in the sugar cane oil. The unsaponifiable fraction is mainly unsaturated hydrocarbons with smaller amounts of sterols and other alcohols.

Acknowledgment

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The Application of Infrared Spectroscopy to Fat and Oil Chemistry[1]

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THE application of spectroscopy to the field of organic chemistry during the past 10 years has been most spectacular. Most oil chemists are familiar with the analytical uses of ultraviolet spectrophotometry and with the proposed change in the approved method for the determination of oil color employing visible spectrophotometry. Another section of the electromagnetic spectrum, the infrared, is now available to the chemist in his research. It is with this that this paper is concerned.

Knowledge of the infrared region of the spectrum and of its potentialities as a powerful analytical tool goes back about 50 years, but practical application on a routine basis is not yet 10 years old. It was during the war, in fact, that the infrared spectrophotometer came of age. The analyses of synthetic rubber and high-octane gasolines as well as the characterization of penicillin are but examples of the many fields in which the infrared spectrophotometer performed functions which would have been impossible by any other available means in the time allowed. Since the war infrared spectrophotometry has found its way into almost every phase of organic chemistry, and the tremendous potential it possesses should not be overlooked by workers in fat and oil chemistry.

The applicability of the infrared and related regions of the spectrum to the analysis of organic molecules is based on the absorption of light energy by these molecules and the atoms of which they are composed. Every combination of atoms has the ability to vibrate in response to energy of a certain frequency (or wave length), and the energy thus absorbed may be determined photometrically. When organic substances are exposed to energy of appropriate wave length, absorption occurs with accompanying conversion of the energy into one of three kinds of molecular or atomic motion, depending upon the wave length of the light. This results in three types of spectra, rotational, electronic, and vibrational. Rotational spectra occur in the far infrared and microwave regions and to date have had little application to organic chemistry. Electronic spectra are those with which research workers are more familiar, forming the basis for visible and ultraviolet spectroscopy. The third type occurs when the absorption of radiant energy gives rise to changes in the vibration of the molecule, and it is the measurement of this absorption which constitutes practical infrared spectroscopy.

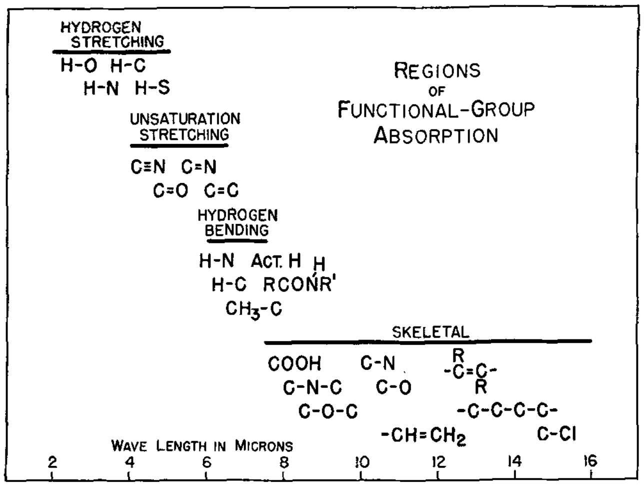

FIG. 1.

It has been established that a molecule having *n* atoms has 3 *n* kinds of motion. Of these, five or six, depending on the molecular symmetry, are motions of the molecule as a rigid unit and do not result in vibrational spectra. The remaining kinds of motion are vibrational in nature, and each has a characteristic frequency. It is possible to derive mathematically the frequencies characteristic of certain functional groups in a simple molecule, and this derivation forms a means of identification for absorption bands in the infrared (1). In practice most absorption bands have been established by empirical means using known compounds.

THE region of the infrared spectrum which is most commonly used at present extends from 2 to 16 microns and is known as the "rock-salt region," since it is the region of high transmission of sodium chlo-

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[1] Presented at the fall meeting of the American Oil Chemists' Society, Chicago, November, 1949.

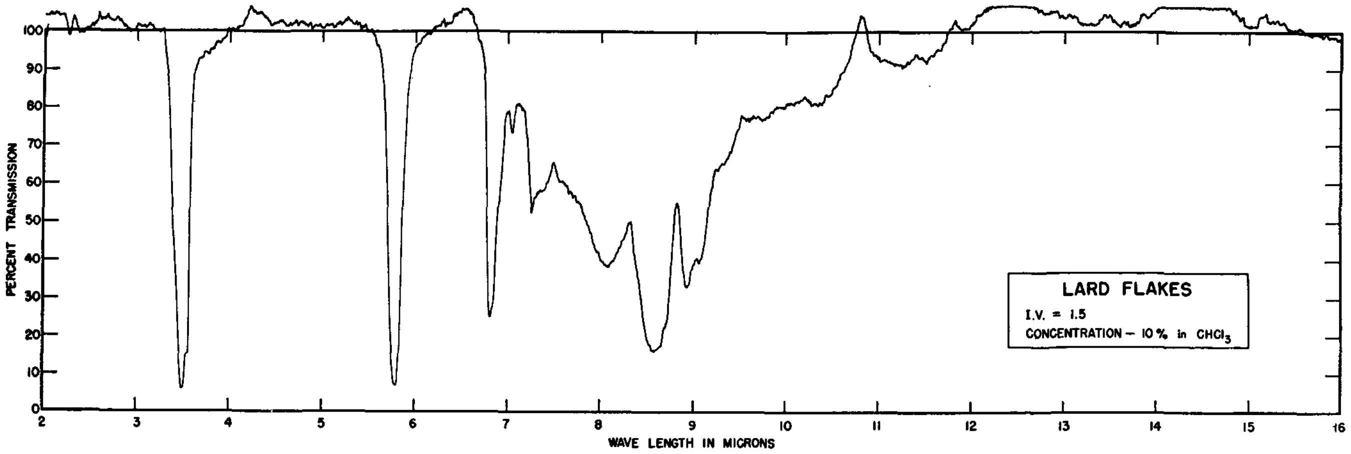

FIG. 2.

ride. Figure 1 presents regions of absorption bands attributed to specific functional groups as observed in this laboratory in studies on fats and fatty-acid derivatives. In the range from 2 to 5 microns, known as the hydrogen-stretching or high-frequency region, there occur absorption bands arising from the stretching vibration of a hydrogen atom attached to some other atom. Most common to organic molecules is the carbon-hydrogen bond which absorbs in the region of 3-3.5 microns. In the adjacent region, from 4.0 to about 6.5 microns, absorption is attributed to unsaturation. Bands here are assigned to carbon-to-carbon double and triple bonds, carbon-to-nitrogen double and triple bonds, and carbon-to-oxygen double bonds.

The hydrogen-bending region covers the range from 6.0 to 7.5 microns and includes absorption arising from $-NH_2$ groups, $-CH_2-$ and $-CH_3$ groups, N-substituted amides, and others.

The balance of the spectrum, 7.5 to 16 microns, referred to as the skeletal region, presents absorptions generally involving all of the atoms in a molecule. Considerable difficulty is encountered in the positive assignment of some of the absorptions occurring in this region. As a result, in characterizing a substance by means of infrared absorption, greatest emphasis is placed on bands in the region of shorter wave length whereas those in the region of higher wave length are confirmatory.

An infrared spectrogram of an unknown substance can be termed a fingerprint of that substance, and an examination of the curve will usually reveal a great many things about the structure and composition of the substance. By reference to the table of frequencies assigned to specific functional groups and by comparison of the spectrogram of an unknown compound with those of known compounds, it is often possible to identify a substance positively. It should also be pointed out that the *absence* of a band at an assigned wave length for a certain functional group is usually sufficient evidence to rule out the presence of that group in the substance. The method is not sufficiently sensitive to discriminate among homologs differing by only a few carbon atoms.

As an example of the type of curve obtained on a commercial infrared spectrophotometer and of the data obtainable from such a curve, the spectrogram of lard flakes is shown in Figure 2. This spectrogram was prepared on a Baird Infrared Recording Spectrophotometer; the absorption due to the solvent was previously eliminated through the double beam principle of the instrument. Beginning at the left or short-wave-length end of the curve, the absorption caused by carbon-to-hydrogen linkages present in the aliphatic chain and in the glycerol molecule is first encountered. This band is a combination of separate bands, resulting from C-H, CH_2, and CH_3 absorptions. The use of a lithium fluoride prism, which has higher resolution in this region, would show this to be several distinct absorption bands. The next minimum is at 5.75 microns and is caused by the presence of the ester carbonyl. The absorption at 6.8 microns is attributed to carbon-hydrogen bending, specifically CH_2 and CH_3 in this case. The active hydrogen adjacent to the carboxyl group in the aliphatic chain is responsible for the band at 7.1 microns, and the terminal methyl groups on the aliphatic chains cause the absorption at 7.25 microns. The broad minima at 8.1, 8.6, and 9.0 microns, in the skeletal region, are characteristic of esters. The balance of the curve is somewhat vague in this instance and of little value. It is evident from the inspection of this one curve that a substantial amount of information about the material under surveillance can be deduced.

INFRARED absorption can be studied in the solid, the liquid, or the vapor state; and appropriate cells are available. However unless extremely thin samples are used, solids and pure liquids may absorb so greatly throughout the spectral region that the spectrograms obtained are almost valueless. Since the obtaining and handling of sufficiently thin samples are difficult, a better approach is through the use of solutions. Solvents should be employed which have good transparency in the infrared, such as CCl_4, $CHCl_3$, and CS_2. If the substance being studied is insoluble, it can be ground in a carrier such as Nujol and smeared on a rock-salt plate or placed between plates in the form of a sandwich.

Quantitative analyses, although not so popular at present as qualitative, are easily performed. In most cases however it is necessary that the components be known and that samples of the pure materials be available in order to establish reference curves. Accuracies of the order of 1 to 2% are possible.

The literature contains many references to the use of infrared spectroscopy, but little is to be found in regard to its application to fat and oil chemistry. The work of Rao and Daubert (2), who characterized vaccenic acid as the *trans* isomer, and of Honn, Bezman, and Daubert (3), who studied the autoxidation of linseed oil by means of infrared absorption, as well as the studies of Shreve, Heether, Knight, and Swern (4) on the *cis-trans* isomers of unsaturated fatty compounds are among the notable recent contributions to the chemistry of fats and oils.

In fatty-acid chemistry, as in all organic chemistry, infrared spectroscopy has already become an indispensable tool. It is being applied to both theoretical and practical problems and has only begun to demonstrate its real value.

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The Nature of Soil to Be Deterged and Its Bonding to the Surface[1]

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Summary

A SOIL is ordinarily composed in varying amounts of oil, wax, or grease; solid particles of diverse types; and special water-soluble or water-dispersible materials such as sugar, salts, starch, etc. Quantitatively the fatty portion on fabrics may run to a substantial fraction of 1% and contains roughly one-third neutral fat, one-third higher fatty acids, one-third other materials, and undetermined. Airborne dust may contain over 20% of fatty matter, over 30 per cent of other organic matter. Soil is retained on fabrics by mechanical forces, chemical forces, electrostatic attraction, and oil-bonding, which itself operates by means of electrical forces on the molecular scale.

The fundamental equations of wetting are presented. They imply that oily soils will gravitate toward the smallest capillaries in fabrics and thus become increasingly difficult to remove as the soiled fabric ages. Polymerization of unsaturated oils and chemical linkage of conjugated unsaturated bonds to active sites on the fibers are also factors in the setting of soil as fabric ages.

For extremely light soiling, the darkening of the fabric is roughly proportional to the amount of soil. As degree of soiling increases, the amounts of soil needed to give proportional darkening become enormously greater. From the viewpoint of detergency this means that the difference between good and bad results depends on removal of the last traces of soil.

The nature of the soil to be removed and the surface from which it is removed has been stressed necessarily, in recent publications by two of us (12, 16). Thus the removal of siliceous soil from metal and from porcelain constitutes two different problems. Likewise the removal of metal particles held by an oily matrix is a different problem with those two types of surface.

Much work on soaps or more recently on synthetic detergents has called for washing tests with some artificial soil. This has in general dealt with a surface of cotton or woolen fabric and a soil of oily nature pigmented with carbon black. Relatively little work has been carried out to determine quantitatively what soil may be, what causes it to adhere to a surface, and the influence of the nature of the fabric or other substrate. So although a limited amount of quantitative work is included in this series, the discussion which follows is largely qualitative and speculative. For simplicity, the numerous terms in use, such as hydrophyllic, lipophyllic, etc., have been roughly translated as either polar or nonpolar. By polar we mean soluble in or preferentially wet by water and other solvents with high dipole moment. By nonpolar we mean soluble in or preferentially wet by nonpolar liquids and not by water. Nonpolar substances may have appreciable dipole moments although not as great as polar substances.

Qualitative Nature of Soil

Soil on clothing, household textiles, dishes, the floor, or other surfaces is always a mixture. The ingredients will vary according to the use and situation of the surface. Many components have been mentioned by different investigators. Those described as being possible components, according to the condition of use, include the following:

Oily, Waxy, or Greasy Soil. This may contain saponifiable oils, including those of both animal and vegetable origin; unsaponifiable matter such as long chain alcohols and mineral oils. All of these substances are nonpolar, not readily wet by water.

Solid Soil. Solid soil may or may not be coated with a greasy film. It may consist of particles of soot, dust, clay, carbon, sand, and iron rust (5, 10). The electrical charge, while generally negative, may occasionally be positive. Dirt particles may be relatively polar such as sand, or nonpolar such as carbon black. All particles coated with oils, waxes, or grease are nonpolar (14).

Special Types of Soil. These may consist of food residues such as sugar, starch, and salts, readily wet by and usually readily soluble in water; proteins such as eggs, blood, and other albuminous matter, readily wet by and partially soluble in water, except at high temperatures. In addition, various stains are encountered which may be more or less water-soluble or which may require special removal treatment other than the usual detergent process.

Perspiration, often an important soil ingredient on clothing, is itself a complex mixture of substances, partly water-soluble, partly insoluble (9). In addi-

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