

# INDUSTRIAL AND ENGINEERING CHEMISTRY

## ANALYTICAL EDITION

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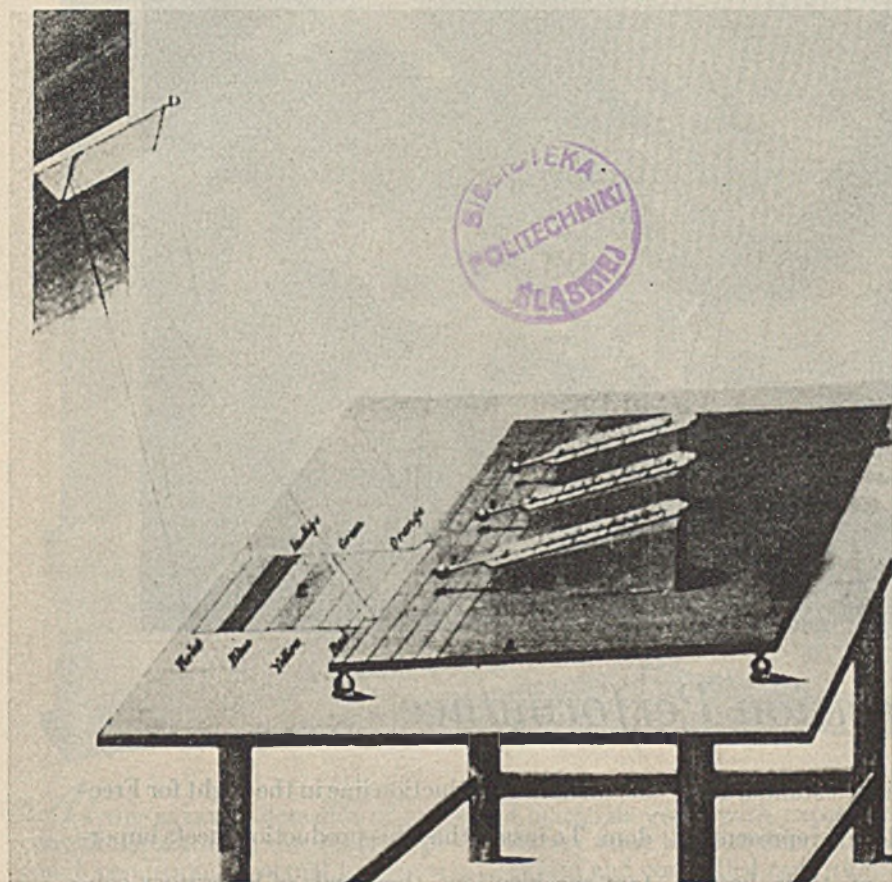
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## Infrared Spectroscopy. Industrial Applications . . . . .

R. B. Barnes, Urner Liddel, and V. Z. Williams 659



Because of the high value of this comprehensive article as a work of reference, a special arrangement has been made to have it republished in permanent book form instead of the usual standard reprint. In addition to the material here presented, the bound reprints will also contain a bibliography of the literature of infrared spectroscopy consisting of some 2000 items. The bibliography was omitted here because of space limitations. The book can be obtained for probably \$2.25 from Reinhold Publishing Corp., 330 West 42nd St., New York 18, N. Y.



Herschel's Drawing of the Apparatus Used in the Discovery of Infrared Radiation

This drawing appeared in a paper by Sir Frederick William Herschel in 1800 and is copied from the "Philosophical Transactions" of that year. The spectrum of sunlight produced by a prism was allowed to fall on a table. The temperature rise produced by radiation beyond the red was measured by one thermometer while the other two were used as controls.

## Book Reviews . . . . . 710

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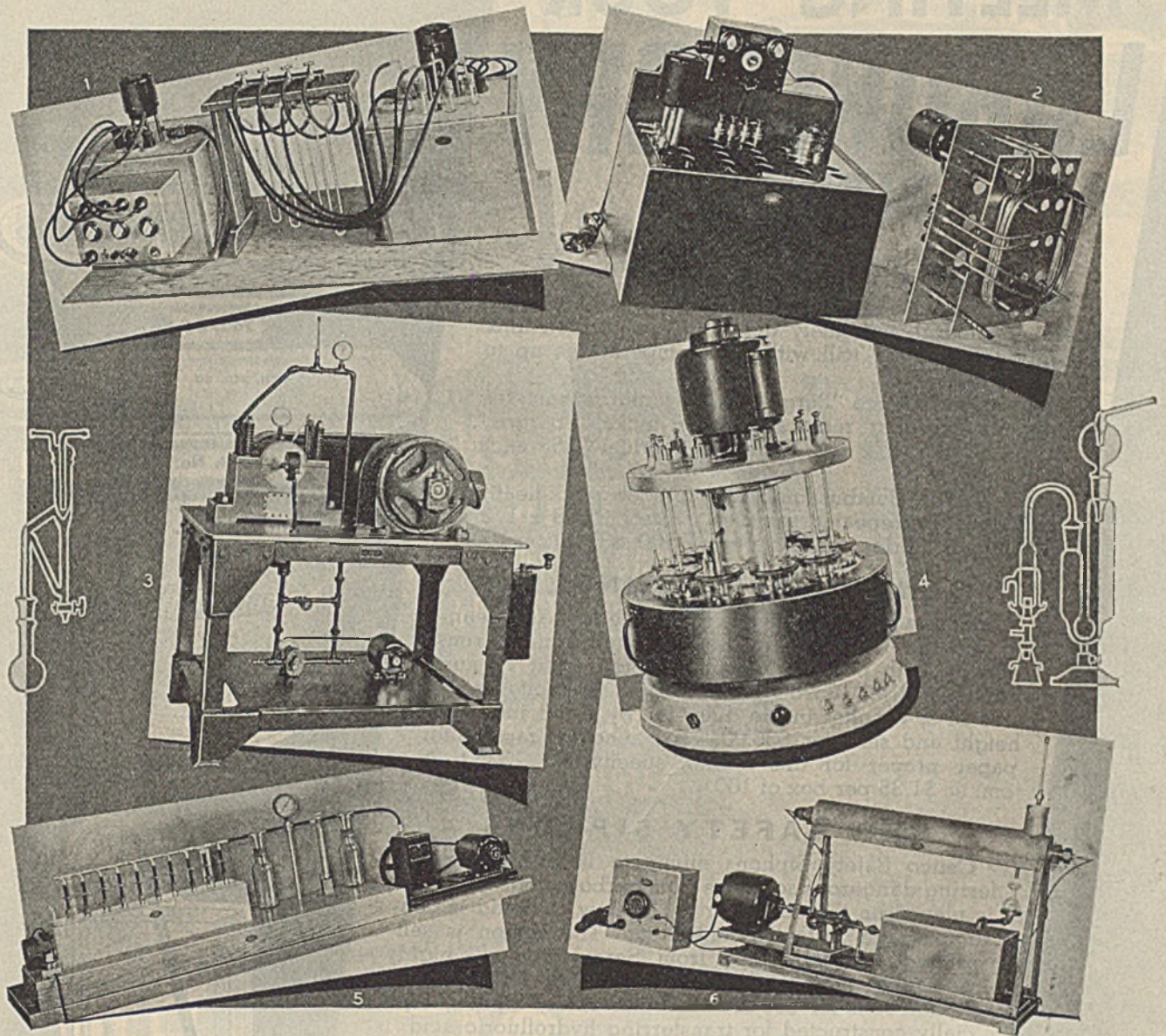
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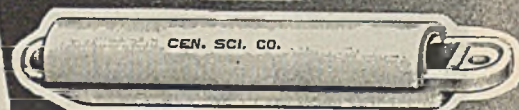
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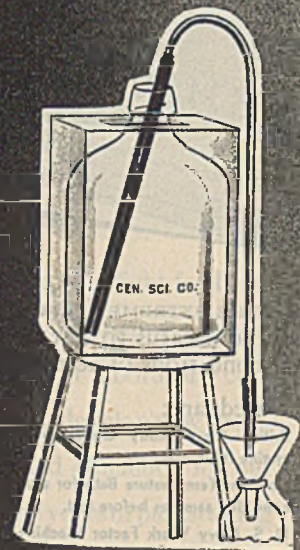
26278 C



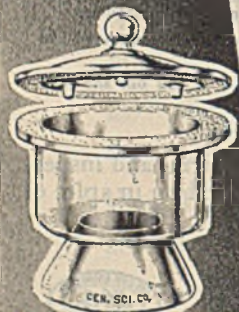
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10007-8



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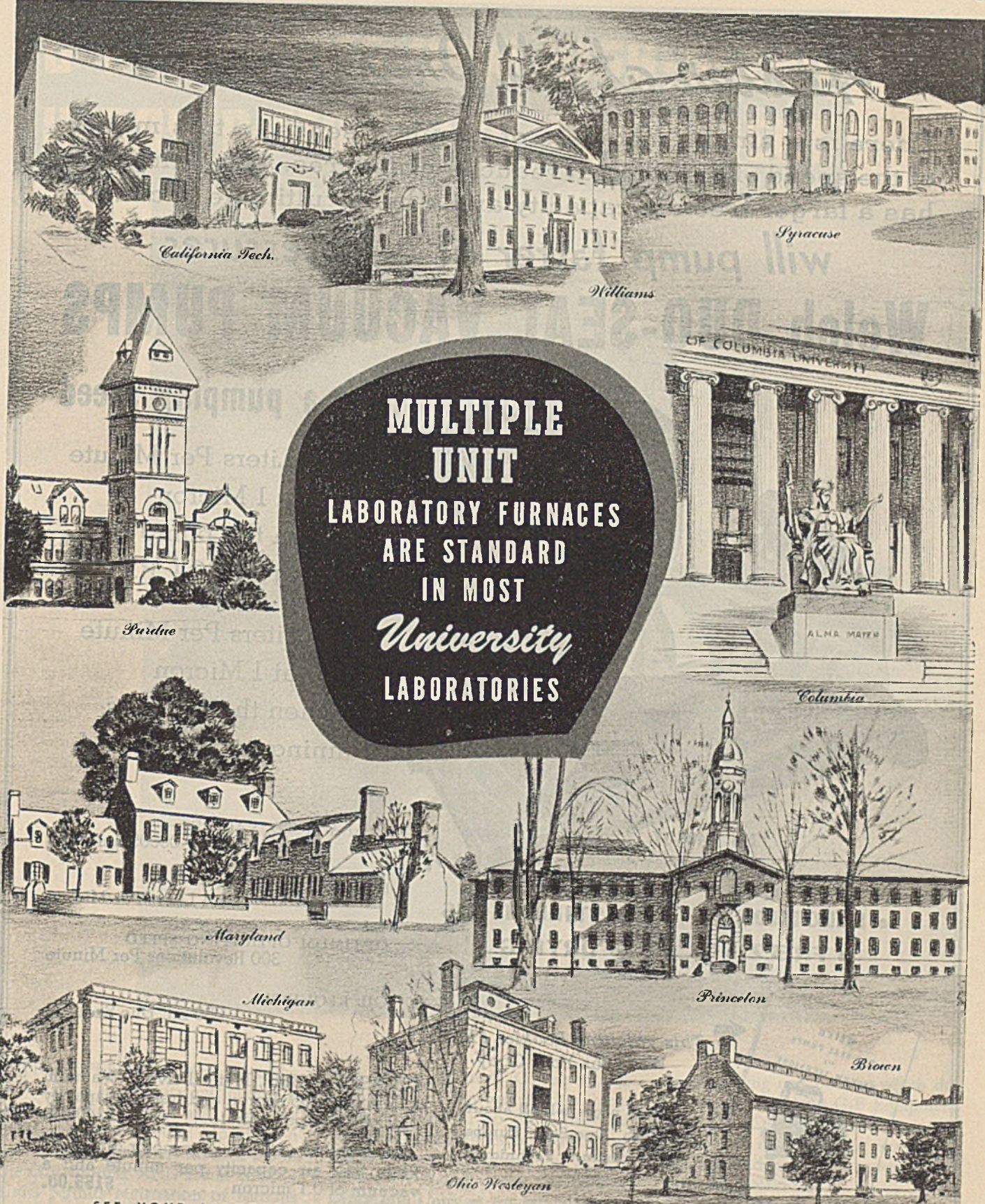
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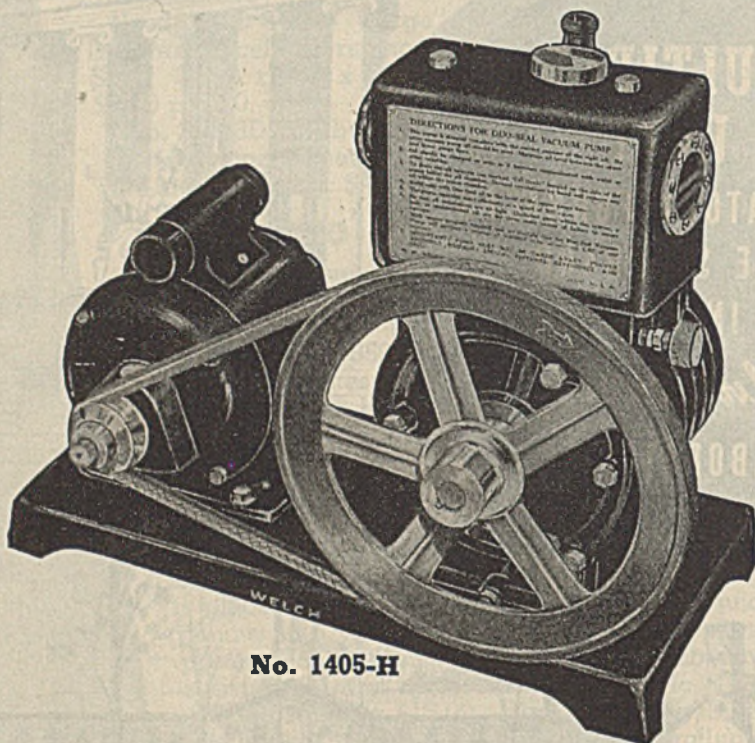


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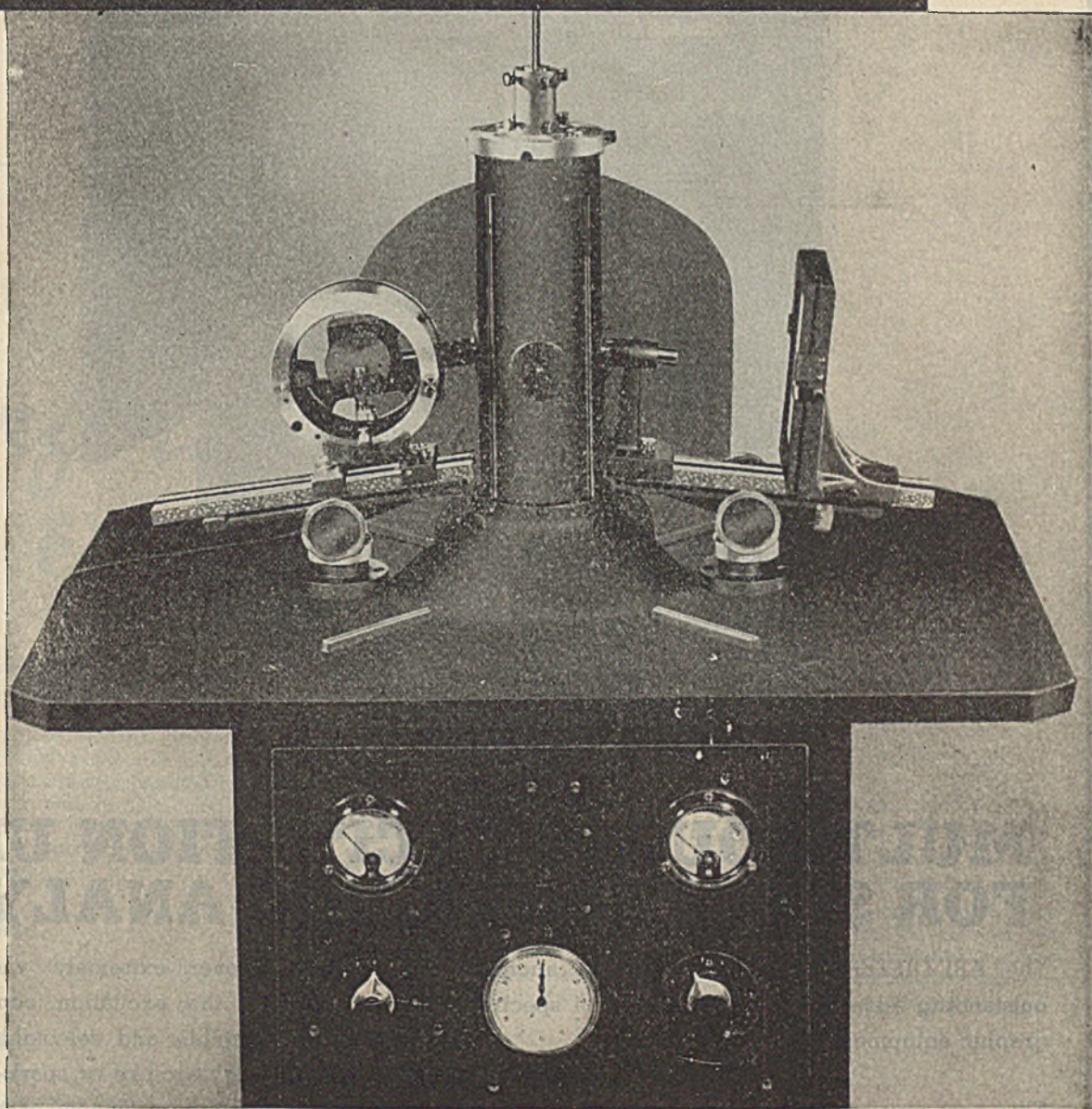
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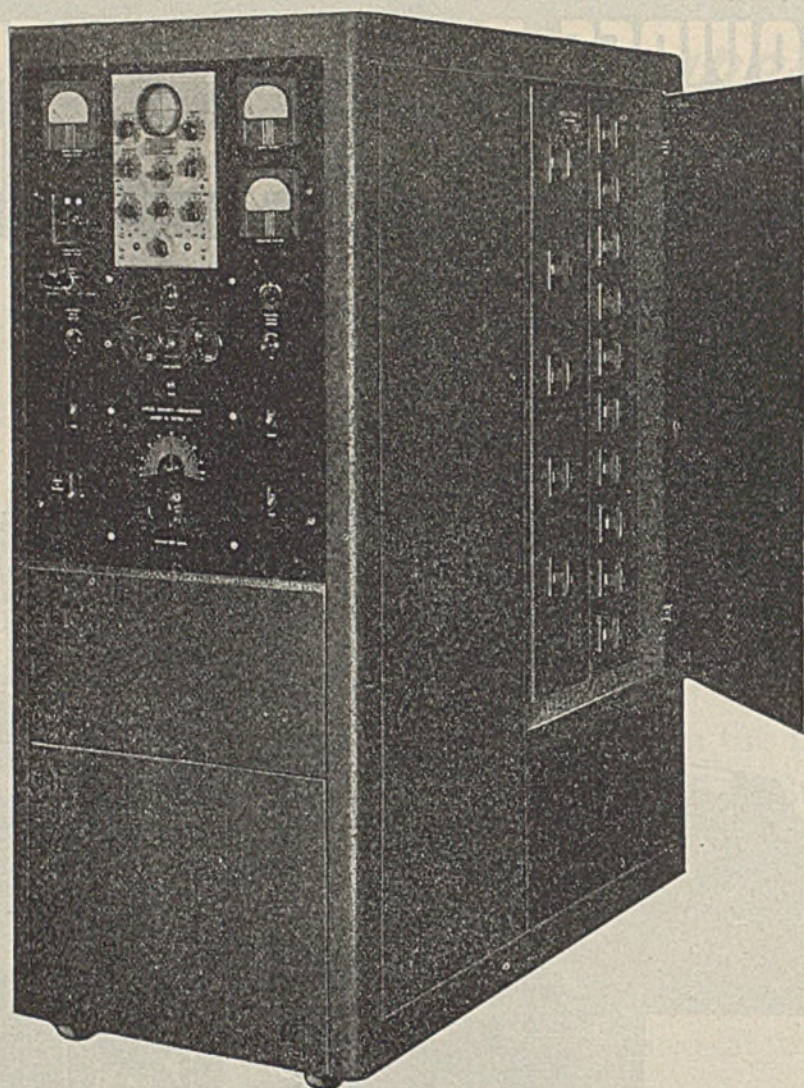
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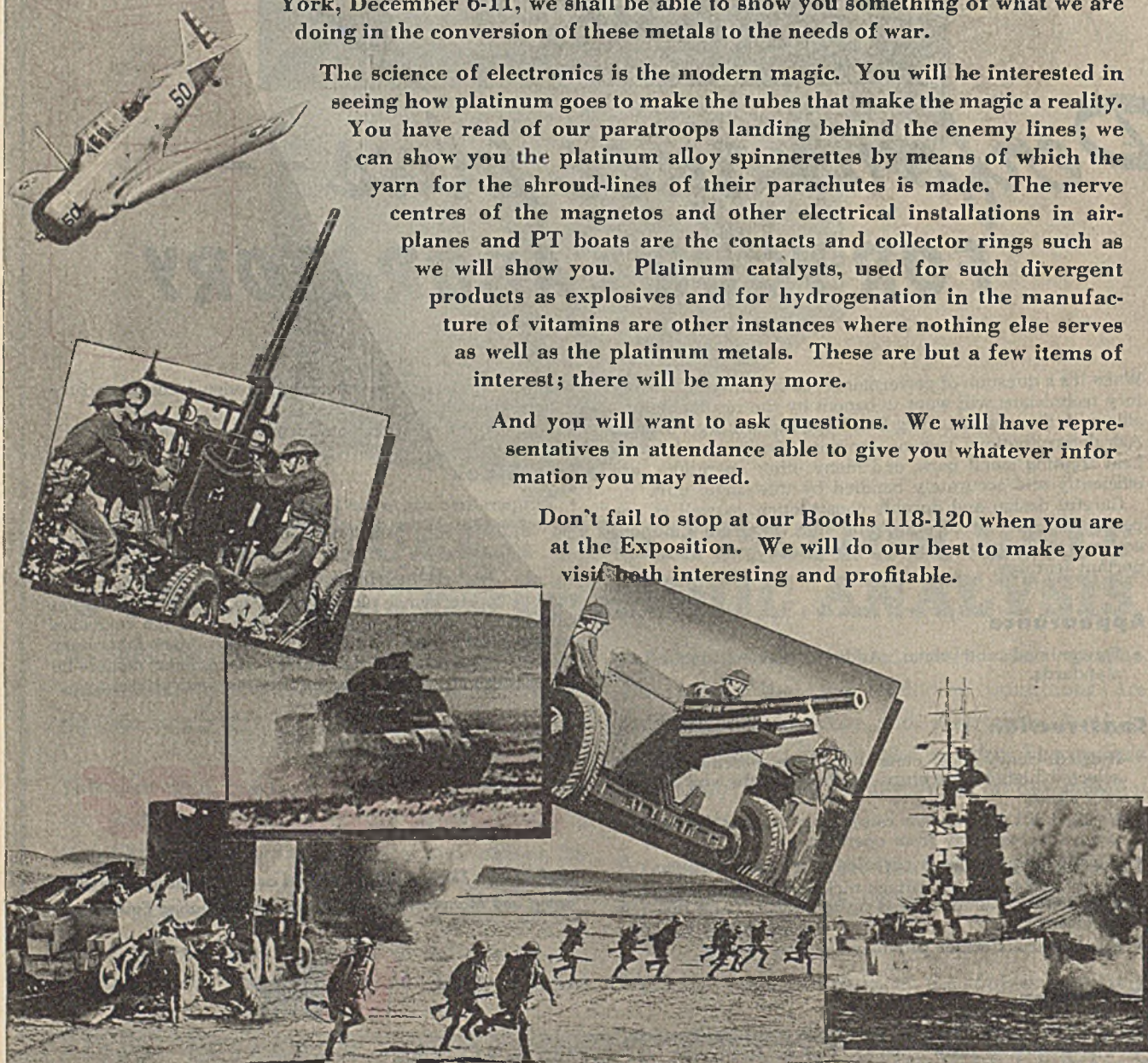
At the 19th Exposition of Chemical Industries, Madison Square Garden, New York, December 6-11, we shall be able to show you something of what we are doing in the conversion of these metals to the needs of war.

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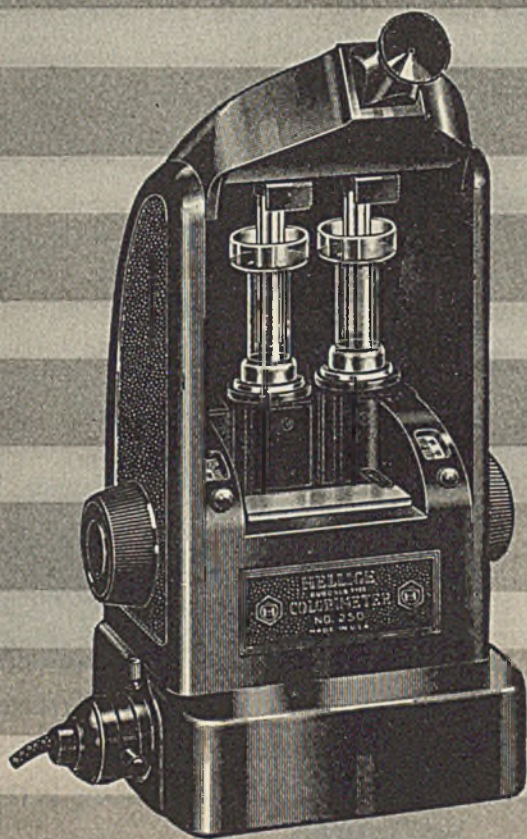
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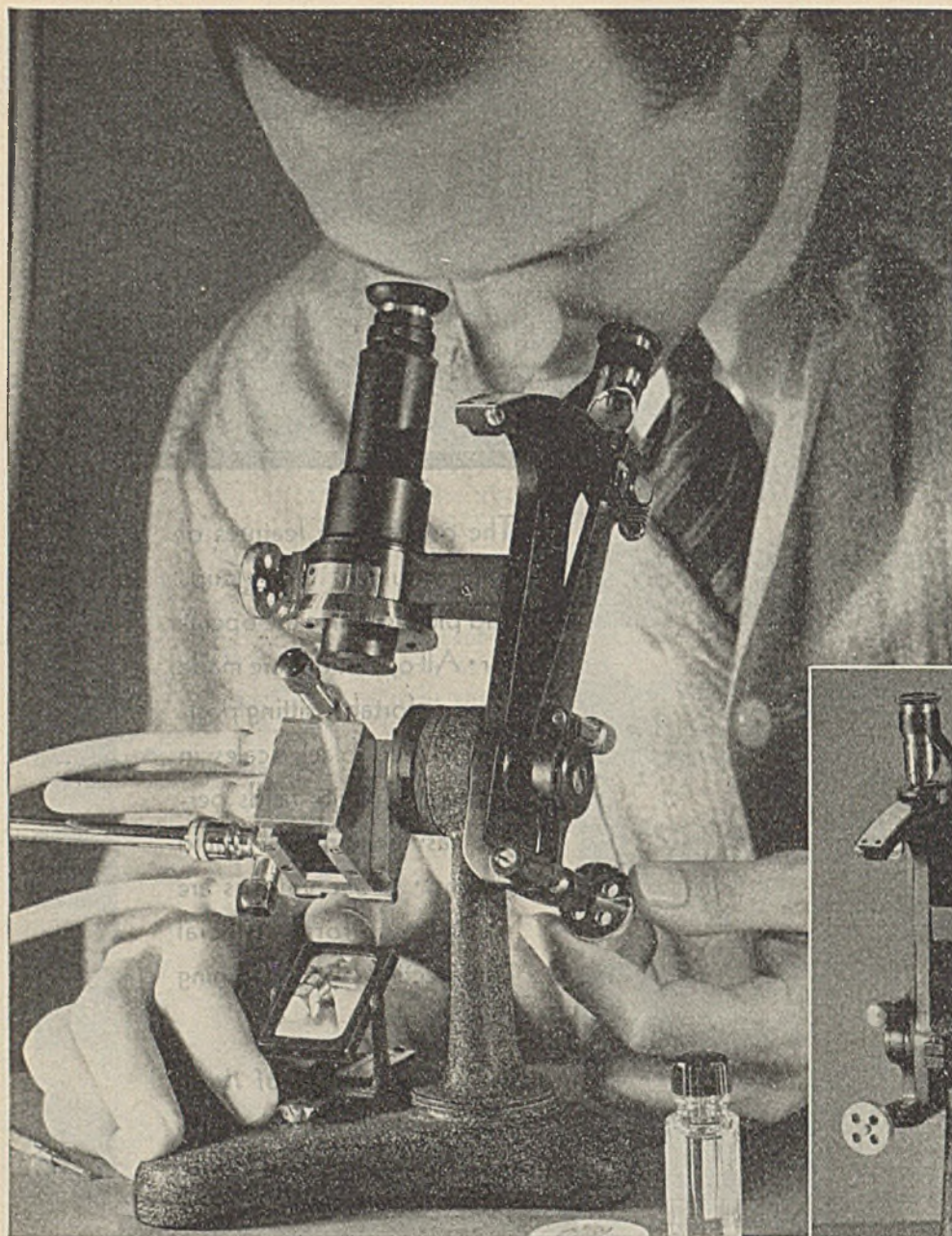
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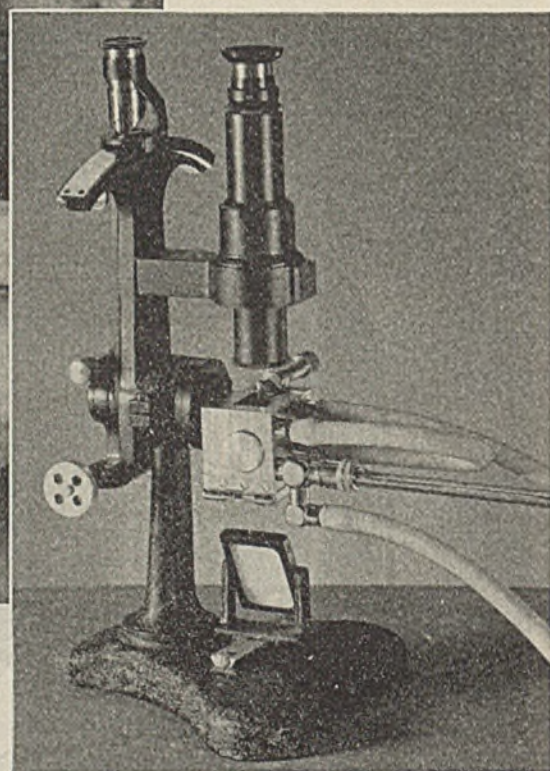
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Below: The Spencer Refractometer without Amici prisms for use with monochromatic light.



## Process Control —Refractive Index

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Instruments are available for essential use.



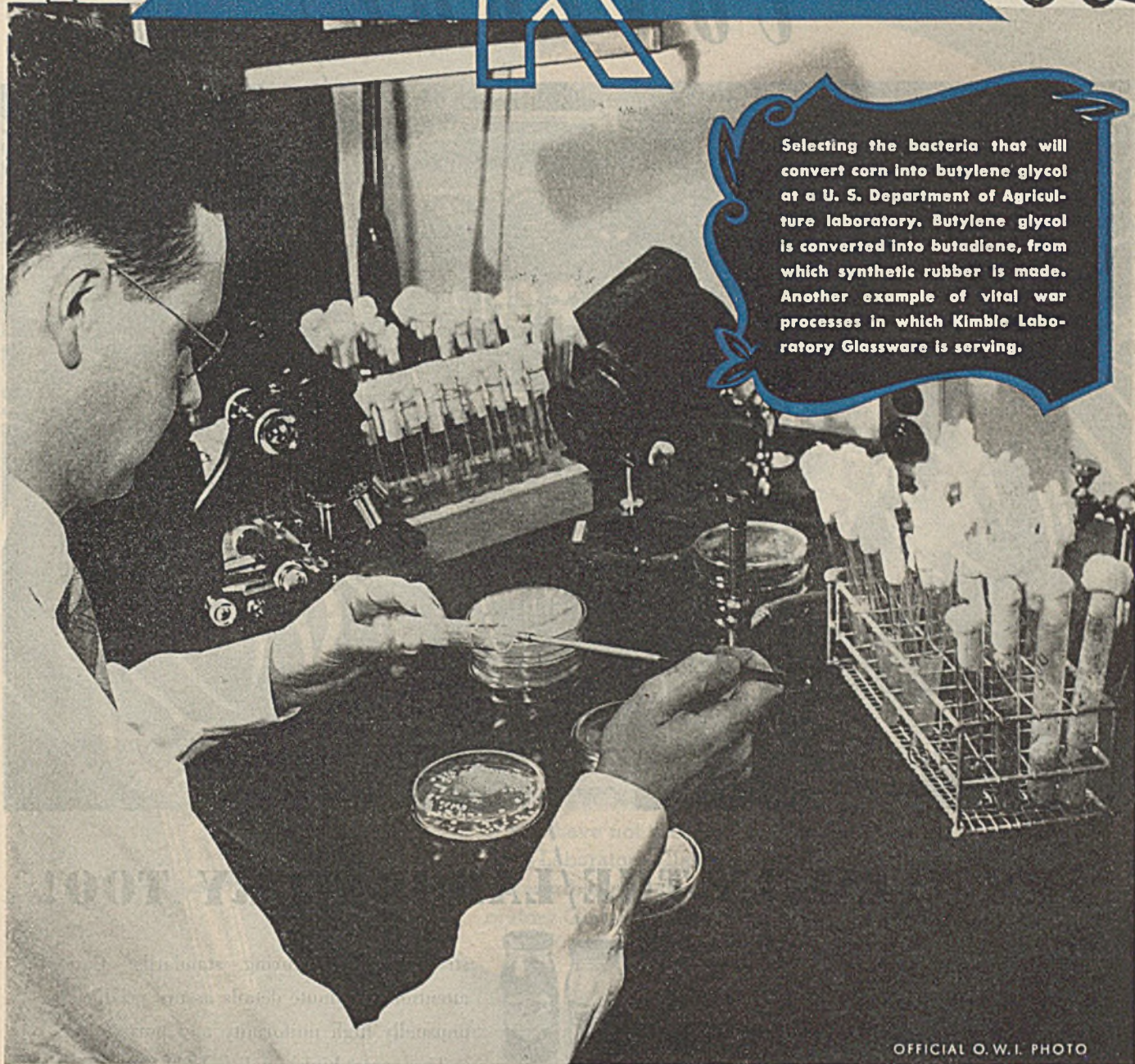
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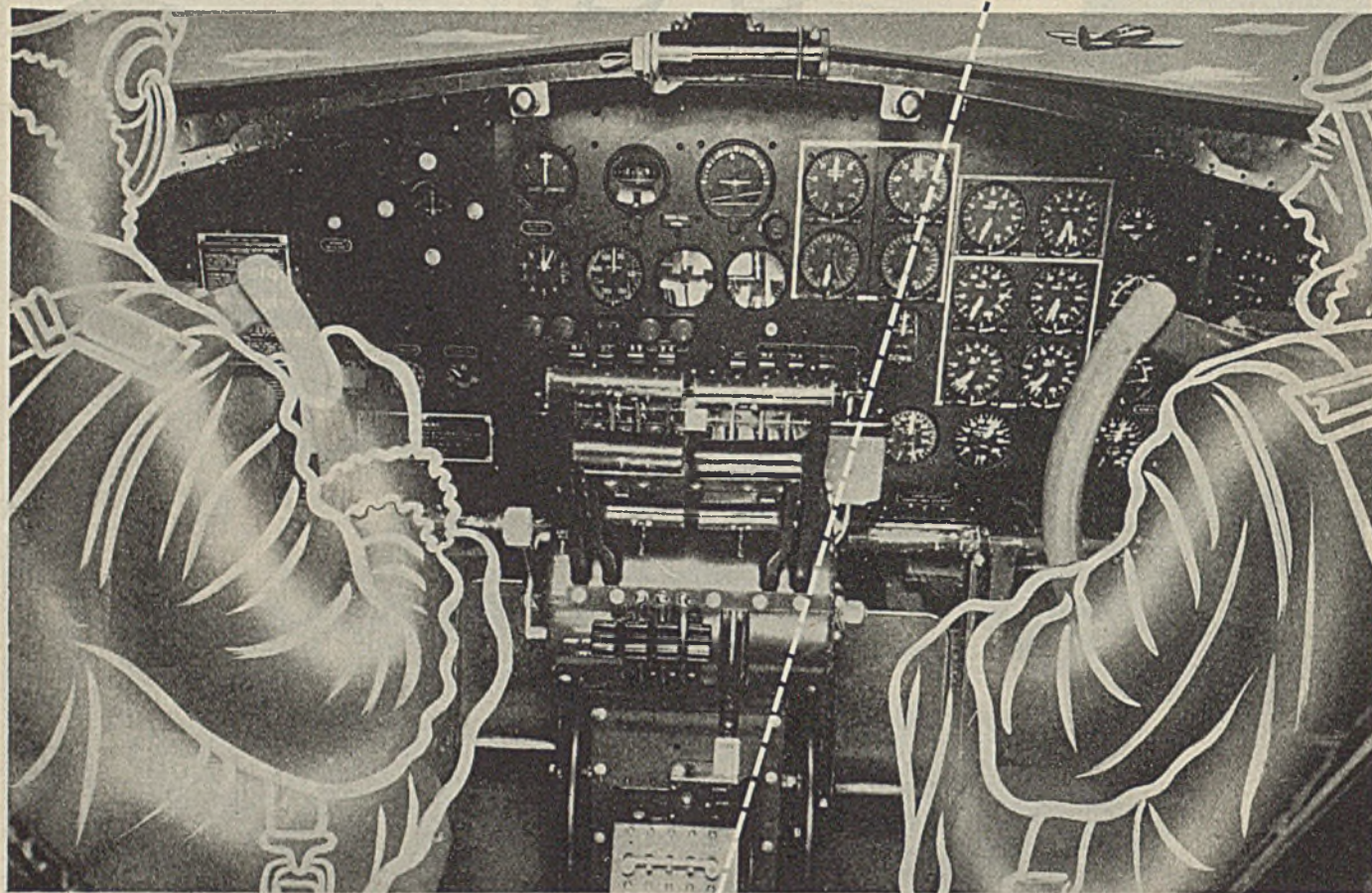
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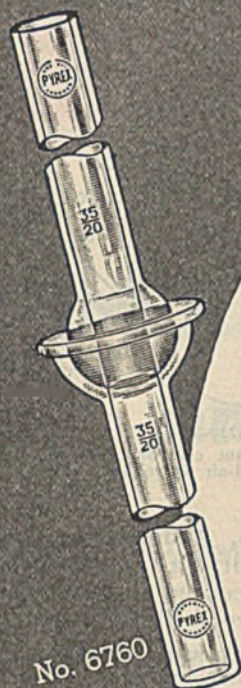
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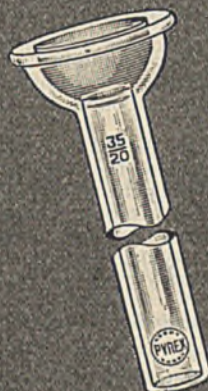
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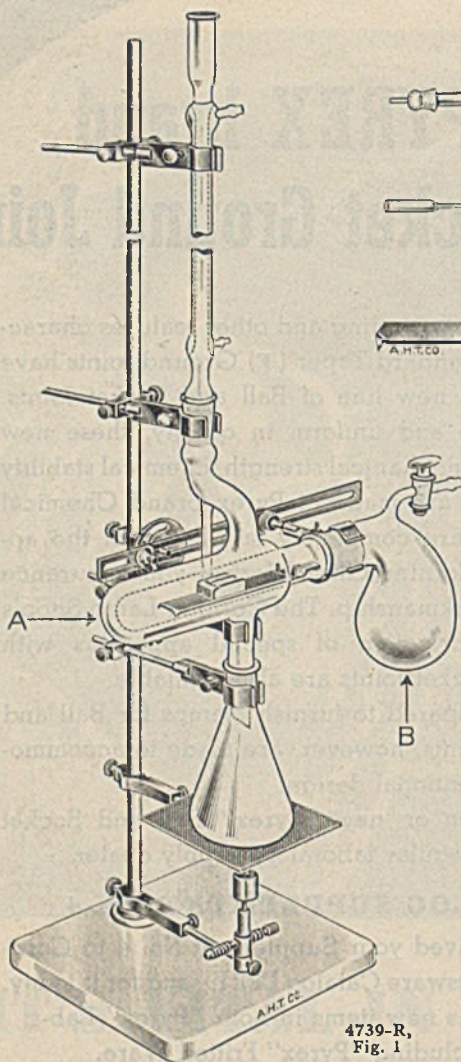
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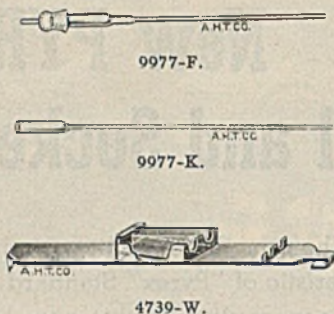


A.H.T. CO. SPECIFICATION

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4739-R, Fig. 1



4739-R, Fig. 2

Showing desiccant chamber detached and supported in mid-air for refilling, etc.

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The by-pass for condensate results in greater temperature uniformity than was possible in the original execution. Temperature range is limited only by the number and variety of constant boiling liquids which are available.

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See H. K. Alber, "Hygroscopic Substances in Microanalysis," *Mikrochemie vereinigt mit Mikrochimica Acta*, Band XXV, Heft 1-4 (1938), p. 47.

**4739-R.** Vacuum Drying Apparatus, Abderhalden Improved, A.H.T. Co. Specification, as above described, complete outfit as shown in illustration, i.e. drying chamber A, desiccant chamber B, condenser and Erlenmeyer flask of Pyrex glass with interchangeable T/S joints throughout, mounted on support with base of Coors porcelain, with necessary Spring-Grip clamps and holders, Chromel wire gauze, and micro burner for use on artificial gases up to 800 B.T.U.; with 4739-W Abderhalden Weighing Tube Support, but without weighing tubes or rubber connections for burner or condenser.....\$60.75

**4739-W.** Weighing Tube Support, Alber, of aluminum, for drying hygroscopic and volatile micro samples, evaporation of liquids, moisture determinations, etc. Takes two weighing tubes such as 9977-F or 9977-K. Ground glass cap of Alber weighing tube can be removed and resealed *in situ* without difficulty. Overall dimensions  $6\frac{3}{8}$  inches long  $\times$   $\frac{11}{16}$  inch wide  $\times$   $\frac{1}{2}$  inch high.....\$6.50

**9977-F.** Micro Weighing Tube, Alber, with ground glass cap, for drying, handling and weighing hygroscopic or

volatile substances. Chamber 30 mm long  $\times$  5 mm inside diameter, total length 150 mm, weight 1.5 to 2 grams; in accordance with specifications of A.C.S. ....\$1.30

**9977-K.** Micro Weighing Tube, Lieb and Krainick, without glass stopper. Chamber 25 mm long  $\times$  4.5 mm inside diameter, total length 155 mm, weight 1.0 to 1.5 grams; in accordance with A.C.S. specifications. See H. Lieb and H. G. Krainick, *Mikrochemie*, Vol. 9 (1931), p. 367.....\$5.00

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# INFRARED SPECTROSCOPY

## Industrial Applications

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*Infrared spectroscopy has proved a powerful tool in solving problems of organic chemistry and finds a widening field in industry. The theory of infrared absorption and its relation to molecular structure are discussed to provide the essential background for detailed descriptions of techniques*

*useful in analysis. Finally a library of 363 representative spectrographs of organic compounds taken in the rock salt region of the infrared spectrum is presented for comparison with those obtained from unknown compounds under investigation.*

THE last half dozen years have seen a rapid rise in the contributions of physicists to the chemical industry. Many important problems, which had previously been attacked solely by chemical methods, are now being studied and solved by the methods of both physics and chemistry or by the tools of physics alone. Physical instruments in increasing variety—among them optical and electron microscopes, mass spectrometers, Geiger counters, polarographs, colorimeters, and optical spectrometers of many kinds—are proving more useful every day as their potentialities and capabilities are tested and proved.

The approach of the physicist to a problem is inherently different from that of the chemist. The physicist concentrates upon the physical characteristics of the material itself, its absorption spectrum, x-ray diffraction pattern, exact mass, electronic configuration and properties, whereas the chemist studies the material in reaction with other substances. From these reactions the chemist deduces a wealth of information relating to the original material in question. His apparatus in general is relatively simple. On the other hand, the physicist may require elaborate apparatus of special design, but once this apparatus is constructed, its applications are versatile and the physicist's methods become direct, accurate, rapid, and usually require only small samples. Fortunately, the results obtained from these two methods of approach supplement each other and suffice in most cases to furnish the desired information.

Whether or not one agrees that this is "a physicist's war", certainly it is a time when physical instruments are of enormous

usefulness. Devices capable of automatic operation have already proved their merit in practically every field of endeavor. In the chemical industry, today more than ever before, is the need for speed and accuracy keenly felt. The urgency of the demands for multiplied production and the stringent shortage of manpower have necessitated abbreviation of the usual sequence from the research laboratory through the pilot plant to the final production. Short cuts must be taken and sometimes the pilot-plant stage must be eliminated entirely. The production engineer must have immediate and continuous checks on the quality of his product in order to duplicate efficiently the results of the research laboratory. Delay in obtaining analytical results quickly might lead to the waste of large quantities of valuable raw materials and products. Here the saving of time by the physicist's methods is proving invaluable. But here, too, the problems of the industrial physicist are greatly multiplied. He must not only adapt his tools or instruments to solve specific problems under ideal conditions in the research laboratory, but he must also modify them to function dependably under conditions of production analysis and control.

A typical application of physics on a widening scale in industry is infrared spectroscopy. One of the first industrial infrared spectrometers was constructed in this laboratory in the latter part of 1936. Numerous applications of this instrument have been eminently successful and have become familiar to a large number of chemists. Daily, this tool is performing analyses impossible by any other method. More common analyses are being completed in a few minutes which previously required hours.

<sup>1</sup> Absent on leave.



Interest in the potentialities of this physical tool has become so widespread that infrared spectrometers may now be found in the laboratories of an impressive list of American companies, and the time will soon arrive when such instruments will be standard equipment in most laboratories and plants.

The underlying basis of applied infrared spectroscopy is the fact that practically all organic substances possess selective absorption at certain frequencies in the infrared portion of the electromagnetic spectrum. Experimentally, as will be shown below, a spectrometer is used to determine the per cent transmission or absorption of the sample at a series of narrow frequency intervals throughout a chosen part of the spectrum. A plot of these transmission or absorption values versus frequency or wave-length units constitutes an infrared spectrum, which is characteristic of the sample being studied and which may be used to describe the sample in much the same manner as boiling point, refractive index value, or melting point. Because the individual absorption bands of which such spectrum is composed arise from the mutual motion of the atoms within the molecule, these spectral characteristics bear a direct relationship to the atomic masses, the molecular configuration in space, and the binding forces present.

Applications of infrared spectroscopy can be divided into two general categories, qualitative and quantitative.

### QUALITATIVE APPLICATIONS OF INFRARED SPECTROSCOPY

#### (a) "Fingerprinting" of compounds

The infrared absorption spectrum of a given compound is a unique fingerprint which cannot be duplicated by any other compound. This characteristic is invaluable in identifying unknowns. Once a large library of absorption curves for known compounds has been amassed, frequently only minutes are required to match the absorption spectrum of an unknown with one of the known curves. Even in cases where no satisfactory match is found, assurance that the unknown is not one of a list of known compounds is useful information.

Since the samples required are small and are in no way damaged or harmed, this method of analysis is particularly useful in connection with chemical research where limited amounts of material are available.

#### (b) Recognition of specific chemical bonds, linkages, or groups

Comparisons of spectra of large numbers of pure compounds have shown that absorption bands occurring at certain frequencies can be correlated with certain bonds or atomic groups within the molecule. For example, a glance at an absorption spectrum gives an indication of the presence or absence of such groups as O—H, N—H, C≡N, C=O, CH<sub>3</sub>, etc. Observed absorption characteristic of hydrocarbon unsaturation can be ascribed to either aliphatic or aromatic structures. More particularly, the position of the absorption band of a carbonyl group in general indicates whether it forms part of an anhydride, ester, ketone, aldehyde, or acid. The appearance of the "methyl band" distinguishes between the terminal methyl groups of a straight chain and an isopropyl or tertiary butyl group. Although all the structural units of a sample may not be determined in this manner, at least a considerable number of the more common ones can be identified.

#### (c) Gross structural features

The appearance and analysis of the absorption spectrum can often be used to determine or verify the spatial configuration of the atoms within a molecule. Examples are *cis-trans* or *ortho-, meta-, and para-isomerism*, the planarity of the aromatic ring, *keto-enol tautomerism*, hydrogen bonding, etc.

#### (d) Qualitative analysis of mixtures

Except in special cases of strong intermolecular interaction, the absorption spectrum of a mixture is equivalent to a simple superposition of the spectra of its individual components. Hence it is possible, by comparing the spectrum of a mixture with the library of spectra of pure compounds, to determine not only the components but also their relative concentrations.

### QUANTITATIVE APPLICATIONS OF INFRARED SPECTROSCOPY

#### (a) Analysis

A mixture of materials can be analyzed quickly and accurately so long as the components present in the mixture are known. From a study of the spectra of the known compounds, it is usually possible to find a frequency at which only one component possesses strong absorption. By setting the spectrometer at this particular frequency and comparing the absorption of an unknown with that of known prepared standards, the amount of the particular component in the unknown can be determined. Usually another characteristic frequency can be found for each of the other components. This rapid method, modified suitably to meet existing conditions, has been applied with an accuracy of 1 per cent or better to a great variety of mixtures from simple ones of two hydrocarbon components to complex mixtures containing up to six terpenes. It is particularly useful for analyzing close boiling isomeric mixtures for, as mentioned above, the absorption spectra are functions of geometrical configuration and are not related to boiling points. A characteristic curve of absorption versus concentration shows the method to be particularly accurate for measuring small amounts of impurities, such as water in oils, oxidation products, etc.

#### (b) Measurements of reaction rates

The principle outlined above can be used for measuring rates of reaction or polymerization as a function of temperature, pressure, or the catalyst used. Samples may be taken from the reaction chamber at suitable time intervals, and the amounts of the reactants consumed and new products formed quickly determined. Since the amount of sample required is so small (less than 1 gram) its removal from the reacting mass has a negligible effect on the reaction.

#### (c) Determination of thermodynamic data

A knowledge of the exact values of the infrared absorption frequencies provides part of the information needed for a mathematical calculation of the thermodynamic constants of the material.

#### (d) Process analysis and control

The analytical methods described can be used in the plant as well as in the research laboratory. Small, sturdy spectrometers which can be set at fixed frequencies have been constructed for such work. Frequently, such control analyses may be made from a by-pass in the production line to give a continuous record of the concentration of one component as a function of time. The output of these spectrometers is an electrical current, which may be used to provide automatic control through suitable relays.

The basic methods described in this paper have been in use in these laboratories since 1937, and are considered to be especially valuable in the present emergency. This paper provides working descriptions of the various experimental techniques involved and a brief discussion of the theoretical basis of infrared spectroscopy. Within the scope of a single paper, however, no attempt can be made to present a complete survey of this field, nor to describe each of the many types of instruments now in use. Rather, the content is restricted to a discussion of the applica-



tions made in this laboratory. Obviously, one of the fundamental requirements for the successful application of infrared spectroscopy is a knowledge of the absorption spectra of a large number of pure compounds. Accordingly a library of 363 spectra has been included.

### EXPERIMENTAL EQUIPMENT AND TECHNIQUE

A graph of the complete electromagnetic spectrum is given in Figure 1. Throughout the spectrum the fundamental relationship holds:  $\lambda\nu = c$ , where  $\lambda$  is the wave length of the radiation,  $\nu$  is the frequency of vibration, and  $c$  is a universal constant, the velocity of light. Because of the various interactions of electromagnetic radiation with matter, each portion of the spectrum is of interest and value to the industrial physicist.

The infrared portion of the spectrum extends from the long wave-length limit of sensitivity of the human eye to the region of ultra short radio waves—that is, from about 7500 Å. ( $0.75\mu$ ) to about 350,000 Å. ( $350\mu$ ). The units most often used in designating portions of the infrared spectrum are: wave-length unit, micron or  $\mu$  ( $1\mu = 10,000 \text{ \AA.} = 10^{-4} \text{ cm.}$ ); and so-called frequency unit, wave number or  $\text{cm.}^{-1}$  [ $1 \text{ cm.}^{-1} = 1/\lambda(\text{cm.})$ ]. The various subdivisions of the infrared spectrum are shown in Figure 1 with dotted lines and are described above the graph. Within very approximate limits these are: the photographic region from  $0.75\mu$  to  $1.3\mu$ ; the overtone region from  $1.3\mu$  to  $2.5\mu$ ; the fundamental vibration region from  $2.5\mu$  to about  $25\mu$ ; and the rotational region from  $25\mu$  to  $350\mu$ . Although each is important and capable of yielding much valuable information, primary interest centers in the fundamental vibration region. Because of the limitations of radiation sources and prism materials, a portion of this range, from  $2.5\mu$  ( $4000 \text{ cm.}^{-1}$ ) to  $15\mu$  ( $667 \text{ cm.}^{-1}$ ), has been most thoroughly investigated.

The infrared spectrometer used in work in this field consists essentially of: (1) a source emitting a continuous range of wave lengths desired; (2) a dispersing means<sup>2</sup> to spread out this radiation in order to provide narrow wave-length bands at accurately known wave-length positions; (3) a means for interposing a sample of suitable thickness into the path for this radiation; and (4) a detector and amplifier to measure accurately the intensity of radiation in each narrow band. Indicative of the difficulties of infrared technique is the fact that no standardized research spectrometers are available today. In other branches of spectroscopy, it is customary to mention a medium Hilger, a large Bausch & Lomb quartz spectrograph, or a General Electric recording spectrophotometer and let a reference to the literature suffice as a description of the instrument. In contrast to this, the various infrared laboratories use instruments constructed according to the individual ideas, designs, and demands of each investigator. Unfortunately, this paper cannot include descriptions of all the various types of instruments in use, nor can it single out any one as being the best. However, a discussion is given of the spectrometer which was used in obtaining the absorption spectra given below.

### THE SPECTROMETER

A schematic drawing of the optical path of the spectrometer is shown in Figure 2. The source is an electrically heated commer-

cial Globar (a silicon carbide rod) having a power consumption of about 400 watts at 115 volts controlled by a voltage regulator. The Globar is thinned in the central section in order to raise the intensity of radiation from the actual source area. The radiation from this source is reflected by the plane mirror,  $M_1$ , to the spherical mirror,  $M_2$ , which focuses the beam at the position marked "cell". The sample is introduced here by means of an electrically driven way with three stop positions so that a shutter, absorption cell, or a control cell can be placed in the same position in the light path. The radiation transmitted through the cell is then focused by  $M_3$  on the entrance slit at  $S$ .  $S$  is a double slit having a common center and two movable outer jaws. The entrance slit is curved to compensate for the image curvature introduced by the prisms. The radiation from  $S$  enters the spectrometer proper through a slot in the plane mirror,  $M_4$ , is rendered parallel by the spherical mirror,  $M_5$ , whose focal length is 40 cm. The beam of radiation is given its first dispersion on passing through the two prisms, and is then reflected back through the prisms by the plane Littrow mirror,  $M_6$ , for a second dispersion. The dispersed beam traverses the path from  $P_1$  to  $M_5$ , to  $M_4$ , through the slot in  $M_5$ , and passes out through the exit slit at  $S$ . The mechanical widths of the two slits control the width of the spectral band and the wave length or frequency of the band center is determined by the rotational setting of the Littrow mirror,  $M_6$ . The narrow band of energy emerging from  $S$  is then reflected at a small angle by the plane mirror,  $M_7$ , to the elliptical mirror,  $M_8$ , which focuses a greatly reduced image of the exit slit,  $S$ , onto a compensated, vacuum thermocouple. The entire instrument, except for the source and the absorption cell, is housed in an airtight aluminum case whose interior is freed of water vapor and carbon dioxide. For this purpose, air purified over large quantities of phosphorus pentoxide and soda lime is supplied at intervals by a circulating system. The radiation from the source enters and leaves the spectrometer case through rock salt windows.

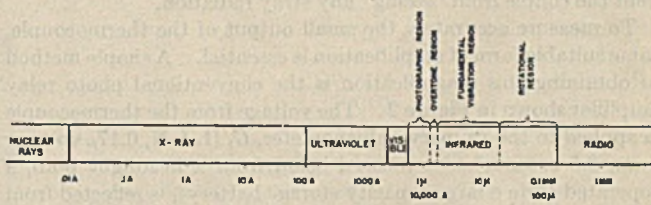


FIGURE 1. GRAPH OF THE ELECTROMAGNETIC SPECTRUM

Since these infrared radiations cannot be photographed and there is no photoelectric element sensitive to this part of the spectrum, the detector must of necessity be some type of thermosensitive element, such as a thermocouple, bolometer, or radiometer.

The order of magnitude of the energies involved illustrates the difficulties encountered in infrared spectroscopy, and accounts for the slow progress in this field as compared with other branches of spectroscopy. The average energy in the dispersed beam produces a voltage at the thermocouple of about 1 microvolt ( $10^{-6}$  volt).<sup>3</sup> Since the thermoelectric coefficient of the elements used is of the order of 100 microvolts per degree centigrade, this represents a temperature difference between hot and cold junctions of the thermocouple of roughly  $0.01^\circ \text{C}$ . Since, as will be seen later, it is necessary for practical purposes that energies of this order of magnitude be measured with an accuracy of 0.5 per cent, the limit of error must be not greater than  $5 \times 10^{-5}^\circ \text{C}$ . Small changes in ambient temperature are minimized by using a two junction couple connected in series opposition, only

<sup>3</sup> Electronic amplification of this output is difficult because of the low resistance ( $10\text{--}20\Omega$ ) and the slow period (one second) of the average thermocouple.

<sup>2</sup> The dispersing medium may be either a grating or a prism. A grating provides greater dispersion but its use involves more experimental difficulties because of the necessity of eliminating higher order radiation. For this reason prisms are more generally used in industrial spectroscopy. A list of prism materials together with their long wave-length transmission cutoffs is given (glass  $1.5\mu$ , quartz  $3\mu$ , lithium fluoride  $5\mu$ , fluorite  $9\mu$ , sodium chloride  $15\mu$ , and potassium bromide  $25\mu$ ). Ideally, best dispersion is obtained by using one material up to its cutoff and then switching to the next material. For a single prism instrument, rock salt is most generally used because it provides the best combination of dispersion and accessible region.



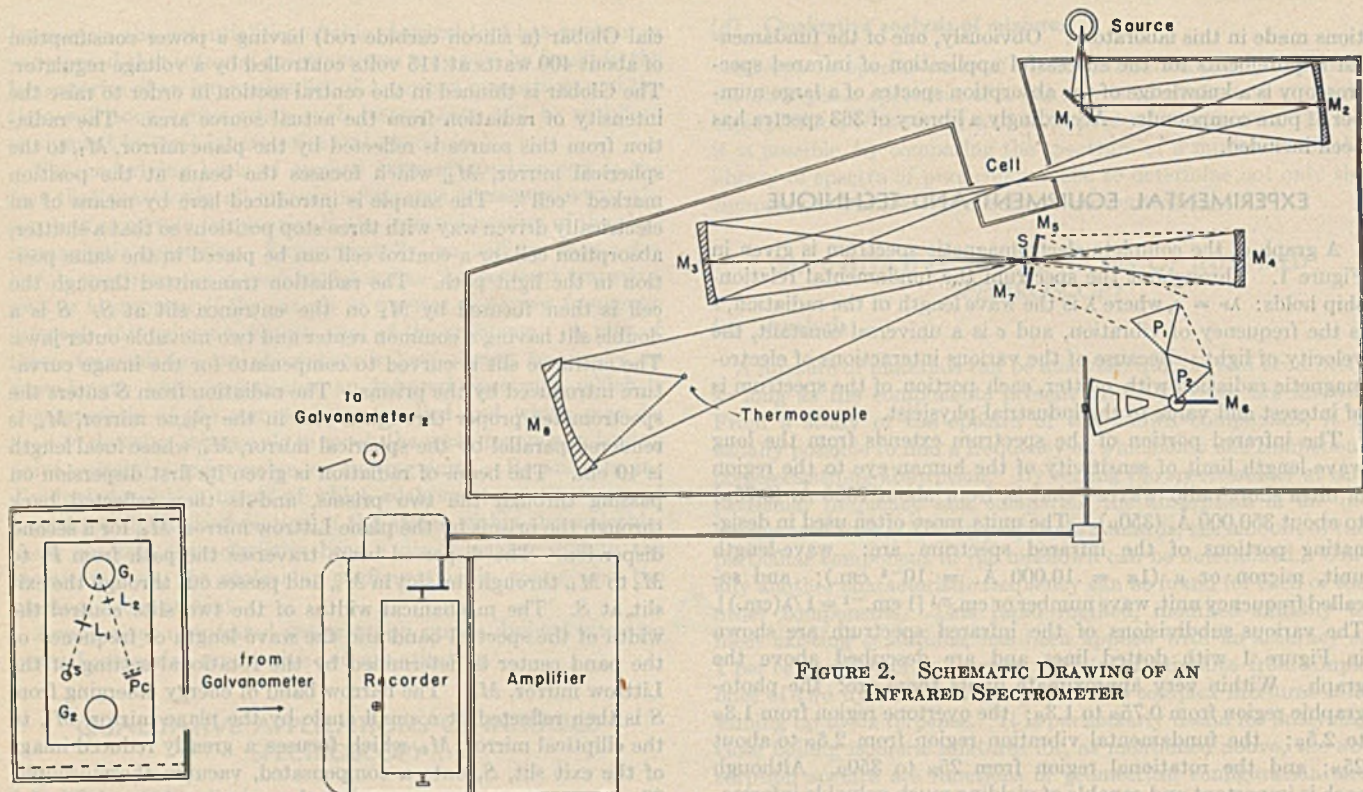


FIGURE 2. SCHEMATIC DRAWING OF AN INFRARED SPECTROMETER

one of the hot junctions being illuminated by the radiation being measured. These values illustrate the excessive care necessary to provide adequate thermal and electrical shielding and to prevent the couple from "seeing" any stray radiation.

To measure accurately the small output of the thermocouple, some suitable form of amplification is essential. A simple method of obtaining this magnification is the conventional photo relay amplifier shown in Figure 2. The voltage from the thermocouple is applied to the primary galvanometer,  $G_1$  (L & N, 0.17 $\mu$  volt per mm., 3.5 seconds). A focused beam from a headlight bulb,  $s$  (operated from a large capacity storage battery), is reflected from the primary galvanometer mirror onto the edge of a barrier layer cell,  $P_c$ . A small deflection of  $G_1$  increases the illumination on  $P_c$  and proportionately increases the current from  $P_c$ , which is fed directly into the recording galvanometer  $G_2$  (L & N, 0.003 $\mu$  volt per mm., 2.5 seconds). By this method any desired degree of angular amplification up to the Brownian motion limit of  $G_1$  can be achieved. In practice, depending upon the stability of the galvanometers, an amplification factor between 0 and 200 is generally used.

The final spectrogram is obtained by recording the deflections of  $G_2$  with an automatic pen recorder<sup>4</sup> built in this laboratory. A pen is mounted on a carriage which holds a twin cathode photoelectric cell (such as an R. C. A. 920). The light beam reflected from  $G_2$  is interrupted at sixty cycles and is focused symmetrically on the two cathodes so that the outputs of the twin photo cells are equal. Any slight deflection of the beam from  $G_2$  upsets the balance between these outputs. This difference is amplified by one of two Thyatron circuits and fed into a split-field, series-wound motor so geared as to drive the carriage in a direction to restore the balance. Thus the pen carriage follows accurately the deflections of the reflected beam from  $G_2$  and draws, automatically, a continuous record of the galvanometer deflections. This

record is drawn on a 12  $\times$  20 inch chart, carried on a rotating drum driven by the same synchronous motor which controls the frequency settings of the Littrow mirror of the spectrometer proper. Suitable calibration marks are made on the record by a small solenoid which deflects the pen at specified frequencies. This solenoid is actuated by a microswitch which is closed once during each rotation of the Littrow shaft. A Veeder counter operated by the same shaft indicates the frequency setting at all times.

In practice, the spectrometer is set at a desired frequency and the slit width and amplification factors are fixed to give the desired spectral slit width and a full scale galvanometer deflection, respectively. The sample is then interposed in the path of the beam, the position of the pen for zero energy is marked on the chart by momentarily inserting an opaque shutter in the light path, and a switch is finally thrown to start the motor. The actual record is a graph of galvanometer deflections as ordinates versus frequency units as abscissas.

This record can be transformed into a per cent transmission graph by a series of calculations using an energy curve covering the same spectral region. In many studies this conversion of the original records to transmission curves is unnecessary.

#### PREPARATION OF SAMPLES

Samples can be studied as vapors, liquids, solutions, or solids. Windows of the absorption cell can be made of any material which is reasonably transparent in the region of the spectrum employed. In addition to the materials already mentioned as being suitable for prisms, sheets of mica, thin nitrocellulose, or silver chloride can be used in special cases. Examples of typical infrared salt window absorption cells are shown in Figure 3.

Vapors are studied in glass or metal tubes whose ends are closed by cell windows attached with a cement such as Glyptal or Apiezon. Either the pressure in the cell or the length of the cell itself may be adjusted to give the desired degree of absorption.

<sup>4</sup> The basic suggestion for this recorder was obtained from a paper by D. J. Pompeo and C. J. Penner, [Rev. Sci. Instruments, 13, 218 (1942)].



In examining liquids, a drop or two of the sample is placed on a plate of salt or other window material on which is laid a U-shaped spacer of thin metal foil to give the required thickness, and then another salt plate is clamped on top of this assembly under uniform pressure. Volatile samples are put in special cells which can be sealed. The average thickness of samples of liquids is about 0.05 mm.

Samples are occasionally studied in solution when the material is a solid or when intermolecular association is to be avoided. Use of this method is greatly restricted since no available solvent is free from absorption throughout the infrared spectrum. Solvents, such as carbon tetrachloride or carbon disulfide whose molecules are nonpolar and consist of a small number of heavy atoms, are most suitable.

It is possible to get good infrared curves from solids if a thin (ca. 0.03 mm.) plate, continuous film, or very finely divided crystalline sample can be obtained. Various methods are employed for producing these. Resinous samples are prepared by laying down a film of suitable thickness from solution and allowing the solvent to evaporate. Satisfactory samples of rubbery materials may be prepared by softening the material to a gluey consistency with a volatile solvent, spreading a thin film on a salt plate and evaporating the solvent in a vacuum desiccator. If melting does not alter the material, the sample can be fused between the plates of a capillary salt cell and allowed to cool, or the sample can be melted on a hot salt plate and smoothed out with a knife or razor blade into a thin layer. Suitable samples may also be obtained by crystallizing the material from solution. If the average particle size of the crystals formed is approximately the same as the wave length of the radiation used for study, the radiation will be scattered rather than transmitted.

To avoid this, the crystals must be either considerably larger or smaller than the wave length being used. Samples of insoluble, infusible materials may be prepared for examination by grinding the substance to as fine a powder as possible, then mulling it thoroughly in a straight-chain aliphatic hydrocarbon, such as Nujol. The resulting paste is pressed between two salt plates. The Nujol will absorb strongly in the characteristic region of the CH frequencies but will leave the rest of the spectrum clear for absorption by the sample.

### THE ORIGIN OF INFRARED SPECTRA

The atoms of any molecule not at absolute zero are constantly oscillating about their positions of equilibrium. The amplitudes of these oscillations are extremely minute ( $10^{-9}$  to  $10^{-10}$  cm.) and their frequencies are high ( $10^{13}$  to  $10^{14}$  cycles per second). Since these frequencies are of the same order of magnitude as those of infrared radiations, some direct relationship might be expected to exist between the motions of the atoms within molecules and their effects on infrared radiation incident upon them. Actually those molecular vibrations which are accompanied by a change of dipole moment, so-called "infrared active" vibrations, absorb, by resonance, all or part of the incident radiation, provided the frequencies of the latter coincide exactly with those of the intramolecular vibrations. Thus, if a sample of molecules of a single kind is irradiated in succession by a series of monochromatic bands of infrared, and the percentage of radiation transmitted is plotted as a function of either wave length or frequency, the resulting graph may be interpreted in terms of intramolecular motion. Although these atomic motions at first thought seem to be very complicated, they may be shown by detailed analysis to be

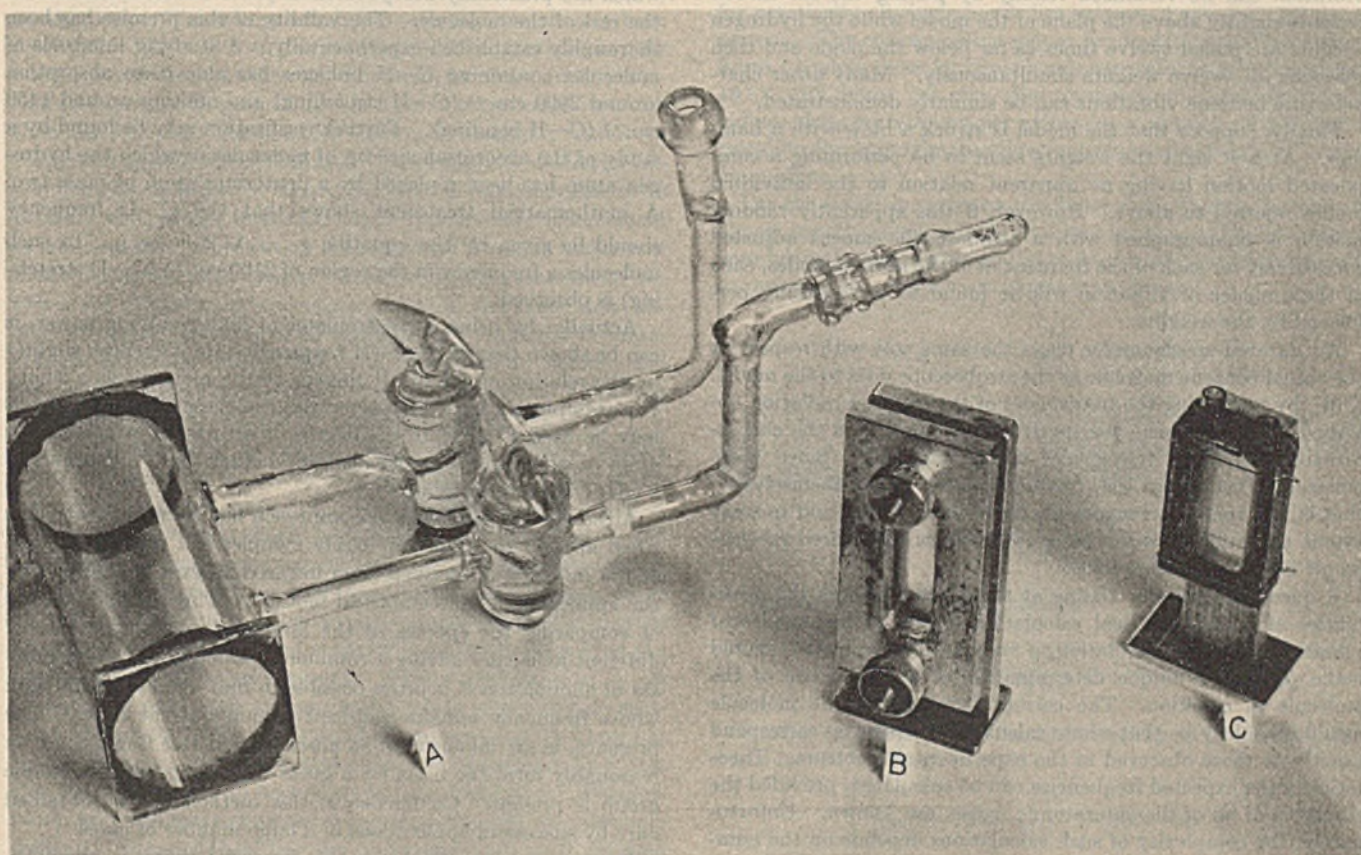


FIGURE 3. TYPICAL INFRARED ABSORPTION CELLS

- A. Vapor cell
- B. Clamped cell for qualitative studies
- C. Fixed cell for quantitative studies



summations of a number of simple oscillations. Each of these simple vibrations is referred to as a "fundamental" or "normal" mode of vibration. Any nonlinear molecule of  $n$  atoms can be shown mathematically to possess  $3n - 6$  such normal modes, whereas a linear molecule possesses  $3n - 5$ . A normal mode of vibration is defined as a mode in which the center of gravity of the molecule does not move, and in which all of the atoms move with the same frequency and in phase. Except for cases of accidental degeneracy, each normal mode is independent of the others in that any one can occur without affecting the others. Hence it is possible for all of these vibrations to occur simultaneously and yet for each one to retain its characteristic frequency. An analysis of an infrared spectrum therefore constitutes an analysis of the mechanics of the molecule in question.

The concept of a normal vibration may be clarified by analogy with a mechanical model. Suppose that a model of the benzene molecule,  $C_6H_6$ , is constructed by using weights in the ratio of 12 to 1, respectively, for the carbon and hydrogen atoms, these weights being held in proper orientation by suitable springs. Suppose further that the carbon-hydrogen springs are now stretched slightly by moving each of the six pair of weights so that the hydrogens are moved twelve times as far from the equilibrium position as are the carbons. If, now, the weights are released simultaneously, a vibration will occur in which the weights move back and forth along the connecting bonds. The center of gravity of the whole model remains at rest and the weights move only along the line of the connecting springs, since no original impetus was given to the weights in any other direction. This is a characteristic vibration of the model, inasmuch as it has a definite frequency which can be measured by a stroboscope, and it does not excite any other vibration in the model. This stretching motion is exactly analogous to one of the  $3n - 6$ , or 30, normal modes of the benzene molecule. Another benzene vibration can be visualized readily by pulling the six carbon weights slightly above the plane of the model while the hydrogen weights are pulled twelve times as far below the plane and then releasing all twelve weights simultaneously. Many other characteristic benzene vibrations can be similarly demonstrated.

Finally, suppose that the model is struck a blow with a hammer. At first sight the weights seem to be performing a complicated motion having no apparent relation to the individual modes referred to above. However, if this apparently random motion is photographed with a stroboscopic camera adjusted successively for each of the frequencies of the normal modes, each of these modes of vibration will be found to be faithfully performed by the weights.

An infrared spectrometer plays the same role with respect to the actual benzene molecule as the stroboscope does to the model. Thus, by measuring the frequencies of the infrared radiation absorbed by a substance, the spectrometer determines the characteristic mechanical frequencies of its molecules. Since these molecular frequencies are functions of the atoms themselves—that is, the spatial arrangement, the valence forces, and to some extent the intermolecular forces—the value of infrared spectroscopic information is obvious.

A question naturally arising at this point concerns the possibilities of a mathematical calculation of the normal modes of vibration. Such a calculation, if successfully completed, should make possible a unique determination of the structure of the molecule in question. The correct structure of the molecule would obviously be that whose calculated frequencies correspond exactly to those observed in the experimental spectrum. Theoretically the expected frequencies can be calculated, provided the strengths of all of the interatomic forces are known. Unfortunately, the complexity of such calculations depends on the number of atoms in the molecules and the symmetry of their geometrical arrangement.

Water, for example, with three atoms involves only a third degree equation, and has accordingly been subjected to thorough

mathematical treatment. Benzene, although composed of twelve atoms, is so symmetrical that a fourth degree equation is the most difficult encountered. The frequencies calculated for this molecule, too, have been found to agree with experimental values. However, if this geometrical symmetry is completely destroyed by substitution, as in ortho-chlorophenol, a rigorous treatment would require the solution of a thirty-third degree equation. Such a task is out of the question. Accordingly, since most of the molecules of interest to the industrial chemist are quite complex, some other method is required to correlate the characteristics of an observed spectrum with the structure of the molecule. Considerable success in this direction has been achieved by a purely empirical approach.

In order to understand the basis for such an empirical method, it will be well to resort again to a discussion of mechanical molecular models. Consider a model of a molecule containing only one C—H bond, such as chloroform,  $Cl_3CH$ . If the C—H spring is stretched and released, the carbon and hydrogen weights vibrate rapidly with a characteristic frequency. The chlorine weights, on the other hand, are so heavy they are almost totally unable to follow the vibration. It is true, at least to a first approximation, that the observed stretching frequency is a characteristic of the C—H spring (bond) and the masses of these two atoms, and is practically independent of the rest of the molecule. Similarly, a bending or deformation can be studied by displacing the hydrogen weight in a direction normal to the axis of molecular symmetry and then releasing it. Again the carbon and hydrogen weights will move characteristically with the remaining weights practically at rest.

These observations lead to the basic premise that, to the extent that atomic forces between a carbon and a hydrogen atom are a function of these two atoms alone, the presence of C—H linkages in a molecule will cause at least two infrared absorptions which are practically independent of the atomic constitution of the rest of the molecule. The validity of this premise has been thoroughly established experimentally. A study of hundreds of molecules containing C—H linkages has shown an absorption around  $2900\text{ cm.}^{-1}$  (C—H stretching) and another around  $1450\text{ cm.}^{-1}$  (C—H bending). Further verification may be found by a study of the absorption spectra of molecules in which the hydrogen atom has been replaced by a deuterium atom of mass two. A mathematical treatment shows that the C—D frequency should be given by the equation  $\nu_{C-D} \cdot \sqrt{2} = \nu_{C-H}$ . In such molecules a frequency in the region of  $2100\text{ cm.}^{-1}$  (C—D stretching) is observed.

Actually, by using a spectrometer of high resolving power, it can be shown that these C—H frequencies are influenced slightly by the relation of the C—H linkage to the molecule as a whole. For example, the exact frequency value of these absorption bands may be used to indicate the degree of saturation of the carbon atom to which the H is attached or whether the C—H occurs in a CH,  $CH_2$ , or  $CH_3$  group.

Although the mathematical approach has been of great value when applied to simple or highly symmetrical molecules, most of the information derived from infrared spectra is obtained by the application of the empirical method. This method consists of comparing the spectra of the largest obtainable number of different molecules having a common atomic group. By a process of elimination it is often possible to find an absorption band whose frequency remains constant throughout the series. The presence, in an unknown, of an absorption at this frequency may reasonably form the basis for a guess that the particular atomic group is present. Confidence in this method can be obtained only by successful applications in a large number of cases.

It must not be assumed from this discussion that it is, or will be, possible to ascribe every observed absorption to a specific atomic group. Indeed, if this were true it would make more difficult the possibility of differentiating clearly between isomeric compounds.



Actually only a few of the observed bands can usually be correlated in this manner. The majority of observed bands arise from normal modes of vibration which are characteristic of the molecule as a whole. These general absorption bands are very sensitive to structural changes, and so furnish us with a "finger-print" of the molecule. They also make possible the analysis of isomeric mixtures and provide the basis for quantitative analyses of other closely related compounds.

The normal vibrations of a molecule do not account for all of the absorption bands observed in its infrared spectrum. For example, in the far infrared there are absorptions caused by the slower rotations of the molecules or the massive lattice vibrations of crystals. Moreover, throughout the whole infrared region absorptions frequently occur at integral multiples (overtone bands) of the fundamentals, or at frequencies which are equal to the sum or difference (combination bands) of fundamentals. These bands in general absorb very much less strongly than do the fundamentals and consequently must be studied with thicker samples. Since they are so sensitive to the over-all molecular structure, they can sometimes be used more successfully for accurate fingerprinting of molecules and for the analysis of mixtures than the fundamental absorptions.

### THE INTENSITY OF INFRARED ABSORPTION BANDS

Except for special cases where intermolecular action occurs, the amount of light transmitted by a sample is governed by Beer's law  $I_\nu/I_{\nu 0} = e^{-k_\nu x}$ .  $I_{\nu 0}$  is the radiation incident on, and  $I_\nu$  the radiation transmitted by, the sample at the frequency  $\nu$ ;  $k_\nu$  is the absorption coefficient of the sample material at the frequency  $\nu$ ;  $c$  is the concentration of a given material in the sample being studied; and  $x$  is the length of the optical path or thickness of the absorbing layer of sample. In general, the infrared data shown are presented as a plot of  $I_\nu/I_{\nu 0}$  as ordinates versus  $\nu$  (or  $\lambda$ ) as abscissas. The factors which influence  $k_\nu$  have already been discussed. The value of this constant will be appreciable only when  $\nu$  is an infrared-active fundamental, overtone, or combination frequency. In general,  $k_\nu$  will have a larger value for polar than for nonpolar compounds. Thus, for example, water, alcohol, and acetone absorb infrared very strongly, while the hydrocarbons absorb weakly. The value of  $k_\nu$  is fairly insensitive to pressure and, except in special cases, is practically independent of temperature. However,  $k_\nu$  is not entirely a unique function of molecular structure for slight variations in its values occur between the solid, liquid, and vapor phases of the same molecule. These changes appear as small shifts in the frequencies or intensities of maximum absorption—i. e., maximum  $k_\nu$  values—and are caused by the varying extent to which the internal vibrations of one molecule are affected by those by its neighbors.

The question may be raised: Why are not infrared spectra plotted as graphs of  $k_\nu$  versus frequency instead of  $I_\nu/I_{\nu 0}$  versus frequency? Graphs using  $I_\nu/I_{\nu 0}$  are functions of both  $c$  and  $x$ , whereas those using  $k_\nu$  should be independent of these factors and accordingly more generally applicable. As will be pointed out in a later section, most infrared spectrometers have varying amounts of scattered light and employ varying spectral slit widths in order to attain the sensitivity and stability required in measuring the spectrum with sufficient accuracy. An accurate value of  $k_\nu$  can be obtained only with an instrument which either has no scattered light or for which the amount of scattered light is known at each frequency. Since  $k_\nu$  is also a function of spectral slit width, this too would have to be known at each frequency. Furthermore, accurate measurements of sample thickness are extremely difficult. Other difficulties also intervene and until infrared spectrometers have been improved materially and standardized, the conventional plots of  $I_\nu/I_{\nu 0}$ , rather than  $k_\nu$ , versus frequency are preferable.

### QUALITATIVE ANALYSIS

As shown by our previous analogy to molecular models, the atoms of an organic molecule are constrained to oscillate about their equilibrium positions by the valence forces which exist between the atoms. To a first approximation and for purposes of illustration only, these vibrations may be considered to obey Hooke's law. To the extent that this is true, any equation set up to describe these motions must be dimensionally similar to that which holds for simple harmonic vibrations, namely,

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

In this expression,  $\nu$  is the frequency in  $\text{cm.}^{-1}$ ,  $c$  is the velocity of light,  $\mu$  is the reduced mass of the vibrating atoms, and  $k$  is the force constant which exists between the atoms. The reduced mass,  $\mu$ , is calculated from the relationship  $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$ , where  $m_1$  and  $m_2$  are the relative masses of the vibrating atoms. This constant,  $k$ , is related to the vibrations by the equation

$$V = \frac{1}{2} kx^2$$

where  $V$  is the potential energy and  $x$  the displacement of the atoms from their equilibrium positions. Upon substituting the proper universal constant, the dimensional formula above may be reduced to

$$\nu = 1307 \sqrt{\frac{k}{\mu}} \text{cm.}^{-1}$$

where  $k$  is used as a pure number and  $\mu$  is expressed in dimensionless atomic mass units.

A brief examination of the literature shows that the value of  $k$  for practically all single bonds lies between 4 and  $6 \times 10^5$  dynes per cm. The corresponding values for double bonds lie between 8 and 12, while those for triple bonds generally lie between 12 and  $18 \times 10^5$  dynes per cm. For purposes of illustration these values, along with the proper values for  $\mu$ , may be substituted to calculate the approximate vibration frequencies for a few typical atom pairs.

For the C—H in methane the value of  $k$  has been found to be almost exactly equal to  $5 \times 10^5$  dynes per cm. Since the carbon is so heavy in comparison to the hydrogen, it remains practically at rest, and the value of  $\mu$  is close to 1. Thus,

$$\nu_{\text{C-H}} = 1307 \sqrt{\frac{5}{1}} = 2920 \text{cm.}^{-1}$$

For the C—O in methyl alcohol the force constant is still very close to  $5 \times 10^5$  dynes per cm., but the value of  $\mu$  jumps to about 6.85, causing  $\nu_{\text{C-O}}$  to be much lower than  $\nu_{\text{C-H}}$ .

$$\nu_{\text{C-O}} = 1307 \sqrt{\frac{5}{6.85}} = 1110 \text{cm.}^{-1}$$

Analogously, for C=O in acetone

$$\nu_{\text{C=O}} = 1307 \sqrt{\frac{12}{6.8}} = 1730 \text{cm.}^{-1}$$

Similar calculations for the C≡N group in HCN lead to a value for

$$\nu_{\text{C=N}} = 1307 \sqrt{\frac{15}{6.5}} = 2000 \text{cm.}^{-1}$$

In the infrared spectra of these four compounds there are strong absorption bands at 2915, 1034, 1744, and 2080  $\text{cm.}^{-1}$ . Moreover, a study of a series of molecules containing one or more of



TABLE I. TYPICAL INTERATOMIC CHARACTERISTICS

Atom Pair	Reduced Mass	$k$	Interatomic Distance A.	Absorption Frequency $\text{Cm.}^{-1}$	Compound
C—C	6	4.50	1.54	993	$\text{C}_2\text{H}_6$
C—O	6.85	5.77	1.43	1034	$\text{CH}_3\text{OH}$
C—N	6.46	...	1.47	1045	$\text{CH}_3\text{NH}_2$
C=C	6	9.77	1.33	1623	$\text{C}_2\text{H}_4$
C=O	6.85	12.06	1.21	1744	$\text{H}_2\text{CO}$
C=N	6.46	...	1.26	1653	$\text{CH}_3\text{CHNOH}$
C C	6	17.2	1.20	1975	$\text{C}_2\text{H}_2$
C O	6.85	...	1.10	2169	CO
C N	6.46	16.6	1.15	2089	HCN
C—H	0.92	5.07	1.07	2915	$\text{CH}_4$
O—H	0.94	...	0.96	3683	$\text{CH}_3\text{OH}$
N—H	0.93	...	1.00	3370	$\text{CH}_3\text{NH}_2$
				3315	
S—H	0.97	...	1.3	2597	$\text{C}_2\text{H}_5\text{SH}$

these linkages shows the characteristic bands approximately at the calculated frequencies. Thus, it is seen that these approximate values of  $k$  and  $\mu$  determine the absorption frequency for a particular atom pair. The slight variations observed in these frequency positions of maximum absorption for molecules that are closely related chemically (hence slight variations in  $k$  and  $\mu$ ) make it possible, in many cases, to use the exact frequency empirically as a means not only of telling that a given atomic group is present but also of determining the relation of this group to the remainder of the molecule.

Conversely, once the value of the absorption frequency of a given band has been determined experimentally, it is often possible to calculate the force constant,  $k$ , or the binding energy between the vibrating atoms.

Published data show that in general the larger the value of  $k$  the shorter the equilibrium distance between the atoms concerned. Table I is presented to show the effect of  $k$  and  $\mu$  upon these interatomic distances and upon the frequencies of absorption.

The above discussion is presented in order to give some indication of the theoretical basis for the fact that certain atomic pairs or groups give rise consistently to absorption bands in a well defined region of the spectrum. However, it is to be emphasized that this treatment of extracting a portion of a molecule and treating this portion mathematically is only an approximation and should not be carried to an extreme. The method is applicable to only a very few types of atomic vibrations and it is definitely impossible to start with published data of interatomic distances or force constants and calculate the entire infrared absorption spectrum of a material by this simple means.

Using an empirical approach the authors have examined repeatedly the spectra of many hundreds of organic compounds, and these searches have rarely failed to reveal interesting correlations between bond frequencies and structural relationships. It would be out of place to cite each of these correlations, but a few are given as illustrations of the type of information which may be obtained through careful study of a large number of infrared spectra. It must be pointed out, however, that the curves used in these studies, some of which are reproduced in a later section, were obtained through the use of the large research type spectrometer described above. Users of lower resolving power instruments may experience difficulty in checking some of the correlations indicated below. In view of the inability of any prism spectrometer to resolve completely the structure of complex bands it is frequently true that the shape of a given region of the spectrum is just as important from a qualitative analysis point of view as the exact values of the absorption maxima or transmission minima. In the interest of economy of space, however, we have chosen, in the remainder of this section, to present the illustrations of constant bond frequencies through the use of line graphs rather than full transmission curves. In these graphs the height of the line may be taken as a rough measure of the intensity of the absorption.

(a) High frequency ( $3\mu$ ) region

In the region from  $3700 \text{ cm.}^{-1}$  to  $2500 \text{ cm.}^{-1}$  occur the absorption bands arising from hydrogen stretching vibrations, the oscillating motion of a hydrogen atom in the direction of its valence bond. Unfortunately, the dispersion of a rock salt prism is not very good in this region and a lithium fluoride prism or a grating is necessary to make available all the qualitative information which the region offers. However, the type of information which can be obtained from a sodium chloride prism is shown in Figure 4.

"Free" hydroxyl vibrations, where the hydrogen is not affected by any atom except the oxygen to which it is bound, have a characteristic absorption between  $3700$  and  $3500 \text{ cm.}^{-1}$ . If the material is concentrated so that "hydrogen bonding" can occur, this absorption becomes broader and stronger and moves to lower frequency. It has been shown that there is a relationship between the energy of the hydrogen bond and the frequency shift from "free" to "associated" state. Because the hydroxyl frequency is exceptionally sensitive to the effects of intermolecular association and internal chelation, it is always necessary to consider the physical state of the sample in interpreting this region. Benzyl alcohol, diluted in carbon tetrachloride, shows the free hydroxyl absorption at  $3640 \text{ cm.}^{-1}$ , while in the pure material this band has shifted to a broad deep absorption centering around  $3350 \text{ cm.}^{-1}$ . Under high dispersion these association bands sometimes show discrete structure which probably arises from the types of molecular aggregates involved.

N—H bonds show a characteristic absorption between  $3500$  and  $3200 \text{ cm.}^{-1}$ . Aniline has two N—H bonds, one at  $3445 \text{ cm.}^{-1}$  and

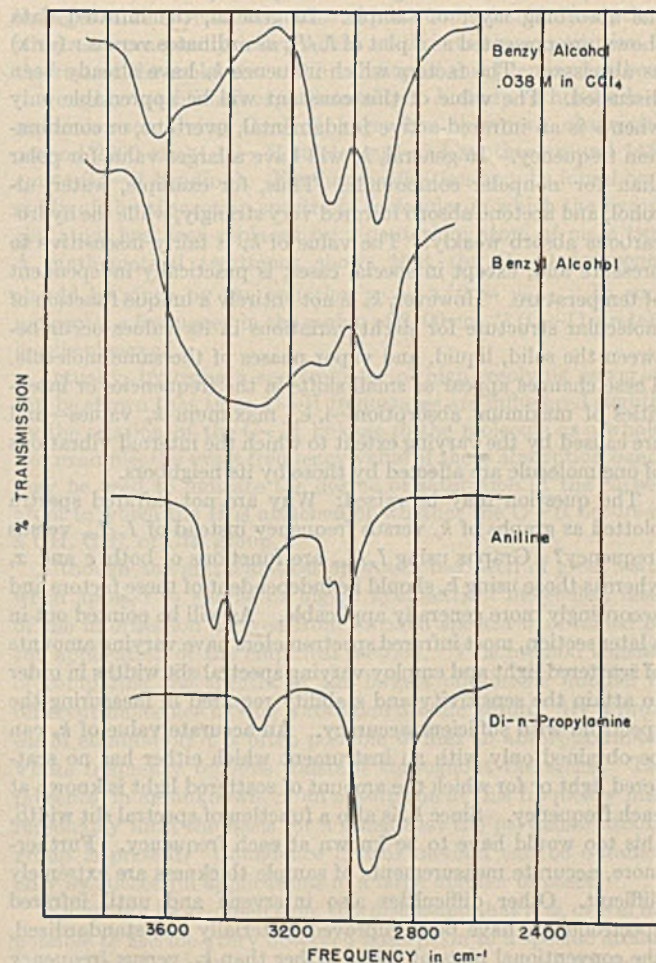


FIGURE 4. CHARACTERISTIC ABSORPTIONS OF X—H BONDS



TABLE 2  
C=O FREQUENCIES

Molecule	Absorption Frequencies				
	1850	1800	1750	1700	1650
<b>Anhydrides</b>					
Acetic anhydride					
Caproic anhydride					
Crotonic anhydride					
Maleic anhydride					
Phthalic anhydride					
<b>Esters</b>					
Methyl acetate					
Allyl acetate					
Dibutyl maleate					
Dibutyl fumarate					
Methyl acrylate					
Diamyl phthalate					
Ethyl carbonate					
Diallyl adipate					
Methyl oleate					
Methyl methacrylate					
Dimethyl itaconate					
Methyl octadecadienate					
Dimethyl phthalate					
Tung oil esters					
<b>Acids</b>					
Maleic acid					
Fumaric acid					
p-Toluic acid					
m-Toluic acid					
o-Toluic acid					
p-Hydroxy benzoic acid					
m-Hydroxy benzoic acid					
o-Hydroxy isobutyric acid					
Undecylenic acid					
<b>Ketones</b>					
Ketobutanol					
Methyl isopropyl ketone					
Acetone					
Acetonyl acetone					
Cyclohexanone					
Acetophenone					
Benzophenone					
Mesityl oxide					
p-Isopropyl benzaldehyde					
Fenchone					
<b>Aldehydes</b>					
Formaldehyde					
Methacrolein					
Salicylaldehyde					
Benzaldehyde					
Furfural					
m-Tolualdehyde					

(b) Unsaturated region

Absorption bands originating in unsaturated bonds between atoms of the second row of the periodic table occur between 2300 and 1300  $\text{cm}^{-1}$

The highest frequencies observed are those of the triple bonds between 2300 and 2000  $\text{cm}^{-1}$  from such linkages as  $\text{C}\equiv\text{C}$ ,  $\text{C}\equiv\text{N}$ , and the  $\text{C}\equiv\text{O}$  of carbon monoxide and carbon dioxide. There is little chance of error in ascribing an observed band in this region to a triple bond origin, for the only other fundamental vibrations which can occur here are the above-mentioned X—D vibrations.

Carbonyl frequencies fall between 1850 and 1650  $\text{cm}^{-1}$  as shown by the line graphs of Table 2. To a certain extent these bands fall in a fairly narrow region of the spectrum according to the relationship of the group to the rest of the molecule. The anhydrides usually show a double band with one minimum between 1850 and 1800  $\text{cm}^{-1}$ , the other between 1800 and 1750  $\text{cm}^{-1}$ . Ester carbonyls are generally in the region from 1750 to 1725  $\text{cm}^{-1}$ , aldehydes and ketones from 1725 to 1690  $\text{cm}^{-1}$ , and acids from 1700 to 1670  $\text{cm}^{-1}$ . These criteria are not always valid, for it can be seen from the graph that low members of a series are often out of line while conjugation tends to lower the characteristic frequencies. Other regions of the spectrum can be used to check the tentative correlation of an observed carbonyl bond. If an acid is suspected, the high frequency region can be examined for hydroxyl absorption. Esters in general show a strong band from 1300 to 1200  $\text{cm}^{-1}$  which probably arises from the single bond carbon oxygen where the carbon is an unsaturated atom. Phthalates in particular show a characteristic triplet at 1275, 1120, and 1070  $\text{cm}^{-1}$ .

Aliphatic carbon-carbon double bond linkages occur between 1660 and 1600  $\text{cm}^{-1}$  as shown by typical examples in Table 3. It is to be noticed that such bands usually occur between 1660 and 1640  $\text{cm}^{-1}$  when the bond is not conjugated. When the bond is conjugated with an aromatic unsaturation, the frequency drops to 1625  $\text{cm}^{-1}$ , whereas, if full aliphatic conjugation occurs, the frequency is nearer 1600  $\text{cm}^{-1}$ . It would be well to repeat the point here that atomic motions give rise to infrared absorption only if the vibration causes a change in dipole moment. Therefore, the  $\text{C}=\text{C}$  absorption may be weak or nonexistent if the bond occurs in a perfectly symmetrical molecule such as ethylene, or

the other at 3368  $\text{cm}^{-1}$ , because of the interaction between the two hydrogen atoms on the same nitrogen. Di-n-propylamine, on the other hand, shows only one absorption band.

C—H frequencies occur between 3200 and 2800  $\text{cm}^{-1}$ . This region is subdivided by the characteristic that the band is usually above 3000  $\text{cm}^{-1}$  if the carbon atom is unsaturated or if the hydrogen occurs in highly halogenated compounds. In normal aliphatic compounds, the band usually occurs below 3000  $\text{cm}^{-1}$ . In benzyl alcohol both saturated and unsaturated carbons and C—H bands are observed in each region, respectively. In aniline, only unsaturated carbon hydrogen bands occur at 3080 and 3040  $\text{cm}^{-1}$ , while di-n-propylamine has only saturated C—H at 2950 to 2870  $\text{cm}^{-1}$ . With higher dispersion the unsaturated C—H region shows structure characteristic of  $\text{CH}$ ,  $\text{CH}_2$ , and  $\text{CH}_3$  groups.

Another bond of interest to the chemist is the S—H group whose characteristic absorption lies in the region of 2500  $\text{cm}^{-1}$ . A study of the simplified Hooke's law treatment of vibrating atoms shows that the reduced mass,  $\mu$ , of an X—H group is approximately doubled if a deuterium atom is substituted for the hydrogen. There may occur situations where it would be desirable to study separately the behavior of two X—H groups whose frequencies coincide. If it is possible to substitute a deuterium atom for one of the hydrogen atoms, the infrared characteristics of the two bonds will differ to permit individual study while their chemical natures are unchanged.

TABLE 3

ALIPHATIC C=C FREQUENCIES

Molecule	Absorption Frequencies				
	1900	1800	1700	1600	1550
Butene-1					
Butene-2					
$\beta$ -Pinene					
Isobutylene					
Di-isocamylene					
Di-isobutylene					
Dipentene					
Cyclohexene					
$\alpha$ -Pinene					
Indene					
Vinyl acetate					
Allyl acetate					
Dimethyl maleate					
Diallyl adipate					
Diallyl sebacate					
Methyl oleate					
Crotonic anhydride					
Methallyl chloride					
Methyl acrylate					
Methyl methacrylate					
Ethyl crotonate					
Stilbene					
Styrene					
p-Methyl styrene					
p-Methyl $\alpha$ -methyl styrene					
2,3-Dimethyl styrene					
2,4-Dimethyl styrene					
Butadiene					
Piperylene					
Isoprene					



in the middle of a long hydrocarbon chain where the atomic structure at each end of the bond is well balanced.

The carbon-carbon unsaturation of the benzene ring is evidenced by an absorption band near  $1600\text{ cm}^{-1}$  and another near  $1500\text{ cm}^{-1}$ . Not only are these bands very characteristic of the phenyl ring itself but their specific positions in conjunction with other bands throughout the spectrum furnish a tentative determination of the manner in which the ring is substituted. There appears to be some correlation between the type of substitution and the position of the overtone bands between  $2000\text{ cm}^{-1}$  and  $1700\text{ cm}^{-1}$  although this evidence is still meager and may be a function of the particular group substituted. In general the  $1500\text{ cm}^{-1}$  band appears to be high for para substituted molecules. Mono substituted aromatic compounds generally have a band from  $1075$  to  $1065\text{ cm}^{-1}$  and from  $720$  to  $700\text{ cm}^{-1}$ ; ortho substituted,  $1125$  to  $1085\text{ cm}^{-1}$  and  $720$  to  $700\text{ cm}^{-1}$ ; meta substituted,  $1170$  to  $1140\text{ cm}^{-1}$  and  $790$  to  $735\text{ cm}^{-1}$ ; and para substituted,  $1120$  to  $1090\text{ cm}^{-1}$  and  $850$  to  $775\text{ cm}^{-1}$ .

TABLE 4  
AROMATIC RING FREQUENCIES

Molecule	Absorption Frequencies					
	2000	1900	1800	1700	1600	1500 1400
Benzene						
Mono Substituted						
Toluene						
Ethyl benzene						
n-Propyl benzene						
n-Butyl benzene						
Isopropyl benzene						
Secondary butyl benzene						
Tertiary butyl benzene						
Tertiary amyl benzene						
Chlorobenzene						
Styrene						
Phenol						
Anisole						
Phenetole						
Ortho Substituted						
o-Xylene						
o-Chlorotoluene						
o-Dichlorobenzene						
Quinacel						
o-Chlor phenol						
o-Ethyl phenol						
o-Bornyl phenol						
o-Benzyl phenol						
o-Cresyl ethyl ether						
o-Cresyl methyl ether						
Meta Substituted						
m-Xylene						
m-Chlorotoluene						
m-Ethyl phenol						
m-Cresyl ethyl ether						
m-Cresyl methyl ether						
Para Substituted						
p-Xylene						
p-Cymene						
p-Ethyl toluene						
p-Chlorotoluene						
p-Methyl styrene						
p-Methyl -methyl styrene						
p-Chlor phenol						
p-Ethyl phenol						
p-Tertiary butyl phenol						
p-Tertiary amyl phenol						
p-Bornyl phenol						
p-Methoxy tertiary amyl benzene						
p-Cresyl ethyl ether						
p-Cresyl methyl ether						

Other common unsaturated bands of interest are the C=O group which absorbs near  $1650\text{ cm}^{-1}$  and  $\text{NO}_2$  which generally has bands near  $1550\text{ cm}^{-1}$  and  $1340\text{ cm}^{-1}$ . In this region bands are also to be expected which arise from water or from unsaturated ring structures whose characteristics are not well known.

Some other characteristic absorptions may be reviewed briefly: The terminal group  $\text{H}_2\text{C}=\text{CHX}$  has an overtone band near  $1800\text{ cm}^{-1}$  and a  $\text{CH}_2$  bending vibration between  $1420$  and  $1400$

$\text{cm}^{-1}$ . The presence of  $\text{CH}_2$  or  $\text{CH}_3$  groups in a material gives rise to absorption between  $1475$  and  $1430\text{ cm}^{-1}$ , while a band at  $1375\text{ cm}^{-1}$  is indicative of the grouping  $\text{C}-\text{CH}_3$ . This  $1375\text{ cm}^{-1}$  band is quite characteristic of the type of methyl structure present. For a tertiary butyl group the band is split with a weak component about  $1385\text{ cm}^{-1}$  and a strong one at  $1367\text{ cm}^{-1}$ , while for isopropyl groups the band is split into a doublet at  $1380$  and  $1370\text{ cm}^{-1}$  of approximately equal intensity. C-Cl bonds have a strong band about  $750\text{ cm}^{-1}$  with an overtone at about twice that frequency. A C-O linkage where the carbon is unsaturated has a band between  $1250$  and  $1200\text{ cm}^{-1}$ , as evidenced by esters and aromatic ethers. If the carbon atom is saturated, this band is at a lower frequency, as in aliphatic ethers, near  $1100\text{ cm}^{-1}$ .

This type of empirical correlation between observed absorption and molecular structure is essential to qualitative analysis and it is here that a great deal of work must be done. At the present time, frequencies above  $1350\text{ cm}^{-1}$  allow fairly definite assignments while those below  $1350\text{ cm}^{-1}$  will necessarily be less definite because these vibrations generally involve all the atoms of a molecule rather than those of a specific part. Moreover, exceptions to any correlation will be found because the exact values of the frequencies are always dependent on the rest of the molecular substitutions or unsaturations, and accidental degeneracies will occur to split an expected single band into a doublet which will confuse the spectrum. However, the information which has already been gained has proved of great value in such applications as indicating the presence or, of equal importance, the absence of specific groups in an unknown material. It will well repay spectroscopists to obtain more data, to group and regroup all available spectra for studying a specific molecular characteristic, and to draw conclusions from these studies which will permit of a standard, rapid infrared approach to the identification of unknown compounds.

## QUANTITATIVE ANALYTICAL TECHNIQUES

It has been pointed out previously that the experimental difficulties which have hindered the general progress of infrared spectroscopy have been the lack of strong energy sources and adequate energy detectors. These two weaknesses are most keenly felt in making accurate intensity measurements. It is only natural, therefore, that in the past one of the most practical applications of infrared, its use for quantitative analysis, should have received very little attention compared with its qualitative applications. However, the fact remains that infrared answers the two prime requisites for analysis: that every compound should have a unique characteristic and that it should retain that characteristic on admixture with other materials. The infrared spectrum of an organic material is a unique characteristic of that material, and the infrared spectrum of a mixture of materials is, in almost all cases, an additive function of the spectra of each component in a pure state. These facts, combined with the characteristics of speed, small sampling, and the ability to recover the sample unchanged have impelled the industrial infrared spectroscopist to improve his experimental techniques to the extent that an appreciable percentage of his time is now spent in performing accurate quantitative analyses.

The fundamental rule correlating component concentration with the absorption intensity of that component is the well known Beer's law  $I_p = I_0 e^{-k_p c x}$  which was discussed under Origin of Infrared Spectra. Theoretically, the application of this law to the analysis of any mixture is quite straightforward. The spectra of each component is obtained in a pure state. By comparison of these spectra, those frequencies are chosen for which one component shows a strong absorption whereas the absorption of the other components is weak. Using pure materials ( $c = 100$  per cent) and known or constant values of  $x$ ,  $k_p$  is determined for each component at each of these chosen frequencies.



With these calibration data obtained, the analysis of an unknown mixture consists first of determining experimentally the per cent transmission ( $I/I_0$ ) for each chosen frequency. The logarithm of these transmissions then furnishes a set of linear equations,  $\log(I_\nu/I_{0\nu}) = x(k_\nu c_a + k_\nu c_b + \dots)$ , which can be solved for the desired concentrations  $c_a, c_b$ , etc. Theoretically the method is straightforward but actually it may be complicated by experimental difficulties or tedious mathematics in case the number of components is large. Therefore, while it may be considered a rigorous method of analysis, in particular cases it is desirable to seek short cuts and more empirical methods of analysis which will shorten the process without sacrificing accuracy.

It is not feasible to discuss all the possible types of analysis which may arise nor to go into great detail on all the methods of treatment which may be used. Rather, the subject is treated by a consideration of the instrumental difficulties attendant upon infrared analysis and the bearing which these difficulties may have on the method to be used; a brief discussion of the possible methods of handling materials in vapor, liquid, or solid state; and finally, a few illustrations of typical analyses.

There are two main characteristics of the analytical instrument to be used which will influence the method of analysis chosen. The first of these is that an infrared spectrometer is apt to suffer from scattered light. The typical infrared source (an approximation to the black body radiator of Figure 5) throws most of its energy into short wave radiation and it is these short wave components which are scattered most strongly. As can be seen from Figure 5, a black body source at  $2000^\circ$  C. has an intrinsic energy at  $1.5\mu$  which is about one hundred times greater than the energy in the  $10\mu$  region where a great deal of analytical work is done. The presence of scattered light in a measurement of  $I/I_0$  makes the direct use of Beer's law inaccurate, especially at low values of  $I/I_0$ . While it is true that the amount of scattered light in an instrument can be determined as a function of  $\nu$ , it is difficult to determine the extent to which this factor is reduced when an arbitrary sample is introduced into the light path.

Careful instrumental technique is required to reduce the short wave scattered light to the point where it is an unappreciable percentage of the longer wave-length energy desired. One method is to introduce at the entrance window of the spectrometer a magnesium oxide filter whose particle size is so chosen as to cut off light of frequency higher than the highest frequency used in the analysis. Again, the shutter used for determining the galvanometer reading for true zero energy may be so chosen that it will stop all radiation at the analytical frequency but will transmit a great portion of the energy at higher frequency. By the use of such devices, as well as careful light baffling inside the spectrometer, the factor of scattered light in analysis can be reduced so that it is negligible.

The other analytical difficulty lies in the relation of the spectral slit width used to the width of the characteristic band whose absorption is to be measured. In the ultraviolet and visible regions, the absorption bands studied are generally much broader than the spectral slit width used. Therefore, it is possible for one ultraviolet or visible spectroscopist to publish a value of the absorption coefficient,  $k_\nu$ , for a pure material, and for another operator to use this value directly with his own instrument.

Unfortunately, this situation does not exist at present for the infrared spectroscopist. Most organic molecules possess absorption bands whose widths at half maximum are of the same order of magnitude as the spectral slit width ( $10$  to  $15\text{ cm.}^{-1}$ ) used to scan the bands. For independent operators to use a published value of  $k_\nu$  on instruments which are not identical, would require an accuracy of frequency setting and spectral slit width that would exceed normal operating conditions. This means that, until infrared instruments are more standardized and instrumental technique becomes more accurate, published values of  $k_\nu$  or plots of  $I/I_0$  vs.  $\nu$  can be used as rough values to indicate the possibilities of analysis, but each spectroscopist must determine

usable values of  $k_\nu$  and limits of error as a function of his own instrument.

The accuracy with which an instrument can be made to repeat a frequency setting and spectral slit width within the time which can be devoted to a given analysis, will determine the general method to be used. If these factors can be reproduced, a previously determined working curve of per cent transmission vs. component concentration or a value of  $k_\nu$  can be used safely over considerable time intervals. If the conditions cannot be repeated with sufficient accuracy, it is necessary to measure standard mixtures together with the unknown until the desired degree of bracketing for interpolation is attained.

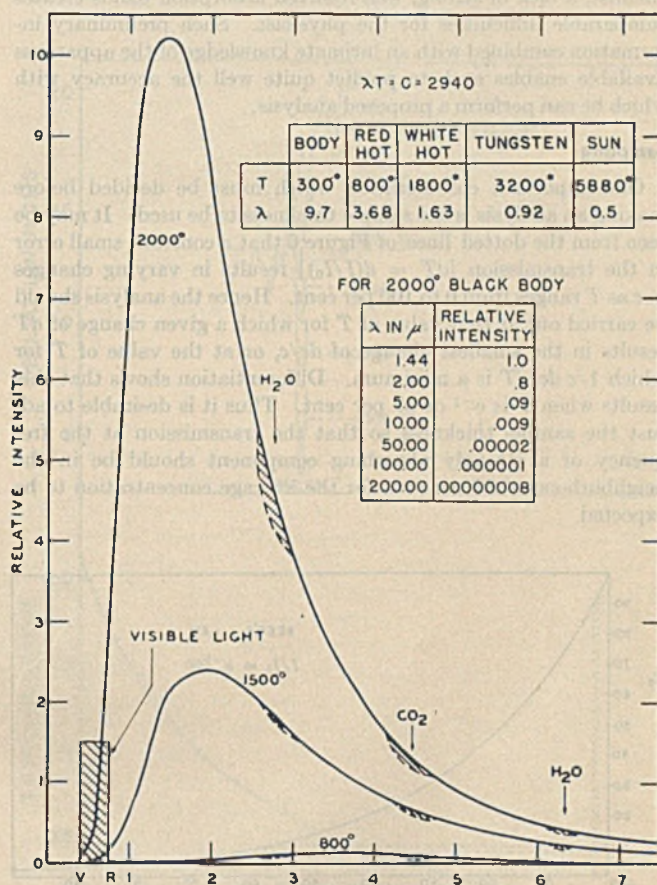


FIGURE 5. EMISSION OF A BLACK BODY RADIATOR

Assuming the possibilities of repeating experimental conditions or running enough standards for correlation, the accuracy of the typical analysis is limited further by the ability of the instrument to measure a per cent transmission. This depends on galvanometer steadiness, sharpness of thermal equilibrium, the stability of the source during the time interval required to measure  $I_{0\nu}$  and  $I_\nu$ , etc. These uncertainties are functions of the instrument only and are fairly independent of the absolute value of  $I_\nu/I_{0\nu}$ . A study of the graph of Beer's law, Figure 6, shows that a given error in the measurement of  $I_\nu/I_{0\nu}$  represents a much smaller error, based on total composition, when the concentration of the component is small than when it is large. That is, spectroscopic analyses are, in general, better at measuring small amounts of impurity than at measuring major components. Therefore, in simple analyses, it is generally better to measure the lesser components directly and obtain the major component by difference, provided all the components present are known.

To a certain extent, a nice analogy can be drawn between the conditions for the physicist's infrared analysis and the chemist's



distillation analysis of a mixture. Each would like to know beforehand all the components involved. In case all the constituents are not certain, the chemist can run a very careful distillation to see if the observed boiling point plateaus correspond to the expected components. The infrared spectroscopist can obtain a careful absorption spectrum of the mixture to check that all observed bands can be correlated with the expected components. The chemist requires the a priori knowledge of boiling points, probabilities of constant boiling mixtures, decomposition, or polymerization in order to predict the possibilities of analysis; the spectroscopist, the a priori knowledge of pure spectra and the possibilities of intermolecular effects which vary with concentration. Where close boiling points are troublesome for the chemist, a lack of strong, well resolved absorption bands creates comparable difficulties for the physicist. Such preliminary information combined with an intimate knowledge of the apparatus available enables each to predict quite well the accuracy with which he can perform a proposed analysis.

### Sampling

One important consideration which must be decided before making an analysis is the sample thickness to be used. It may be seen from the dotted lines of Figure 6 that a constant small error in the transmission [ $dT = d(I/I_0)$ ] results in varying changes in  $c$  as  $T$  ranges from 0 to 100 per cent. Hence the analysis should be carried out at that value of  $T$  for which a given change of  $dT$  results in the smallest change of  $dc/c$ , or at the value of  $T$  for which  $1/c \, dc/dT$  is a minimum. Differentiation shows that this results when  $T$  is  $e^{-1}$  or 37 per cent. Thus it is desirable to adjust the sample thickness so that the transmission at the frequency of a strongly absorbing component should be in the neighborhood of 37 per cent for the average concentration to be expected.

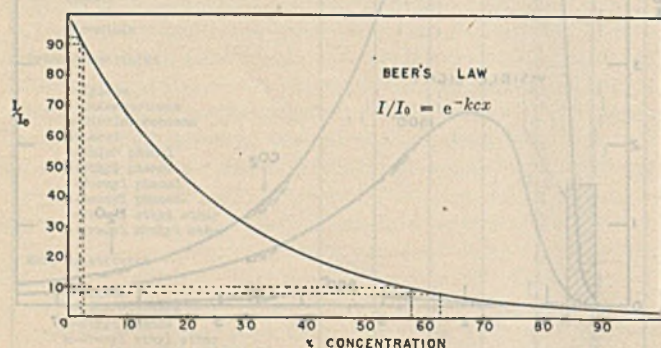


FIGURE 6. GRAPH OF BEER'S LAW

The above considerations apply only to the measurement of a single component in the presence of a nonabsorbing medium. In the case of a multicomponent analysis further study shows that the value of  $T$  should be lower than 37 per cent by a function of the absorption coefficients of these other components. Fortunately the function  $1/c \, dc/dT$  does not vary rapidly with  $T$ , so that no appreciable accuracy is lost if  $x$  is so chosen that  $T$  lies between 25 and 50 per cent.

In considering analysis of samples in the gas, liquid, or solid state, gas analysis presents the most favorable situation for two reasons. In the first place, the sample thickness, the product of pressure by cell length, can be regulated by a choice of either factor. For any given cell length, the pressure can be varied easily to ensure the best value of  $T$  at each frequency. Moreover, since the cell length is of the order of centimeters it can be measured easily and the pressure can be measured accurately by means of a mercury or Octoil manometer. In the second place, vapor analysis is favorable because there is little interference from intermolecular effects. For molecules possessing some degree of

geometrical symmetry there are vibrations which do not result in infrared absorption because they do not involve a change of dipole moment. However, in the liquid or solid state, these vibrations may give rise to absorption, inasmuch as the selection rules are modified by intermolecular reactions. It is true that these absorptions are weak but they may become appreciable in using a thick sample to bring out a slight impurity. Therefore, the favorable analytical situation of one component absorbing strongly against a weak background from the other components is more probable in the vapor than in the liquid or solid state. Gas cells generally vary from 1 to 20 cm. and the pressures may run from a few millimeters of mercury to atmospheric pressure (or greater).

The sample thickness for liquids varies from less than 0.01 mm. for very polar materials to 10 mm. to bring out overtone or combination bands. Working with such small dimensions poses the problem of an absorption cell which will repeat its thickness to better than 0.5 per cent. The simplest way to meet this problem is to make a cell of fixed thickness which can be cleaned and refilled. For a given analysis it is not necessary that the sample thickness be known accurately, but it is necessary that it be repeated accurately. Cells for this purpose can be made by clamping two rock salt plates together with an appropriate metal foil spacer to fix the thickness. Holes may be drilled in the top of the cell plates and glass or brass tubes inserted for corking volatile materials. The cells may be sealed by using a mercury amalgamated spacer or by coating with a suitable material such as Apiezon wax, Duco cement, or Glyptal resin. If the liquids are volatile the cell can be cleaned by a stream of dry air; if not, air combined with a suitable volatile solvent can be used. For fixed cells less than 0.05 mm., capillary action restricts the ease of cleaning and refilling. If it is necessary to work with a sample thickness less than 0.05 mm. in order to get the required transmission, it is best to dilute the sample with some material which has weak absorption at the frequencies of interest. However, since all solvents show some infrared absorption, it is usually desirable to use as thin a cell as is compatible with the solubility of the material in question. The cell thickness chosen for a given analysis should give the best compromise of transmission values at the chosen frequencies or more than one fixed cell must be used.

There are occasions where a choice can be made between studying a mixture in a liquid or completely vaporized state. As a rule this choice can be made only after experimenting with each method. While vapor studies have the advantages discussed above, it is also true that values of  $k$ , vary considerably as the material goes from the liquid to the vapor state and it may happen that an impurity band will show a greater value of  $k$ , relative to the background in the liquid state.

The sample thickness for solids is of the same order of magnitude as that for liquids. If the solid material can be dissolved in a suitable solvent, the methods of liquid analysis can be used. If it is not soluble, then the problem of repeating a sample thickness becomes so difficult that the time involved would be prohibitive in the general case. There is some possibility of working with known amounts deposited from solution or mulled in Nujol where the same plates and spacer conditions could be repeated. However, this method, at best, is not very satisfactory. The easiest method of attack is to repeat the sample thickness as closely as possible by identical methods of preparation. The analyses can then be made for component ratio by measurements of relative band depths or by including a known amount of some new material to be used as an internal standard.

### Typical analyses

A few typical analyses have been chosen to illustrate the various methods of treatment which may be used. Most of these are applications which have been made in this laboratory as actual analyses or to determine the accuracy which might be expected



if the analysis were undertaken. The absorption spectra on which they are based are given in the section on Library of Reference Curves.

#### I. DETERMINATIONS OF A SINGLE COMPONENT—I. e., MEASUREMENT AT A SINGLE FREQUENCY

##### 1. Impurity Analysis

The simplest analysis which is encountered is the measurement of a material for a small amount of an expected impurity. An example of such an analysis is the determination of cyclohexanone in cyclohexane shown in Figure 7. The obvious frequency for analysis is the strong carbonyl absorption of cyclohexanone at  $1718\text{ cm.}^{-1}$  where cyclohexane itself has very weak absorption. Four possible methods of analysis are discussed in the light of experimental conditions and the accuracy desired.

a. Record Comparison. This method of analysis is based upon the automatic absorption records of galvanometer deflection obtained for a series of known standard mixtures. An unknown can then be determined by visual comparison of the absorption record of the unknown with those of the known series. The method is rough at best and can be used only with a recording spectrometer, but it is rapid and eliminates the necessity of having to set the instrument accurately at the absorption maximum. A series of such standard absorptions is shown in Figure 7, A. The sharp background absorption structure, which is caused by residual water vapor in the instrument, is useful as an internal frequency calibration standard.

b. Working Curve. A more accurate method of analysis consists of measuring the per cent transmission of an unknown sample of cyclohexane, and determining the per cent of cyclohexanone present by reading directly from a working curve such as that shown in Figure 7, B. This working curve was obtained by setting the instrument at  $1718\text{ cm.}^{-1}$ , and measuring the per cent transmission of the series of known standards with an auxiliary galvanometer lamp and scale. With this method the per cent transmission includes the scattered light contribution and the sample cell absorption since the measurement of  $I_0$  is made with nothing in the light path. Hence the accuracy of the analysis is dependent on the constancy of the cell window absorption, which must be checked from time to time.

A study of Figure 7, B reveals some characteristics that have been discussed previously. The curve at low concentration is almost a straight line as would be expected from an expansion of  $e^{-x}$  where  $x \ll 1$ . With a knowledge of the accuracy with which a per cent transmission can be measured, the error in measuring the concentration can be determined from the slope of the curve at any point. Assuming that the error in reading  $I/I_0$  is  $\pm 1$  per cent, the corresponding error in concentration is  $\pm 0.01$  per cent at 0.1 per cent,  $\pm 0.02$  per cent at 0.5 per cent, and  $\pm 0.1$  per cent at 2 per cent concentrations, respectively. This shows that the absolute error,  $dc/c$ , is a desirable minimum in the neighborhood of 37 per cent transmission where  $dc/c$  is equal to  $0.02/0.5$ . The absorption cell chosen (0.2 mm. thickness) should be used when the cyclohexanone is expected to be about 0.5 per cent concentration. If the impurity is expected to be considerably less than 0.5 per cent, greater analytical accuracy would be obtained with a thicker cell, whereas for concentrations greater than 0.5 per cent a thinner cell should be used.

c. Beer's Law Graph. In Figure 7, C the per cent transmission values of 7, B have been corrected for scattered light and absorption cell plus pure cyclohexane absorption. A plot of  $\log I/I_0$  vs. concentration shows a fairly straight line with some deviation at the high concentrations. In this particular analysis there is no gain in accuracy and a loss in time in going to the straight-line log plot. However, there might arise a case in which there is insufficient material to make up a series of standards, or an unknown impurity may be observed which cannot be identified to make possible a series of known standards. In the latter case the amount of impurity in one sample may be taken as an

arbitrary unit of concentration. A measurement of this sample and the pure material determines  $k_v$ , the slope of the straight line of Figure 7, C. Then the concentrations of this impurity in other unknowns may be measured in terms of the arbitrary unit chosen.

d. Special Methods. It is not strictly true to say that the accuracy of a concentration analysis is always limited by the accuracy of determining a per cent transmission. An exception to this is illustrated by a special method of analysis which can be used for measuring a small concentration of an impurity which does not present a favorable case for analysis—i. e., does not have a strong absorption at a frequency for which the major component absorbs very weakly. A frequency can be chosen, preferably

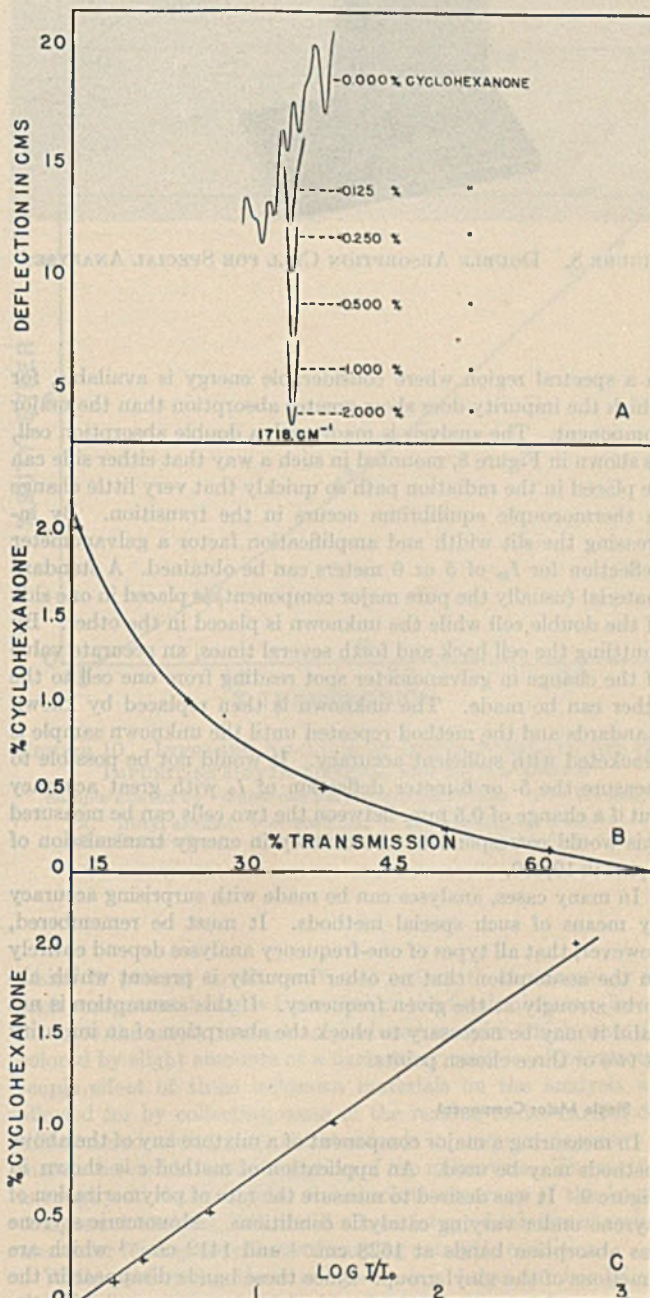


FIGURE 7. ONE COMPONENT INFRARED ANALYSIS FOR CYCLOHEXANONE IN CYCLOHEXANE

$x = 0.2\text{ mm.}$ ; spectral slit, ca.  $8\text{ cm.}^{-1}$

- Automatic record comparison
- Empirical working curve
- Beer's law graph



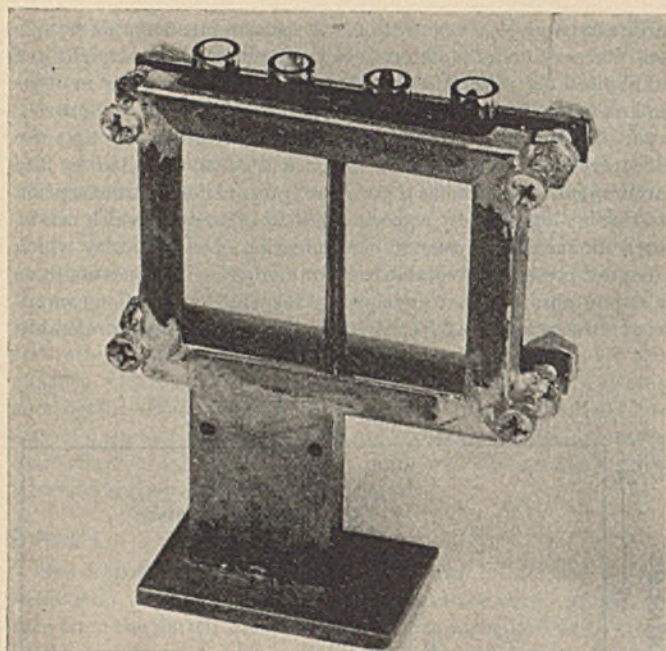


FIGURE 8. DOUBLE ABSORPTION CELL FOR SPECIAL ANALYSES

in a spectral region where considerable energy is available, for which the impurity does show greater absorption than the major component. The analysis is made with a double absorption cell, as shown in Figure 8, mounted in such a way that either side can be placed in the radiation path so quickly that very little change in thermocouple equilibrium occurs in the transition. By increasing the slit width and amplification factor a galvanometer deflection for  $I_{0p}$  of 5 or 6 meters can be obtained. A standard material (usually the pure major component) is placed in one side of the double cell while the unknown is placed in the other. By shuttling the cell back and forth several times, an accurate value of the change in galvanometer spot reading from one cell to the other can be made. The unknown is then replaced by known standards and the method repeated until the unknown sample is bracketed with sufficient accuracy. It would not be possible to measure the 5- or 6-meter deflection of  $I_0$  with great accuracy but if a change of 0.5 mm. between the two cells can be measured this would correspond to an accuracy in energy transmission of 1 part in 10,000.

In many cases, analyses can be made with surprising accuracy by means of such special methods. It must be remembered, however, that all types of one-frequency analyses depend entirely on the assumption that no other impurity is present which absorbs strongly at the given frequency. If this assumption is not valid it may be necessary to check the absorption of an impurity at two or three chosen points.

## 2. Single Major Component

In measuring a major component of a mixture any of the above methods may be used. An application of method *c* is shown in Figure 9. It was desired to measure the rate of polymerization of styrene under varying catalytic conditions. Monomeric styrene has absorption bands at  $1628 \text{ cm.}^{-1}$  and  $1412 \text{ cm.}^{-1}$  which are functions of the vinyl group. Since these bands disappear in the polymer, they may be used as unique measurements for the amount of monomer present. Using the per cent transmission at these frequencies of the starting material as 100 per cent concentration a value of  $k_{1628}$  and  $k_{1412}$  was obtained after making correction for scattered light and background absorption. These values of  $k$  were then used to determine the concentration of

monomer in subsequent samples. Figure 9 shows a typical reaction rate curve obtained on small samples extracted from the reaction kettle at given time intervals. The scattering of the points from a smooth curve indicates the accuracy to be  $\pm 1$  per cent of total composition.

## II. DETERMINATION OF TWO COMPONENTS

### 1. Impurities

*a.* Independent Absorption Frequencies. In favorable cases of analyzing for two or more impurities, the analytical bands can sometimes be chosen so that, where one impurity has a strong absorption, the major component and the other impurity have practically the same small absorption. An example is the analysis of butyl ether and butyl alcohol in butyl acrylate. The working curve method was used as shown in Figure 10. The point scattering shows an accuracy of  $\pm 0.5$  per cent.

*b.* Dependent Absorption Frequencies. There may arise occasions where the favorable situation above does not hold. An example is the analysis of acrylonitrile for water and ethylene cyanhydrin. Each impurity has a hydroxyl absorption, water at  $3430 \text{ cm.}^{-1}$  and cyanhydrin at  $3350 \text{ cm.}^{-1}$ . The analyses were made on an instrument which had a negligible amount of scattered light and the quartz absorption cell thickness was so adjusted that Beer's law would hold over the transmission range used. The per cent transmissions of known standards were obtained by dividing the sample transmission by that of pure acrylonitrile so that the resultant transmissions could be ascribed to the impurity alone. From these transmissions, values of  $k_p$  were obtained for each impurity at each frequency. Unknowns were then analyzed by determining the log of the per cent transmission at each frequency and solving the two simultaneous equations for the concentrations. The accuracy of the analysis was  $\pm 0.5$  per cent for cyanhydrin and slightly better than this for water.

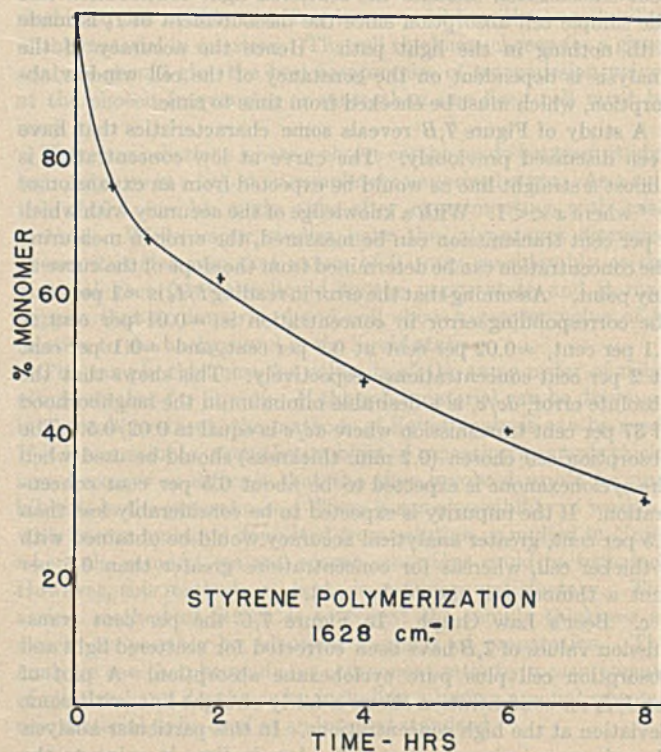


FIGURE 9. INFRARED MEASUREMENT OF A RATE OF STYRENE POLYMERIZATION  
0.3 gm. sample in 10 cc. of  $\text{CCl}_4$   
 $x = 1 \text{ mm.}$   
 $\nu = 1628 \text{ cm.}^{-1}$   
Spectral slit, ca.  $9 \text{ cm.}^{-1}$



## 2. Two Major Components

For two major materials any of the above methods may be used. In cases where the two bands chosen are unique and independent of other impurities, very rapid analysis can be made by using deflection ratios instead of per cent transmissions. For example, it may be desired to obtain the ratio of butane to isobutane in an unknown mixture of these two materials. Isobutane has a strong band at  $1175\text{ cm.}^{-1}$  whereas butane is analyzed at  $975\text{ cm.}^{-1}$ . An analysis can be made simply by obtaining galvanometer deflections as a measure of the radiation passing through the sample at each frequency. The ratio of the two deflections can then be correlated with the ratio of the concentrations by means of a working curve previously obtained on known standards. The method is desirable in that it does not require a cell evacuation to determine  $I_0$  nor is its accuracy sensitive to small variations in the total gas pressure used.

## III. DETERMINATION OF MULTICOMPONENTS

### 1. Impurities

There may be a case where the favorable situation of the butyl acrylate impurities does not exist and yet it is not expedient to use Beer's law directly. A working curve method may be used by applying the proper corrections to the graphs before interpreting the results.

A terpene is converted catalytically to *p*-cymene with the resultant impurities, *p*-menthane, dipentene, and dimethylstyrene. It is desired to analyze *p*-cymene for these three major impurities. A comparison of  $k_p$ 's for the four pure materials shows that *p*-menthane can be analyzed directly but that the dipentene and the dimethylstyrene impurity absorptions must each be corrected for the amount of the other impurities present.

The working curves for this analysis are shown in Figure 11. Because a large number of samples was involved, it was expected that there would be some change in transmission of the fixed absorption cell with use. Therefore, the working curves are plotted in terms of the difference in transmission at each chosen frequency between pure *p*-cymene and the unknown mixture. By measuring pure *p*-cymene at intervals throughout the analyses this change in cell absorption could be accounted for automatically.

The working curve for *p*-menthane, which had to be determined as the first step in the analysis, is shown in Figure 11, A. At the dimethylstyrene frequency, the absorption of *p*-menthane is less than that of *p*-cymene. Therefore, it was necessary to add the correction given in the caption of Figure 11, B. After this correction was made, the concentration of dimethylstyrene was determined. The standards used for this working graph were made up with varying concentrations of *p*-menthane in order to determine this correction. At the frequency of dipentene absorption both *p*-menthane and dimethylstyrene have absorptions which are greater than *p*-cymene and approximately equal. Therefore, the correct factor must be subtracted as indicated in the caption to Figure 11, C. In each case the point scattering of the standards shows an accuracy of the order of  $\pm 1$  per cent.

In order to check the analysis, two standard mixtures were prepared and analyzed as unknowns. The results of these analyses are as follows:

	$X_1$ , %		$X_1$ , %	
	Actual	Infrared	Actual	Infrared
<i>p</i> -Menthane	10.7	10.0	7.5	6.5
Dimethylstyrene	7.1	7.0	5	4.5
Dipentene	3.6	4.0	2.5	2.5

This method of analysis has been extended to the case of measuring five impurities in the presence of a major component

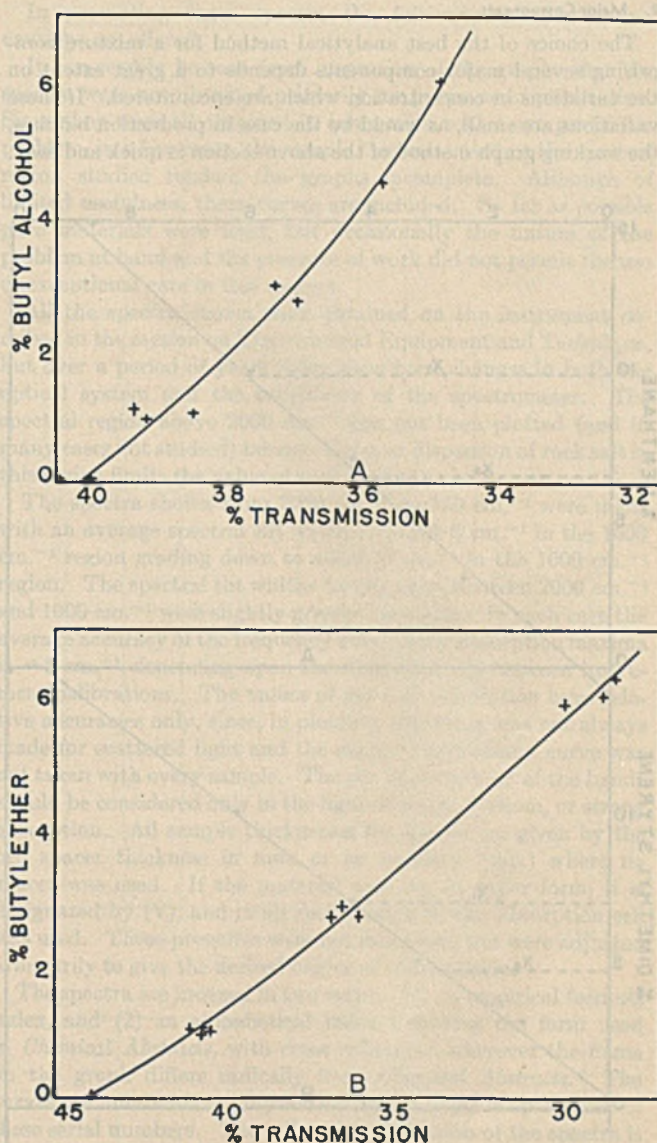


FIGURE 10. INFRARED ANALYSIS OF BUTYL ACRYLATE FOR THE IMPURITIES BUTYL ALCOHOL AND BUTYL ETHER

Sample diluted by volume one part to two parts  $\text{CCl}_4$ .  $x = 0.1\text{ mm.}$

A. Butyl alcohol  $\nu = 1030\text{ cm.}^{-1}$ ; spectral slit, ca.  $6\text{ cm.}^{-1}$   
 B. Butyl ether  $\nu = 1125\text{ cm.}^{-1}$ ; spectral slit, ca.  $6\text{ cm.}^{-1}$

which is present to 60 or 70 per cent with the accuracy for each component being  $\pm 1$  per cent of the total mixture. In one instance the catalytic reaction produced samples which were discolored by slight amounts of a dark, tarry residue. The spectroscopic effect of these unknown materials on the analysis was allowed for by collecting some of the residue under careful distillation and adding it to the standards in amounts necessary to match the visible light absorption of the unknowns. The method is rough and detracts from the absolute accuracy of the known component analysis, but it still allows for good relative measurements for testing the effects of varying catalytic conditions.

While performing these analyses on a large number of unknowns, it was found advisable to check the standards at frequent intervals. Once the working graphs were determined, the time of analysis for each unknown, including standard mixture calibration, sampling, and computation was about 0.5 hour in the sense that fifteen analyses could be made in an 8-hour day.



## 2. Major Components

The choice of the best analytical method for a mixture comprising several major components depends to a great extent on the variations in concentration which are encountered. If these variations are small, as would be the case in production batches, the working graph method of the above section is quick and easy.

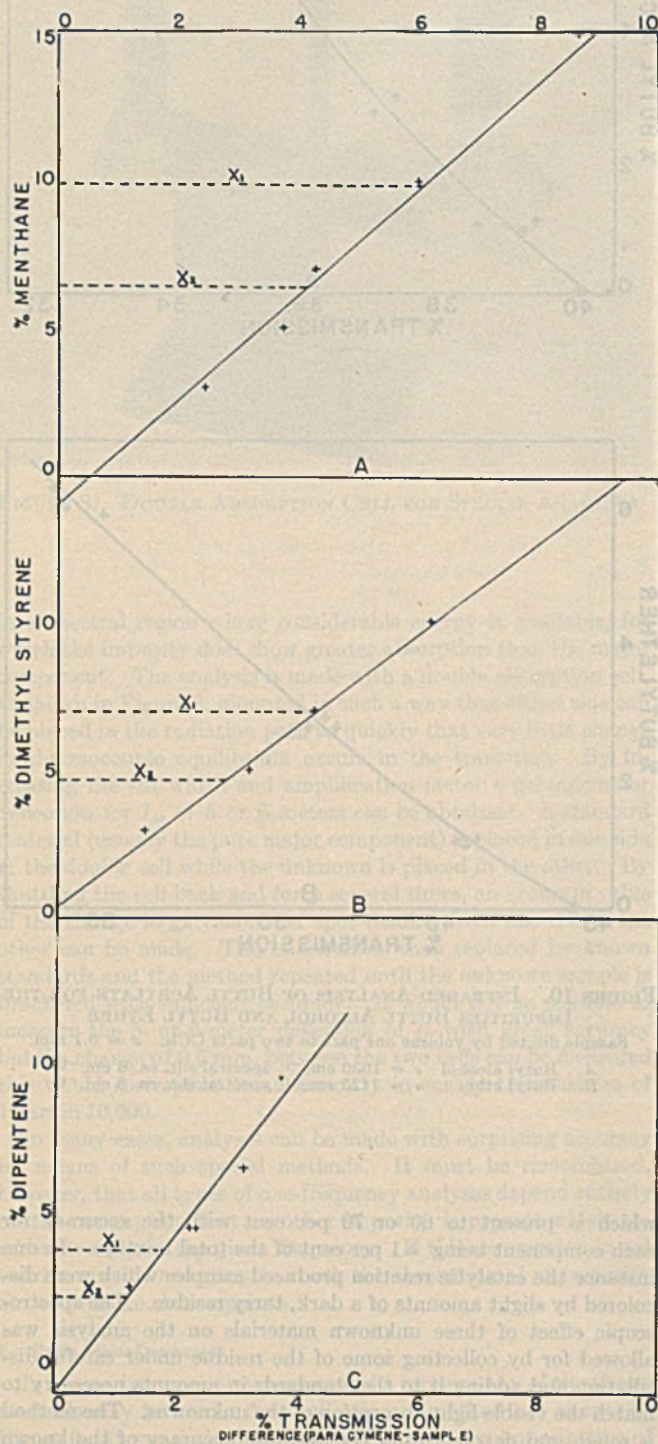


FIGURE 11. INFRARED ANALYSIS OF *p*-CYMENE FOR *p*-MENTHANE, DIMETHYLSTYRENE, AND DIPENTENE

$x = 0.1$  mm.

- A. Working curve for *p*-menthane  
 $\nu = 1177$  cm.<sup>-1</sup>; spectral slit, ca. 6 cm.<sup>-1</sup>
- B. Working curve for dimethylstyrene  
 $\nu = 1570$  cm.<sup>-1</sup>; spectral slit, ca. 9 cm.<sup>-1</sup>  
Correction: For every 5 per cent of *p*-menthane present, add 0.7 per cent to difference percentage before plotting.
- C. Working curve for dipentene  
 $\nu = 963$  cm.<sup>-1</sup>; spectral slit, ca. 5 cm.<sup>-1</sup>  
Correction: For every 5 per cent of total *p*-menthane plus dimethylstyrene, subtract 0.6 per cent from difference percentage before plotting.

Over small ranges of concentration the working graphs will approximate straight lines. In such cases changes in absorption cell condition can be checked at intervals and a point determined through which the straight line of known slope may be drawn. This method has been applied to mixtures of substituted anilines and the results obtained agreed within  $\pm 1$  per cent with distillation analyses on the same samples. However, if the concentrations vary over a wide range, a direct calculational application of Beer's law would be accurate but time-consuming, while a method of working graphs on semilog paper would be fast with some sacrifice in accuracy.

## PRESENT STATUS OF INFRARED SPECTROSCOPY IN INDUSTRY

The initial phase of infrared spectroscopy in industry was exploratory in nature. It has been known for many years that such correlations as those described in the section on Qualitative Analysis could be made between observed spectral characteristics and the molecular structure of the material being studied. The fact that an infrared absorption spectrum is a unique characteristic of a compound had suggested that this spectral region could be useful for identification and analysis of unknown materials and mixtures. Starting with this basic knowledge, spectroscopists in those companies which have shown an interest in the field have had to construct their own spectrometers, build up a reference library of absorption spectra of pure materials, establish structural correlations, and develop their own methods of quantitative analysis. Not only has this fundamental work been done, but also sufficient preliminary applications and results have been derived to prove conclusively that infrared pays its own way and is rapidly becoming a practical necessity to any research or production organization handling organic chemicals.

Industrial infrared spectroscopy is now entering its second phase—the development from proving potentialities under ideal research conditions to widespread applications under any practical conditions which might occur. This expansion does not imply that all efforts must be bent toward making infrared techniques routine but it does imply that the basis upon which infrared research is conducted has changed. It has passed the stage of hiring a trained infrared spectroscopist with the general instruction that he should build an instrument and then proceed to demonstrate its utility. Neither sufficient time nor trained personnel is available to permit such an approach. With the large number of companies now interested in conducting infrared research, it is necessary that commercial spectrometers be available, that there be sufficient background information in the literature so that an operator may be put on one of these instruments to produce results immediately without having to spend a long time acquiring basic data.

The first person to recognize this demand was the infrared spectroscopist already at work in the field. He was called upon to study the possibility of performing analyses which were difficult or tedious by chemical methods. Once a satisfactory analysis had been established, his research instrument was generally tied up for a month or more on routine work while research on further exploratory problems suffered. For his own protection, the spectroscopist has had to develop simple, compact instruments having sufficient resolving power to handle the majority of the analytical problems which might be encountered. With such instruments available, the role of the research spectrometer in analysis may be restricted to obtaining the pure spectra of the components involved. From these spectra the analytical frequencies can be chosen and the rest of the analysis performed by means of the small spectrometer. For convenience in setting to these frequencies, mechanical stops are provided. These small instruments can be operated in the infrared laboratory or moved to the site of the chemical reaction if operating conditions are favorable.



In accordance with the mutual desire of the industrial spectroscopist and the instrument maker, these small instruments are being made commercially available. The manufacturer is always anxious to produce an instrument which has been designed, proved practical, and has a growing market. The research spectroscopist does not, in general, desire to carry out analyses on production samples once the details of analysis have been worked out. He prefers to refer the production man to a commercial source of instruments which will answer the requirements. Therefore, as far as small routine instruments are concerned, favorable progress is being made.

Unfortunately, this does not mean that the spectroscopist can turn back happily to problems intended for his research spectrometer. There are at least two important advances in the instrumentology of research spectrometers which must be made before the spectroscopist can devote himself entirely to the results obtained and not have to worry about the means of producing them. In the first place, most infrared spectra are obtained today as records of frequency *vs.* galvanometer deflection superimposed upon the radiation background. To obtain full significance from these results it is necessary to convert them to frequency *vs.* per cent transmission or log of per cent transmission. This conversion as it is now done involves considerable tedious labor and it is highly desirable that the instrument make this conversion automatically. In short, infrared needs a spectrophotometer to replace its present spectrometer. In the second place, most infrared recording is done by means of a very sensitive galvanometer amplifier. Unless the stability conditions of the building in which the instrument is used are favorable, such a mechanically sensitive device is not satisfactory. Certainly, under the conditions which exist in the average laboratory or plant, an improved detecting system is required. Therefore, it is highly desirable that a means of electronic amplification of thermocouple output be devised to replace the present use of galvanometers. There is a growing tendency to use pen recorders rather than photographic methods for recording the galvanometer deflections. This means that an electronic stage must be interposed between the galvanometer beam and the actual record. If the entire amplification from the radiation detector to the record could be done electronically, the use of some type of a split beam instrument would answer the instrumental problems of the infrared spectroscopist.

It will be a natural step for the manufacturer to go from the small routine spectrometer to the research type of instrument and it is to be hoped that the combination of instrument maker and spectroscopist will solve these problems in the near future. It will then remain for the spectroscopist to refine his analytical techniques and to broaden his knowledge and application of structural correlations, in order that infrared spectroscopy can make its maximum contribution to the advance of science.

#### LIBRARY OF REFERENCE CURVES

As shown above, it is very desirable to have available for reference purposes the per cent transmission curves for as many organic compounds as possible. These curves serve a threefold purpose. They may be used for studying correlations between molecular structure and spectral characteristics, for identification of unknown materials, and for determining in advance the possibilities of qualitative and quantitative infrared analysis of mixtures.

In presenting these spectra the following comments and cautions are offered:

It can readily be seen from inspection of the graphs that the spectra were not obtained primarily for purposes of publication. Since they were all obtained in connection with some particular problem, in a few cases, the sample thickness used or the spectral region studied renders the graphs incomplete. Although of limited usefulness, these curves are included. So far as possible pure materials were used, but occasionally the nature of the problem at hand and the pressure of work did not permit the use of exceptional care in this respect.

All the spectra shown were obtained on the instrument described in the section on Experimental Equipment and Technique, but over a period of years there have been changes in both the optical system and the sensitivity of the spectrometer. The spectral region above 2000  $\text{cm}^{-1}$  has not been plotted (and in many cases not studied) because the poor dispersion of rock salt in this region limits the value of such studies.

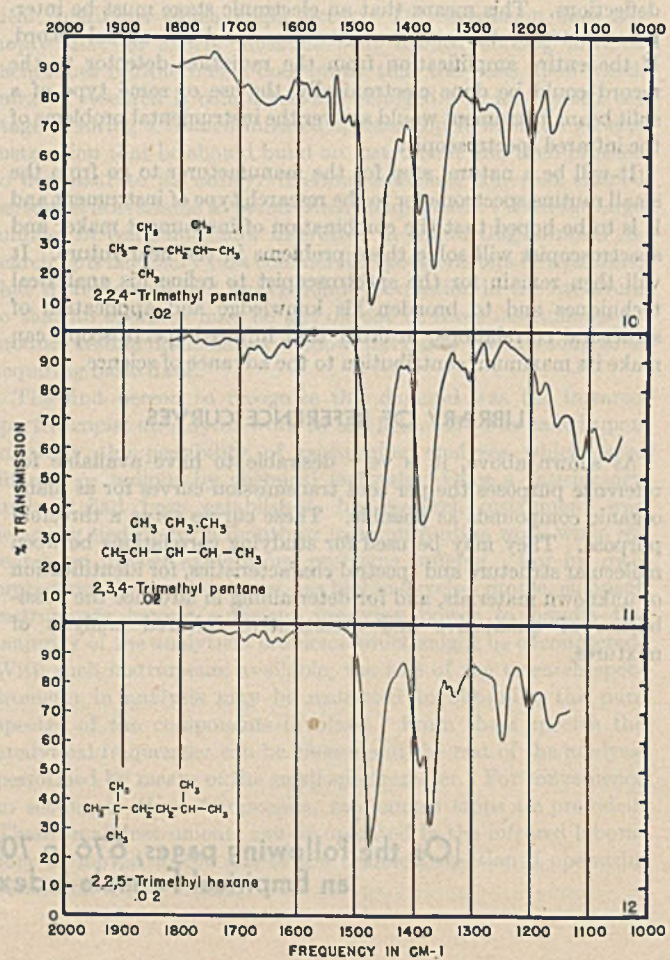
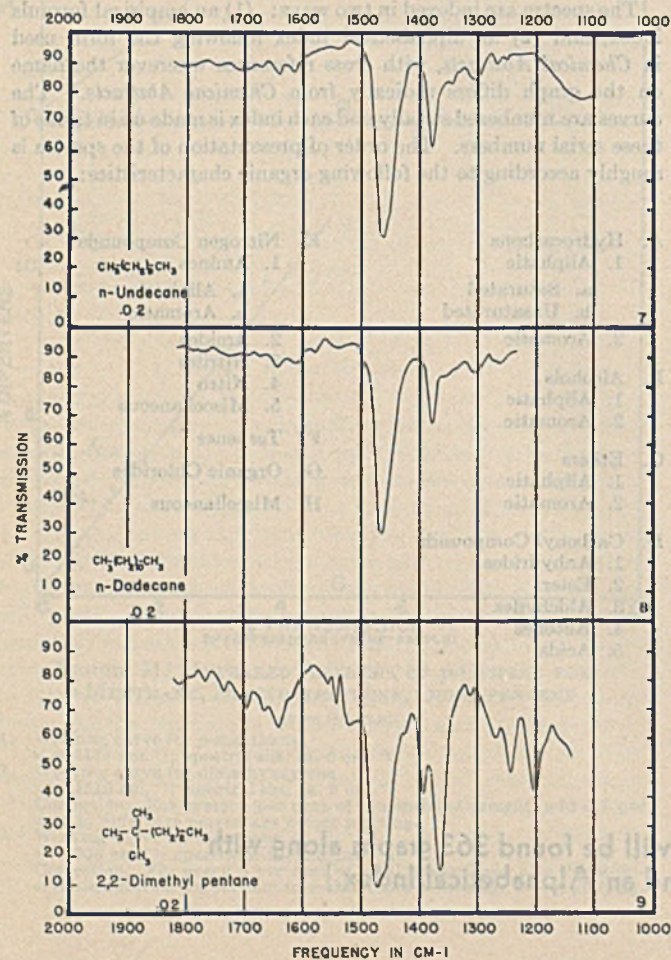
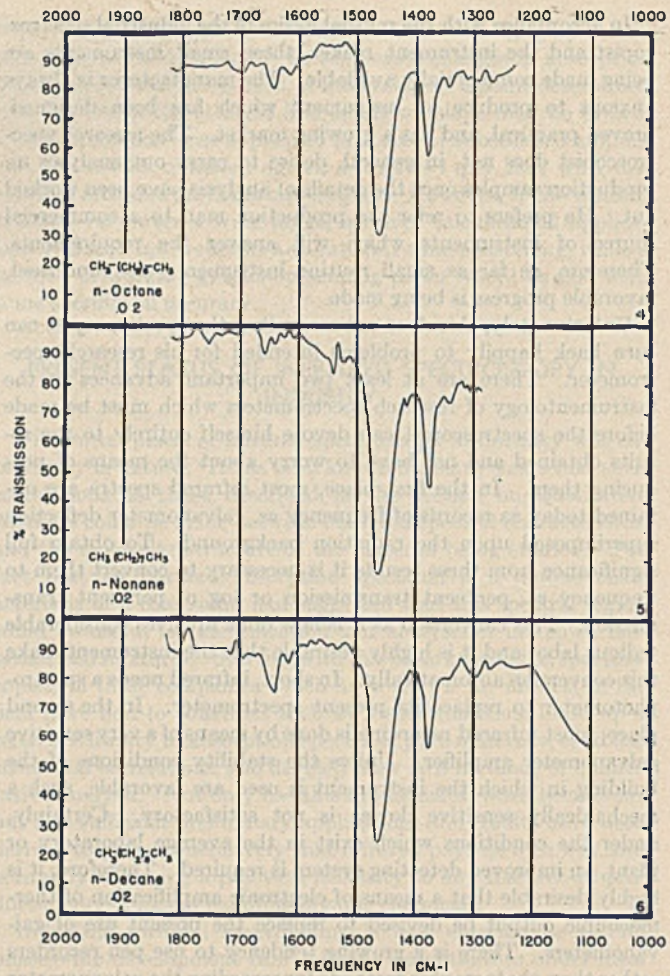
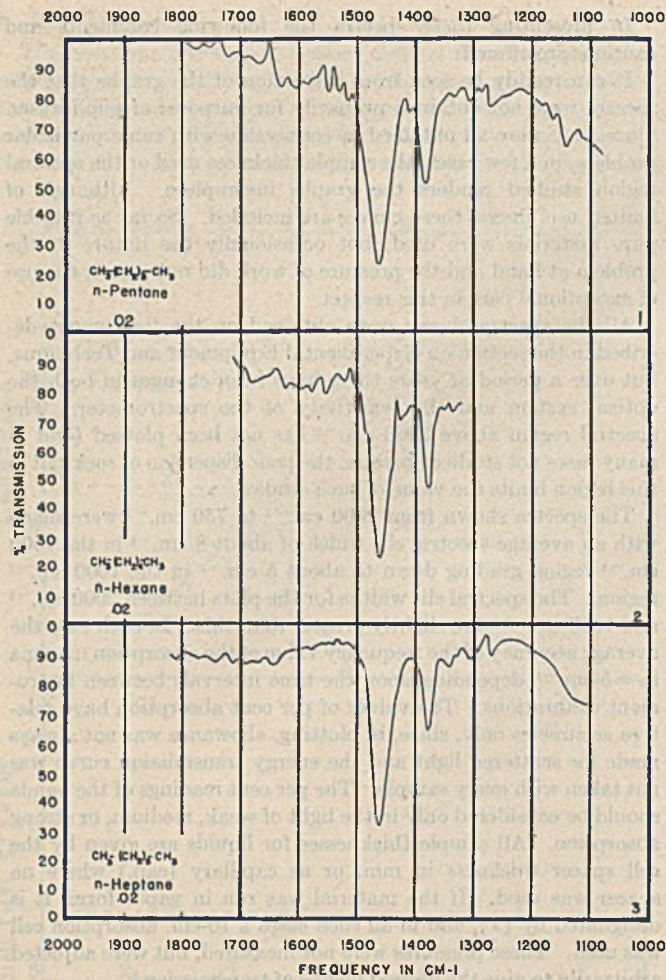
The spectra shown from 2000  $\text{cm}^{-1}$  to 750  $\text{cm}^{-1}$  were made with an average spectral slit width of about 8  $\text{cm}^{-1}$  in the 1600  $\text{cm}^{-1}$  region grading down to about 5  $\text{cm}^{-1}$  in the 1000  $\text{cm}^{-1}$  region. The spectral slit widths for the plots between 2000  $\text{cm}^{-1}$  and 1000  $\text{cm}^{-1}$  were slightly greater than this. In each case the average accuracy of the frequency value of the absorption maxima is  $\pm 5 \text{ cm}^{-1}$ , depending upon the time intervals between instrument calibrations. The values of per cent absorption have relative accuracies only, since, in plotting, allowance was not always made for scattered light and the energy transmission curve was not taken with every sample. The per cent readings of the bands should be considered only in the light of weak, medium, or strong absorption. All sample thicknesses for liquids are given by the cell spacer thickness in mm. or as capillary (cap.) where no spacer was used. If the material was run in vapor form, it is designated by (V), and in all such cases a 10-cm. absorption cell was used. These pressures were not measured, but were adjusted arbitrarily to give the desired degree of transmission.

The spectra are indexed in two ways: (1) an empirical formula index, and (2) an alphabetical index following the form used in *Chemical Abstracts*, with cross references wherever the name on the graph differs radically from *Chemical Abstracts*. The curves are numbered serially and each index is made up in terms of these serial numbers. The order of presentation of the spectra is roughly according to the following organic characteristics:

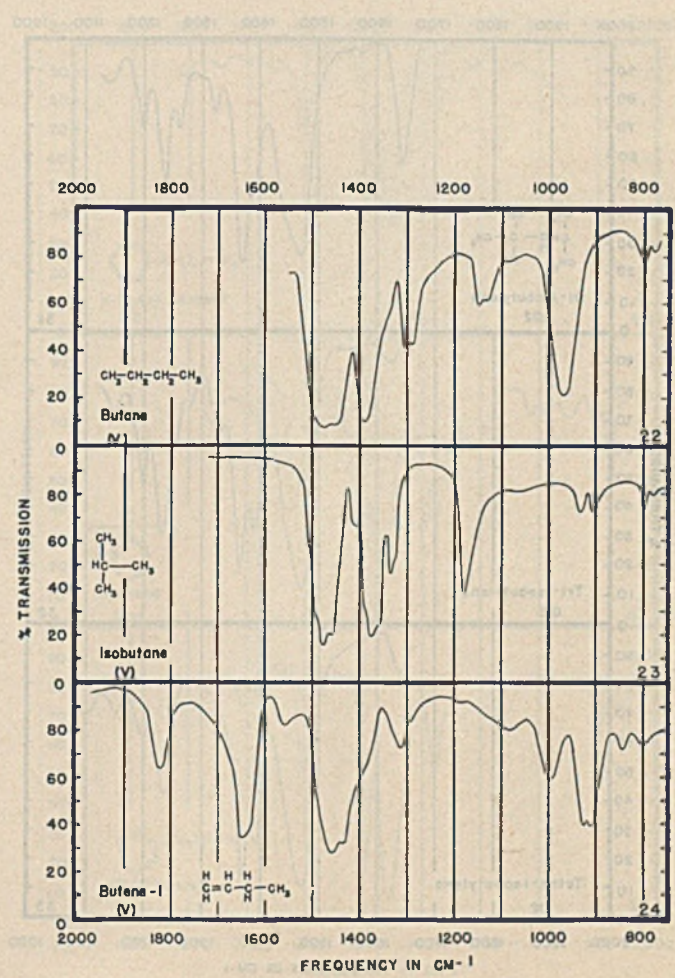
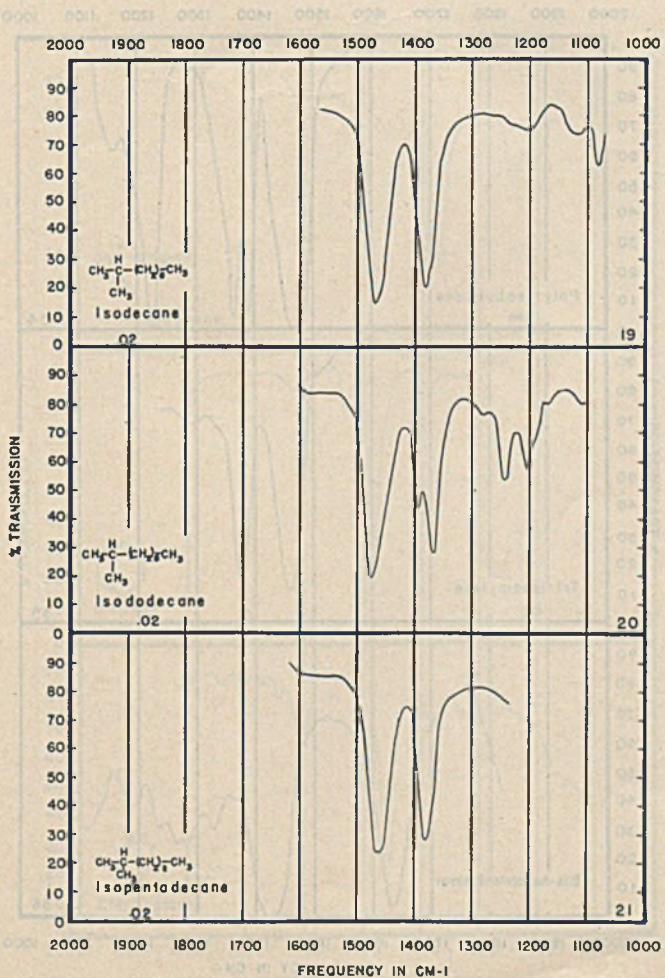
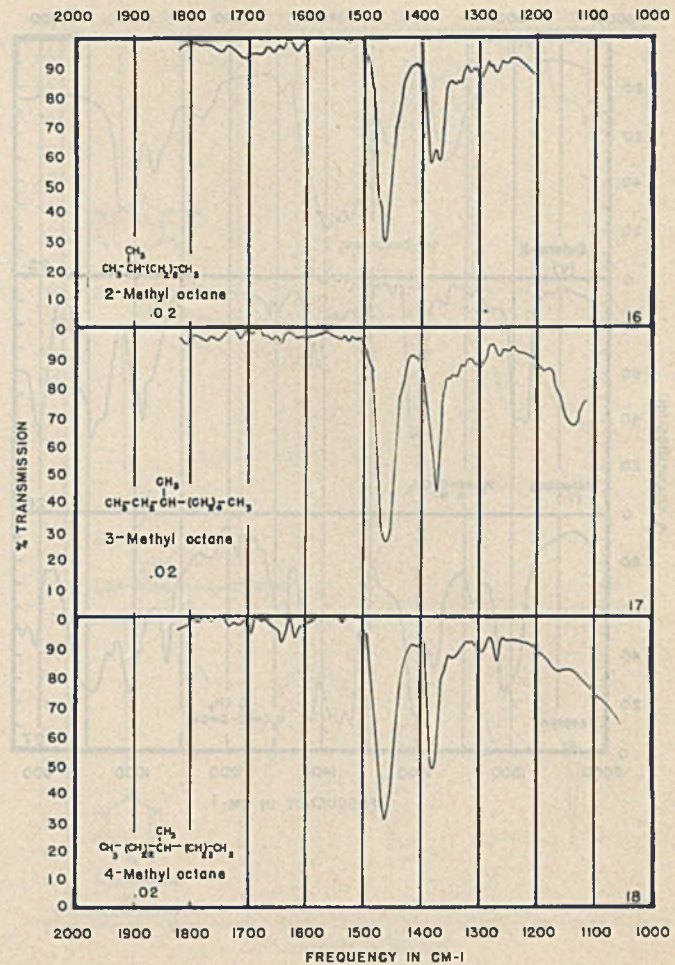
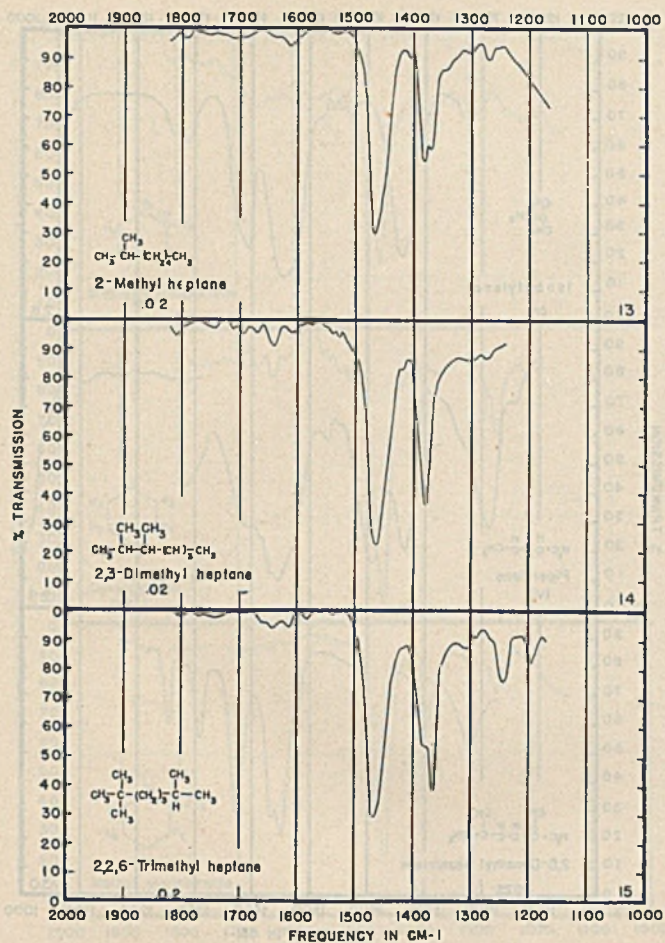
- |  |   |
|--|---|
| <p>A. Hydrocarbons</p> <ol style="list-style-type: none"> <li>1. Aliphatic               <ol style="list-style-type: none"> <li>a. Saturated</li> <li>b. Unsaturated</li> </ol> </li> <li>2. Aromatic</li> </ol> | <p>E. Nitrogen Compounds</p> <ol style="list-style-type: none"> <li>1. Amines               <ol style="list-style-type: none"> <li>a. Aliphatic</li> <li>b. Aromatic</li> </ol> </li> <li>2. Amides</li> <li>3. Nitriles</li> <li>4. Nitro</li> <li>5. Miscellaneous</li> </ol> |
| <p>B. Alcohols</p> <ol style="list-style-type: none"> <li>1. Aliphatic</li> <li>2. Aromatic</li> </ol>   | <p>F. Terpenes</p>  |
| <p>C. Ethers</p> <ol style="list-style-type: none"> <li>1. Aliphatic</li> <li>2. Aromatic</li> </ol>   | <p>G. Organic Chlorides</p>   |
| <p>D. Carbonyl Compounds</p> <ol style="list-style-type: none"> <li>1. Anhydrides</li> <li>2. Esters</li> <li>3. Aldehydes</li> <li>4. Ketones</li> <li>5. Acids</li> </ol>                                      | <p>H. Miscellaneous</p>   |

[On the following pages, 676 to 709, will be found 363 graphs along with an Empirical Formula Index and an Alphabetical Index.]

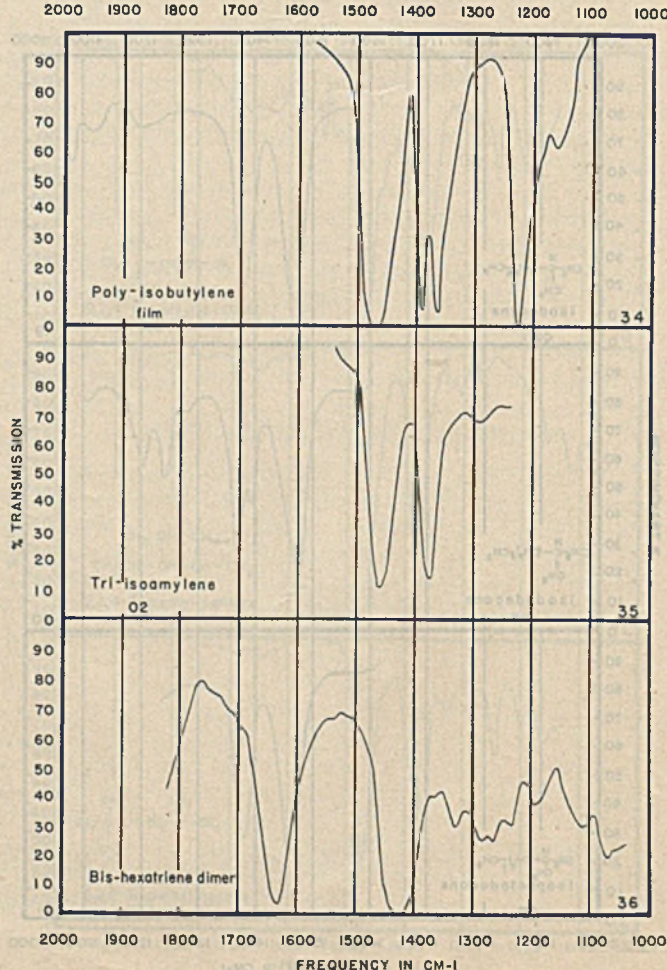
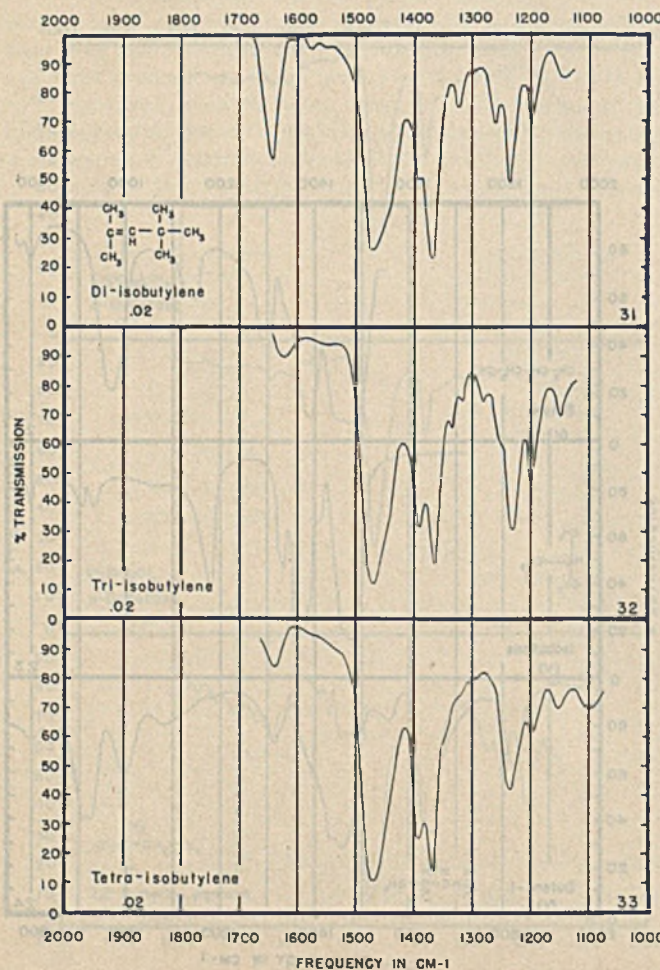
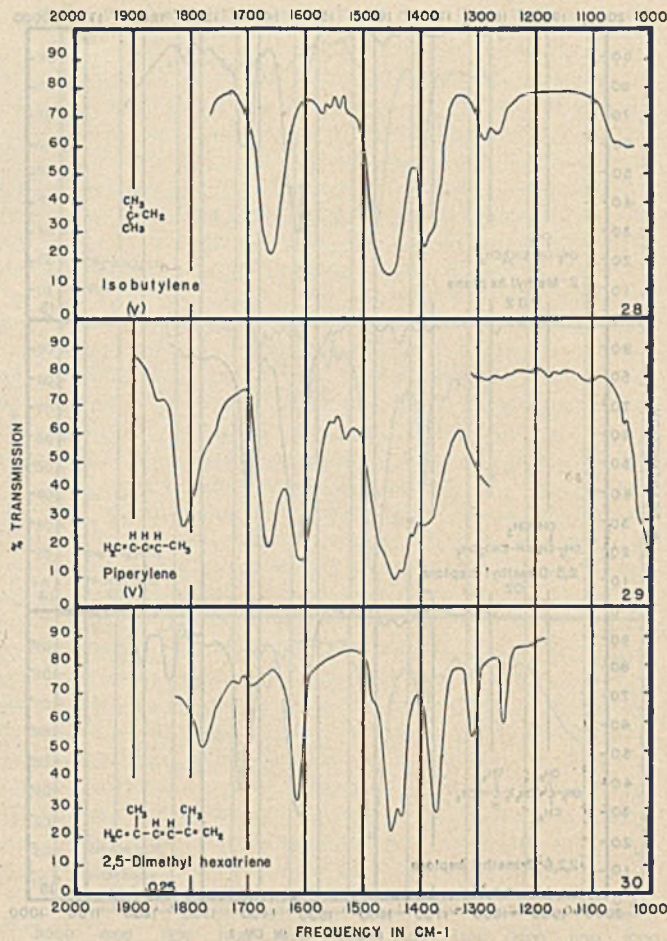
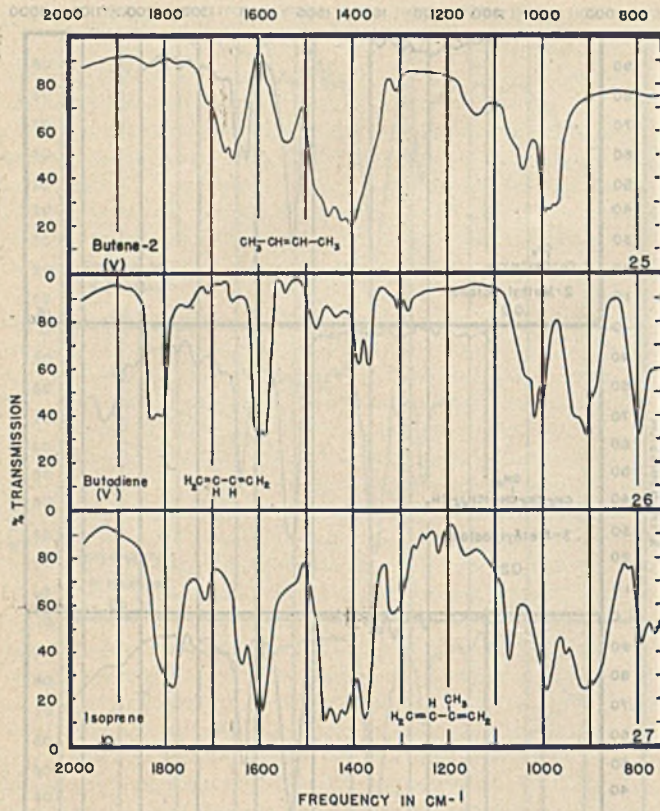




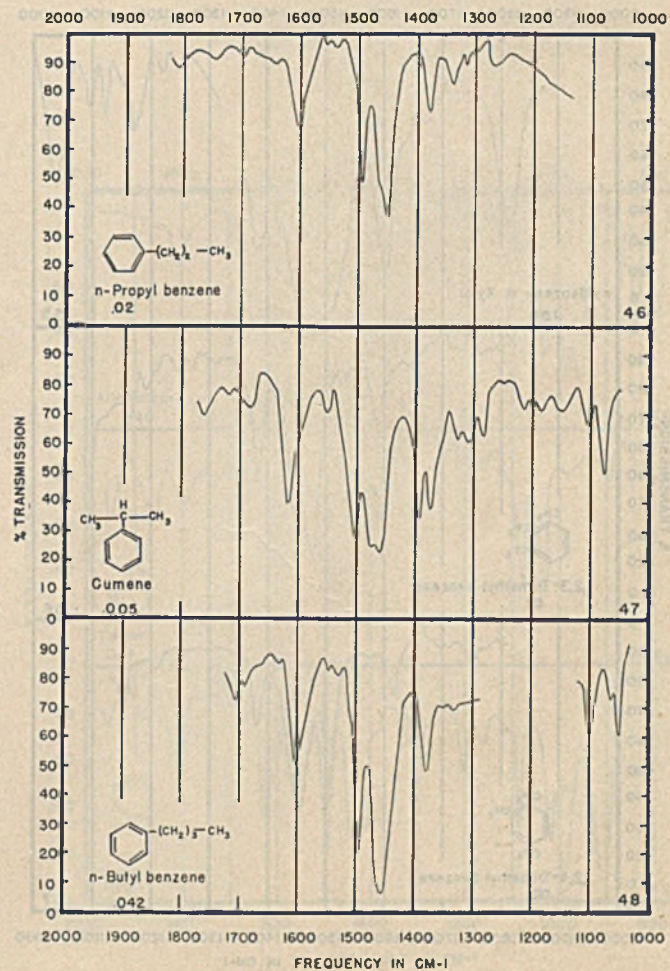
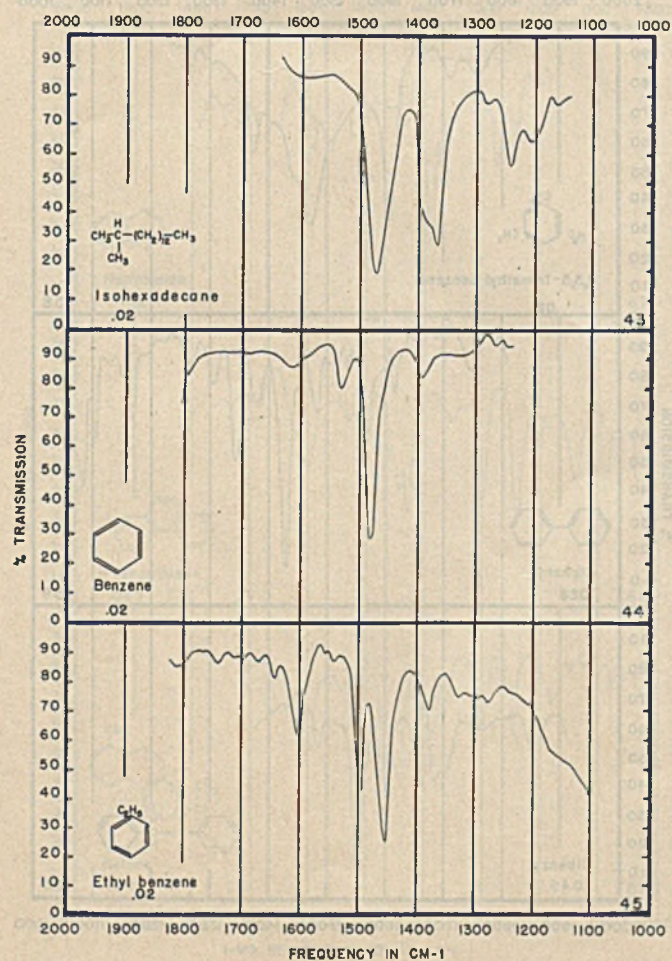
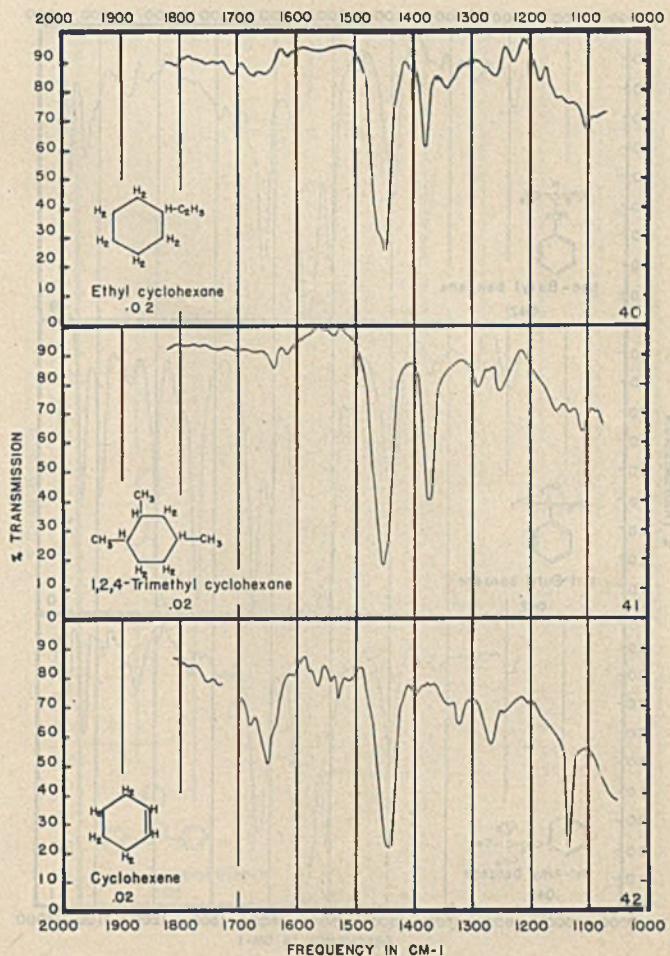
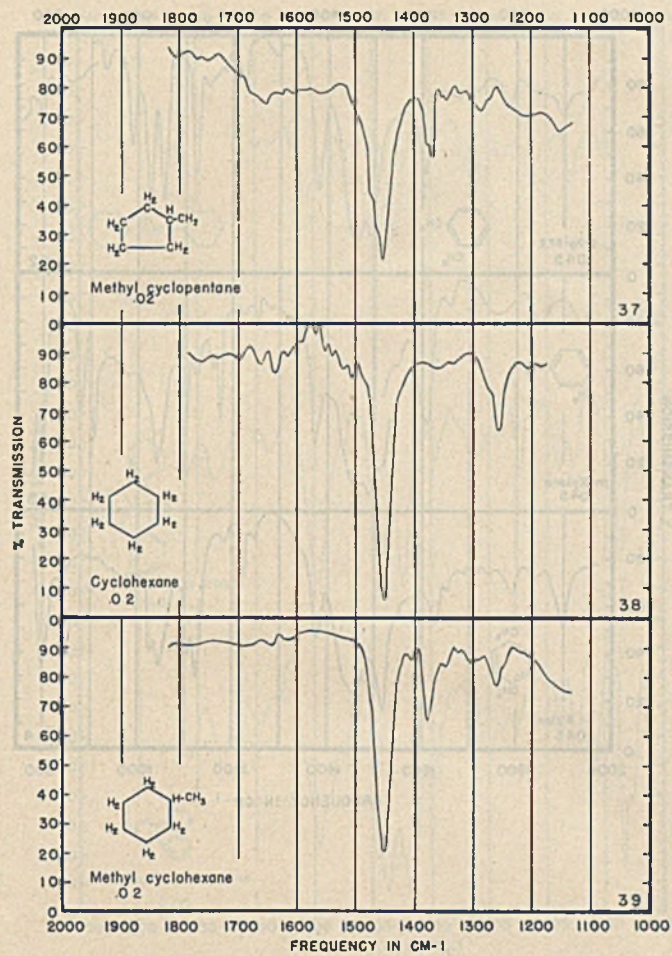




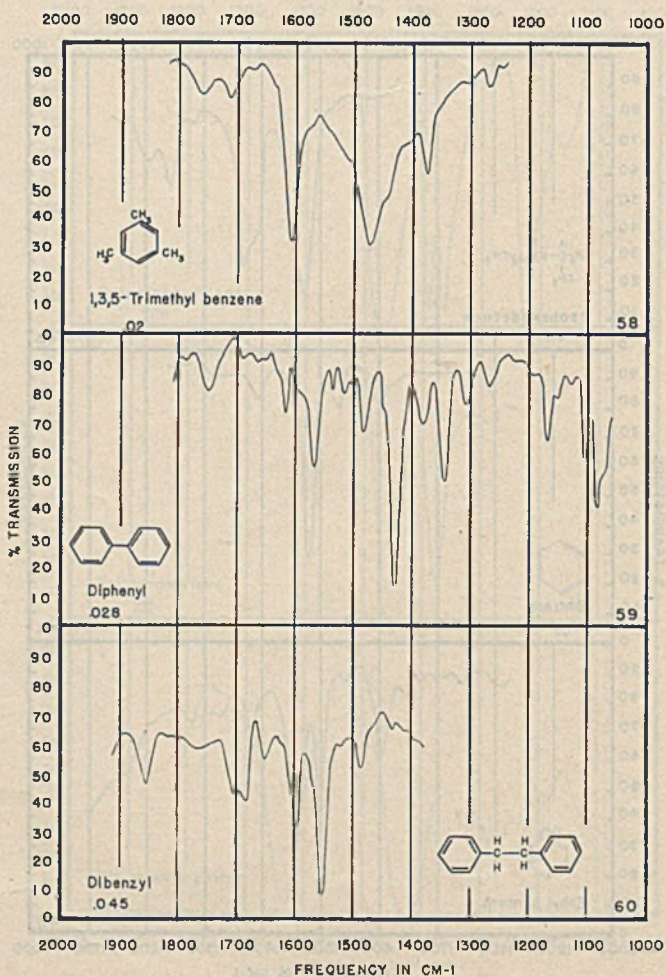
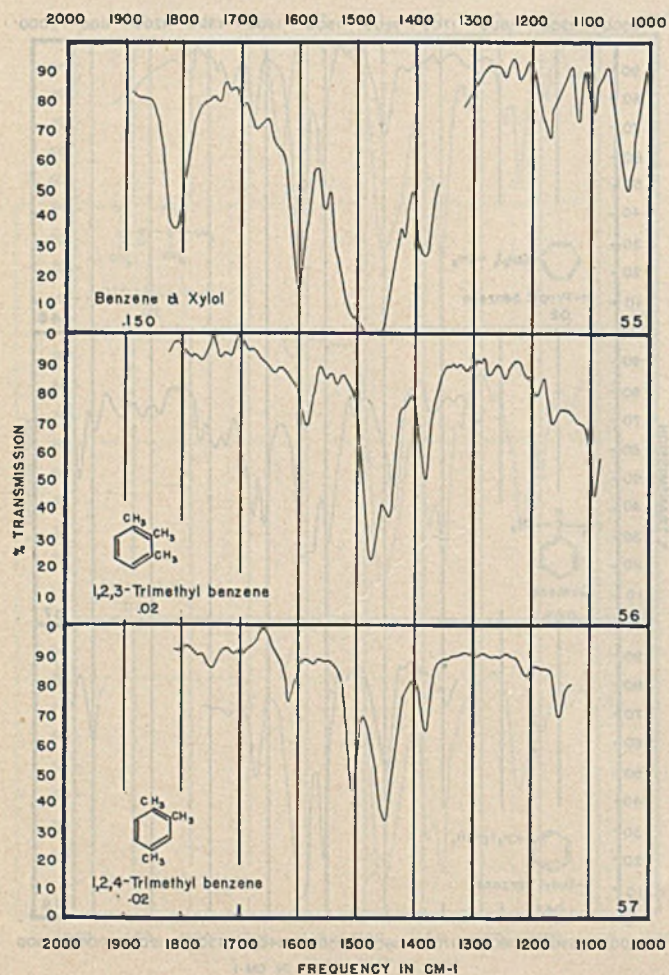
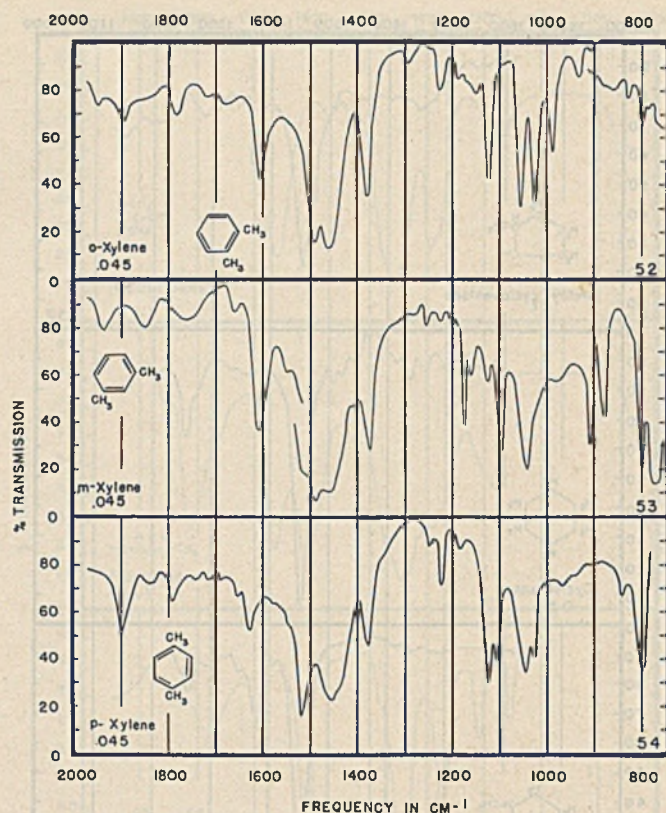
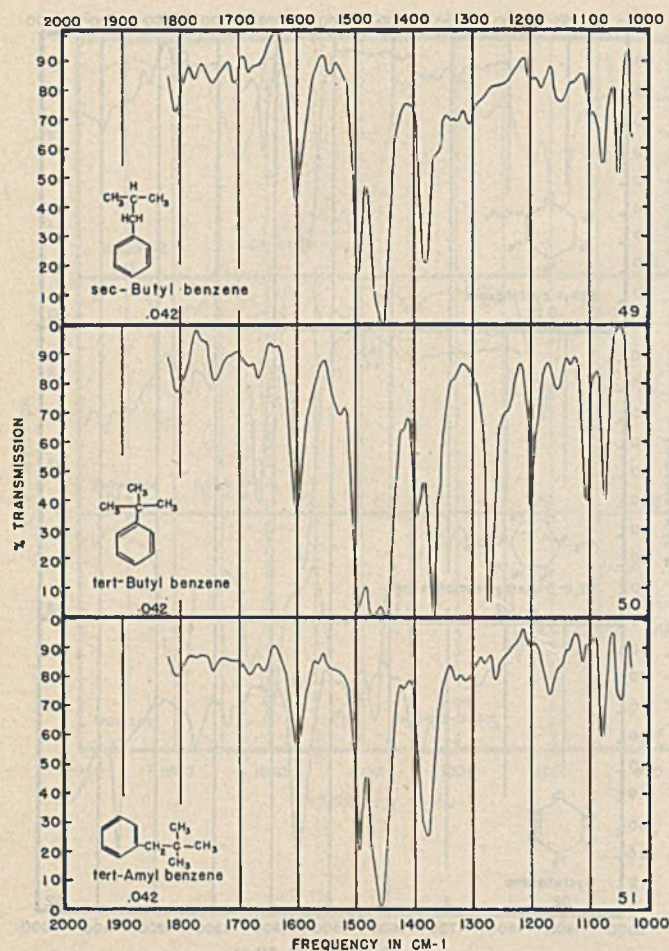




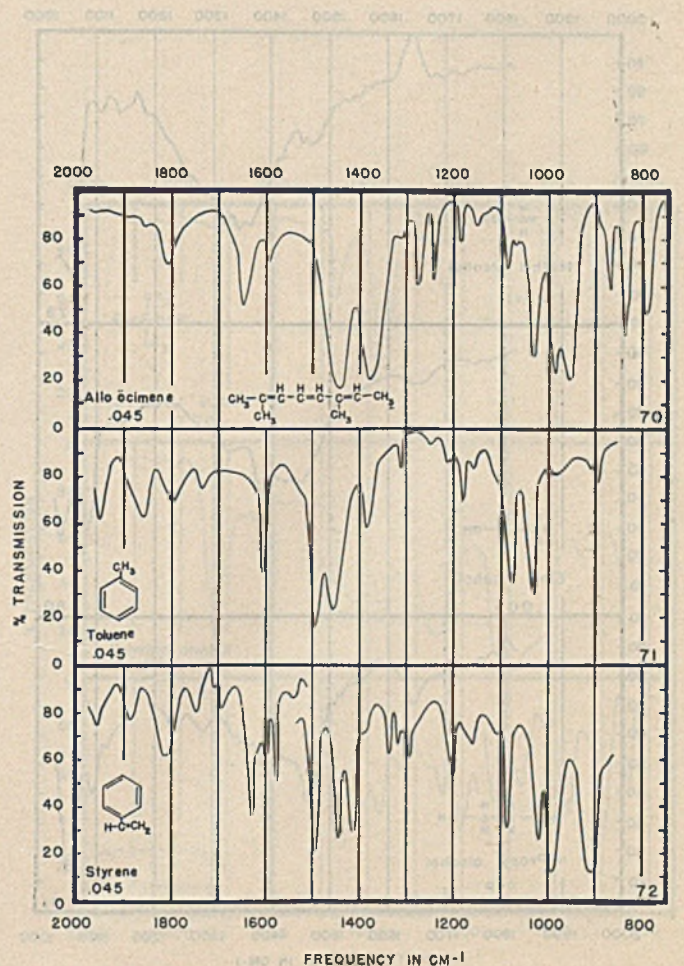
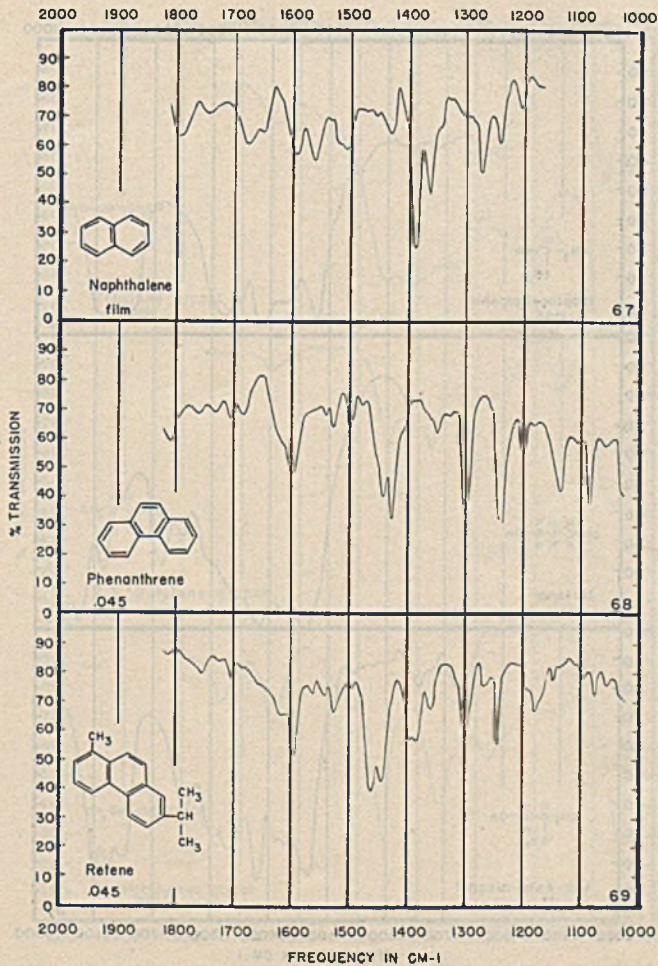
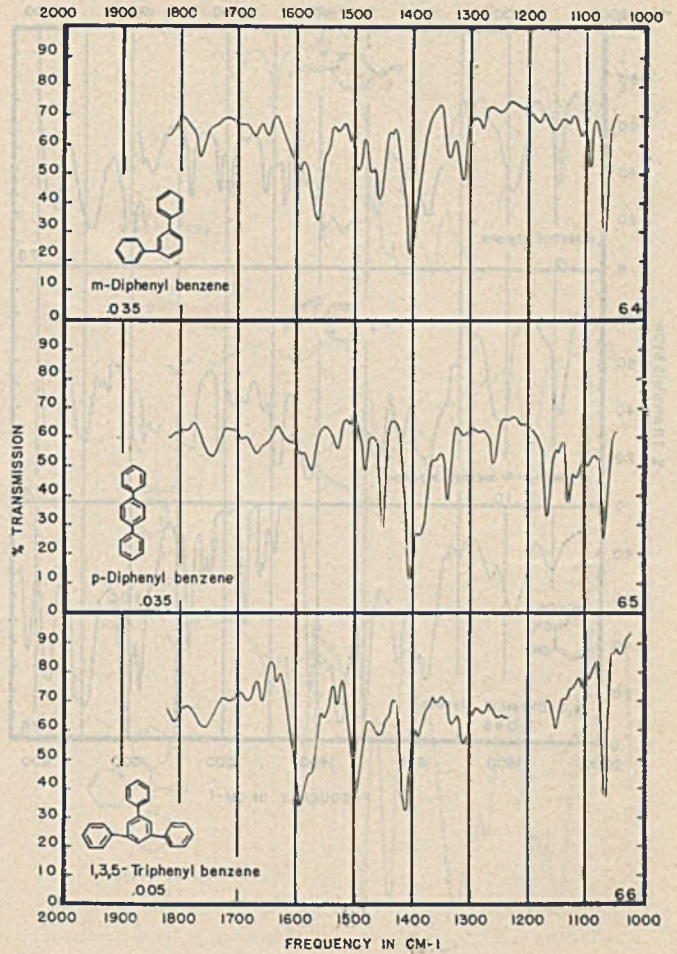
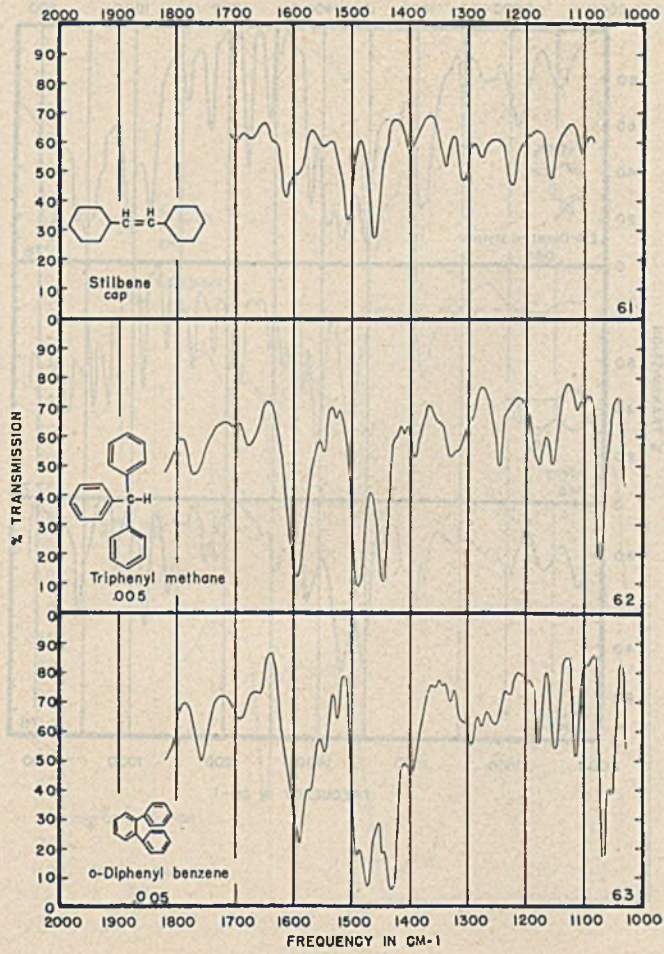




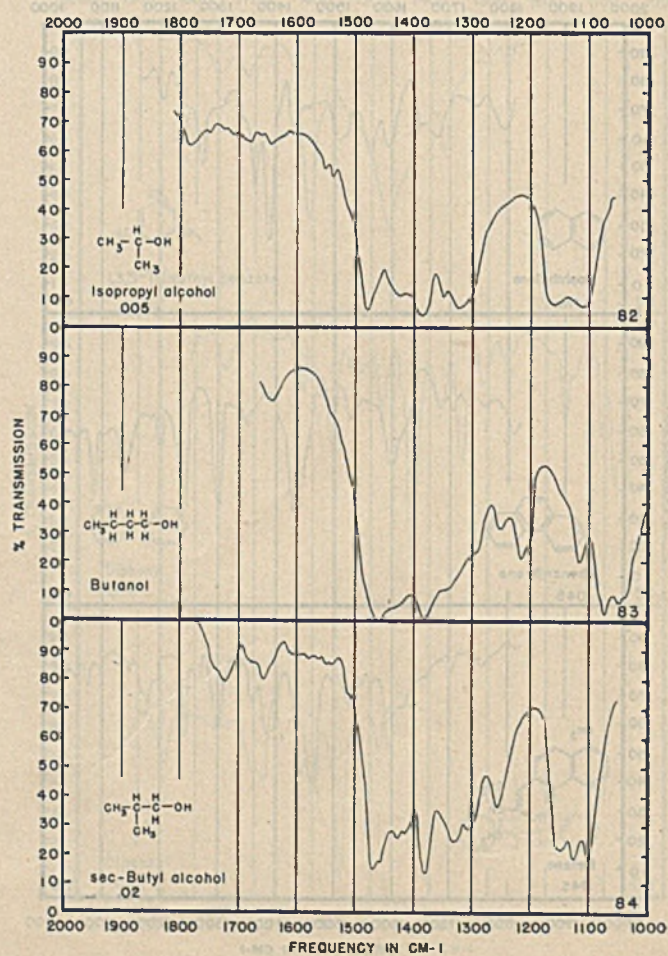
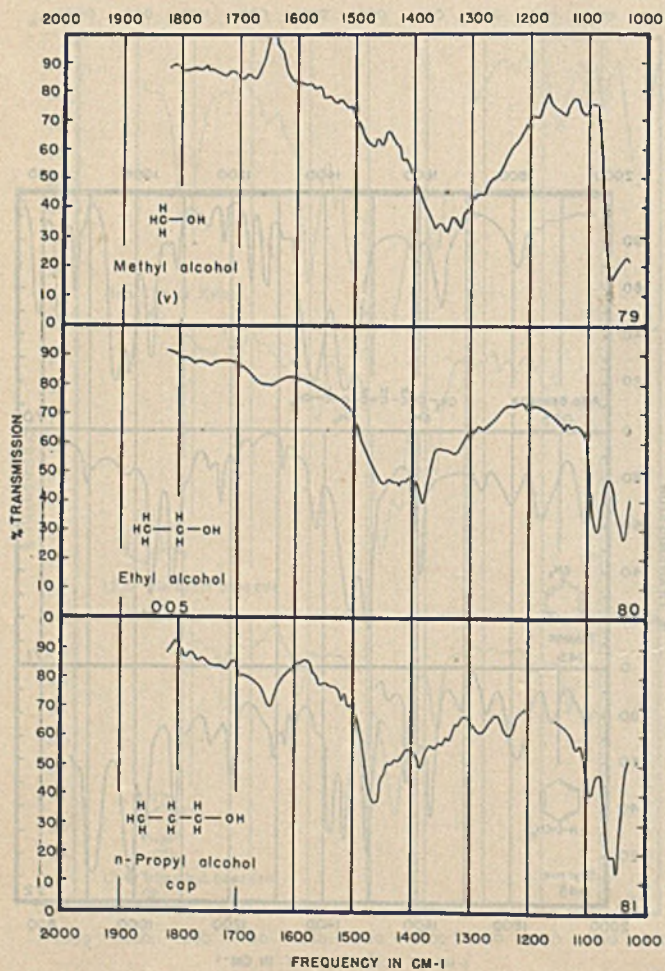
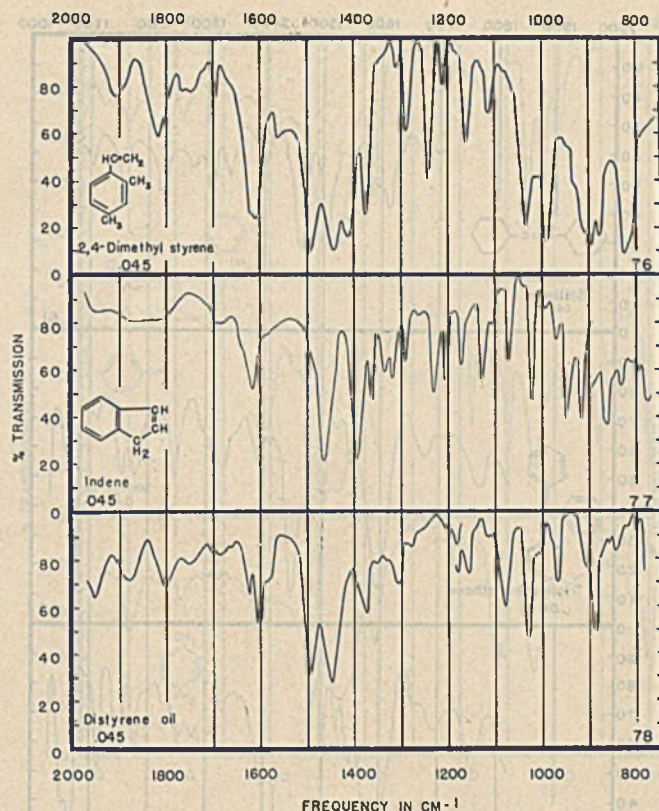
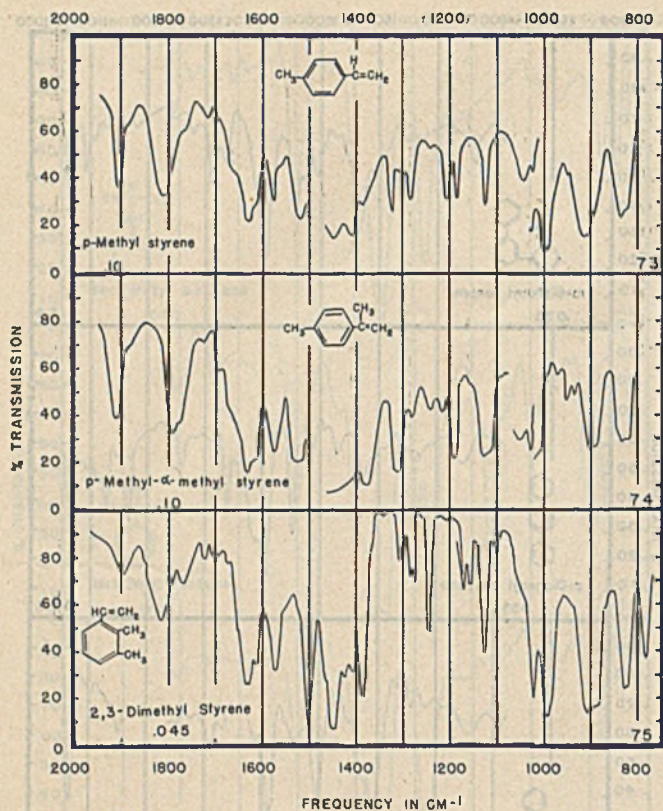




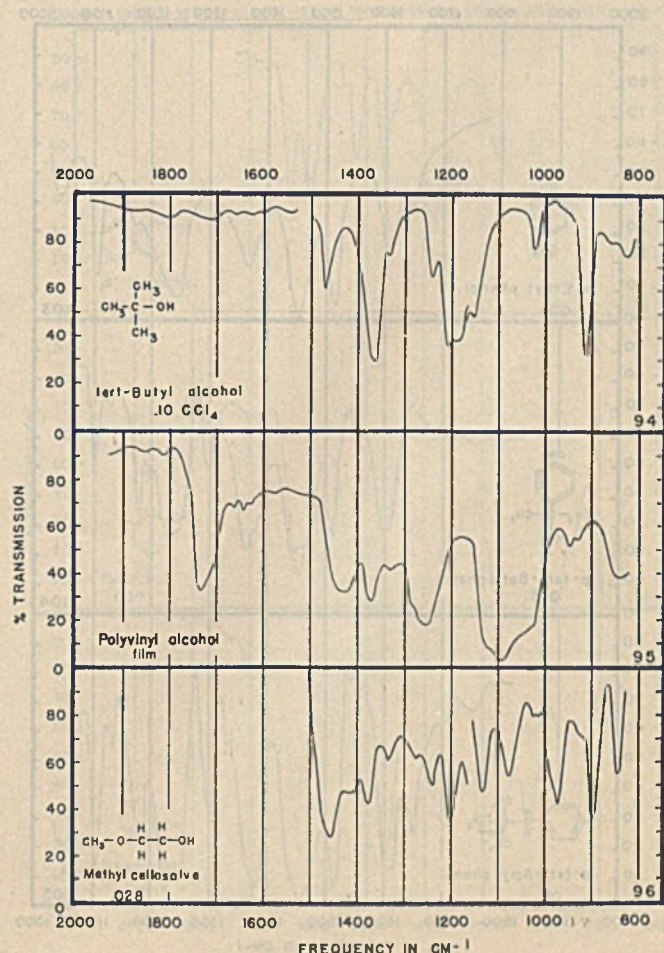
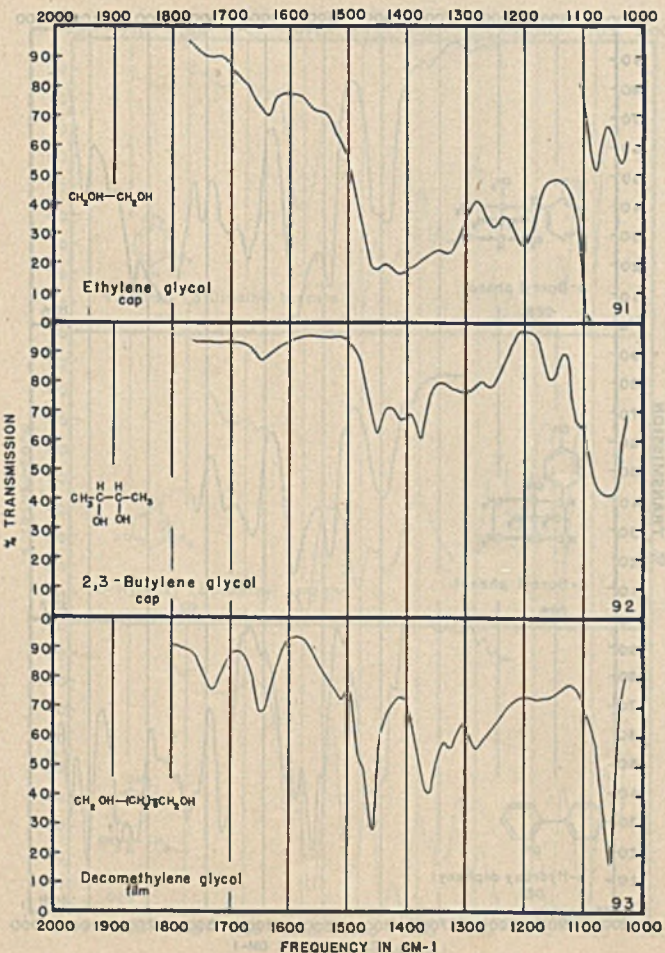
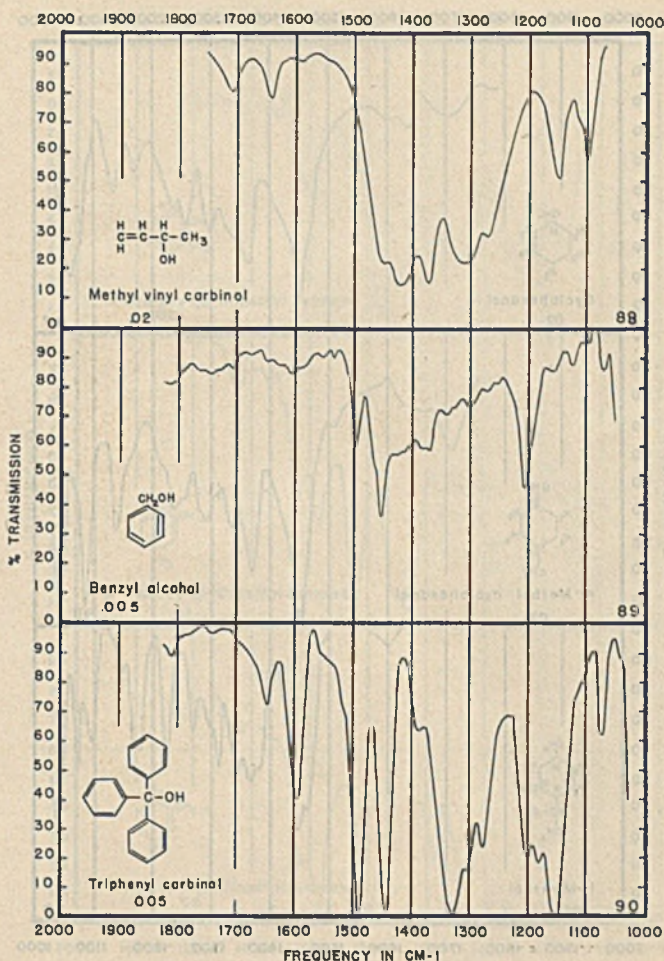
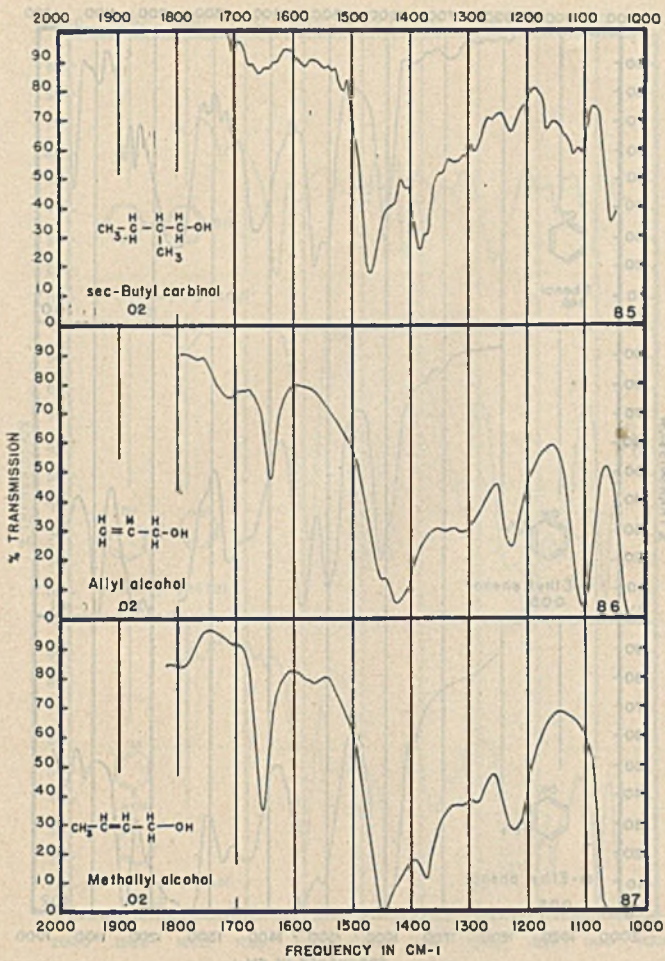




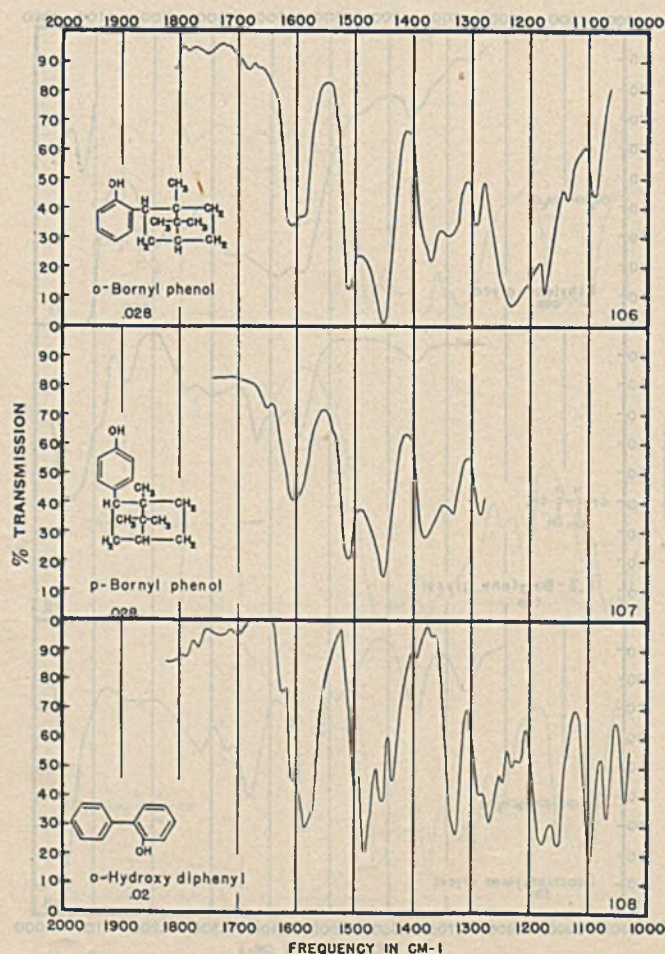
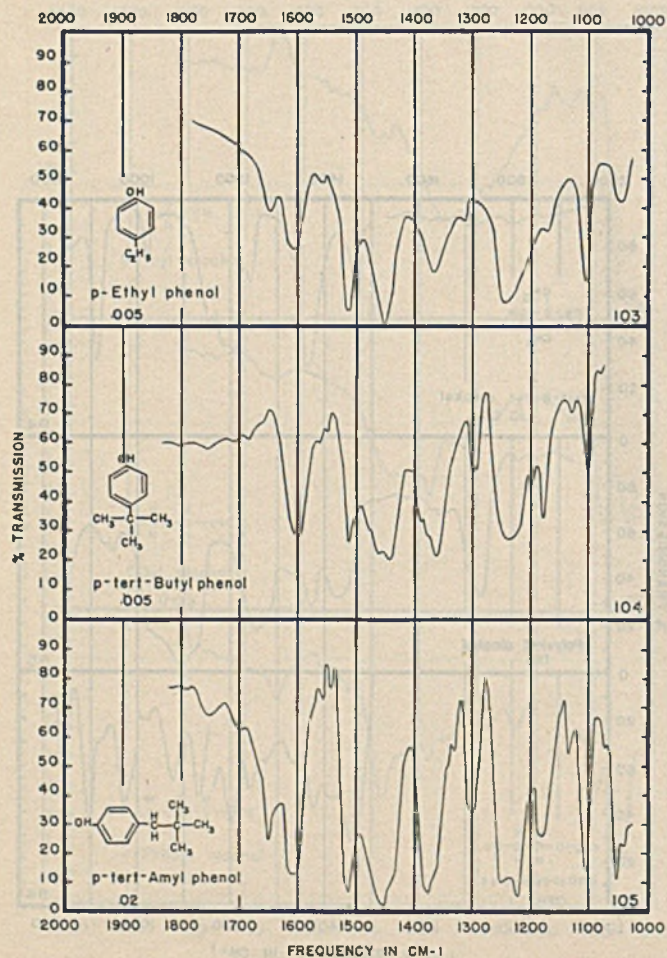
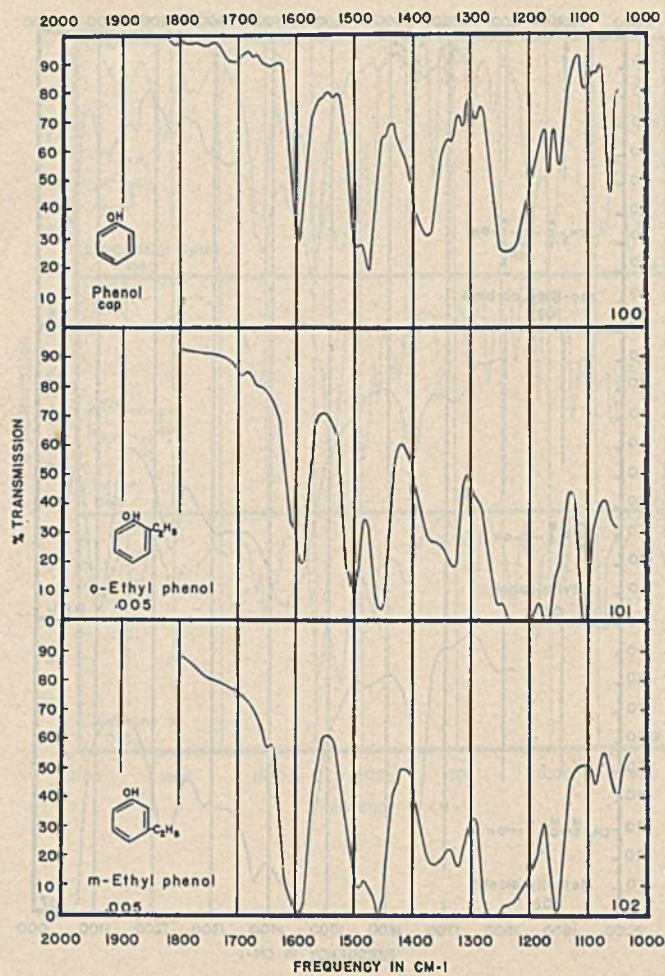
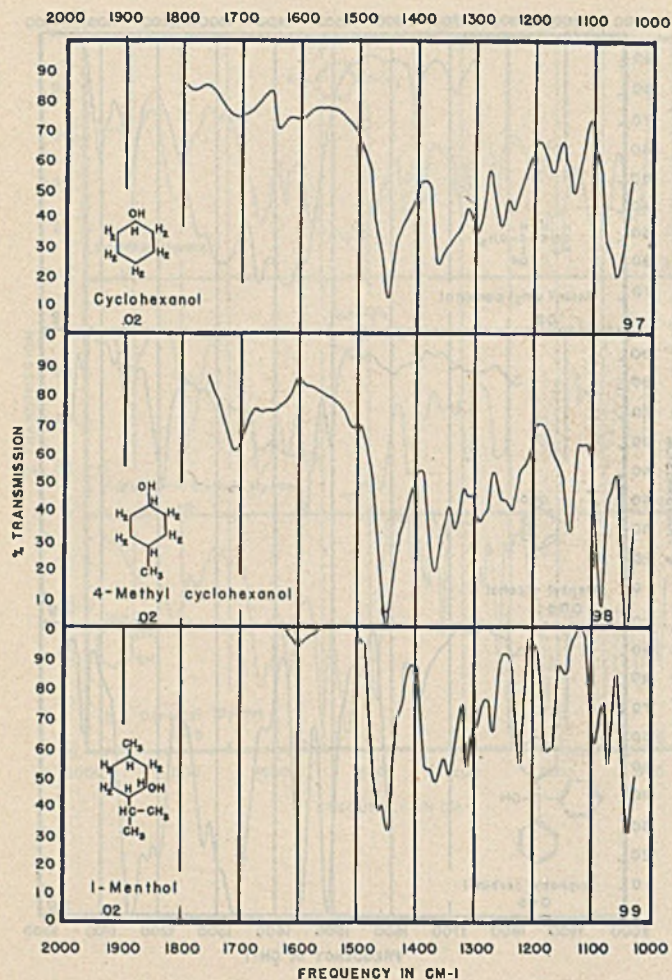




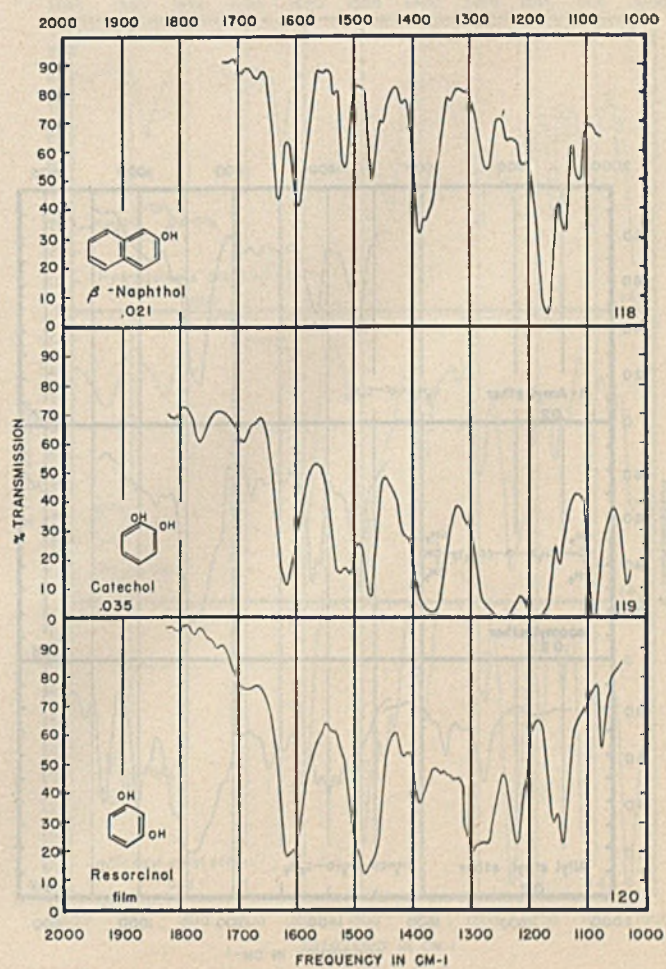
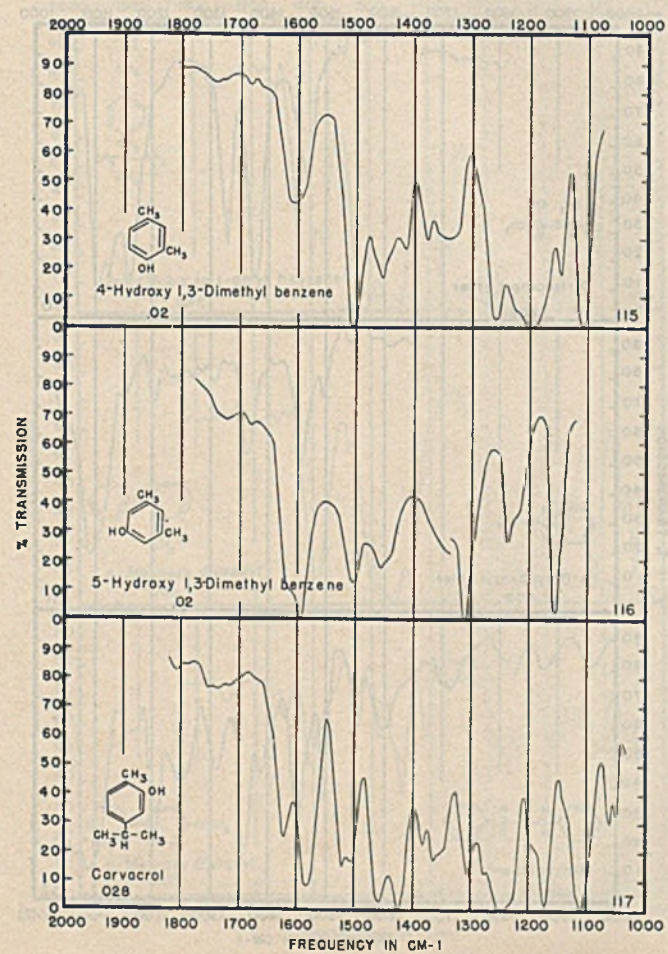
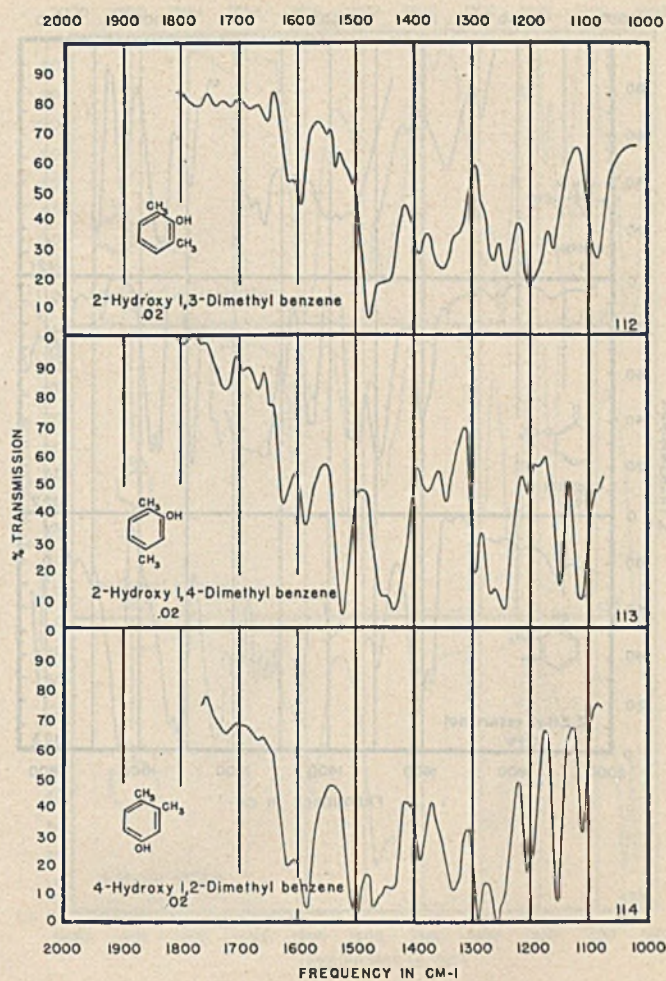
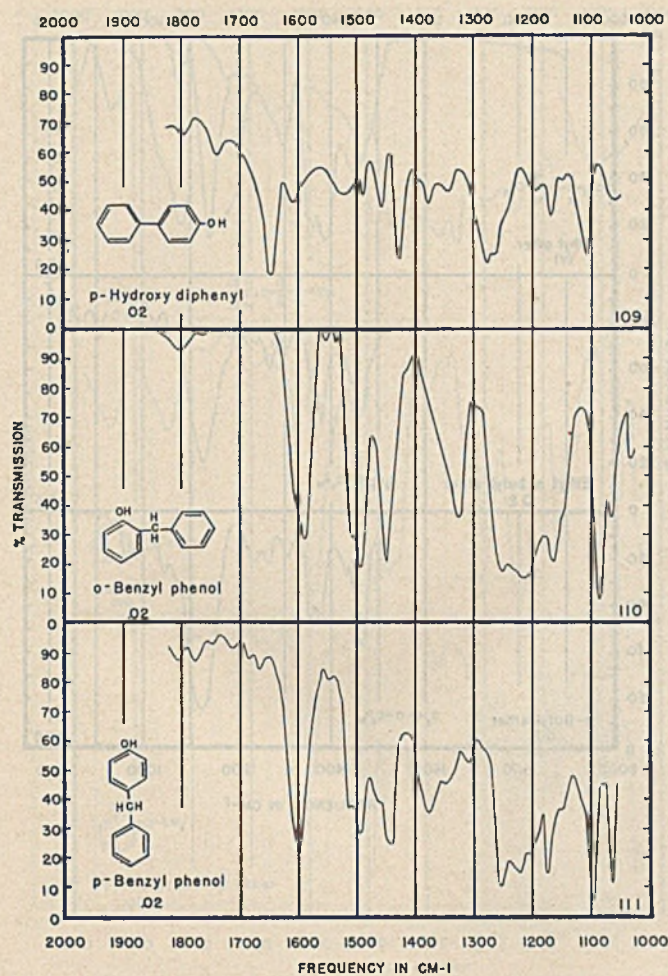




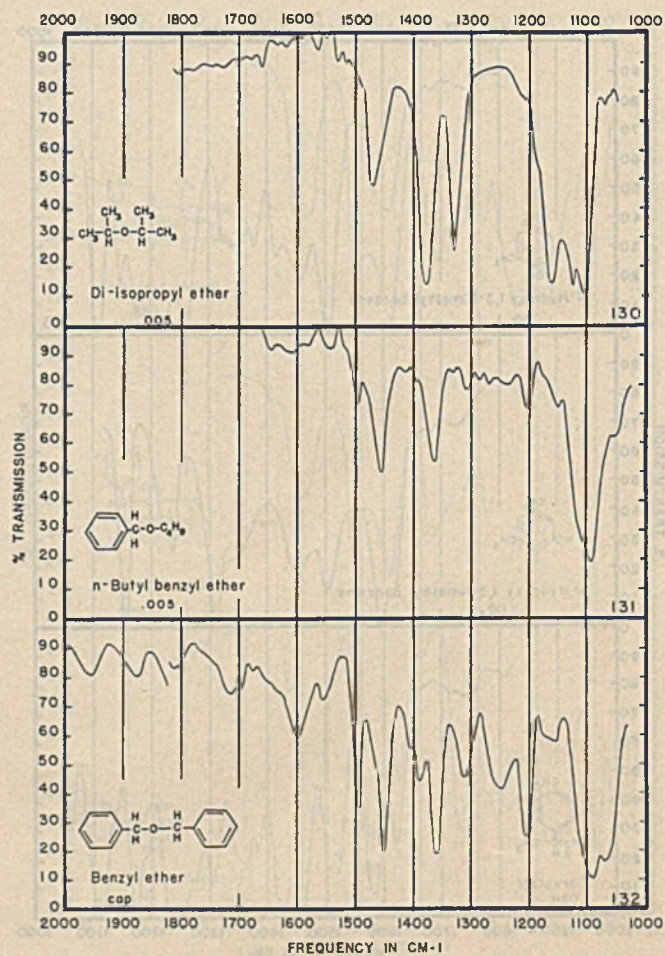
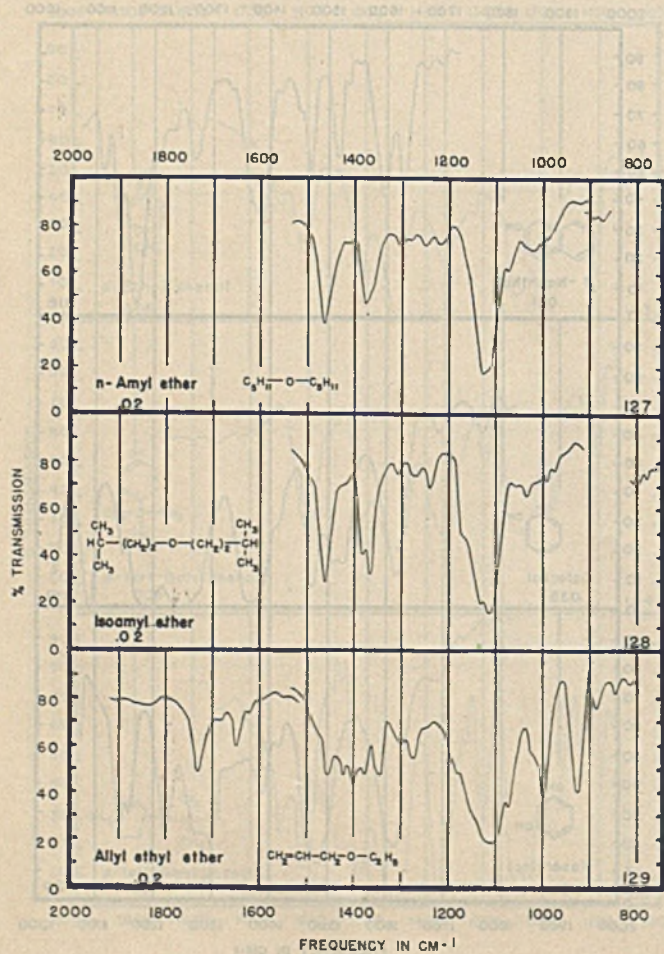
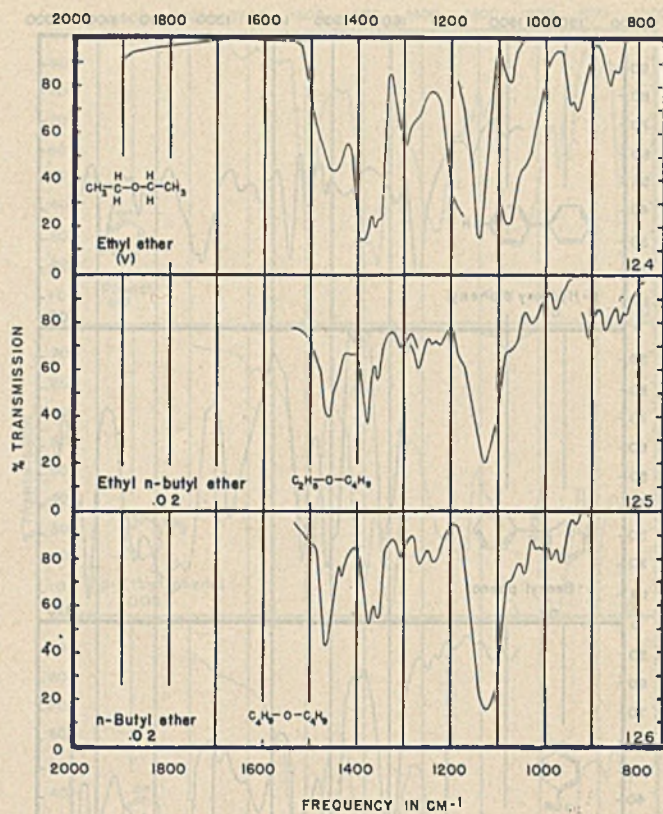
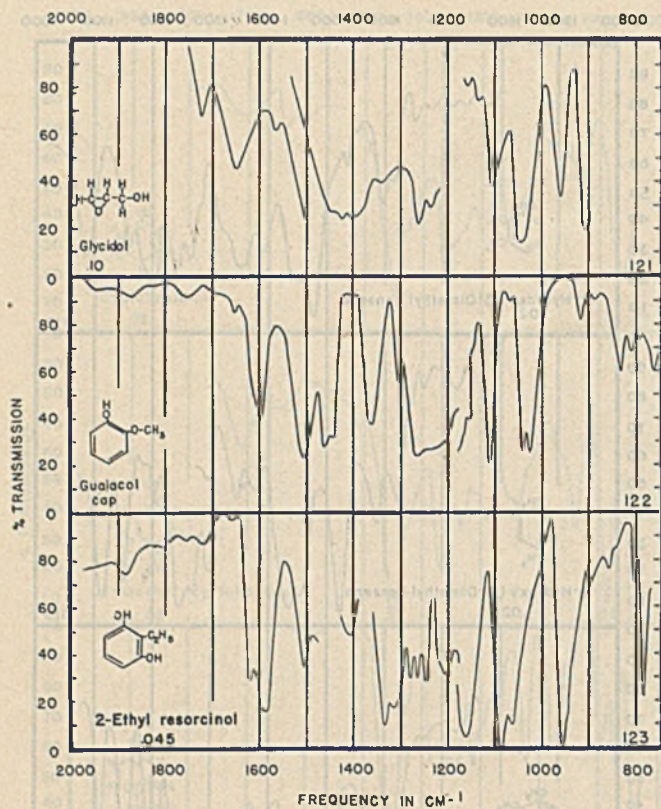




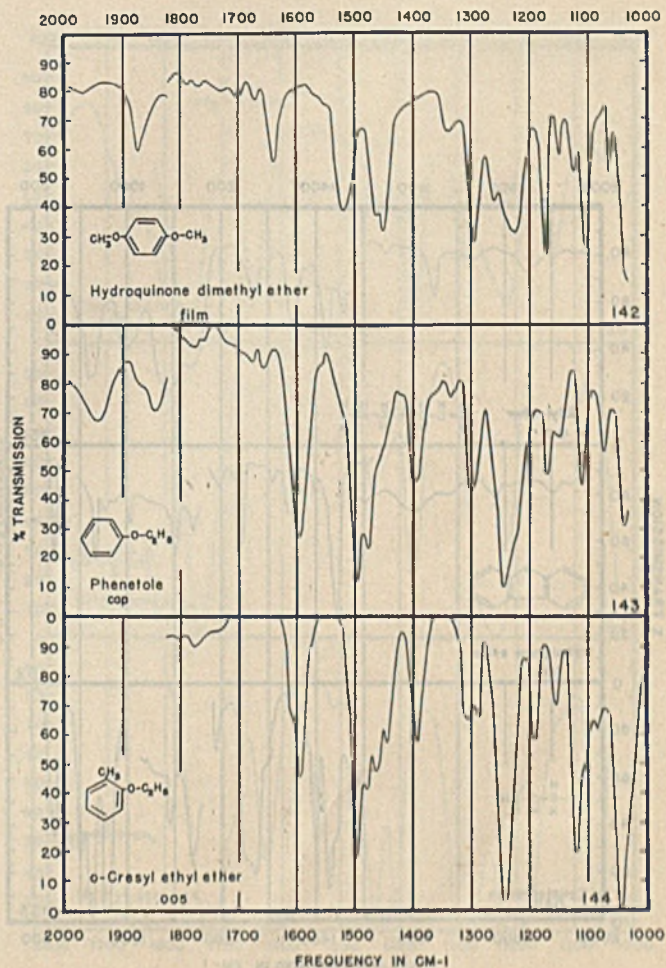
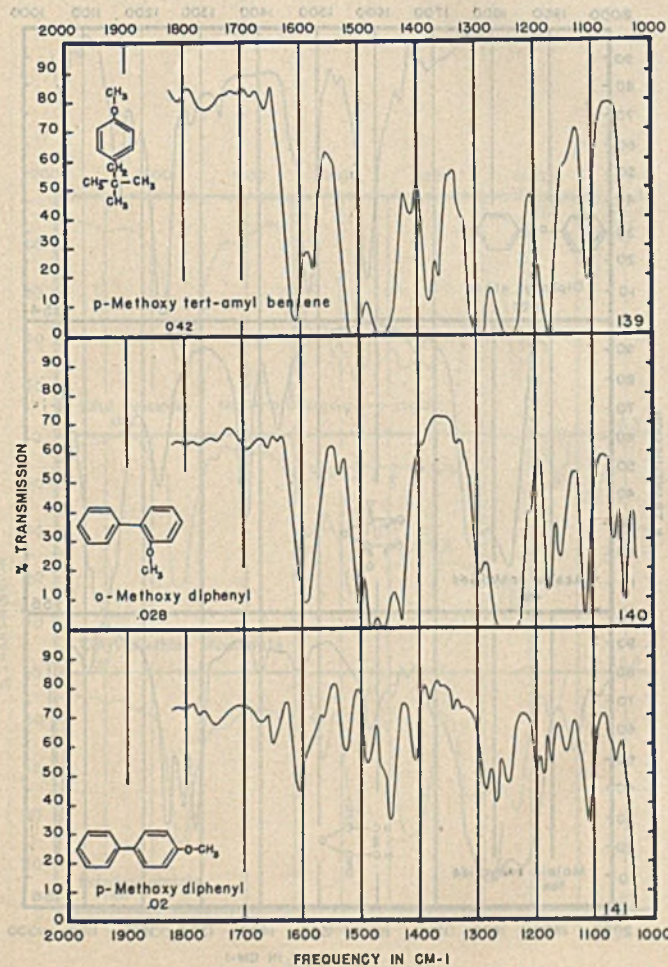
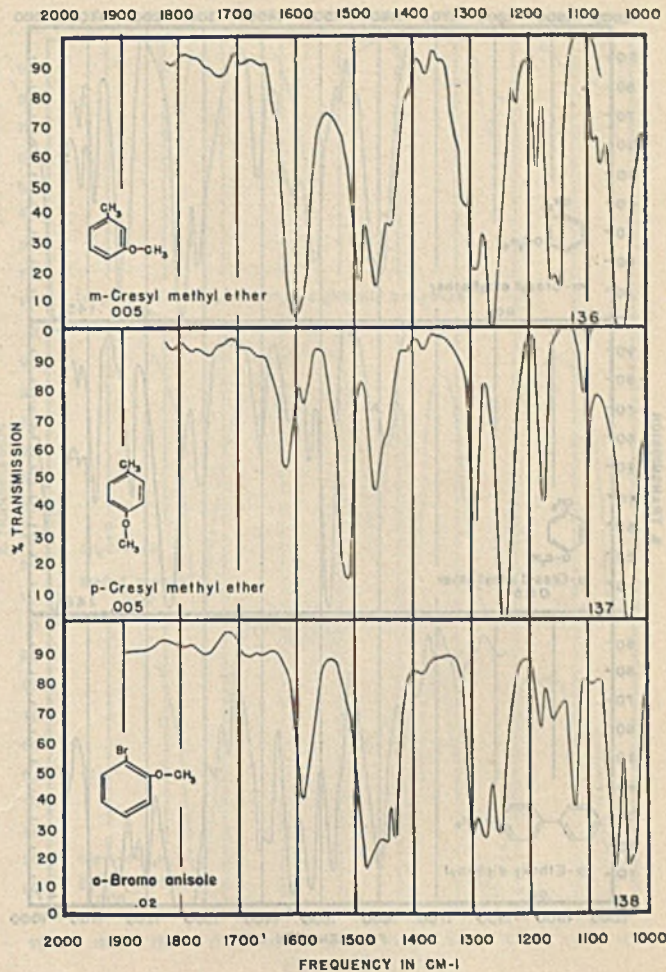
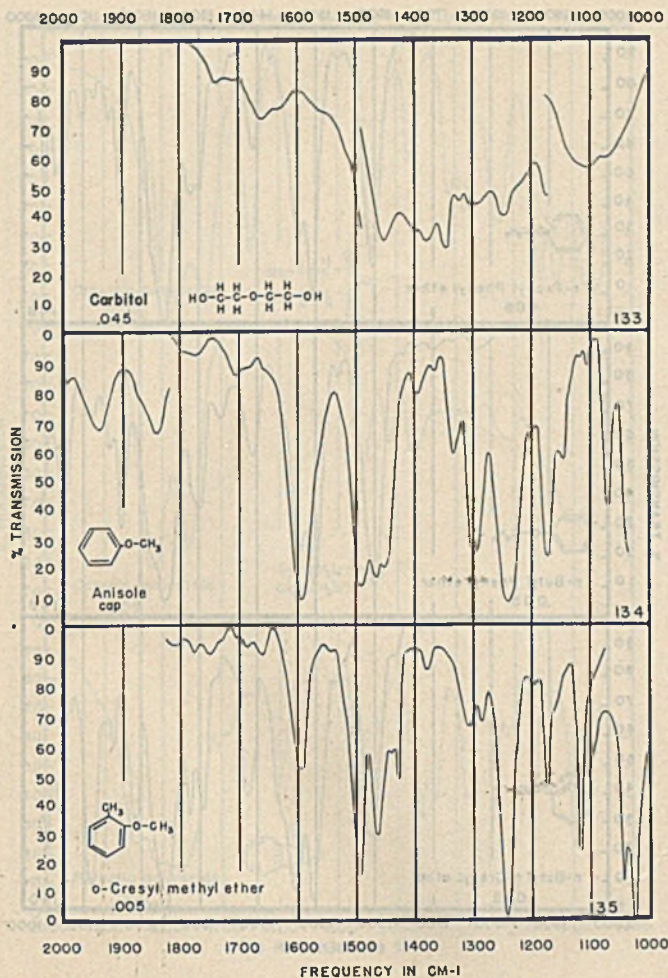




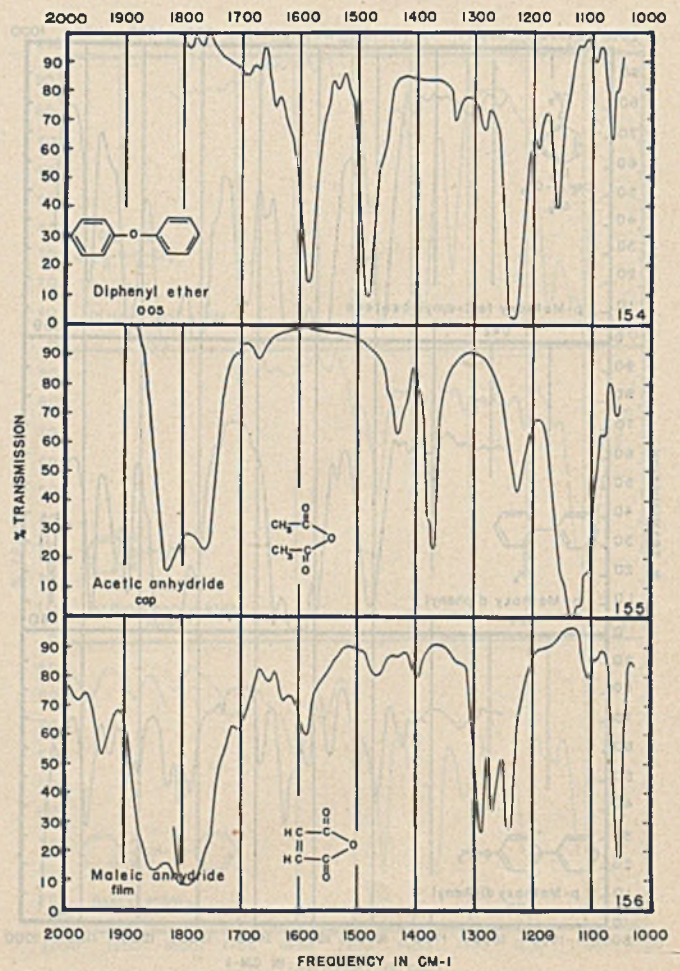
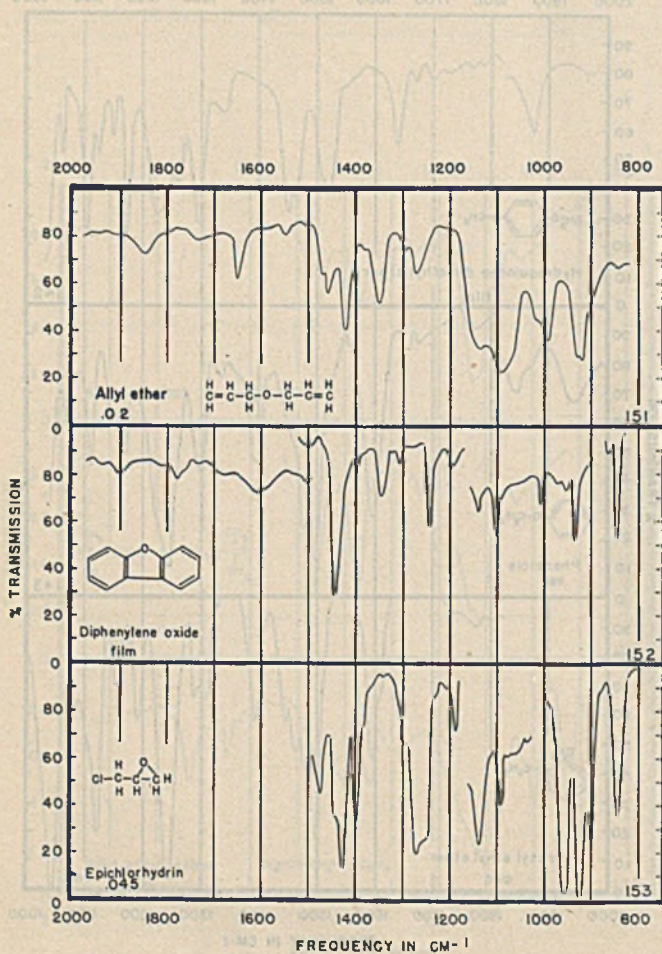
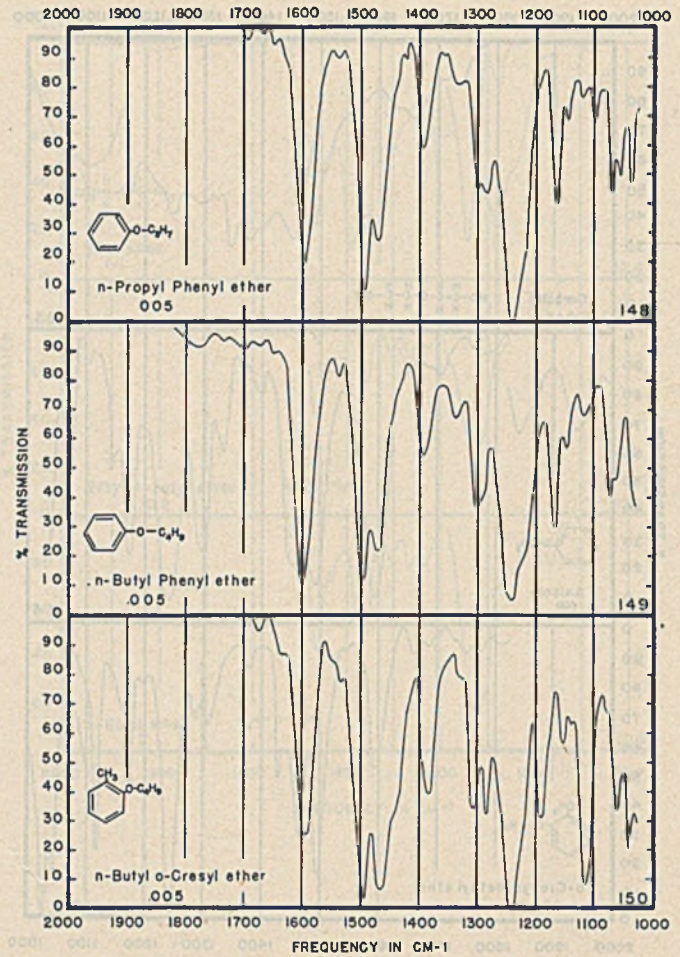
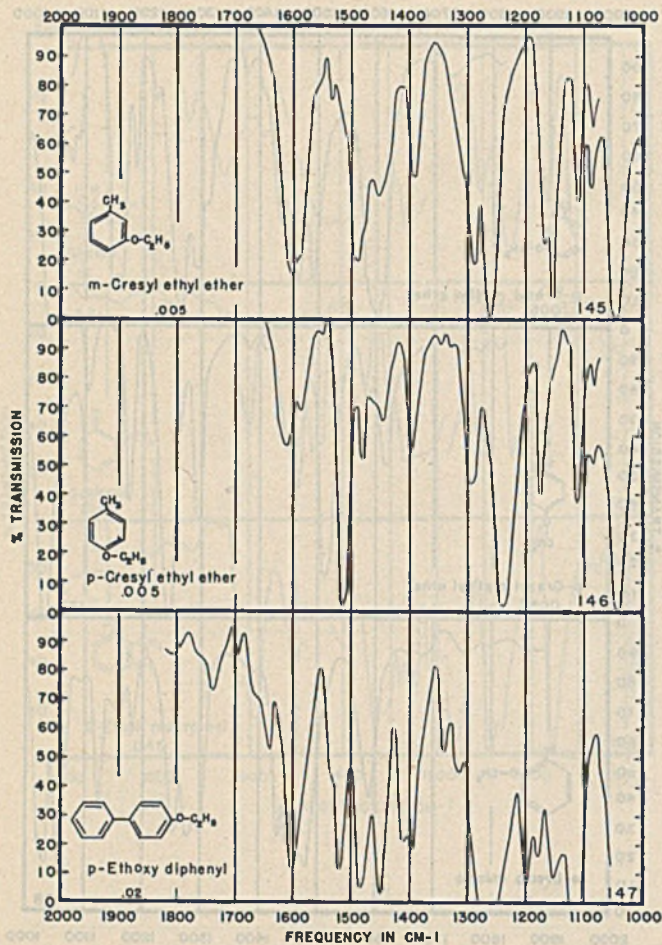




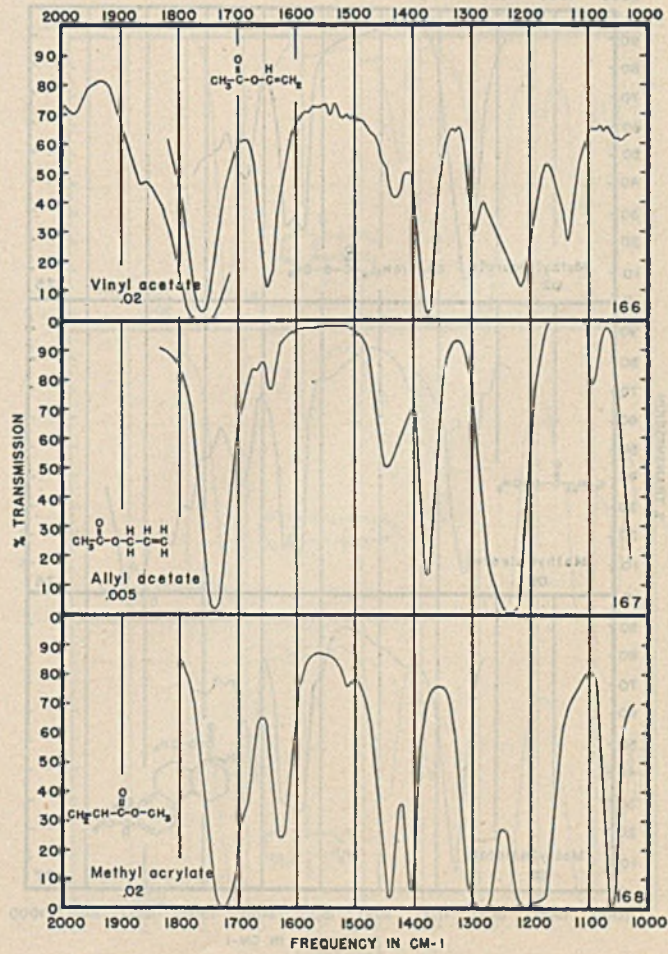
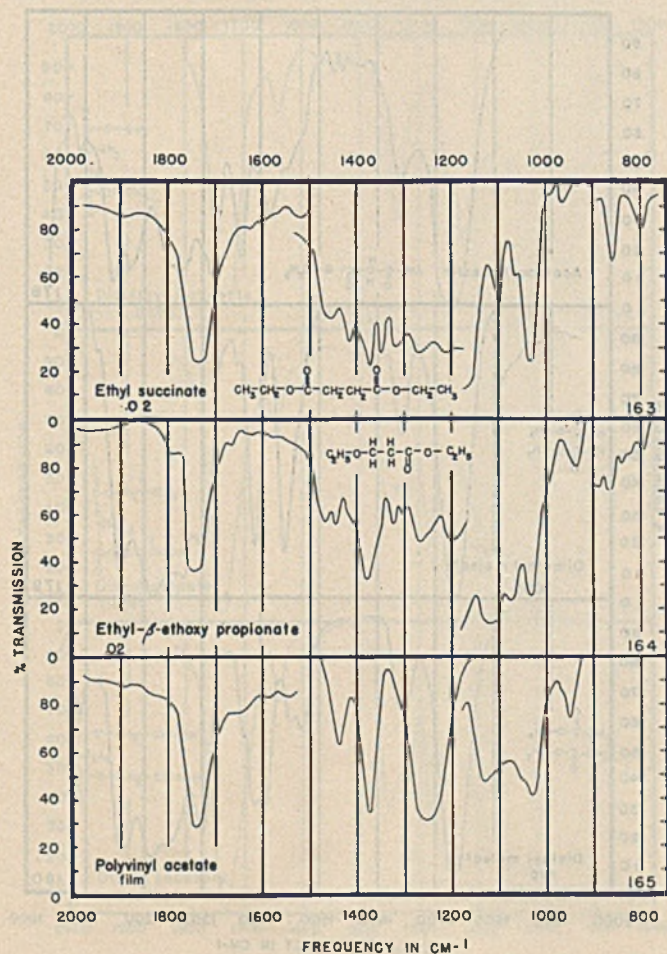
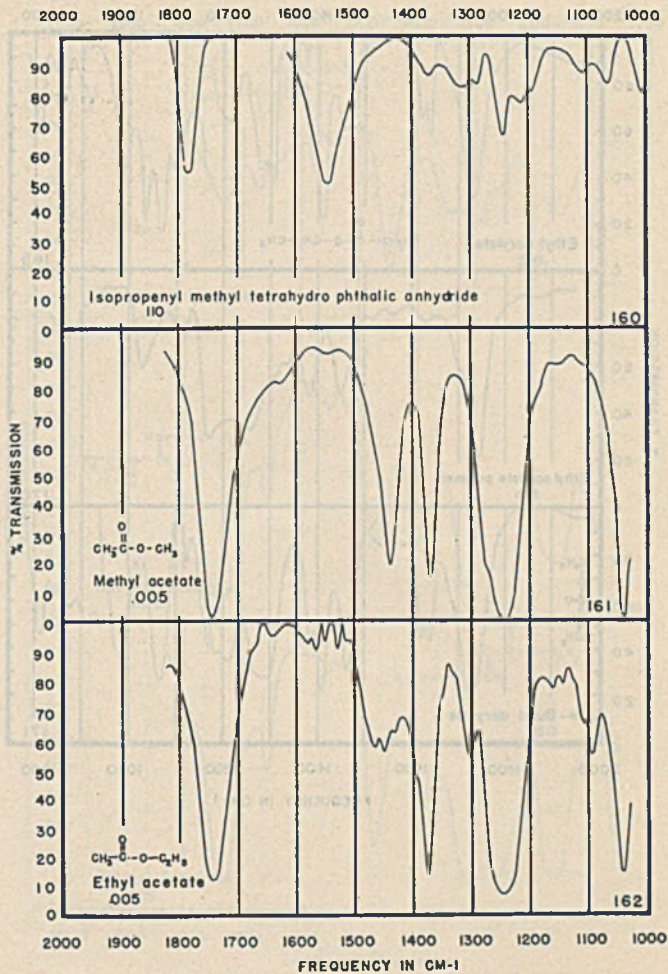
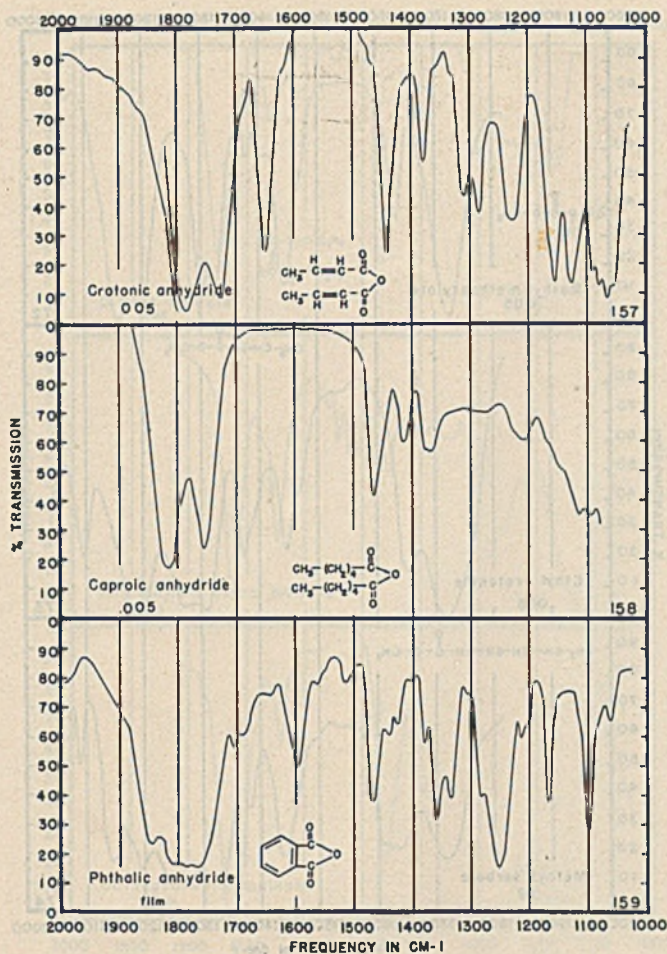




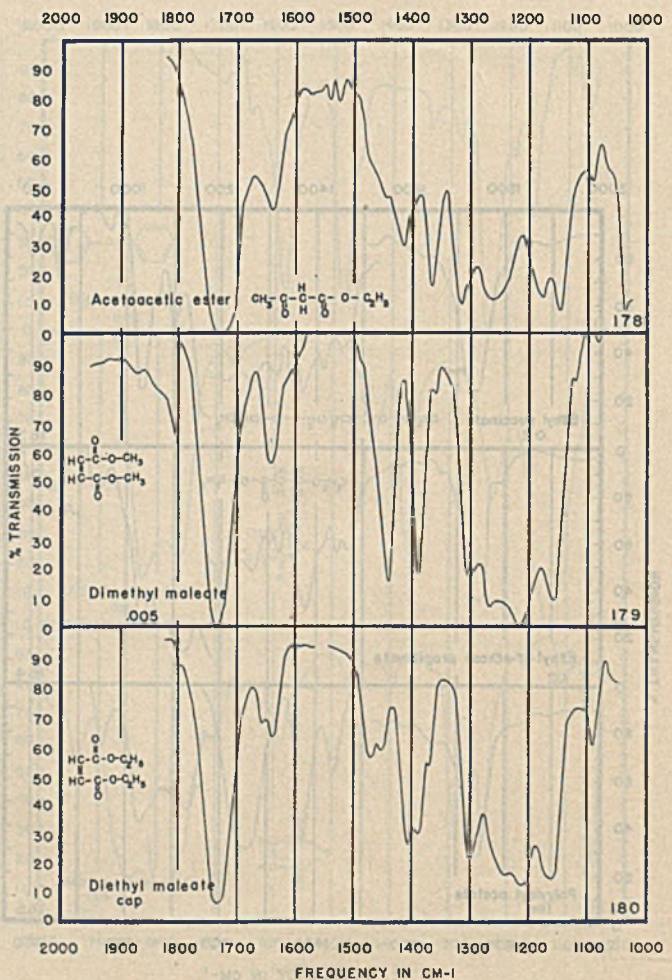
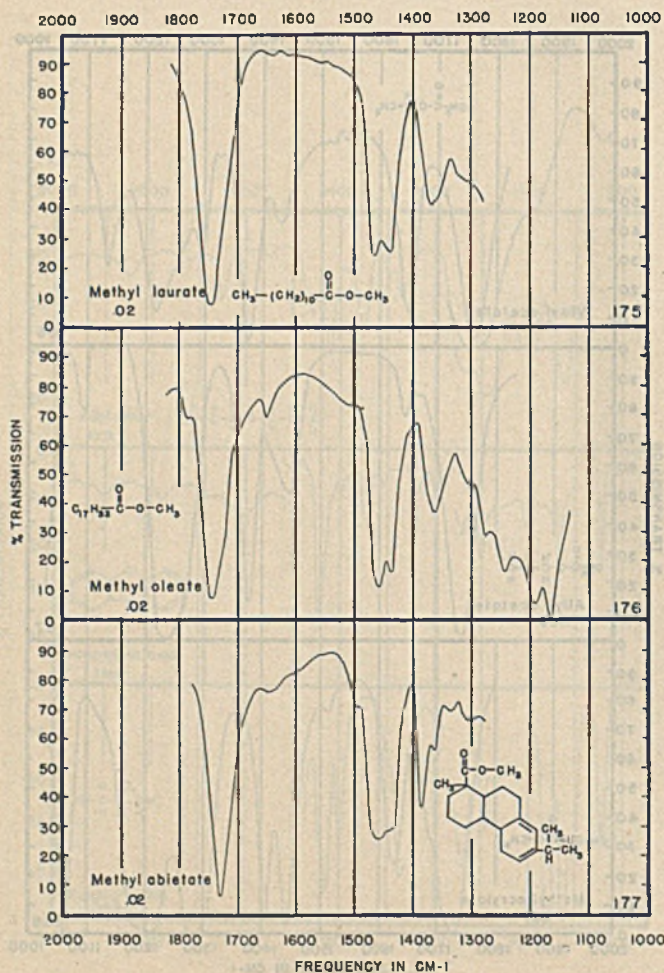
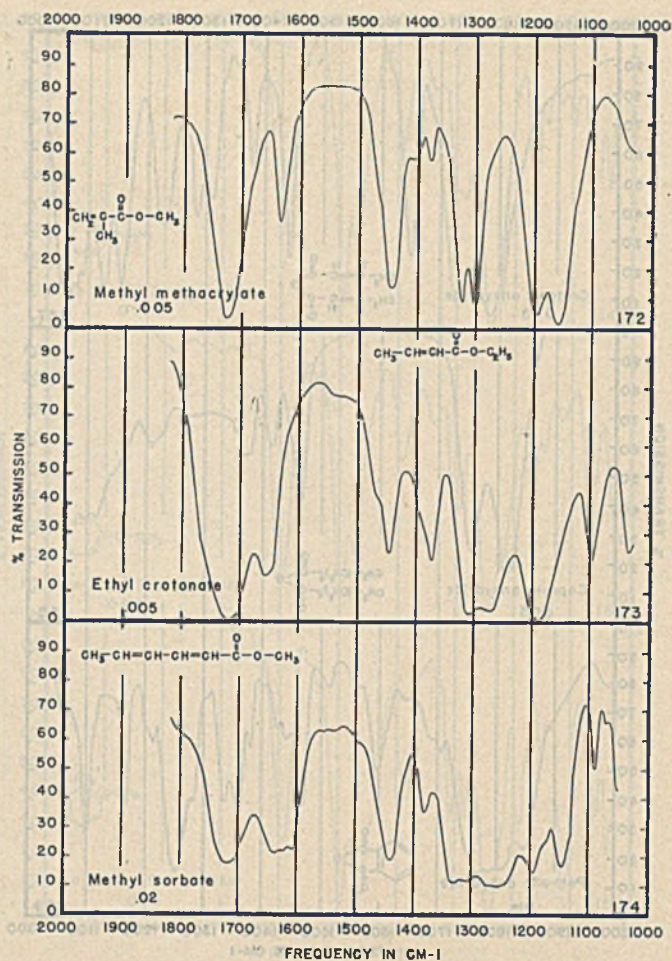
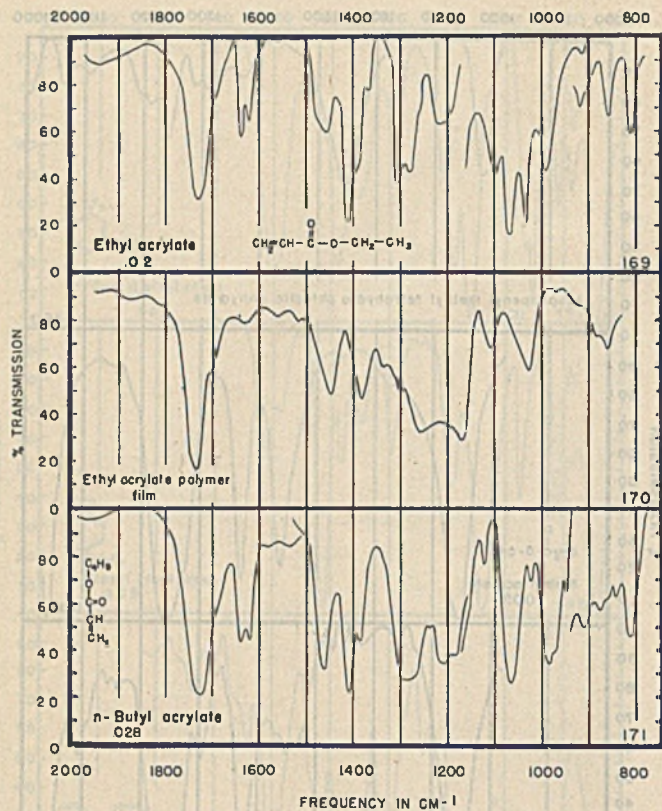




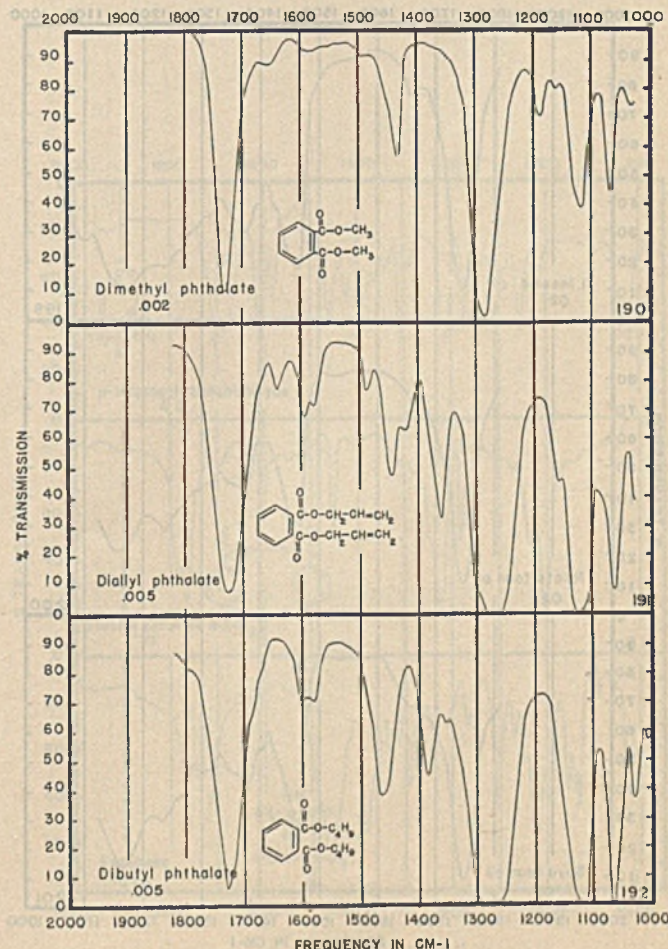
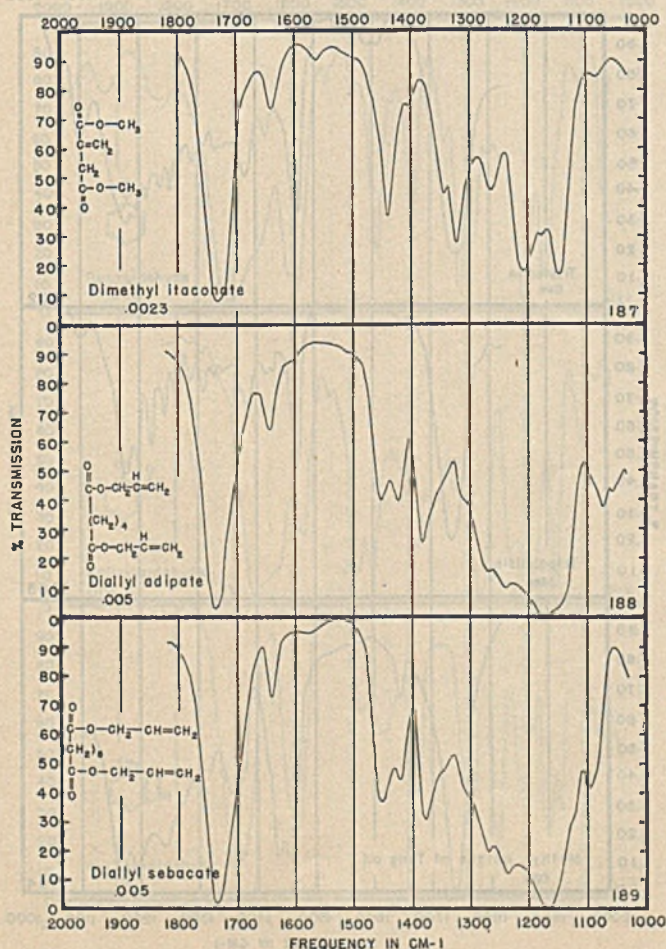
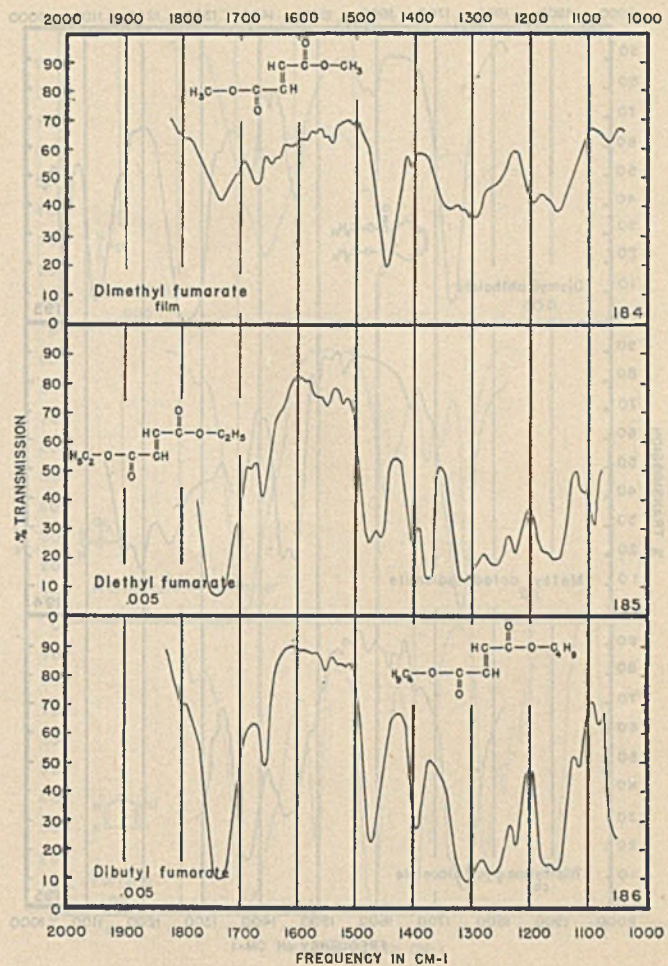
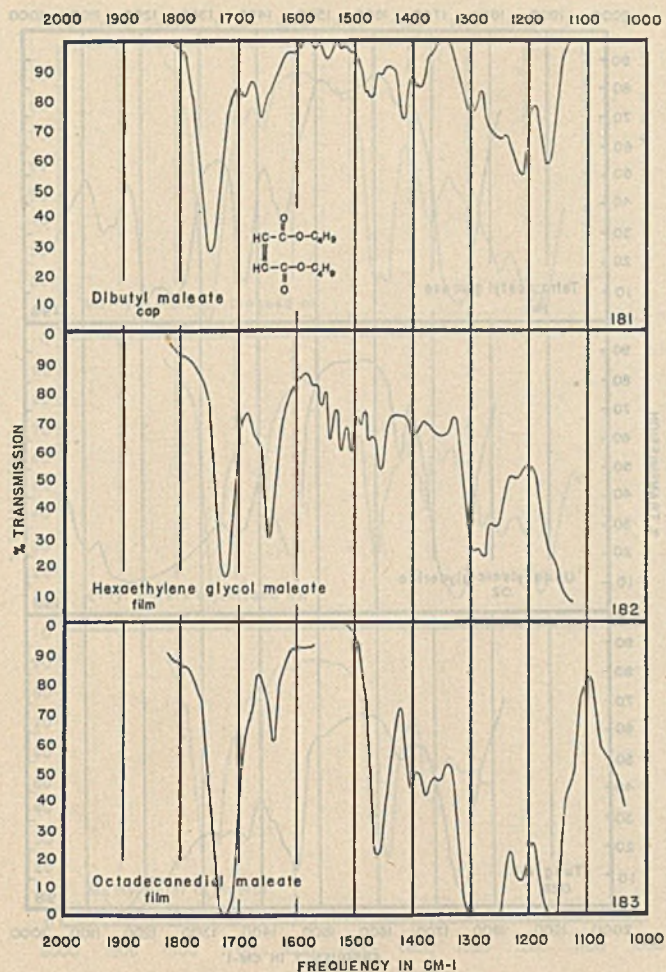




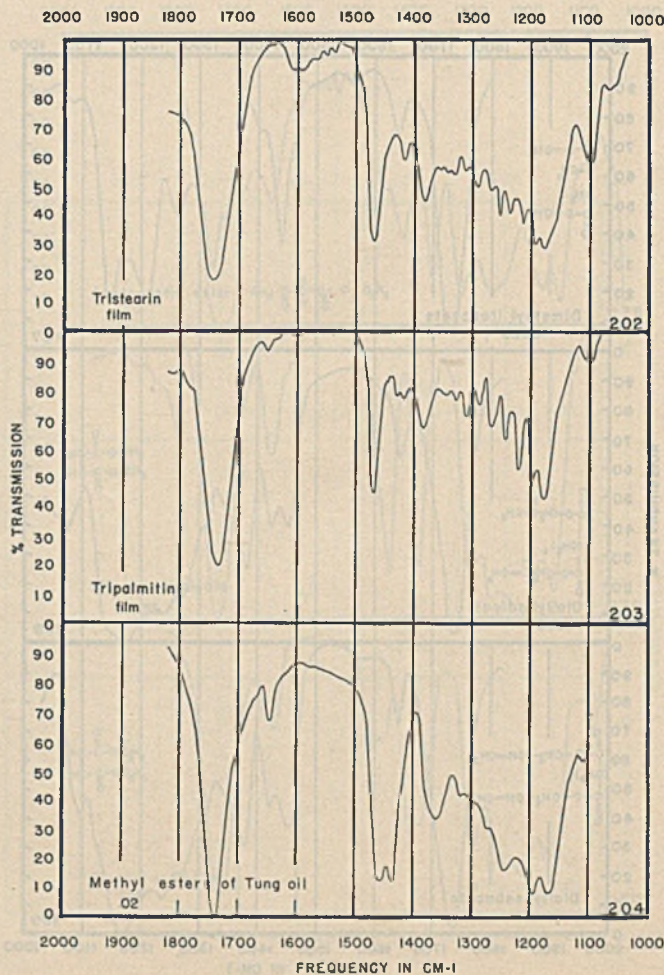
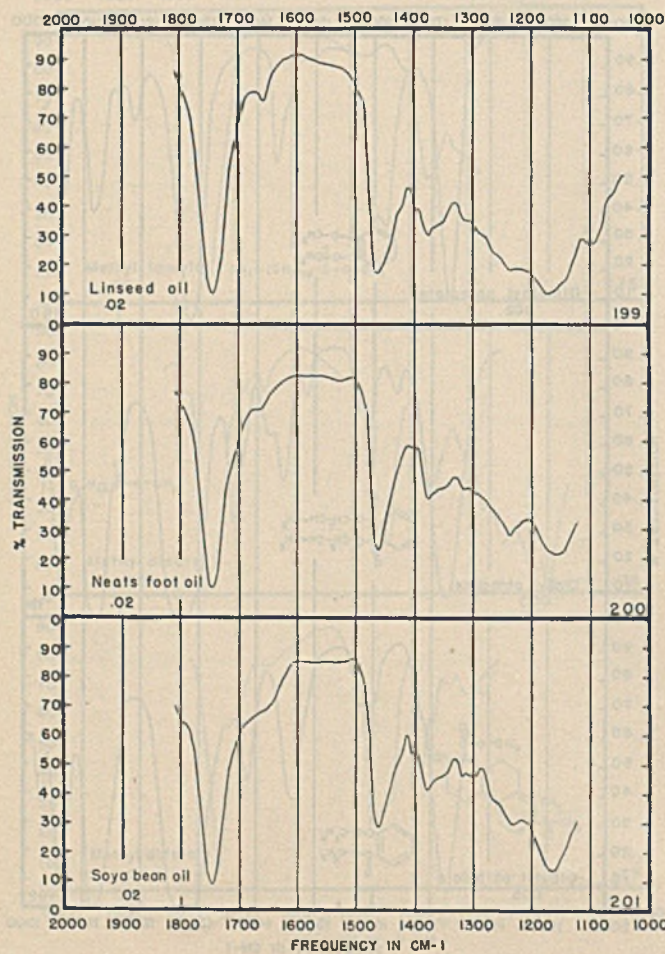
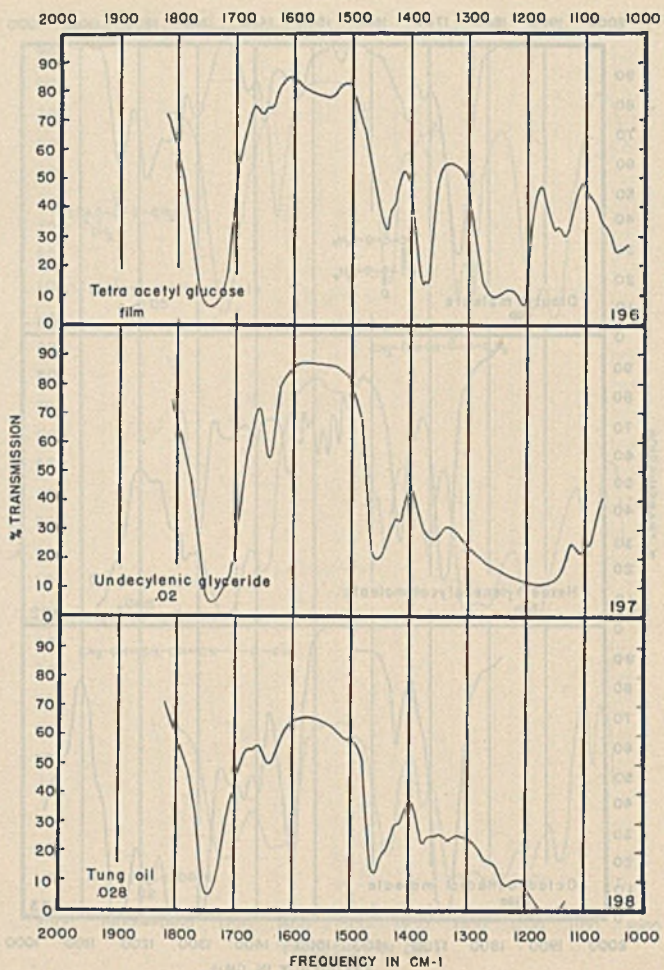
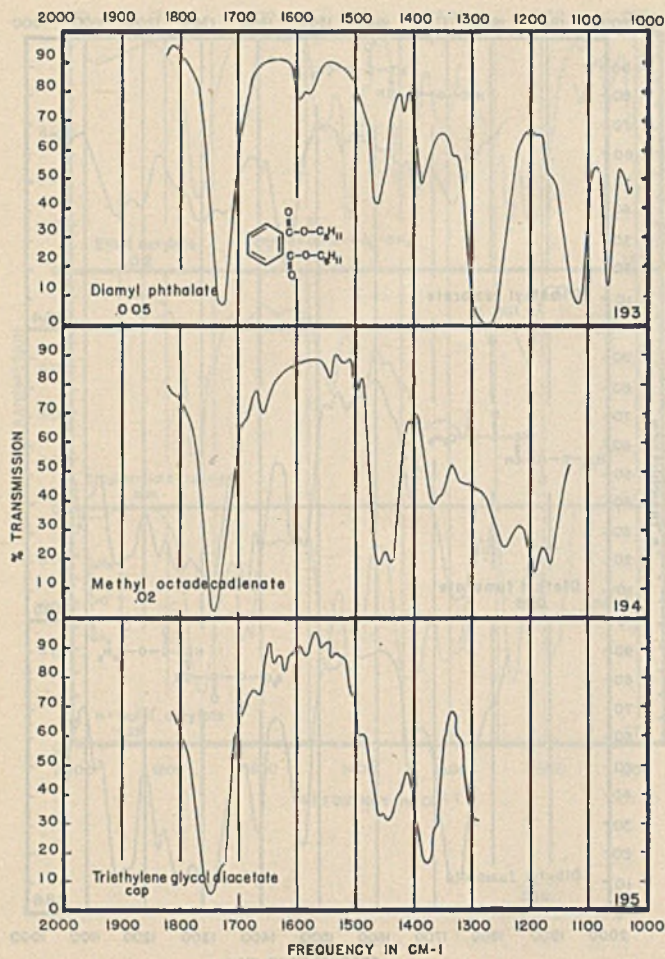




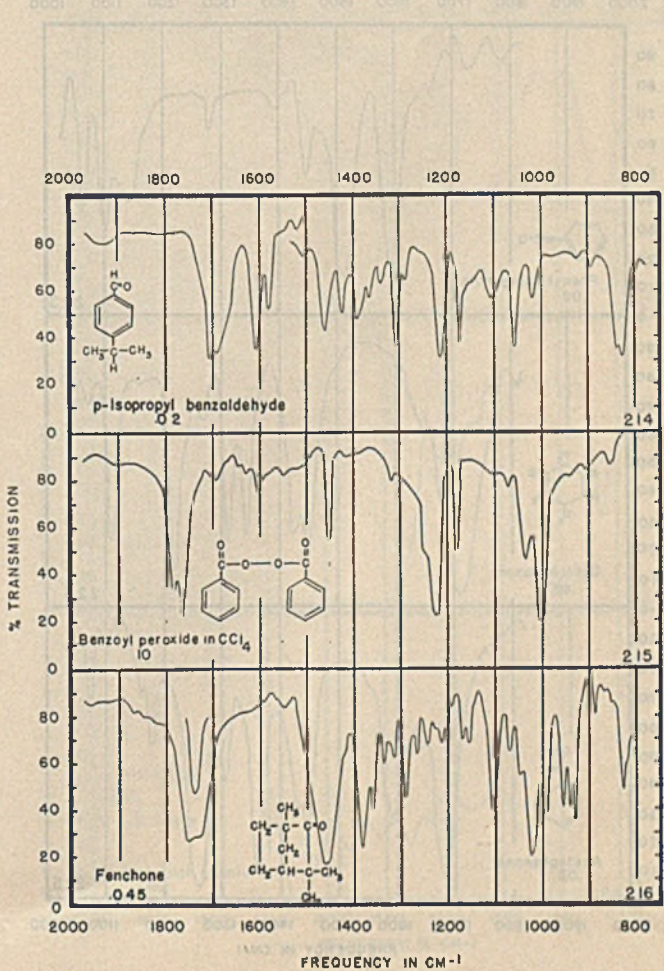
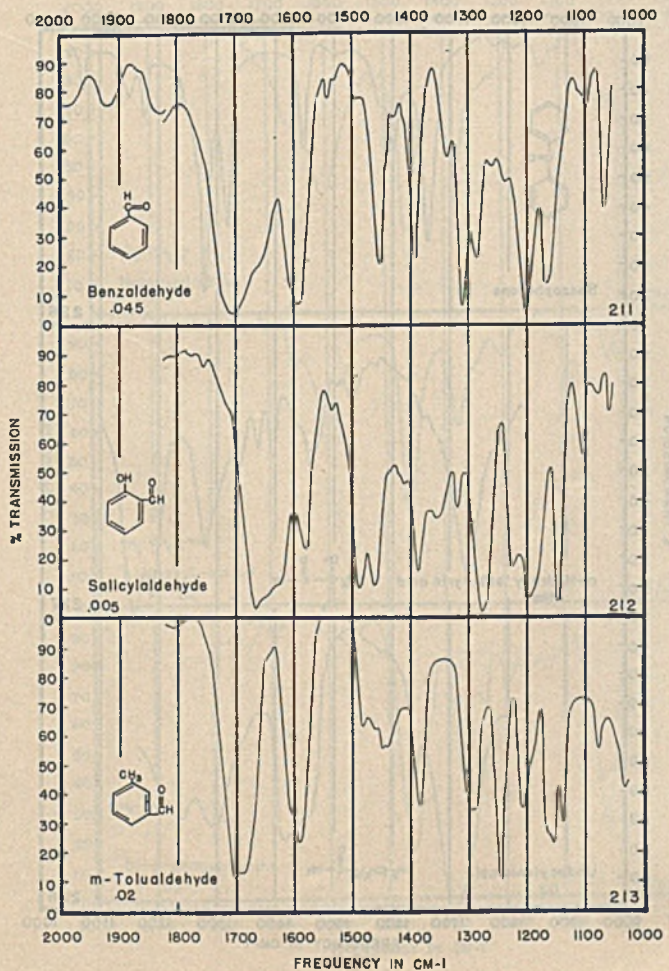
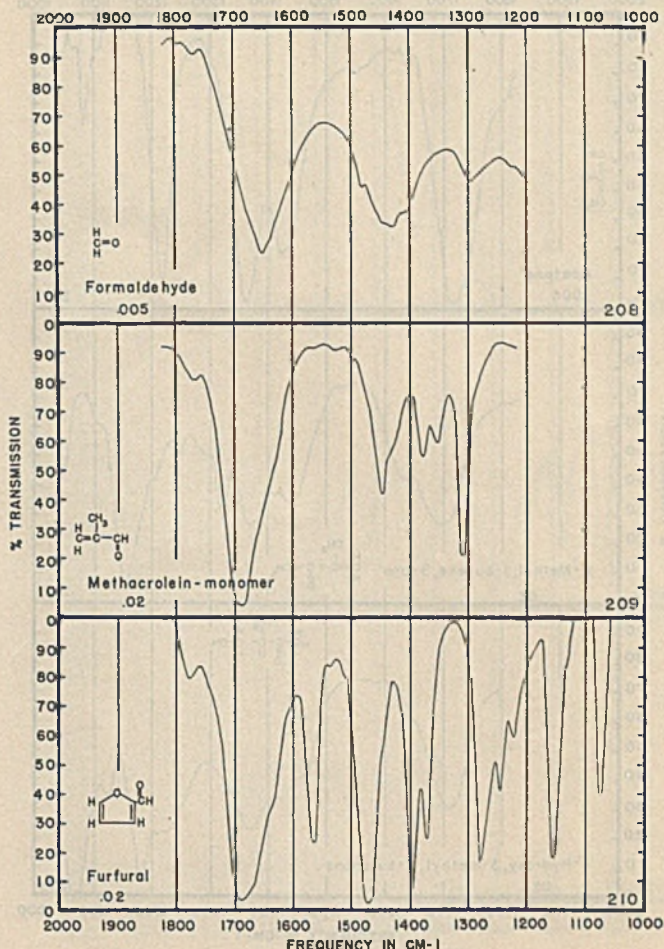
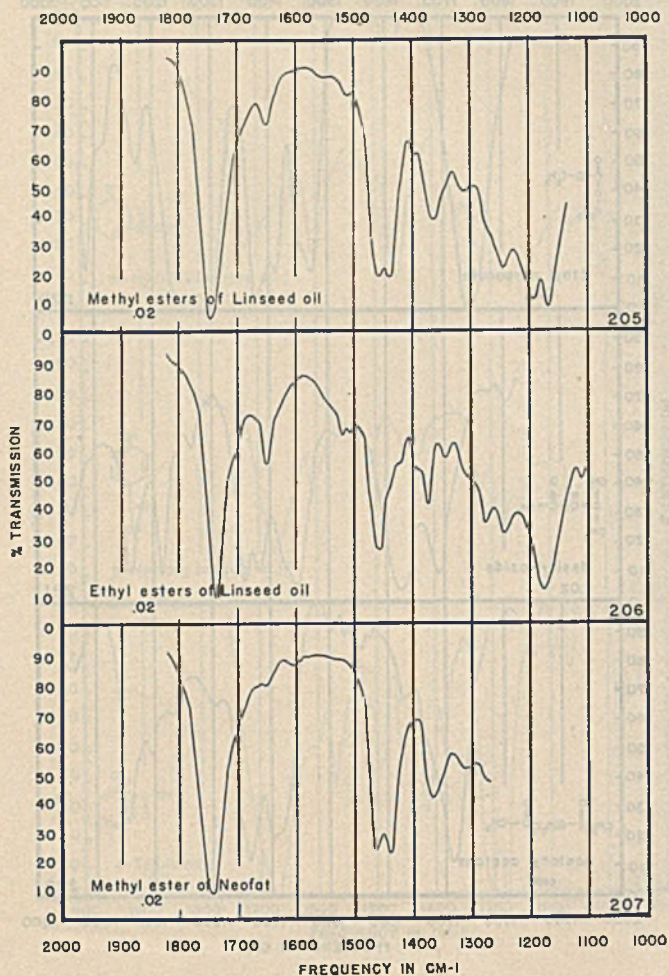




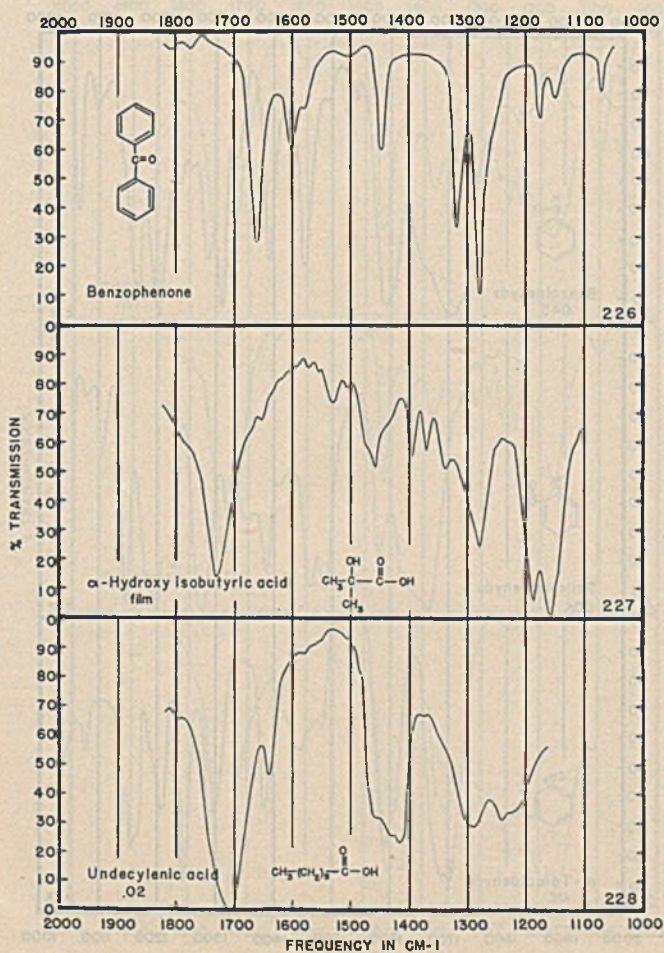
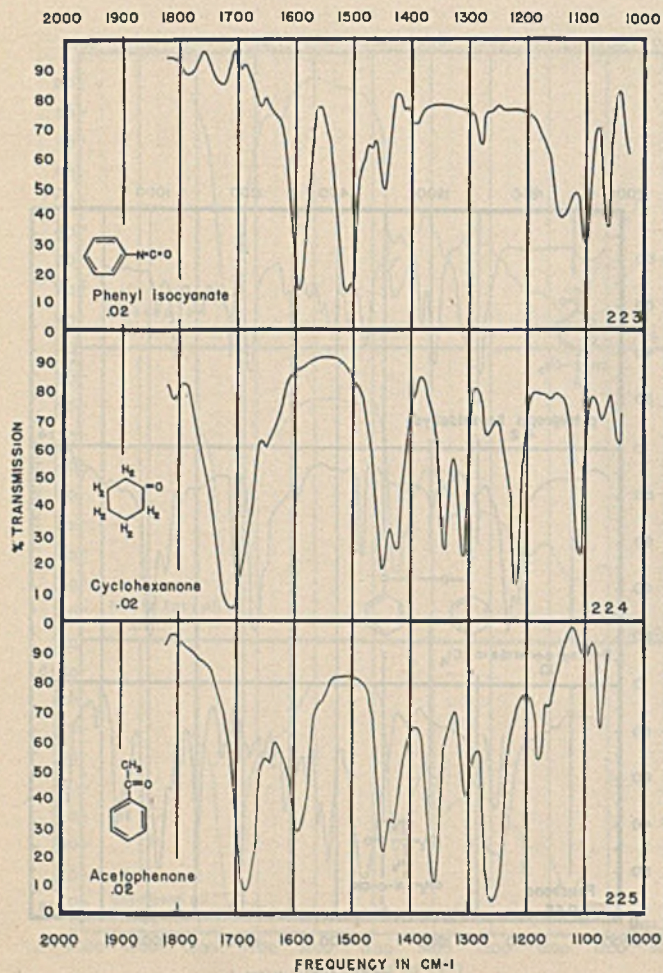
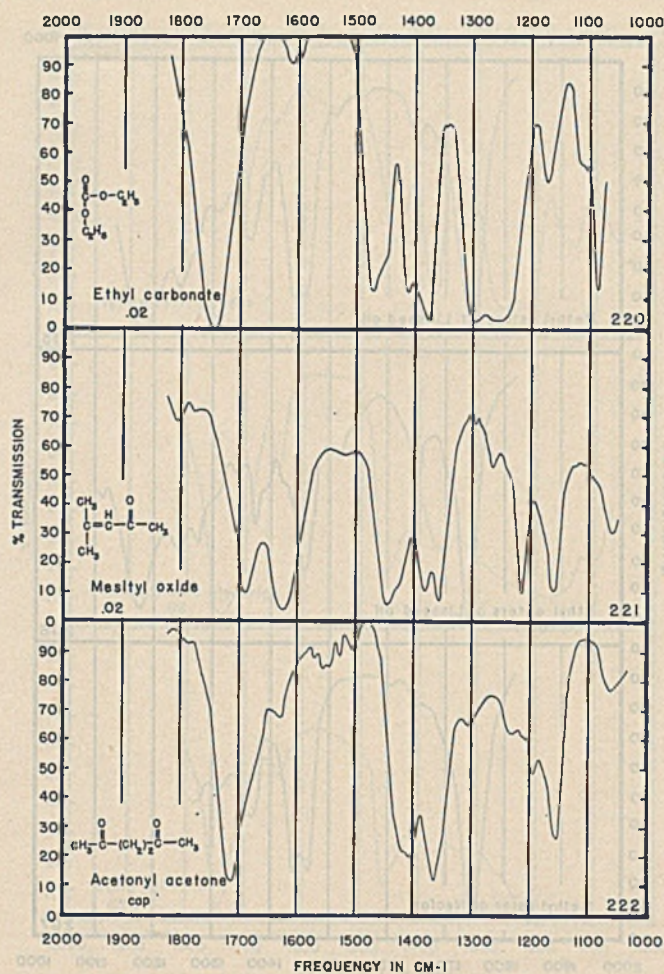
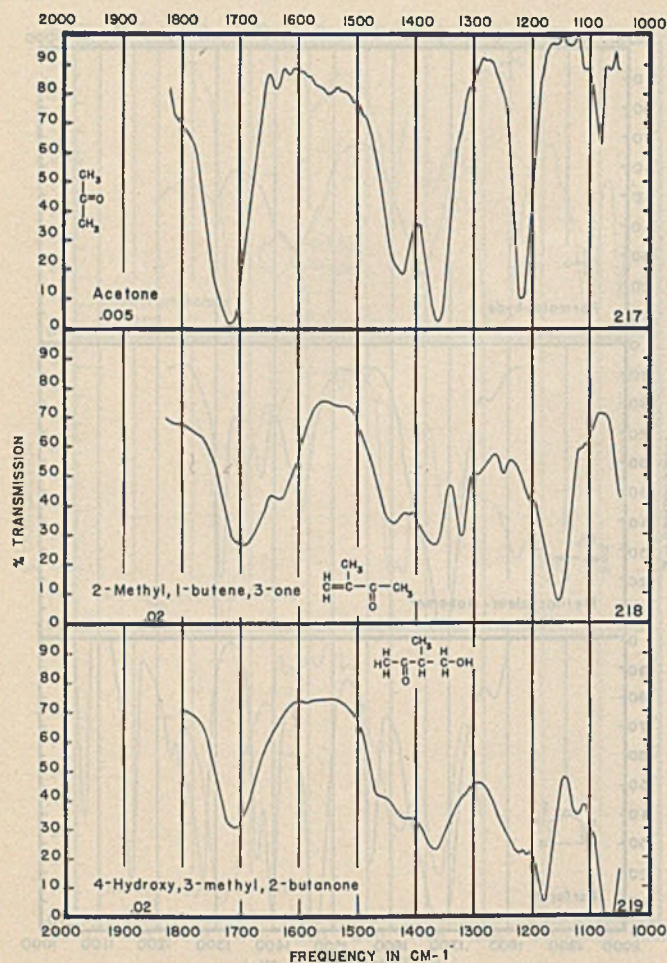




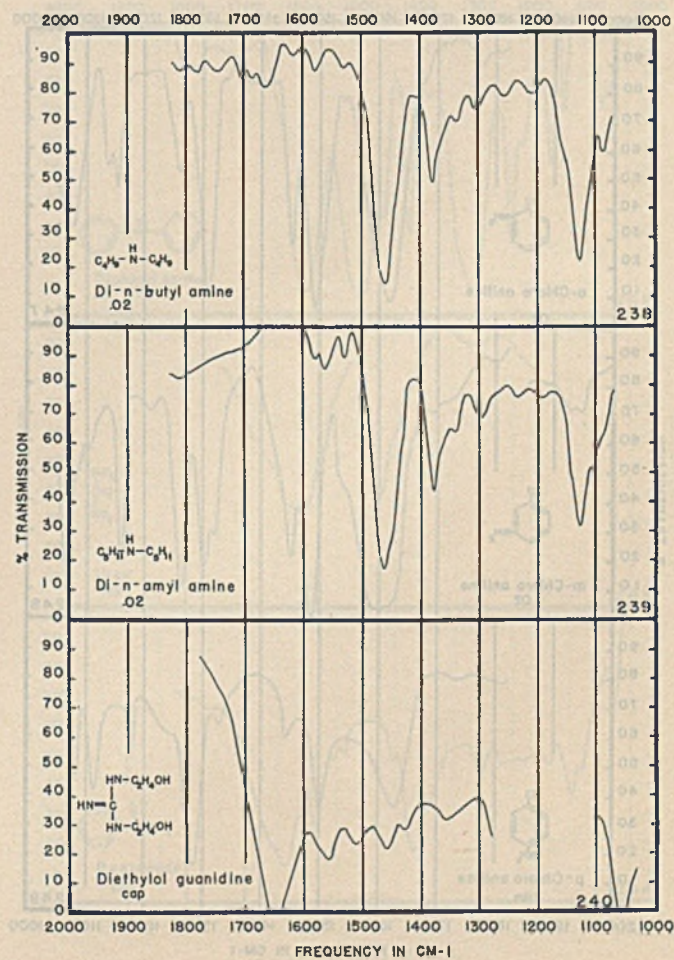
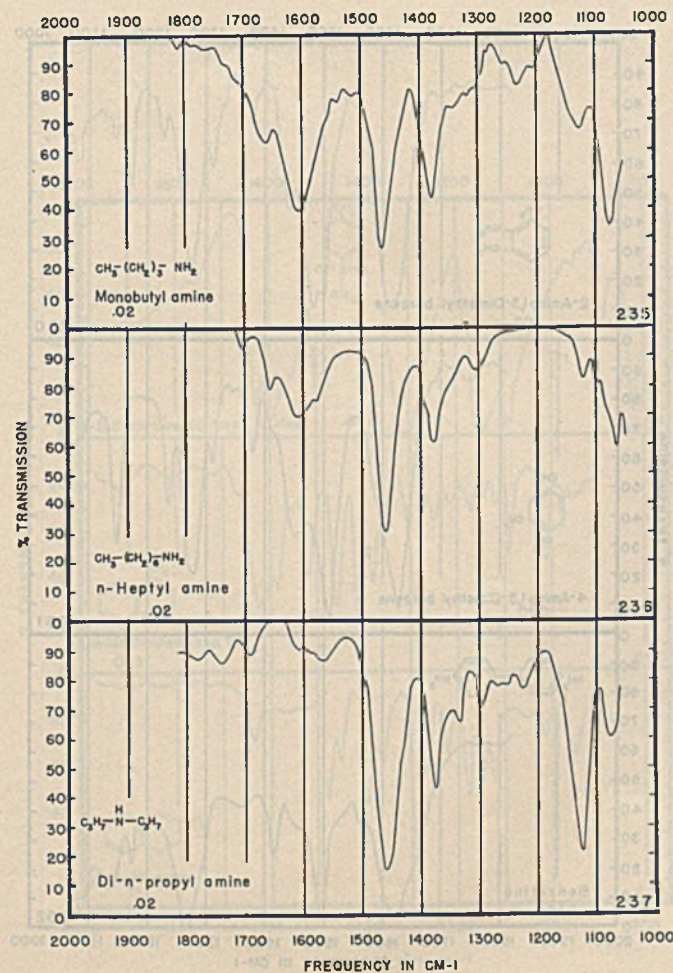
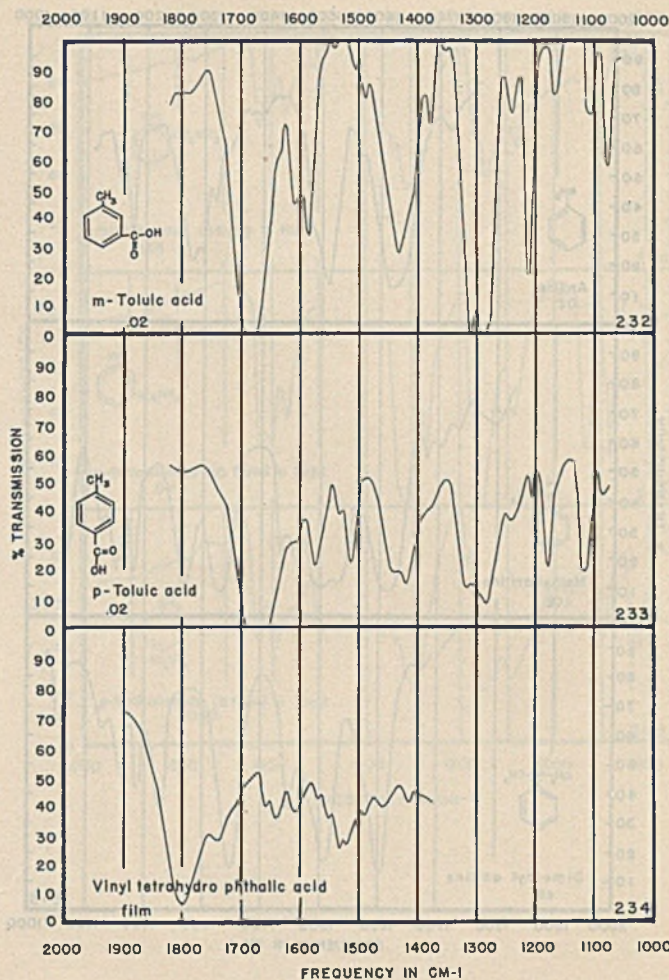
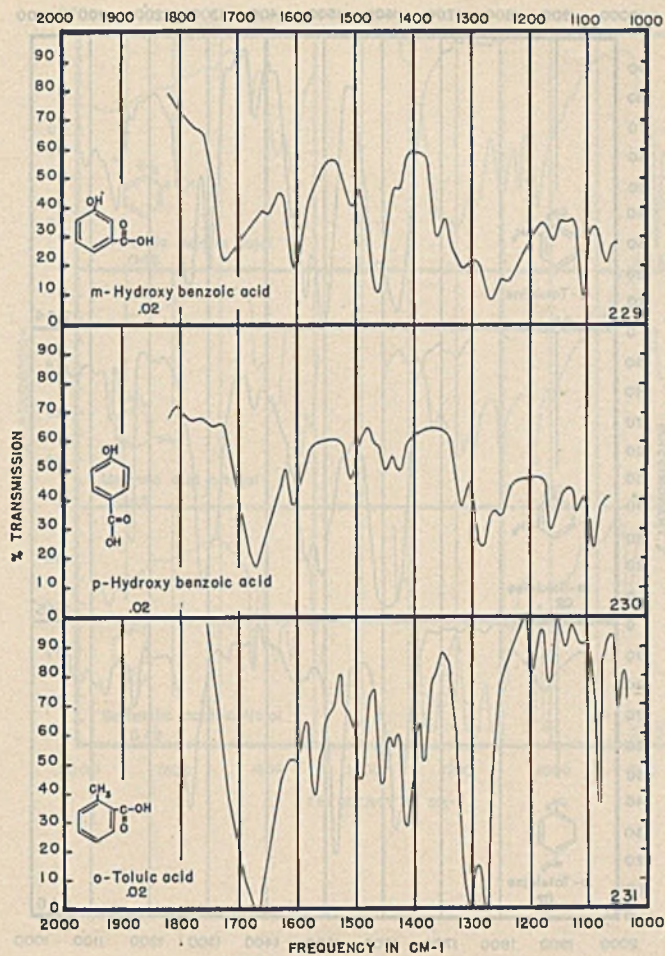




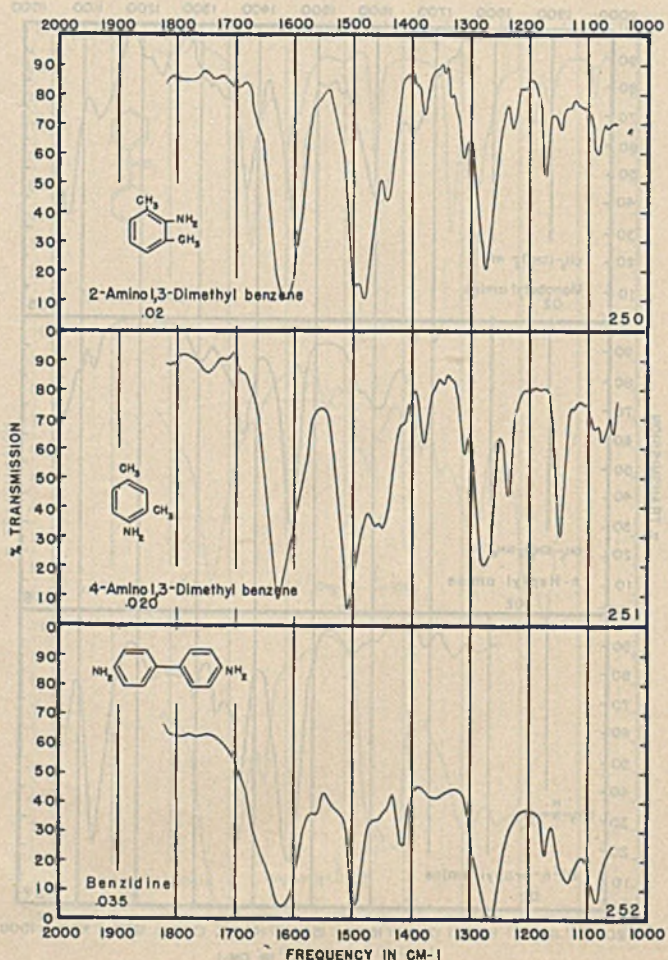
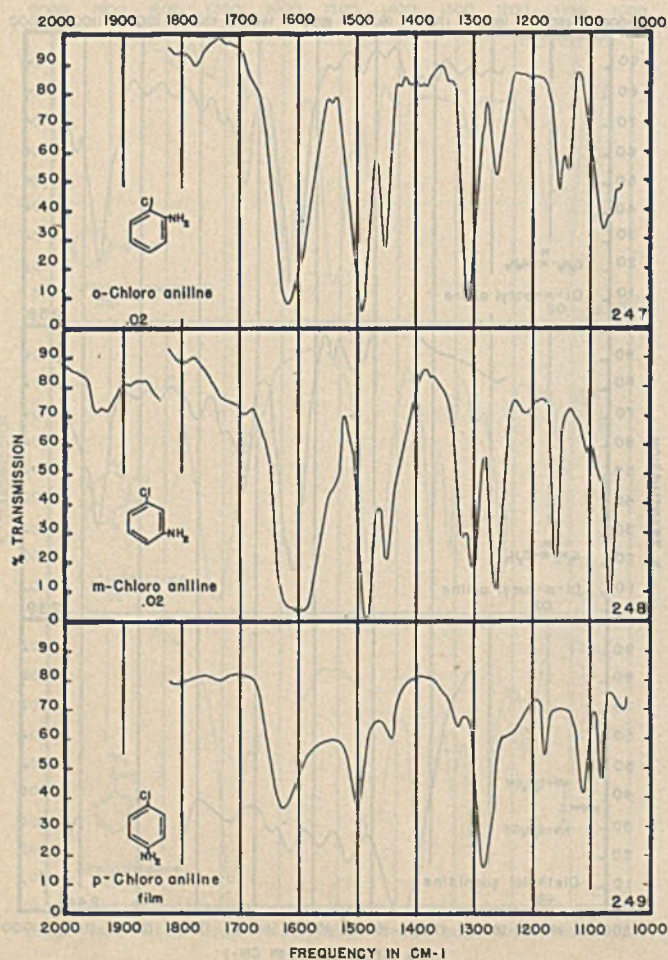
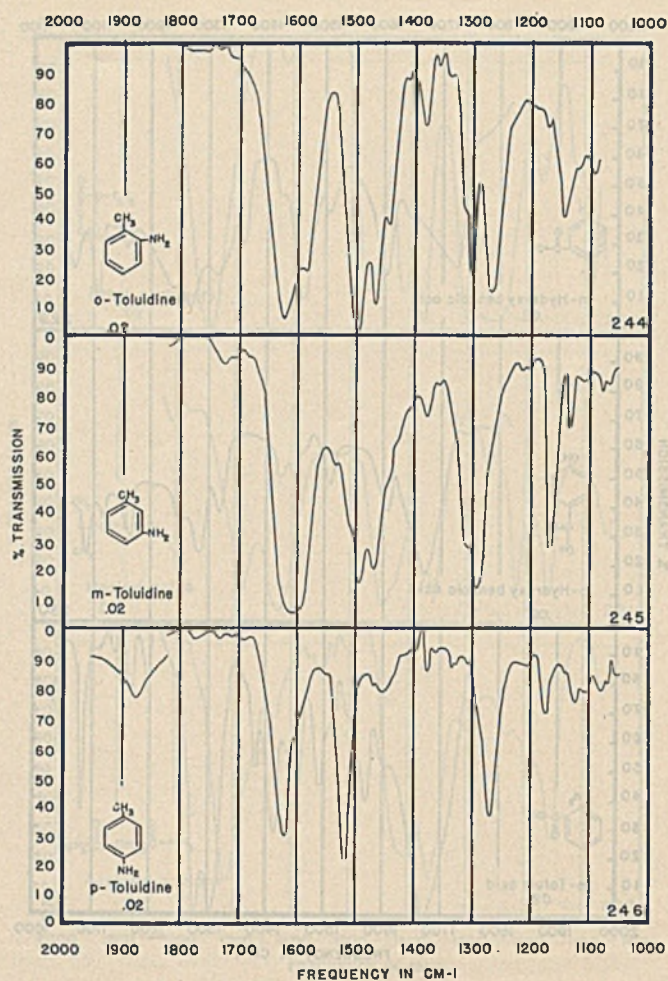
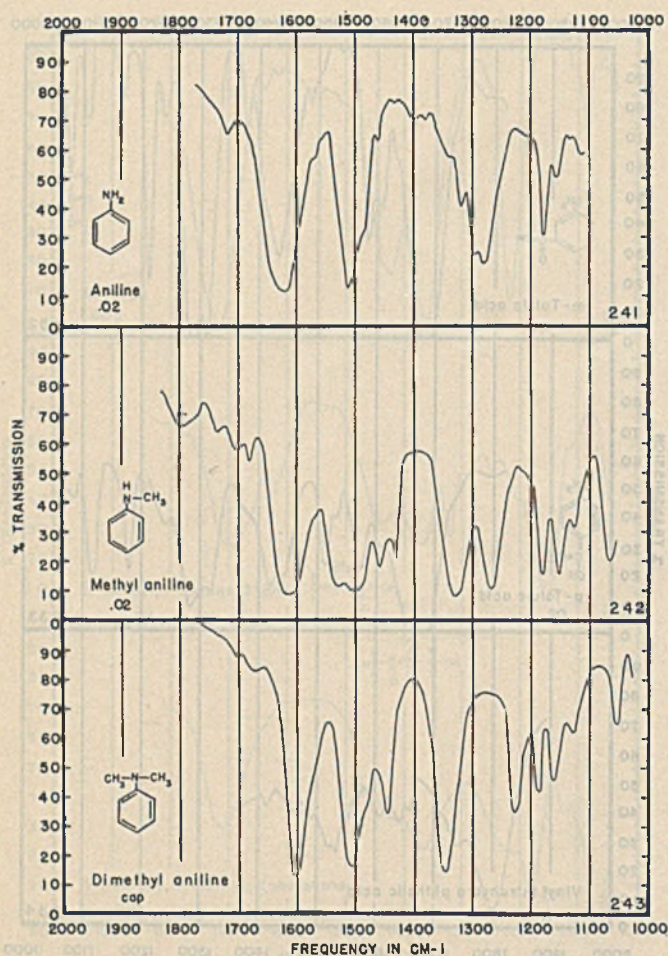




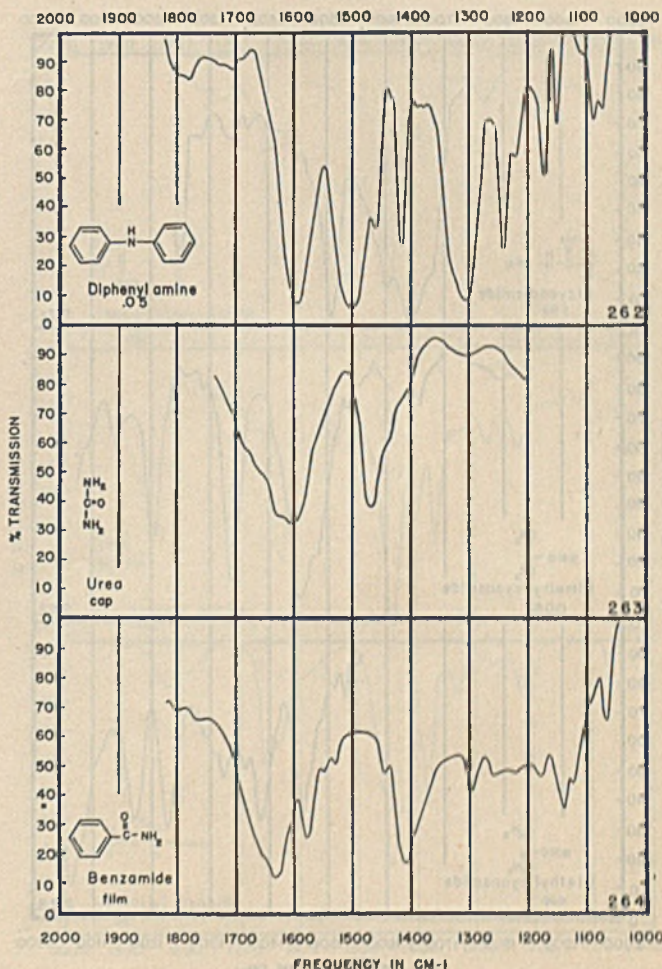
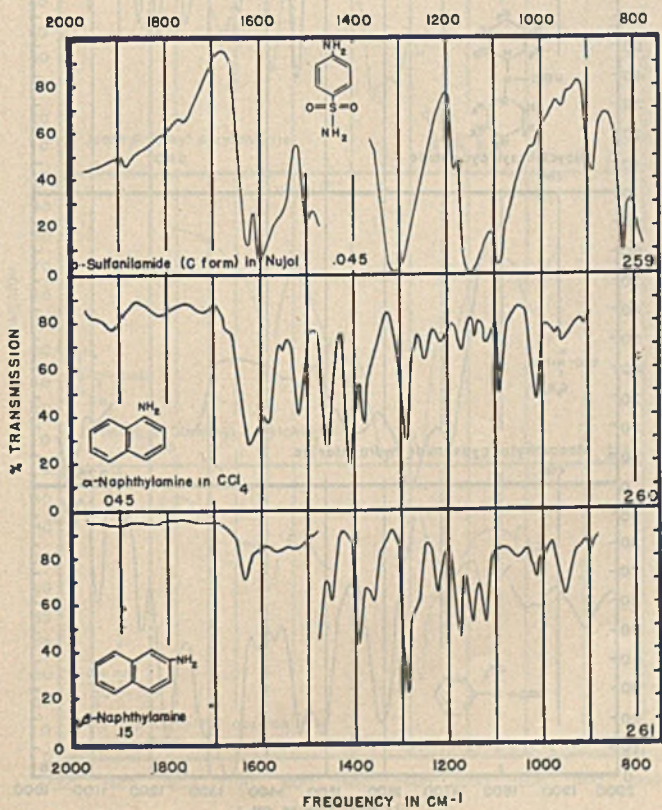
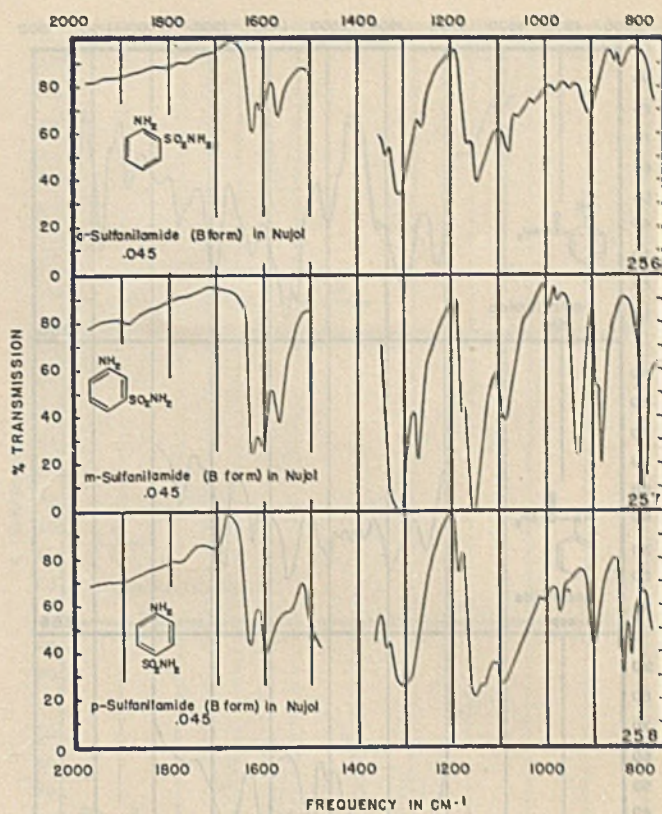
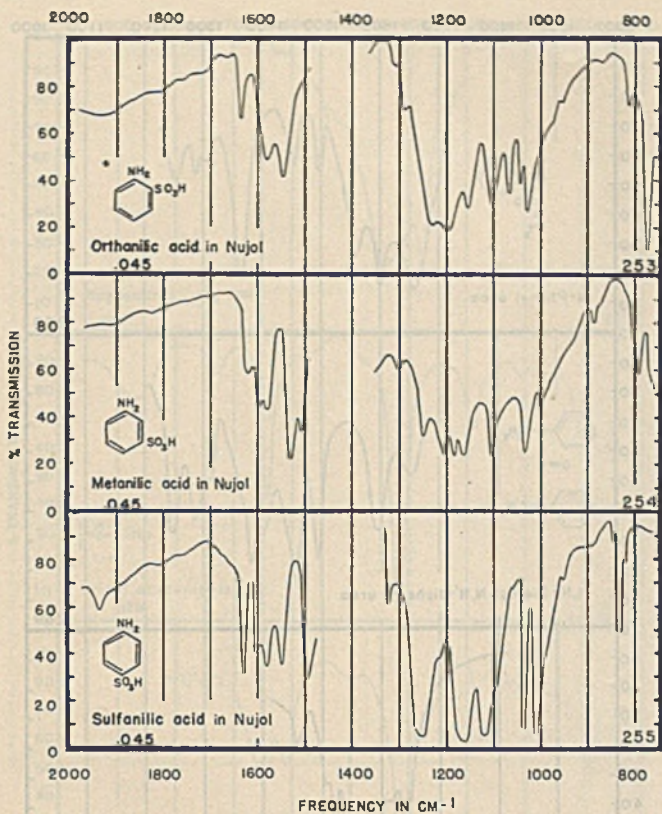




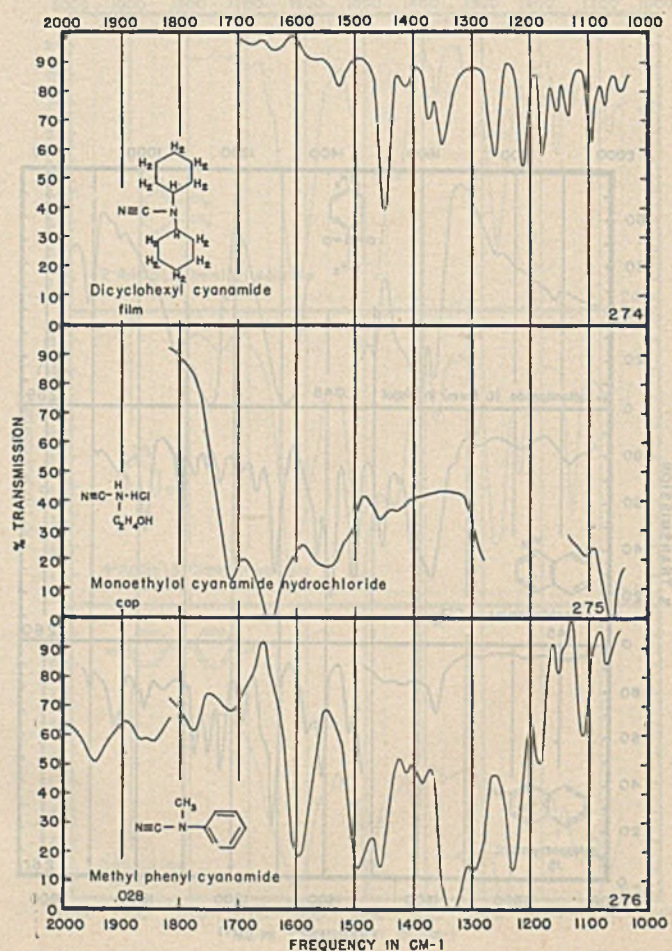
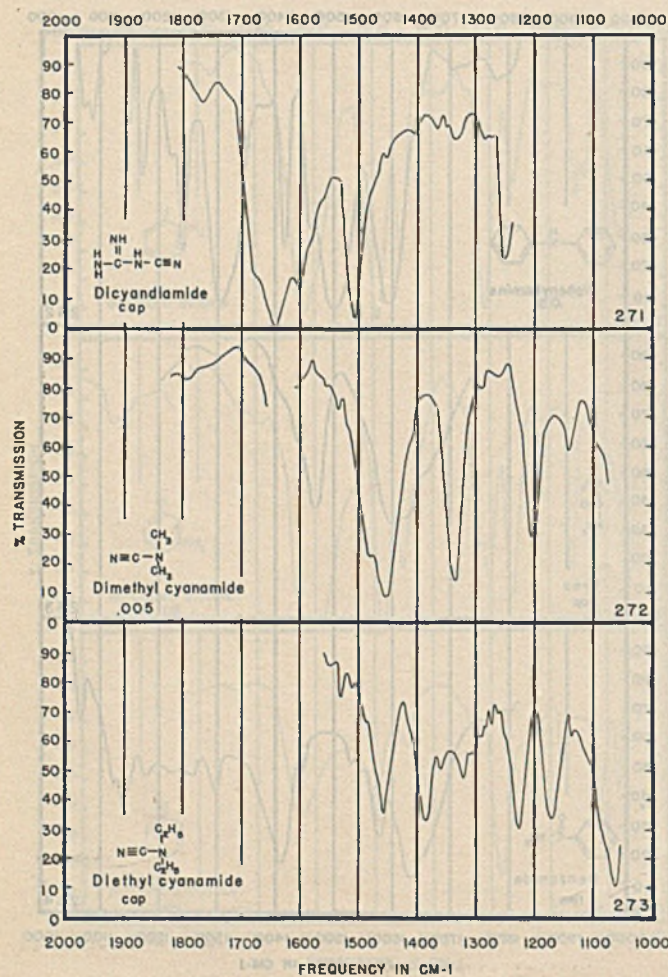
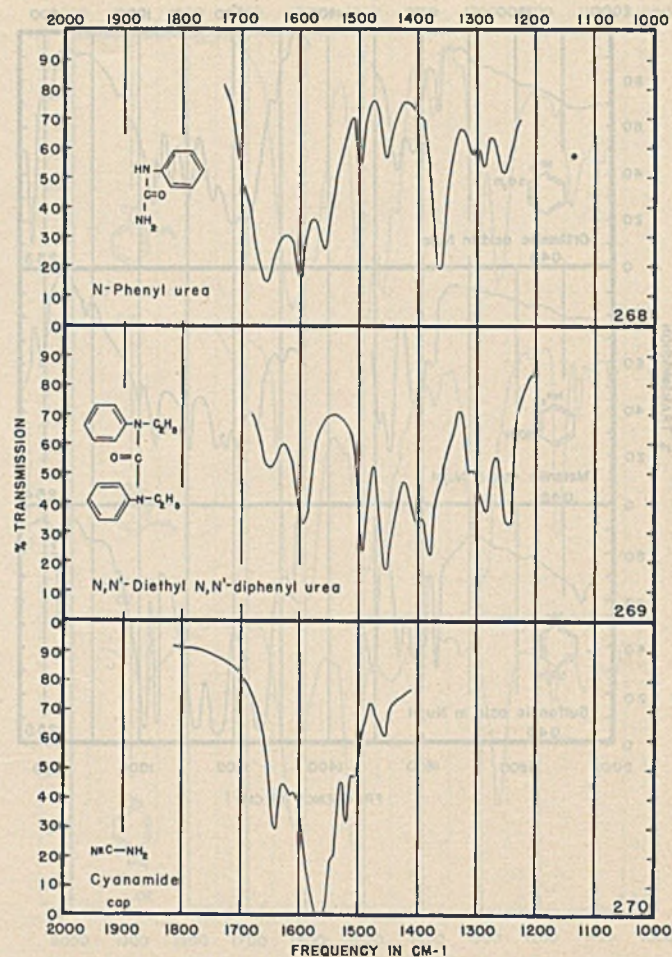
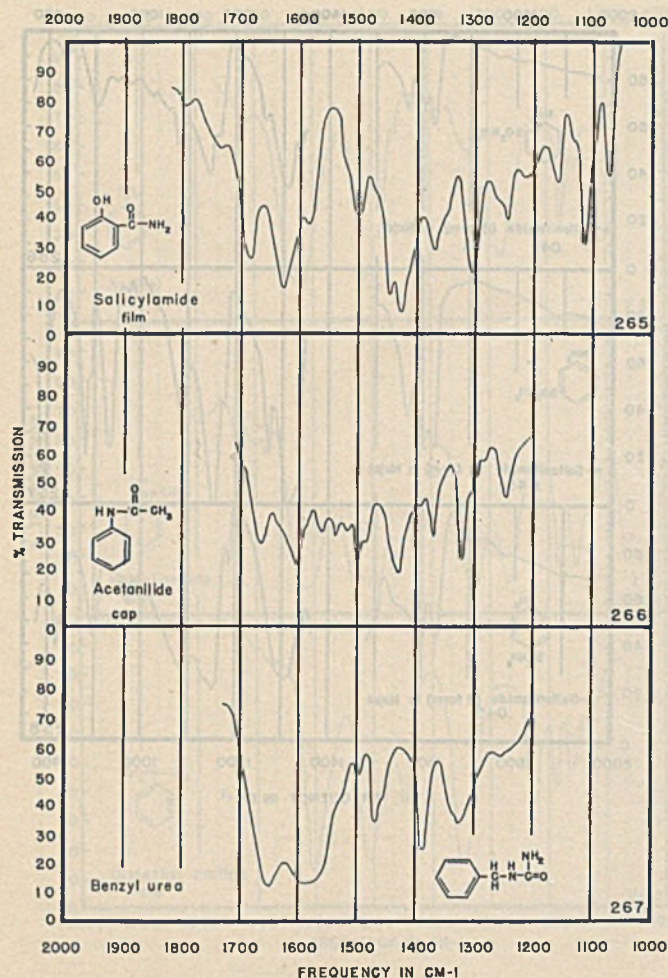




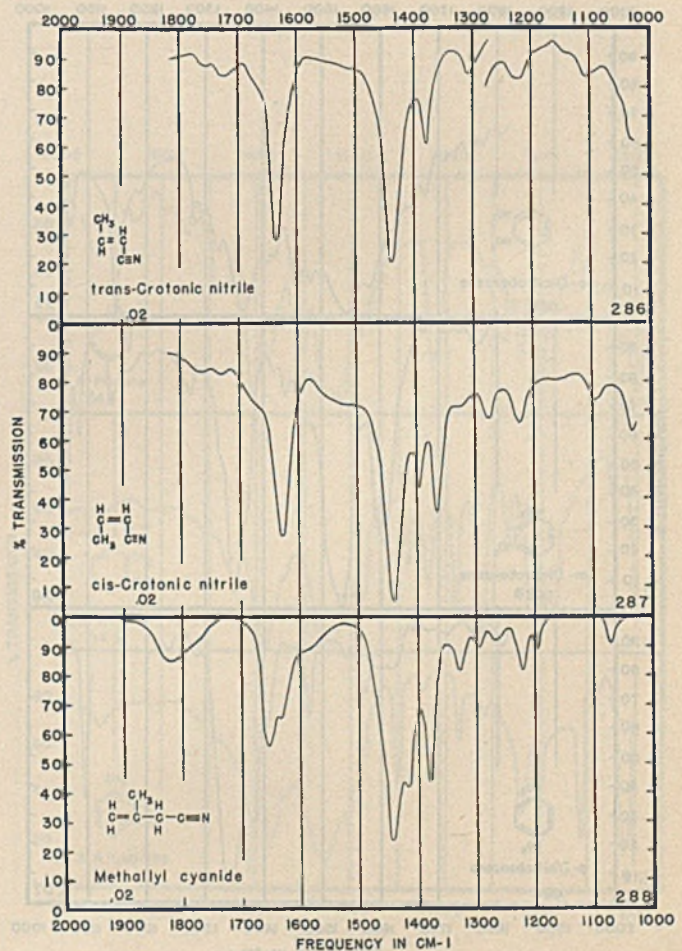
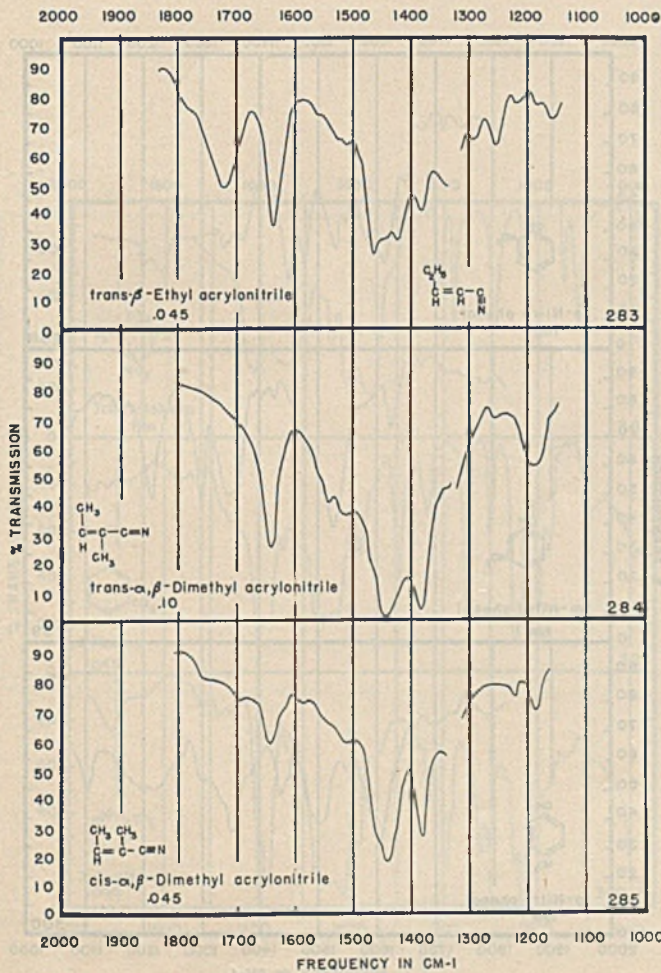
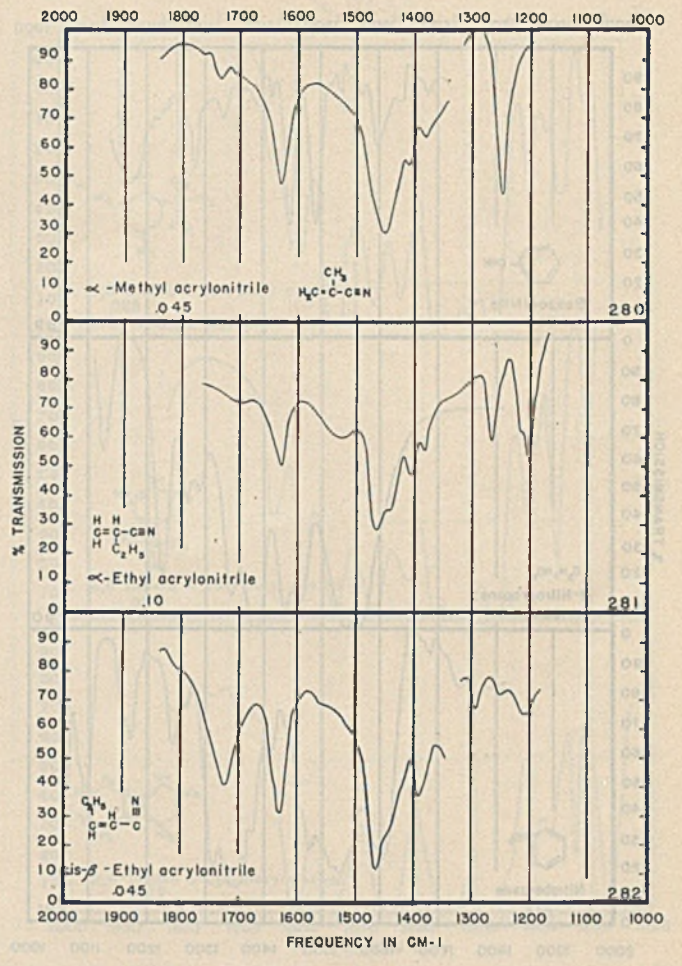
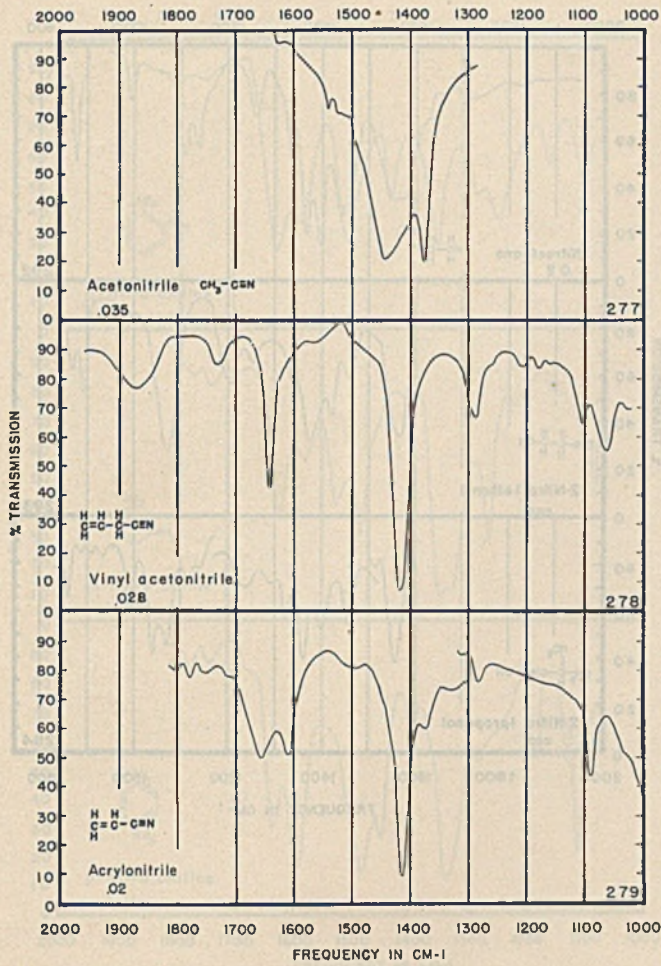




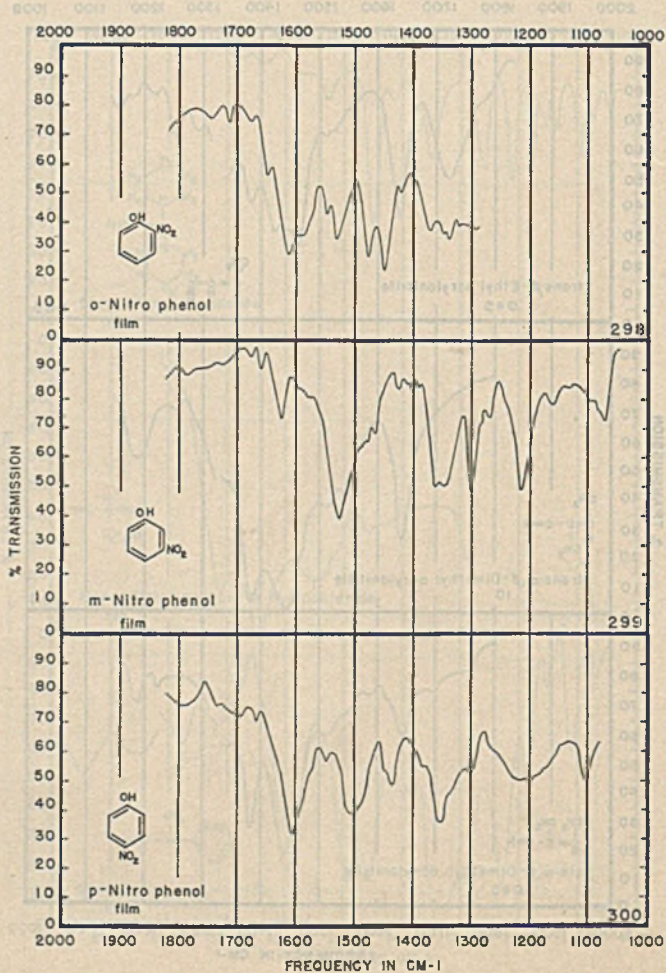
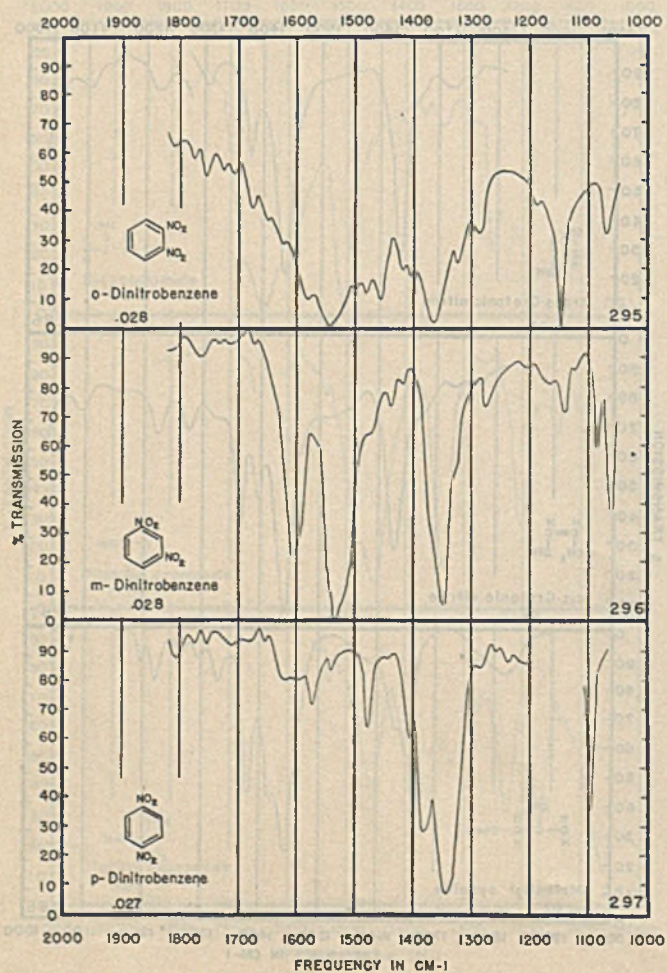
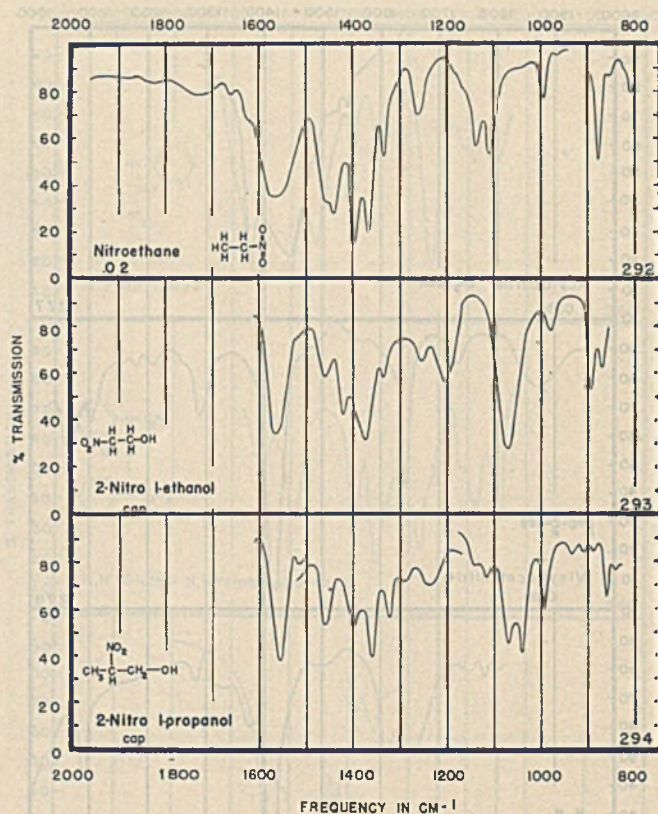
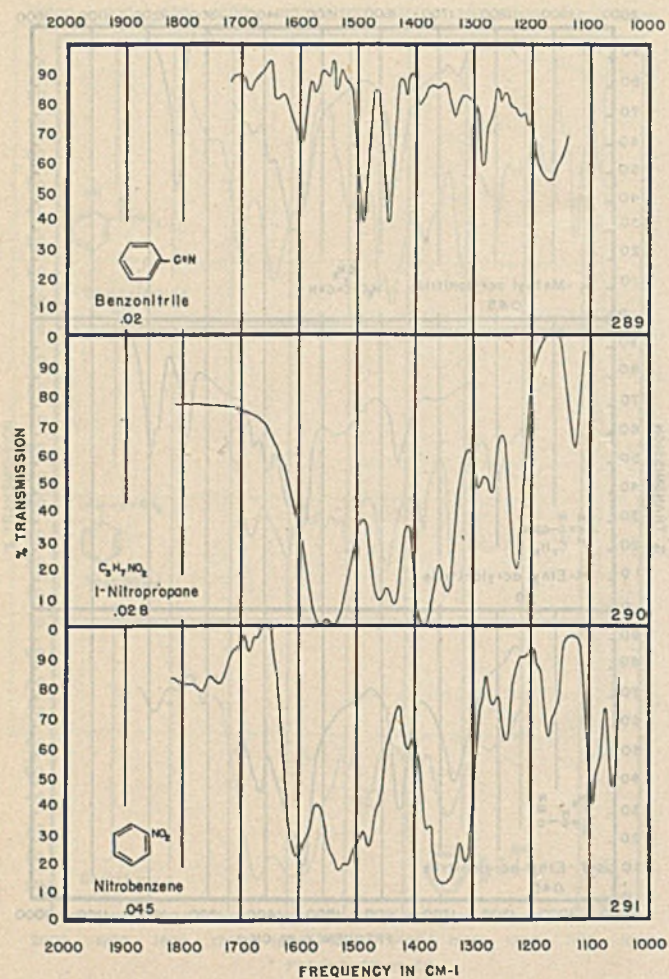




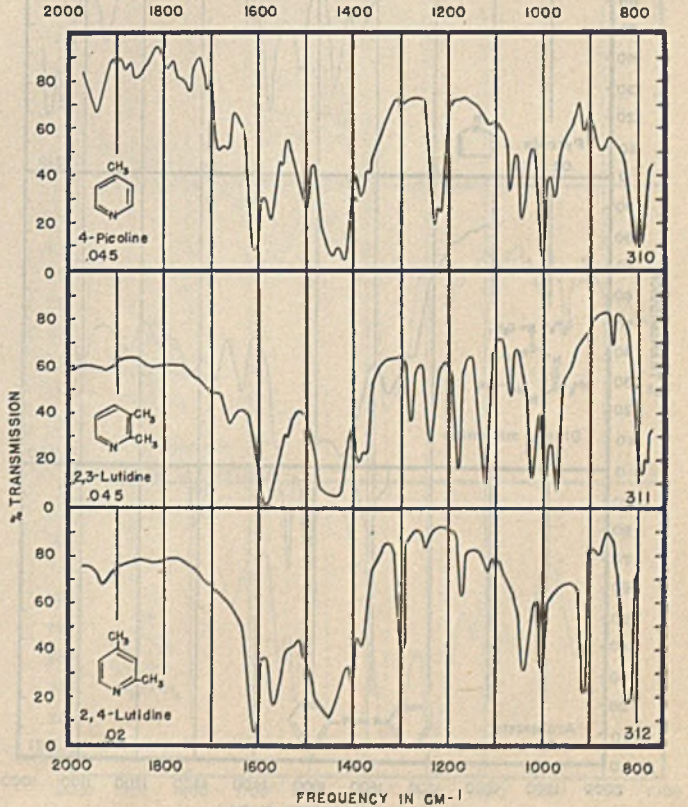
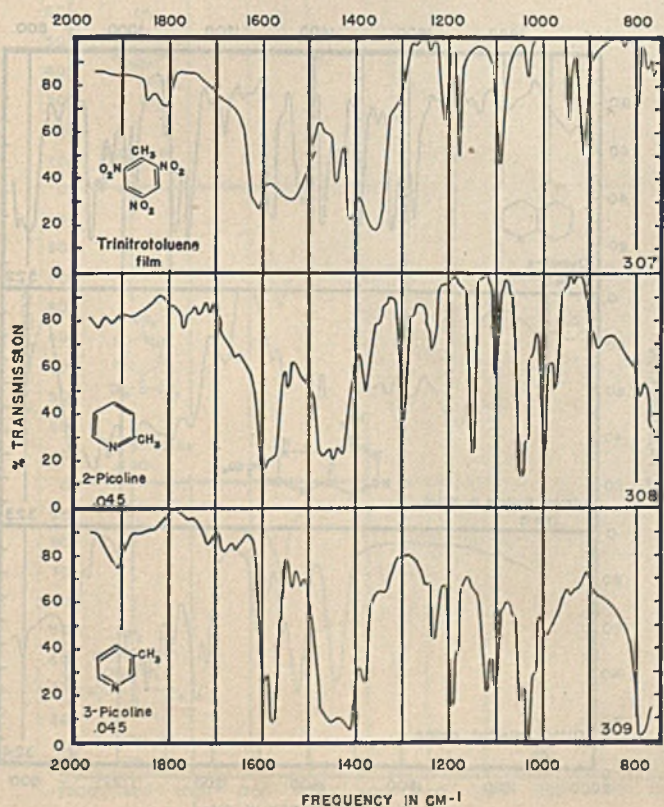
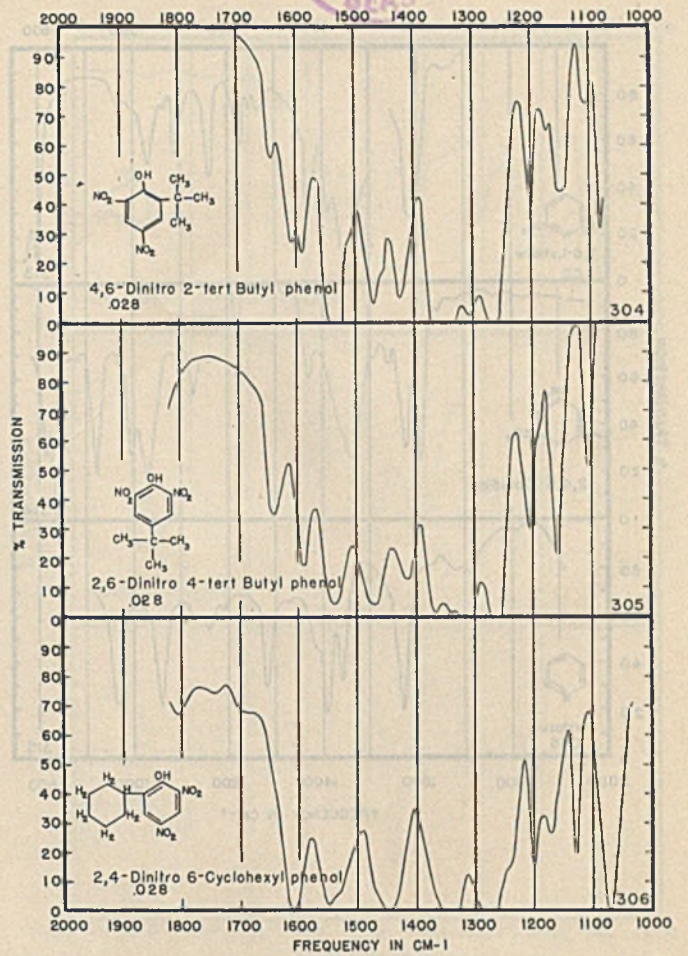
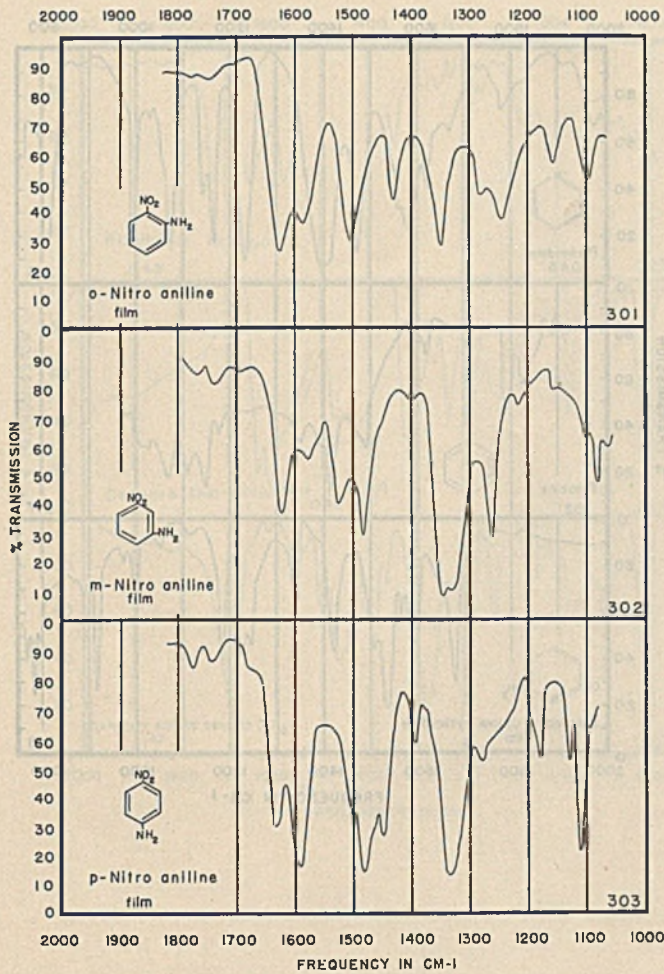




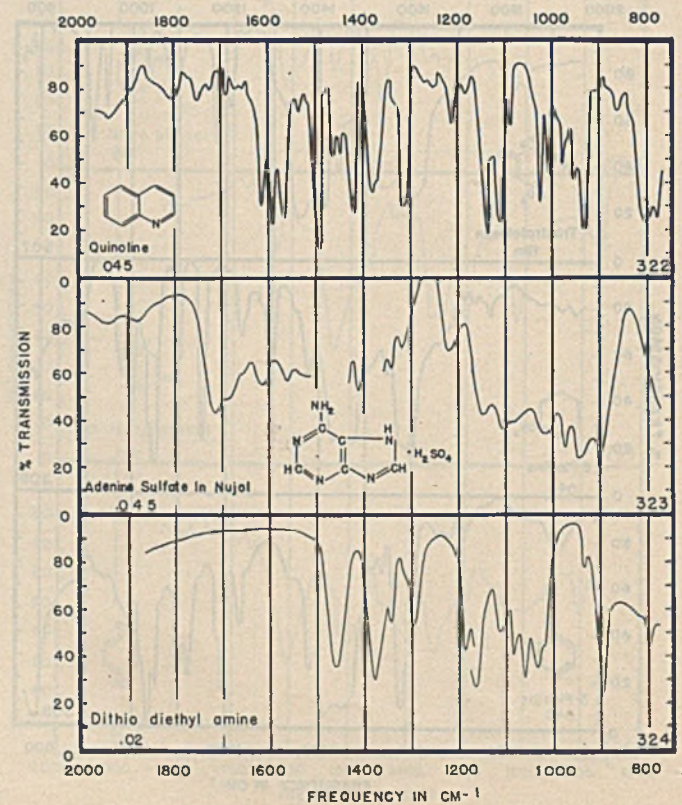
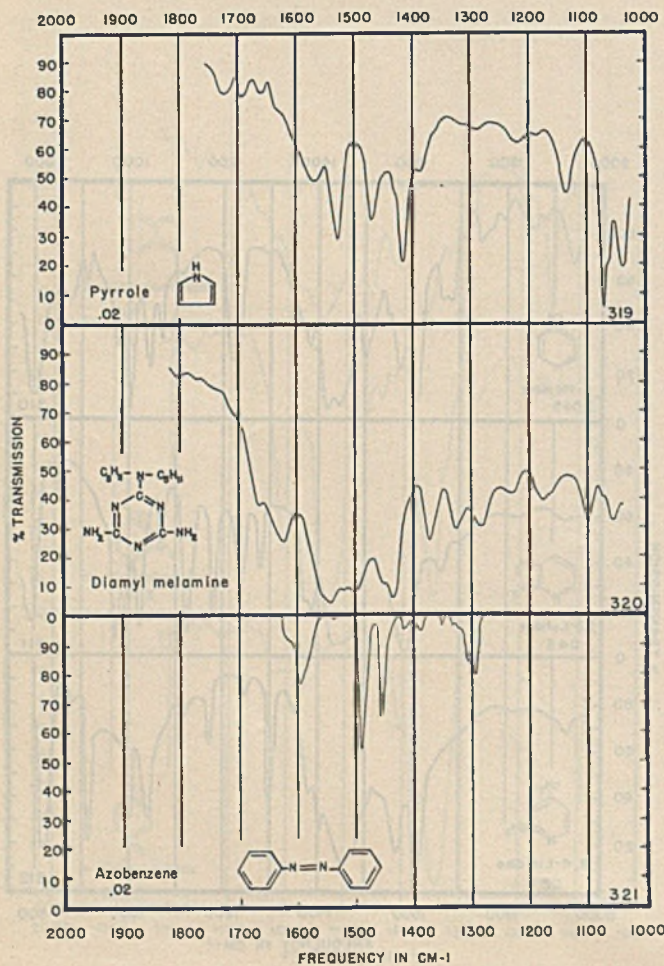
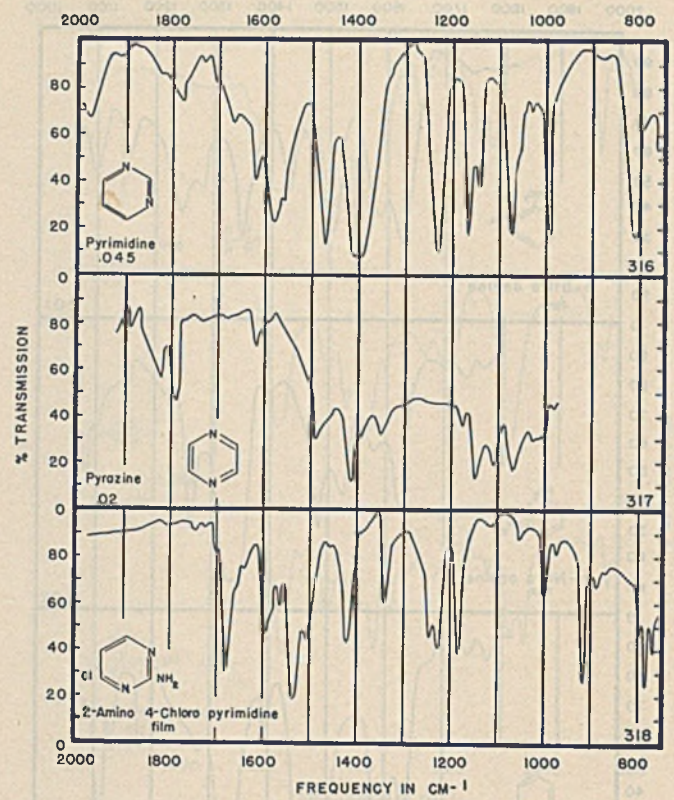
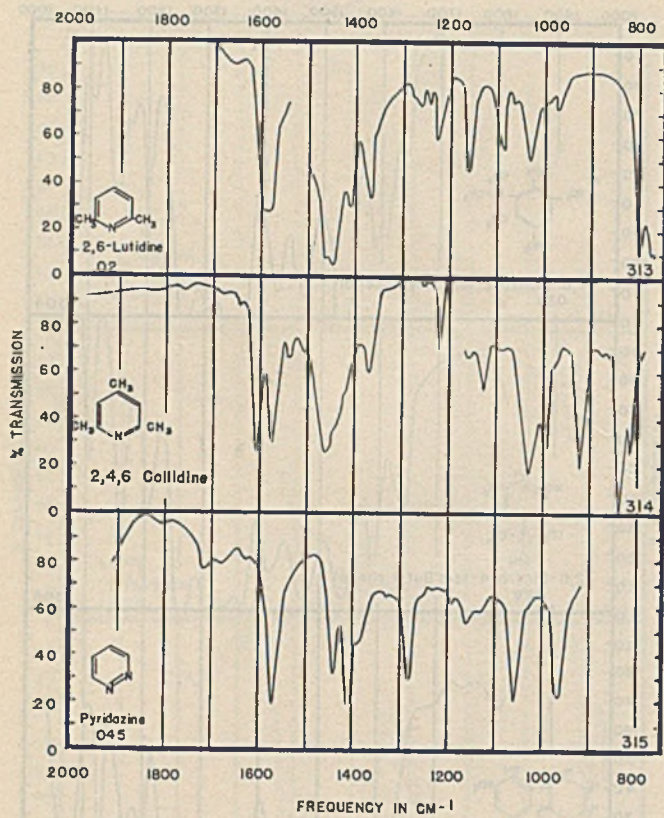




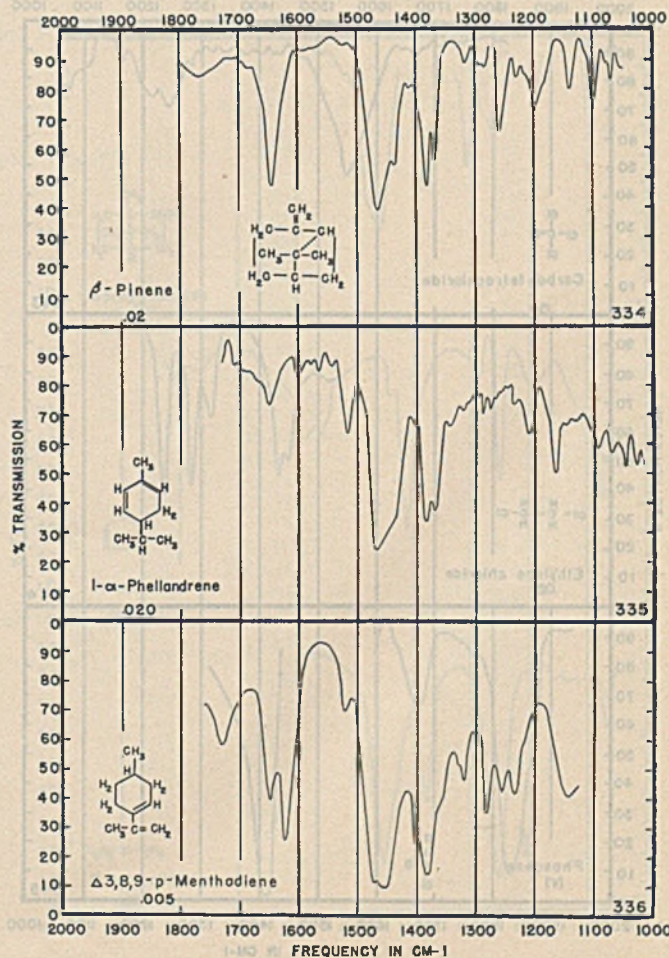
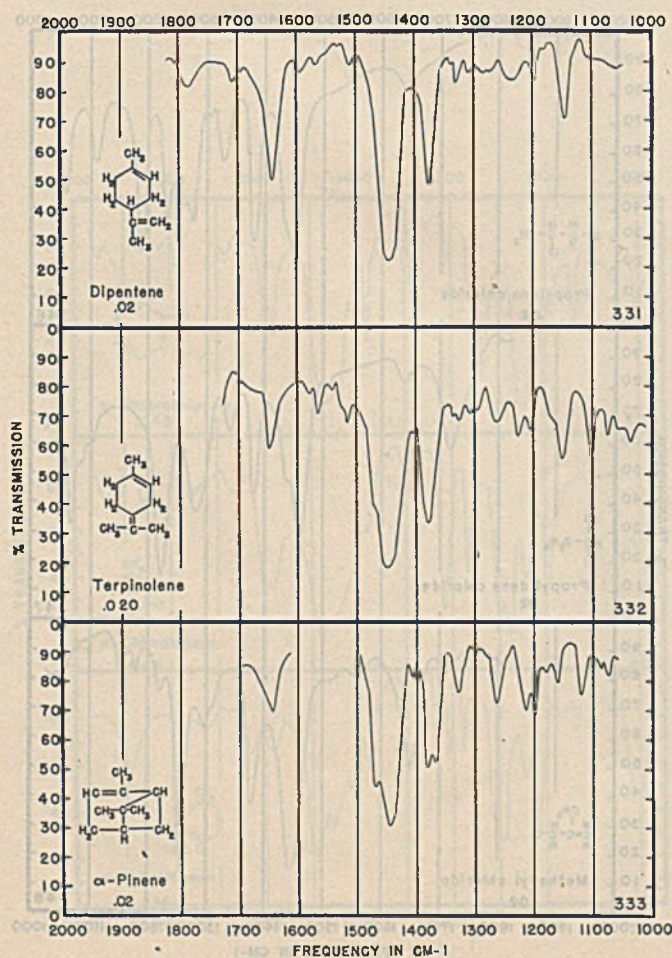
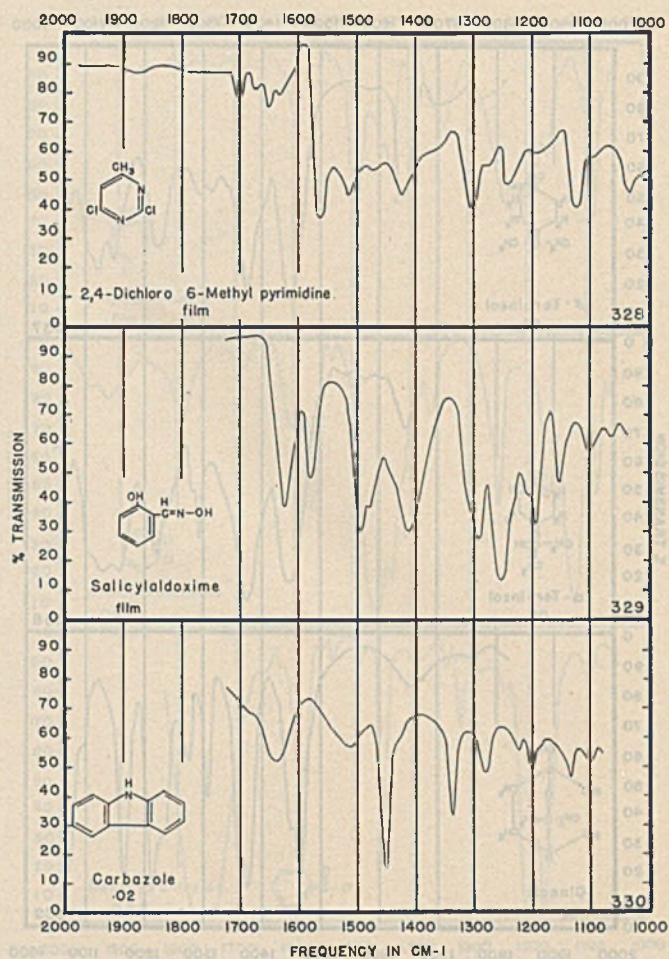
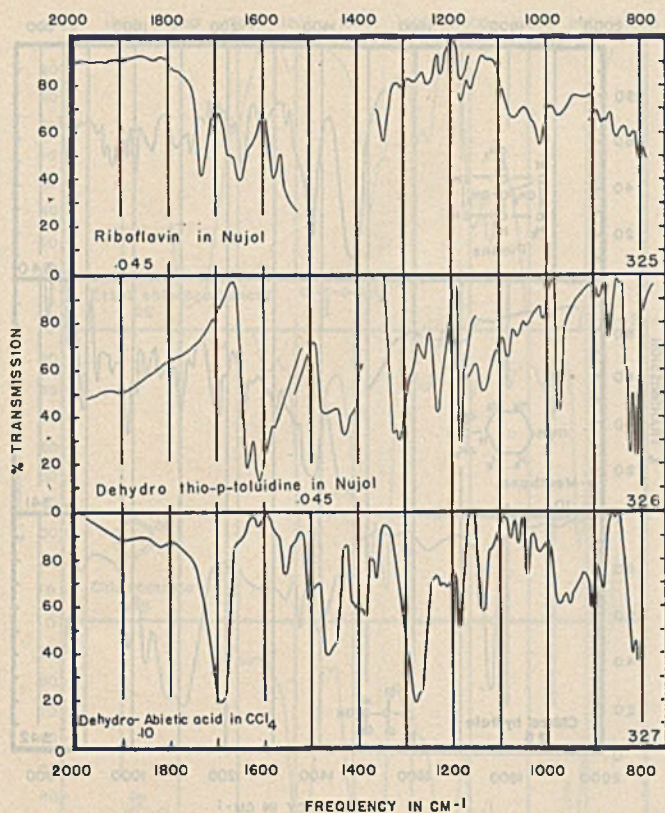




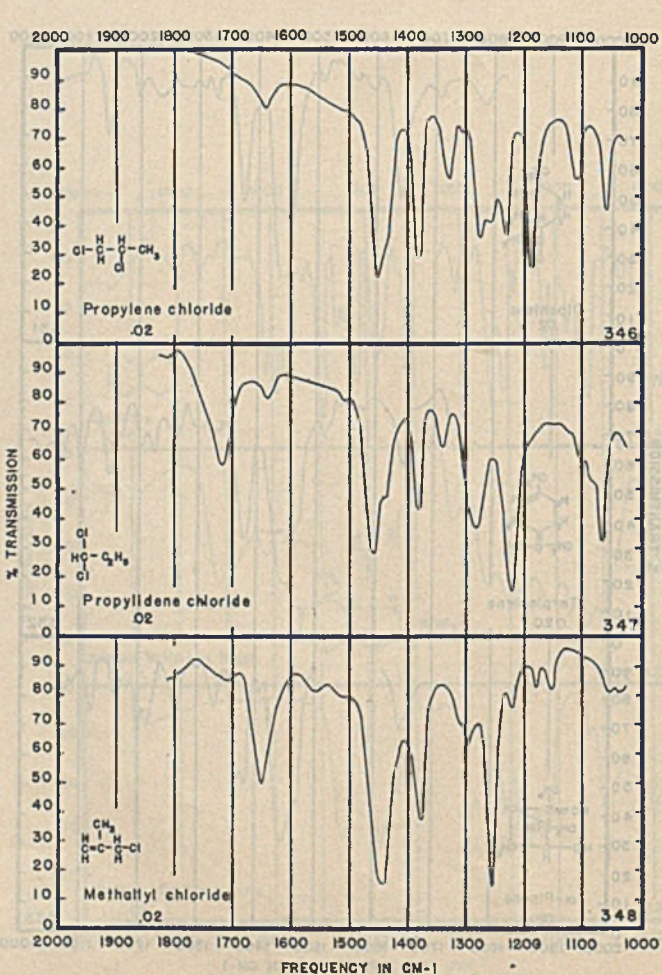
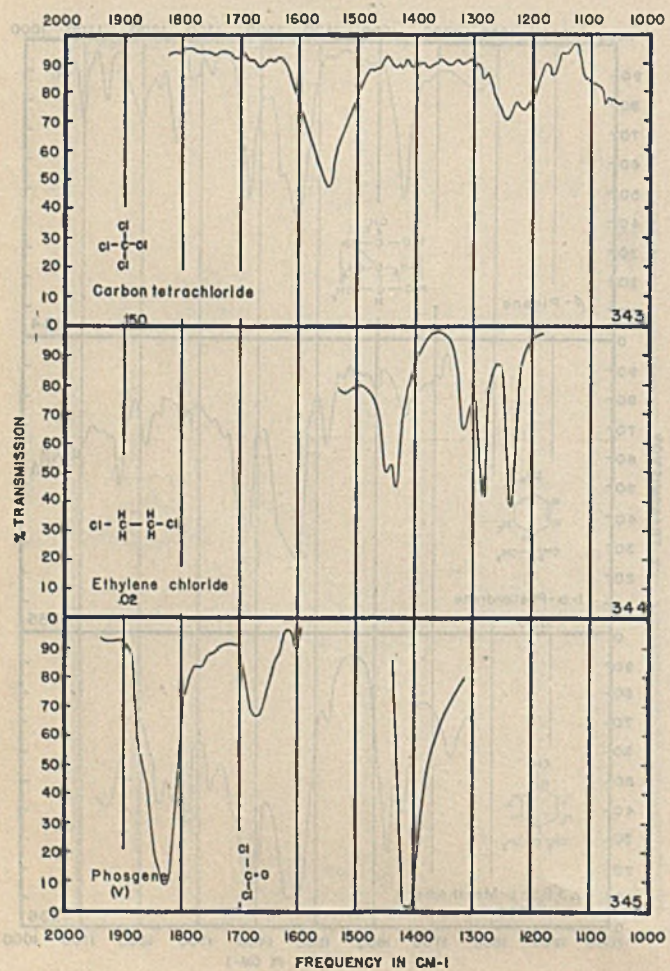
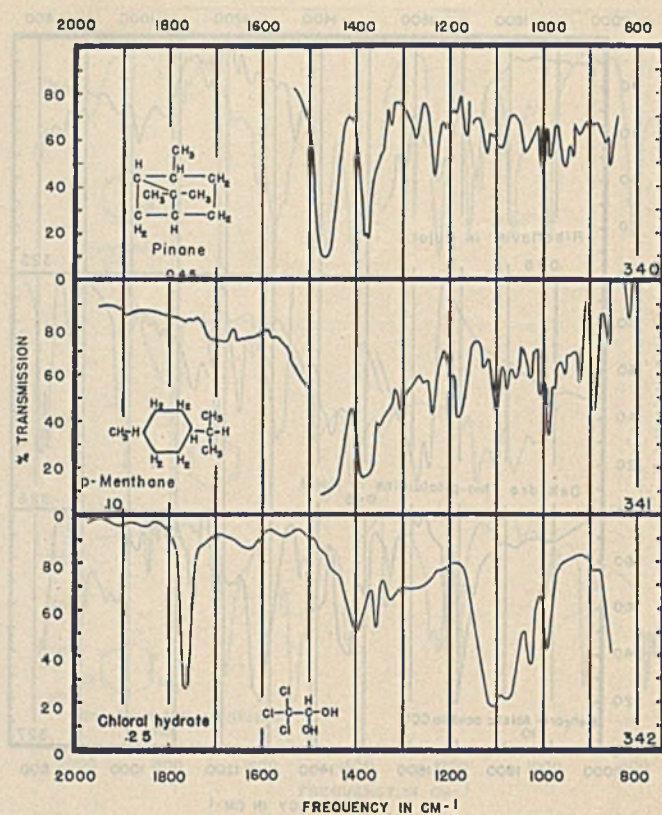
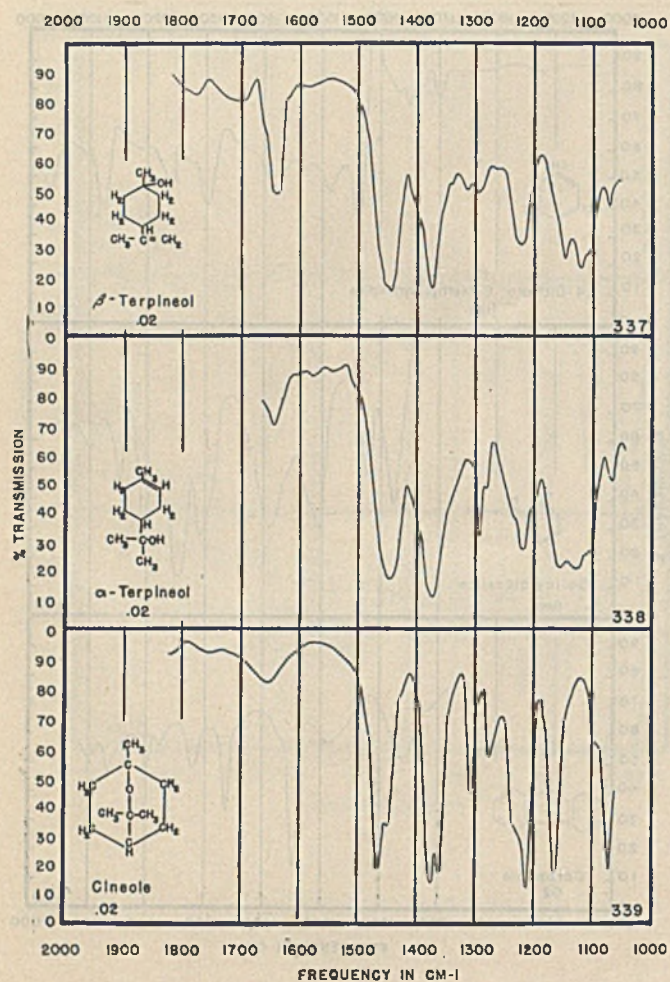




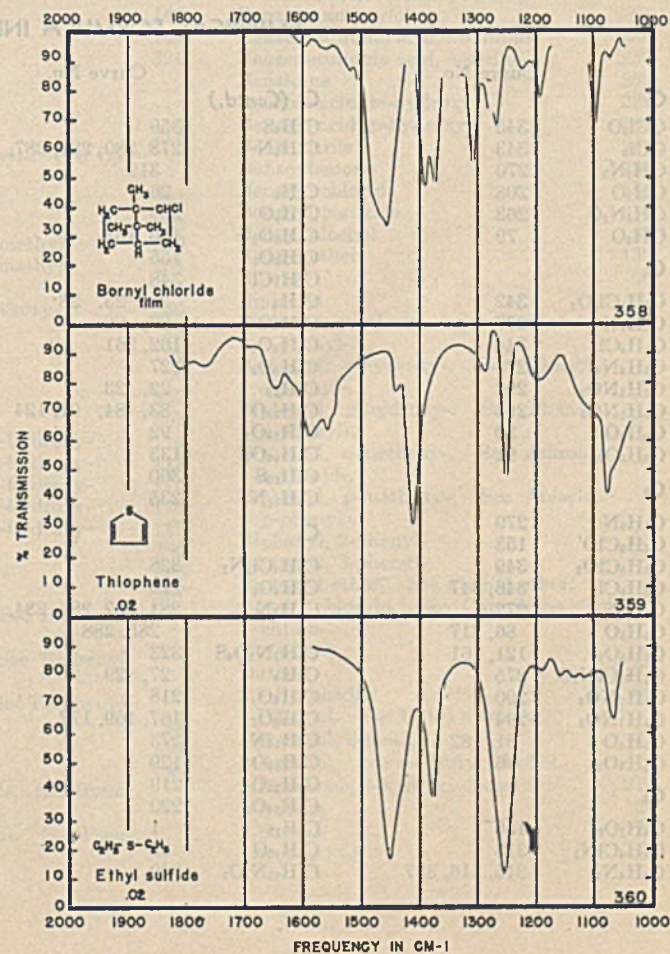
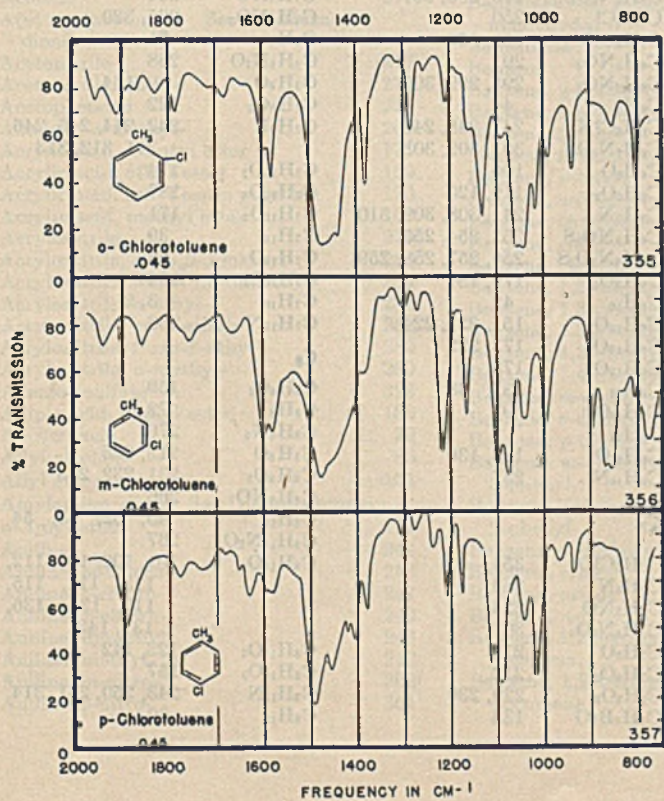
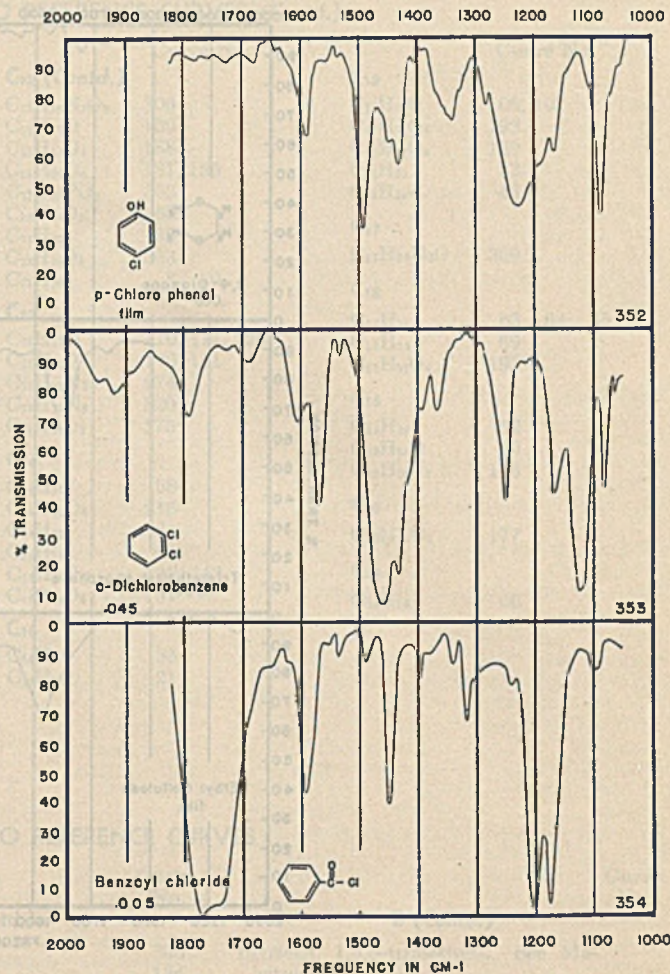
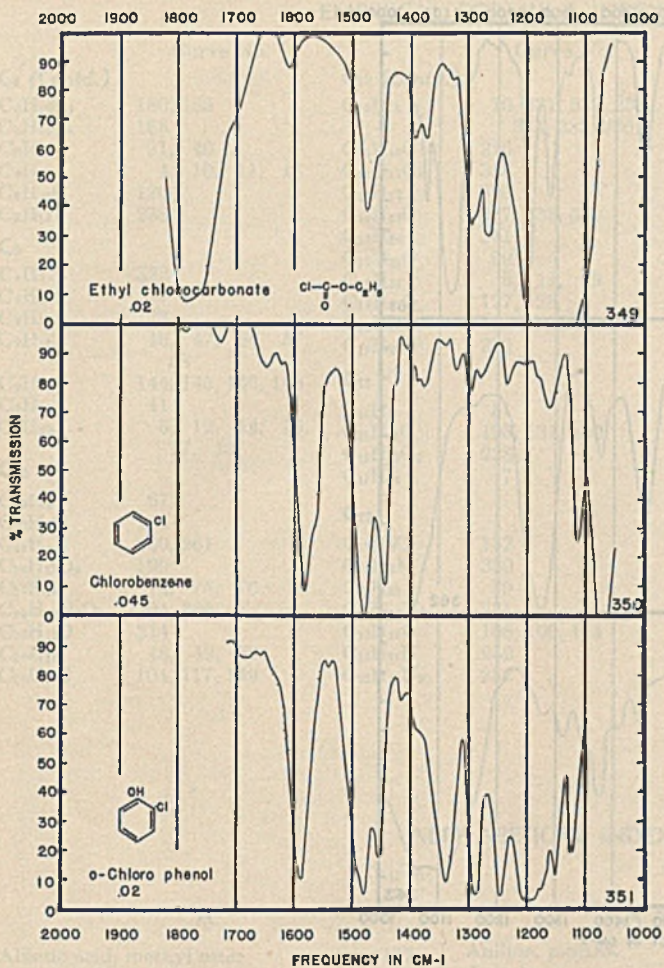




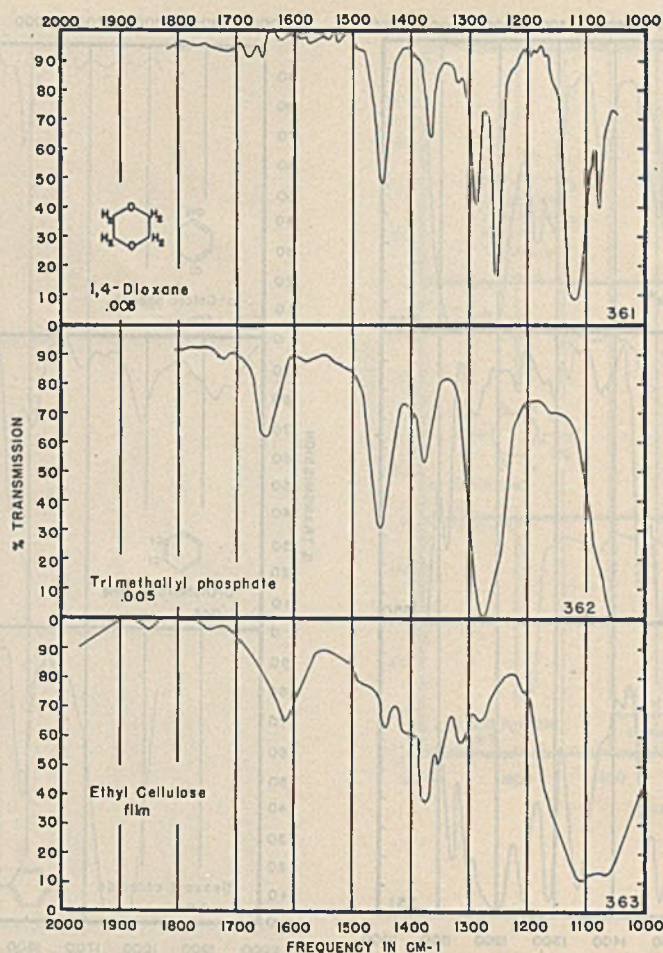












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# BOOK REVIEWS

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## A. S. T. M. Methods of Chemical Analysis of Metals

The 1943 volume of A. S. T. M. Methods of Chemical Analysis of Metals contains tentative recommended practices for reagents and apparatus, two sampling methods, and seventeen standard and tentative methods of chemical analysis, comprising four methods for analyzing ferrous metals, ten methods for nonferrous metals and alloys, and three methods of quantitative spectrochemical analysis of nonferrous metals. Published as information only are methods for the chemical analysis of special brasses and bronzes, and of white metal bearing alloys; also a procedure for aluminum in solder metal, and methods of sampling wrought metals and alloys for determination of chemical composition. The book also includes a list of standard samples of metals issued by the National Bureau of Standards and a good index.

Work leading to the issuance of the book has been under way for many months, particularly in Committee E-3 on Chemical Analysis of Metals headed by G. E. F. Lundell of the National Bureau of Standards. Committee E-2 on Spectrographic Analysis formulated the methods of spectrochemical analysis.

The book, 323 pages, is available at \$3 per copy from the American Society for Testing Materials, 260 South Broad St., Philadelphia 2, Penna. Individual test methods are available in separate pamphlet form.

## Spectrographic Analysis

Two tentative methods developed by Committee E-2 of the American Society for Testing Materials cover tentative spectrochemical methods for the determination of impurities in tin alloys (E51-43T) and in lead alloys (E49-43T).

The method involving lead alloys gives a procedure for the determination of 0.001 to 0.30 per cent of antimony, arsenic, barium, bismuth, copper, iron, magnesium, nickel, silver, strontium, tin, and zinc in lead, lead-calcium, and lead-antimony alloys, with an average precision of  $\pm 10$  per cent of the amount of the element sought. It is also applicable to other alloys of high lead content except those containing a large proportion of tin.

The method for tin alloys covers the determination of 0.001 to 1.0 per cent of antimony, and 0.001 to 0.3 per cent of aluminum, arsenic, bismuth, copper, iron, lead, nickel, and zinc in solders, bronzes, tin base die-cast alloys, and other alloys high in tin.

An additional procedure making use of photometric measurement has been included in the tentative method of quantitative spectrochemical analysis of zinc alloy die castings for minor constituents and impurities (E27-40T).

The revised methods of test for quantitative spectrochemical analysis of zinc for lead, iron, and cadmium (E26-35T) may be applied to any grade of zinc, providing the lead, iron, and cadmium contents are less than 0.1 per cent.

**Semimicro Qualitative Analysis.** *James T. Dobbins.* x + 423 pages. John Wiley & Sons, Inc., New York, N. Y., 1943. Price, \$3.00.

A textbook containing a set of experiments illustrating the fundamental principles; a complete systematic scheme of separation of the anions; and methods reducing time required for a complete analysis.

**Semimicro Qualitative Analysis.** *John F. Flagg and Willard R. Line.* viii + 140 pages. D. Van Nostrand Co., Inc., New York, N. Y., 1943. Price, \$1.50.

A course in applied chemical equilibrium. Includes chapters on basic theory and notes adjoining the laboratory procedures, in which the application of the theory is pointed out.

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## Delivery of Laboratory Equipment

Limitation Order L-144, governing the delivery of laboratory equipment, was amended October 9, 1943, in order to simplify and clarify the provisions of the order and reduce the number of applications to be filed by users of laboratory equipment.

Restrictions are entirely eliminated on the delivery of any item costing less than \$50, a quantity of the same item costing \$50 or more, a miscellaneous order aggregating \$200 or more, accessories and attachments when sold separately, or parts or materials to be used for repair and maintenance of existing instruments.

Form WPB-1414 is required for instruments included in List A costing \$50 or more.

List A. Analytical balances (sensitivity 0.2 mg. or more sensitive), calorimeters, centrifuges, hydrogen-ion meters (electrometric), metaloscopes, microscopes (except Brinell and tool makers), microtomes, potentiometers, Wheatstone bridges, and resistance boxes, refractometers, spectrographs, spectrosopes, spectrometers, and spectrophotometers, and vacuum pumps (1 micro or higher vacuum).

## Laboratories' Rating for Reagent Chemicals Raised

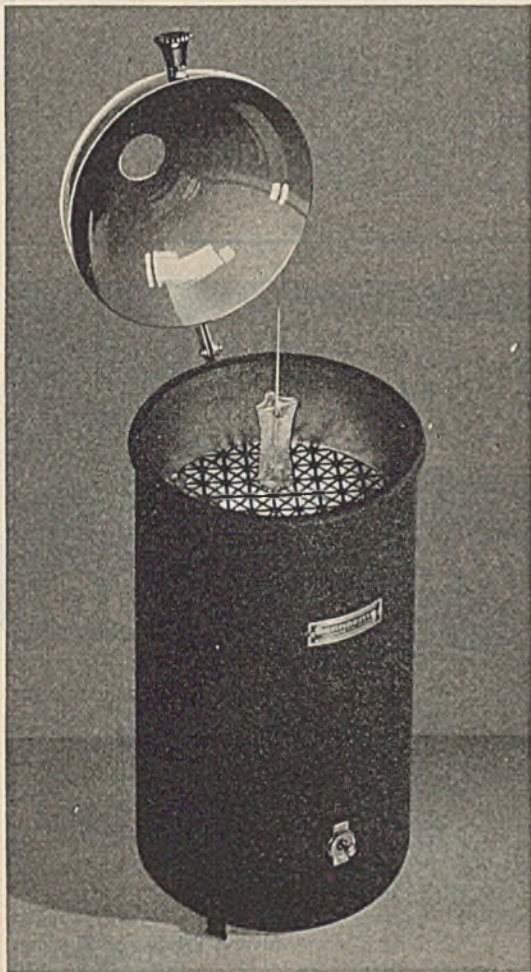
Preference ratings on deliveries of reagent chemicals for laboratory use were reassigned September 28 by the War Production Board through issuance of Preference Rating Order P-135 as amended. Preference rating AA-1 is assigned to deliveries of any reagent chemical to any laboratory to which a serial number has been assigned under Preference Rating Order P-43, governing laboratory equipment, and to any laboratory owned and operated by the Army or Navy. Preference Rating AA-2 is assigned to deliveries of any reagent chemical to any laboratory lacking a serial number under Order P-43 or to a distributor or producer of reagent chemicals. Order P-135 formerly assigned a blanket rating of AA-2X to reagent chemicals for laboratories.

The amended order defines "laboratory" as meaning "any person engaged in the business of carrying on scientific or technological investigation, testing, development or experimentation, to the extent that he is so engaged. The term includes research laboratories, production control laboratories, clinical laboratories, and instructional laboratories. It does not include any person to the extent that he is engaged in the manufacture of products for commercial sale, even though the place in which the products are manufactured may be called a laboratory."

Supplementary Order P-135-a also was amended to exempt from certification the delivery to or acceptance of delivery by a laboratory of not more than 10 per cent of the quantity of reagent chemicals in any period which are exempt from specific authorization under the small order clause.



# Sargent RADIANT HEATING OVEN



Although principally designed to provide an inexpensive unit for quick and convenient drying of electrodes in connection with the determination of lead as lead dioxide, this infra red drying oven has a wide variety of other applications. For example, it is excellently suited for such operations as evaporating, drying precipitates, paraffin melting, drying solids, etc. Drying efficiency is well illustrated by the fact that lead dioxide is thoroughly dried in one to two minutes.

The oven consists of a cylindrical case containing a General Electric R-40, 250 watt drying lamp with self reflector, a hinged, chromium plated, hemispherical dome, a chromium plated perforated shelf and an on-off switch mounted on the case. The reflector contained within the drying lamp reflects the radiant heat upward thus directing all energy to the working area of the oven. Further concentration of heat is accomplished by the chromium plated dome which acts as a highly effective heat reflector so reducing to a minimum heat loss by radiation. By means of this design a maximum temperature of approximately 500° F is developed within ten minutes. The fast upward flow of air provided by the open bottom and vent hole in dome also contributes greatly to the high drying rate of this oven.

The filament of the drying lamp develops a large component of radiant energy in the near infra red spectral region at wavelengths having high penetration. The average service life of these lamps is 5000 hours.

Overall dimensions: height, 13½ inches; diameter, 6½ inches. Inside dimensions: height from top of perforated shelf to top of dome, 5¼ inches; diameter, 5⅞ inches. Electrodes having a total height exceeding 5¼ inches can be placed in the oven by permitting the electrode stems to project out of the vent hole in the dome.

**S-64050** Sargent Infra Red Drying Oven—Complete with General Electric R-40, 250 watt drying lamp, perforated shelf and cord and plug. For operation from standard 115 volt A.C. or D.C. circuits.....**\$18.00**

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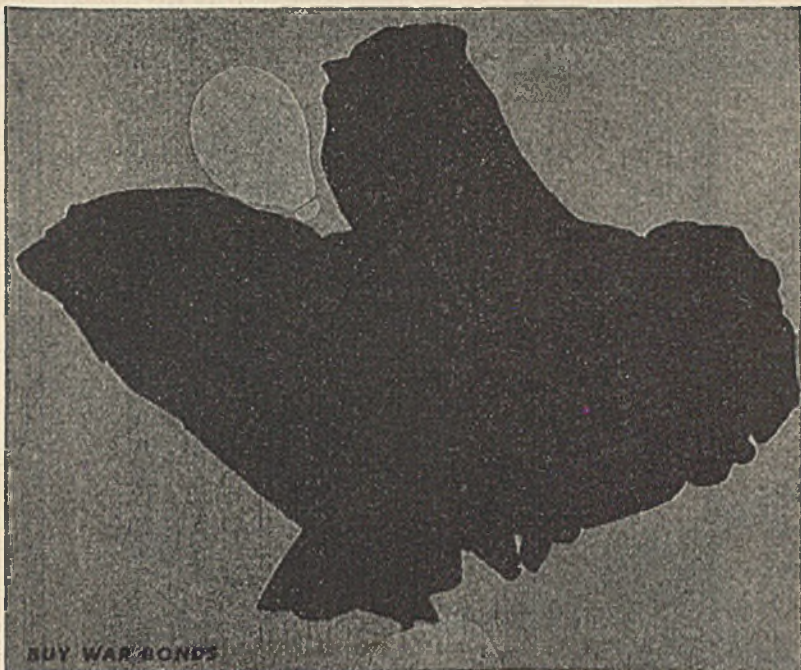
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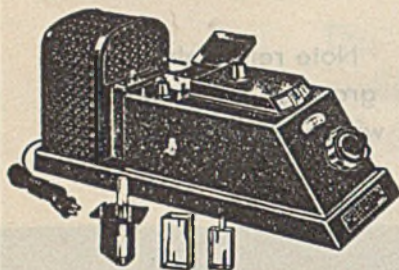
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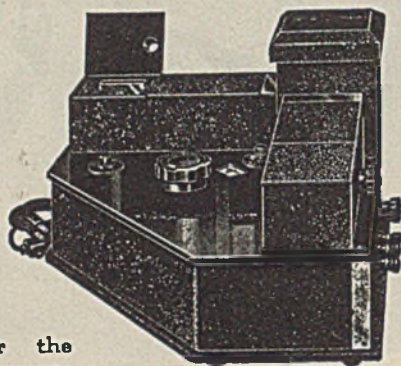


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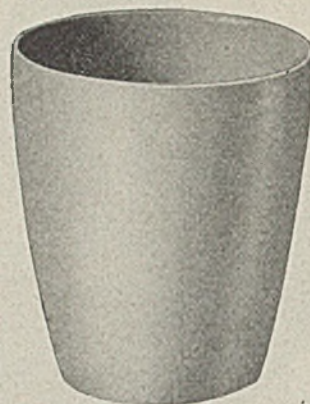
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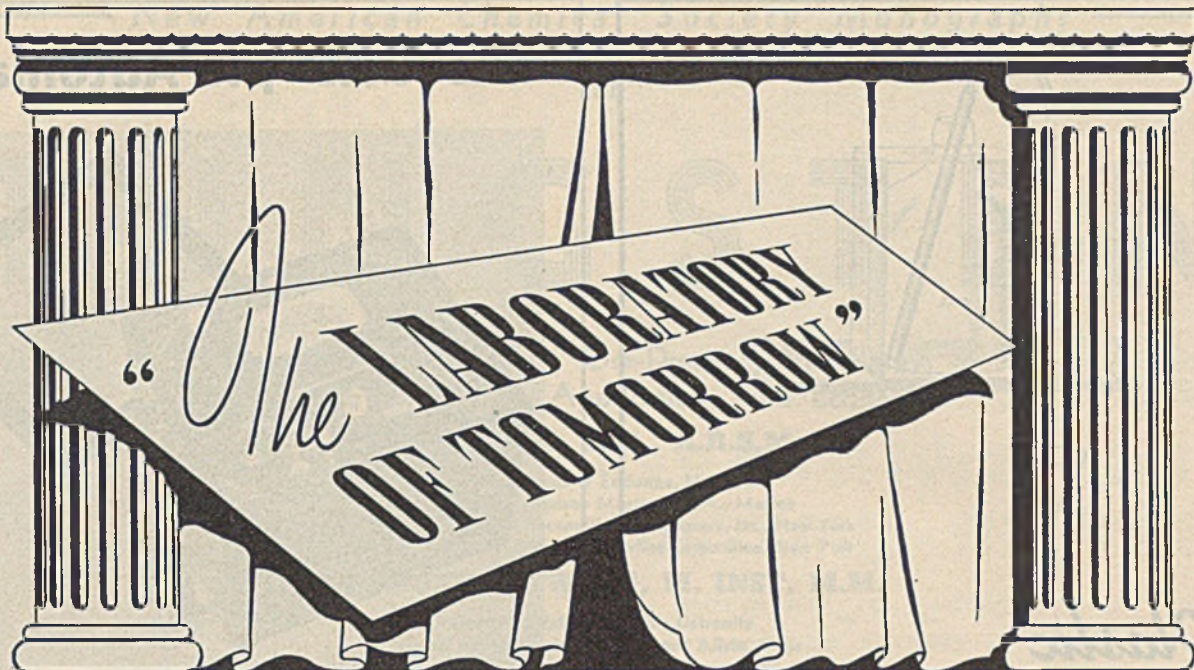
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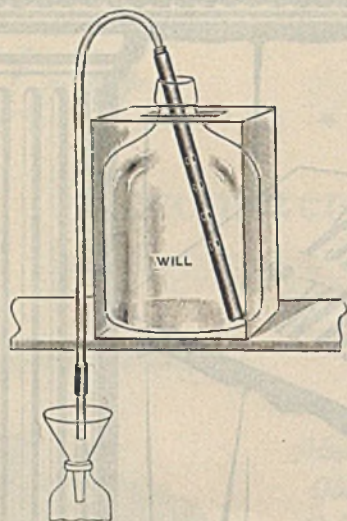
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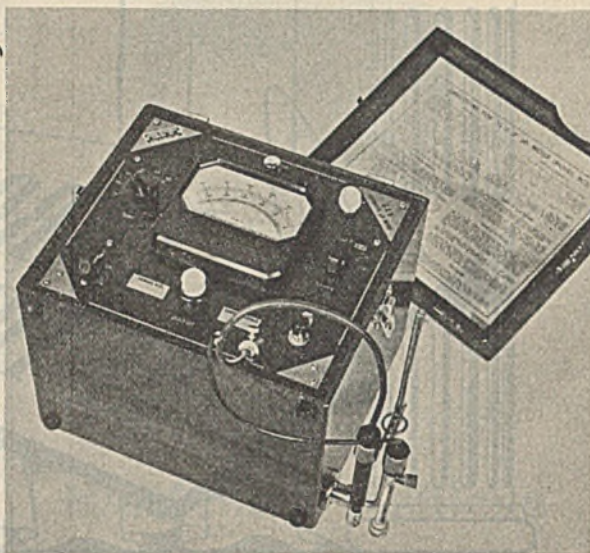
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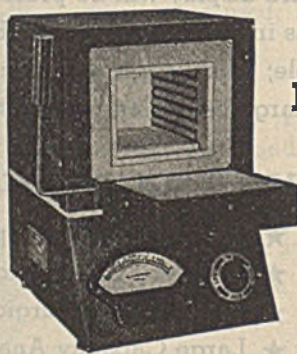
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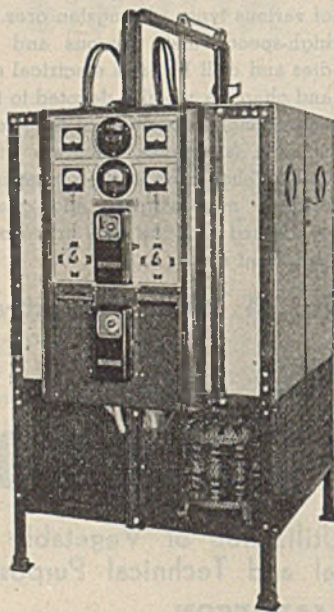


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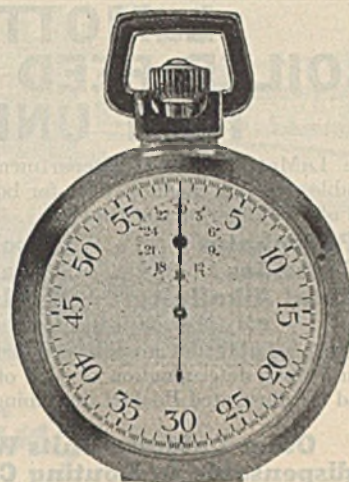
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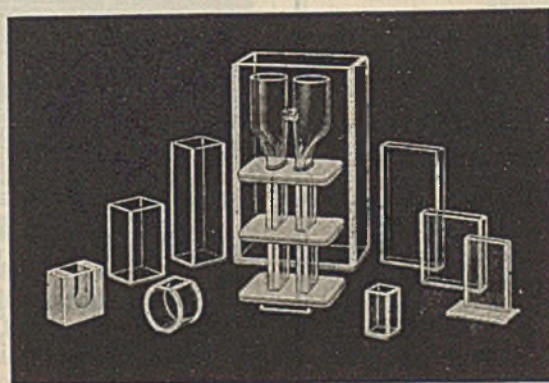
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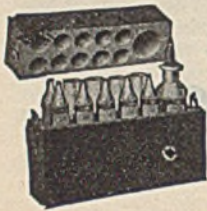
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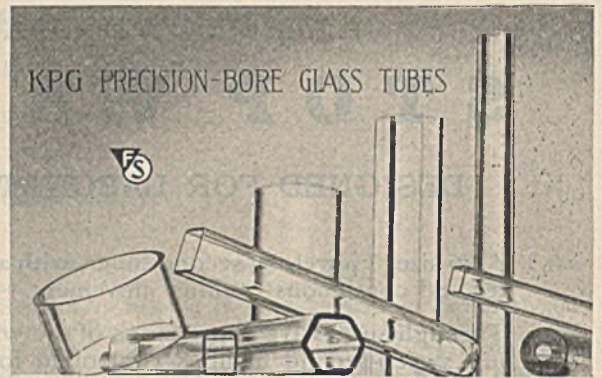
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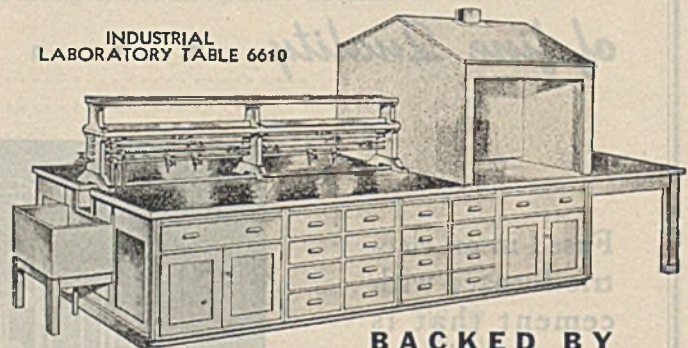
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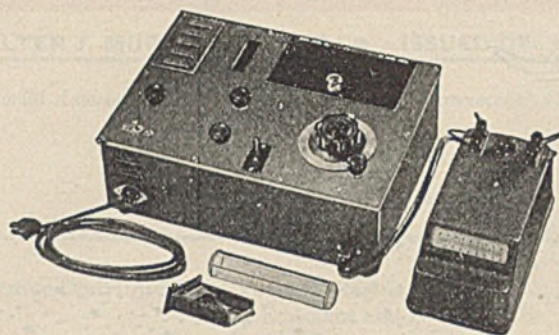
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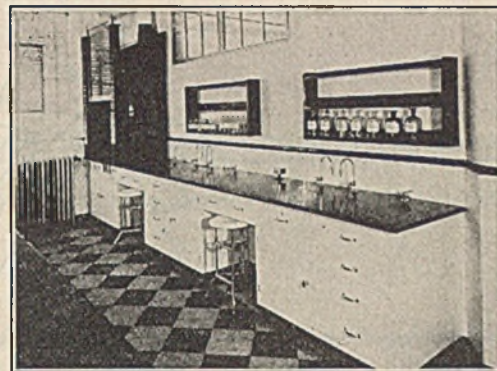
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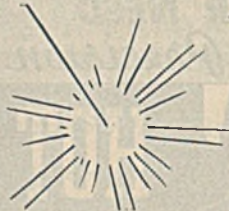
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