahlers and McTaggart (5) have suggested infrared spectroscopic methods for quantitative determination of hydroxyl, ketone, and ester groups, avoiding hydrogen bonding effects by use of very dilute solutions.

Van Tamelen and Shamma (69) suggest an interesting method, based on infrared spectra, for the determination of the position of double bonds by means of a study of iodolactonization reaction products. A band at 5.6 μ indicates that the starting acid was probably β-γ or γ-Δ unsaturated. Absorption at 5.75 μ demonstrates the probable presence of a Δ-ϵ double bond.

Fingerprint Technique

The infrared portion of the electromagnetic spectrum may be considered as extending from the edge of the visible region, about 1 μ, to the beginning of microwave spectroscopy, about 1000 μ. In contrast to this great expanse practically all applications of infrared spectroscopy to chemical problems have been confined to the "rock salt" region—so-called because common salt is the material used for all optics, including prisms, windows, lenses, etc.—between 1 and 15 μ. Use of different materials for prisms and other optical components has extended the usable infrared region to about 25 μ (KBr), and to about 40 μ (CsBr or KRS, a thallium bromoiodide). Beyond about 40 μ measurements can be made only with the use of grating instruments. Isolated measurements in the infrared spectra to about 300 μ, using grating instruments, have been reported.

Probably 95–98% of the applications of any significance in the chemistry of fats and oils have been made in the region between 2 and 15 μ. As observed earlier, the lower half of this region from about 2 to 8 μ has been called the "group frequency" region

because in this region are found bands which can more or less readily be correlated to the vibrations of specific functional groups. Beyond 8 or 9 μ the vibrations appear to be associated with larger groups, often of the molecule as a unit. Hence they are very characteristic of specific molecules, and this region has been referred to as a fingerprint of the molecule and the technique used in this region as the fingerprint technique.

The fingerprint technique, as the name implies, consists merely of comparing the spectrum of an unknown material with a series of standards and identification by direct "fingerprint" comparison. Let us for a moment consider identifications by means of fingerprints. A fingerprint is lifted at the scene of a crime by the local police and sent to the Federal Bureau of Investigation for identification. A group of experts make the fingerprint search, identify the suspect, and wire description. Apprehension follows within a few hours. What happens however if a fingerprint matching the one lifted from the scene of the crime is not found in the files of the Federal Bureau of Investigation? Nothing. As far as fingerprint identification is concerned, the local officers are no farther ahead than if they had not found a print. The success of the technique depends upon an elaborate fingerprint file. So in an attempted identification of a molecule by its infrared fingerprint a large collection of infrared spectra of pure compounds is required. This requirement has delayed the development of the fingerprint method of chemical identification and promoted the "group frequency" type of qualitative analysis.

However the potential advantages of being able to identify any molecule by a direct comparison of its infrared absorption spectra are so great that several large organizations are combining efforts to obtain and maintain a fingerprint file of all known molecules. Through the American Society of Testing Materials these spectra are being made available.

As soon as a file of infrared fingerprints, anywhere near adequate to permit identifications, has been established another problem is presented. The number of molecules is so great that visual comparisons to identify the unknown would soon become prohibitive in time. This problem has received considerable attention and some progress made toward its solution. From the A.S.T.M. instead of obtaining a three- or four-foot long infrared spectral curve, one purchases an IBM card on which all the specific, characteristic absorption data, as well as some pertinent chemical data, for a particular compound have been coded. An infrared fingerprint identification is made by use of an IBM sorter which rapidly rejects cards which do not have a required absorption maximum, an observed region of transparency, or a particular chemical grouping. (Recent reports describe uses of combinations of these factors in a simultantous multiple sort which greatly speeds up this part of the identification.) At the present time well over 10,000 cards are available. An intense program is just getting into full swing involving the cooperation of more than 100 abstractors who are covering the literature to obtain data on an ever-increasing number of compounds. Once a library of cards is established, chemical qualitative analysis consists in merely obtaining an infrared absorption spectra of the unknown and a series of sorts by means of an IBM machine. This technique is no longer a wild proposal. It is today being used in scores of chemical organizations. It is mentioned because, while not actually used in any specific fat and oil application, as far as we know, it is of course readily applicable to fat and oil analyses and its implications are so great that it should not be overlooked. The analytical laboratory of tomorrow, consisting of merely one or more streamlined automatically recording infrared spectrophotometers, an IBM sorter, and files of IBM punched cards, will differ greatly in appearance from the typical wet-method analytical laboratory of today.

Conclusions

Considerable strides have been made in the applications of infrared absorption spectra to solutions of problems of the fat and oil industry. As in applications in other fields, these advances have not been without some difficulties. In the recent review (50) previously referred to, the three main problems facing infrared absorption spectroscopy and its application to fats and oils were discussed. These three problems are:

Need for good quantitative spectra of very carefully prepared pure compounds, measured under instrumental conditions which can be reproduced in future measurements of samples for analysis;

Increased resolution (as seen in some of the examples, several identifications and determinations are being made, if at all, only with difficulty due to insufficient resolution);

and

Difficulties in interchange of quantitative infrared absorption data between different laboratories. (Instruments are not usually standardized hence absorptivities cannot be used for quantitative determinations in another laboratory using a different instrument.)

These problems are faced by users of infrared absorption techniques in all fields. The importance of the applications is sufficient guarantee that they will be completely solved. The tremendous activity in the application of infrared absorption spectroscopy to fats and oils, as evidenced by the number of technical publications during the last four or five years, is only the beginning, only the introduction of infrared spectroscopy to fat and oil chemistry. In the immediate future it can be expected to exert considerable influence upon the methods of analysis, upon production control, and upon research in fat and oil chemistry.

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Dilatometric Measurements

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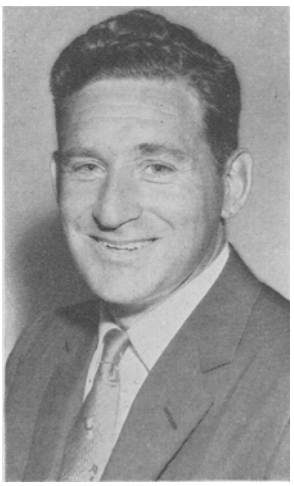
DILATOMETRY IS ESSENTIALLY a measurement of changes in specific volume. It is useful in the field of fats and oils to detect or analyze phase transformations because fats expand when they melt and generally contract when they undergo polymorphic change to a more stable form.



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Dilatometric measurements have great value in the margarine and shortening industries because they characterize fats over a wide temperature range. Plastic fats are mixtures of liquid oil and small crystals of solid fat, and their consistency is largely dependent upon their solid fat content. It is, of course, advantageous to know if a fat will produce a product with desirable consistency characteristics before the product is plasticized. Since dilatometry provides a fairly simple means of estimating solid fat contents at various temperatures, it is useful both for consistency control and for formulation work.

According to Andersen (1), dilatometry has been used as an analytical method in some margarine establishments since the early 1920's. The first publication on this subject appears to have been by Norman in 1931 (2). Hofgaard published dilatometric data on a large number of fats in 1938 and also pointed out the relationship between dilatometric curves and solid fat content (3). Since his work was published in Danish, it was not widely read in this country at that time.

Interest in dilatometric measurements in this country before 1940 is indicated by a number of publications (4, 5). However the first extensive studies which appeared in the literature were by Bailey and co-workers in a series of articles beginning in 1944 (6, 7, 8).

When the specific volume of a fat is plotted against temperature over a wide temperature range, one obtains an irregular curve similar to the one in Figure 1. There is a linear volume-temperature relationship only at temperatures below T_S, where the fat is completely solidified and above T_L, where the fat is completely liquefied. When extending the solid and liquid