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ANALYTICAL CHEMISTRY

OCTOBER 1947

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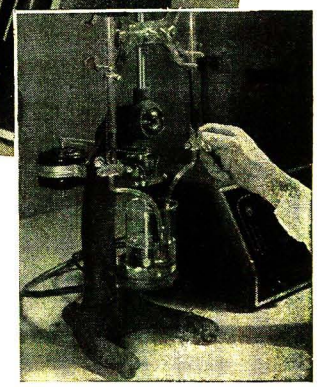

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14. Dissolved Oxygen
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INDUSTRIAL AND ENGINEERING CHEMISTRY *covering the field of...*

ANALYTICAL CHEMISTRY

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Issued October 22, 1947

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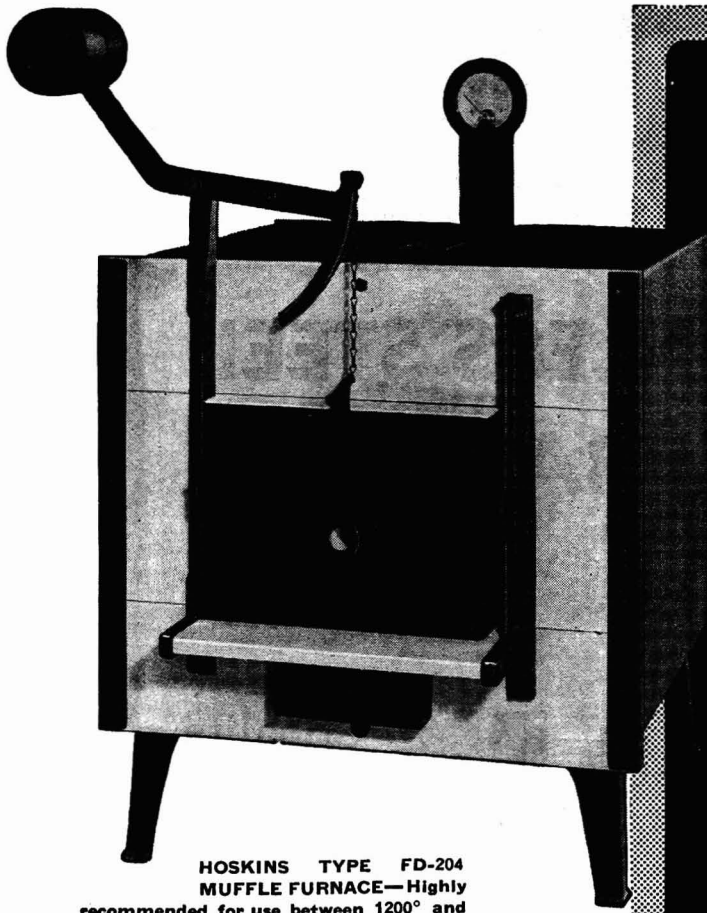

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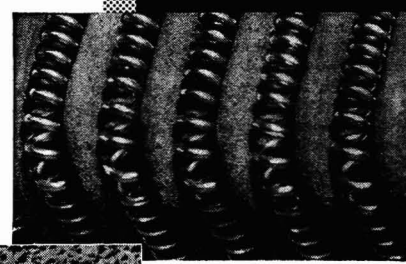
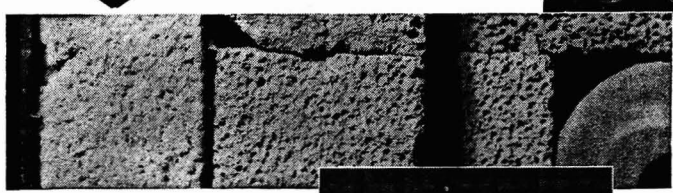
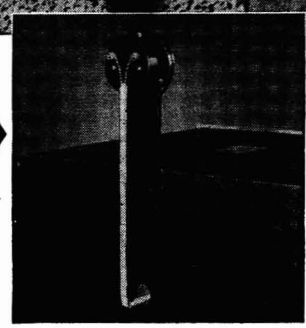


Heavy 13 ga. (.072") CHROMEL Heating Element Wire assures long-life, trouble-free service in Hoskins 110-V Unit.

4½ inches of protective insulation keeps heat in, power costs down. Makes for safer, more comfortable working conditions, too.



Type PBM Pyrometer . . . small inexpensive, suitable for approximate temperature measurements. Installed on Hoskins Type FD (and FH) Muffle Furnaces at slight additional cost.



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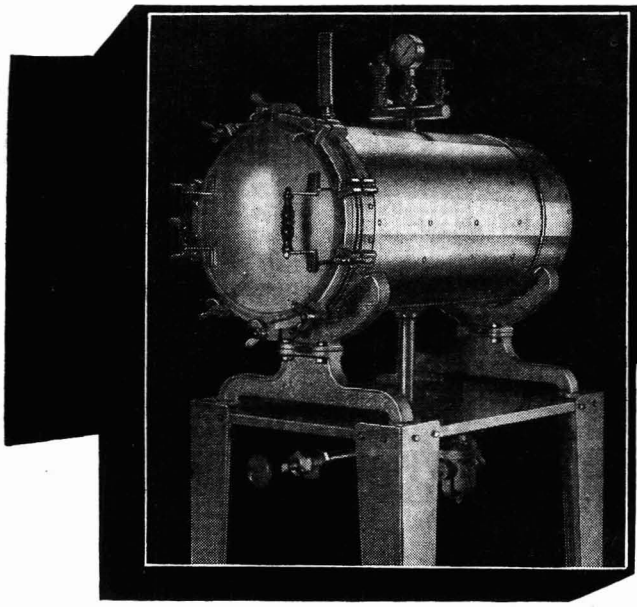

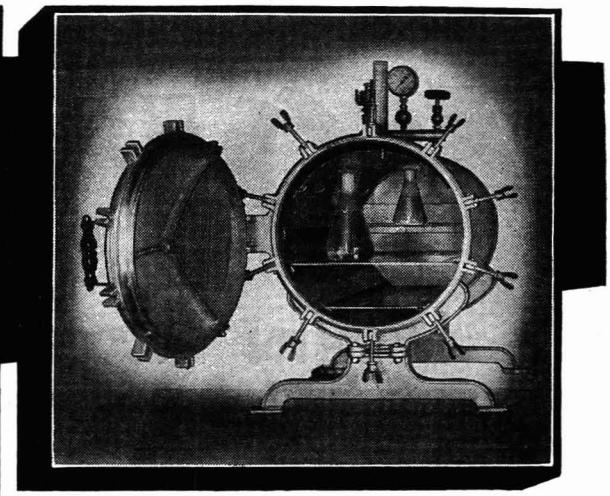

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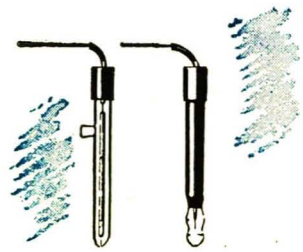
...THE INDUSTRY'S MOST COMPLETE LINE OF MODERN pH ELECTRODES IS AVAILABLE FOR USE WITH BECKMAN pH INSTRUMENTS

REMEMBER THIS important fact about modern pH equipment —glass electrode pH instruments are the most advanced and efficient type of pH equipment obtainable. *But no glass electrode instrument is better than the versatility, accuracy and dependability of the electrode assemblies available for use with it.*

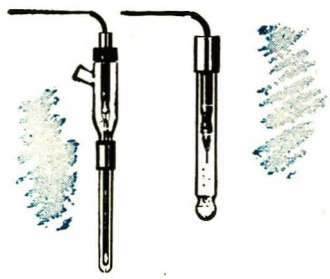
And that is another of the many vital advantages that are yours when you select BECKMAN pH Instruments—for Beckman, *pioneer of modern glass electrode pH equipment*, not only provides the finest and most advanced pH instruments, but also the industry's most complete line of electrodes for use with these instruments.

Illustrated below are only a few of the more than 90 different types of interchangeable Beckman pH Electrodes that assure maximum accuracy, convenience and wide-range adaptability to users of Beckman pH Meters—the pH instruments that are the recognized standard of the industry.

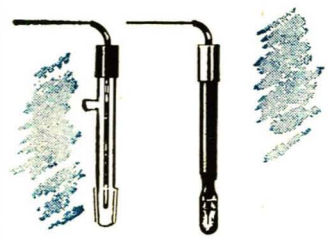
No matter what *your* pH problem, there is a Beckman pH Instrument and a Beckman Glass Electrode assembly to meet your exact requirements for both industrial and research applications. So why restrict your operations with anything less than the *complete* pH facilities provided by Beckman?



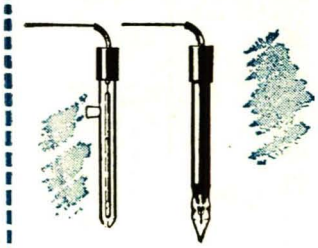
HIGH pH GLASS ELECTRODES. Pioneered by Beckman, these glass electrodes permit accurate measurement of high pH solutions with negligible error *even in the presence of sodium ions.* Ideal for use on detergents, soaps and many other applications where regular glass electrodes are useless.



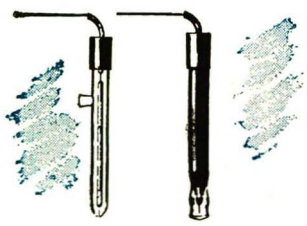
HIGH TEMPERATURE GLASS ELECTRODES. Another development pioneered by Beckman, these electrodes can be used directly in high temperature process solutions to 100° C. (212° F.) without damage. Eliminates special sampling devices and greatly simplifies control of hot processing solutions.



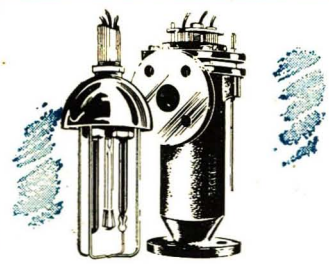
RUGGED DUTY GLASS ELECTRODES. Still another Beckman development, these electrodes are specially designed for direct immersion in tanks and flow lines where abrasion is severe (paper pulps, ore slurries, etc.). Not only abrasion resistant, but also withstand more than 100 lbs. pressure on immersion end.



PENETRATION TYPE GLASS ELECTRODES. The pointed application end greatly simplifies direct pH measurements of cheeses, fish, fruits and similar semi-solids where penetration of outer surface is desired for internal pH measurements.

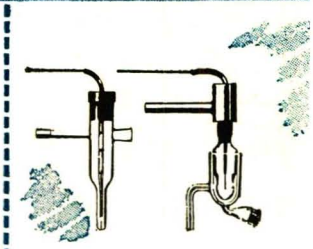


SURFACE TYPE GLASS ELECTRODES. On these Beckman electrodes the application end is nearly flat in order to simplify pH measurements on skin, hides and moist surfaces of materials where pH measurements of outer surfaces are desired.



IMMERSION AND FLOW TYPE ASSEMBLIES. Can be placed directly in flow lines, vats, tanks, etc., to permit direct and continuous pH measurements on process solutions. Far simpler, quicker and more accurate than sampling devices. Can be used with various types of Beckman electrodes.

MICRO GLASS ELECTRODES. One of dozens of specialized Beckman pH electrodes for science and laboratory investigations. This type permits quick, convenient and accurate pH measurements on samples of less than one drop.



HYPODERMIC GLASS ELECTRODES. One of many specialized Beckman pH electrodes for medical use. In this type, 0.5 ml blood samples can be injected from hypodermic needle through membrane with minimum exposure to air. Other types are also available.

THE ABOVE ARE ONLY TYPICAL of the wide selection of glass electrodes available for use with Beckman pH Instruments . . . one more reason why Beckman pH Instruments are recognized throughout the world for their dependability, accuracy and versatility. *Beckman Instruments, National Technical Laboratories, South Pasadena 15, Calif.*

BECKMAN

INSTRUMENTS CONTROL MODERN INDUSTRIES

the analyst's column

A LARGE part of this issue deals with Raman spectroscopy, a branch of spectroscopy that is well known but has not been developed to the point where it is as useful to the analyst as infrared. Contributing to this tardy development is the lack of commercial instruments and spectra of compounds of known composition. About four well-known instrument companies are working on the design of a Raman instrument, so that in the not distant future this lack of purchasable equipment should be solved. None of the companies is far enough along to permit disclosing of details. The paucity of published spectra is being remedied with time, and your editors are glad to make available the excellent work of M. R. Fenske and his co-workers.

THE symposium on purity and identity held at the New York meeting of the ACS was very well attended and brought together the views and philosophy of organic and physical chemists concerning the ultimate criteria of purity, which was designated by Eyring for crystalline substances where $\tilde{S} = 0$ at 0 Å., and the practical definition which can be considered when existing methods are incapable of separating the system in two or more fractions with different properties. This criterion of purity, of course, may change with the development of new techniques.

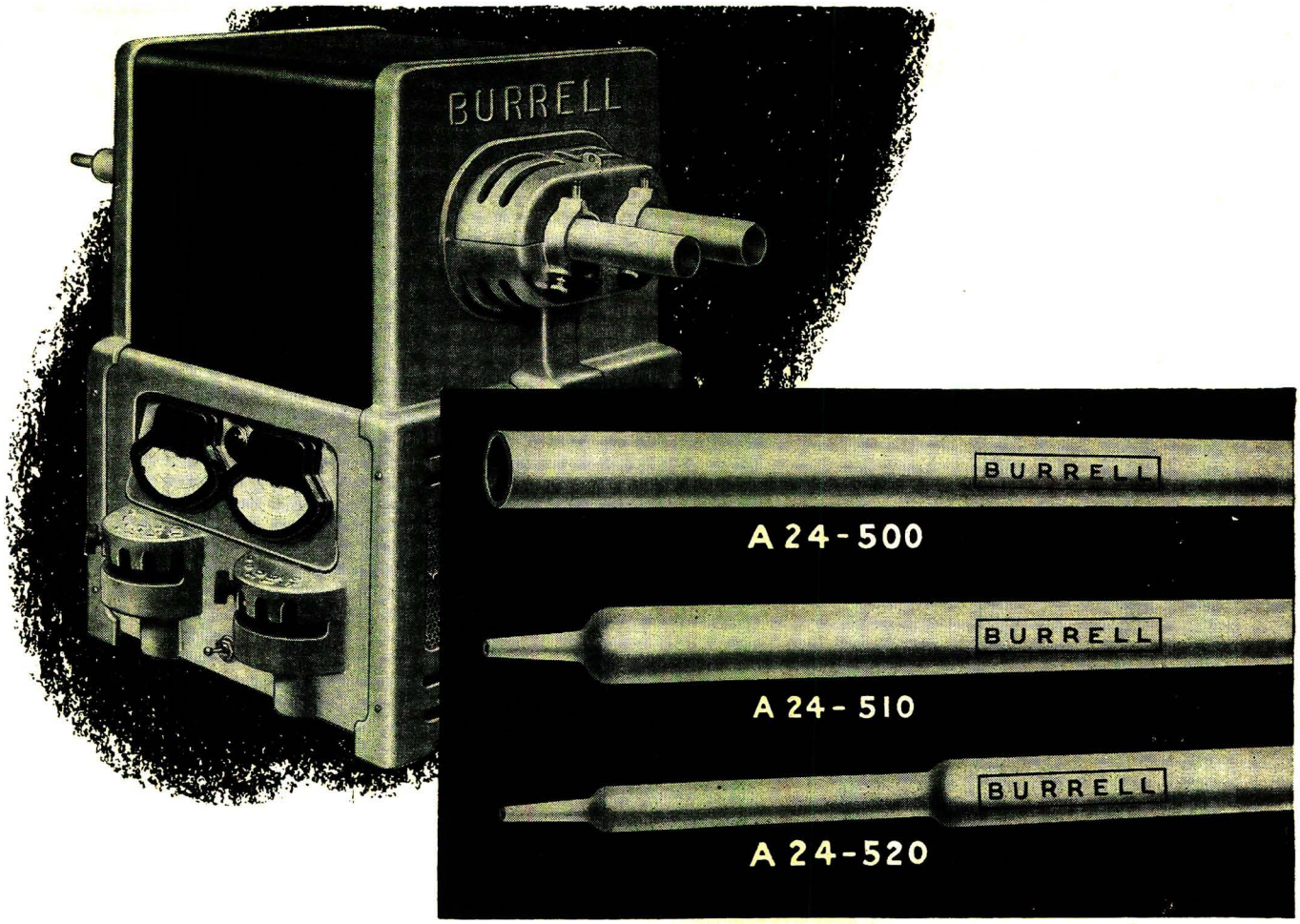
At the dinner of the Division of Analytical and Micro Chemistry, Dr. Mellon raised some problems in the teaching of analysis. He discussed the type of analytical chemistry now taught, with which we are all familiar, and then rightly asked how and whether this should be supplanted by the newer analytical chemistry which is developing. His thesis was that you should not throw out the old until you are reasonably sure that what you substitute will accomplish your desired improvement. Desires and accomplishment are often far apart. We are in accord with Dr. Mellon's conservatism but feel that the answer is in a dynamic approach to this problem. It was, therefore, with much anticipation that we received an announcement of a symposium on this subject to be held at the 1948 Spring Meeting, where all views can be considered and perhaps some conclusions drawn as to how analytical courses can be improved. It has always seemed to us that analysis is used to teach inorganic and physical chemistry. Let's teach analysis in its own right and add organic analysis to bring the subject up to date.

The Anachems (Association of Analytical Chemists), affiliated with the Detroit Section, are doing a splendid job for analytical chemistry and analysts in their area. It was, therefore, not surprising to learn that they are sponsoring a joint meeting with the other divisions of the Detroit Section on November 3. Ralph Müller will speak on "Modern Analyses—a New Science."

THE Instrument Society of America held a meeting on September 8 to 12 in Chicago, attended by 7000. In addition to the 139 instrument exhibits, there were several technical sessions. Some papers of interest to analysts are abstracted on page 817.

THE use of radioactive isotopes in medicine and in inorganic and physical chemistry is not new. However, general analytical applications are appearing from time to time, about which analysts should know and which they should apply to their own problems. Little has been published as yet, but the paper by Buchdahl and Polglase, this journal (1946), is typical. Robley Evans at the Instrument Society of America conference gave an excellent paper on this subject (see abstract, page 817). With the ready availability of isotopes, the analyst should give these techniques careful thought as to their applicability in solving unusual problems, especially in trace analysis.

Associate Editor



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BURRELL high temperature tubes are a synthetic product, the result of an exclusive process in which the ingredients combine to form natural Mullite crystals when fired at temperatures in excess of 3100°F. This process gives a stronger, harder, more homogeneous structure with a low coefficient of expansion and high resistance to thermal shock.

BURRELL high temperature tubes are:

- Dense, vitreous, and gas tight
- Straight and accurately sized
- Smooth inside, easily cleaned
- Free from devitrification
- Not distorted at high temperatures
- Unconditionally guaranteed to withstand temperatures up to 2900°F., thus providing a wide margin of safety when used in Burrell Furnaces at temperatures up to 2650°F.

These tubes are recommended as standard equipment for use in the determination of carbon and sulfur by the combustion method in iron and steel analysis, and for other applications which require the maintenance of gas atmospheres at high temperatures.

BURRELL tubes are available from stock in the three types illustrated above, in diameters from ¾-inch I.D. to 1¾-inch I.D. Lengths from 24 to 36 inches. Larger sizes supplied on special order.

Complete information on Burrell high temperature combustion tubes is given in Bulletin 201. For your copy write to: Burrell Technical Supply Co., 1936-42 Fifth Avenue, Pittsburgh 19, Penna.

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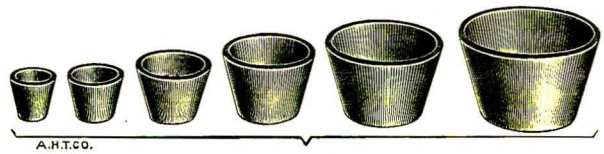

5115-T. Showing complete series of six Adapter sizes.

FILTER ADAPTERS, Neoprene Tapered Collar Type, A. H. T. Co. Specification. For supporting funnels, Gooch-type crucibles, micro filter tubes, etc., in vacuum-type filtration assemblies. Particularly suitable for Buechner and fritted glass funnels, porcelain filters without headpieces, and for reverse flow methods of cleaning filter crucibles. A unique feature of the design is that the adapter need not be fitted closely around the funnel stem but is equally effective when any part of funnel body makes contact provided negative pressure is applied. Can be used singly or in combination with adjacent sizes, forming a positive gas-tight seal which is broken gently and automatically when vacuum is released. Eliminates both boring of special size hole in rubber stopper and the difficulties which accompany use and removal of stopper from flask used in the customary way.

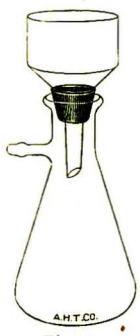

Fig. 1
Showing Size 3 Adapter in use supporting an 80 mm Buechner Funnel in the neck of a 500 ml Filter Flask.

The set consists of six concentric sizes with side walls tapering at angle of approximately 17° and varying in height between 20 and 40 mm. Minimum inside diameters range from 5 to 38 mm diameter; can be used in receivers with mouths 15 to 60 mm inside diameter. Will withstand steam pressure sterilization.

Fig. 3
Showing Size 1 Adapter in use supporting a Micro Funnel in a 125 x 16 mm Test Tube with side arm.

5115-T. Filter Adapters, Neoprene, Tapered Collar Type, A. H. T. Co. Specification. Complete set of six sizes, as above described..... 2.25
Code Word..... *Fociz*
10% discount in lots of 12 sets; 20% discount in lots of 72 sets.

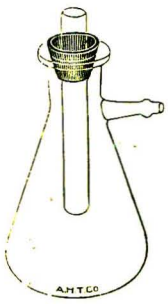

Fig. 2
Showing Size 3 Adapter supporting Coors Porcelain Filter Cylinder 155 x 15 mm in the neck of a 500 ml Filter Flask.

5115-V. Filter Adapters, single sizes, as supplied in 5115-T complete set.

Size No.	1	2	3	4	5	6
Outside diameter at top, mm.	22	28	37	46	58	70
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Wall thickness, mm.	2.5	2.5	3	3	3	4
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Each	.30	.35	.38	.40	.45	.50
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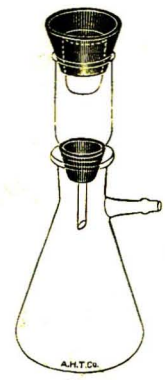

Fig. 4
Showing Size 5 Adapter in use supporting a 25 ml Gooch Crucible in a Filter Tube which, in turn, is supported by Size 3 Adapter in the neck of a 500 ml Filter Flask.

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ANALYTICAL CHEMISTRY

Walter J. Murphy, Editor

Fisher Award

In March of this year we printed an editorial entitled "The Profession of Analytical Chemist," which attracted considerable attention and brought to the editor's desk a large number of interesting comments. In the editorial we offered a practical program for increasing the prestige of the analytical chemist, and number three in the list of suggestions was one proposing the establishment of an award for outstanding original work in the field of analytical chemistry.

Within a few days after the appearance of this editorial, we received a letter from C. G. Fisher, president of the Fisher Scientific Co., Pittsburgh, Pa., offering to finance such an award. It is with great pleasure that we announce that the Board of Directors has accepted the administrative responsibility of the Fisher Award in Analytical Chemistry. The award consists of $1000 and a medallion. An additional allowance of not more than $150 is provided for actual traveling expenses to the meeting at which the award will be presented. The purpose of the award is to recognize and encourage outstanding contributions to the science of analytical chemistry, pure and applied, carried out in the United States or Canada.

Details concerning this new award will be found on page 819 of this issue.

The profession of analytical chemistry is greatly indebted to C. G. Fisher for his generous action.

More Than Just a Change in Name

The Analytical Edition of Industrial and Engineering Chemistry will become Analytical Chemistry beginning with the January 1948 issue.

During the current year we have unofficially designated this publication as Analytical Chemistry, but as long as subscribers to I&EC received both Industrial and Analytical editions, it was impossible because of postal regulations and rules laid down by the Audit Bureau of Circulation to use the title "Analytical Chemistry" officially.

The final step in the complete separation of the two editions of Industrial and Engineering Chemistry was accomplished at the American Chemical Society Meeting last month when the Board of Directors, the Council Policy Committee, the Council Committee on Publications, and the Council approved the joint recommendation of the editor and business manager that separate subscription lists be maintained for the two journals.

We believe that it is unnecessary to refer now to the several successive logical steps which have been taken, culminating in the establishment of a journal devoted exclusively to analytical chemistry. Today this publication is recognized nationally and internationally as the outstanding journal serving the broad field of analytical chemistry and it is the firm intention of the editors to continue and further to expand the present positive dynamic type of editorial policy.

The Advisory Board has been increased from nine to twelve and a system of rotation has been adopted. We are pleased to announce that I. M. Kolthoff of the University of Minnesota, K. K. Chen of the Lilly Research Laboratories, and W. J. Sweeney of the Standard Oil Development Co. have accepted 4-year appointments to the board, beginning January 1, 1948.

Under the plan of rotation suggested by your editor, the following members of the board will serve one year: Clarke, Cunningham, and Willard; Chapman, Churchill, and Lundell will serve two years; Mellon, Müller, and Oser will remain on the board for three years. In this way three new members will be appointed each year and due consideration will be given to their selection, so that at all times the board will be representative of the various fields of activity within the broad field of analytical chemistry.

In conclusion, we wish to point out that this issue contains a larger number of paginated pages than we have printed in any prior issue during 1947. The Board of Directors has made available additional funds to finance more pages during the remainder of this year in order to reduce the present backlog of manuscripts waiting publication. We hope that additional paper can be obtained to increase the number of pages in the November and December issues.

We are slightly optimistic that increased paper supplies will be available in 1948 and that we shall be in a position next year to reduce substantially the time lapse between acceptance and publication. Readers will also note that beginning with this issue we have resumed the practice of printing a footnote giving date of receipt of manuscripts.

Raman Spectra of Hydrocarbons

M. R. FENSKE, W. G. BRAUN, R. V. WIEGAND[1], DOROTHY QUIGGLE R. H. MCCORMICK, AND D. H. RANK
School of Chemistry and Physics, The Pennsylvania State College, State College, Pa.

The Raman spectra of 172 pure hydrocarbons are presented both as reproductions of the original records obtained from a recording spectrograph and in tabular form as scattering coefficients and depolarization factors. Data are presented for 76 paraffins, 32 naphthenes, 29 olefins, 3 diolefins, 30 aromatics, and 2 other hydrocarbons. Direct comparisons of spectra are possible because a uniform intensity scale has been used. The spectrograph employed records the Raman spectrum as a graph with coordinates linear in both wave length and intensity. Raman spectra can be used for the qualitative and quantitative analysis of hydrocarbon mixtures. A few nine-component mixtures have been analyzed successfully. In general, Raman spectroscopy in hydrocarbon analyses is best used as a complement to rather than a substitute for the infrared and ultraviolet techniques.

RECENT advances in the applications of the newer physical methods of analyses have contributed greatly to the manufacture and quality control of various chemicals. The petroleum industry in particular has used these methods in the conversion and synthesis of various hydrocarbons and in the control of distillation, extraction, and other separational processes in both the laboratory and the refinery. Some of these applications have been described in review articles (*9, 17, 18, 24, 27*).

Most of the research on spectroscopic methods of analysis has been concerned with the application of infrared and ultraviolet absorption methods (*3, 4, 5, 8*), and today these are used rather extensively. Many improvements in instrumentation were made during the war and several good infrared and ultraviolet spectrophotometers are now available commercially. Most of these instruments are either of the direct indicating or recording type and have been designed for maximum economy in work and time.

The application of Raman spectroscopy to the analysis of hydrocarbon mixtures, on the other hand, has been rather limited even though, in many cases, it offers advantages over both the infrared and ultraviolet techniques. Recording spectrometers for this work have not been available and the photographic procedure generally used has not been sufficiently fast or accurate for general analytical purposes. The earlier features of this method of analysis have been described by Goubeau (*11*) and Glockler (*10*), and the more recent advances by Stamm (*25*). All this work was done by recording the Raman spectra photographically. These photographic methods, however, are time-consuming and are always attended by the inherent difficulties of development and photometry.

The work described in this paper was started in 1943 and was directed toward the development of a Raman spectrograph having as the principal objectives: (1) that the instrument be direct recording; (2) that it be semiautomatic; (3) that the actual time for running the instrument and processing the record be as short as possible; and (4) that the spectra be reproducible.

Preliminary investigations (*20*) showed that the Raman spectra of hydrocarbons could be recorded directly by using a multiplier phototube to scan the spectra. Additional work was carried out at these laboratories to make a direct-recording Raman spectrograph and develop techniques to satisfy the conditions given above. The instrument which was constructed for this purpose has recently been described (*23*). The analytical results and the spectra of the pure hydrocarbons presented here were obtained with this apparatus.

The basis for applying Raman spectroscopy to hydrocarbon analysis is dependent upon the fact that when a beam of a monochromatic exciting light passes through a transparent medium some of the light is absorbed and may be re-emitted. If this re-emitted light is examined by means of a spectrograph, very weak spectral lines or bands will appear on either side of the line of the exciting light. These weak lines, which are called Raman lines, are characteristic of the substance illuminated and are therefore a "fingerprint" of that substance. The frequency differences between the exciting light and the Raman lines are independent of the frequency of the exciting light—i.e., the frequency differences are the same for exciting lights of different wave lengths. In order to have a convenient system of units and to conform with past usage these frequency differences are expressed as wave number shifts and written $\Delta\nu$cm.$^{-1}$

It is beyond the scope of this paper to discuss in any detail the theoretical concepts of the Raman effect. The comprehensive monographs of Kohlrausch (*14*), Hibben (*13*), Glockler (*10*), Sutherland (*26*), and Herzberg (*12*) have treated rather exhaustively the fundamental principles and reviewed the experimental data. The paper by Stamm (*25*) is brief but rather complete. To these the reader is referred for more details.

Since the Raman spectra are characteristic of the scattering substances, both in the wave number shift and the intensities of the various lines, they can be used like any other physical property as a means of identification. Experimentally it has been found that for many mixtures of hydrocarbons the intensities of the Raman lines of a constituent are directly proportional to the volume fraction of that constituent present. A qualitative analysis of a mixture may therefore be made by determining the frequencies (wave number shifts) of the various lines of its Raman spectrum and comparing these data with those obtained for pure compounds. The quantitative analysis is made by determining the ratios of the intensities of the Raman lines of a substance in the spectrum of the mixture with those of the same lines in the spectrum of the pure compound.

FIELD OF USEFULNESS

Although, like the ultraviolet and infrared absorption methods, the analysis by Raman spectroscopy involves the measurement of the characteristics of a spectrum, different principles and techniques are used. The types of analyses which can be made, the concentrations of the components which are most suitable for analyses, and the sensitivities of the methods are different. Consequently, the choice of the spectroscopic method to be used for an analysis depends on the operator's knowledge of the type of sample, the number of components present, and the past history and treatment of the sample. No one spectroscopic method is universal in hydrocarbon analytical work. The ultraviolet and infrared absorption methods and Raman spectroscopy will probably be used as complements rather than as substitutes for each other in analytical work.

[1] Present address, Montana State College, Bozeman, Mont.

Ultraviolet absorption spectrophotometry is well suited for the determination of conjugated diolefins and the aromatic hydrocarbons of lower molecular weight. The absorption spectra of the higher molecular weight aromatics—namely, those having nine or more carbon atoms—become similar and accurate analyses are often difficult, if not impossible. The ultraviolet method is normally not sensitive to olefins, paraffins, or naphthenes; it is particularly useful when only a few aromatics must be determined in a mixture of other hydrocarbons.

The limitations of infrared absorption spectrophotometry, on the other hand, are not so specific and analyses can be made on mixtures containing paraffins, olefins, naphthenes, and aromatics. Some difficulties are usually experienced with mixtures of paraffins and naphthenes which contain aromatics; with mixtures of naphthenes and paraffins which contain small amounts of alcohols, ethers, ketones, and esters; with materials containing water; and with certain other systems where a small amount of strongly absorbing compound can mask the absorption of the other materials present.

Both the ultraviolet and infrared methods are sensitive to small amounts of an absorbing material and are often useful for the detection and estimation of small concentrations of certain impurities in an otherwise relatively pure material. Both methods are more accurate for determining small concentrations than they are for large concentrations of an absorbing constituent.

Although in practice most of the hydrocarbon samples subjected to analysis by the infrared absorption methods are relatively simple—that is, they contain from two to four components—as many as nine individual hydrocarbons may be determined in one sample. For ultraviolet absorption analyses the samples should be less complex, and a maximum of perhaps four hydrocarbons which absorb should be determined in a single sample.

Since the relationship between the volume fraction concentration of a compound and the intensity of the Raman lines is a linear one for most hydrocarbon mixtures, the concentrations of compounds as high as 100% can be determined without difficulty. For the infrared and ultraviolet absorption methods the relationship between transmission and concentration is logarithmic. On the other hand, the Raman spectra are usually not sensitive to small concentrations such as 1 to 5% and in a mixture these minor components may even be missed qualitatively. This is no disadvantage when only the concentration of the major constituent is desired.

Mixtures having as many as nine components have been analyzed by their Raman spectra at these laboratories. However, such complex analyses are rather unusual and the study of the spectra and the computations involved become rather tedious. The time required for an analysis depends on the number of components and the similarity of their spectra. Usually about one hour is required for preparing the sample, scanning the spectrum, and processing the record. This is required for all samples. In addition, examination of the spectrograms and the qualitative and quantitative analysis of 2- or 3-component mixtures take about 0.5 to 1 hour except for routine work where the time will be somewhat less. For 5-component mixtures the examination of the spectrograms and the analytical computations may take as long as 3 hours.

The sample size required for the regular Raman tubes is 35 ml., although some analyses have been made, using specially designed tubes, on as little as 12 ml. with the present apparatus. It is believed, however, that recording instruments could be built which would use considerably smaller sample tubes.

DEFINITIONS AND TERMS

The many papers which have been published on the Raman effect have been consistent in most of their designations of the various units. The ones most frequently used to define the Raman effect refer to spectral position, intensity, and degree of polarization.

Spectral Position. The actual position where the Raman frequencies occur in the spectrum is of little importance, since it is an effect which can be produced by an exciting light of any frequency. The important fact is that the frequency difference, preferably measured in the number of vibrations per centimeter, between the exciting radiation and the Raman line is the same no matter where in the spectrum the effect occurs. This difference is usually expressed in wave numbers or vibrations per centimeter and is designated as the Raman shift or wave number shift, $\Delta\nu$ in cm.$^{-1}$

To express the frequency, ν, in the usual unit, cycles or vibrations per second, would lead to awkward numbers. Hence another unit, obtained by dividing vibrations per second by the velocity of light, c, in centimeters per second, is used. This unit has the dimensions of vibrations per centimeter, and is equal to the reciprocal of the wave length, λ:

$$\lambda\nu = c; \quad \therefore \quad \nu/c = 1/\lambda$$

Intensity Measurements. For quantitative analytical work the intensities of each line must be known in addition to the Raman shift. Unfortunately, intensity measurements have not been made on any absolute or comparative basis and each investigator has chosen a system to suit his own work. The most frequently used system is to correlate the intensities of the various lines on a basis of 0 to 10 where 0 is the intensity of the weakest and 10 the intensity of the strongest line in each spectrum. For the correlation of molecular structure and Raman spectra this method has been satisfactory; however, for analytical work there is a serious disadvantage: it does not allow the intensity comparison of a line in one spectrum with a line in another, since each spectrum is usually on a different basis.

In all the work done at these laboratories, intensities have been measured relative to the $\Delta\nu$ = 459 cm.$^{-1}$ line of carbon tetrachloride. The unit of intensity is the "scattering coefficient" and is defined as the ratio of the intensity of the hydrocarbon Raman line to that of the $\Delta\nu$ = 459 cm.$^{-1}$ line of carbon tetrachloride. Since all the intensities are on this same basis, the spectra of known pure compounds may be compared directly with unknown mixtures and the analysis is straightforward.

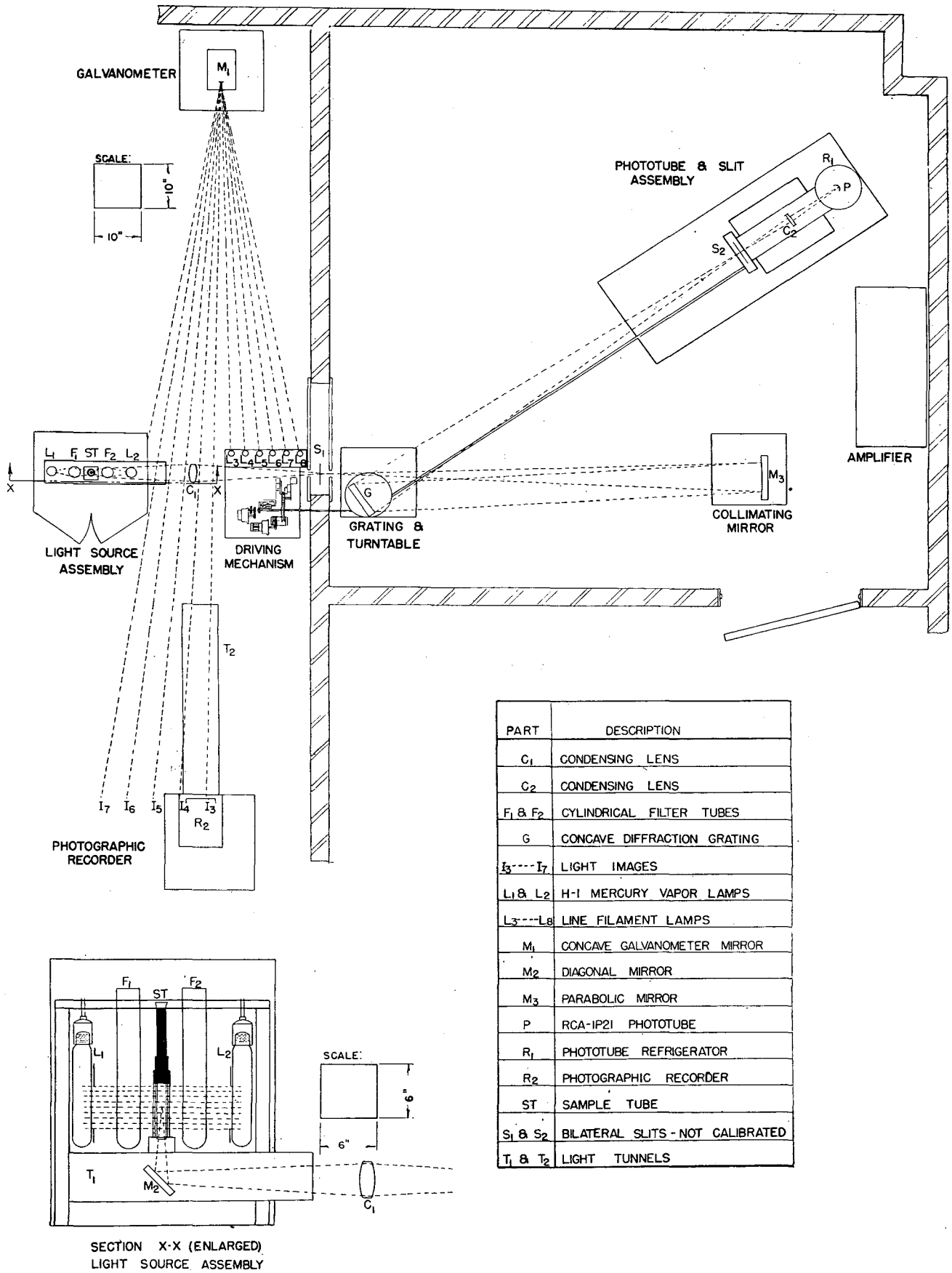
Degree of Polarization. The polarization of the Raman lines is defined by the depolarization factor, ρ_n (*12*, *14*), which is the ratio of the intensities of the perpendicular component (the electric vector vibrating in the vertical plane) to the parallel component (the electric vector vibrating in the horizontal plane) of the Raman line. The parallel component is always preponderant and according to theory the value of ρ_n approaches 0 for symmetrical types of vibrations and 6/7 for asymmetrical types.

For most hydrocarbon analytical work this value has little application; however, for the delineation of molecular structure and for the assignment of molecular vibrations it is important.

APPARATUS

A schematic drawing of the instrument and optical path is shown in Figure 1.

The exciting lights, L_1 and L_2, are mercury vapor lamps supplied from a voltage-regulated line. The light from these lamps is focused by means of the cylindrical filter tubes, F_1 and F_2, and concentrated in the sample tube, ST. Scattered light arising from this illumination passes out the end of the sample tube and is directed to the first condensing lens, C_1, by means of diagonal mirror M_2. This condensing lens focuses the light from the sample on the entrance slit, S_1, of the spectrograph. Light entering the spectrograph falls on collimating mirror M_3 and is directed as a parallel beam to the concave diffraction grating. The spectrum diffracted from the grating comes to focus on a parabola passing through the exit slit, S_2, the collimating mirror, M_3.



PART	DESCRIPTION
C_1	CONDENSING LENS
C_2	CONDENSING LENS
F_1 & F_2	CYLINDRICAL FILTER TUBES
G	CONCAVE DIFFRACTION GRATING
I_3----I_7	LIGHT IMAGES
L_1 & L_2	H-I MERCURY VAPOR LAMPS
L_3---L_8	LINE FILAMENT LAMPS
M_1	CONCAVE GALVANOMETER MIRROR
M_2	DIAGONAL MIRROR
M_3	PARABOLIC MIRROR
P	RCA-IP21 PHOTOTUBE
R_1	PHOTOTUBE REFRIGERATOR
R_2	PHOTOGRAPHIC RECORDER
ST	SAMPLE TUBE
S_1 & S_2	BILATERAL SLITS - NOT CALIBRATED
T_1 & T_2	LIGHT TUNNELS

Figure 1. Schematic Diagram of Spectrograph

and the grating, G. The grating can be rotated by means of a motor drive so that the spectrum passes the exit slit at a rate of about 11 Å. per minute.

Individual lines are focused on the phototube, P, by means of lens C_2. The phototube (RCA-1P21) used here as a detector is a cascade type which greatly amplifies the initial photocurrent before it leaves the tube. The signal is further magnified by an amplifier and the fluctuations produced in the plate current are passed through the galvanometer, producing rotation of the galvanometer coil. The movement of the coil is recorded by the movement of the light images, I_3 to I_7, produced by the rotation of galvanometer mirror M_1. The movement of the light images together with the movement of the paper past the slit of the recorder produces a continuous curve showing the Raman spectrum of the sample.

To aid in the analysis of the spectrum a mechanism for putting wave length calibration lines on the trace is connected directly to the driving mechanism..

Light Source. The divergent light from the mercury vapor lamps (Type H-1, 400-watt) is focused in the horizontal plane by means of the cylindrical filter tubes, F_1 and F_2, so that an intense beam passes through the center of the Raman tube. Since there is an overlapping of the Raman spectra produced by the 4078 and 4047Å. lines with that of the 4358 Å. mercury line, these first two must be filtered out. For this reason both tubes are filled with a solution of sodium nitrite which serves as a filter to remove the 4078 and 4047 Å. radiation, as well as a small amount of the ultraviolet light which may not have been removed by the glass envelopes of the lamps. For the present unit a tube 6.25 cm. (2.5 inches) in diameter and containing a solution of about 35 grams of sodium nitrite per 100 grams of water has been found to be most satisfactory.

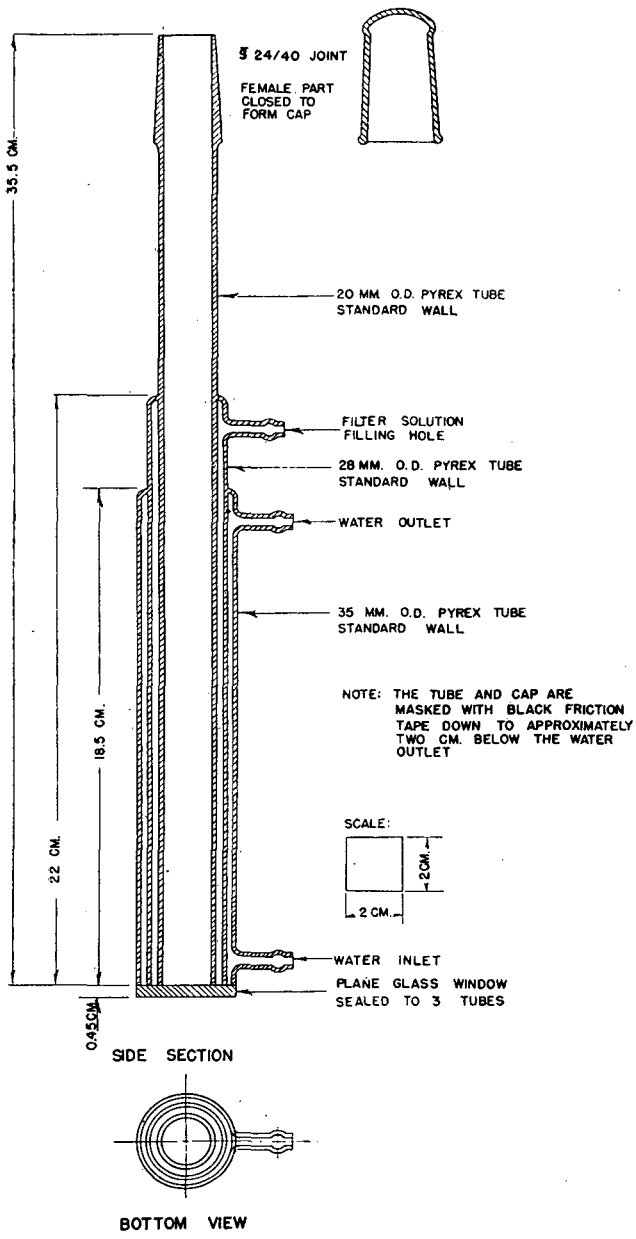


Figure 2. Raman Sample Tube

The Raman sample tube as shown in Figure 2 was designed for this apparatus, so that an additional filter solution could be placed in the light path and constant-temperature water circulated around the tube. The arrangement shown has the advantage over previously used separate filter holders and cooling systems in that there are fewer glass-to-air surfaces, resulting in less surface reflection losses. The elimination of ring seals at the bottom of the tube allows the sample to be irradiated as far down as the plane window. The all-glass construction facilitates cleaning. (The sample tubes were made by the Pyrocell Manufacturing Co., 207-211 East 84th St., New York 28, N. Y.)

Distilled water is circulated through the outer jacket of the tube from a constant-temperature supply by means of a small centrifugal pump.

The inner jacket has one opening through which a filter solution can be added to remove as completely as possible the mercury continuum between 4400 and 4700 Å. A saturated solution of praseodymium ammonium nitrate has proved to be most efficient for this purpose. Since this salt was rather difficult to purify, a commercial mixture of approximately 50% praseodymium, 30%, neodymium, and 20% lanthanum salts was tried and found satisfactory (supplied by Lindsay Light and Chemical Co., West Chicago, Ill.).

The sample tubes shown in Figure 2 require a 35-ml. sample; however, when only smaller amounts of material are available a tube of somewhat similar design is used in which glass wedges are cemented into the tube to fill part of the useless volume. Samples as small as 12 ml. have been used in these modified tubes.

Immediately below the sample tube a slide containing a Polaroid disk may be inserted. Either the parallel or the perpendicular component of the Raman lines can be selected for recording by rotation of the Polaroid. The method of determining depolarization factors from the records of the two components has been reported in the literature (*21*).

Spectrograph. The grating mounting is a stigmatic type similar to that described by Meggers and Burns (*16*) except that the grating is mounted on a turntable and an exit slit is used to make the instrument a monochromator. The diffraction grating was ruled at Johns Hopkins University on a Pyrex mirror. The grating has a ruled area of 7 by 3.25 inches with 15,000 lines per inch and a radius of curvature of 15 feet.

The grating and its support bracket are mounted on a precision turntable which can be turned by means of a motor drive, so that the spectrum passes by the exit slit at a rate of 11 Å. per minute. A suitable gear mechanism is provided for a small revolution counter, which indicates directly the wave length in Ångströms, and for a switch mechanism which places fiducial marks on the record at 5 and 25 Å. intervals. The 5 Å. marks are placed on the record by flashing a light in front of the recorder, so that the entire slit is illuminated and a line approximately equal to the width of the slit appears on the finished record. The darker 25 Å. marks are recorded by a brighter light in front of the slit. For this purpose a two-filament automobile lamp serves very well, one filament being used for the 5 Å. marks and two for the 25 Å. marks.

The collimating mirror, M_3, is made from a 25-cm. (10-inch) Pyrex telescope blank ground and polished to a parabola having a focal length of 94.5 inches. The mirror is front-surface aluminized. The mounting bracket is adjustable, so that the mirror may be properly aligned and focused.

The entrance and exit slits of the spectrometer are bilateral and adjustable. Both slits are set at 0.6-mm. opening which gives a resolution of about 15 $cm.^{-1}$ for the spectrograph. The exit slit assembly may be removed and a plate holder inserted for photographic recording if desired.

A simple one-element condensing lens, C_2, serves to focus the light passing through the slit onto the sensitive surface of the phototube.

Detector. A specially designed refrigerator compartment, R_1, is used to house the phototube assembly, so that the unit can be kept at dry ice temperature while in use. This refrigeration is necessary to reduce the fluctuations in the thermal dark current of the tube. The phototube, an RCA 1P21 multiplier type, and the voltage divider supplying the tube are enclosed in an air-

tight case in the center of the refrigerator. A light tunnel, containing two glass windows to minimize heat transfer, allows light focused by lens C_2 to fall on the photosensitive surface of the tube.

For all the Raman work which has been done with this detector a potential of about 110 volts per stage has been used. This is supplied from a set of 24 radio B-batteries in series with a voltage divider.

Amplifier and Recorder. The signal from the phototube is passed to a one-stage direct current amplifier employing an RH-507 amplifier-electrometer tube. The grid bias and the plate and filament currents are supplied from Willard low discharge wet

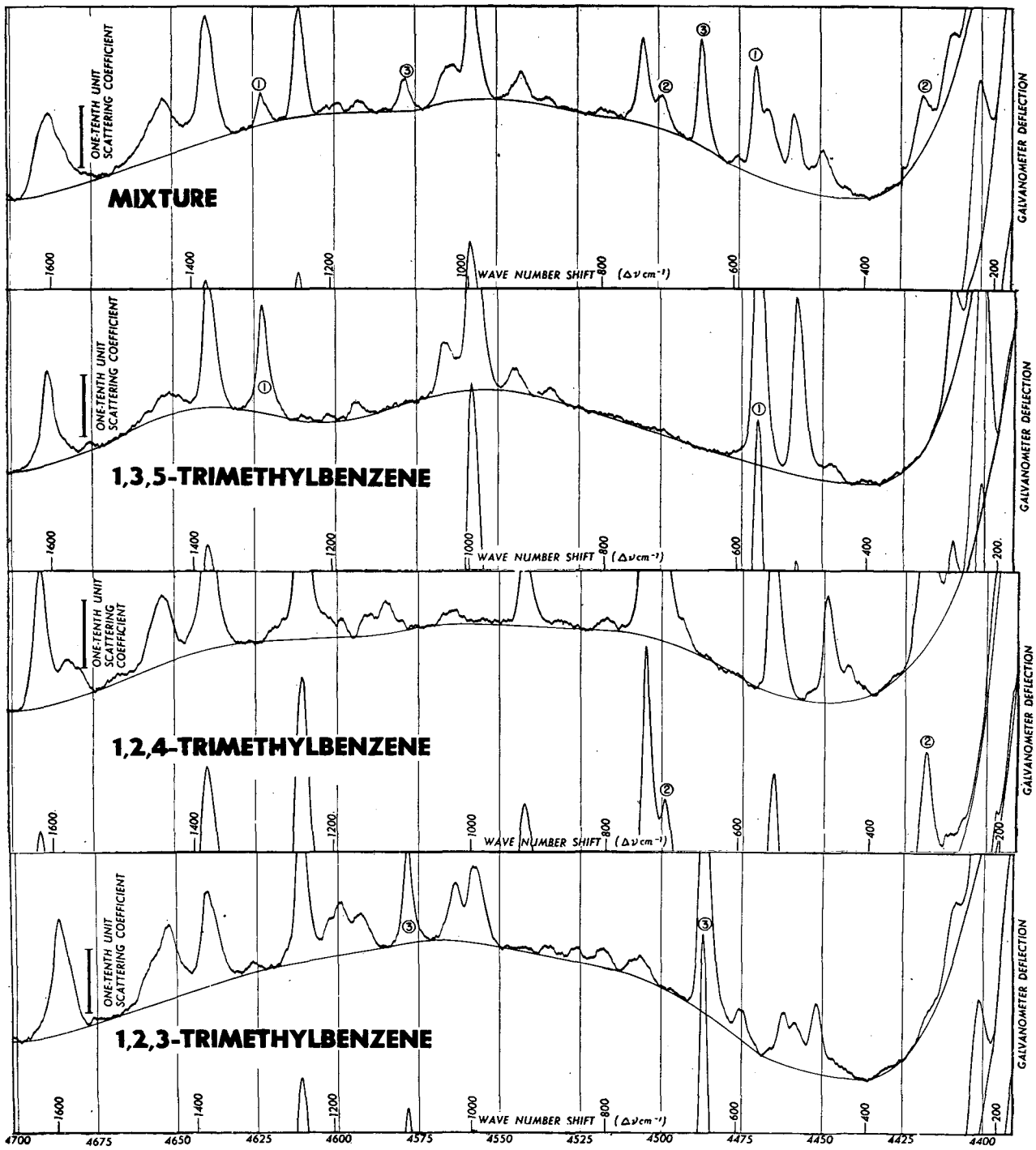


Figure 3. Raman Spectra of a Known Mixture and Its Components

	Composition, Volume %	
	Known	Determined
1,3,5-Trimethylbenzene	33.3	33.6
1,2,4-Trimethylbenzene	33.3	33.4
1,2,3-Trimethylbenzene	33.4	33.0
Total	100.0	100.0

storage batteries. These batteries provide an exceptionally steady output which, together with proper shielding, good insulation, and drying of the amplifier case make the unit extremely stable for long periods of time.

The plate current from the amplifier is led to an opposing potentiometer circuit which cancels the steady plate current and leaves the variable signal to be fed to the recording galvanometer. A variable shunt across the galvanometer allows the sensitivity to be changed.

The recorder automatically feeds the photographic paper from a 250-foot roll past the recording slit, on which the galvanometer light images are focused, and into a receiver. The entire unit is light-tight, provision having been made for shearing off the record and closing the receiver so that the photographic paper can be removed to the darkroom for processing.

The system of multiple lights and a concave galvanometer mirror for use with the photographic recorder allows deflections of approximately 30 inches to be recorded on paper only 6 inches wide (*19*).

ANALYTICAL PROCEDURE

Treatment of Sample. The method of obtaining the Raman spectra requires that the samples examined be relatively free of dust, turbidity, colored material, and fluorescing impurities. The presence of an excess of any of these may make the spectra obtained unsuited for analytical work. Their removal is usually necessary.

Dust and suspended matter in a sample cause an increase in background by reason of the Tyndall effect, the suspended material scattering the light of the mercury continuum. The random movements of the particles cause fluctuations in the amount of this scattered light with resulting errors in the Raman line intensity measurements, particularly with recording instruments.

Fluorescent impurities are often present in hydrocarbon samples and may originate from oxidation of the hydrocarbon, contamination by stopcock lubricants, rubber, material extracted from corks and plastic bottle caps, and countless other sources. The usual effect of these is to increase the amount of continuous radiation entering the spectrograph. Since the random fluctuations in the output of the phototube increase with increasing amounts of light, strongly fluorescing samples will cause random fluctuations which can entirely mask the rather weak Raman radiations. This can make the record useless for analytical work.

Samples which are colored in themselves or which contain colored impurities where the absorbing region lies in the wavelength region of their Raman spectrum do not lend themselves to analysis by the Raman technique. If either the exciting light or the Raman spectrum is absorbed there will be a decrease in the intensity of the Raman lines and any quantitative comparison with external standards becomes difficult. Some work done in these laboratories has shown that a sample which has a transmittance between 4300 and 4700 Å., of 99% through a 1-cm. path will have Raman lines only 90% as intense as those of a sample whose transmittance is 100%.

Several methods of treating samples to remove these materials have been described (*11*, *14*). The one which appeared most satisfactory for hydrocarbon analysis was a simple distillation where the distillate was collected directly in the Raman tube. In the case of mixtures, the distillations must be carried to dryness in order to avoid any effects of fractionation and consequent changes in sample composition. In almost all the cases encountered, the dust and the fluorescent and colored contaminants were removed by this simple distillation; however, some samples of aromatic hydrocarbons, which had been obtained from hydrocarbon mixtures by extraction with aniline, remained colored even after this treatment. It was found that a distillation in which the vapor was passed through hot activated silica gel cleaned the samples sufficiently to obtain satisfactory Raman spectra. Known samples treated in this manner showed no detectable change in composition due to selective adsorption.

Production of Spectrograms. The usual procedure in recording the spectrum of a sample is to place in the apparatus a tube containing pure carbon tetrachloride. The short section of the spectrum which includes the $\Delta\nu = 459$ cm.$^{-1}$ line of this material is next scanned for intensity calibration purposes. The tube containing the sample for analysis is then inserted in the instrument and the spectrum from 1700 to 150 cm.$^{-1}$ (4725 to 4385 Å.) recorded. A second carbon tetrachloride calibration mark is recorded for a check of the first calibration and if, after processing the recording, the two standard deflections of carbon tetrachloride, taken before and after the determination of the spectrum of the sample, are found to agree within 2 or 3%, the spectrogram of the sample is used for the analytical work.

Analysis of Records. For qualitative analytical work the number of possible compounds which must be looked for in an unknown sample may be considerably narrowed down by a knowledge of the source of the sample, the boiling point range, refractive index, bromine number, etc. The analysis then usually involves only the direct visual comparison of a few spectrograms of known compounds with the spectrogram of the unknown. An alternate method lies in calculating the wave number shifts of the Raman lines of the unknown sample and comparing these data with the tables prepared for the pure compounds, similar to those given in this paper.

For quantitative work a base line curve, as shown in Figure 3, must be drawn on the spectrogram. Since the intensities of the Raman lines are directly proportional to the galvanometer deflections, and hence proportional to the heights of the lines above the base line on the spectrogram, the various lines suitable for analytical purposes are measured. The scattering coefficients or the ratios of the heights of these lines to the height of the $\Delta\nu = 459$ cm.$^{-1}$ line of carbon tetrachloride are then calculated. The scattering coefficients of the corresponding lines of the pure compounds are next obtained in the same manner. The concentration of the compound present for which the analysis is being made ordinarily is the ratio of the scattering coefficient for one of these lines in the mixture to that of the corresponding line in the pure material.

For most hydrocarbon mixtures, particularly those in which the components are all of the same molecular type, there is a direct proportionality between the scattering coefficient and the volume fraction of the compound present. For mixtures of dissimilar types, such as aromatics and paraffins, there may be deviations from this direct proportionality and additional calibrations may be necessary before accurate analyses can be made.

In determining the percentage of each component present it is desirable to choose positions on the trace where only single substances have moderately strong lines. If the number of components in a mixture is sufficiently small and the spectrum of each component contains several lines, it is usually possible to find more than one peak in the clear for each substance. Figure 3 shows the spectrum of a mixture and the spectra of the pure hydrocarbons in it. The various Raman lines used in the analysis for each of the components have been marked with circled numbers.

If the values obtained from the various peaks for one compound do not check each other sufficiently well, the spectra of the components believed to be present should be rechecked to determine whether some interference has been overlooked or whether the sample is colored. The position of the base line curve should also be checked to see if a slight change in its location could account for the discrepancy. When values are found for all the substances which have peaks in the clear, these may be used to apply corrections on peaks where a component of known percentage may be interfering with a component whose percentage is still unknown. For complex mixtures it may be necessary to apply several corrections to a peak in order to obtain a value for one of the components which cannot be found simply. When corrections are applied to a peak, they must not be a substantial part of its height or the error caused by uncertainty in the base

Table I. Analysis of Known Hydrocarbon Mixtures

Compound	Boiling Point, Corrected to 760 Mm. of Hg, ° C.	Known Composition, Volume %, A	Determined Composition, Volume %, B	Difference, A−B
1,2,3-Trimethylbenzene	176.1	50.0	50.1	−0.1
1,3,5-Trimethylbenzene	164.7	50.0	50.2	−0.2
		100.0	100.3	
1-Methyl-4-isopropylbenzene	177.1	43.4	42.7	0.7
1,2,3-Trimethylbenzene	176.1	56.6	56.7	−0.1
		100.0	99.4	
1-Methyl-3-ethylbenzene	161.3	13.9	16.1	−2.2
1-Methyl-4-ethylbenzene	162.0	13.4	15.6	−2.2
n-Propylbenzene	159.2	72.7	72.2	0.5
		100.0	103.9	
1,2,3-Trimethylbenzene	176.1	33.3	33.0	0.3
1,2,4-Trimethylbenzene	169.2	33.3	33.4	−0.1
1,3,5-Trimethylbenzene	164.7	33.4	33.6	−0.2
		100.0	100.0	
1-Methyl-3-ethylbenzene	161.3	10.6	9.1	1.5
1-Methyl-4-ethylbenzene	162.0	10.2	8.5	1.7
n-Propylbenzene	159.2	65.3	70.3	−5.0
1,3,5-Trimethylbenzene	164.7	13.9	14.1	−0.2
		100.0	102.0	
1,3,5-Trimethylbenzene	164.7	35.2	34.0	1.2
n-Propylbenzene	159.2	15.6	15.6	0.0
1-Methyl-2-ethylbenzene	165.2	17.2	16.2	1.0
1,2,4-Trimethylbenzene	169.2	13.7	12.7	1.0
tert-Butylbenzene	169.1	18.3	19.3	−1.0
		100.0	97.8	
Ethylbenzene	136.2	50.0	50.1	−0.1
2,2,5-Trimethylhexane	124.1	50.0	50.4	−0.4
		100.0	100.5	
1,2-Dimethylbenzene	144.4	13.3	13.8	−0.5
Isopropylbenzene	152.4	16.7	16.1	0.6
n-Propylbenzene	159.2	16.7	15.3	1.4
1-Methyl-3-ethylbenzene	161.3	13.3	14.6	−1.3
1-Methyl-4-ethylbenzene	162.0	3.3	4.2	−0.9
2-Cyclopentylbutane	154.4	36.7	36.7	0.0
		100.0	100.7	
1-Methyl-2-ethylbenzene	165.2	3.9	3.8	0.1
1,2,4-Trimethylbenzene	169.2	5.4	5.2	0.2
1,3,5-Trimethylbenzene	164.7	15.1	15.9	−0.8
Paraffin-naphthene mixture[a]	...	75.6	74.5	1.1
		100.0	99.4	
n-Propylbenzene	159.2	6.1	5.2	0.9
1-Methyl-3-ethylbenzene	161.3	8.9	9.5	−0.6
1-Methyl-4-ethylbenzene	162.0	1.6	2.3	−0.7
1,3,5-Trimethylbenzene	164.7	2.4	2.3	0.1
Paraffin-naphthene mixture[a]	...	81.0	82.0	−1.0
		100.0	101.3	
2-Methylpentane	60.3	30.8	32.6	−1.8
3-Methylpentane	63.3	30.8	29.5	1.3
n-Hexane	68.7	38.4	37.9	0.5
		100.0	100.0	
3-Methylpentane	63.3	30.8	31.6	0.8
n-Hexane	68.7	38.4	38.5	−0.1
Methylcyclopentane	71.8	30.8	30.7	0.1
		100.0	100.8	
n-Hexane	68.7	38.4	36.2	2.2
Methylcyclopentane	71.8	30.8	31.5	−0.7
Cyclohexane	80.7	30.8	33.7	−2.9
		100.0	101.4	

[a] Petroleum fraction having a boiling point of approximately 160° C. This mixture had been extensively extracted with 98% sulfuric acid to remove aromatic hydrocarbons.

line location will be prohibitive. This doubt in the position of the base line makes it nearly impossible to use simultaneous equations for peaks common to several components and still obtain good results. As a final check on the values obtained, the total should equal 100%. If the total is over this, the base line should be checked to see if it has been drawn too low. If the total is less than 100%, the sample should be checked for color, the base line should be checked to see if it is drawn too high, and, finally, the qualitative analyses should be checked to see that no components have been overlooked.

ANALYTICAL RESULTS

To test the reliability of the method of analysis several known mixtures of hydrocarbons were analyzed. The analyst was not given any information about the samples except the approximate boiling point range and the knowledge that he had at his disposal the spectra of the pure components from which the blends were prepared. The selection of the components for these blends, although dictated somewhat by the availability of the materials used, was such that the samples were in general similar to the fractions which might be obtained from a fractional distillation—that is, they consisted of a mixture of close-boiling materials. The mixtures examined were blends of aromatics, paraffins, naphthenes and aromatics, naphthenes and paraffins, and paraffins and aromatics.

The results of some typical analyses are given in Table I. The percentage error in the analyses, based on the total sample, varies somewhat from compound to compound and is largest in mixtures where the components have similar spectra and in mixtures which have a large number of compounds present. In the former case the analytical difficulties are encountered in overlapping lines, while in the latter the principal difficulty is the uncertainty of the base line location. In general, the Raman analyses have been found to be correct to within 2 percentage units.

CORRELATION OF RAMAN DATA AND MOLECULAR STRUCTURE

Since the Raman spectrum of a material bears a direct relationship to the characteristic frequencies of the various parts of a molecule, the careful examination of the spectrum of a compound should provide information on its molecular configuration. Such knowledge is useful in the study of petroleum fractions where certain types of compounds, which have either not been prepared or are not available for study in their pure state, are to be identified. As additional improvements are made in distillation, extraction, and other separational processes for the higher boiling naphtha and gas oil fractions these correlations, together with those based on the infrared spectra (*3*), should be invaluable in studying the composition of petroleum fractions.

Of specific interest in the analysis of hydrocarbon mixtures are certain correlations between the Raman spectra and molecular structure which have been made in the course of this work, as well as those which have been published by Kohlrausch, Pongratz, Reitz, and their co-workers (*15*) and by many others (*13*). These are summarized in the following paragraphs.

Aliphatic Olefins. Compounds having a C=C bond show a strong Raman line between 1600 and 1685 cm.$^{-1}$, the exact position depending on the configuration of the rest of the molecule. In general, the depolarization factor, ρ_n, for this line is low—namely, between 0.15 and 0.3.

In compounds of the type CH_2=CHR, and CH_2=CRR′, where R is any hydrocarbon radical, the strong Raman line lies between about 1640 and 1655 cm.$^{-1}$, while in compounds of the type HRC=CHR′, RR′C=CHR″, and RR′C=CR″R‴

Table II. Spectra Numbers and Properties of Pure Paraffin Hydrocarbons

Name of Compound	Spectrum No.	Boiling Point at 760 Mm. of Hg, ° C. Determined	Boiling Point at 760 Mm. of Hg, ° C. Literature values[a]	Refractive Index at 20° C., n_D^{20} Determined	Refractive Index at 20° C., n_D^{20} Literature values[a]	Estimated Purity, Mole %[b]	Source of Compound[c]
5-carbon atom							
n-Pentane	1	36.1	36.07	1.3577	1.3575	.....	A
2-Methylbutane	2	27.9	27.85	1.3538	1.3537	.....	A
6-carbon atom							
n-Hexane	3	68.7	68.74	1.3749	1.3749	.....	A
2-Methylpentane	4	60.25	60.27	1.3713	1.3715	.....	A
3-Methylpentane	5	63.15	63.28	1.3764	1.3765	.....	A
2,2-Dimethylbutane	6	49.65	49.74	1.3687	1.3688	.....	A
2,3-Dimethylbutane	7	57.95	57.99	1.3750	1.3750	.....	A
7-carbon atom							
n-Heptane	8	98.4	98.43	1.3877	1.3876	.....	A
2-Methylhexane	9	.....	90.05	....	1.3849	99.77 ± 0.07	D
3-Methylhexane	10	91.85	91.95	1.3887	1.3887	.....	A
3-Ethylpentane	11	93.55	93.47	1.3934	1.3934	.....	C
2,2-Dimethylpentane	12	79.1	79.21	1.3821	1.3822	99.31	A
2,3-Dimethylpentane	13	89.75	89.79	1.3916	1.3920	.....	A
2,4-Dimethylpentane	14	80.4	80.51	1.3815	1.3815	98.66	A
3,3-Dimethylpentane	15	86.1	86.07	1.3909	1.3909	.....	C
2,2,3-Trimethylbutane	16	80.9	80.87	1.3895	1.3895	99.7	E
8-carbon atom							
n-Octane	17	125.6	125.67	1.3976	1.3975	.....	C
2-Methylheptane	18	117.75	117.65	1.3952	1.3950	.....	C
3-Methylheptane	19	118.89	118.93	1.3985	1.3985	.....	C
4-Methylheptane	20	117.63	117.71	1.3978	1.3979	.....	C
3-Ethylhexane	21	118.55	118.54	1.4017	1.4016	.....	C
2,2-Dimethylhexane	22	106.9	106.84	1.3937	1.3935	.....	C
2,3-Dimethylhexane	23	115.6	115.61	1.4011	1.4013	.....	A
2,4-Dimethylhexane	24	109.35	109.43	1.3953	1.3953	.....	D
2,5-Dimethylhexane	25	109.2	109.1	1.3926	1.3925	.....	D
3,3-Dimethylhexane	26	111.95	111.97	1.4003	1.4001	.....	C
3,4-Dimethylhexane	27	117.45	117.73	1.4039	1.4042	.....	C
2-Methyl-3-ethylpentane	28	115.75	115.65	1.4040	1.4040	.....	C
3-Methyl-3-ethylpentane	29	118.28	118.26	1.4078	1.4078	.....	C
2,2,3-Trimethylpentane	30	109.85	109.84	1.4029	1.4030	.....	A
2,2,4-Trimethylpentane	31	99.23	99.24	1.3913	1.3915	.....	C
2,3,3-Trimethylpentane	32	114.7	114.76	1.4072	1.4075	.....	A
2,3,4-Trimethylpentane	33	113.45	113.47	1.4043	1.4042	99.38	A
9-carbon atom							
n-Nonane	34	150.8	150.80	1.4053	1.4055	.....	A
2-Methyloctane	35	.....	143.26	1.4035	1.4031	.....	B
3-Methyloctane	36	.....	144.18	....	1.4062	.....	B
4-Methyloctane	37	.....	142.48	....	1.4061	.....	B
3-Ethylheptane	38	.....	143.0	1.4095	1.4092	.....	B
4-Ethylheptane	39	.....	141.2	....	1.4109	.....	B
2,2-Dimethylheptane	40	.....	130.5	1.4032	1.402	.....	B
3,3-Dimethylheptane	41	.....	137.3	1.4090	1.4085	.....	B
3,4-Dimethylheptane	42	140.7	140.5	1.4115	1.4108	.....	B
3,5-Dimethylheptane	43	136.0	136.0	1.4067	1.407	.....	B
4,4-Dimethylheptane	44	135.2	138.0	1.4076	1.408	.....	B
2-Methyl-3-ethylhexane	45	138.0	139.0	1.4106	1.411	.....	B
2-Methyl-4-ethylhexane	46	133.8	136.0	1.4063	1.407	.....	B
3-Methyl-3-ethylhexane	47	140.6	143.0	1.4142	1.415	.....	B
3-Methyl-4-ethylhexane	48	140.4	143.0	1.4134	1.416	.....	B
2,2,4-Trimethylhexane	49	126.6	126.5	1.4034	1.4033	.....	B
2,2,5-Trimethylhexane	50	124.1	124.09	1.3996	1.3996	.....	A
2,3,3-Trimethylhexane	51	.....	138.0	1.4143	1.4143	.....	B
2,3,4-Trimethylhexane	52	139.1	140.0	1.4144	1.415	.....	B
2,3,5-Trimethylhexane	53	.....	131.37	....	1.4060	.....	B
2,4,4-Trimethylhexane	54	130.45	131	1.4072	1.4075	.....	B
3,3,4-Trimethylhexane	55	139.9	139	1.4178	1.4178	.....	B
2,2-Dimethyl-3-ethylpentane	56	133.6	133.83	1.4125	1.4123	.....	B
2,4-Dimethyl-3-ethylpentane	57	136.6	136.73	1.4138	1.4137	.....	B
2,2,3,4-Tetramethylpentane	58	133.0	133.01	1.4146	1.4146	.....	B
2,2,4,4-Tetramethylpentane	59	.....	122.28	1.4072	1.4068	.....	B
2,3,3,4-Tetramethylpentane	60	141.2	141.54	1.4222	1.4220	.....	B
10-carbon atom							
n-Decane	61	174.05	174.0[d]	1.4119	1.4114[d]	.....	A
2,2,6-Trimethylheptane	62	148.2	148.93[d]	1.4059	1.4078[d]	.....	B
2,3,6-Trimethylheptane	63	156.0	155.2[d]	1.4122	1.4130[d]	.....	B
2,2,3,3-Tetramethylhexane	64	159.8	159.0[d]	1.4281	1.4264[d]	.....	B
2,2,3,4-Tetramethylhexane	65	154.3	156.5[e]	1.4226	1.4224[e]	.....	B
2,2,3,5-Tetramethylhexane	66	148.4	.....	1.4142	.....	.....	B
2,2,4,5-Tetramethylhexane	67	148.2	.....	1.4132	1.4133[d]	.....	B
3,3,4,4-Tetramethylhexane	68	170.9	165.5[d]	1.4379	1.4340[d]	.....	B
11-carbon atom							
n-Undecane	69	195.9	195.8[d]	1.4174	1.4173[d]	.....	A
2,2,4,6-Tetramethylheptane	70	161.9	162.0[d]	1.4127	1.4127[d]	.....	B
12-carbon atom							
n-Dodecane	71	216.26	216.26[d]	1.4217	1.4216[d]	.....	B
2,2,3,5,6-Pentamethylheptane	72	188.8	.....	1.4283	.....	.....	B
2,2,4,6,6-Pentamethylheptane	73	177.8	177.2[d]	1.4189	1.4191[d]	.....	B
13-carbon atom							
n-Tridecane	74	106.8 at 10 mm.	236.5[d]	1.4256	.....	.....	B
14-carbon atom							
n-Tetradecane	75	121.1 at 10 mm.	253.5[d]	1.4290	1.4289[d]	.....	B
7-Methyltridecane	76	115.3 at 10 mm.	.....	1.4291	.....	.....	B

this frequency is shifted to about 1660 to 1685 cm.$^{-1}$ Compounds of these latter three types may show geometrical isomerism and in these cases the frequency is greater by at least 15 units for the trans- than for the cis-isomers.

Compounds which have the structure RHC=CHR′, where a hydrogen atom is present on both of the carbons which are connected by the double bond, show a Raman line between 1420 and 1428 cm.$^{-1}$ Pentene-1 and 2-methyl-1-butene are exceptions. This also holds in the cases of the diolefins studied.

In general, normal monoolefins and some diolefins have strong lines between 1290 and 1300 cm.$^{-1}$. The depolarization factor of the line varies from about 0.2 to 0.25 for the mono-olefins while for diolefins it is 0.3 or greater.

Mononuclear Aromatics. The Raman spectra of the aromatic hydrocarbons have, in general, lines which are quite intense, and sharp as compared with the rather wide bands of comparatively

[a] All physical properties except those marked [d] and [e] are from (*2*). Values from (*2*) are given only to nearest 0.01° C. in boiling point and 0.0001 in refractive index.

[b] Purities listed were determined by freezing point measurements. It is believed that all other materials were 98 mole % pure or higher.

[c] Source of compounds:
A. Petroleum Refining Laboratory, School of Chemistry and Physics, Pennsylvania State College.
B. Organic Research Laboratory, School of Chemistry and Physics, Pennsylvania State College.
C. American Petroleum Institute Research Project 45 at Ohio State University.
D. American Petroleum Institute Research Project 6 at National Bureau of Standards.
E. Esso Laboratories, Standard Oil Development Co.
F. Anglo-Iranian Oil Co., Sunbury-on-Thames, England.

[d] (*6*).
[e] (*7*).

Table III. Spectra Numbers and Properties of Pure Olefin Hydrocarbons

Name of Compound	Spectrum No.	Boiling Point at 760 Mm. of Hg, ° C. Determined	Boiling Point at 760 Mm. of Hg, ° C. Literature values[a]	Refractive Index at 20° C., n_D^{20} Determined	Refractive Index at 20° C., n_D^{20} Literature values[a]	Estimated Purity, Mole %[b]	Source of Compound[c]
Olefins							
5-carbon atom							
1-Pentene	77	30.0	29.97	1.3718	1.3714	.....	A
cis-2-Pentene	78	....	37.1	....	1.3820	99.55 ± 0.15	D
trans-2-Pentene	79	....	36.36	....	1.3793	99.91 ± 0.05	D
2-Methyl-1-butene	80	31.05	31.10	1.3776	1.3778	.....	A
2-Methyl-2-butene	81	38.6	38.53	1.3874	1.3874	.....	A
6-carbon atom							
2,3-Dimethyl-1-butene	82	55.6	55.64	1.3902	1.3904	.....	A
3,3-Dimethyl-1-butene	83	....	41.24	....	1.3760	99.7	B
7-carbon atom							
1-Heptene	84	93.65	93.3	1.3998	1.3994	.....	A
8-carbon atom							
1-Octene	85	121.25	121.27	1.4088	1.4088	.....	A
2,3,3-Trimethyl-1-pentene	86	118.5	108.	1.4188	1.418	.....	B
2,3,4-Trimethyl-1-pentene	87	117.15	108.	1.4136	1.415	.....	B
2,3,4-Trimethyl-2-pentene	88	116.5	116.26	1.4274	1.4275	.....	B
2,4,4-Trimethyl-1-pentene	89	101.55	101.44	1.4096	1.4086	.....	B
2,4,4-Trimethyl-2-pentene	90	103.9	104.91	1.4176	1.4160	.....	B
3,3,4-Trimethyl-1-pentene	91	....	105.	1.4144	1.414	.....	B
3-Methyl-2-isopropyl-1-butene	92	113.55	104.	1.4085	1.409	.....	B
3,3-Dimethyl-2-ethyl-1-butene	93	117.2	110.0	1.4159	1.416	.....	B
9-carbon atom							
3,3-Dimethyl-2-isopropyl-1-butene	94	121.6	121.6[d]	1.4168	1.4174[d]	.....	B
2,3,3,4-Tetramethyl-1-pentene	95	134.55	132.6[d]	1.4303	1.4305[d]	.....	B
10-carbon atom							
2,6,6-Trimethyl-1-heptene	96	150.4	....	1.4202	.....	.....	B
2,4,4,5-Tetramethyl-1-hexene	97	158.1	....	1.4350	.....	.....	B
Diolefins							
5-carbon atom							
2-Methyl-1,3-butadiene	98	....	34.08	1.4218	1.4216	.....	A
7-carbon atom							
2-Methyl-1,5-hexadiene	99	88.85	88.1[d]	1.4187	1.4184[d]	.....	B
9-carbon atom							
2,3,3,4-Tetramethyl-1,4-pentadiene	100	127.7	....	1.4402	.....	.....	B

[a] All physical properties except those marked [d] are from (*2*). Values taken from (*2*) are given only to nearest 0.01° C. in boiling point and 0.0001 in refractive index.

[b] Purities listed were determined by freezing point measurements. It is believed that all other materials were 98 mole % pure or higher.

[c] Sources of compounds:
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C. American Petroleum Institute Research Project 45 at Ohio State University.
D. American Petroleum Institute Research Project 6 at National Bureau of Standards.
E. Esso Laboratories, Standard Oil Development Co.
F. Anglo-Iranian Oil Co., Sunbury-on-Thames, England.

[d] (*6*).

Table IV. Spectra Numbers and Properties of Pure Naphthene Hydrocarbons-Alkylcyclopentanes

Name of Compound	Spectrum No.	Boiling Point at 760 Mm. of Hg, ° C. Determined	Boiling Point at 760 Mm. of Hg, ° C. Literature values[a]	Refractive Index at 20° C., n_D^{20} Determined	Refractive Index at 20° C., n_D^{20} Literature values[a]	Estimated Purity, Mole %[b]	Source of Compound[c]
5-carbon atom							
Cyclopentane	101	49.2	49.26	1.4065	1.4065	99.9+	A
6-carbon atom							
Methylcyclopentane	102	71.8	71.81	1.4098	1.4097	99.63	A
7-carbon atom							
Ethylcyclopentane	103	103.45	103.45	1.4197	1.4198	97.1	A
1,1-Dimethylcyclopentane	104	.....	87.5	1.4137	1.4135	.....	B
cis-1,2-Dimethylcyclopentane	105	99.1	99.25	1.4200	1.4221	.....	B
trans-1,2-Dimethylcyclopentane	106	91.85	91.85	1.4118	1.4119	.....	A
cis-1,3-Dimethylcyclopentane	107	90.5 at 725 mm.	.....	1.4081 at 25° C.	.....	.....	D
trans-1,3-Dimethylcyclopentane	108	89.4 at 725 mm.	90.97	1.4065 at 25° C.	1.4088	99.4 ± 0.12	D
8-carbon atom							
n-Propylcyclopentane	109	131.0	130.8[d]	1.4263	1.4266[d]	.....	A
Isopropylcyclopentane	110	126.4	126.4[d]	1.4260	1.4260[d]	.....	A
1-Methyl-1-ethylcyclopentane	111	121.45	.....	1.4269	.....	.....	B
cis-1-Methyl-3-ethylcyclopentane	112	121.0	.....	1.4202	.....	.....	B
1,1,2-Trimethylcyclopentane	113	113.7	114.0[d]	1.4228	1.4238[d]	.....	B
1,1,3-Trimethylcyclopentane	114	104.9	115–16[d]	1.4111.	1.4223[d]	.....	C
cis,cis,cis-1,2,3-Trimethylcyclopentane	115	122.8	.....	1.4263	.....	.....	B
cis,cis,trans-1,2,3-Trimethylcyclopentane	116	117.2	.....	1.4218	.....	.....	B
cis,trans,cis-1,2,3-Trimethylcyclopentane	117	109.9	.....	1.4133	.....	.....	B
cis,cis,trans-1,2,4-Trimethylcyclopentane	118	116.9	.....	1.4183	.....	.....	B
cis,trans,cis-1,2,4-Trimethylcyclopentane	119	109.0	.....	1.4103	.....	.....	B
9-carbon atom							
2-Cyclopentylbutane	120	154.4	154.6[d]	1.4360	1.4361[d]	.....	A
10-carbon atom							
2-Cyclopentylpentane	121	176.5	177.5[d]	1.4393	1.4438[d]	.....	A
12-carbon atom							
2-Cyclopentylheptane	122	219.0	.....	1.4450	.....	.....	A

[a] All physical properties except those marked [d] are from (*2*). Values from (*2*) are given only to nearest 0.01° C. in boiling point and 0.0001 in refractive index.

[b] Purities listed were determined by freezing point measurements. It is believed that all other materials were 98 mole % pure or higher.

[c] Sources of compounds:
A. Petroleum Refining Laboratory, School of Chemistry and Physics, Pennsylvania State College.
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E. Esso Laboratories, Standard Oil Development Co.
F. Anglo-Iranian Oil Co., Sunbury-on-Thames, England.

[d] (*6*).

Table V. Spectra Numbers and Properties of Pure Naphthene Hydrocarbons-Alkylcyclohexanes

Name of Compound	Spectrum No.	Boiling Point at 760 Mm. of Hg, ° C. Determined	Boiling Point at 760 Mm. of Hg, ° C. Literature values[a]	Refractive Index at 20° C., n_D^{20} Determined	Refractive Index at 20° C., n_D^{20} Literature values[a]	Estimated Purity, Mole %[b]	Source of Compound[c]
6-carbon atom							
Cyclohexane	123	80.8	80.74	1.4263	1.4262	.....	A
7-carbon atom							
Methylcyclohexane	124	100.8	100.94	1.4231	1.4231	.....	A
8-carbon atom							
Ethylcyclohexane	125	131.7	131.79	1.4330	1.4330	.....	A
1,1-Dimethylcyclohexane	126	....	119.50	....	1.4289	99.81 ± 0.03	D
cis-1,2-Dimethylcyclohexane	127	129.65	129.73	1.4360	1.4360	.....	A
trans-1,2-Dimethylcyclohexane	128	123.35	123.42	1.4270	1.4270	.....	A
cis-1,4-Dimethylcyclohexane	129	124.3	124.32	1.4296	1.4297	.....	A
trans-1,4-Dimethylcyclohexane	130	119.3	119.35	1.4209	1.4209	.....	A
9-carbon atom							
n-Propylcyclohexane	131	156.6	154.9–155.0[d]	1.4370	1.4370[d]	.....	A
Isopropylcyclohexane	132	154.4	154.4[d]	1.4410	1.4408[d]	.....	A

[a] All physical properties except those marked [d] are from (*2*). Values from (*2*) are given only to the nearest 0.01° C. in boiling point and 0.0001 in refractive index.

[b] Purities listed were determined by freezing point measurements. It is believed that all other materials were 98 mole % pure or higher.

[c] Source of compounds:
A. Petroleum Refining Laboratory, School of Chemistry and Physics, Pennsylvania State College.
B. Organic Research Laboratory, School of Chemistry and Physics, Pennsylvania State College.
C. American Petroleum Institute Research Project 45 at Ohio State University.
D. American Petroleum Institute Research Project 6 at National Bureau of Standards.
E. Esso Laboratories, Standard Oil Development Co.
F. Anglo-Iranian Oil Co., Sunbury-on-Thames, England.

[d] (*6*).

Table VI. Spectra Numbers and Properties of Pure Cyclo-olefin Hydrocarbons

Name of Compound	Spectrum No.	Boiling Point at 760 Mm. of Hg, ° C. Determined	Boiling Point at 760 Mm. of Hg, ° C. Literature values[a]	Refractive Index at 20° C., n_D^{20} Determined	Refractive Index at 20° C., n_D^{20} Literature values[a]	Estimated Purity, Mole[b] %	Source of Compound[c]
Methylenecyclobutane	133	42.2	41.9[d]	1.4210	1.4204[d]	..	B
1-Methyl-1-cyclopentene	134	75.6	75.85[d]	1.4319	.....	..	B
3-Methyl-1-cyclopentene	135	65.2	.....	1.4215	1.4248[d]	..	B
cis-3,4-Dimethyl-1-cyclopentene	136	....	.....	1.4300	.....	..	B
1,2,3-Trimethyl-1-cyclopentene	137	121.9	121.0[d]	1.4457	1.4445[d]	..	B
2,3,3-Trimethyl-1-cyclopentene	138	110.65	108.5[e]	1.4345	1.4324[d]	..	B
2,3,4-Trimethyl-1-cyclopentene	139	112.3	.....	1.4345	.....	..	B
Cyclohexene	140	....	83.19[d]	1.4464	1.4467[d]	..	A

[a] All physical properties except those marked [d] and [e] are from (*2*). Values taken from (*2*) are given only to nearest 0.01° C. in boiling point and 0.0001 in refractive index.

[b] Purities listed were determined by freezing point measurements. It is believed that all other materials were 98 mole % pure or higher.

[c] Sources of compounds:
A. Petroleum Refining Laboratory, School of Chemistry and Physics, Pennsylvania State College.
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C. American Petroleum Institute Research Project 45 at Ohio State University.
D. American Petroleum Institute Research Project 6 at National Bureau of Standards.
E. Esso Laboratories, Standard Oil Development Co.
F. Anglo-Iranian Oil Co., Sunbury-on-Thames, England.

[d] (*6*).
[e] (*7*).

Table VII. Spectra Numbers and Properties of Pure Aromatic Hydrocarbons

Name of Compound	Spectrum No.	Boiling Point at 760 Mm. of Hg, ° C. Determined	Boiling Point at 760 Mm. of Hg, ° C. Literature values[a]	Refractive Index at 20° C., n_D^{20} Determined	Refractive Index at 20° C., n_D^{20} Literature values[a]	Estimated Purity, Mole %[b]	Source of Compound[c]
6-carbon atom							
Benzene	141	80.1	80.10	1.5012	1.5011	.....	A
7-carbon atom							
Methylbenzene (toluene)	142	110.65	110.63	1.4969	1.4969	.....	A
8-carbon atom							
Ethylbenzene	143	136.25	136.19	1.4959	1.4958	.....	A
1,2-Dimethylbenzene (*o*-xylene)	144	144.4	144.42	1.5053	1.5052	.....	A
1,3-Dimethylbenzene (*m*-xylene)	145	139.15	139.10	1.4972	1.4972	.....	E
1,4-Dimethylbenzene (*p*-xylene)	146	138.4	138.35	1.4958	1.4958	.....	A
9-carbon atom							
n-Propylbenzene	147	159.25	159.22	1.4919	1.4920	.....	A
Isopropylbenzene	148	152.4	152.40	1.4910	1.4913	.....	A
1-Methyl-2-ethylbenzene	149	165.15	165.15	1.5042	1.5044	99.1	A
1-Methyl-3-ethylbenzene	150	161.4	161.30	1.4965	1.4965	95.8	A
1-Methyl-4-ethylbenzene	151	161.95	162.05	1.4948	1.4950	95.3	A
1,2,3-Trimethylbenzene	152	176.1	176.15	1.5140	1.5139	.....	A
1,2,4-Trimethylbenzene	153	169.2	169.25	1.5049	1.5048	.....	A
1,3,5-Trimethylbenzene	154	164.7	164.70	1.4992	1.4991	.....	A
10-carbon atom							
n-Butylbenzene	155	183.1	183.28	1.4900	1.4900	.....	A
Isobutylbenzene	156	....	172.80	....	1.4865	99.87 ± 0.09	D
sec-Butylbenzene	157	173.15	173.30	1.4900	1.4902	.....	A
tert-Butylbenzene	158	169.1	169.10	1.4926	1.4927	.....	A
1-Methyl-2-isopropylbenzene	159	178.35	178.3	1.5006	1.5006	99.9	F
1-Methyl-3-isopropylbenzene	160	175.20	175.2	1.4930	1.4930	99.96	F
1-Methyl-4-isopropylbenzene	161	177.15	177.10	1.4905	1.4909	.....	A
1,2-Dimethyl-3-ethylbenzene	162	193.80	193.91	1.5117	1.5117	99.6	F
1,2-Dimethyl-4-ethylbenzene	163	189.55	189.75	1.5032	1.5031	99.6	F
1,3-Dimethyl-2-ethylbenzene	164	189.95	190.01	1.5107	1.5107	99.84	F
1,3-Dimethyl-4-ethylbenzene	165	188.45	188.41	1.5039	1.5038	99.95	F
1,3-Dimethyl-5-ethylbenzene	166	183.65	183.75	1.4981	1.4981	99.93	F
1,4-Dimethyl-2-ethylbenzene	167	186.45	186.91	1.5043	1.5043	99.8	F
1,2-Diethylbenzene	168	183.30	184.5	1.5034	1.5034	99.85	F
1,3-Diethylbenzene	169	181.2	181.14	1.4953	1.4955	99.4	A
1,4-Diethylbenzene	170	183.60	183.75	1.4947	1.4947	99.65	F

[a] Physical properties from (*2*) are given only to nearest 0.01° C. in boiling point and 0.0001 in refractive index.

[b] Purities listed were determined by freezing point measurements. It is believed that all other materials were 98 mole % pure or higher.

[c] Sources of compounds:
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B. Organic Research Laboratory, School of Chemistry and Physics, Pennsylvania State College.
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D. American Petroleum Institute Research Project 6 at National Bureau of Standards.
E. Esso Laboratories, Standard Oil Development Co.
F. Anglo-Iranian Oil Co., Sunbury-on-Thames, England.

Table VIII. Spectra Numbers and Properties of Miscellaneous Pure Hydrocarbons

Name of Compound	Spectrum No.	Boiling Point at 760 Mm. of Hg, ° C. Determined	Boiling Point at 760 Mm. of Hg, ° C. Literature values[a]	Refractive Index at 20° C., n_D^{20} Determined	Refractive Index at 20° C., n_D^{20} Literature values[a]	Estimated Purity, Mole %[b]	Source of Compound[c]
Indene	171	182.57	181.8–182.3[d]	1.5766	1.5764[d]	..	A
Hydrindene	172	177.85	177.5–178.5[d]	1.5383	1.5383[d]	..	A

[a] All physical properties except those marked [d] are from (*2*). Values taken from (*2*) are given only to nearest 0.01° C. in boiling point and 0.0001 in refractive index.
[b] Purities listed were determined by freezing point measurements. It is believed that all other materials were 98 mole % pure or higher.
[c] Sources of compounds:
A. Petroleum Refining Laboratory, School of Chemistry and Physics, Pennsylvania State College.
B. Organic Research Laboratory, School of Chemistry and Physics, Pennsylvania State College.
C. American Petroleum Institute Research Project 45 at Ohio State University.
D. American Petroleum Institute Research Project 6 at National Bureau of Standards.
E. Esso Laboratories, Standard Oil Development Co.
F. Anglo-Iranian Oil Co., Sunbury-on-Thames, England.
[d] (*6*)

low intensity obtained for many of the paraffins and olefins. All the aromatics have in common one or two rather strong lines near 1600 cm.$^{-1}$, believed by many investigators to correspond to the 1650 cm.$^{-1}$ line of the C=C group found in olefins. In addition, all substituted aromatics, where a methyl group is attached directly to the ring, show a rather strong line between 1373 and 1393 cm.$^{-1}$ (scattering coefficient = 0.05 to 0.25). Also, in common with all substituted aromatics, where the substituting group contains the CH_3 group, is a Raman line between 1430 and 1460 cm.$^{-1}$

Monosubstituted Aromatics. All monosubstituted aromatics retain some of the strong Raman lines of benzene with but slight shifts of frequency. The lines most characteristic of this group are at about 617, 1001, 1030, and 1200 cm.$^{-1}$ The line at 614 to 620 cm.$^{-1}$ (scattering coefficient greater than 0.1, depolarization factor = 0.65 to 0.88) is easily distinguished from lines of other compounds in this range by its comparatively high intensity and by its depolarization factor. The Raman line at 999 to 1006 cm.$^{-1}$ is very intense (scattering coefficient = 0.55 to 0.9, depolarization factor = 0.1 to 0.2) but polysubstituted compounds where the substitution is in the 1,3-position also have lines in this region which cannot be distinguished from the lines characteristic of monosubstitution. The Raman line at 1025 to 1035 cm.$^{-1}$ for monosubstituted aromatics (scattering coefficient = 0.1 to 0.28, depolarization factor = 0.1 to 0.2) occurs with strong lines for 1,2-disubstituted molecules in the region of 1030 to 1050 cm.$^{-1}$ although, in general, the scattering coefficients for these disubstituted compounds are somewhat greater than for the lines of the monosubstituted type.

The Raman line for monosubstituted compounds at 1183 to 1208 cm.$^{-1}$ (scattering coefficient = 0.11 to 0.3) lies in the same region as that characteristic of 1,4-disubstituted molecules.

Disubstituted Aromatics. Characteristic of 1,2-disubstitution is a strong Raman line between 1030 and 1050 cm.$^{-1}$ (scattering coefficient = 0.23 to 0.45) and in approximately the same range as a line of the monosubstituted molecule. Between 1313 and 1330 cm.$^{-1}$ all polysubstituted aromatics where substitution is in the 1,2 position have a weak Raman line (scattering coefficient = 0.015 to 0.11). The 1600 cm.$^{-1}$ Raman line common to all aromatics is generally split into a pair of lines approximately 20 to 25 cm.$^{-1}$ apart for 1,2-disubstituted aromatics.

The 1,3-disubstitution is characterized by a rather strong Raman line (scattering coefficient = 0.1 to 0.18, depolarization factor = 0.7 to 0.9) between 638 and 641 cm.$^{-1}$ as well as a strong line between 1187 and 1200 cm.$^{-1}$ (scattering coefficient = 0.15 to 0.35). The latter line occurs in the same region as one of the monosubstituted type.

Trisubstituted Aromatics. 1,2,3- and 1,2,4-trisubstituted aromatic hydrocarbons show strong Raman lines between 465 and 480 cm.$^{-1}$ The 1,2,3- lines lie between 479 and 482 cm.$^{-1}$ (scattering coefficient = 0.1, depolarization factor = 0.64 to 0.76) while those of the 1,2,4- type lie between 465 and 476 cm.$^{-1}$ (scattering coefficient = 0.08 to 0.22, depolarization factor = 0.3 to 0.5).

A Raman line at 990 to 995 cm.$^{-1}$ with a high intensity (scattering coefficient = 0.45 to 0.7) occurs only for the 1,3,5-trisubstitution. The 1,3-disubstituted and 1,2,3-trisubstituted molecules may have lines in this region but can generally be distinguished *from the 1,3,5- lines* either because of their lesser intensity or because they are located closer to 1000 cm.$^{-1}$

In the 1,2,3- and the 1,3,5-trisubstituted and probably in all the hexasubstituted aromatics, the 1600 cm.$^{-1}$ line is not split into a pair as in the case of the 1,2-disubstituted compounds.

Alkyl Cyclopentanes. Cyclopentane, its monosubstituted, its 1,1- and 1,2-disubstituted, and its 1,1,2-trisubstituted compounds can be recognized by their characteristic line between 884 and 899 cm.$^{-1}$ The intensity of this line decreases as the length of the side chain increases. The depolarization factor is low.

The 1,3-disubstituted and the 1,1,3- and 1,2,3-trisubstituted compounds do not show a strong line in this region.

All the cyclopentanes have a common line between 1450 and 1470 cm.$^{-1}$ In general, this line lies below 1460 cm.$^{-1}$ except when the substitution is in the 1,3-position.

CATALOG OF SPECTRA

The usefulness of any spectrographic method of analysis depends in part on the availability of a set of reference spectra of the pure materials which are apt to be present in the sample under examination. For qualitative purposes the spectra of the unknown and known materials can be compared visually. For quantitative analytical work accurate values of the wave number shifts and scattering coefficients must be known. In the present study on hydrocarbon mixtures the spectra of a large number of relatively pure hydrocarbons have been measured and assembled. These are presented here both as reproductions of the original records obtained with the recording spectrograph and as tables for quantitative analytical purposes.

Such spectra enable the spectroscopist to foresee the difficulties attending a particular analysis, and possibly, with the aid of similar infrared and ultraviolet spectrograms now being distributed by the American Petroleum Institute (*1*), to select the best method for making the analysis.

In common with all other spectroscopic methods of analysis, the reproducibility and accuracy of the Raman procedure are dependent upon certain instrument constants. Accordingly, for the best quantitative work each spectrograph must be calibrated with a complete set of the known pure hydrocarbons which will be found in the samples to be analyzed.

The limitations which govern the applicability of the data concern only the intensity values. The wave number shifts and depolarization factors should, of course, be independent of the instrument used. The main reason for the discrepancy between intensities measured on different instruments is the combined effect of the variation of the degree of polarization of the Raman lines and the difference between the various instruments in transmitting the two polarized components of unpolarized light. The number of reflecting surfaces and their inclination to the path of the light through the spectrograph determine the fraction of each kind of polarized light which will be transmitted. For the instrument described here the ratio of the amount of the parallel polarized component of unpolarized light to that of the perpendicularly polarized component is 0.9, while for an older prism instrument (*22*) the ratio is 0.3. This difference in the transmittances causes a considerable difference in the scattering coefficients of the various lines in the spectrum of carbon tetrachloride. The scattering coefficient of the $\Delta\nu$ = 313 cm.$^{-1}$ (depolarized) line is 0.82 for the grating instrument and 0.66 for the prism instrument.

A second factor which may cause variations in intensities among different instruments is the combined effect of the spec-

trograph resolution and the Raman line width. In order that enough light flux may be obtained at the phototube when recording Raman spectra photoelectrically it is necessary to open the slits more than is sometimes required for photographic work. Although most Raman lines have a considerable width and may be wider than the slits, some are also narrower and their shape and apparent intensity on the recording will vary with the slit width.

All the spectra presented here were obtained using the 4358 Å. mercury line as the exciting frequency, and since the 4347 and 4339 Å. mercury lines could not be removed some very weak Raman lines due to them are shown in the records. The intensities of these triply excited Raman lines for the 4358, 4347, and 4339 Å. mercury lines are in the ratio of about 1:1/15:1/30, respectively. Since the main utility of these spectra will be for analytical work and since these triply excited lines occur only for strong Raman lines, they have been included in the tabular data given here. The wave number shifts have been calculated as though they originated from the 4358 Å. mercury line.

The values recorded for the Raman frequencies in the tabular data are correct to within ± 5 cm.$^{-1}$ Experimental data have been reported exclusively rather than the values corrected to agree with the averages reported by other investigators. The values for the depolarization factors listed in the tabular data are believed to be most accurate where the Raman lines are isolated and somewhat less accurate where the lines are relatively close together. The latter values are, however, still useful for the assignment of molecular vibrations.

The spectra presented are divided into groups according to molecular structure, each group being then arranged in order of molecular weight and of increasing complexity of structure. The groups are: paraffins, olefins and diolefins, naphthenes (including alkylcyclopentanes and alkylcyclohexanes), aromatics, and miscellaneous hydrocarbons.

The indexes of the spectra, given in Tables II to VIII list in addition to the name and the spectrum number the physical properties of the compounds examined, the best literature data on the properties (*2*, *6*, *7*), the sources, and, when known, the purities of the hydrocarbons. In many cases the purities have not been separately determined. However, the physical properties and the methods of preparation indicate that the purities are 98 mole % or higher.

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On the following pages (712 to 765) will be found data in the form of graphs and tables on the Raman spectra of 172 hydrocarbons. Indexes for these graphs and tables are given in Tables II to VIII.

Raman Spectral Data for Hydrocarbons

No. 1. *n*-Pentane

$\Delta\nu$, cm.$^{-1}$	Scattering Coefficient	ρ
336	0.020	..
400	0.075	0.3
468	0.019	..
764	0.024	..
841	0.080	0.2
866	0.064	0.3
911	0.019	0.9
1031	0.048	..
1075	0.051	0.87
1148	0.026	..
1308	0.050	0.67
1457	0.144	0.74

No. 2. 2-Methylbutane

368	0.024	..
459	0.063	..
765	0.112	0.1
794	0.086	0.2
907	0.052	0.5
953	0.038	0.7
1019	0.053	0.6
1036	0.056	..
1154	0.043	0.7
1175	0.043	0.6
1280	0.015	..
1301	0.015	..
1343	0.031	0.5
1460	0.139	0.75

No. 3. *n*-Hexane

186	0.026	..
311	0.031	..
371	0.035	..
404	0.015	..
820	0.034	0.2
870	0.037	..
894	0.062	0.3
1009	0.024	0.6
1044	0.045	0.4
1082	0.049	0.74
1142	0.026	0.4
1306	0.064	0.89
1452	0.156	0.88

No. 4. 2-Methylpentane

325	0.037	0.3
382	0.009	..
442	0.064	..
734	0.014	..
815	0.091	0.2
892	0.031	..
954	0.040	0.6
1041	0.046	0.4
1154	0.049	0.6
1176	0.036	0.8
1306	0.032	0.9
1344	0.030	0.8
1458	0.143	0.85

No. 5. 3-Methylpentane

191	0.032	..
311	0.008	..
387	0.022	..
445	0.56	..
750	0.061	..
819	0.047	..
882	0.029	0.9
974	0.044	0.6
1046	0.066	0.3
1162	0.036	0.5
1282	0.026	0.7
1360	0.021	..
1459	0.145	0.81

No. 6. 2,2-Dimethylbutane

194	0.020	..
260	0.013	..
344	0.041	0.8
361	0.044	0.5
411	0.017	..
484	0.029	..
612	0.017	..
659	0.018	..
714	0.287	0.08
873	0.051	0.89
929	0.094	0.76
1021	0.036	0.7
1080	0.022	..
1221	0.073	0.86
1258	0.053	0.76
1313	0.020	0.9
1458	0.179	0.84

No. 7. 2,3-Dimethylbutane

477	0.033	..
502	0.029	..
730	0.161	0.09
754	0.091	0.2
868	0.035	0.7
939	0.117	0.57
1038	0.041	0.7
1165	0.060	0.62
1200	0.035	0.5
1306	0.044	0.7
1348	0.031	0.9
1461	0.134	0.77

No. 8. *n*-Heptane

185	0.017	..
309	0.061	0.4
393	0.013	..
775	0.009	..
836	0.042	0.3
903	0.044	0.3
1081	0.055	0.83
1140	0.028	0.6
1307	0.066	0.76
1450	0.158	0.84

No. 9. 2-Methylhexane

311	0.101	0.2
410	0.037	..
430	0.045	..
612	0.016	..
732	0.012	..
782	0.062	..
822	0.093	..
877	0.062	0.3
896	0.076	0.4
928	0.033	0.9
957	0.062	0.9
1010	0.016	..
1040	0.041	0.3
1073	0.064	0.6
1148	0.066	0.6
1179	0.054	0.7
1213	0.016	0.9
1309	0.076	0.74
1345	0.056	0.73
1393	0.025	0.5
1464	0.243	0.73

No. 10. 3-Methylhexane

326	0.035	..
436	0.032	..
768	0.023	..
816	0.027	..
876	0.033	0.8
929	0.031	..
984	0.045	..
1036	0.074	0.4
1158	0.047	0.6
1300	0.033	0.7
1356	0.018	..
1456	0.171	0.80

No. 11. 3-Ethylpentane

230	0.005	..
306	0.016	..
397	0.041	0.2
447	0.041	0.3
546	0.012	..
735	0.076	0.1
832	0.040	..
901	0.065	0.88
1007	0.064	0.67
1039	0.077	0.62
1164	0.038	0.9
1279	0.033	0.6
1307	0.027	0.9
1367	0.019	..
1461	0.156	0.76

No. 12. 2,2-Dimethylpentane

324	0.061	..
340	0.069	0.56
496	0.052	..
693	0.013	..
746	0.165	0.08
880	0.070	0.61
928	0.091	0.70
1044	0.060	0.5
1105	0.025	..
1210	0.070	0.56
1254	0.052	0.64
1275	0.025	..
1320	0.023	0.7
1458	0.165	0.82

No. 13. 2,3-Dimethylpentane

315	0.018	..
425	0.026	..
459	0.027	..
553	0.014	..
710	0.041	..
747	0.067	..
789	0.017	..
849	0.033	0.7
915	0.058	0.5
960	0.060	0.62
1041	0.047	0.3
1166	0.053	0.6
1185	0.033	0.7
1289	0.030	0.8
1311	0.033	0.9
1356	0.021	..
1457	0.143	0.81

No. 14. 2,4-Dimethylpentane

306	0.054	0.5
414	0.019	..
466	0.069	0.3
750	0.013	..
810	0.167	0.1
869	0.011	..
924	0.056	0.4
956	0.068	1.
986	0.018	..
1039	0.010	..
1164	0.081	0.67
1254	0.020	..
1328	0.055	0.7
1348	0.062	0.72
1462	0.144	0.79

No. 15. 3,3-Dimethylpentane

238	0.009	..
351	0.030	0.5
376	0.031	0.5
410	0.022	..
443	0.018	..
482	0.022	..
594	0.006	..
638	0.014	..
695	0.203	0.07
854	0.052	0.8
917	0.062	0.76
934	0.047	0.8
1007	0.061	0.7
1031	0.050	0.6
1085	0.043	0.3
1200	0.050	0.85
1217	0.050	0.8
1236	0.034	0.8
1296	0.019	0.9
1345	0.019	0.9
1396	0.015	0.9
1456	0.166	0.93

No. 16. 2,2,3-Trimethylbutane

364	0.038	0.7
449	0.017	..
520	0.040	..
630	0.026	..
686	0.248	0.1
830	0.034	0.9
920	0.179	0.65
1000	0.010	..
1090	0.021	..
1110	0.021	..
1220	0.079	0.86
1255	0.058	0.82
1331	0.036	0.9
1460	0.129	0.78

No. 17. *n*-Octane

189	0.020	..
285	0.056	..
811	0.014	..
851	0.026	..
889	0.041	0.3
969	0.015	..
1036	0.039	0.4
1070	0.060	0.58
1083	0.062	0.55
1144	0.028	..
1207	0.006	..
1307	0.072	0.71
1453	0.158	0.74
1464	0.133	0.77

No. 18. 2-Methylheptane

289	0.049	..
317	0.021	..
384	0.015	..
406	0.019	..
434	0.015	..
458	0.006	..
758	0.013	..
814	0.046	..
890	0.024	..
958	0.030	0.8
1066	0.034	0.6
1084	0.029	0.6
1149	0.035	0.4
1177	0.022	0.4
1214	0.005	..
1311	0.047	0.9
1344	0.030	0.9
1461	0.133	0.79

No. 19. 3-Methylheptane

306	0.036	..
765	0.034	..
820	0.032	..
874	0.034	..
898	0.056	..
980	0.032	..
1044	0.048	..
1073	0.042	..
1156	0.042	0.4
1306	0.038	1.
1352	0.016	..
1454	0.175	0.76

No. 20. 4-Methylheptane

316	0.075	0.3
418	0.018	..
451	0.018	..
824	0.043	..
874	0.034	..
910	0.033	..
1042	0.070	0.7
1156	0.043	0.5
1304	0.046	1.
1450	0.150	1.

No. 21. 3-Ethylhexane

338	0.028	..
434	0.025	..
754	0.023	..
823	0.025	..
886	0.049	..
914	0.032	..
1042	0.096	0.43
1156	0.042	0.6
1301	0.033	0.6
1459	0.201	0.80

No. 22. 2,2-Dimethylhexane

303	0.084	0.4
339	0.031	0.7
465	0.019	..
495	0.035	..
746	0.108	..
874	0.053	..
912	0.087	0.60
928	0.097	0.71
1067	0.042	0.5
1105	0.030	0.3
1204	0.058	0.56
1251	0.083	0.79
1320	0.038	0.7
1456	0.177	0.75

Raman Spectral Data for Hydrocarbons (*Continued*)

No. 23. 2,3-Dimethylhexane

$\Delta\nu$, cm.$^{-1}$	Scattering Coefficient	ρ
316	0.032	0.4
402	0.012	..
457	0.019	..
723	0.030	..
765	0.050	..
788	0.021	..
849	0.023	..
871	0.026	0.3
901	0.049	0.3
951	0.030	0.9
1009	0.026	0.4
1055	0.037	0.6
1163	0.045	0.7
1192	0.029	0.8
1244	0.008	..
1311	0.054	0.7
1354	0.018	..
1457	0.140	0.81

No. 24. 2,4-Dimethylhexane

189	0.022	..
313	0.037	0.3
420	0.028	..
447	0.043	..
510	0.011	..
768	0.040	..
823	0.083	0.1
859	0.009	..
909	0.024	0.8
960	0.046	0.8
997	0.027	0.9
1049	0.014	..
1165	0.062	0.83
1241	0.012	..
1274	0.012	..
1349	0.032	0.8
1458	0.161	0.80
1465	0.156	0.69

No. 25. 2,5-Dimethylhexane

187	0.023	..
263	0.025	..
311	0.026	..
440	0.039	..
778	0.031	..
840	0.082	..
911	0.017	0.7
963	0.056	0.82
1051	0.019	..
1096	0.011	..
1154	0.051	0.7
1175	0.047	0.7
1305	0.040	0.9
1341	0.077	1.
1369	0.025	..
1459	0.155	0.84
1467	0.145	0.79

No. 26. 3,3-Dimethylhexane

324	0.045	..
366	0.038	..
492	0.038	..
722	0.124	..
852	0.038	..
912	0.038	0.9
1019	0.056	0.6
1045	0.062	0.5
1100	0.032	..
1208	0.058	0.76
1306	0.030	..
1454	0.169	0.94

No. 27. 3,4-Dimethylhexane

338	0.023	..
430	0.040	..
471	0.023	..
738	0.031	..
898	0.023	..
984	0.048	..
1039	0.067	..
1169	0.040	..
1286	0.035	..
1456	0.162	0.89

No. 28. 2-Methyl-3-ethylpentane

229	0.015	..
319	0.026	..
389	0.011	0.9
448	0.029	0.5
477	0.024	..
556	0.027	..
605	0.008	..
720	0.059	..
767	0.011	..
821	0.032	0.2
864	0.022	0.9
913	0.035	0.8
949	0.048	0.5
1044	0.079	0.5
1133	0.015	..
1166	0.042	0.7
1183	0.031	0.5
1274	0.022	0.7
1317	0.027	0.9
1370	0.019	..
1460	0.146	0.78

No. 29. 3-Methyl-3-ethylpentane

380	0.041	..
408	0.054	..
475	0.017	..
681	0.186	..
875	0.081	0.80
960	0.047	1.
1022	0.095	0.52
1088	0.057	0.2
1192	0.049	0.7
1279	0.033	..
1348	0.032	..
1388	0.032	..
1454	0.192	0.85

No. 30. 2,2,3-Trimethylpentane

319	0.063	0.7
388	0.026	..
456	0.027	..
526	0.083	..
607	0.013	..
657	0.022	..
717	0.168	0.08
827	0.030	0.7
892	0.071	0.3
927	0.112	0.67
975	0.068	0.5
1029	0.038	..
1082	0.023	..
1220	0.062	0.82
1245	0.056	1.
1313	0.015	..
1350	0.015	..
1457	0.163	0.70

No. 31. 2,2,4-Trimethylpentane

189	0.012	..
301	0.046	0.6
423	0.010	..
512	0.050	..
695	0.013	..
749	0.166	0.06
829	0.029	..
904	0.063	0.66
931	0.076	0.82
959	0.029	0.9
1023	0.011	..
1106	0.034	0.6
1179	0.017	0.8
1212	0.056	0.76
1254	0.053	0.76
1292	0.028	0.5
1361	0.021	0.9
1460	0.167	0.79
1473	0.134	0.80

No. 32. 2,3,3-Trimethylpentane

371	0.044	0.5
422	0.025	..
470	0.032	..
534	0.021	..
676	0.178	0.1
826	0.022	0.9
900	0.060	0.7
929	0.119	0.66
1016	0.048	0.5
1047	0.025	..
1089	0.031	..
1114	0.020	..
1218	0.055	0.7
1236	0.044	0.9
1302	0.017	..
1336	0.030	0.6
1458	0.147	0.89
1473	0.131	0.87

No. 33. 2,3,4-Trimethylpentane

318	0.026	..
417	0.026	..
472	0.077	..
572	0.033	..
695	0.011	..
756	0.134	0.1
816	0.033	0.7
895	0.050	..
935	0.067	0.70
956	0.057	0.79
1000	0.050	0.4
1168	0.066	0.61
1185	0.061	0.68
1325	0.064	1.
1355	0.027	1.
1461	0.149	0.76

No. 34. *n*-Nonane

261	0.032	..
836	0.030	..
872	0.038	..
891	0.047	0.2
1078	0.052	0.90
1140	0.032	..
1305	0.084	0.93
1452	0.158	0.72

No. 35. 2-Methyloctane

190	0.029	..
256	0.034	..
391	0.018	..
790	0.018	..
826	0.036	..
886	0.018	..
961	0.021	..
1079	0.029	0.9
1148	0.034	0.9
1175	0.019	..
1310	0.048	0.79
1345	0.029	..
1457	0.143	0.78

No. 36. 3-Methyloctane

229	0.014	..
272	0.020	..
295	0.016	..
388	0.013	..
422	0.016	..
470	0.013	..
600	0.011	..
709	0.011	..
770	0.027	..
846	0.020	..
919	0.017	..
967	0.021	..
1041	0.057	0.3
1069	0.054	0.6
1089	0.036	0.3
1113	0.020	..
1155	0.042	0.5
1211	0.019	0.8
1286	0.043	0.7
1311	0.066	0.5
1360	0.046	0.3
1459	0.182	0.76

No. 37. 4-Methyloctane

290	0.035	0.6
414	0.015	..
439	0.018	..
455	0.018	..
739	0.019	..
830	0.032	0.4
874	0.035	0.4
893	0.056	0.7
941	0.016	0.6
1044	0.056	0.6
1066	0.060	0.6
1155	0.051	0.8
1210	0.012	..
1309	0.079	0.84
1459	0.194	0.77

No. 38. 3-Ethylheptane

300	0.026	..
457	0.014	..
752	0.019	..
836	0.024	..
894	0.040	..
941	0.027	..
1047	0.061	0.3
1161	0.031	..
1282	0.024	..
1310	0.034	1.
1457	0.169	0.86

No. 39. 4-Ethylheptane

194	0.035	..
318	0.061	0.4
433	0.021	0.7
612	0.011	..
727	0.031	0.4
773	0.027	0.4
812	0.040	0.3
848	0.039	0.5
897	0.066	0.5
960	0.021	0.5
1047	0.112	0.5
1076	0.053	0.3
1154	0.047	0.6
1207	0.011	0.5
1244	0.014	..
1282	0.034	0.5
1306	0.074	0.59
1456	0.228	0.84

No. 40. 2,2-Dimethylheptane

188	0.028	..
283	0.033	..
348	0.017	..
414	0.012	..
750	0.068	..
930	0.070	0.78
1068	0.033	..
1112	0.019	..
1202	0.033	0.7
1251	0.049	0.5
1314	0.042	0.87
1455	0.170	0.80
1469	0.135	0.88

No. 41. 3,3-Dimethylheptane

190	0.019	..
242	0.013	..
305	0.053	..
478	0.029	..
724	0.096	..
884	0.053	..
939	0.041	..
1023	0.038	0.4
1060	0.044	0.5
1104	0.038	..
1200	0.042	0.7
1320	0.026	0.7
1401	0.015	..
1452	0.184	0.80
1472	0.122	0.85

Raman Spectral Data for Hydrocarbons (*Continued*)

No. 42. 3,4-Dimethylheptane

Δν, cm.⁻¹	Scattering Coefficient	ρ
189	0.021	..
305	0.025	0.6
329	0.022	0.6
428	0.020	..
730	0.022	..
751	0.024	..
795	0.018	..
845	0.025	..
891	0.035	..
931	0.014	..
969	0.028	0.4
988	0.031	0.4
1035	0.047	0.3
1166	0.037	0.8
1301	0.032	0.9
1359	0.015	..
1455	0.161	0.76
1465	0.147	0.79

No. 43. 3,5-Dimethylheptane

Δν, cm.⁻¹	Scattering Coefficient	ρ
318	0.020	..
444	0.032	..
767	0.045	..
824	0.055	..
892	0.019	..
936	0.019	..
987	0.060	0.6
1039	0.044	..
1160	0.053	0.82
1283	0.023	0.7
1304	0.014	..
1356	0.035	0.65
1456	0.179	0.78

No. 44. 4,4-Dimethylheptane

Δν, cm.⁻¹	Scattering Coefficient	ρ
185	0.035	..
318	0.078	0.3
343	0.056	0.4
435	0.011	..
465	0.024	..
493	0.041	..
546	0.013	..
607	0.006	..
701	0.011	..
753	0.077	0.1
856	0.024	0.8
879	0.056	0.82
915	0.036	0.6
933	0.028	0.9
1047	0.093	0.62
1108	0.030	0.4
1195	0.053	0.67
1211	0.056	0.67
1271	0.008	..
1318	0.047	0.6
1367	0.013	..
1393	0.009	..
1449	0.166	0.87
1464	0.136	0.69

No. 45. 2-Methyl-3-ethylhexane

Δν, cm.⁻¹	Scattering Coefficient	ρ
191	0.020	..
310	0.030	..
401	0.014	..
464	0.019	..
564	0.014	..
722	0.029	..
891	0.042	..
953	0.031	..
1052	0.068	0.5
1165	0.035	..
1312	0.037	0.7
1457	0.129	0.70

No. 46. 2-Methyl-4-ethylhexane

Δν, cm.⁻¹	Scattering Coefficient	ρ
310	0.025	..
419	0.030	..
450	0.035	..
749	0.046	..
825	0.067	0.2
881	0.018	..
918	0.028	0.9
955	0.030	0.8
1042	0.049	0.4
1092	0.009	..
1164	0.050	0.79
1238	0.010	..
1282	0.016	..
1311	0.016	0.6
1342	0.030	1.
1457	0.195	0.73

No. 47. 3-Methyl-3-ethylhexane

Δν, cm.⁻¹	Scattering Coefficient	ρ
330	0.051	0.3
369	0.033	..
413	0.016	..
485	0.022	..
539	0.011	..
706	0.115	0.07
852	0.020	..
879	0.047	0.5
898	0.036	0.7
939	0.015	..
999	0.034	0.9
1037	0.092	0.60
1104	0.039	0.3
1191	0.053	0.62
1229	0.026	0.7
1291	0.021	0.8
1304	0.023	0.7
1347	0.010	..
1454	0.197	0.80

No. 48. 3-Methyl-4-ethylhexane

Δν, cm.⁻¹	Scattering Coefficient	ρ
337	0.048	..
439	0.037	..
480	0.018	..
728	0.035	..
825	0.031	..
854	0.023	1.
917	0.062	0.68
985	0.046	0.7
1046	0.104	0.50
1126	0.015	..
1163	0.049	0.9
1210	0.018	..
1281	0.029	0.8
1361	0.021	..
1461	0.195	0.68

No. 49. 2,2,4-Trimethylhexane

Δν, cm.⁻¹	Scattering Coefficient	ρ
188	0.020	..
305	0.038	..
490	0.034	..
744	0.152	..
827	0.035	..
889	0.048	0.7
927	0.087	0.82
999	0.017	..
1034	0.033	..
1106	0.029	..
1161	0.020	..
1210	0.054	0.4
1250	0.055	0.6
1286	0.041	..
1359	0.017	..
1456	0.197	0.89

No. 50. 2,2,5-Trimethylhexane

Δν, cm.⁻¹	Scattering Coefficient	ρ
248	0.033	..
302	0.044	0.8
374	0.007	..
407	0.014	..
479	0.048	..
746	0.079	..
828	0.086	0.2
917	0.093	0.81
929	0.090	0.85
958	0.046	0.8
1025	0.020	..
1125	0.017	..
1206	0.058	0.6
1257	0.062	0.78
1322	0.028	0.6
1345	0.033	0.7
1458	0.165	0.74

No. 51. 2,3,3-Trimethylhexane

Δν, cm.⁻¹	Scattering Coefficient	ρ
232	0.018	..
322	0.037	..
363	0.022	0.5
377	0.023	0.6
410	0.011	..
483	0.041	..
559	0.011	..
691	0.112	0.1
709	0.078	0.2
794	0.015	..
838	0.018	0 8
894	0.059	0.5
928	0.084	0.74
950	0.043	0.8
1041	0.062	0.6
1100	0.029	0.6
1114	0.027	0.5
1191	0.037	0.9
1210	0.055	0.9
1230	0.044	0.9
1256	0.015	..
1317	0.058	0.9
1457	0.164	0.86

No. 52. 2,3,4-Trimethylhexane

Δν, cm.⁻¹	Scattering Coefficient	ρ
325	0.025	..
404	0.016	..
462	0.057	..
596	0.016	..
754	0.069	..
812	0.037	0.3
874	0.038	..
918	0.032	0.6
957	0.044	0.87
1000	0.030	..
1029	0.024	..
1166	0.068	0.53
1292	0.023	..
1330	0.030	..
1460	0.177	0.79

No. 53. 2,3,5-Trimethylhexane

Δν, cm.⁻¹	Scattering Coefficient	ρ
315	0.033	0.6
428	0.031	0.3
459	0.034	..
731	0.034	..
765	0.059	..
820	0.096	..
884	0.029	0.7
926	0.023	0.5
957	0.073	0.89
1006	0.026	0.3
1164	0.068	0.6
1190	0.037	0.6
1253	0.014	..
1278	0.021	..
1318	0.071	0.7
1346	0.066	0.9
1395	0.043	0.6
1464	0.175	0.81

No. 54. 2,4,4-Trimethylhexane

Δν, cm.⁻¹	Scattering Coefficient	ρ
311	0.030	0.5
422	0.012	..
478	0.020	..
511	0.022	..
721	0.127	0.1
822	0.040	0.2
871	0.027	0.4
931	0.070	0.7
978	0.014	..
1018	0.029	0.6
1051	0.018	..
1105	0.040	0.6
1172	0.030	0.8
1205	0.050	0.6
1229	0.029	0.6
1274	0.019	..
1302	0.023	..
1355	0.027	0.5
1455	0.179	0.73

No. 55. 3,3,4-Trimethylhexane

Δν, cm.⁻¹	Scattering Coefficient	ρ
339	0.044	0.6
484	0.024	0.6
532	0.027	0.8
704	0.150	0.21
774	0.015	..
822	0.035	1.
881	0.038	0.6
916	0.057	0.68
977	0.058	0.7
1024	0.052	0.5
1084	0.026	..
1192	0.052	..
1211	0.076	0.68
1294	0.023	0.8
1349	0.020	1.
1455	0.190	0.80

No. 56. 2,2-Dimethyl-3-ethylpentane

Δν, cm.⁻¹	Scattering Coefficient	ρ
187	0.024	..
308	0.038	..
346	0.036	..
461	0.016	..
479	0.016	..
533	0.084	..
585	0.008	..
696	0.021	..
727	0.047	..
789	0.036	..
851	0.014	..
925	0.133	0.64
1014	0.046	0.6
1027	0.067	0.53
1045	0.038	0.4
1093	0.016	..
1121	0.011	..
1201	0.046	0.6
1226	0.062	0.79
1235	0.062	0.5
1310	0.017	..
1356	0.013	..
1410	0.019	..
1454	0.168	0.79
1466	0.155	0.71

No. 57. 2,4-Dimethyl-3-ethylpentane

Δν, cm.⁻¹	Scattering Coefficient	ρ
324	0.047	..
480	0.058	..
573	0.040	..
720	0.022	..
795	0.042	..
843	0.020	0.8
886	0.037	0.9
947	0.099	0.61
1047	0.051	0.5
1175	0.055	0.6
1276	0.022	0.5
1327	0.050	0.6
1468	0.159	0.74

No. 58. 2,2,3,4-Tetramethylpentane

Δν, cm.⁻¹	Scattering Coefficient	ρ
186	0.023	..
324	0.047	..
370	0.015	..
457	0.014	..
516	0.047	..
575	0.041	..
655	0.016	..
712	0.207	0.09
864	0.119	0.4
922	0.135	0.71
993	0.045	..
1028	0.028	..
1090	0.017	..
1115	0.018	..
1186	0.032	0.9
1227	0.075	1.
1244	0.063	0.68
1305	0.043	..
1463	0.151	0.80

Raman Spectral Data for Hydrocarbons (*Continued*)

No. 59 2,2,4,4-Tetramethylpentane

Δν, cm.⁻¹	Scattering Coefficient	ρ
275	0.066	0.85
315	0.052	0.5
374	0.031	..
551	0.070	..
674	0.021	..
731	0.305	0.06
875	0.110	0.42
920	0.174	0.73
1173	0.061	0.6
1249	0.206	0.73
1454	0.191	0.70
1475	0.114	0.65

No. 60 2,3,3,4-Tetramethylpentane

371	0.058	0.7
467	0.092	0.2
566	0.009	..
614	0.021	..
671	0.248	0.06
786	0.029	..
872	0.060	..
922	0.195	0.55
956	0.041	0.6
1028	0.026	..
1087	0.036	..
1123	0.025	..
1186	0.036	..
1227	0.102	0.68
1321	0.060	0.80
1460	0.171	0.76
1470	0.169	0.75

No. 61. *n*-Decane

250	0.024	..
850	0.031	..
887	0.024	..
1074	0.051	1.
1136	0.026	..
1306	0.090	0.72
1450	0.182	0.72

No. 62. 2,2,6-Trimethylheptane

189	0.016	..
242	0.065	0.6
341	0.040	0.9
468	0.024	..
745	0.082	..
810	0.061	..
833	0.031	..
923	0.078	0.75
1052	0.024	0.6
1125	0.020	..
1201	0.046	0.7
1249	0.055	0.7
1319	0.037	0.8
1455	0.163	0.78

No. 63. 2,3,6-Trimethylheptane

190	0.026	..
235	0.026	0.6
310	0.013	..
422	0.019	..
462	0.014	..
727	0.023	..
766	0.047	..
825	0.060	0.2
875	0.015	0.9
930	0.048	0.7
953	0.047	0.7
1014	0.015	..
1047	0.016	..
1102	0.013	0.9
1168	0.050	0.9
1307	0.048	0.8
1344	0.059	0.6
1456	0.144	0.87

No. 64. 2,2,3,3-Tetramethylhexane

312	0.099	0.3
367	0.030	..
475	0.062	0.9
523	0.076	0.3
589	0.043	0.9
615	0.048	0.7
675	0.205	0.1
804	0.013	0.9
860	0.144	0.47
920	0.146	0.89
1040	0.113	0.79
1085	0.053	0.9
1110	0.054	0.9
1229	0.159	0.65
1239	0.153	0.78
1272	0.040	0.8
1320	0.030	0.9
1453	0.181	0.89
1474	0.114	0.97

No. 65. 2,2,3,4-Tetramethylhexane

318	0.032	0.6
373	0.019	..
451	0.013	..
476	0.012	..
517	0.045	..
604	0.028	0.9
661	0.015	..
714	0.124	0.1
772	0.016	..
800	0.010	..
851	0.058	0.5
894	0.028	0.9
926	0.079	0.7
962	0.039	0.5
987	0.028	0.7
999	0.033	0.5
1036	0.039	0.5
1089	0.015	..
1214	0.058	0.6
1243	0.052	0.9
1356	0.034	0.9
1392	0.043	0.9
1460	0.166	0.96

No. 66. 2,2,3,5-Tetramethylhexane

262	0.036	0.4
306	0.033	0.9
378	0.023	0.7
412	0.021	..
463	0.019	..
504	0.037	..
528	0.037	..
666	0.017	..
724	0.124	0.2
762	0.018	..
819	0.116	0.3
865	0.051	0.9
926	0.109	0.54
959	0.079	0.9
1014	0.015	..
1036	0.026	0.6
1100	0.028	..
1127	0.035	0.9
1176	0.044	0.7
1205	0.059	0.8
1246	0.076	0.7
1335	0.066	0.7
1347	0.066	0.7
1460	0.184	0.74

No. 67. 2,2,4,5-Tetramethylhexane

189	0.015	0.7
242	0.017	..
299	0.025	0.7
486	0.028	0.3
560	0.017	..
748	0.087	0.1
772	0.104	0.1
793	0.034	..
876	0.047	0.9
928	0.102	0.84
950	0.059	0.7
1003	0.021	0.7
1035	0.020	0.5
1114	0.020	..
1148	0.025	..
1206	0.049	0.6
1250	0.049	0.9
1288	0.046	0.9
1362	0.015	0.9
1459	0.161	0.88

No. 68 3,3,4,4-Tetramethylhexane

191	0.015	..
353	0.139	0.3
400	0.029	0.7
460	0.040	0.8
558	0.010	..
601	0.025	..
658	0.259	0.09
840	0.076	0.7
914	0.083	0.76
926	0.123	0.82
1017	0.123	0.70
1061	0.076	0.6
1216	0.111	0.77
1237	0.068	0.82
1311	0.025	0.8
1400	0.042	0.6
1452	0.222	0.79
1477	0.126	0.59

No. 69. *n*-Undecane

191	0.022	..
245	0.020	..
403	0.008	..
767	0.017	..
836	0.034	0.7
881	0.042	..
1003	0.025	..
1075	0.073	0.07
1131	0.032	0.6
1207	0.011	..
1305	0.109	0.81
1385	0.027	..
1446	0.191	0.79

No. 70 2,2,4,6-Tetramethylheptane

190	0.020	..
250	0.033	0.8
301	0.016	..
352	0.016	..
483	0.025	..
741	0.109	0.09
812	0.086	0.1
896	0.038	0.9
924	0.071	0.9
954	0.044	0.9
1117	0.018	0.7
1166	0.029	0.6
1201	0.037	0.6
1253	0.042	0.9
1302	0.018	..
1350	0.019	0.5
1460	0.168	0.73

No. 71. *n*-Dodecane

190	0.043	..
226	0.012	..
311	0.008	..
396	0.012	..
478	0.018	..
609	0.018	..
713	0.011	..
843	0.029	0.4
885	0.026	0.3
1029	0.031	0.6
1080	0.049	0.9
1132	0.024	0.5
1205	0.028	..
1273	0.034	0.9
1302	0.057	0.9
1382	0.024	..
1447	0.106	0.73

No. 72 2,2,3,5,6-Pentamethylheptane

193	0.020	..
228	0.024	..
318	0.021	0.5
377	0.018	..
451	0.012	..
499	0.032	..
551	0.011	..
720	0.040	0.2
743	0.067	..
775	0.053	..
878	0.052	0.9
927	0.113	0.82
950	0.071	0.9
1002	0.043	0.6
1028	0.024	..
1054	0.021	..
1103	0.011	..
1161	0.023	0.6
1226	0.049	0.9
1243	0.047	0.9
1323	0.038	0.5
1459	0.160	0.78

No. 73 2 2,4,6,6-Pentamethylheptane

240	0.043	0.6
327	0.024	0.7
349	0.024	0.9
395	0.007	..
444	0.007	..
507	0.047	..
547	0.010	..
704	0.017	..
757	0.197	0.08
872	0.054	0.8
924	0.133	0.84
1018	0.015	0.6
1084	0.026	0.7
1113	0.017	..
1209	0.074	0.7
1248	0.092	0.83
1282	0.041	0.7
1355	0.017	0.8
1456	0.198	0.82

No. 74. *n*-Tridecane

191	0.029	..
233	0.012	..
316	0.008	..
405	0.008	..
475	0.013	..
603	0.009	..
722	0.009	..
842	0.039	..
891	0.036	0.4
965	0.018	..
1037	0.043	0.6
1076	0.074	0.6
1132	0.038	0.4
1205	0.014	0.5
1305	0.100	0.80
1446	0.189	0.74

No. 75. *n*-Tetradecane

191	0.020	0.9
232	0.017	..
304	0.010	..
401	0.010	0.9
485	0.011	..
602	0.006	..
841	0.043	0.6
879	0.042	0.4
921	0.010	..
1009	0.025	0.6
1075	0.069	0.6
1132	0.029	..
1210	0.013	..
1305	0.120	0.89
1384	0.038	..
1447	0.204	0.78

Raman Spectral Data for Hydrocarbons (*Continued*)

No. 76. 7-Methyltridecane

Δν, cm.⁻¹	Scattering Coefficient	ρ
188	0.032	..
235	0.011	..
314	0.009	..
409	0.006	..
607	0.012	..
747	0.017	..
796	0.028	..
842	0.048	..
880	0.048	..
973	0.025	0.8
1022	0.032	0.6
1073	0.065	..
1138	0.037	0.9
1152	0.032	0.6
1208	0.022	..
1306	0.101	0.75
1448	0.201	0.82

No. 77. 1-Pentene

226	0.017	..
384	0.050	0.5
430	0.036	0.7
625	0.037	0.3
770	0.015	..
846	0.065	0.3
872	0.050	0.6
911	0.032	0.9
1009	0.029	0.6
1044	0.053	0.6
1091	0.039	0.2
1235	0.050	0.4
1292	0.145	0.37
1424	0.113	0.56
1450	0.100	0.67
1550	0.016	..
1593	0.018	..
1650	0.224	0.11

No. 78. *cis*-2-Pentene

310	0.036	0.8
464	0.052	0.9
602	0.024	..
794	0.018	..
859	0.113	0.9
957	0.034	..
1024	0.105	0.3
1069	0.042	..
1112	0.025	..
1207	0.058	0.88
1268	0.148	0.77
1376	0.039	0.7
1408	0.042	0.9
1458	0.123	0.74
1532	0.015	..
1605	0.028	..
1667	0.227	0.14

No. 79. *trans*-2-Pentene

303	0.018	..
409	0.066	0.3
484	0.122	0.3
606	0.015	..
708	0.018	..
750	0.031	0.9
803	0.037	0.6
850	0.021	0.4
873	0.022	..
940	0.022	0.9
1020	0.040	0.3
1064	0.064	0.4
1207	0.024	0.9
1252	0.033	..
1276	0.057	0.8
1311	0.117	0.46
1382	0.054	0.4
1454	0.140	0.72
1550	0.021	..
1582	0.018	..
1621	0.019	..
1680	0.215	0.13

No. 80. 2-Methyl-1-butene

394	0.060	0.7
420	0.046	0.9
481	0.017	..
524	0.021	..
605	0.010	..
667	0.016	..
705	0.042	..
769	0.151	0.1
884	0.042	0.8
933	0.025	0.9
1011	0.069	0.4
1082	0.079	0.2
1248	0.017	..
1281	0.020	..
1395	0.107	0.51
1421	0.161	0.55
1435	0.167	0.51
1554	0.008	..
1600	0.016	..
1659	0.237	0.17

No. 81. 2-Methyl-2-butene

260	0.010	..
387	0.064	0.53
443	0.071	0.90
526	0.086	0.3
712	0.022	..
768	0.193	0.18
801	0.034	0.8
958	0.019	..
1034	0.036	0.4
1056	0.049	0.3
1072	0.037	0.7
1110	0.028	..
1216	0.012	..
1286	0.013	..
1343	0.096	0.54
1390	0.172	0.53
1453	0.202	0.85
1625	0.024	..
1684	0.241	0.21

No. 82. 2,3-Dimethyl-1-butene

307	0.023	..
336	0.020	0.9
432	0.021	0.8
486	0.019	0.7
519	0.027	..
548	0.019	0.5
707	0.074	0.2
728	0.118	0.2
885	0.076	0.67
954	0.066	0.3
996	0.016	..
1034	0.006	..
1100	0.077	0.7
1162	0.012	..
1208	0.008	..
1305	0.055	0.8
1400	0.104	0.58
1450	0.117	0.78
1550	0.004	..
1595	0.012	..
1652	0.194	0.16

No. 83. 3,3-Dimethyl-1-butene

304	0.086	0.9
353	0.070	0.6
519	0.048	0.3
615	0.012	..
657	0.020	..
715	0.268	0.06
879	0.056	0.3
922	0.115	0.74
999	0.033	..
1026	0.027	..
1067	0.017	..
1209	0.099	0.69
1272	0.044	0.56
1311	0.111	0.3
1390	0.033	0.4
1424	0.074	0.4
1456	0.108	0.71
1549	0.007	..
1592	0.021	..
1648	0.177	0.13

No. 84. 1-Heptene

308	0.011	..
425	0.010	..
630	0.017	..
765	0.008	..
834	0.039	0.4
911	0.035	0.8
967	0.011	..
1027	0.025	..
1069	0.046	0.9
1107	0.035	0.3
1215	0.022	..
1299	0.140	0.47
1422	0.097	0.54
1445	0.124	0.80
1592	0.011	..
1647	0.188	0.12

No. 85. 1-Octene

288	0.034	..
364	0.011	..
433	0.013	..
636	0.014	..
815	0.028	..
850	0.038	0.2
884	0.049	0.4
905	0.044	0.6
1009	0.041	0.6
1071	0.056	0.6
1108	0.038	0.5
1206	0.018	0.6
1298	0.161	0.53
1423	0.108	0.61
1445	0.163	0.84
1590	0.011	..
1647	0.187	0.1

No. 86 2,3,3-Trimethyl-1-pentene

319	0.012	..
368	0.033	0.6
472	0.037	0.5
566	0.009	..
607	0.013	..
661	0.240	0.09
691	0.056	..
830	0.043	0.7
906	0.052	0.7
948	0.061	0.7
1008	0.048	0.6
1058	0.048	0.3
1176	0.048	0.7
1210	0.055	0.7
1338	0.012	..
1388	0.074	0.53
1410	0.107	0.53
1462	0.151	0.86
1648	0.154	0.21

No. 87 2,3,4-Trimethyl-1-pentene

193	0.034	0.6
276	0.014	..
346	0.027	..
465	0.026	0.9
526	0.079	..
560	0.019	..
603	0.009	..
694	0.036	..
759	0.093	0.2
828	0.033	0.9
890	0.048	0.9
910	0.062	0.4
954	0.041	0.9
1001	0.015	..
1025	0.019	..
1038	0.021	..
1091	0.026	..
1128	0.043	0.6
1163	0.026	..
1181	0.022	0.9
1213	0.009	..
1275	0.019	..
1325	0.031	0.5
1341	0.036	0.9
1413	0.069	0.4
1461	0.120	0.79
1599	0.015	0.9
1656	0.185	0.22

No. 88 2,3,4-Trimethyl-2-pentene

308	0.035	..
379	0.015	0.9
422	0.020	..
484	0.053	0.5
507	0.064	0.2
586	0.047	0.8
616	0.023	..
680	0.161	0.1
834	0.037	0.9
904	0.065	0.2
955	0.027	0.6
1058	0.064	0.7
1106	0.078	0.6
1194	0.030	..
1276	0.011	..
1333	0.026	..
1394	0.100	0.4
1463	0.170	0.78
1672	0.220	0.26

No. 89 2,4,4-Trimethyl-1-pentene

299	0.063	0.8
383	0.034	0.5
411	0.021	..
457	0.014	..
558	0.072	..
626	0.008	..
686	0.123	0.09
767	0.099	0.1
827	0.034	..
909	0.096	0.89
932	0.078	0.9
1004	0.017	..
1046	0.015	..
1160	0.041	0.7
1206	0.047	0.9
1244	0.077	0.84
1299	0.015	..
1333	0.013	..
1417	0.126	0.62
1457	0.144	0.93
1592	0.008	..
1653	0.150	0.18

No. 90 2,4,4-Trimethyl-2-pentene

327	0.064	0.4
499	0.027	..
565	0.075	..
704	0.016	..
762	0.201	0.1
820	0.029	0.6
925	0.091	0.77
1030	0.020	..
1075	0.042	..
1162	0.029	0.9
1205	0.053	0.7
1261	0.015	..
1359	0.053	0.5
1392	0.133	0.45
1457	0.188	0.71
1622	0.013	..
1675	0.166	0.26

No. 91 3,3,4-Trimethyl-1-pentene

298	0.019	..
363	0.023	0.9
500	0.037	..
525	0.032	..
676	0.079	..
697	0.097	..
761	0.018	..
825	0.033	0.8
908	0.067	0.5
932	0.097	0.6
1006	0.018	..
1031	0.018	..
1103	0.021	..
1187	0.028	0.7
1251	0.014	..
1369	0.076	0.4
1424	0.077	0.5
1462	0.117	0.91
1590	0.009	..
1647	0.128	0.1

Raman Spectral Data for Hydrocarbons (*Continued*)

No. 92
3-Methyl-2-isopropyl-1-butene

$\Delta\nu$, cm.$^{-1}$	Scattering Coefficient	ρ
214	0.084	0.9
311	0.044	..
343	0.035	..
467	0.038	..
493	0.018	..
706	0.087	..
743	0.075	..
825	0.026	0.8
904	0.136	0.3
955	0.047	0.9
1052	0.017	..
1102	0.154	0.46
1177	0.011	..
1304	0.090	0.6
1383	0.059	..
1408	0.069	..
1464	0.151	0.56
1652	0.142	0.2

No. 93
3,3-Dimethyl-2-ethyl-1-butene

226	0.015	0.8
350	0.061	0.6
381	0.032	0.6
468	0.029	0.9
511	0.007	..
639	0.056	..
694	0.207	0.1
821	0.030	0.8
908	0.088	0.4
923	0.099	0.72
1012	0.058	0.6
1065	0.084	0.2
1209	0.082	0.77
1274	0.022	0.7
1411	0.106	0.56
1445	0.153	0.72
1457	0.162	0.69
1541	0.007	..
1589	0.009	..
1644	0.145	0.2

No. 94
3,3-Dimethyl-2-isopopyl-1-butene

189	0.014	..
213	0.041	0.9
302	0.054	0.6
346	0.047	0.6
387	0.018	0.7
418	0.015	..
475	0.027	0.7
530	0.045	..
597	0.010	..
637	0.024	..
694	0.229	0.08
800	0.009	..
817	0.010	..
875	0.134	0.2
927	0.105	0.69
956	0.033	0.6
1026	0.021	0.6
1098	0.094	0.3
1130	0.028	0.6
1207	0.078	0.61
1274	0.015	0.6
1316	0.018	0.5
1354	0.054	0.4
1410	0.064	0.49
1455	0.133	0.60
1468	0.136	0.62
1574	0.015	..
1647	0.110	0.2

No. 95
2,3,3,4-Tetramethyl-1-pentene

192	0.034	0.5
290	0.015	0.8
381	0.046	0.9
449	0.028	0.9
487	0.052	0.4
517	0.041	0.2
564	0.016	0.7
608	0.032	..
663	0.244	0.06
716	0.028	..
797	0.039	0.8
891	0.067	0.6
924	0.099	0.67
952	0.083	0.5
1007	0.033	0.3
1066	0.041	0.5
1106	0.024	0.5
1181	0.053	0.7
1216	0.039	0.8
1282	0.021	0.6
1329	0.051	0.8
1411	0.131	0.56
1448	0.130	0.84
1463	0.138	0.87
1588	0.011	..
1648	0.146	0.21

No. 96
2,6,6-Trimethyl-1-heptene

187	0.039	..
248	0.029	..
339	0.047	0.9
390	0.023	0.9
425	0.034	0.9
482	0.037	..
547	0.034	..
695	0.023	..
745	0.113	0.09
820	0.038	..
881	0.030	0.9
922	0.075	0.88
1039	0.029	0.5
1068	0.035	0.5
1134	0.017	..
1191	0.030	0.9
1252	0.052	0.7
1318	0.033	0.7
1397	0.058	0.5
1450	0.156	0.76
1600	0.009	..
1657	0.155	0.2

No. 97
2,4,4,5-Tetramethyl-1-hexene

189	0.041	0.6
244	0.025	..
323	0.010	..
399	0.011	..
436	0.014	..
500	0.039	..
555	0.007	..
580	0.018	..
616	0.008	..
673	0.117	0.1
741	0.026	..
810	0.037	0.3
848	0.049	0.3
893	0.086	0.5
913	0.088	0.6
952	0.058	0.6
1015	0.020	..
1073	0.011	..
1101	0.012	..
1157	0.029	0.9
1214	0.066	0.7
1255	0.015	..
1321	0.041	0.8
1416	0.097	0.55
1453	0.134	0.80
1551	0.008	..
1598	0.008	..
1650	0.130	0.2

No. 98. 2-Methyl-1,3-butadiene

283	0.038	0.93
420	0.077	0.81
474	0.006	1.
525	0.177	0.38
629	0.016	..
779	0.088	0.2
894	0.166	0.78
955	0.078	..
998	0.053	..
1017	0.033	..
1072	0.248	0.39
1203	0.024	..
1244	0.061	..
1295	0.565	0.25
1392	0.200	0.56
1428	0.418	0.45
1544	0.075	0.43
1588	0.222	0.35
1643	1.5	0.26

No. 99. 2-Methyl-1,5-hexadiene

319	0.023	..
389	0.051	0.7
418	0.053	0.7
530	0.015	..
626	0.029	0.5
706	0.021	..
766	0.056	..
833	0.044	0.2
890	0.043	0.9
913	0.041	0.6
1015	0.040	0.5
1115	0.023	..
1212	0.034	..
1240	0.028	..
1301	0.155	0.25
1424	0.228	0.47
1553	0.012	..
1596	0.024	..
1652	0.372	0.14

No. 100. 2,3,3,4-Tetramethyl-1,4-pentadiene

188	0.052	0.9
276	0.021	..
377	0.075	0.8
403	0.118	0.5
438	0.023	..
507	0.037	0.8
574	0.045	..
589	0.037	..
649	0.293	0.07
727	0.035	..
804	0.029	0.7
843	0.009	..
896	0.091	0.69
935	0.062	0.6
957	0.089	0.3
1021	0.083	0.3
1113	0.011	..
1148	0.048	0.8
1166	0.041	0.6
1210	0.009	..
1279	0.031	0.8
1383	0.162	0.60
1406	0.234	0.54
1459	0.129	0.63
1548	0.008	..
1596	0.024	..
1651	0.318	0.22

No. 101. Cyclopentane

608	0.013	..
717	0.010	..
794	0.010	..
834	0.028	..
889	0.394	0.12
1033	0.150	0.82
1208	0.035	0.8
1273	0.043	0.8
1453	0.145	0.72
1481	0.054	0.5

No. 102. Methylcyclopentane

310	0.010	0.8
428	*0.013*	..
534	0.034	..
798	0.044	..
843	0.070	..
892	0.130	0.1
992	0.053	0.74
1012	0.058	0.64
1088	0.034	0.9
1206	0.017	..
1306	0.019	0.9
1354	0.011	0.7
1456	0.157	0.77

No. 103. Ethylcyclopentane

393	0.061	0.3
414	0.036	0.3
545	0.015	0.7
609	0.009	..
762	0.026	..
853	0.041	..
893	0.106	0.09
938	0.019	..
1030	0.092	0.45
1094	0.029	0.5
1129	0.015	..
1204	0.012	..
1293	0.017	0.8
1364	0.011	..
1396	0.010	..
1453	0.183	0.79

No. 104
1,1-Dimethylcyclopentane

301	0.006	0.9
350	0.034	0.8
398	0.010	..
561	0.074	..
606	0.006	..
725	0.056	..
809	0.034	..
838	0.018	..
888	0.122	0.2
949	0.045	..
1034	0.060	0.9
1060	0.041	0.7
1162	0.023	..
1237	0.076	0.8
1309	0.024	0.8
1397	0.020	0.7
1458	0.175	0.88

No. 105
cis-1,2-Dimethylcyclopentane

288	0.008	..
330	0.017	0.7
376	0.012	0.9
491	0.043	0.6
572	0.015	0.6
704	0.020	0.4
760	0.140	0.2
836	0.027	0.9
884	0.119	0.3
952	0.032	0.9
977	0.026	0.9
1020	0.060	0.7
1082	0.026	0.8
1106	0.029	0.8
1169	0.018	0.9
1196	0.030	0.8
1274	0.026	0.9
1308	0.035	0.9
1353	0.026	0.9
1390	0.021	0.6
1459	0.158	0.9

Raman Spectral Data for Hydrocarbons (*Continued*)

No. 106 *trans*-1,2-Dimethylcyclopentane

Δν, cm.⁻¹	Scattering Coefficient	ρ
256	0.024	..
376	0.007	..
496	0.074	..
526	0.027	..
603	0.016	..
768	0.071	0.1
803	0.028	..
862	0.020	..
896	0.074	0.1
956	0.031	0.9
1021	0.035	..
1081	0.046	0.6
1150	0.022	0.9
1203	0.016	..
1292	0.016	..
1344	0.031	0.6
1366	0.017	..
1405	0.006	..
1460	0.156	0.79

No. 107 *cis*-1,3-Dimethylcyclopentane

190	0.033	0.5
230	0.011	..
377	0.028	..
412	0.020	..
474	0.006	..
549	0.036	0.4
607	0.014	..
702	0.012	..
801	0.205	0.2
878	0.014	..
938	0.014	..
981	0.029	0.5
1035	0.036	0.5
1088	0.038	0.6
1141	0.035	0.7
1190	0.023	0.6
1207	0.035	0.7
1306	0.041	0.6
1356	0.031	0.6
1464	0.168	0.81

No. 108 *trans*-1,3-Dimethylcyclopentane

357	0.011	..
422	0.027	..
460	0.014	..
513	0.074	0.3
719	0.011	..
775	0.046	..
823	0.164	0.1
952	0.018	..
987	0.039	0.6
1028	0.026	0.9
1093	0.016	..
1146	0.043	0.9
1210	0.027	0.3
1317	0.043	0.7
1348	0.024	0.5
1463	0.159	0.78

No. 109. *n*-Propylcyclopentane

319	0.053	..
363	0.036	..
443	0.020	..
837	0.047	..
893	0.105	0.2
1029	0.084	0.76
1099	0.033	0.7
1130	0.023	0.5
1187	0.017	..
1301	0.039	0.8
1352	0.025	..
1454	0.176	0.80

No. 110. Isopropylcyclopentane

334	0.055	0.2
417	0.036	0.8
462	0.065	0.1
560	0.008	..
611	0.010	..
842	0.031	..
896	0.083	0.2
960	0.034	0.6
984	0.021	..
1037	0.048	0.76
1142	0.026	0.6
1172	0.018	0.5
1205	0.020	0.6
1306	0.025	0.6
1326	0.035	0.6
1364	0.030	0.8
1398	0.007	..
1455	0.156	0.78

No. 111 1-Methyl-1-ethylcyclopentane

358	0.043	0.3
406	0.020	0.7
428	0.025	0.5
572	0.030	0.3
714	0.054	..
802	0.013	..
892	0.095	0.2
994	0.076	0.78
1032	0.070	0.6
1072	0.035	0.4
1121	0.020	0.5
1225	0.044	0.8
1341	0.014	0.7
1405	0.018	..
1456	0.191	0.74

No. 112 *cis*-1-Methyl-3-ethylcyclopentane

303	0.014	..
394	0.054	0.2
525	0.024	0.5
606	0.009	..
781	0.025	..
838	0.087	0.2
940	0.021	0.7
998	0.040	0.6
1045	0.046	0.4
1139	0.028	0.4
1213	0.009	..
1293	0.021	0.9
1316	0.024	0.8
1360	0.021	0.8
1411	0.011	..
1461	0.149	0.75

No. 113 1,2,2-Trimethylcyclopentane

188	0.016	..
273	0.023	0.7
358	0.042	0.8
414	0.014	..
507	0.043	0.4
548	0.015	0.7
616	0.030	0.3
692	0.112	0.08
832	0.045	0.9
890	0.136	0.6
935	0.074	0.3
1010	0.038	0.5
1060	0.046	0.6
1097	0.042	0.9
1182	0.021	0.9
1230	0.060	0.8
1286	0.029	0.7
1348	0.025	0.9
1397	0.015	0.9
1458	0.168	0.90

No. 114 1,1,3-Trimethylcyclopentane

191	0.047	0.4
341	0.042	0.7
403	0.018	..
526	0.057	0.2
562	0.025	..
744	0.065	0.2
790	0.098	0.09
841	0.023	..
940	0.054	0.8
996	0.032	0.3
1050	0.034	0.9
1091	0.022	0.6
1126	0.014	0.8
1184	0.039	0.7
1231	0.047	0.6
1311	0.033	0.6
1355	0.017	0.5
1463	0.189	0.83

No. 115. *cis,cis,cis*-1,2,3-Trimethylcyclopentane

191	0.019	..
239	0.010	0.9
311	0.026	0.5
357	0.014	0.7
408	0.009	0.9
465	0.102	0.3
600	0.046	0.3
666	0.008	..
708	0.032	0.2
762	0.173	0.1
801	0.014	0.4
863	0.083	0.3
901	0.013	0.9
964	0.056	0.5
983	0.037	0.9
1018	0.053	0.7
1039	0.036	0.6
1112	0.033	0.6
1168	0.039	0.7
1200	0.010	0.7
1258	0.043	0.7
1308	0.060	0.9
1354	0.020	0.9
1392	0.013	..
1457	0.164	0.74

No. 116. *cis,cis,trans*-1,2,3-Trimethylcyclopentane

263	0.013	0.7
296	0.011	..
382	0.019	0.3
441	0.017	..
516	0.040	0.3
569	0.023	0.7
745	0.158	0.1
812	0.007	..
867	0.040	..
919	0.011	0.9
954	0.025	..
973	0.023	0.7
1030	0.027	0.7
1086	0.039	0.9
1163	0.009	..
1205	0.013	0.6
1298	0.024	0.7
1348	0.026	0.8
1377	0.012	..
1465	0.147	0.9

No. 117. *cis, trans, cis*-1,2,3-Trimethylcyclopentane

236	0.013	..
260	0.039	0.6
310	0.007	..
404	0.004	..
434	0.005	..
492	0.125	0.2
513	0.078	0.2
603	0.023	0.5
708	0.005	0.7
766	0.081	0.2
814	0.045	0.2
876	0.036	..
949	0.015	0.9
990	0.021	0.5
1035	0.015	..
1073	0.028	0.7
1106	0.014	..
1162	0.055	0.87
1214	0.025	0.3
1277	0.013	0.4
1337	0.051	0.87
1355	0.040	0.9
1468	0.168	0.78

No. 118. *cis, cis, trans*-1,2,4-Trimethylcyclopentane

368	0.018	..
422	0.022	0.8
495	0.077	0.5
513	0.058	0.2
755	0.123	0.1
851	0.035	0.5
937	0.046	0.5
977	0.022	0.9
1026	0.049	0.3
1065	0.035	0.5
1090	0.028	0.6
1151	0.035	0.7
1173	0.035	0.4
1313	0.045	0.8
1352	0.035	0.8
1464	0.189	0.82

No. 119. *cis,trans,cis*-1,2,4-Trimethylcyclopentane

255	0.025	0.8
409	0.035	..
488	0.079	0.2
527	0.030	0.9
598	0.012	..
714	0.011	..
768	0.138	0.2
813	0.060	..
937	0.044	0.6
1031	0.035	0.4
1053	0.042	0.7
1073	0.031	0.6
1150	0.065	0.76
1212	0.012	..
1286	0.012	..
1314	0.029	0.8
1348	0.041	0.9
1413	0.012	..
1465	0.203	0.86

No. 120. 2-Cyclopentylbutane

332	0.068	0.3
382	0.016	..
408	0.017	..
432	0.012	..
484	0.018	..
506	0.014	..
612	0.012	..
831	0.023	..
859	0.015	..
898	0.066	..
948	0.014	..
999	0.025	0.6
1033	0.082	0.49
1094	0.015	..
1145	0.025	..
1196	0.024	..
1282	0.022	..
1313	0.024	0.7
1351	0.014	0.9
1455	0.174	0.77

Raman Spectral Data for Hydrocarbons (*Continued*)

No. 121. 2-Cyclopentylpentane

Δν, cm.⁻¹	Scattering Coefficient	ρ
313	0.078	0.3
429	0.024	0.6
511	0.007	..
613	0.011	..
748	0.010	..
843	0.035	0.2
869	0.028	0.3
899	0.081	0.1
976	0.007	..
1041	0.083	0.60
1144	0.023	0.9
1306	0.039	1.
1455	0.167	0.79

No. 122. 2-Cyclopentylheptane

241	0.017	..
420	0.013	..
605	0.012	..
852	0.036	..
897	0.063	..
971	0.014	..
1035	0.052	0.7
1065	0.045	0.7
1144	0.016	0.6
1185	0.010	..
1310	0.056	0.9
1456	0.176	0.78

No. 123. Cyclohexane

381	0.026	..
423	0.047	0.8
703	0.014	..
743	0.040	
802	0.435	0.13
975	0.028	0.7
1031	0.303	0.79
1161	0.044	0.3
1213	0.014	..
1270	0.248	0.77
1351	0.040	0.8
1397	0.011	1.
1451	0.219	0.81

No. 124. Methylcyclohexane

186	0.024	..
313	0.015	..
339	0.012	..
406	0.048	0.7
444	0.079	0.3
546	0.061	0.1
612	0.006	..
668	0.017	..
715	0.029	..
771	0.284	0.17
844	0.071	0.2
974	0.070	0.79
1037	0.122	0.92
1064	0.044	1.
1093	0.062	0.78
1168	0.046	0.3
1210	0.037	0.6
1264	0.091	0.77
1310	0.025	0.5
1350	0.066	0.65
1449	0.170	0.67
1458	0.156	0.65

No. 125. Ethylcyclohexane

364	0.049	0.5
447	0.056	0.4
538	0.031	..
752	0.102	0.2
790	0.102	0.2
838	0.066	..
912	0.020	..
1016	0.120	0.65
1034	0.188	0.70
1063	0.033	0.9
1095	0.045	0.6
1165	0.049	0.3
1194	0.025	1.
1263	0.139	0.71
1352	0.058	0.90
1452	0.247	0.82

No. 126 1,1-Dimethylcyclohexane

Δν, cm.⁻¹	Scattering Coefficient	ρ
190	0.037	..
320	0.069	0.58
355	0.019	0.9
399	0.016	0.9
456	0.049	0.6
555	0.041	..
603	0.013	..
648	0.017	..
703	0.311	0.07
778	0.020	0.7
827	0.078	0.3
846	0.043	0.3
919	0.054	0.4
934	0.061	0.64
962	0.072	0.75
1028	0.112	0.65
1082	0.047	0.9
1153	0.024	0.6
1189	0.090	0.47
1268	0.104	0.68
1294	0.064	0.60
1351	0.017	0.7
1446	0.193	0.67

No. 127 *cis*-1,2-Dimethylcyclohexane

331	0.020	..
412	0.061	0.2
472	0.020	..
539	0.048	..
593	0.027	..
673	0.017	..
729	0.269	0.09
805	0.023	..
841	0.081	0.3
945	0.051	0.8
981	0.061	0.3
1009	0.089	0.80
1058	0.052	1.
1097	0.078	0.68
1163	0.055	0.76
1231	0.028	0.7
1259	0.096	0.79
1314	0.052	0.74
1345	0.023	..
1453	0.176	0.75

No. 128 *trans*-1,2-Dimethylcyclohexane

312	0.009	..
417	0.047	0.5
439	0.057	0.5
499	0.184	0.09
552	0.006	..
690	0.012	..
749	0.206	0.16
819	0.046	0.3
857	0.035	..
948	0.053	0.6
1009	0.067	0.86
1081	0.070	0.69
1111	0.030	0.7
1169	0.075	0.51
1225	0.052	0.79
1256	0.034	0.7
1300	0.038	0.7
1359	0.097	0.78
1459	0.166	0.69

No. 129 *cis*-1,4-Dimethylcyclohexane

258	0.011	..
312	0.011	..
371	0.052	0.4
432	0.019	..
469	0.071	0.4
638	0.057	..
706	0.014	..
761	0.248	0.12
785	0.084	0.57
955	0.082	0.9
979	0.054	0.7
1003	0.056	0.4
1057	0.103	0.87
1103	0.064	0.63
1168	0.041	0.6
1212	0.041	0.8
1268	0.081	0.79
1309	0.025	..
1350	0.058	0.7
1450	0.128	0.71
1466	0.136	0.71

No. 130 *trans*-1,4-Dimethylcyclohexane

Δν, cm.⁻¹	Scattering Coefficient	ρ
376	0.096	0.4
457	0.097	0.2
475	0.053	0.6
762	0.281	0.18
954	0.040	0.8
1008	0.019	..
1067	0.176	0.75
1173	0.074	0.4
1189	0.075	0.79
1255	0.093	0.76
1313	0.040	0.7
1358	0.095	0.74
1467	0.170	0.78

No. 131. *n*-Propylcyclohexane

301	0.083	0.3
443	0.062	0.3
738	0.025	..
784	0.119	0.2
842	0.048	..
882	0.028	..
970	0.020	..
1035	0.164	0.76
1108	0.039	0.6
1164	0.031	..
1194	0.018	..
1268	0.102	0.79
1298	0.035	0.7
1357	0.041	0.8
1453	0.202	0.81

No. 132. Isopropylcyclohexane

313	0.035	..
338	0.013	..
415	0.022	..
436	0.031	..
466	0.032	..
495	0.030	..
570	0.033	..
770	0.122	0.2
828	0.036	0.5
854	0.046	..
891	0.013	..
953	0.054	0.5
1038	0.163	0.76
1123	0.027	..
1166	0.047	0.6
1199	0.035	0.6
1251	0.036	0.6
1271	0.101	0.71
1301	0.040	0.5
1348	0.037	0.5
1455	0.189	0.89

No. 133. Methylenecyclobutane

357	0.277	0.75
659	0.172	0.26
879	0.143	0.64
907	0.213	0.62
956	0.498	0.12
1198	0.083	0.64
1389	0.183	0.58
1432	0.156	0.67
1686	0.299	0.20

No. 134 1-Methyl-1-cyclopentene

326	0.066	0.7
428	0.049	0.7
519	0.010	..
574	0.090	0.4
647	0.035	..
793	0.035	0.8
818	0.040	0.7
876	0.165	0.2
923	0.029	0.9
1011	0.105	0.61
1153	0.034	0.5
1210	0.053	0.7
1262	0.028	0.7
1299	0.013	..
1339	0.048	0.7
1384	0.059	0.7
1450	0.328	0.67
1564	0.009	..
1607	0.020	..
1668	0.258	0.1

No. 135 3-Methyl-1-cyclopentene

Δν, cm.⁻¹	Scattering Coefficient	
343	0.057	0.9
485	0.045	..
579	0.029	0.6
803	0.098	0.2
841	0.027	0.9
896	0.053	0.4
938	0.070	0.5
965	0.102	0.3
1056	0.057	0.7
1108	0.219	0.50
1210	0.041	0.7
1294	0.033	0.6
1351	0.023	..
1455	0.184	0.71
1517	0.014	..
1559	0.022	..
1621	0.254	0.11

No. 136 *cis*-3,4-Dimethyl-1-cyclopentene

271	0.083	0.9
339	0.027	0.9
385	0.020	0.9
460	0.034	0.9
505	0.034	0.6
621	0.053	0.2
649	0.043	0.2
712	0.053	0.3
747	0.180	0.2
844	0.015	0.7
934	0.085	0.4
992	0.053	0.8
1011	0.044	0.4
1066	0.059	0.6
1109	0.198	0.46
1208	0.007	..
1280	0.051	0.4
1343	0.049	0.5
1396	0.030	..
1455	0.192	0.61
1560	0.019	..
1617	0.212	0.09

No. 137 1,2,3-Trimethyl-1-cyclopentene

291	0.038	0.9
400	0.039	0.5
476	0.006	..
531	0.034	0.4
576	0.021	0.6
610	0.042	0.6
684	0.062	0.2
732	0.017	0.7
768	0.010	..
813	0.012	0.7
888	0.024	0.3
974	0.045	0.9
1019	0.020	0.9
1094	0.028	0.9
1109	0.027	0.9
1174	0.015	0.9
1220	0.016	0.7
1292	0.018	0.7
1328	0.024	0.5
1390	0.082	0.
1455	0.240	0.72
1552	0.005	..
1594	0.016	0.3
1643	0.027	0.5
1693	0.220	0.24.

Raman Spectral Data for Hydrocarbons (*Continued*)

No. 138
2,3,3-Trimethyl-1-cyclopentene

$\Delta\nu$, cm.$^{-1}$	Scattering Coefficient	ρ
224	0.014	0.7
274	0.044	0.8
349	0.088	0.77
431	0.007	..
566	0.056	0.6
593	0.042	..
652	0.259	0.9
699	0.103	0.0
793	0.019	0.7
823	0.017	..
889	0.035	..
921	0.121	0.40
1022	0.093	0.54
1109	0.040	0.7
1204	0.094	0.84
1226	0.048	0.6
1295	0.046	0.5
1332	0.042	0.3
1389	0.061	0.4
1452	0.267	0.58
1560	0.008	..
1605	0.015	..
1665	0.187	0.15

No. 139
2,3,4-Trimethyl-1-cyclopentene

260	0.053	0.9
306	0.020	0.9
404	0.027	..
451	0.055	0.2
516	0.027	0.9
565	0.101	0.2
660	0.031	0.5
717	0.011	..
770	0.097	0.3
824	0.011	0.9
892	0.040	0.3
920	0.017	..
966	0.008	..
1019	0.063	0.53
1090	0.029	0.6
1143	0.021	0.5
1205	0.016	0.7
1276	0.011	0.5
1302	0.011	0.7
1341	0.051	0.7
1386	0.028	0.8
1460	0.238	0.69
1608	0.014	..
1668	0.180	0.15

No. 140. Cyclohexene

190	0.041	..
280	0.056	1.
391	0.089	0.49
454	0.030	0.8
492	0.036	0.9
641	0.023	0.5
721	0.020	0.4
768	0.027	..
825	0.350	0.09
879	0.033	0.7
906	0.045	0.2
967	0.030	0.6
1047	0.075	0.64
1066	0.108	0.58
1142	0.014	1.
1226	0.208	0.47
1246	0.095	0.67
1268	0.095	0.75
1350	0.042	0.4
1438	0.286	0.58
1456	0.161	0.53
1599	0.017	..
1658	0.220	0.09

No. 141. Benzene

603	0.235	0.88
845	0.061	1.
885	0.050	0.2
930	0.152	0.09
988	2.02	0.11
1171	0.269	0.85
1581	0.221	0.81
1596	0.167	0.80

No. 142. Toluene

209	0.228	1.
336	0.035	1.
407	0.012	..
456	0.035	0.5
511	0.210	0.61
558	0.008	..
617	0.144	0.73
723	0.063	0.3
778	0.516	0.09
834	0.027	0.9
879	0.013	..
896	0.033	0.4
942	0.066	..
999	0.917	0.07
1028	0.268	0.10
1102	0.013	..
1148	0.109	0.54
1176	0.088	0.54
1204	0.265	0.13
1319	0.012	..
1375	0.108	0.42
1433	0.028	0.6
1516	0.012	..
1546	0.017	1.
1584	0.156	0.76
1600	0.230	0.70

No. 143. Ethylbenzene

291	0.027	..
390	0.018	..
481	0.080	0.4
550	0.036	0.6
616	0.139	0.88
709	0.021	0.8
750	0.159	0.23
765	0.266	0.17
839	0.021	0.9
900	0.041	0.3
966	0.186	0.31
1001	0.754	0.11
1029	0.282	0.10
1058	0.079	0.2
1097	0.016	..
1155	0.088	0.86
1180	0.107	0.40
1199	0.214	0.13
1322	0.041	0.5
1384	0.014	..
1445	0.102	0.81
1548	0.018	..
1586	0.130	0.82
1602	0.243	0.74

No. 144. 1,2-Dimethylbenzene

172	0.100	0.78
251	0.199	0.75
309	0.019	..
431	0.022	..
500	0.170	0.65
575	0.324	0.30
629	0.017	..
674	0.050	..
736	0.778	0.12
856	0.021	..
930	0.022	..
985	0.130	0.1
1051	0.452	0.10
1114	0.030	0.4
1156	0.100	0.54
1226	0.388	0.11
1285	0.019	0.7
1323	0.010	..
1381	0.192	0.35
1446	0.109	0.68
1584	0.126	0.57
1604	0.208	0.62

No. 145. 1,3-Dimethylbenzene

202	0.085	0.90
219	0.202	0.68
271	0.072	0.65
476	0.024	..
512	0.228	0.60
530	0.334	0.25
621	0.020	..
664	0.035	..
721	0.504	0.16
767	0.026	0.6
890	0.033	0.5
940	0.042	0.2
998	0.675	0.12
1033	0.090	0.2
1091	0.042	0.5
1167	0.042	1.
1199	0.029	..
1247	0.232	0.15
1264	0.092	0.1
1318	0.017	..
1376	0.210	0.59
1439	0.050	0.5
1594	0.119	0.68
1607	0.135	0.68

No. 146. 1,4-Dimethylbenzene

308	0.256	0.94
384	0.030	0.9
453	0.276	0.37
583	0.023	..
639	0.174	0.89
678	0.016	..
700	0.017	..
768	0.054	..
824	0.670	0.14
1032	0.030	0.6
1101	0.023	..
1146	0.037	0.3
1187	0.186	0.22
1202	0.483	0.13
1311	0.051	0.8
1374	0.192	0.45
1446	0.065	0.4
1578	0.045	0.8
1616	0.239	0.72

No. 147. *n*-Propylbenzene

251	0.036	0.87
312	0.051	0.4
480	0.057	0.41
558	0.019	..
614	0.114	0.88
740	0.110	0.2
804	0.105	0.1
810	0.114	0.1
884	0.039	0.5
942	0.031	..
1000	0.665	0.15
1028	0.228	0.24
1091	0.053	0.3
1154	0.064	0.65
1179	0.079	0.30
1199	0.184	1.
1282	0.022	..
1337	0.035	0.5
1440	0.102	0.88
1548	0.015	0.7
1587	0.115	0.72
1601	0.197	0.73

No. 148. Isopropylbenzene

304	0.079	0.44
395	0.008	..
453	0.067	0.2
554	0.028	0.6
614	0.104	0.64
680	0.021	..
734	0.256	0.13
757	0.045	0.3
835	0.018	0.7
890	0.062	0.52
942	0.047	0.2
999	0.654	0.13
1026	0.212	0.13
1081	0.034	0.3
1104	0.041	0.09
1153	0.062	0.91
1180	0.069	0.61
1208	0.149	0.15
1283	0.025	0.5
1303	0.046	0.60
1382	0.009	..
1445	0.075	0.62
1456	0.074	0.69
1543	0.013	..
1583	0.094	0.62
1602	0.181	0.59

No. 149
1-Methyl-2-ethylbenzene

205	0.042	0.64
312	0.058	0.4
450	0.036	0.8
491	0.074	1.
545	0.068	0.3
579	0.139	0.44
615	0.007	1.
668	0.031	0.4
718	0.375	0.15
752	0.044	1.
786	0.026	..
817	0.038	..
857	0.014	..
963	0.088	0.40
986	0.087	0.1
1033	0.232	0.11
1055	0.278	0.13
1104	0.012	..
1156	0.092	..
1213	0.283	0.11
1243	0.012	0.4
1280	0.016	0.7
1319	0.042	0.49
1376	0.078	0.44
1446	0.129	0.76
1550	0.021	..
1584	0.103	0.69
1602	0.193	0.61

No. 150
1-Methyl-3- thylbenzene

213	0.139	0.95
306	0.029	0.5
430	0.022	..
506	0.124	0.77
521	0.201	0.36
579	0.021	1.
614	0.014	..
660	0.026	0.7
716	0.330	0.16
786	0.037	1.
882	0.038	0.7
942	0.046	..
1000	0.619	0.12
1057	0.081	..
1097	0.039	..
1169	0.040	1.
1242	0.146	0.1
1324	0.049	0.4
1373	0.077	0.63
1442	0.098	0.96
1593	0.130	0.86
1607	0.151	0.85

Raman Spectral Data for Hydrocarbons (*Continued*)

No. 151
1-Methyl-4-ethylbenzene

$\Delta\nu$, cm.$^{-1}$	Scattering Coefficient	ρ
217	0.041	0.49
296	0.024	0.7
357	0.083	0.5
390	0.037	0.4
456	0.069	0.4
584	0.019	..
638	0.147	0.77
720	0.036	0.4
747	0.041	..
808	0.416	0.11
815	0.389	0.10
963	0.065	0.94
998	0.038	..
1059	0.088	0.2
1100	0.019	..
1142	0.021	..
1186	0.248	0.12
1198	0.336	0.11
1318	0.058	0.5
1374	0.102	0.52
1444	0.112	1.
1511	0.013	0.23
1614	0.221	0.66

No. 152. 1,2,3-Trimethylbenzene

225	0.151	0.90
262	0.071	0.80
304	0.021	..
480	0.119	0.76
511	0.080	0.68
531	0.094	0.94
596	0.046	0.3
652	0.627	0.17
750	0.039	0.4
808	0.024	0.81
848	0.017	0.7
893	0.014	0.8
995	0.129	0.23
1024	0.095	0.25
1092	0.168	0.15
1160	0.057	0.95
1189	0.081	0.25
1203	0.063	0.40
1246	0.224	0.16
1319	0.020	1.
1380	0.165	0.46
1438	0.119	0.60
1464	0.071	0.65
1539	0.015	0.5
1594	0.193	0.73

No. 153. 1,2,4-Trimethylbenzene

202	0.047	1.
275	0.022	0.7
314	0.236	0.87
432	0.064	0.63
465	0.198	0.50
490	0.024	0.6
548	0.296	0.40
603	0.013	..
686	0.060	0.3
716	0.208	0.24
741	0.477	0.16
802	0.017	0.5
871	0.016	0.6
920	0.146	0.18
1023	0.031	0.7
1122	0.043	..
1147	0.035	..
1186	0.023	..
1208	0.040	..
1244	0.336	0.16
1325	0.015	0.7
1378	0.254	0.50
1443	0.120	0.80
1576	0.065	0.70
1618	0.200	0.69

No. 154. 1,3,5-Trimethylbenzene

225	0.482	0.85
268	0.111	0.77
453	0.034	0.7
509	0.304	0.69
570	0.555	0.11
884	0.025	0.7
935	0.043	0.3
995	0.487	0.11
1035	0.102	0.09
1104	0.011	..
1160	0.031	..
1248	0.014	..
1298	0.210	0.13
1377	0.216	0.38
1425	0.036	0.65
1437	0.036	0.74
1546	0.014	0.9
1605	0.168	0.81

No. 155. *n*-Butylbenzene

224	0.031	0.8
286	0.042	0.3
496	0.033	0.6
571	0.026	0.7
620	0.102	0.83
744	0.063	0.2
781	0.067	0.2
815	0.082	0.2
842	0.015	0.9
895	0.056	0.3
945	0.057	..
1005	0.552	0.1
1034	0.195	0.1
1052	0.078	0.4
1106	0.073	0.3
1160	0.057	0.73
1187	0.092	0.31
1204	0.178	0.2
1303	0.038	0.9
1336	0.032	0.5
1450	0.114	0.79
1552	0.013	0.7
1595	0.088	0.82
1613	0.187	0.75

No. 156. Isobutylbenzene

254	0.145	0.83
311	0.103	0.3
425	0.050	0.6
495	0.071	0.67
620	0.133	0.9
740	0.127	0.2
812	0.259	0.2
909	0.050	0.5
952	0.152	0.39
1006	0.720	0.13
1034	0.240	0.11
1058	0.030	..
1120	0.110	0.71
1164	0.114	0.79
1183	0.114	0.60
1212	0.247	0.21
1286	0.091	0.45
1347	0.095	0.46
1455	0.152	0.78
1553	0.025	0.5
1613	0.253	0.78

No. 157. *sec*-Butylbenzene

312	0.045	0.5
461	0.064	..
559	0.014	..
619	0.110	0.82
731	0.131	..
749	0.067	..
805	0.038	..
850	0.045	0.7
902	0.020	0.6
948	0.056	0.3
1001	0.611	0.11
1032	0.212	0.1
1095	0.049	0.5
1159	0.060	0.76
1188	0.073	0.49
1209	0.163	0.1
1339	0.018	..
1460	0.141	0.77
1612	0.198	0.83

No. 158. *tert*-Butylbenzene

314	0.086	0.78
341	0.069	0.66
386	0.017	0.9
458	0.011	..
528	0.103	0.25
615	0.101	0.83
645	0.033	..
702	0.366	0.17
762	0.030	0.74
836	0.054	0.58
901	0.051	0.85
929	0.110	0.63
1000	0.588	0.17
1030	0.284	0.19
1113	0.122	0.32
1156	0.076	0.78
1194	0.155	0.77
1265	0.062	0.2
1444	0.116	0.93
1463	0.092	0.97
1599	0.164	0.93

No. 159
1-Methyl-2-isopropylbenzene

217	0.088	0.81
302	0.051	0.49
339	0.020	..
393	0.017	..
459	0.031	0.9
487	0.113	0.4
507	0.092	0.4
556	0.032	..
594	0.110	0.60
657	0.036	..
716	0.433	0.14
757	0.043	0.9
807	0.065	0.46
892	0.076	0.4
937	0.010	..
960	0.017	0.9
985	0.028	..
1040	0.434	0.13
1078	0.045	..
1115	0.053	0.70
1168	0.105	0.78
1233	0.320	0.11
1313	0.039	0.9
1390	0.075	0.45
1464	0.113	0.84
1560	0.016	0.9
1592	0.094	0.65
1615	0.202	0.86

No. 160
1-Methyl-3-isopropylbenzene

220	0.108	0.9
299	0.063	0.42
465	0.086	0.25
523	0.152	0.32
581	0.025	0.9
603	0.020	..
653	0.025	..
711	0.340	0.18
783	0.030	0.9
849	0.034	0.9
918	0.070	..
947	0.059	0.2
1003	0.688	0.11
1053	0.034	..
1100	0.050	0.66
1176	0.052	0.9
1248	0.154	0.1
1286	0.047	..
1313	0.050	0.66
1341	0.018	..
1386	0.086	0.39
1459	0.104	0.57
1601	0.113	0.70
1619	0.152	0.72

No. 161
1-Methyl-4-isopropylbenzene

215	0.043	0.89
299	0.083	0.5
380	0.048	1.
436	0.097	0.2
526	0.013	..
584	0.013	..
638	0.140	0.83
720	0.013	1.
745	0.016	..
801	0.436	0.12
885	0.064	0.79
954	0.038	1.
998	0.008	..
1056	0.118	0.2
1103	0.057	0.51
1146	0.025	..
1188	0.137	0.2
1205	0.314	0.09
1282	0.037	0.6
1303	0.065	0.67
1378	0.086	0.42
1442	0.077	0.62
1458	0.094	0.62
1612	0.232	0.76

No. 162
1,2-Dimethyl-3-ethylbenzene

190	0.079	0.9
253	0.119	0.9
328	0.059	0.57
482	0.119	0.80
529	0.107	0.9
583	0.063	0.2
651	0.056	0.15
812	0.055	0.5
859	0.020	0.6
898	0.018	0.9
945	0.038	0.9
963	0.091	0.57
993	0.083	..
1036	0.125	0.31
1063	0.148	0.2
1107	0.178	0.22
1169	0.069	0.82
1192	0.051	..
1248	0.308	0.15
1273	0.040	..
1329	0.071	0.2
1387	0.186	0.50
1458	0.170	0.68
1549	0.020	..
1600	0.239	0.76

No. 163
1,2-Dimethyl-4-ethylbenzene

191	0.080	0.70
251	0.024	..
306	0.059	0.4
365	0.149	0.46
436	0.036	..
476	0.085	0.66
550	0.208	0.28
646	0.014	..
705	0.114	0.22
742	0.562	0.13
818	0.026	..
876	0.024	..
904	0.104	0.23
971	0.057	0.70
1000	0.038	0.7
1028	0.031	0.76
1062	0.133	0.30
1126	0.057	..
1155	0.026	..
1184	0.017	..
1245	0.344	0.13
1329	0.081	0.40
1386	0.213	0.43
1453	0.202	0.78
1587	0.073	0.54
1625	0.234	0.70

Raman Spectral Data for Hydrocarbons (*Continued*)

No. 164 1,3-Dimethyl-2-ethylbenzene

Δν, cm.⁻¹	Scattering Coefficient	ρ
235	0.187	0.90
320	0.051	0.6
351	0.072	0.83
479	0.127	0.90
533	0.170	0.90
554	0.122	0.2
594	0.044	..
648	0.759	0.13
767	0.039	0.9
794	0.031	0.8
885	0.036	0.7
959	0.122	0.87
995	0.141	0.2
1061	0.252	0.18
1095	0.208	0.22
1168	0.072	0.9
1192	0.083	..
1250	0.371	0.12
1322	0.090	0.49
1384	0.212	0.51
1462	0.194	0.81
1601	0.240	0.76

No. 165 1,3-Dimethyl-4-ethylbenzene

214	0.102	0.87
284	0.014	..
374	0.096	0.51
458	0.081	0.35
485	0.085	0.46
553	0.254	0.42
627	0.017	..
677	0.041	..
730	0.453	0.17
789	0.039	..
820	0.025	..
927	0.127	0.2
967	0.076	0.29
1065	0.108	0.26
1126	0.032	0.2
1216	0.081	0.2
1240	0.193	0.10
1250	0.202	0.11
1328	0.066	0.46
1383	0.205	0.67
1406	0.068	0.87
1459	0.174	0.81
1513	0.020	0.9
1587	0.065	0.87
1625	0.251	0.75

No. 166 1,3-Dimethyl-5-ethylbenzene

219	0.162	0.9
275	0.091	0.9
318	0.023	..
346	0.025	..
459	0.045	..
511	0.224	0.70
554	0.360	0.12
602	0.151	0.2
786	0.017	0.9
893	0.059	0.42
944	0.059	..
1001	0.665	0.14
1034	0.111	0.2
1070	0.109	0.3
1172	0.026	0.9
1293	0.196	0.1
1334	0.159	0.25
1384	0.245	0.38
1452	0.143	0.62
1556	0.019	..
1618	0.189	0.77

No. 167 1,4-Dimethyl-2-ethylbenzene

289	0.090	0.72
326	0.113	0.78
465	0.222	0.38
537	0.244	0.31
599	0.038	0.9
656	0.017	..
711	0.278	0.23
735	0.285	0.16
795	0.053	0.46
898	0.186	0.21
963	0.061	0.4
1000	0.078	0.2
1063	0.091	0.3
1133	0.027	0.3
1159	0.013	0.7
1184	0.017	..
1211	0.050	0.2
1245	0.358	0.12
1325	0.065	0.3
1383	0.248	0.42
1457	0.192	0.67
1588	0.076	0.60
1626	0.227	0.69

No. 168. 1,2-Diethylbenzene

223	0.034	..
280	0.020	..
337	0.061	0.4
354	0.038	..
468	0.065	0.6
484	0.073	0.67
540	0.073	0.3
587	0.114	0.55
654	0.031	..
711	0.386	0.14
751	0.079	0.5
784	0.068	0.4
807	0.034	..
865	0.022	..
964	0.179	0.63
1035	0.367	0.14
1060	0.292	0.17
1104	0.020	..
1161	0.102	0.63
1212	0.345	0.14
1245	0.026	..
1277	0.022	..
1328	0.112	0.38
1381	0.020	..
1460	0.232	0.69
1553	0.020	..
1590	0.126	0.69
1612	0.290	0.72

No. 169. 1,3-Diethylbenzene

299	0.032	0.4
451	0.028	..
513	0.074	0.3
548	0.022	..
617	0.035	0.6
663	0.020	..
717	0.209	0.17
796	0.032	0.7
867	0.012	..
902	0.030	0.4
950	0.073	0.4
971	0.107	0.59
1005	0.643	0.11
1069	0.129	0.2
1109	0.039	0.4
1176	0.046	0.6
1242	0.148	0.1
1331	0.089	0.3
1452	0.151	0.87
1600	0.120	0.64
1617	0.148	0.75

No. 170. 1,4-Diethylbenzene

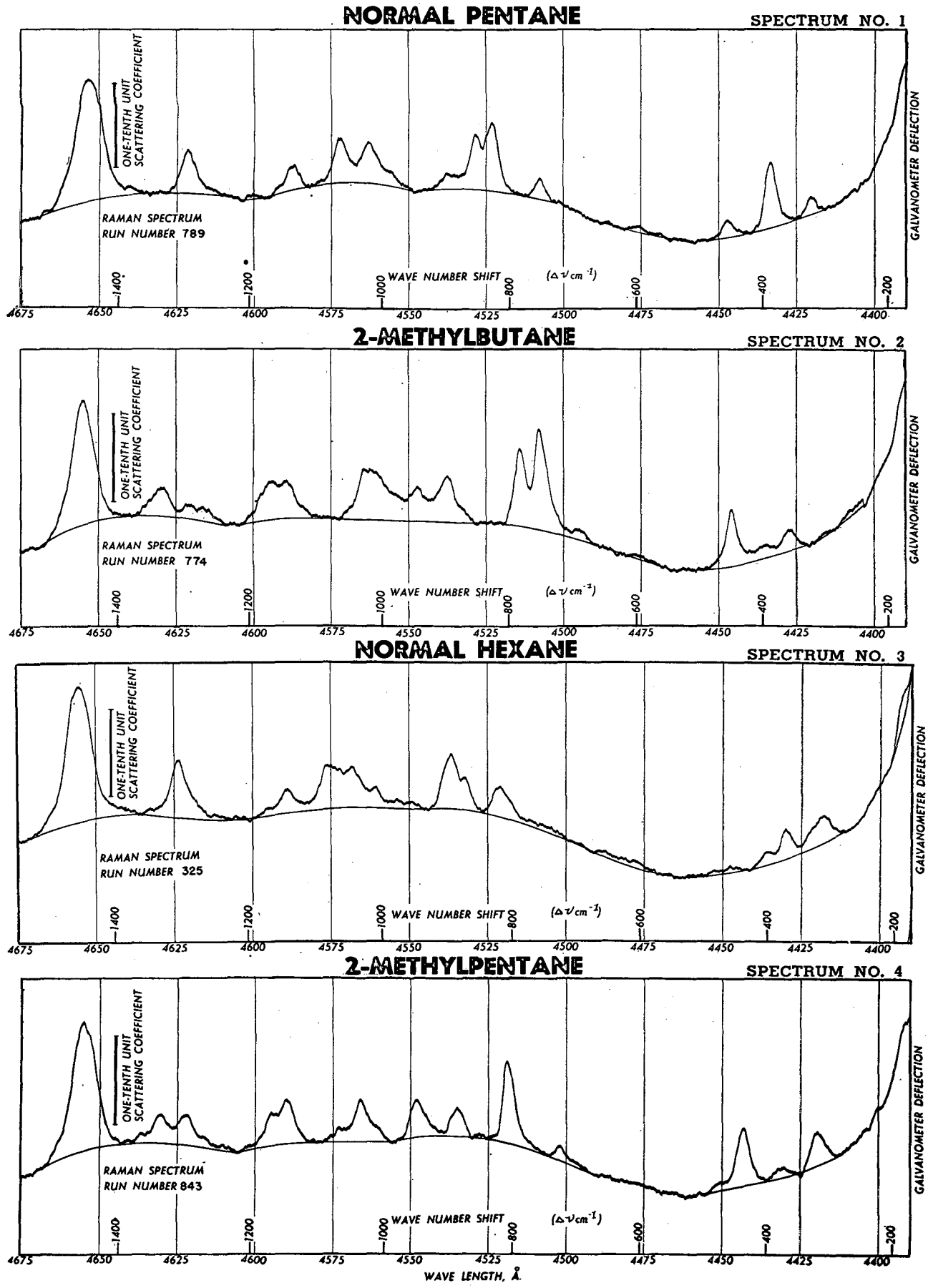
374	0.077	0.3
446	0.024	..
583	0.010	..
641	0.099	0.9
700	0.020	..
741	0.065	..
796	0.536	0.11
962	0.130	0.70
1062	0.203	0.20
1190	0.315	0.17
1199	0.334	0.15
1326	0.109	0.45
1380	0.027	0.5
1452	0.195	0.78
1563	0.027	0.83
1624	0.324	0.64

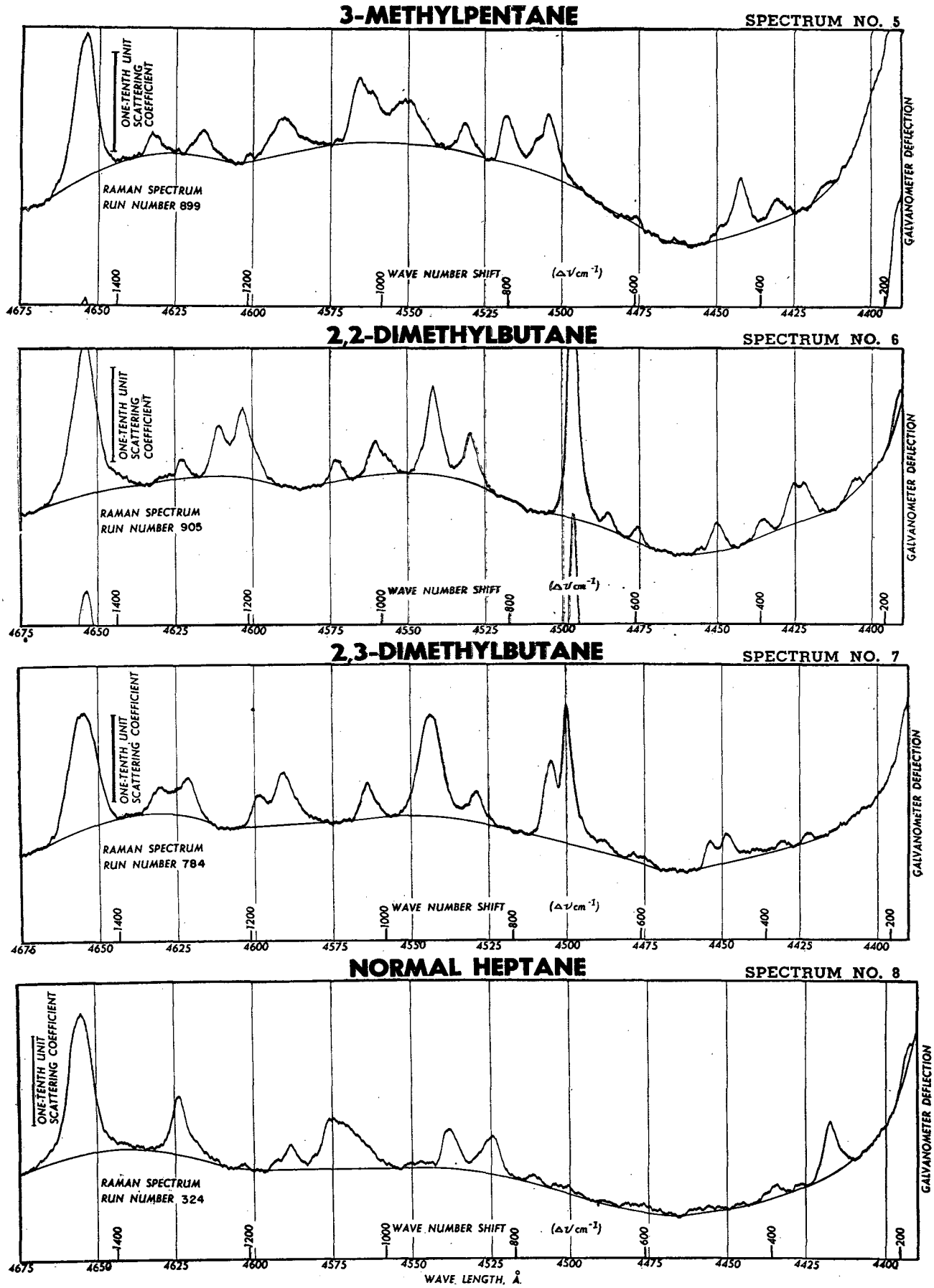
No. 171. Indene

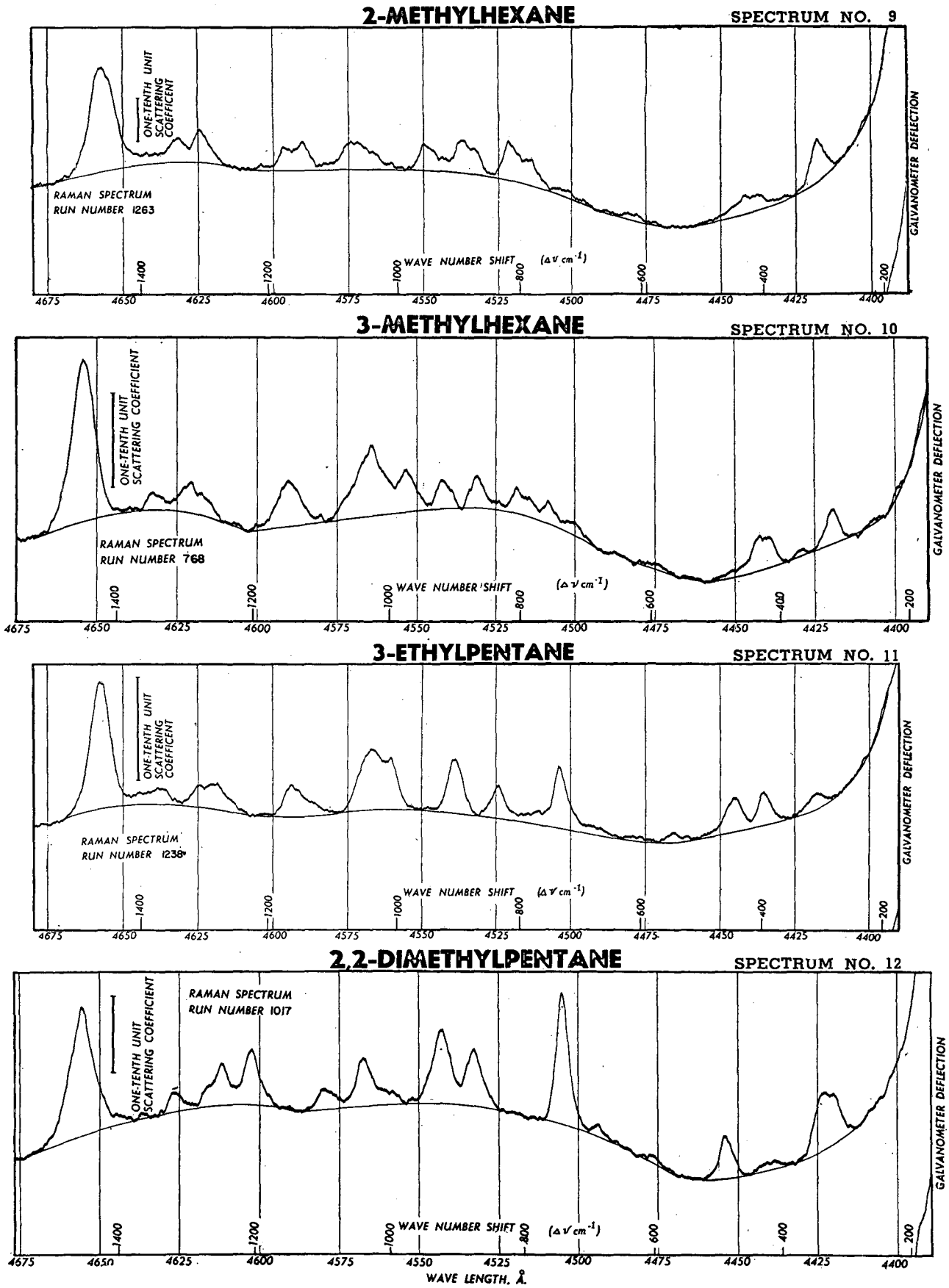
386	0.071	0.6
482	0.013	0.3
532	0.221	0.30
591	0.286	0.65
623	0.039	0.4
672	0.036	0.1
730	0.500	0.11
770	0.088	0.60
835	0.266	0.19
861	0.182	0.53
928	0.130	0.73
947	0.221	0.40
1022	0.708	0.12
1072	0.146	0.23
1112	0.396	0.40
1153	0.101	0.28
1209	0.955	0.29
1227	0.367	0.38
1294	0.104	0.28
1316	0.127	0.46
1366	0.546	0.48
1398	0.377	0.39
1463	0.578	0.46
1498	0.055	0.4
1558	1.143	0.33
1614	1.123	0.47

No. 172. Hydrindene

180	0.033	0.99
252	0.037	0.9
412	0.022	0.9
456	0.015	0.5
513	0.284	0.45
578	0.077	0.97
608	0.025	0.9
742	0.222	0.33
850	0.181	0.29
905	0.052	0.72
917	0.022	0.9
968	0.042	0.2
1000	0.105	0.39
1025	0.432	0.15
1153	0.093	0.60
1202	0.223	0.29
1268	0.060	0.56
1318	0.081	0.35
1378	0.022	1.
1437	0.282	0.76
1460	0.111	0.86
1585	0.118	0.83
1603	0.138	0.82

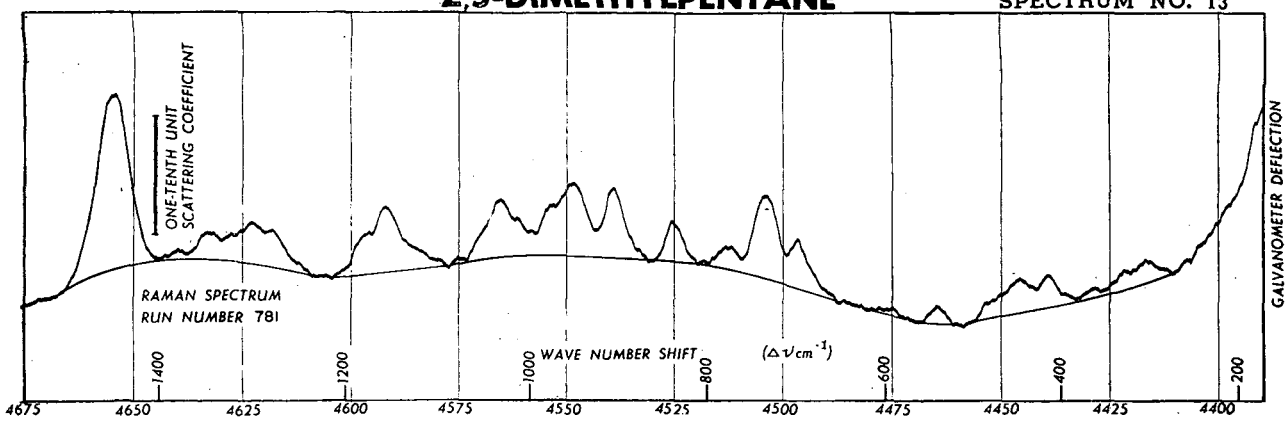

NORMAL PENTANE
SPECTRUM NO. 1
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 789
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2-METHYLBUTANE
SPECTRUM NO. 2
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 774
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
NORMAL HEXANE
SPECTRUM NO. 3
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 325
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2-METHYLPENTANE
SPECTRUM NO. 4
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 843
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1400 1200 1000 800 600 400 200
4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400
WAVE LENGTH, Å.


3-METHYLPENTANE
SPECTRUM NO. 5
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 899
WAVE NUMBER SHIFT (Δν/cm⁻¹)
GALVANOMETER DEFLECTION
2,2-DIMETHYLBUTANE
SPECTRUM NO. 6
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 905
WAVE NUMBER SHIFT (Δν/cm⁻¹)
GALVANOMETER DEFLECTION
2,3-DIMETHYLBUTANE
SPECTRUM NO. 7
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 784
WAVE NUMBER SHIFT (Δν/cm⁻¹)
GALVANOMETER DEFLECTION
NORMAL HEPTANE
SPECTRUM NO. 8
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 324
WAVE NUMBER SHIFT (Δν/cm⁻¹)
GALVANOMETER DEFLECTION
WAVE LENGTH, Å
4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400
1400 1200 1000 800 600 400 200


2-METHYLHEXANE
SPECTRUM NO. 9
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM
RUN NUMBER 1263
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
3-METHYLHEXANE
SPECTRUM NO. 10
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 768
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
3-ETHYLPENTANE
SPECTRUM NO. 11
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM
RUN NUMBER 1238
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2,2-DIMETHYLPENTANE
SPECTRUM NO. 12
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 1017
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
WAVE LENGTH, Å.

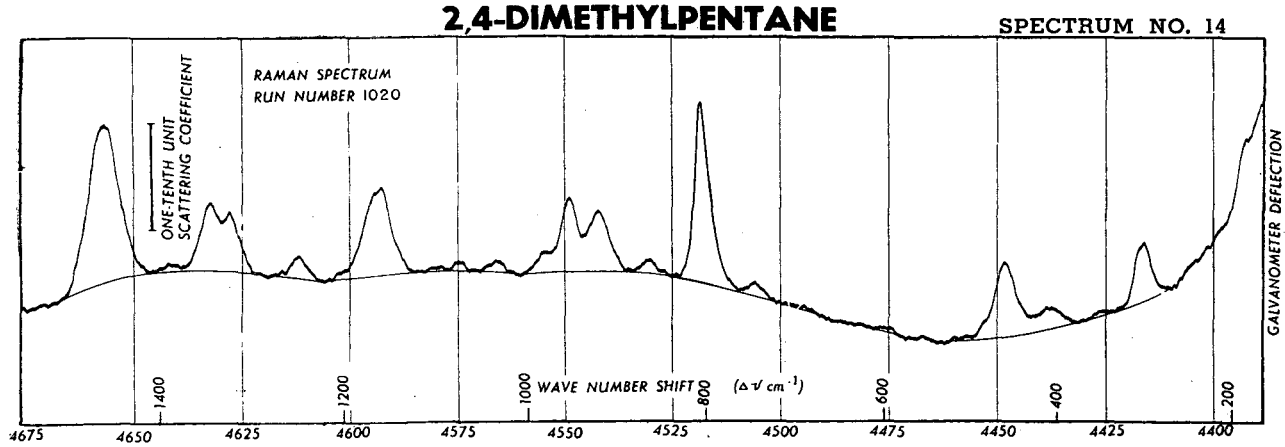
2,3-DIMETHYLPENTANE

SPECTRUM NO. 13



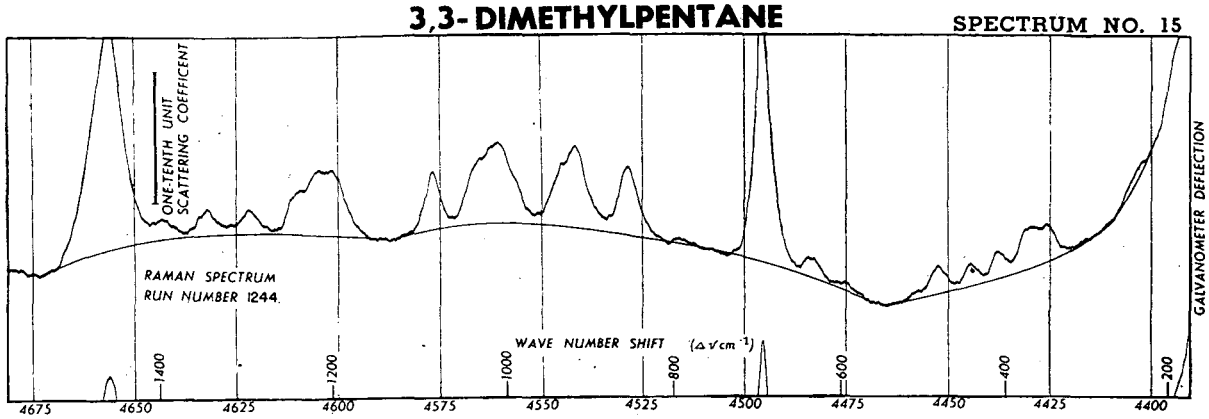
2,4-DIMETHYLPENTANE

SPECTRUM NO. 14



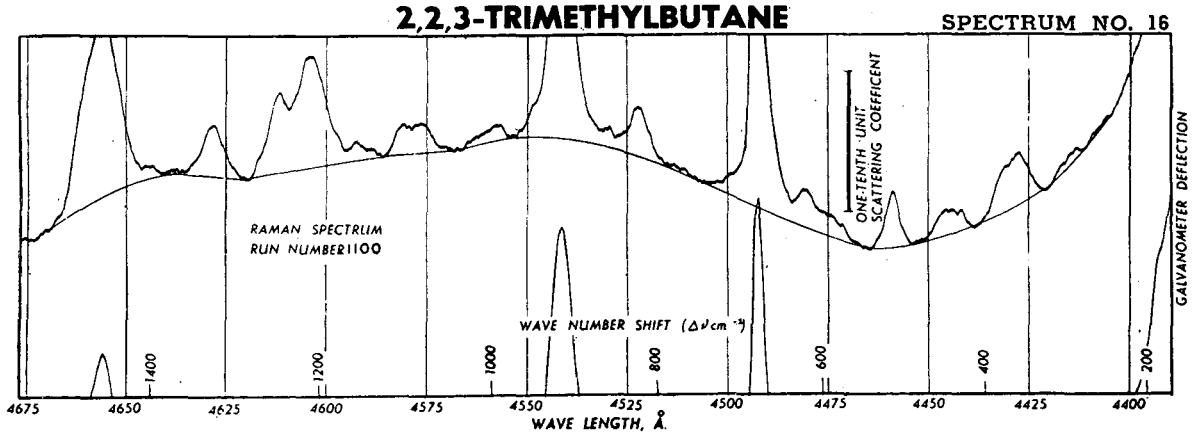
3,3-DIMETHYLPENTANE

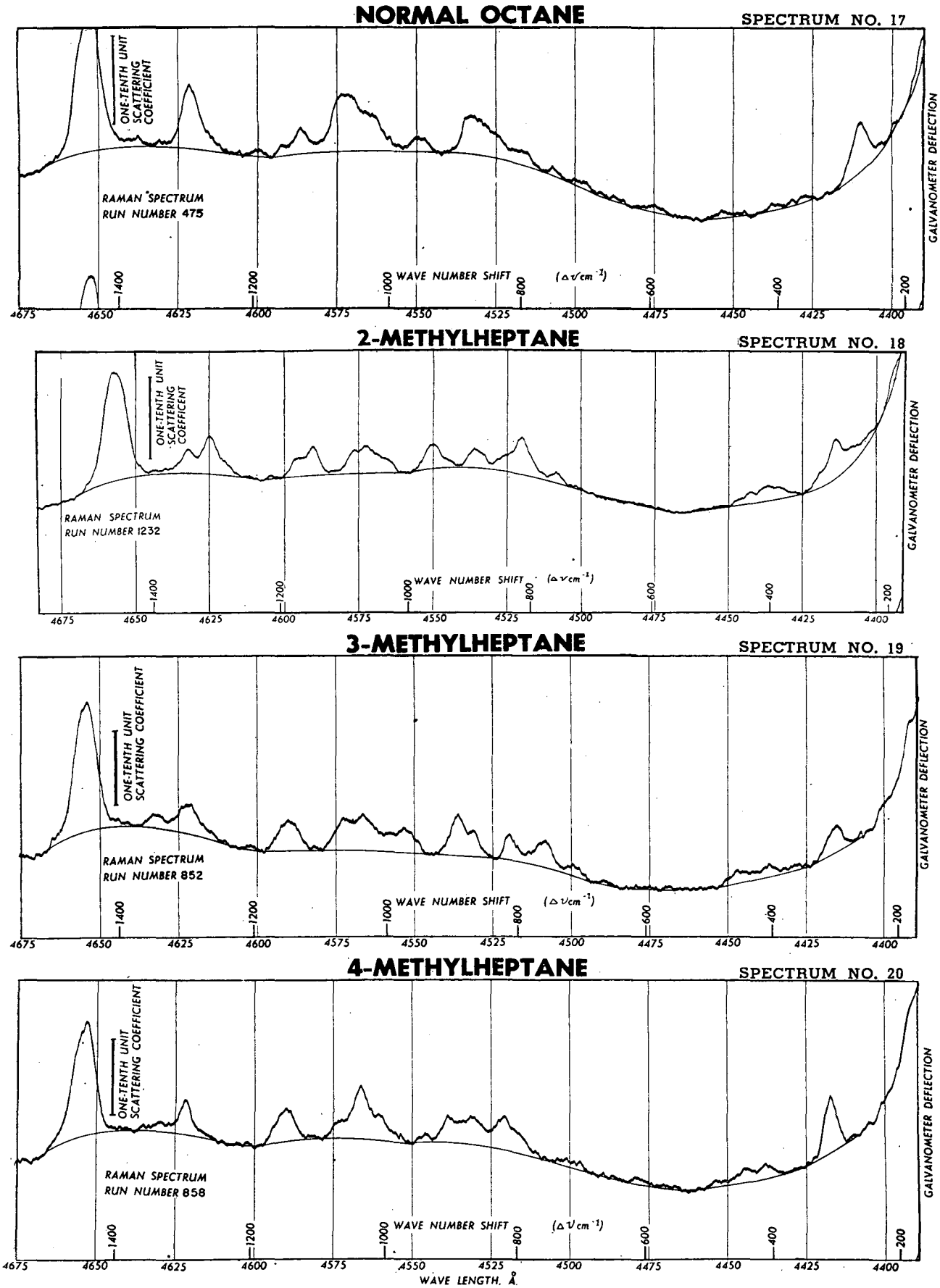
SPECTRUM NO. 15

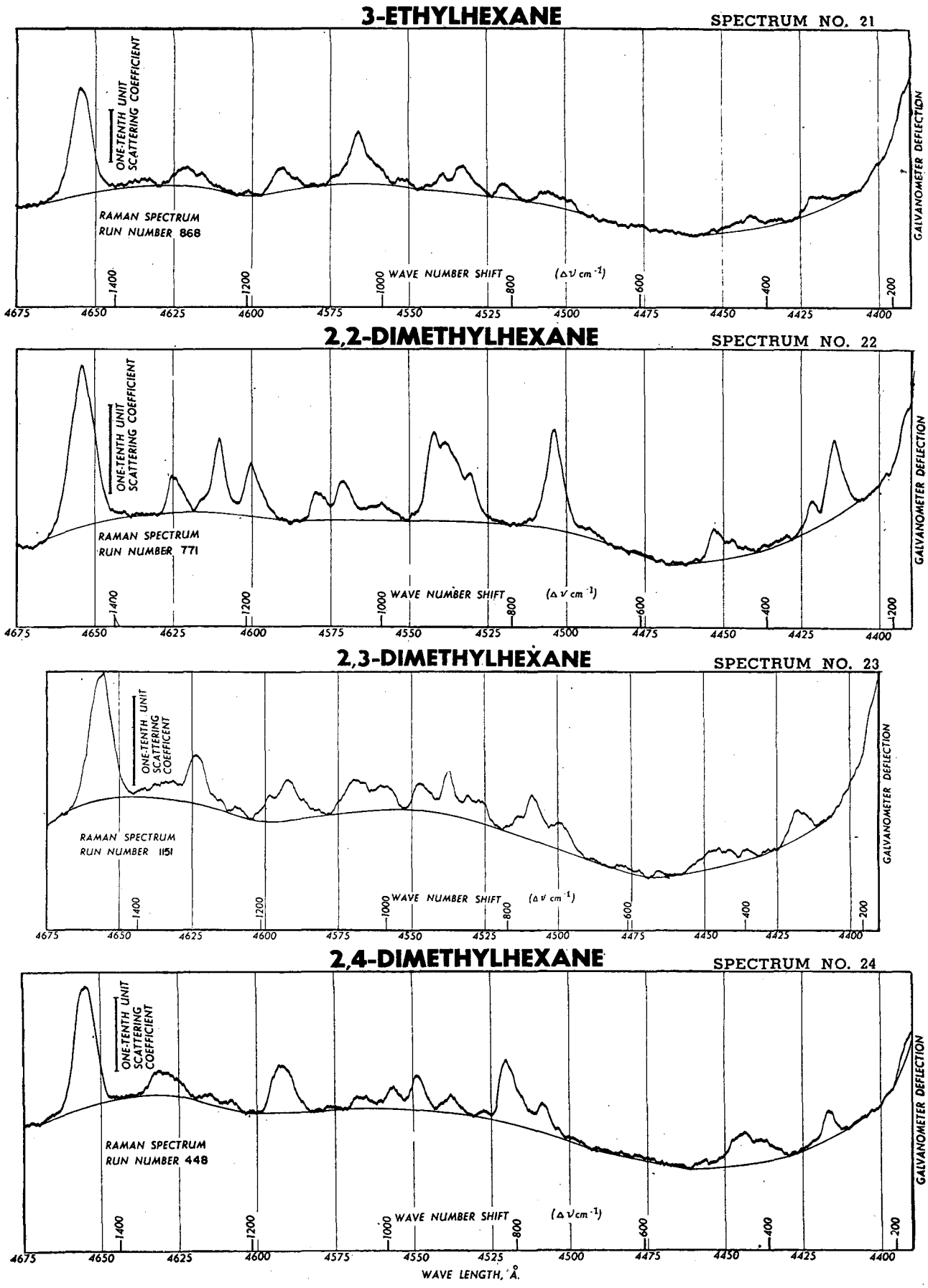


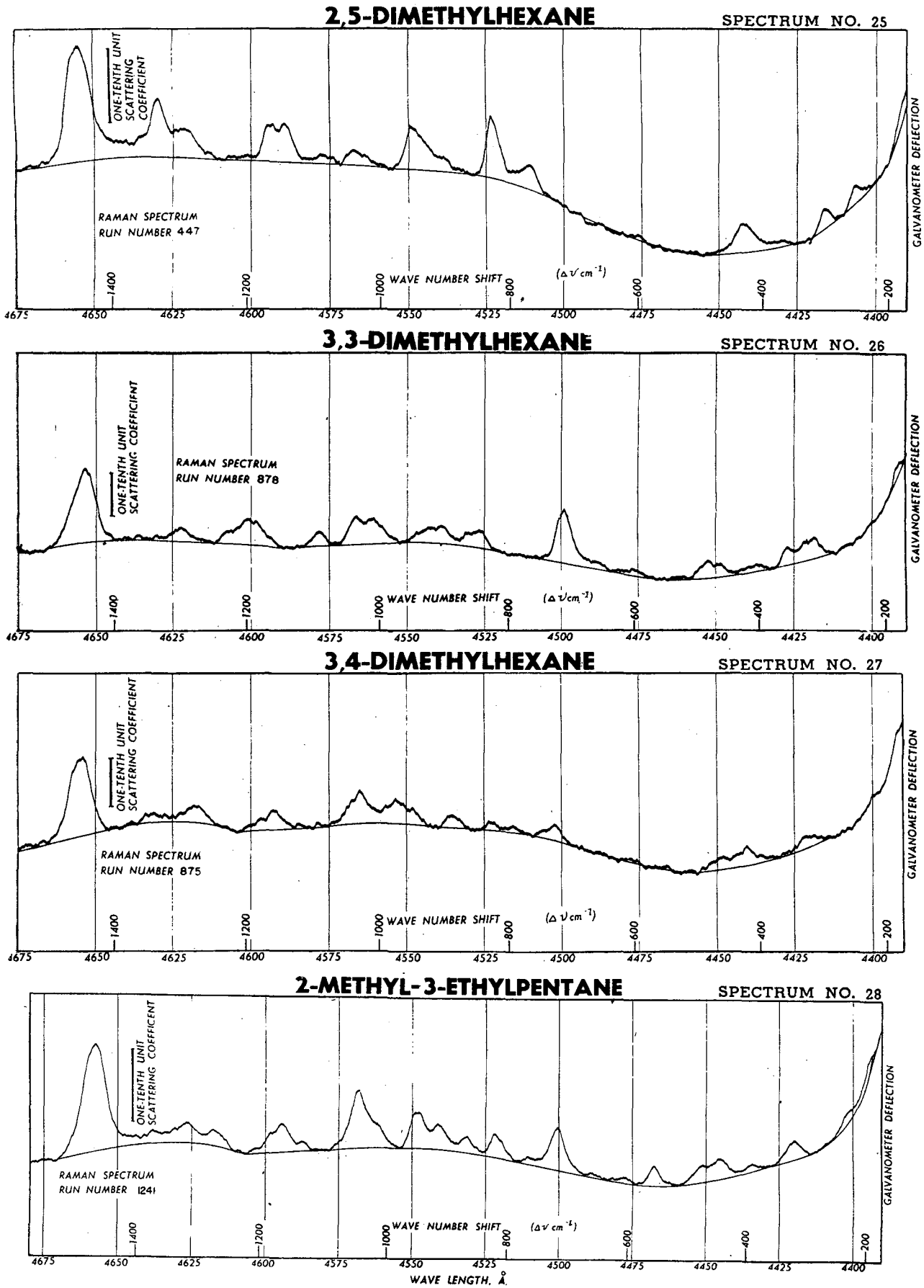
2,2,3-TRIMETHYLBUTANE

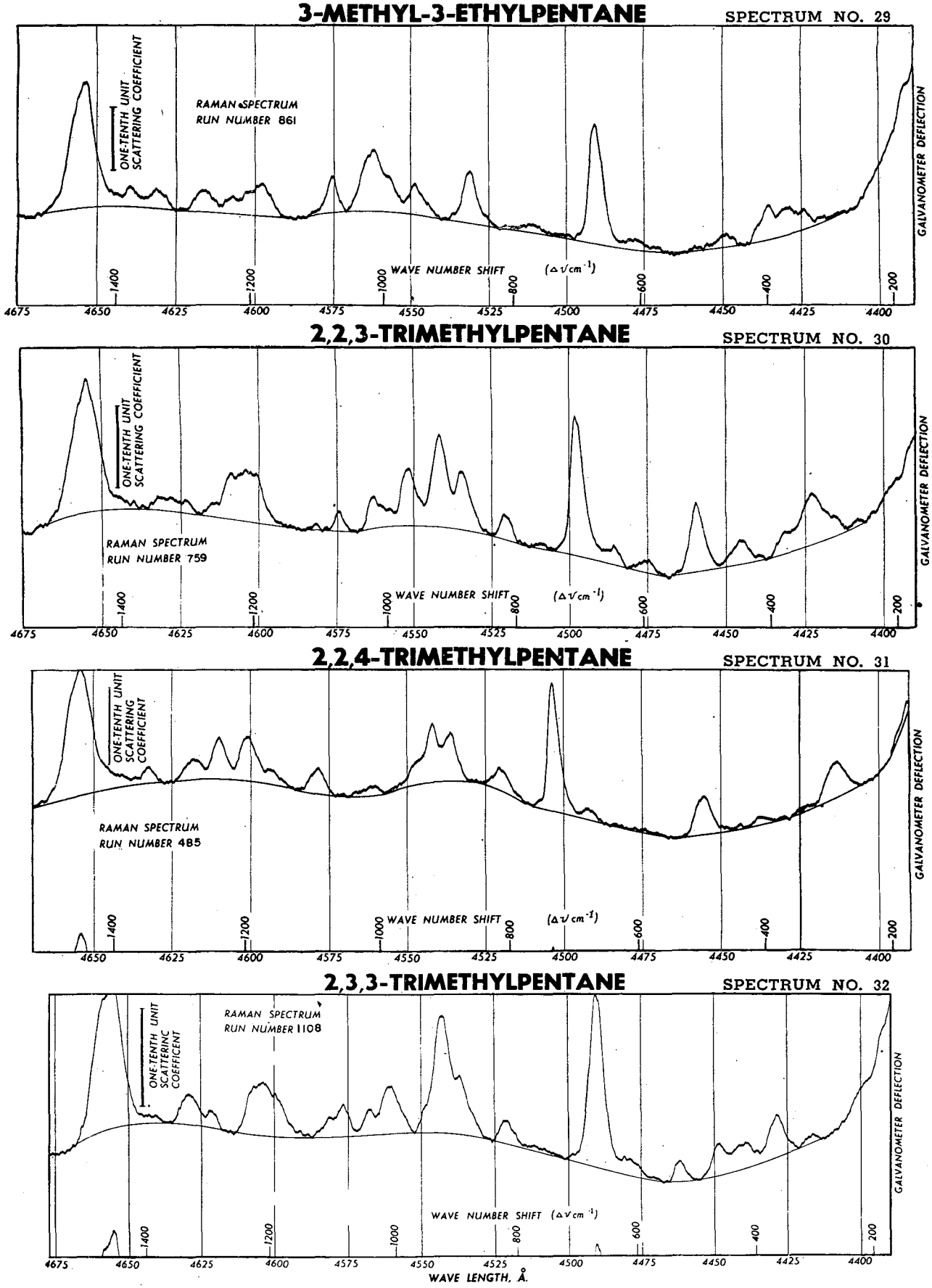
SPECTRUM NO. 16

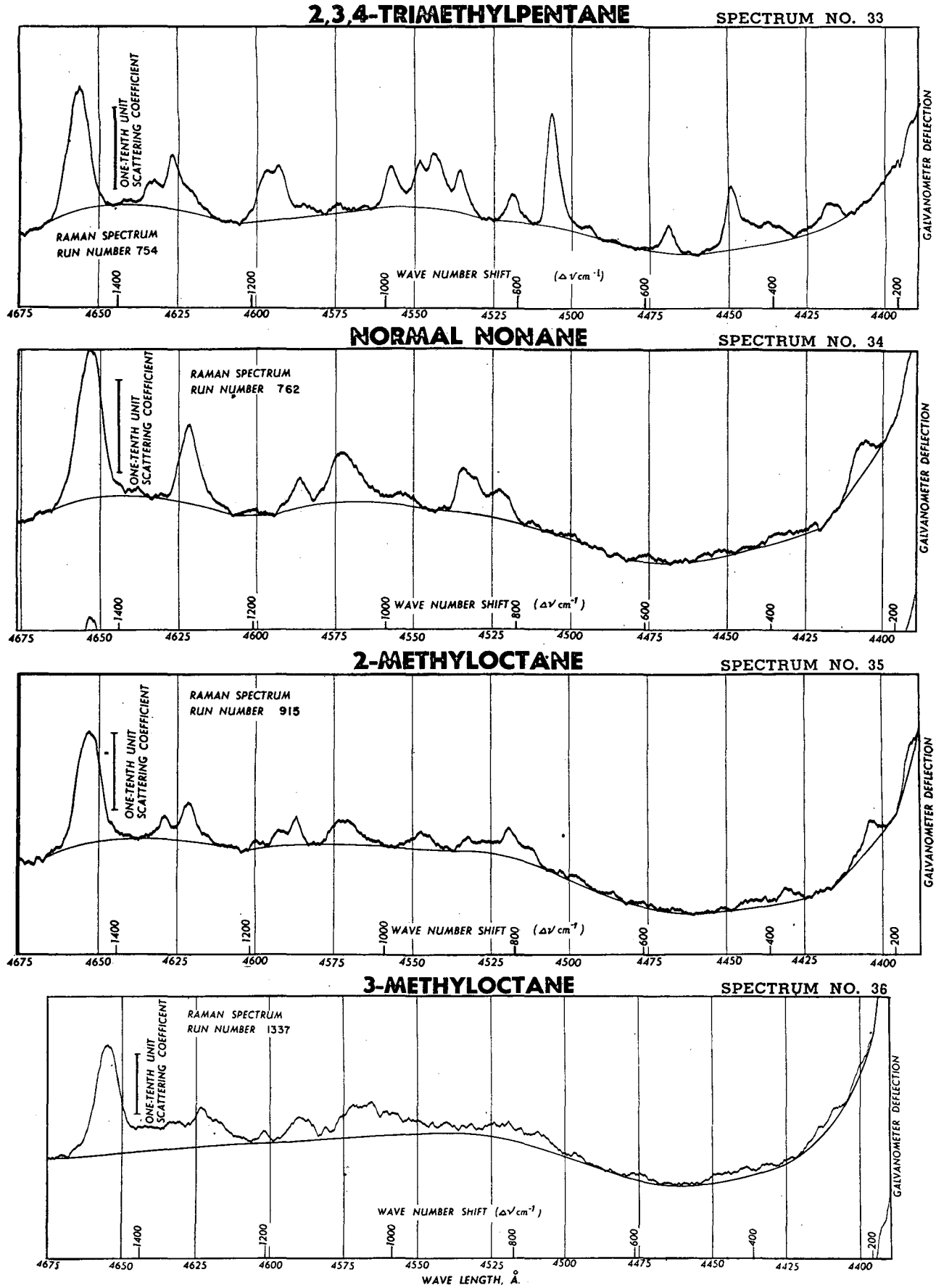


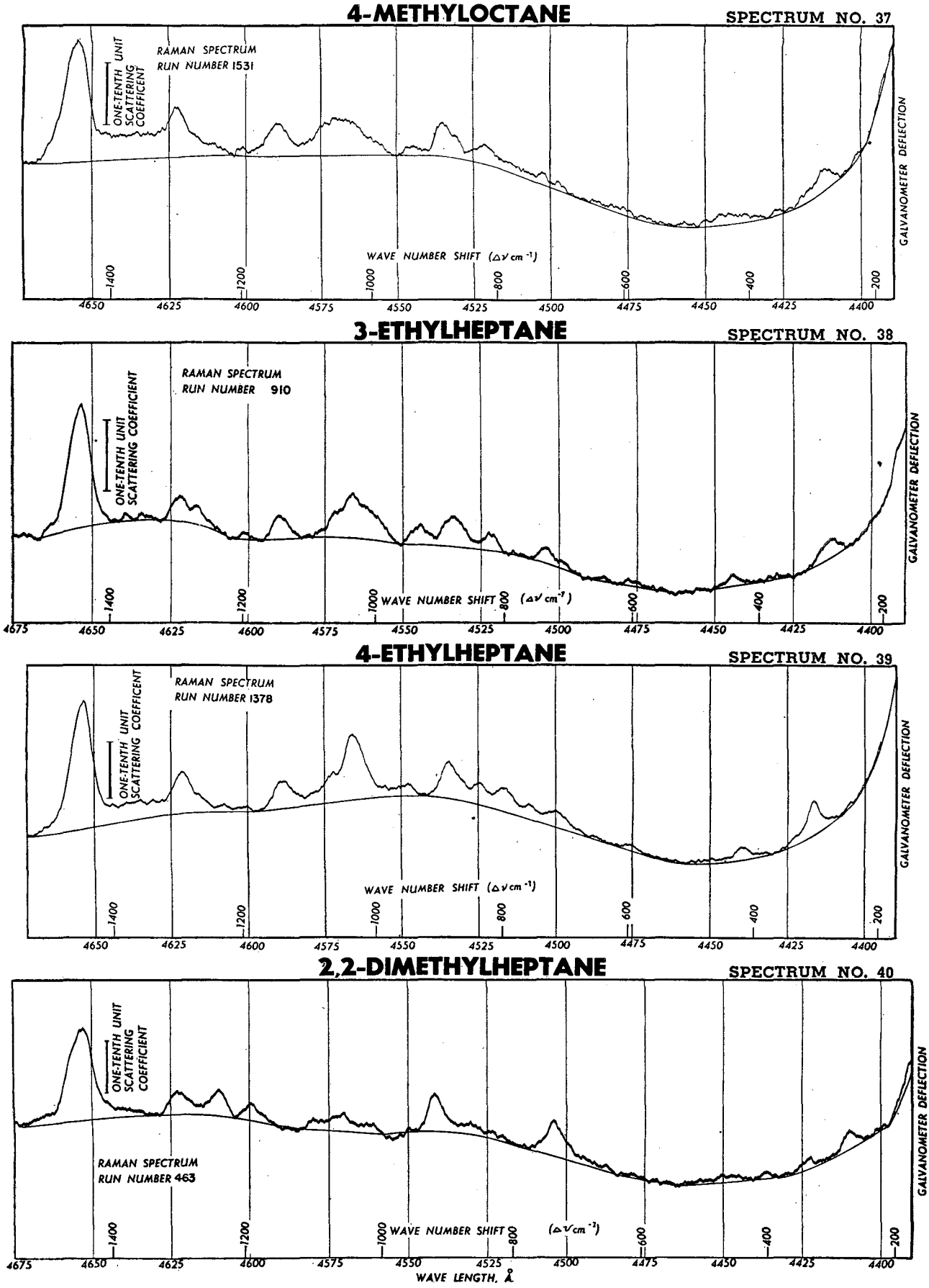

NORMAL OCTANE
SPECTRUM NO. 17
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM RUN NUMBER 475
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2-METHYLHEPTANE
SPECTRUM NO. 18
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM RUN NUMBER 1232
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
3-METHYLHEPTANE
SPECTRUM NO. 19
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM RUN NUMBER 852
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
4-METHYLHEPTANE
SPECTRUM NO. 20
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM RUN NUMBER 858
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1400 1200 1000 800 600 400 200
4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400
WAVE LENGTH, Å

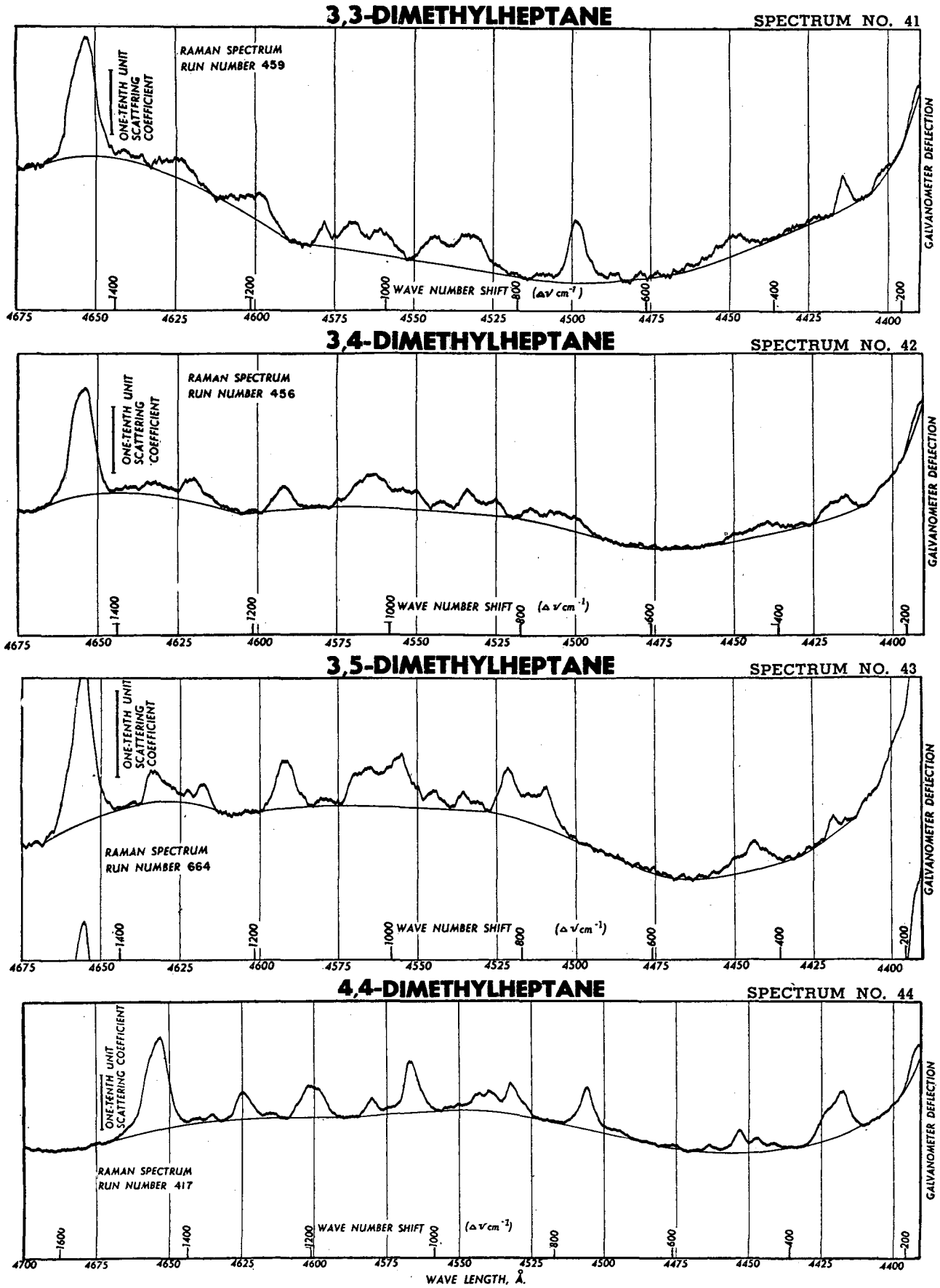

3-ETHYLHEXANE
SPECTRUM NO. 21
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 868
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2,2-DIMETHYLHEXANE
SPECTRUM NO. 22
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 771
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2,3-DIMETHYLHEXANE
SPECTRUM NO. 23
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 1151
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2,4-DIMETHYLHEXANE
SPECTRUM NO. 24
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 448
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1400 1200 1000 800 600 400 200
4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400
WAVE LENGTH, Å.


2,5-DIMETHYLHEXANE
SPECTRUM NO. 25
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 447
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
3,3-DIMETHYLHEXANE
SPECTRUM NO. 26
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 878
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
3,4-DIMETHYLHEXANE
SPECTRUM NO. 27
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 875
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2-METHYL-3-ETHYLPENTANE
SPECTRUM NO. 28
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 1241
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1400 1200 1000 800 600 400 200
4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400
WAVE LENGTH, Å


3-METHYL-3-ETHYLPENTANE
SPECTRUM NO. 29
RAMAN SPECTRUM
RUN NUMBER 861
ONE-TENTH UNIT SCATTERING COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2,2,3-TRIMETHYLPENTANE
SPECTRUM NO. 30
RAMAN SPECTRUM
RUN NUMBER 759
ONE-TENTH UNIT SCATTERING COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2,2,4-TRIMETHYLPENTANE
SPECTRUM NO. 31
RAMAN SPECTRUM
RUN NUMBER 485
ONE-TENTH UNIT SCATTERING COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2,3,3-TRIMETHYLPENTANE
SPECTRUM NO. 32
RAMAN SPECTRUM
RUN NUMBER 1108
ONE-TENTH UNIT SCATTERING COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
WAVE LENGTH, Å.

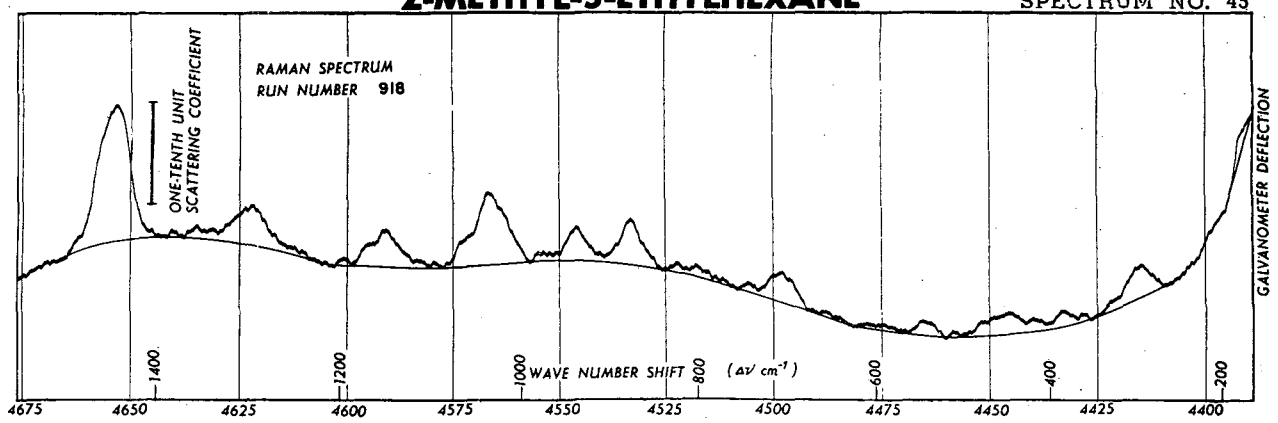

2,3,4-TRIMETHYLPENTANE
SPECTRUM NO. 33
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 754
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
NORMAL NONANE
SPECTRUM NO. 34
RAMAN SPECTRUM
RUN NUMBER 762
2-METHYLOCTANE
SPECTRUM NO. 35
RAMAN SPECTRUM
RUN NUMBER 915
3-METHYLOCTANE
SPECTRUM NO. 36
RAMAN SPECTRUM
RUN NUMBER 1337
WAVE LENGTH, Å.


4-METHYLOCTANE
SPECTRUM NO. 37
RAMAN SPECTRUM
RUN NUMBER 1531
ONE-TENTH UNIT
SCATTERING
COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
3-ETHYLHEPTANE
SPECTRUM NO. 38
RAMAN SPECTRUM
RUN NUMBER 910
ONE-TENTH UNIT
SCATTERING COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
4-ETHYLHEPTANE
SPECTRUM NO. 39
RAMAN SPECTRUM
RUN NUMBER 1378
ONE-TENTH UNIT
SCATTERING COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2,2-DIMETHYLHEPTANE
SPECTRUM NO. 40
RAMAN SPECTRUM
RUN NUMBER 463
ONE-TENTH UNIT
SCATTERING
COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
WAVE LENGTH, Å


3,3-DIMETHYLHEPTANE
SPECTRUM NO. 41
RAMAN SPECTRUM
RUN NUMBER 459
ONE-TENTH UNIT SCATTERING COEFFICIENT
GALVANOMETER DEFLECTION
WAVE NUMBER SHIFT (Δν cm⁻¹)
3,4-DIMETHYLHEPTANE
SPECTRUM NO. 42
RAMAN SPECTRUM
RUN NUMBER 456
ONE-TENTH UNIT SCATTERING COEFFICIENT
GALVANOMETER DEFLECTION
WAVE NUMBER SHIFT (Δν cm⁻¹)
3,5-DIMETHYLHEPTANE
SPECTRUM NO. 43
RAMAN SPECTRUM
RUN NUMBER 664
ONE-TENTH UNIT SCATTERING COEFFICIENT
GALVANOMETER DEFLECTION
WAVE NUMBER SHIFT (Δν cm⁻¹)
4,4-DIMETHYLHEPTANE
SPECTRUM NO. 44
RAMAN SPECTRUM
RUN NUMBER 417
ONE-TENTH UNIT SCATTERING COEFFICIENT
GALVANOMETER DEFLECTION
WAVE NUMBER SHIFT (Δν cm⁻¹)
WAVE LENGTH, Å.

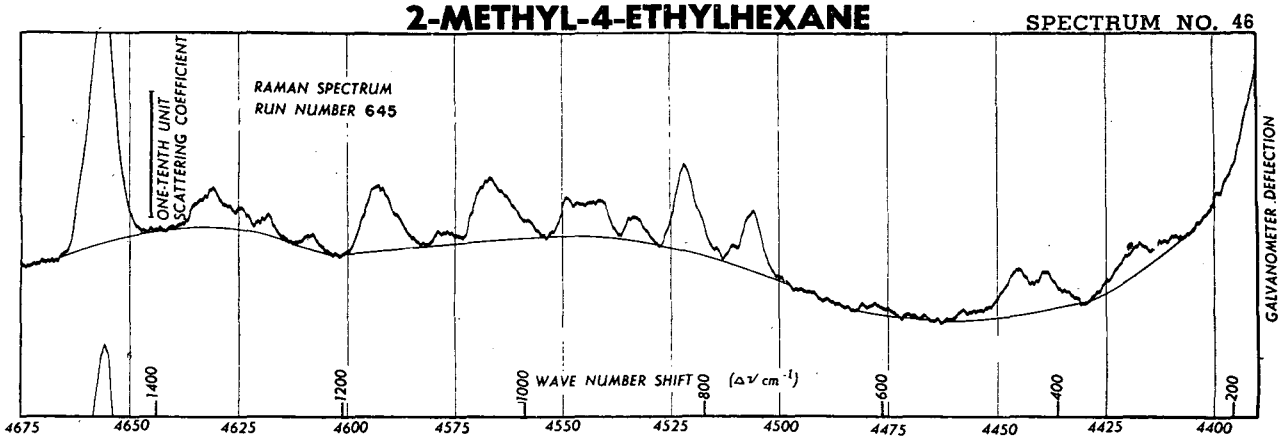
2-METHYL-3-ETHYLHEXANE

SPECTRUM NO. 45



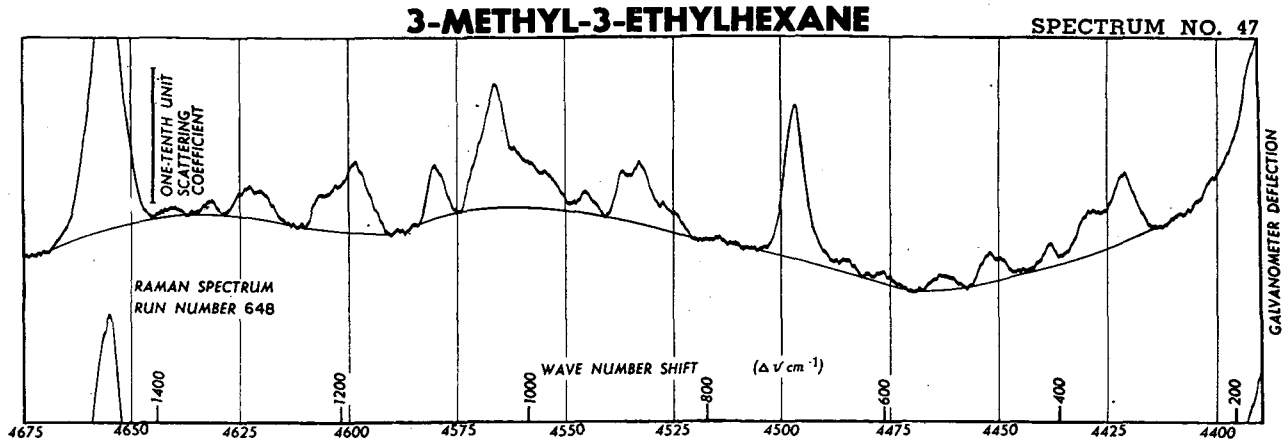
2-METHYL-4-ETHYLHEXANE

SPECTRUM NO. 46



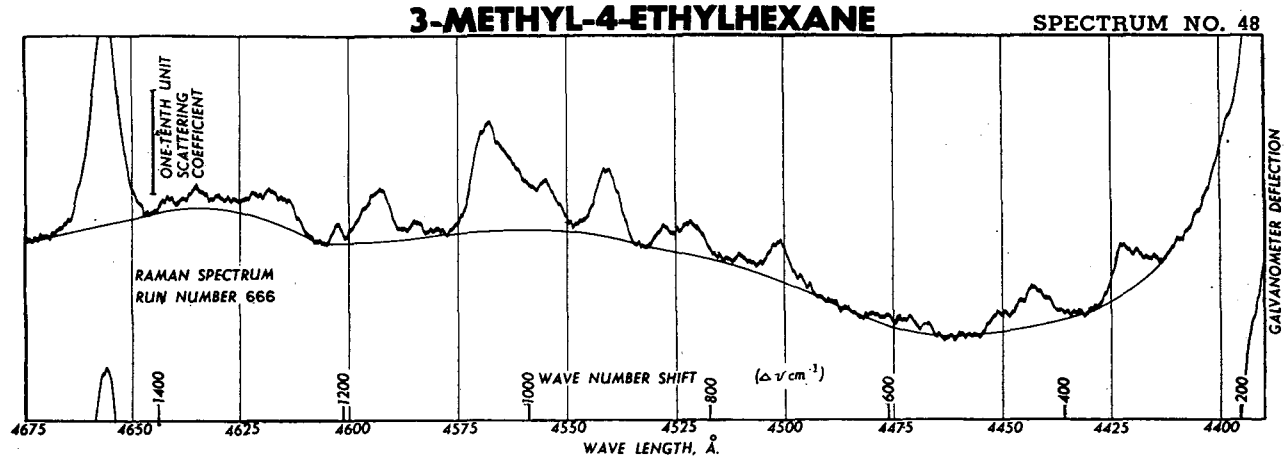
3-METHYL-3-ETHYLHEXANE

SPECTRUM NO. 47

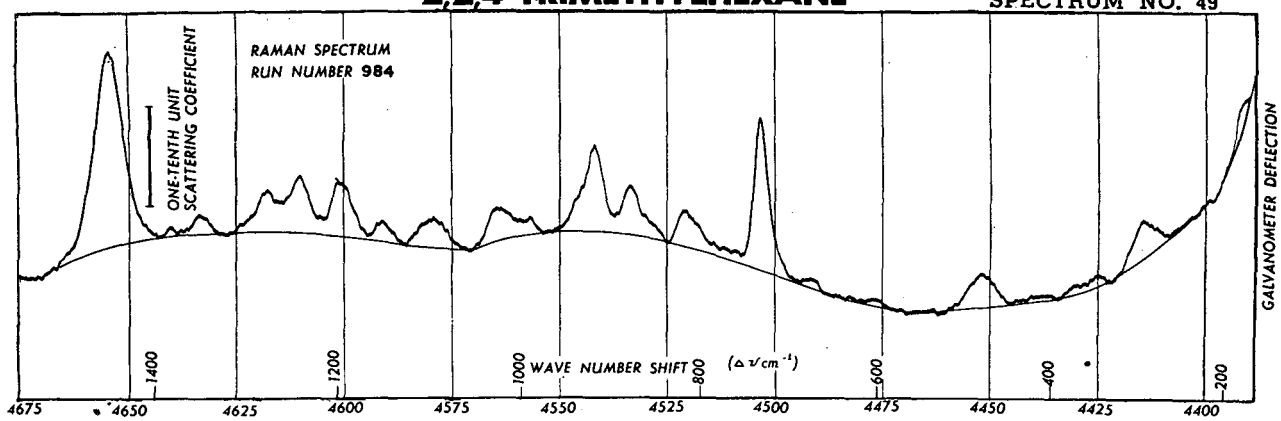


3-METHYL-4-ETHYLHEXANE

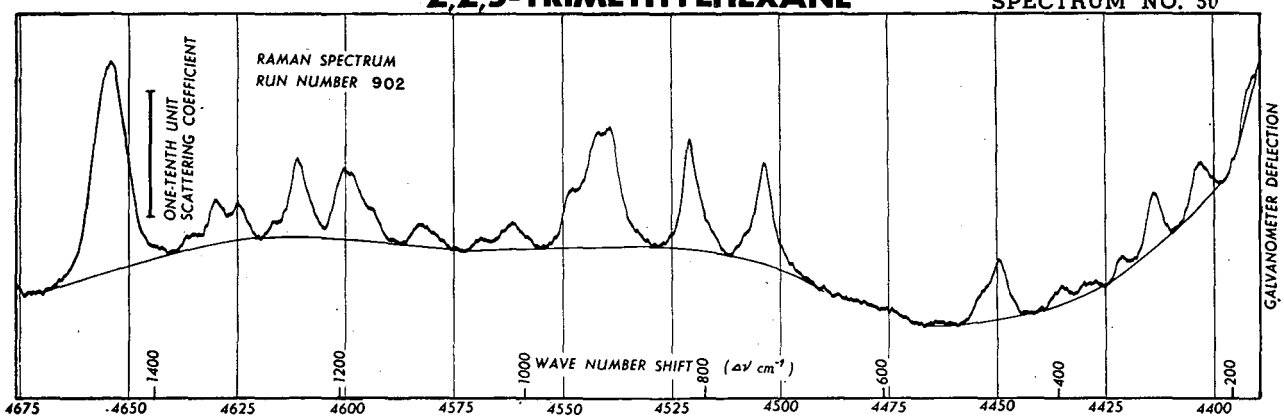
SPECTRUM NO. 48



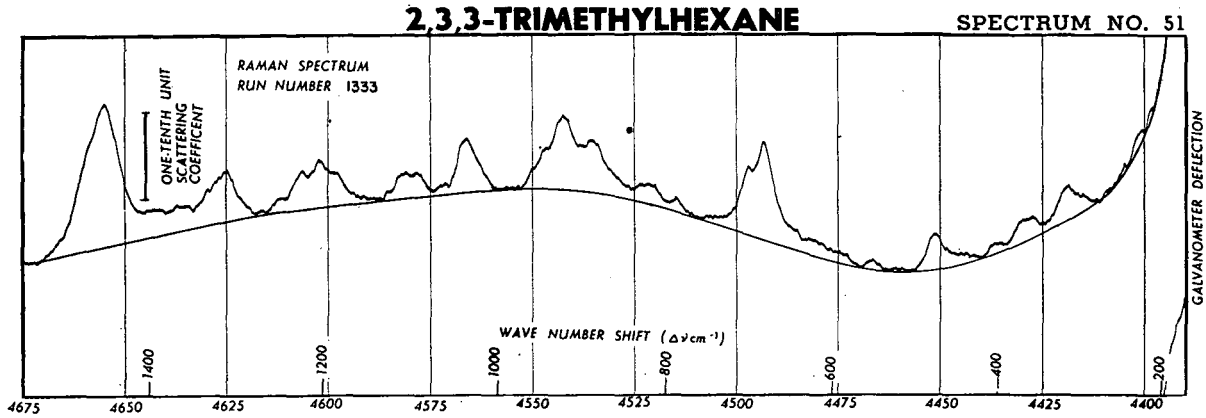
2,2,4-TRIMETHYLHEXANE — SPECTRUM NO. 49



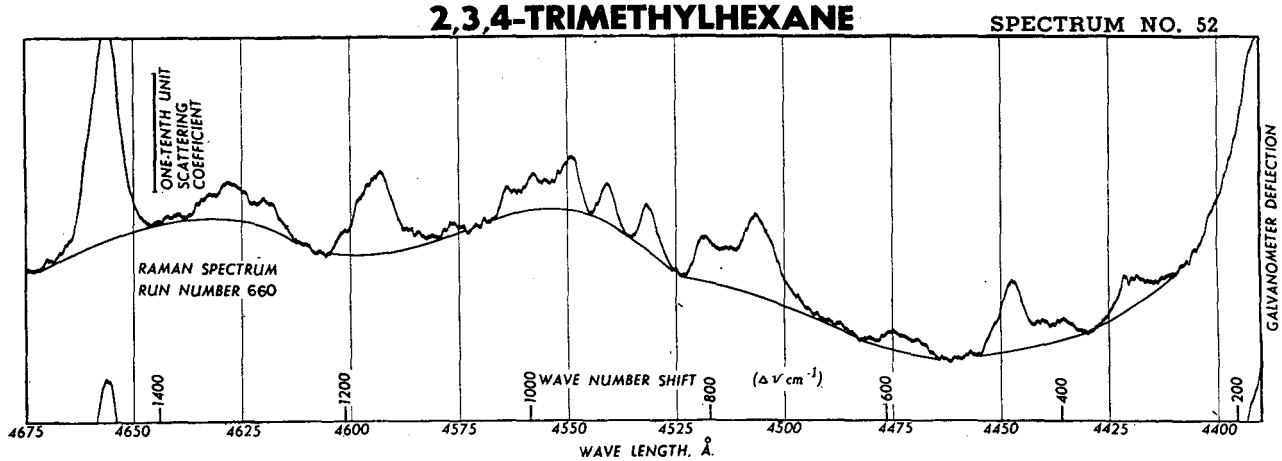
2,2,5-TRIMETHYLHEXANE — SPECTRUM NO. 50



2,3,3-TRIMETHYLHEXANE — SPECTRUM NO. 51

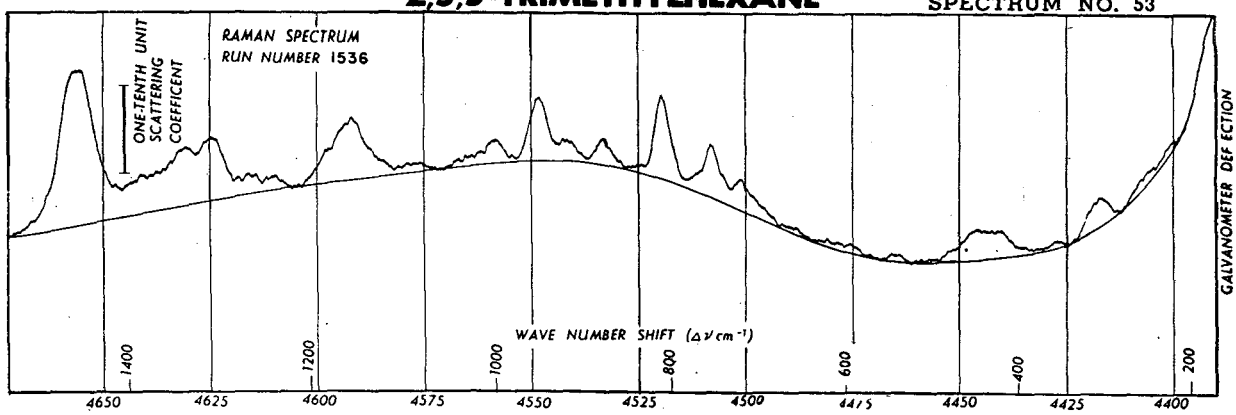


2,3,4-TRIMETHYLHEXANE — SPECTRUM NO. 52



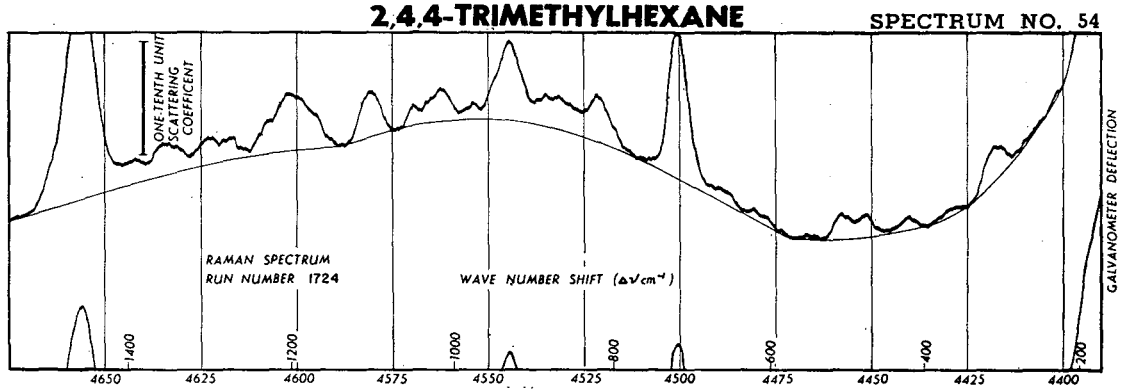
2,3,5-TRIMETHYLHEXANE

SPECTRUM NO. 53



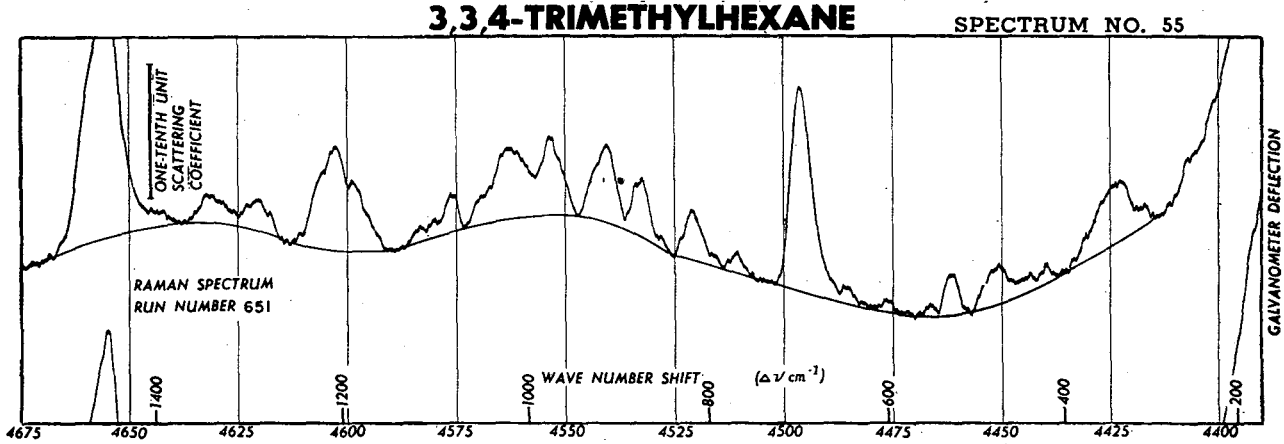
2,4,4-TRIMETHYLHEXANE

SPECTRUM NO. 54



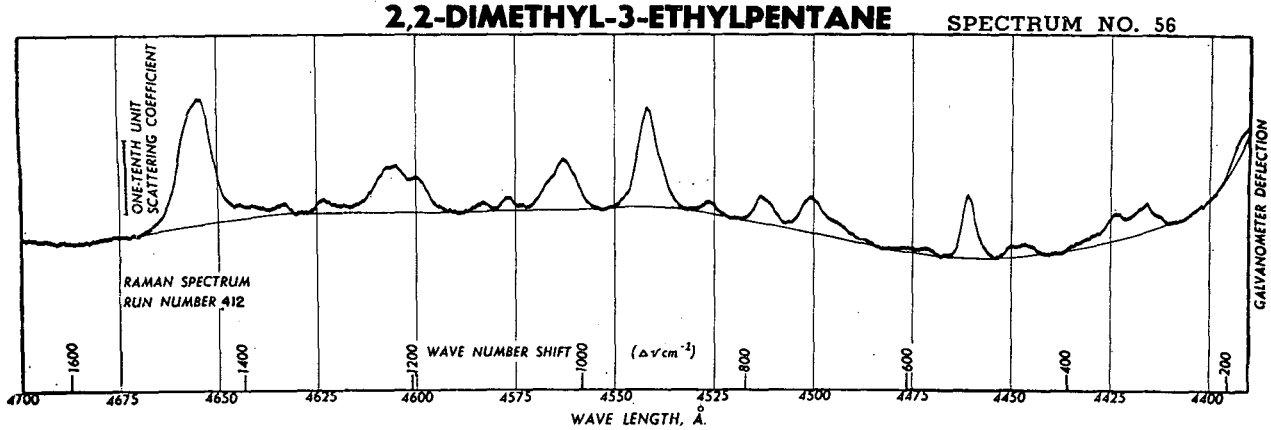
3,3,4-TRIMETHYLHEXANE

SPECTRUM NO. 55



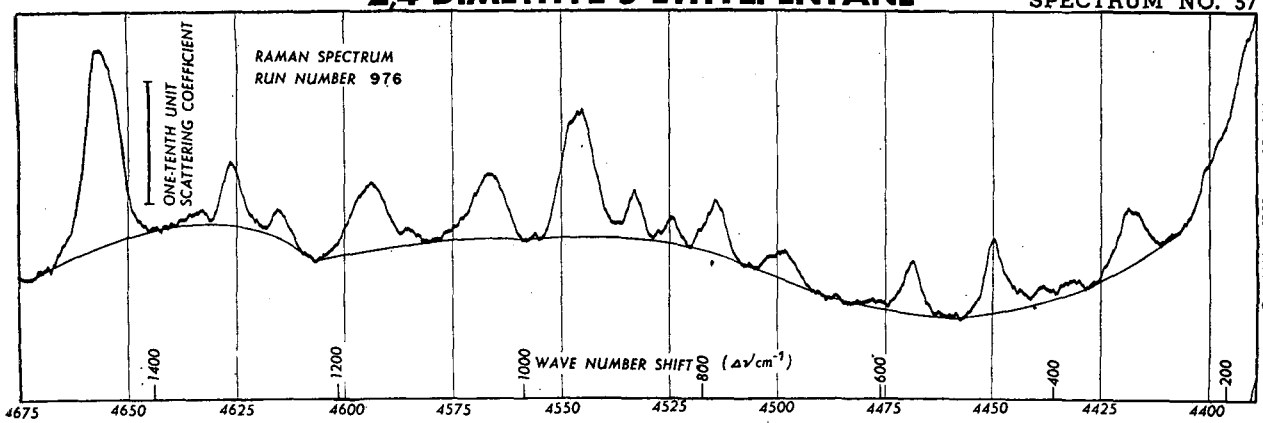
2,2-DIMETHYL-3-ETHYLPENTANE

SPECTRUM NO. 56



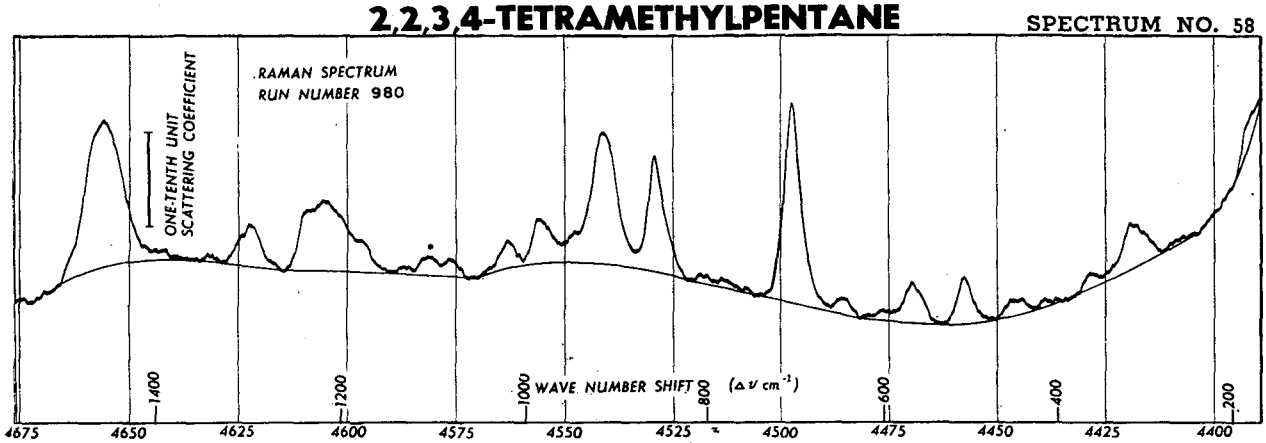
2,4-DIMETHYL-3-ETHYLPENTANE

SPECTRUM NO. 57



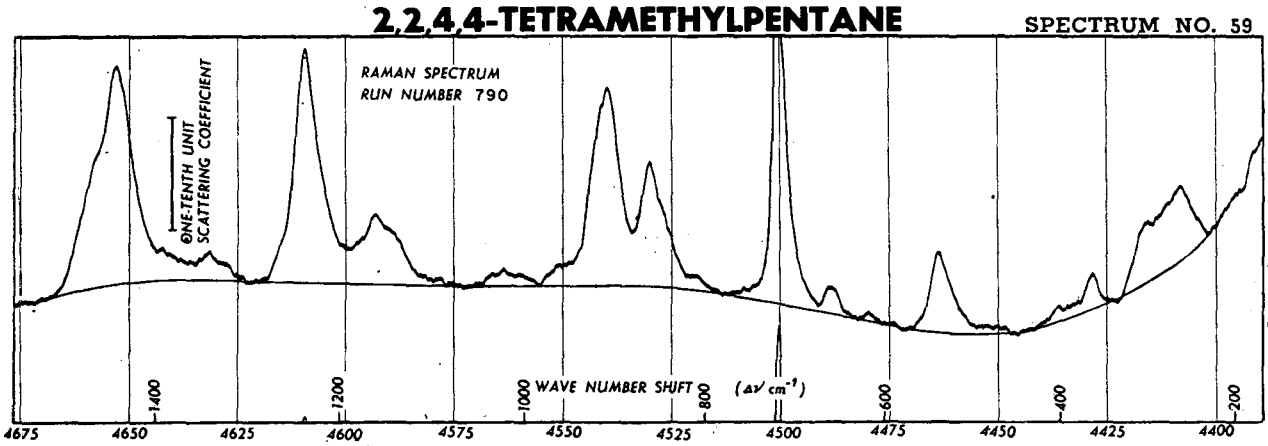
2,2,3,4-TETRAMETHYLPENTANE

SPECTRUM NO. 58



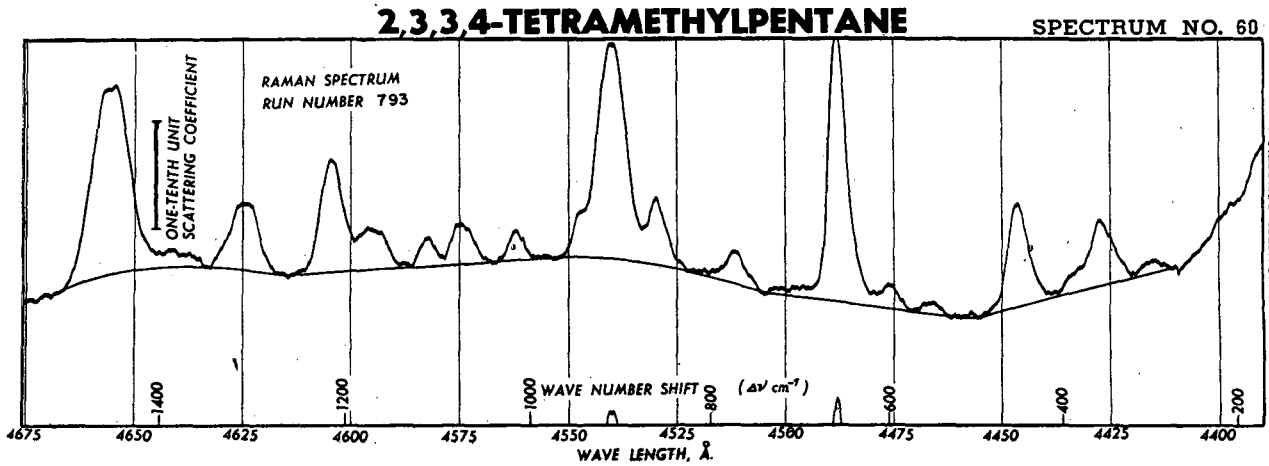
2,2,4,4-TETRAMETHYLPENTANE

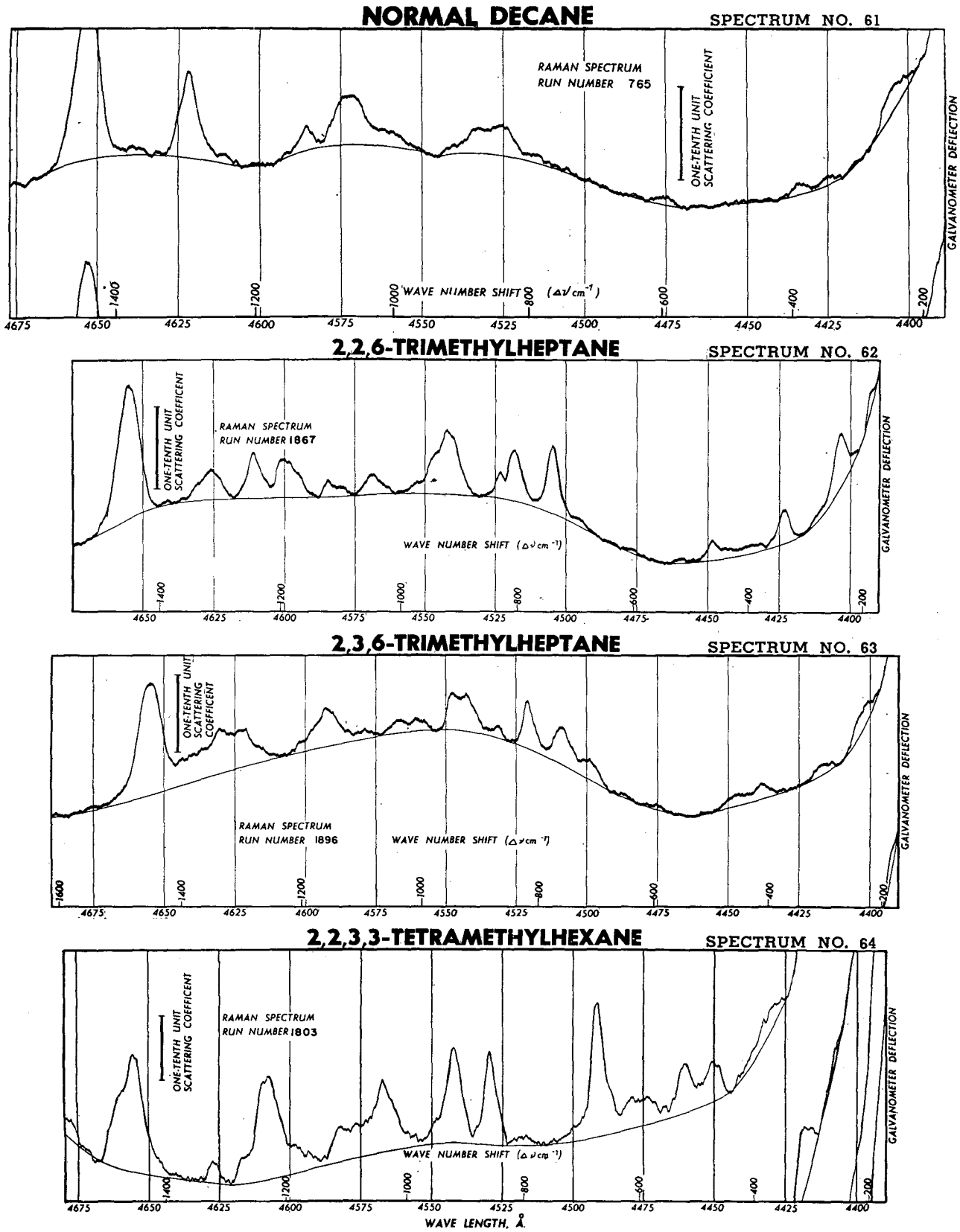
SPECTRUM NO. 59

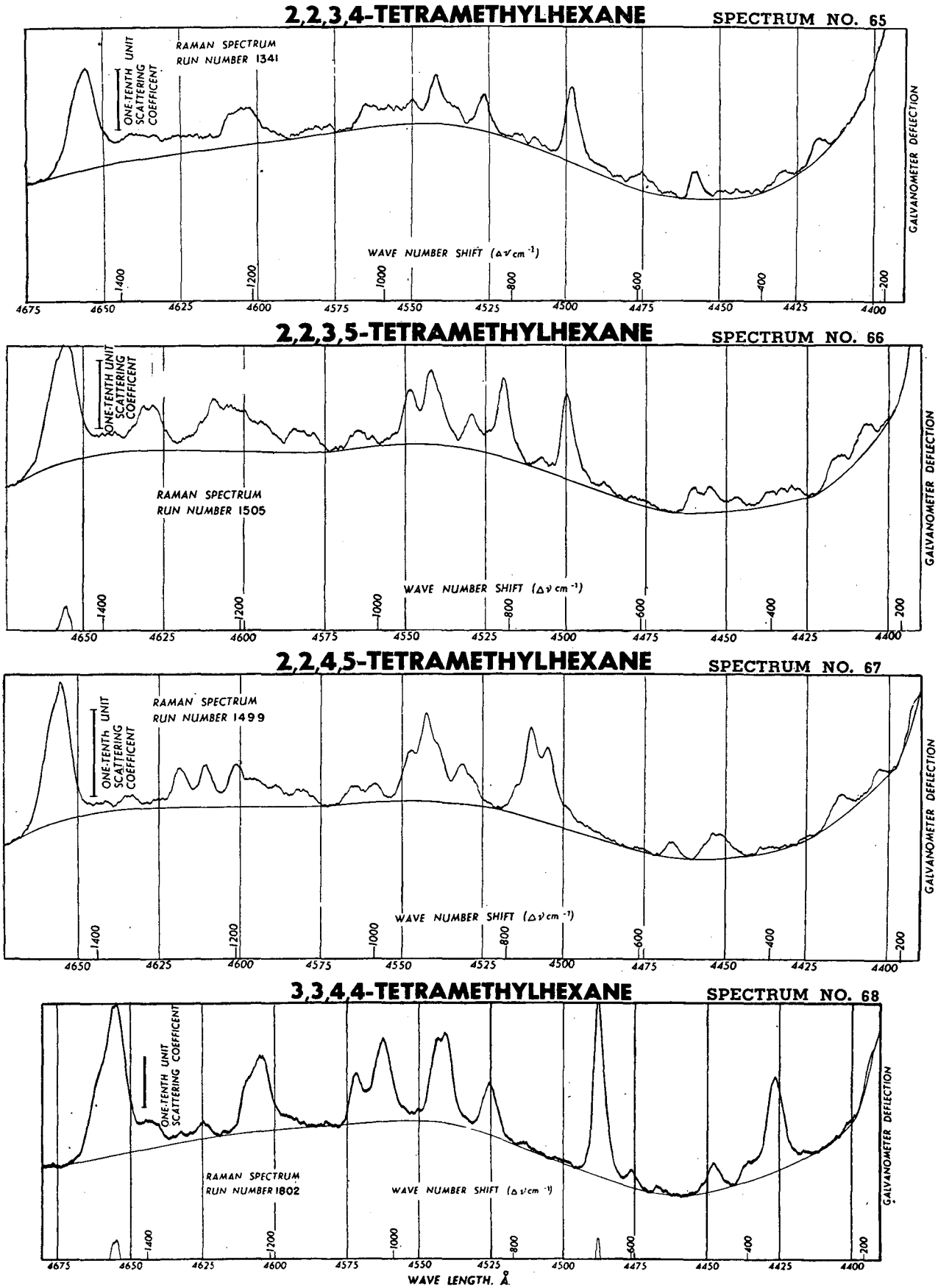


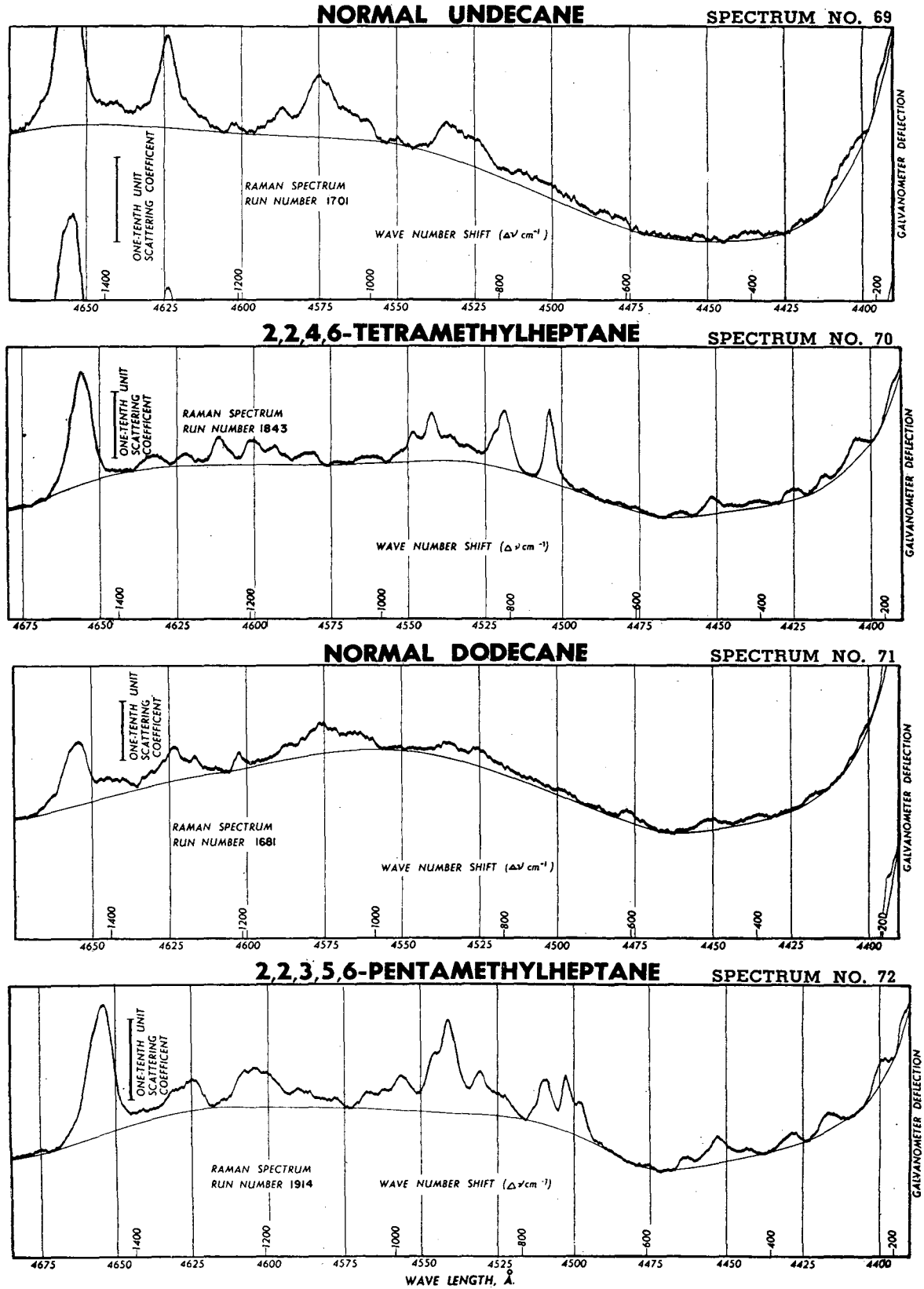
2,3,3,4-TETRAMETHYLPENTANE

SPECTRUM NO. 60

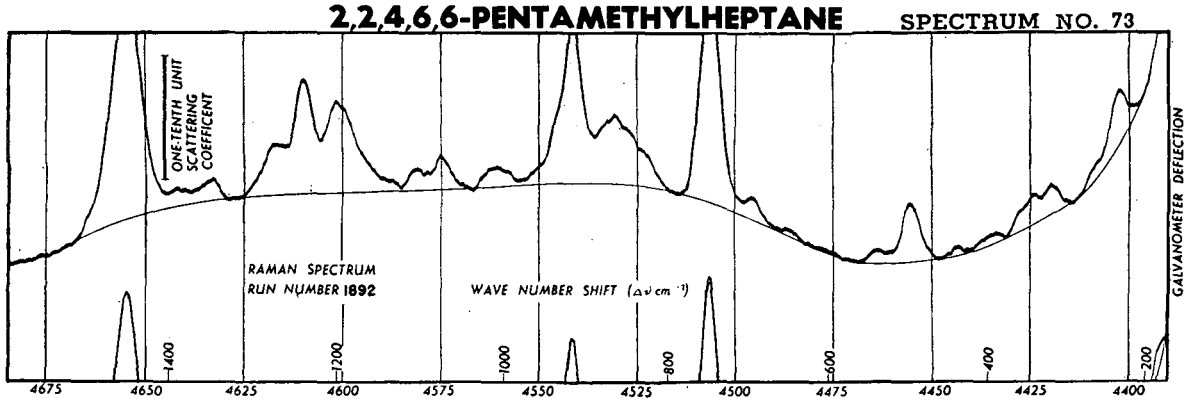



NORMAL DECANE
SPECTRUM NO. 61
RAMAN SPECTRUM
RUN NUMBER 765
ONE-TENTH UNIT
SCATTERING COEFFICIENT
GALVANOMETER DEFLECTION
WAVE NUMBER SHIFT (Δν/cm⁻¹)
2,2,6-TRIMETHYLHEPTANE
SPECTRUM NO. 62
RAMAN SPECTRUM
RUN NUMBER 1867
2,3,6-TRIMETHYLHEPTANE
SPECTRUM NO. 63
RAMAN SPECTRUM
RUN NUMBER 1896
2,2,3,3-TETRAMETHYLHEXANE
SPECTRUM NO. 64
RAMAN SPECTRUM
RUN NUMBER 1803
WAVE LENGTH, Å

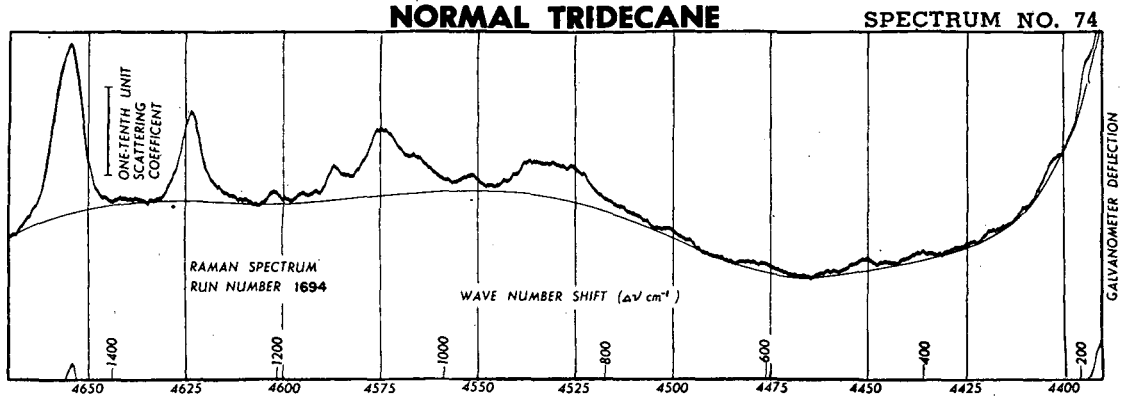

2,2,3,4-TETRAMETHYLHEXANE
SPECTRUM NO. 65
RAMAN SPECTRUM
RUN NUMBER 1341
ONE-TENTH UNIT SCATTERING COEFFICENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2,2,3,5-TETRAMETHYLHEXANE
SPECTRUM NO. 66
RAMAN SPECTRUM
RUN NUMBER 1505
2,2,4,5-TETRAMETHYLHEXANE
SPECTRUM NO. 67
RAMAN SPECTRUM
RUN NUMBER 1499
3,3,4,4-TETRAMETHYLHEXANE
SPECTRUM NO. 68
RAMAN SPECTRUM
RUN NUMBER 1802
WAVE LENGTH, Å


NORMAL UNDECANE
SPECTRUM NO. 69
RAMAN SPECTRUM
RUN NUMBER 1701
ONE-TENTH UNIT SCATTERING COEFFICENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2,2,4,6-TETRAMETHYLHEPTANE
SPECTRUM NO. 70
RAMAN SPECTRUM
RUN NUMBER 1843
ONE-TENTH UNIT SCATTERING COEFFICENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
NORMAL DODECANE
SPECTRUM NO. 71
RAMAN SPECTRUM
RUN NUMBER 1681
ONE-TENTH UNIT SCATTERING COEFFICENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2,2,3,5,6-PENTAMETHYLHEPTANE
SPECTRUM NO. 72
RAMAN SPECTRUM
RUN NUMBER 1914
ONE-TENTH UNIT SCATTERING COEFFICENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
WAVE LENGTH, Å.

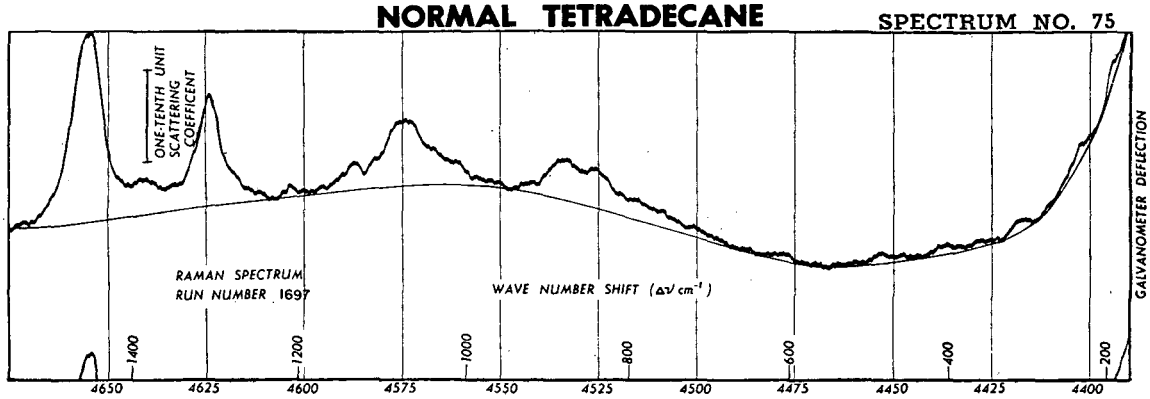
2,2,4,6,6-PENTAMETHYLHEPTANE SPECTRUM NO. 73



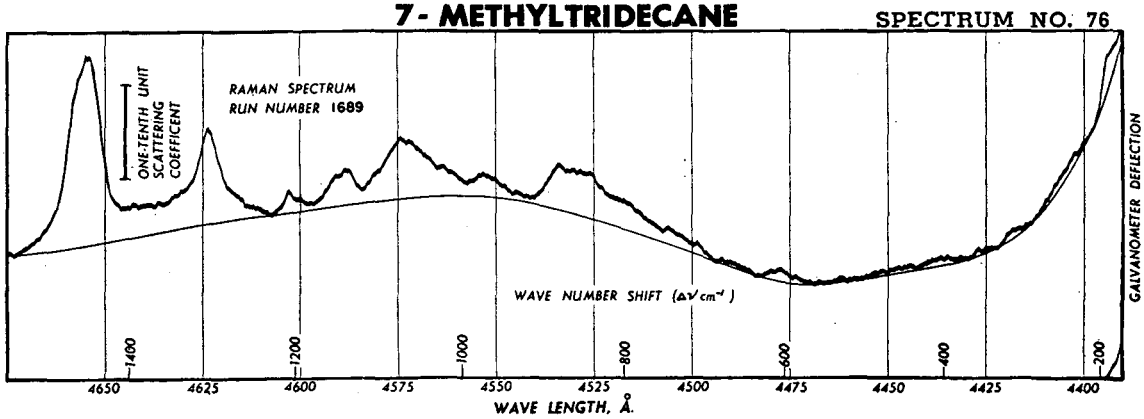
NORMAL TRIDECANE SPECTRUM NO. 74

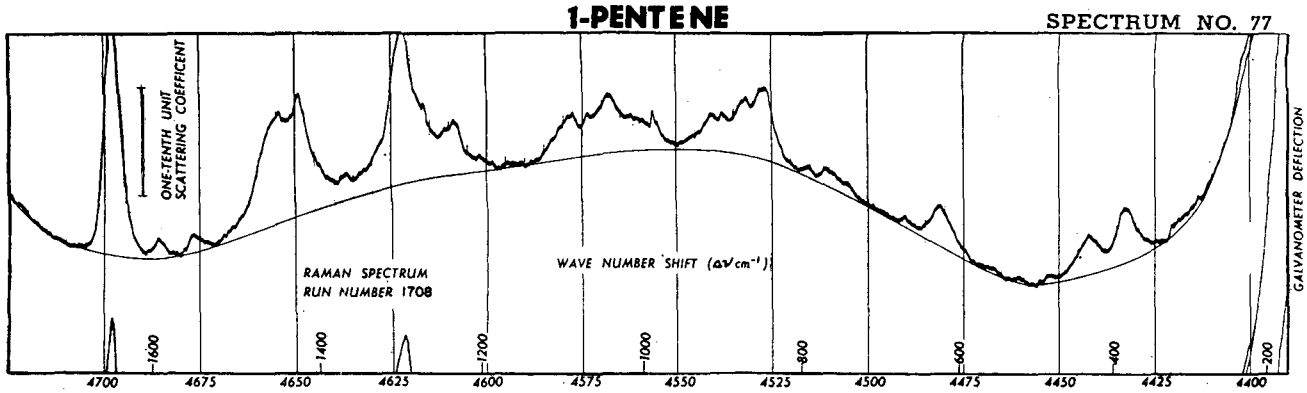


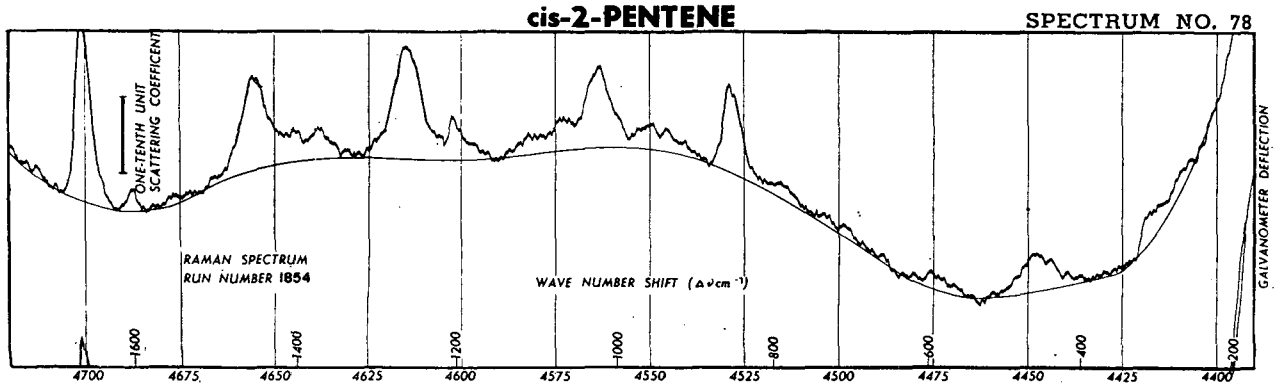
NORMAL TETRADECANE SPECTRUM NO. 75

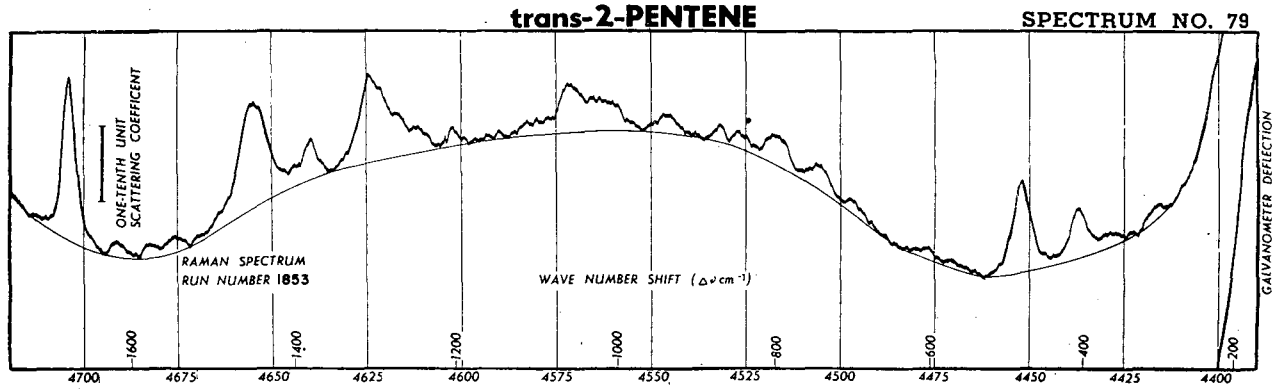


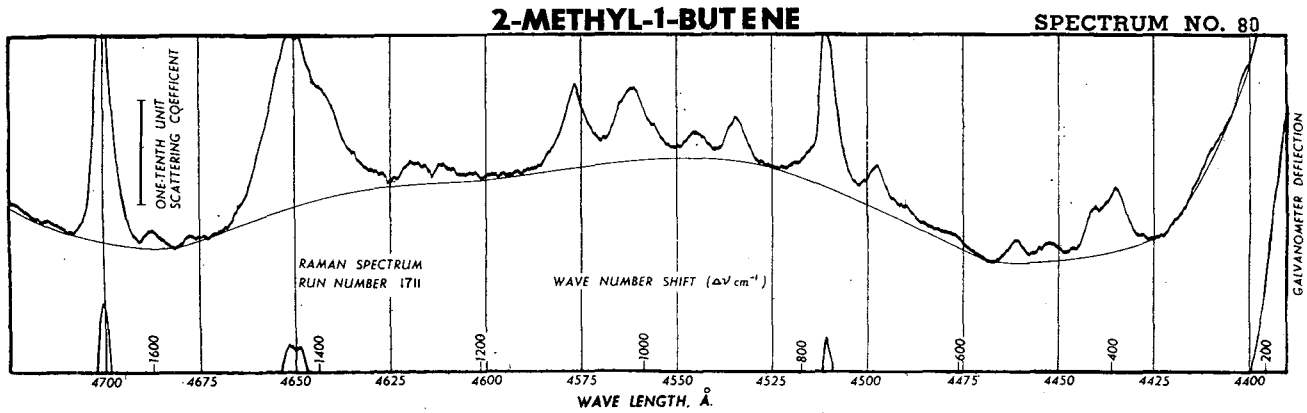
7-METHYLTRIDECANE SPECTRUM NO. 76

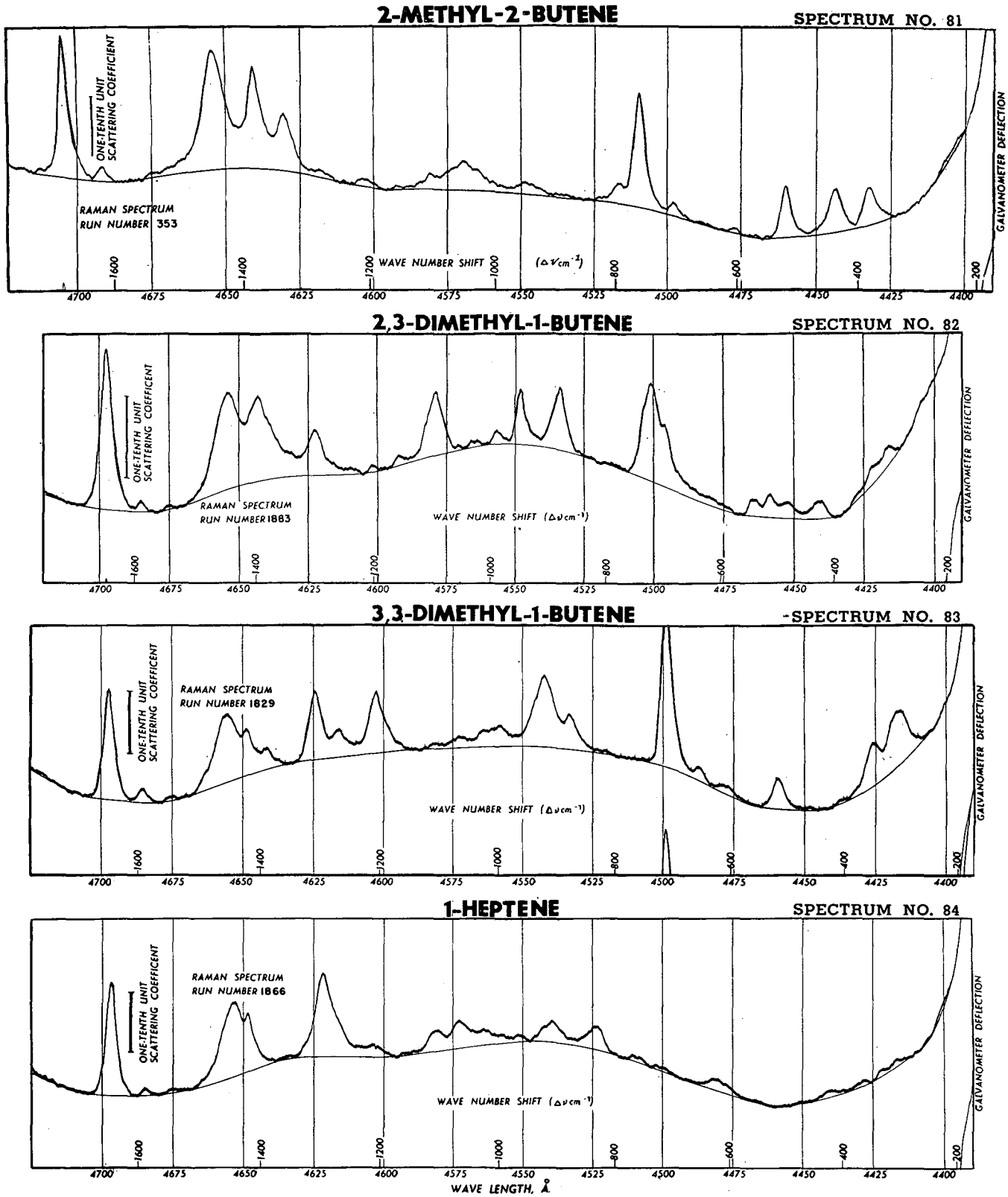


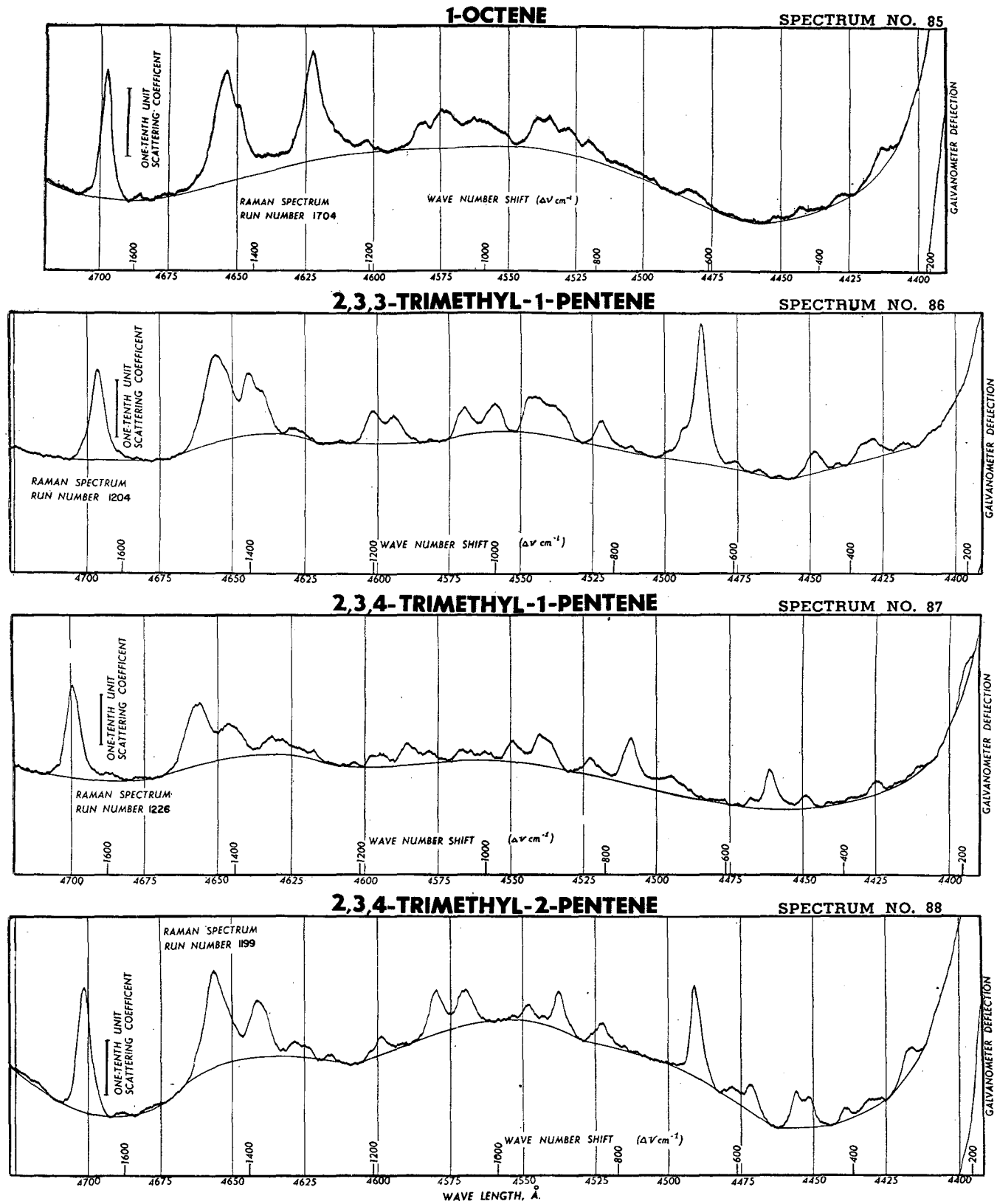

1-PENTENE
SPECTRUM NO. 77
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM
RUN NUMBER 1708
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1600 1400 1200 1000 800 600 400 200
4700 4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400


cis-2-PENTENE
SPECTRUM NO. 78
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM
RUN NUMBER 1854
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1600 1400 1200 1000 800 600 400 200
4700 4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400


trans-2-PENTENE
SPECTRUM NO. 79
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM
RUN NUMBER 1853
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1600 1400 1200 1000 800 600 400 200
4700 4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400

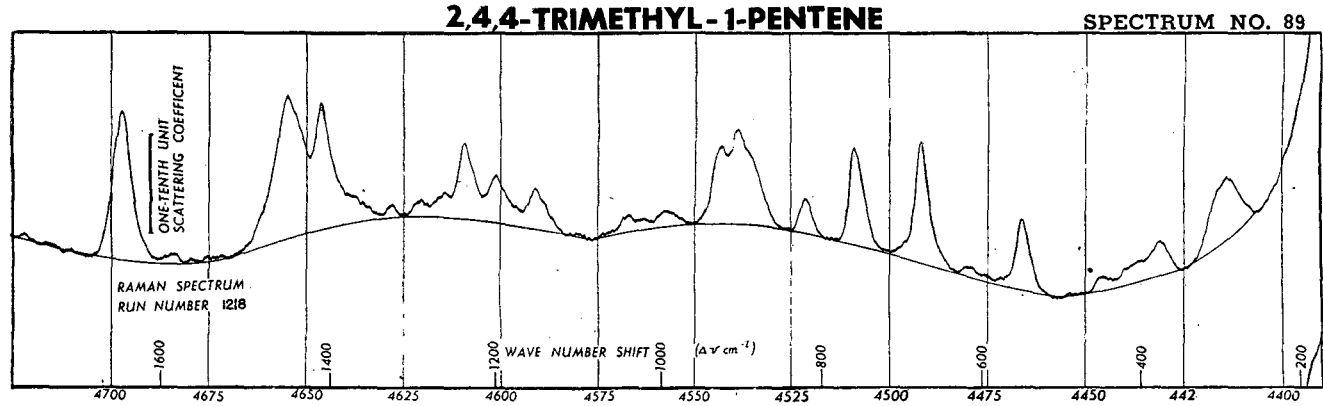

2-METHYL-1-BUTENE
SPECTRUM NO. 80
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM
RUN NUMBER 1711
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1600 1400 1200 1000 800 600 400 200
4700 4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400
WAVE LENGTH, Å.


2-METHYL-2-BUTENE
SPECTRUM NO. 81
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM RUN NUMBER 353
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2,3-DIMETHYL-1-BUTENE
SPECTRUM NO. 82
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM RUN NUMBER 1883
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
3,3-DIMETHYL-1-BUTENE
-SPECTRUM NO. 83
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM RUN NUMBER 1829
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1-HEPTENE
SPECTRUM NO. 84
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM RUN NUMBER 1866
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1600 1400 1200 1000 800 600 400 200
4700 4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400
WAVE LENGTH, Å


1-OCTENE
SPECTRUM NO. 85
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM
RUN NUMBER 1704
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2,3,3-TRIMETHYL-1-PENTENE
SPECTRUM NO. 86
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM
RUN NUMBER 1204
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2,3,4-TRIMETHYL-1-PENTENE
SPECTRUM NO. 87
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM
RUN NUMBER 1226
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2,3,4-TRIMETHYL-2-PENTENE
SPECTRUM NO. 88
RAMAN SPECTRUM
RUN NUMBER 1199
ONE-TENTH UNIT SCATTERING COEFFICENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
WAVE LENGTH, Å.

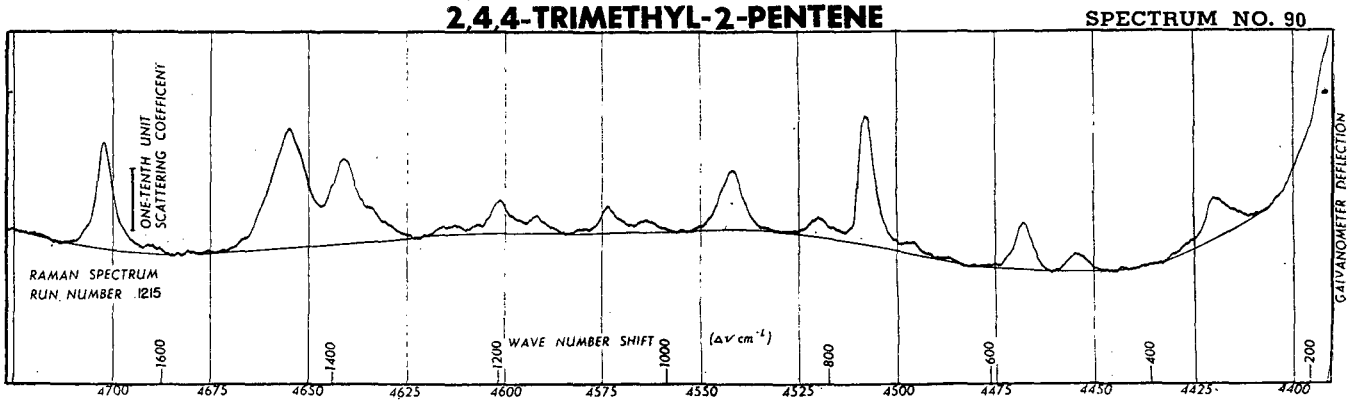
2,4,4-TRIMETHYL-1-PENTENE

SPECTRUM NO. 89



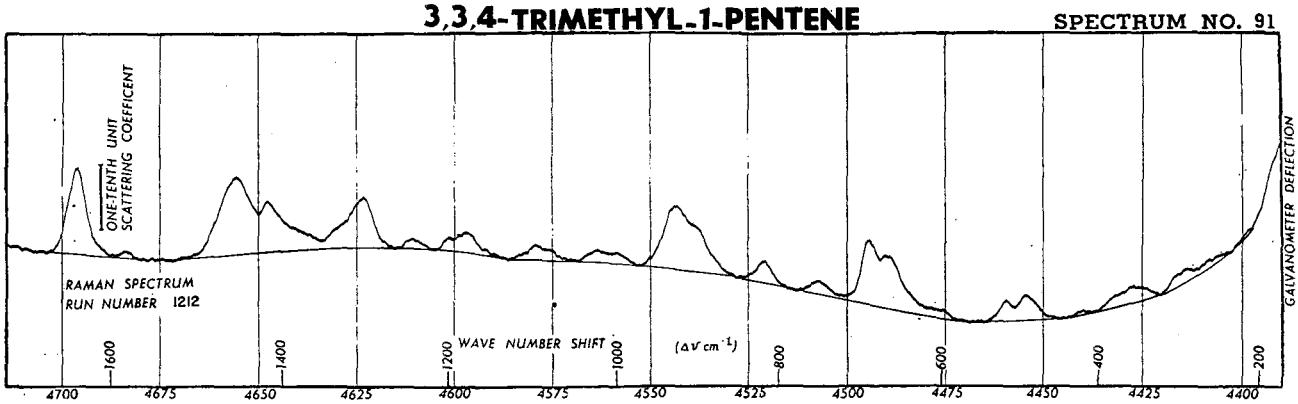
2,4,4-TRIMETHYL-2-PENTENE

SPECTRUM NO. 90



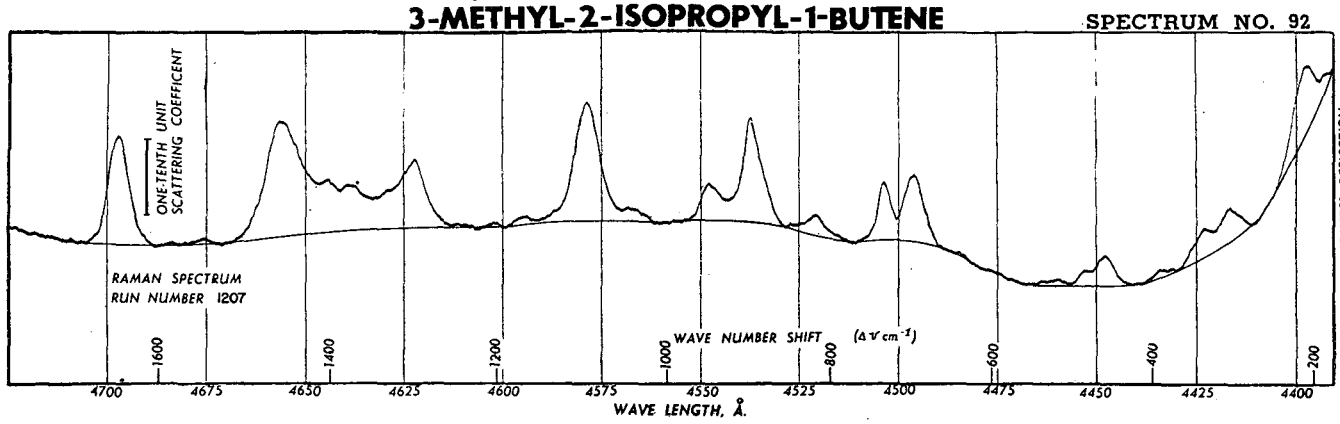
3,3,4-TRIMETHYL-1-PENTENE

SPECTRUM NO. 91



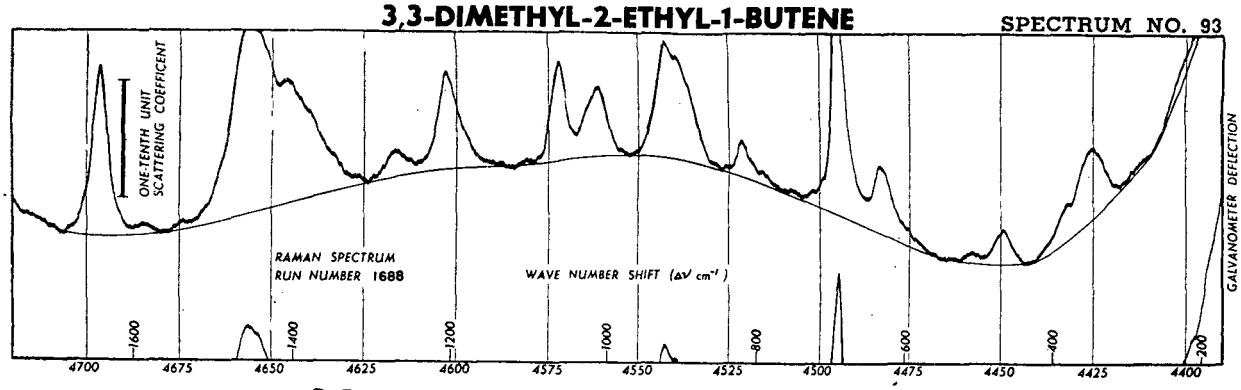
3-METHYL-2-ISOPROPYL-1-BUTENE

SPECTRUM NO. 92



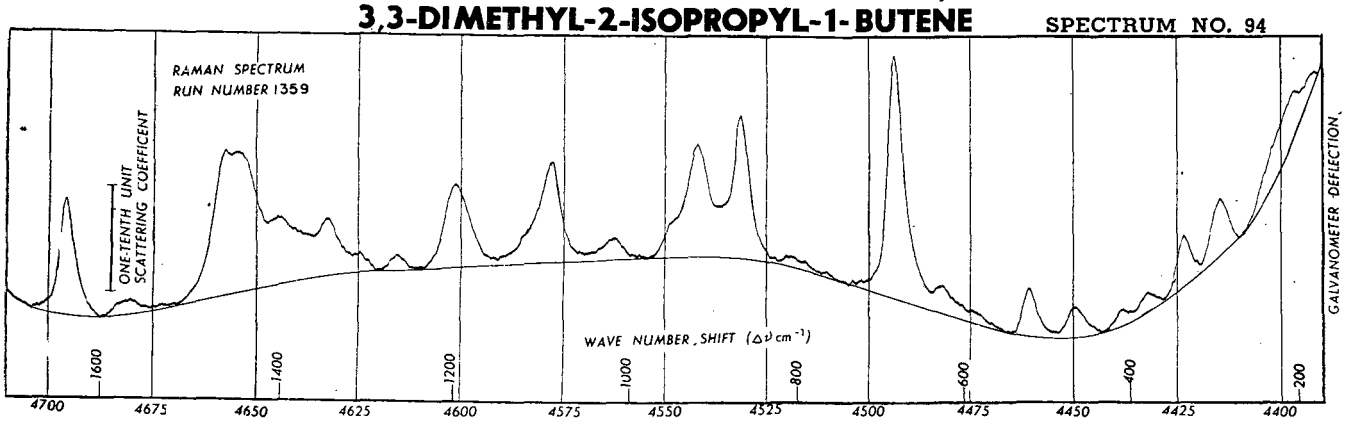
3,3-DIMETHYL-2-ETHYL-1-BUTENE

SPECTRUM NO. 93



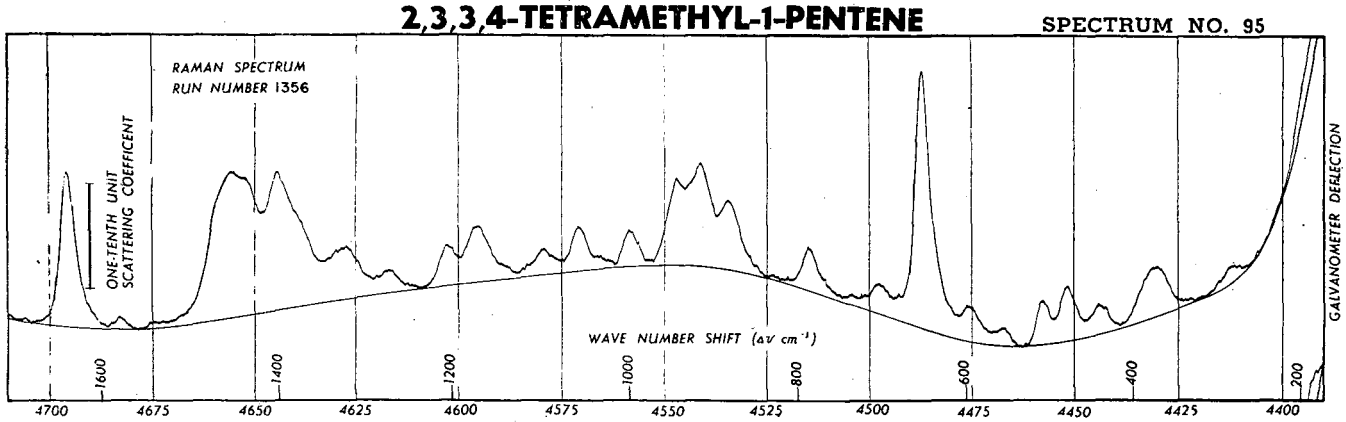
3,3-DIMETHYL-2-ISOPROPYL-1-BUTENE

SPECTRUM NO. 94



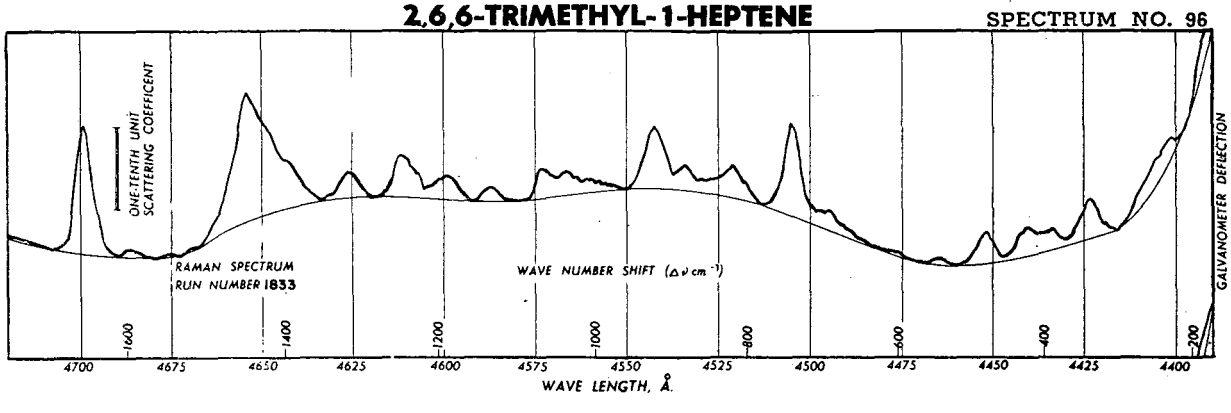
2,3,3,4-TETRAMETHYL-1-PENTENE

SPECTRUM NO. 95



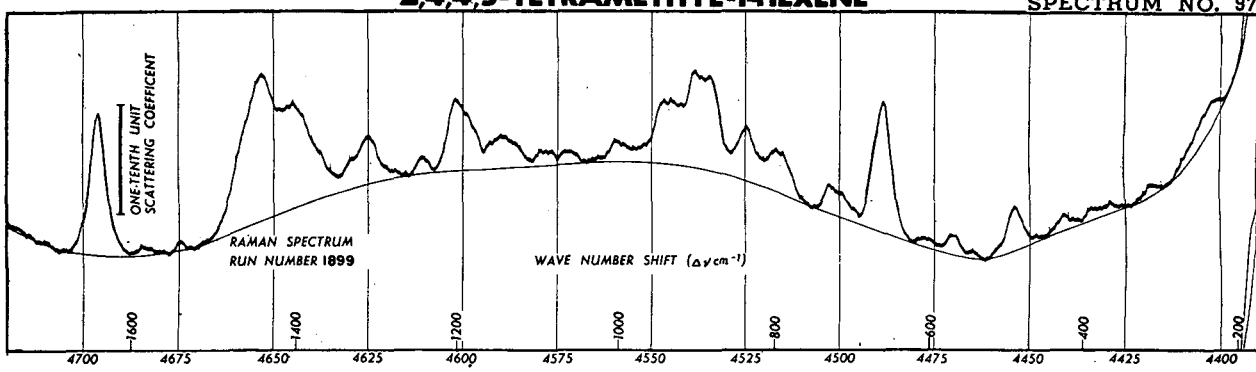
2,6,6-TRIMETHYL-1-HEPTENE

SPECTRUM NO. 96



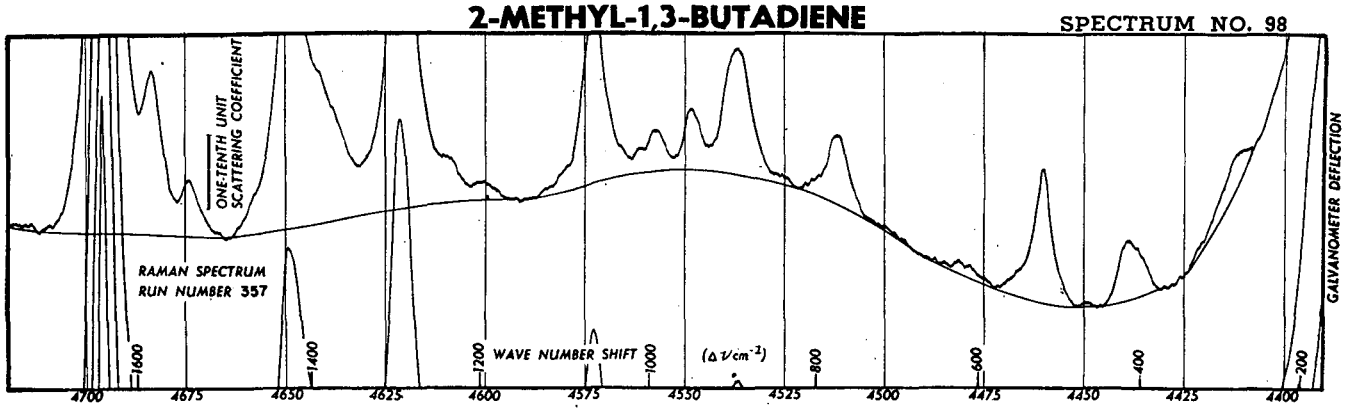
2,4,4,5-TETRAMETHYL-1-HEXENE

SPECTRUM NO. 97



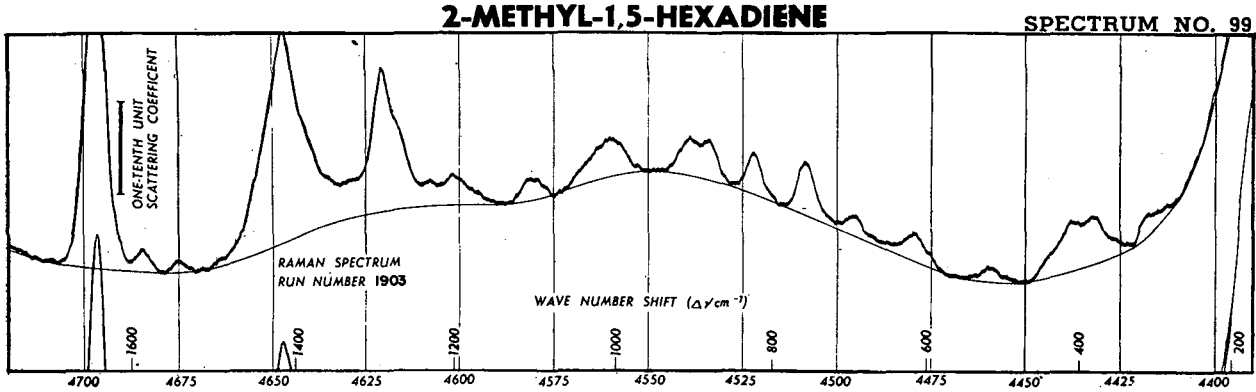
2-METHYL-1,3-BUTADIENE

SPECTRUM NO. 98



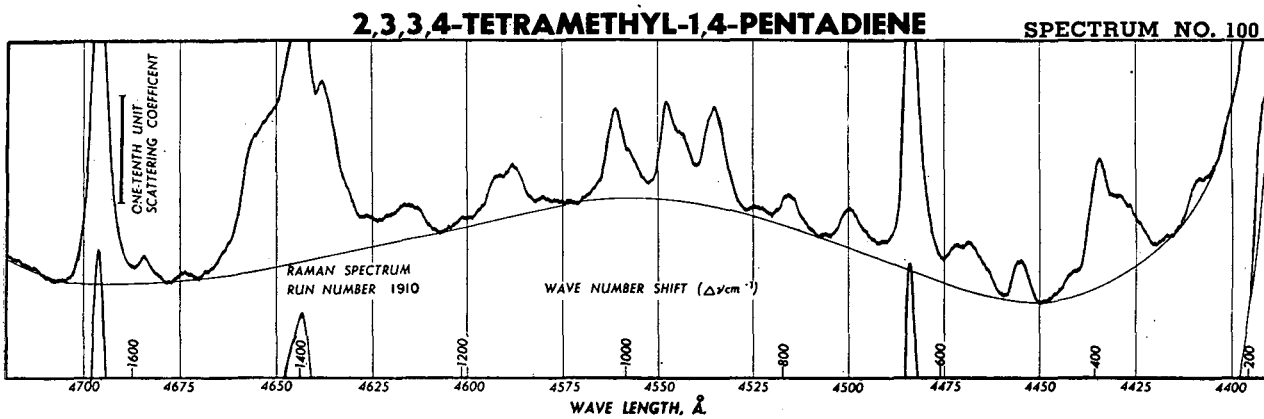
2-METHYL-1,5-HEXADIENE

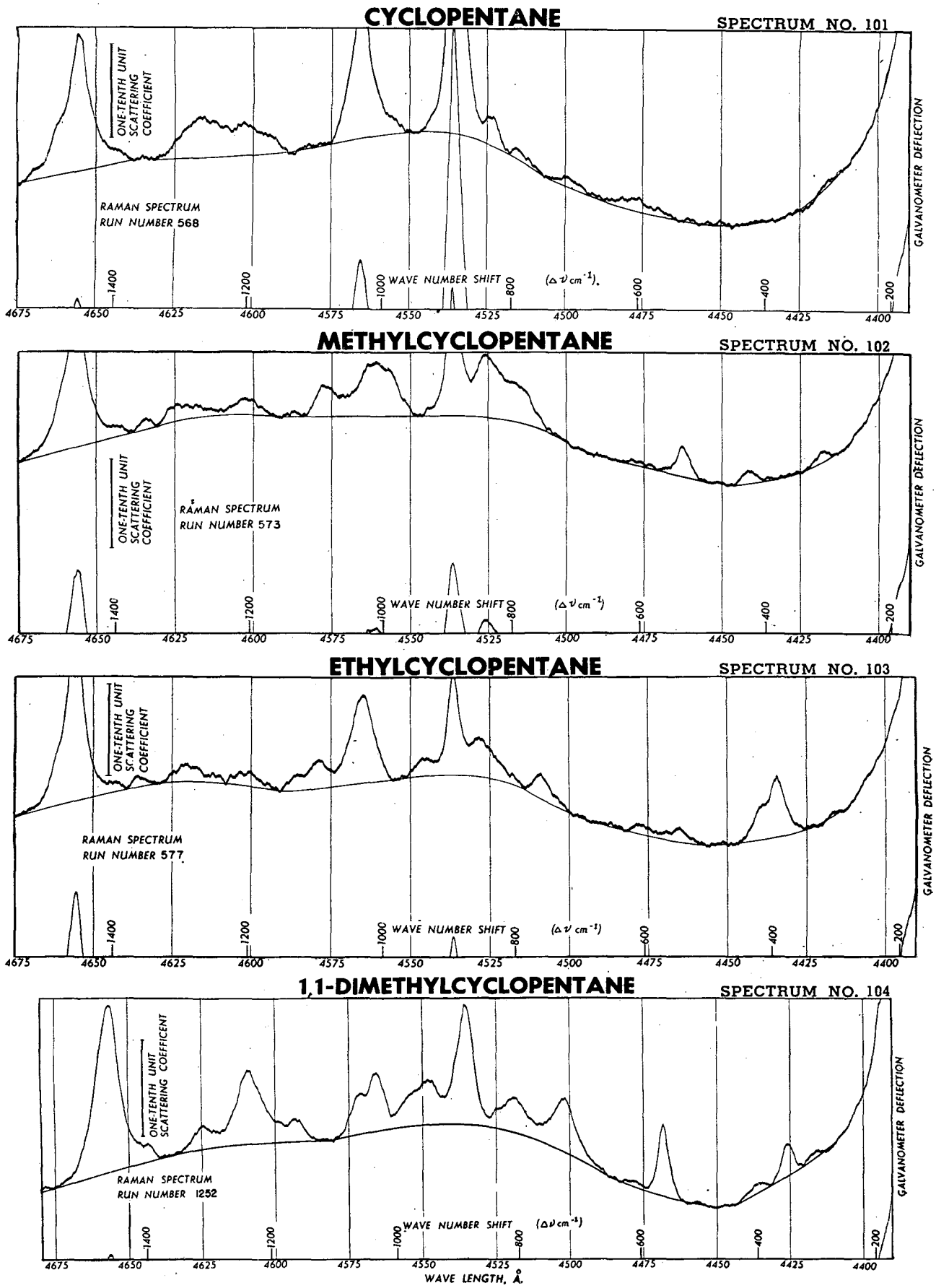
SPECTRUM NO. 99

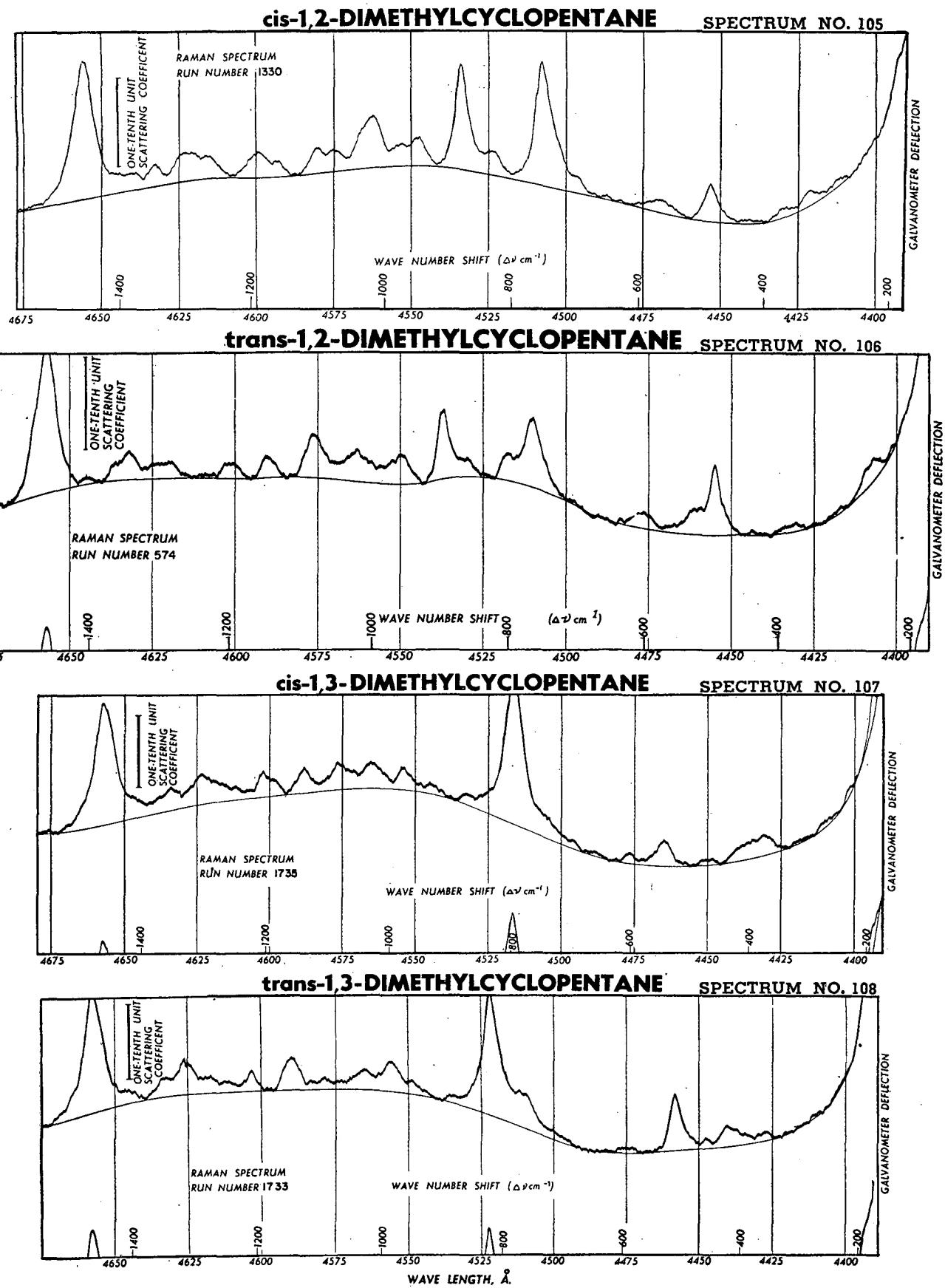


2,3,3,4-TETRAMETHYL-1,4-PENTADIENE

SPECTRUM NO. 100

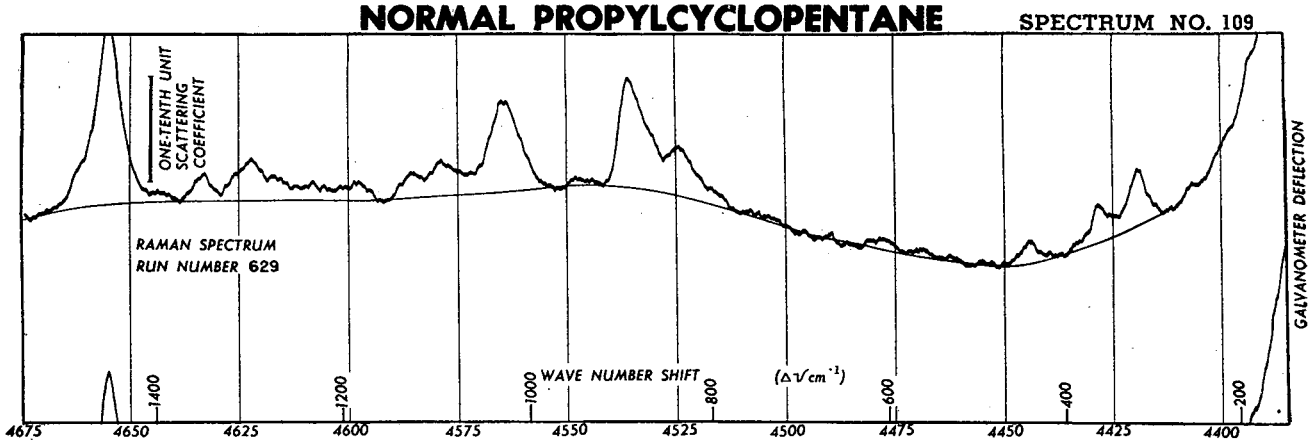



CYCLOPENTANE
SPECTRUM NO. 101
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM RUN NUMBER 568
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
METHYLCYCLOPENTANE
SPECTRUM NO. 102
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM RUN NUMBER 573
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
ETHYLCYCLOPENTANE
SPECTRUM NO. 103
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM RUN NUMBER 577
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1,1-DIMETHYLCYCLOPENTANE
SPECTRUM NO. 104
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM RUN NUMBER 1252
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
WAVE LENGTH, Å
4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400
1400 1200 1000 800 600 400 200


cis-1,2-DIMETHYLCYCLOPENTANE
SPECTRUM NO. 105
RAMAN SPECTRUM
RUN NUMBER 1330
ONE-TENTH UNIT SCATTERING COEFFICENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
trans-1,2-DIMETHYLCYCLOPENTANE
SPECTRUM NO. 106
RAMAN SPECTRUM
RUN NUMBER 574
ONE-TENTH UNIT SCATTERING COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
cis-1,3-DIMETHYLCYCLOPENTANE
SPECTRUM NO. 107
RAMAN SPECTRUM
RUN NUMBER 1735
ONE-TENTH UNIT SCATTERING COEFFICENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
trans-1,3-DIMETHYLCYCLOPENTANE
SPECTRUM NO. 108
RAMAN SPECTRUM
RUN NUMBER 1733
ONE-TENTH UNIT SCATTERING COEFFICENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
WAVE LENGTH, Å.

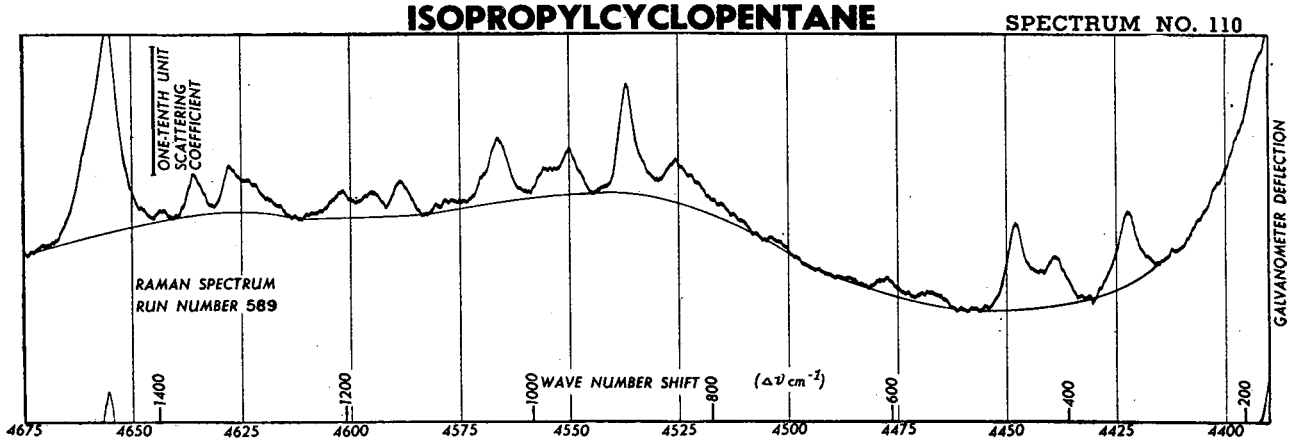
NORMAL PROPYLCYCLOPENTANE

SPECTRUM NO. 109



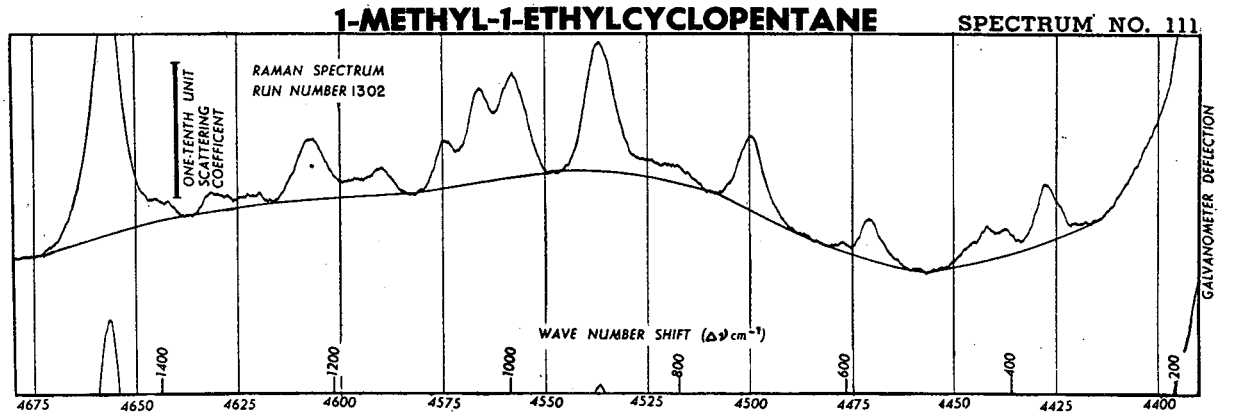
ISOPROPYLCYCLOPENTANE

SPECTRUM NO. 110



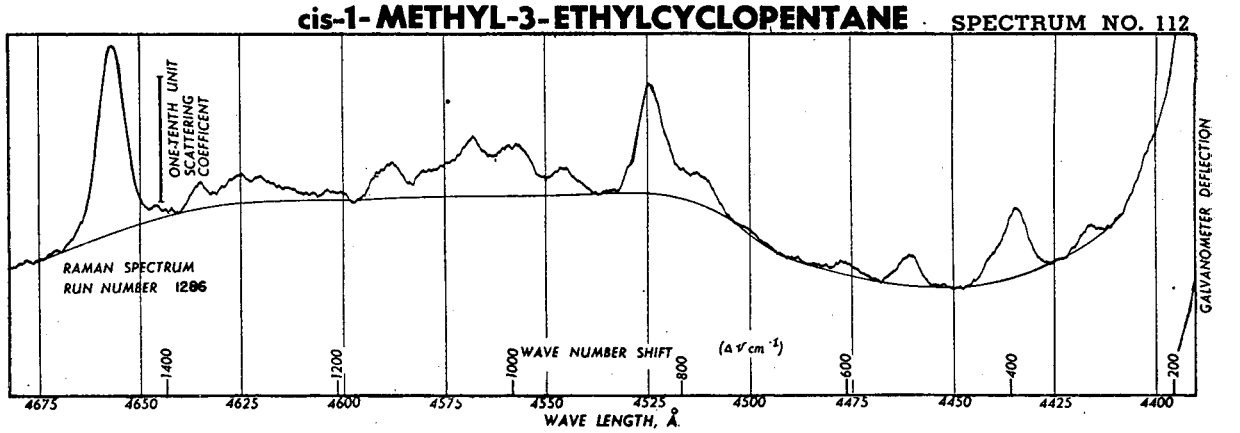
1-METHYL-1-ETHYLCYCLOPENTANE

SPECTRUM NO. 111

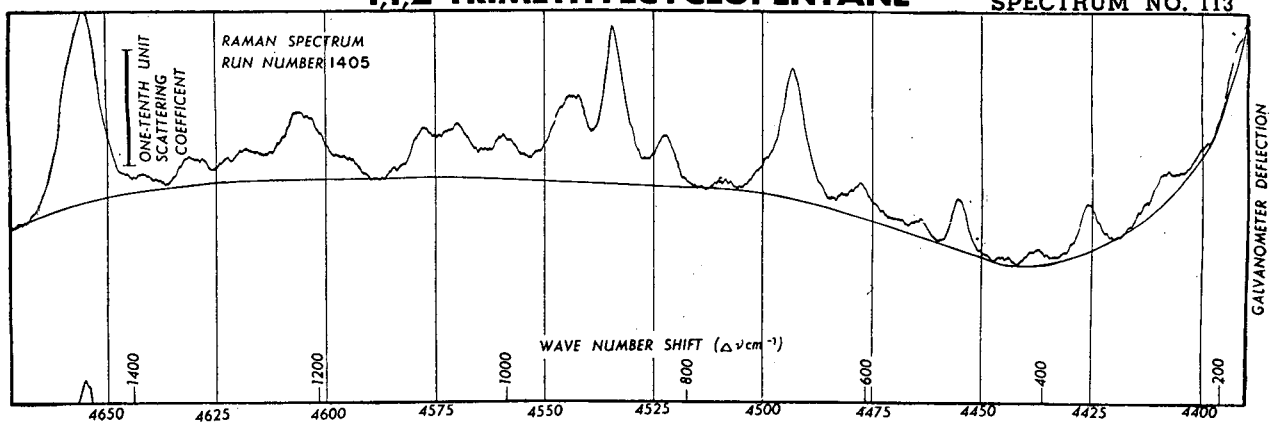


cis-1-METHYL-3-ETHYLCYCLOPENTANE

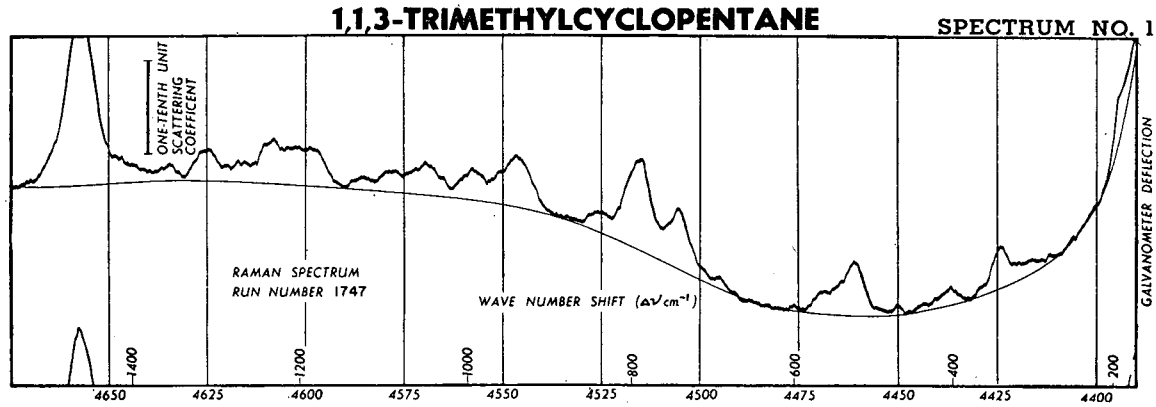
SPECTRUM NO. 112



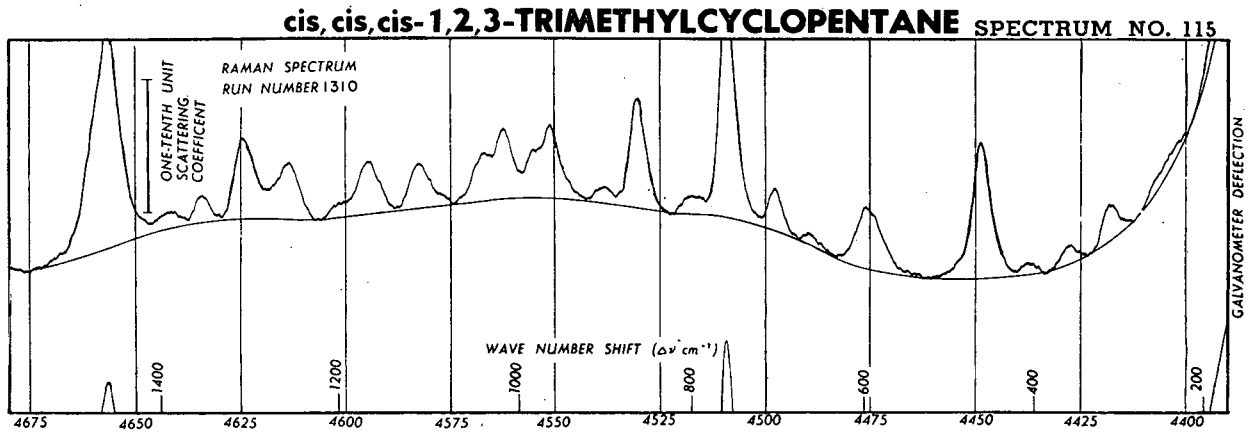
1,1,2-TRIMETHYLCYCLOPENTANE SPECTRUM NO. 113



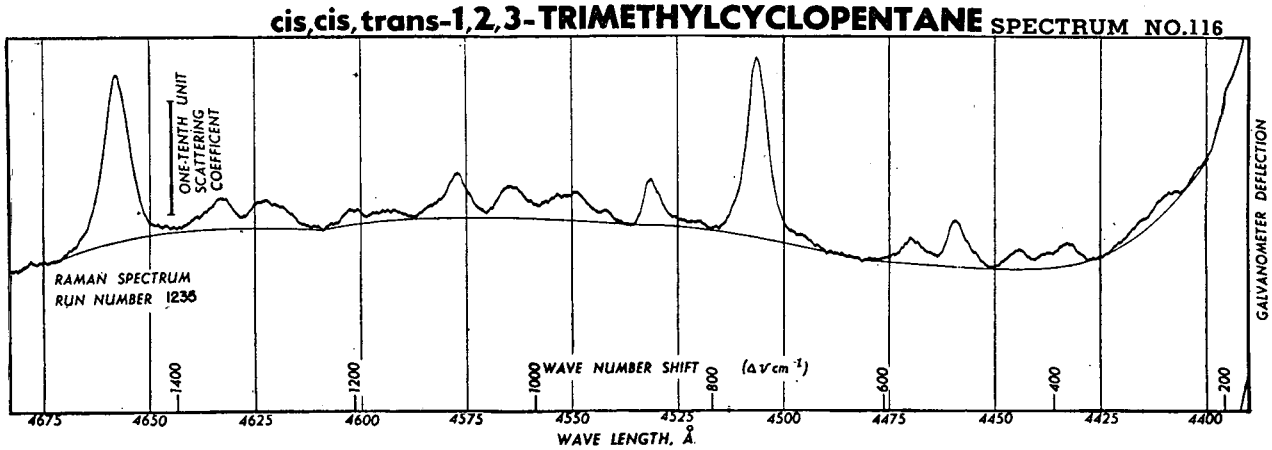
1,1,3-TRIMETHYLCYCLOPENTANE SPECTRUM NO. 114

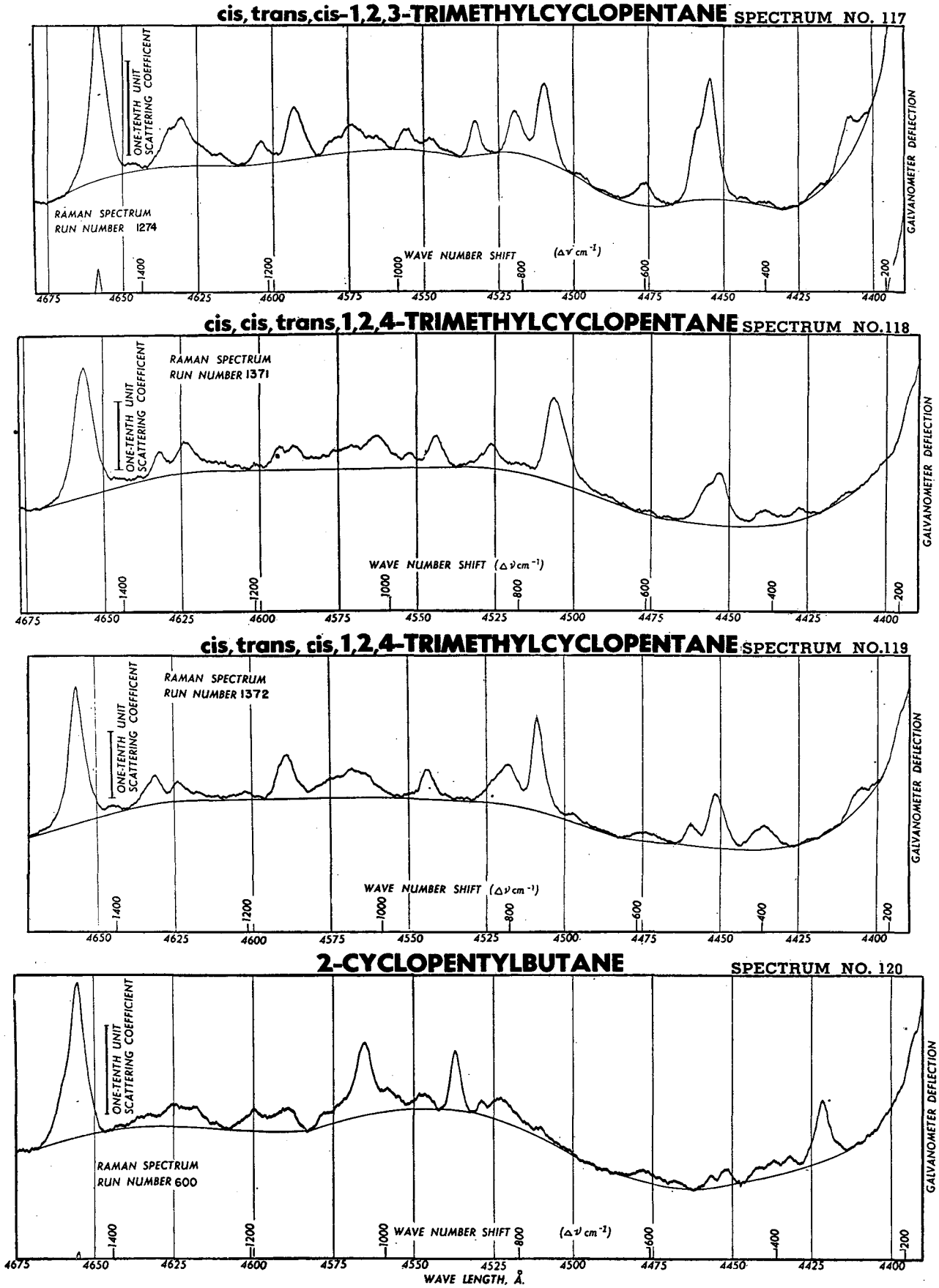


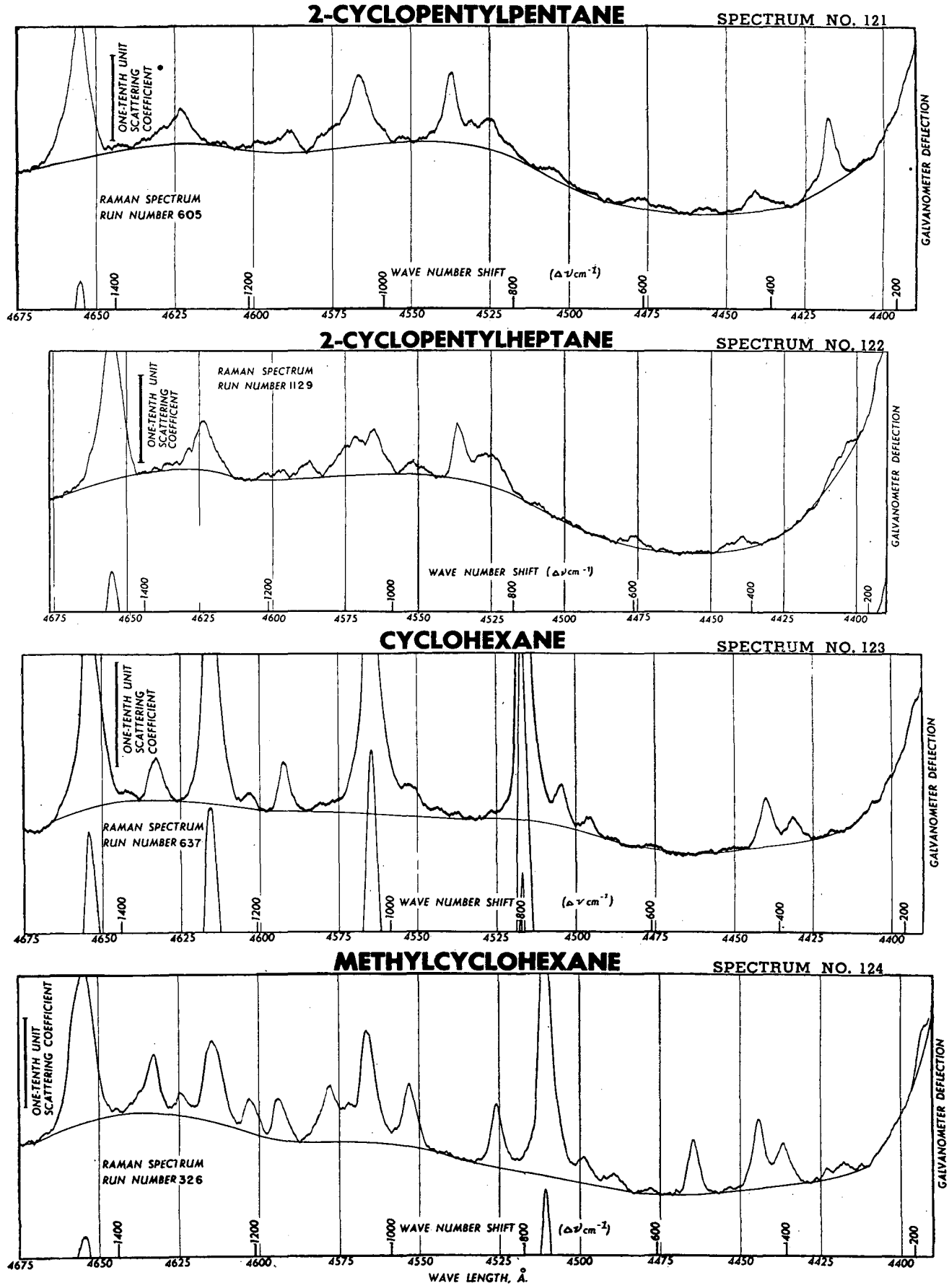
cis, cis, cis-1,2,3-TRIMETHYLCYCLOPENTANE SPECTRUM NO. 115

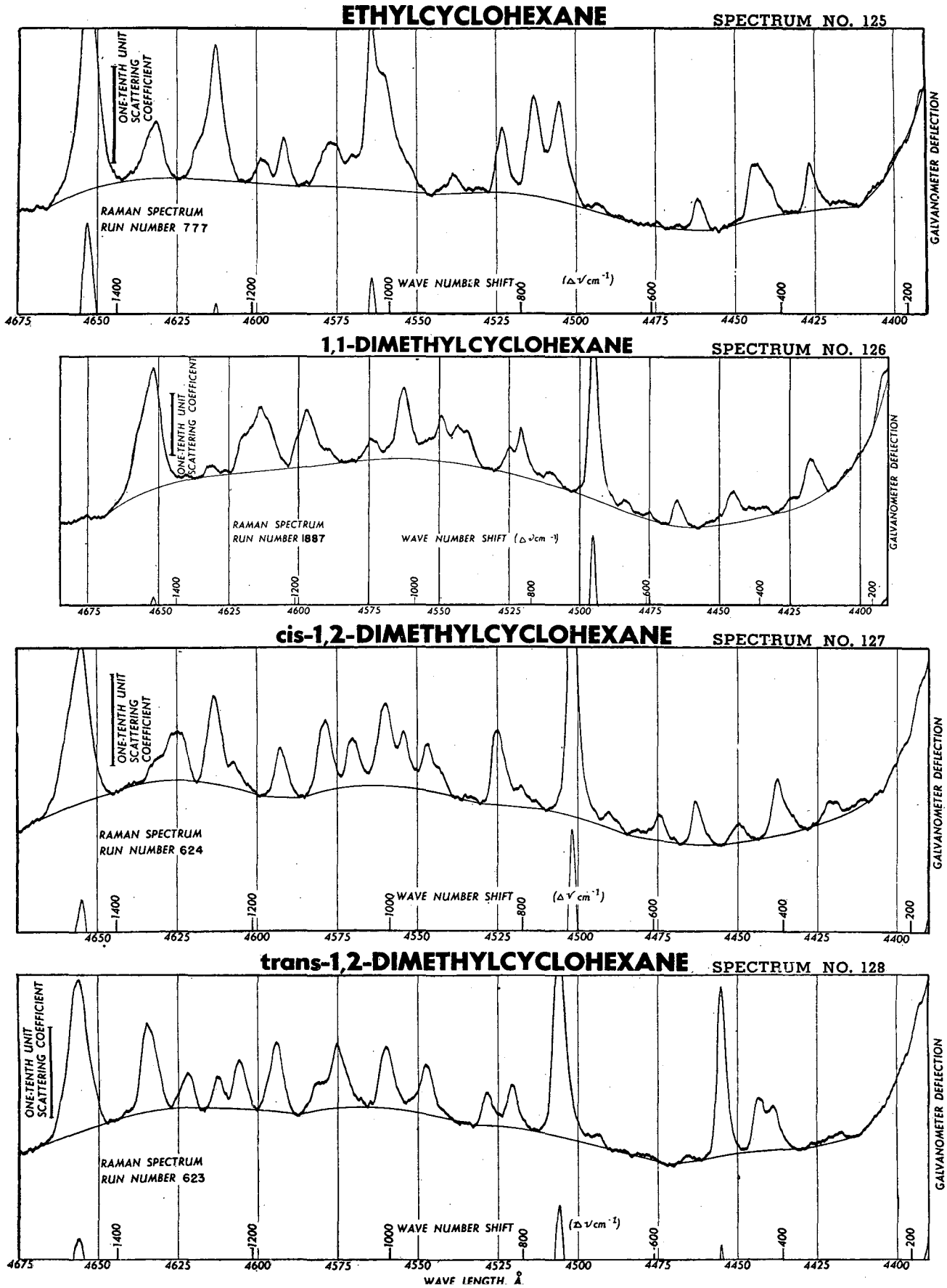


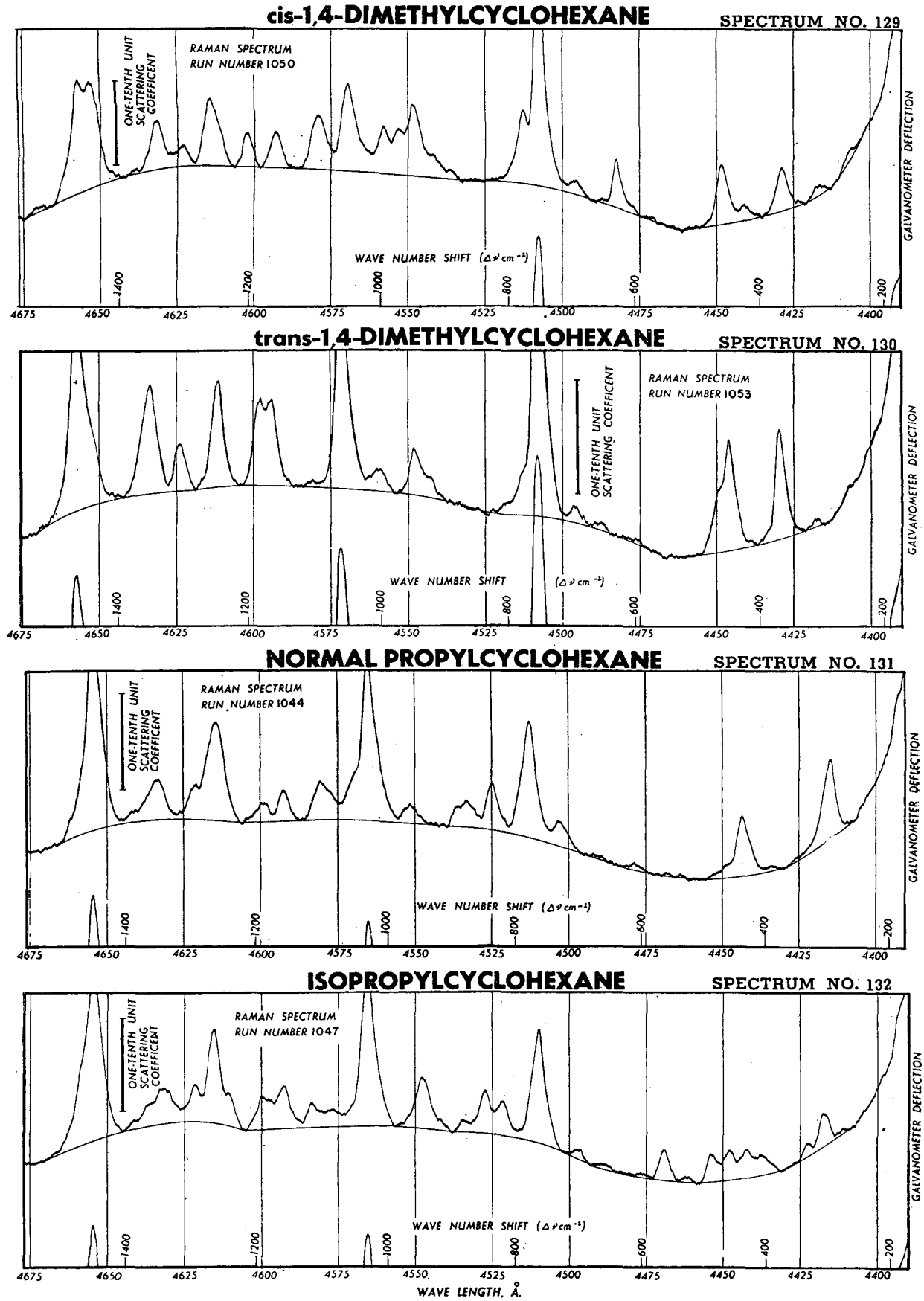
cis, cis, trans-1,2,3-TRIMETHYLCYCLOPENTANE SPECTRUM NO. 116




cis, trans, cis-1,2,3-TRIMETHYLCYCLOPENTANE SPECTRUM NO. 117
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM RUN NUMBER 1274
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
cis, cis, trans-1,2,4-TRIMETHYLCYCLOPENTANE SPECTRUM NO.118
RAMAN SPECTRUM RUN NUMBER 1371
cis, trans, cis-1,2,4-TRIMETHYLCYCLOPENTANE SPECTRUM NO.119
RAMAN SPECTRUM RUN NUMBER 1372
2-CYCLOPENTYLBUTANE SPECTRUM NO. 120
RAMAN SPECTRUM RUN NUMBER 600
WAVE LENGTH, Å.

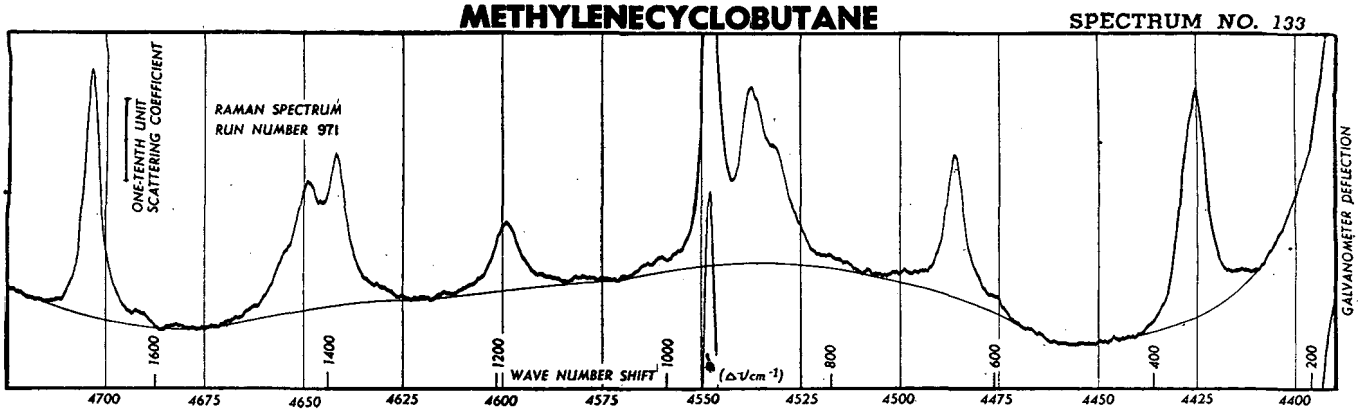

2-CYCLOPENTYLPENTANE
SPECTRUM NO. 121
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 605
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
2-CYCLOPENTYLHEPTANE
SPECTRUM NO. 122
RAMAN SPECTRUM
RUN NUMBER 1129
CYCLOHEXANE
SPECTRUM NO. 123
RAMAN SPECTRUM
RUN NUMBER 637
METHYLCYCLOHEXANE
SPECTRUM NO. 124
RAMAN SPECTRUM
RUN NUMBER 326
WAVE LENGTH, Å.


ETHYLCYCLOHEXANE
SPECTRUM NO. 125
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 777
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1,1-DIMETHYLCYCLOHEXANE
SPECTRUM NO. 126
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM
RUN NUMBER 1887
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
cis-1,2-DIMETHYLCYCLOHEXANE
SPECTRUM NO. 127
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 624
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
trans-1,2-DIMETHYLCYCLOHEXANE
SPECTRUM NO. 128
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 623
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
WAVE LENGTH, Å


cis-1,4-DIMETHYLCYCLOHEXANE
SPECTRUM NO. 129
RAMAN SPECTRUM
RUN NUMBER 1050
ONE-TENTH UNIT SCATTERING COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
trans-1,4-DIMETHYLCYCLOHEXANE
SPECTRUM NO. 130
RAMAN SPECTRUM
RUN NUMBER 1053
ONE-TENTH UNIT SCATTERING COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
NORMAL PROPYLCYCLOHEXANE
SPECTRUM NO. 131
RAMAN SPECTRUM
RUN NUMBER 1044
ONE-TENTH UNIT SCATTERING COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
ISOPROPYLCYCLOHEXANE
SPECTRUM NO. 132
RAMAN SPECTRUM
RUN NUMBER 1047
ONE-TENTH UNIT SCATTERING COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1400 1200 1000 800 600 400 200
4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400
WAVE LENGTH, Å.

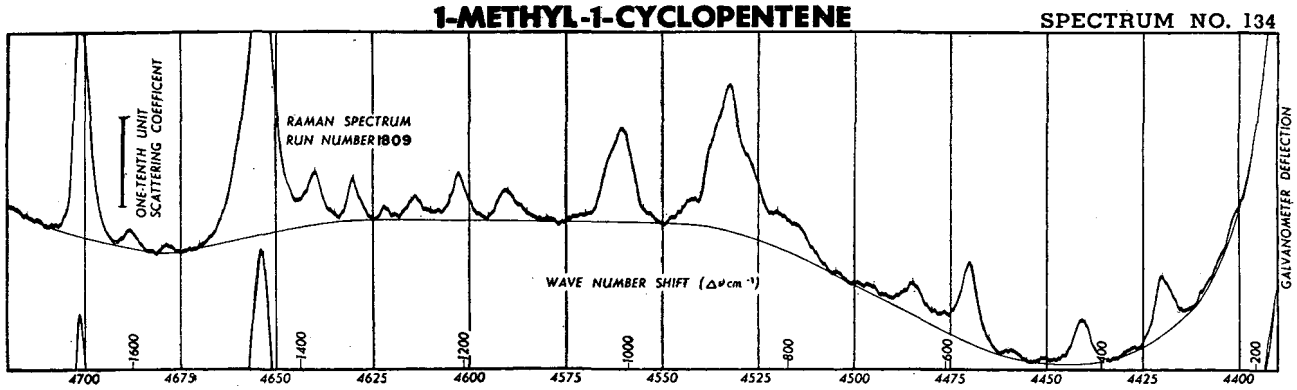
METHYLENECYCLOBUTANE

SPECTRUM NO. 133



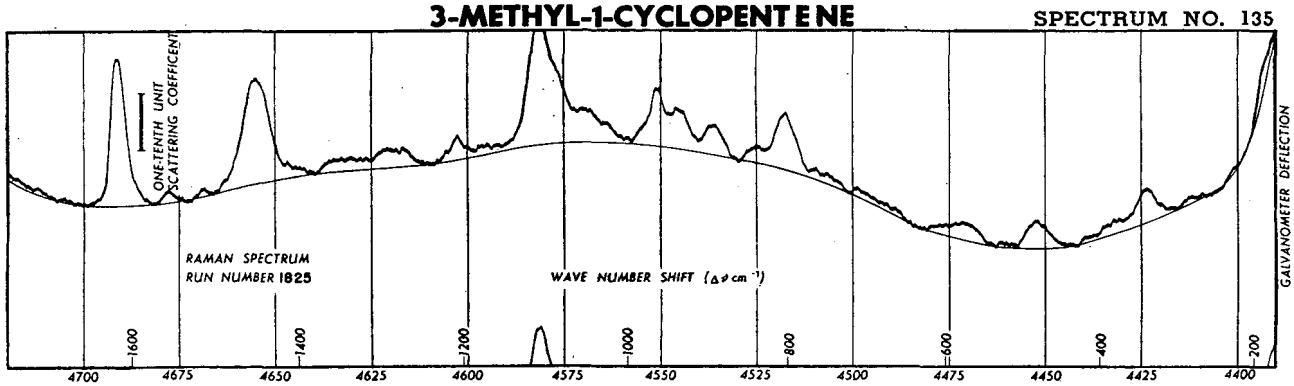
1-METHYL-1-CYCLOPENTENE

SPECTRUM NO. 134



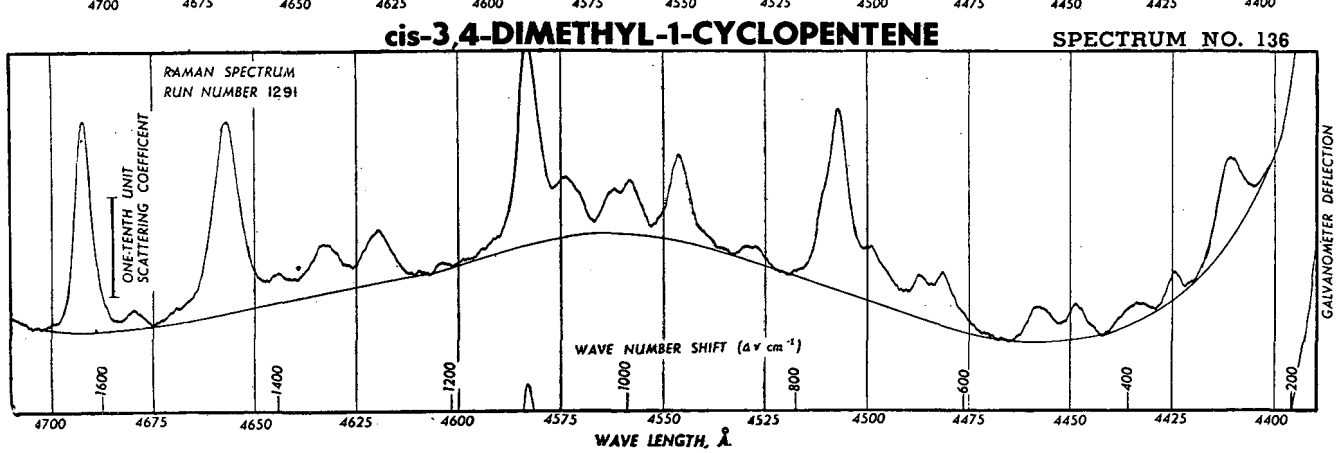
3-METHYL-1-CYCLOPENTENE

SPECTRUM NO. 135

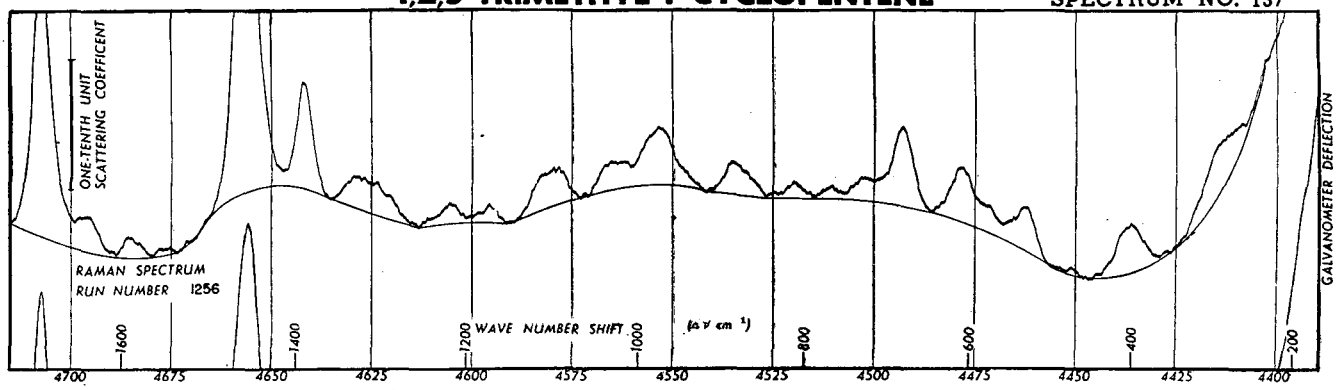


cis-3,4-DIMETHYL-1-CYCLOPENTENE

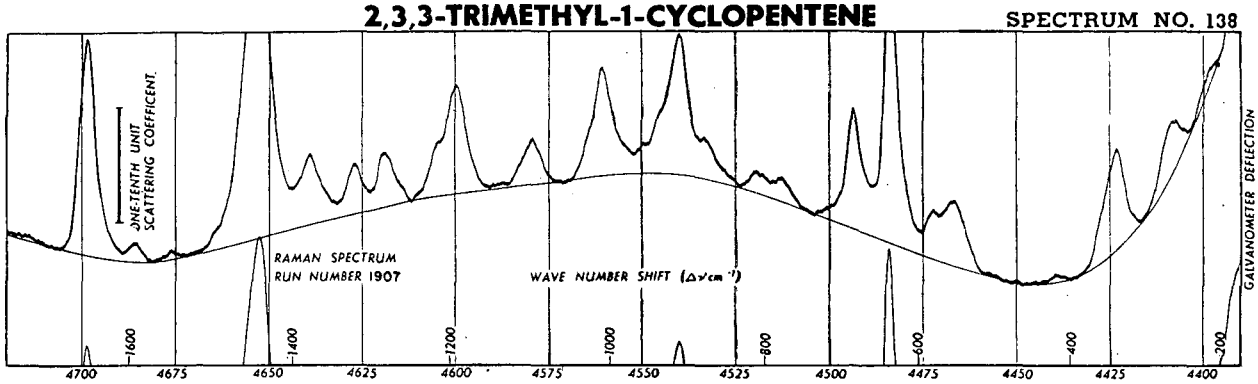
SPECTRUM NO. 136



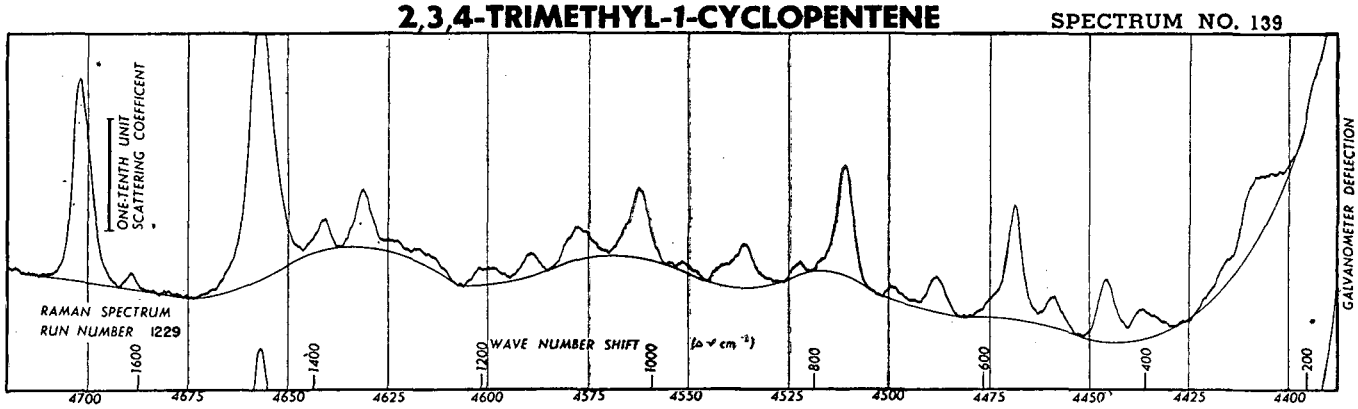
1,2,3-TRIMETHYL-1-CYCLOPENTENE SPECTRUM NO. 137



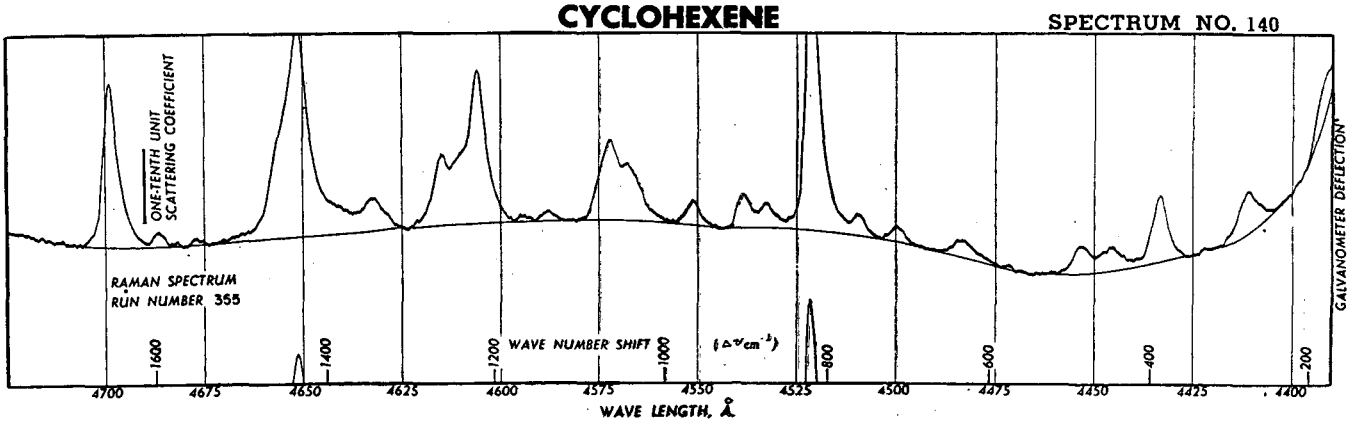
2,3,3-TRIMETHYL-1-CYCLOPENTENE SPECTRUM NO. 138

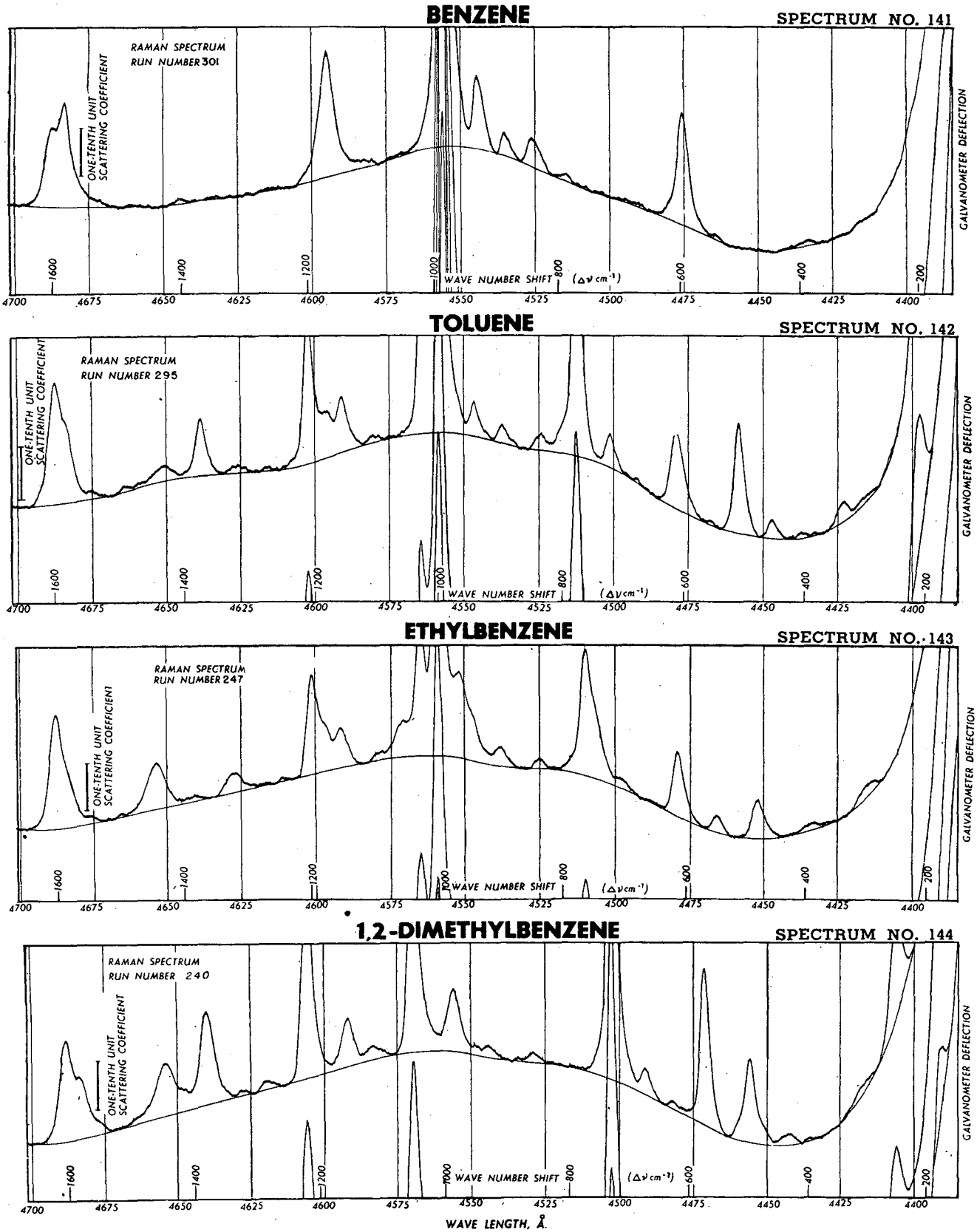


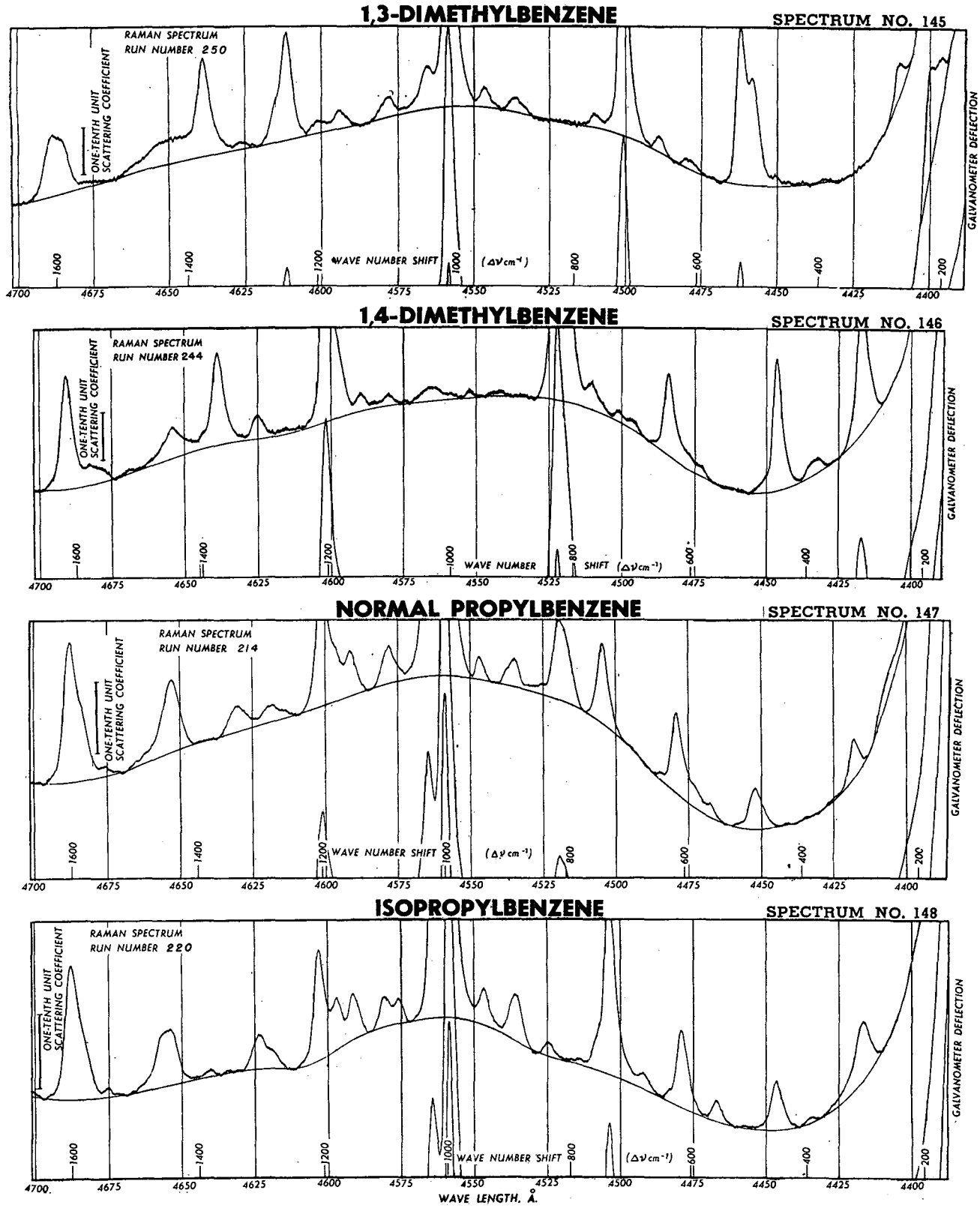
2,3,4-TRIMETHYL-1-CYCLOPENTENE SPECTRUM NO. 139

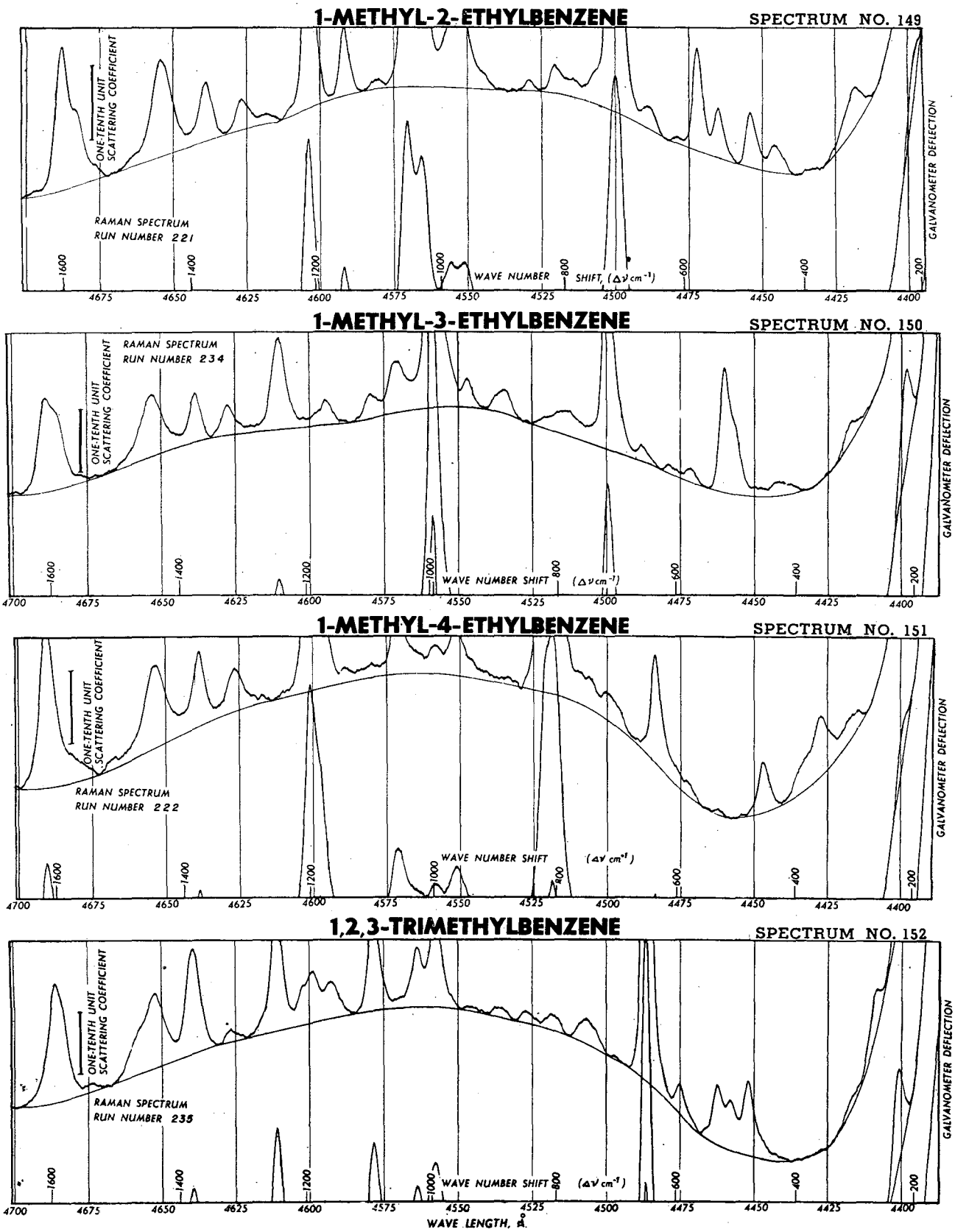


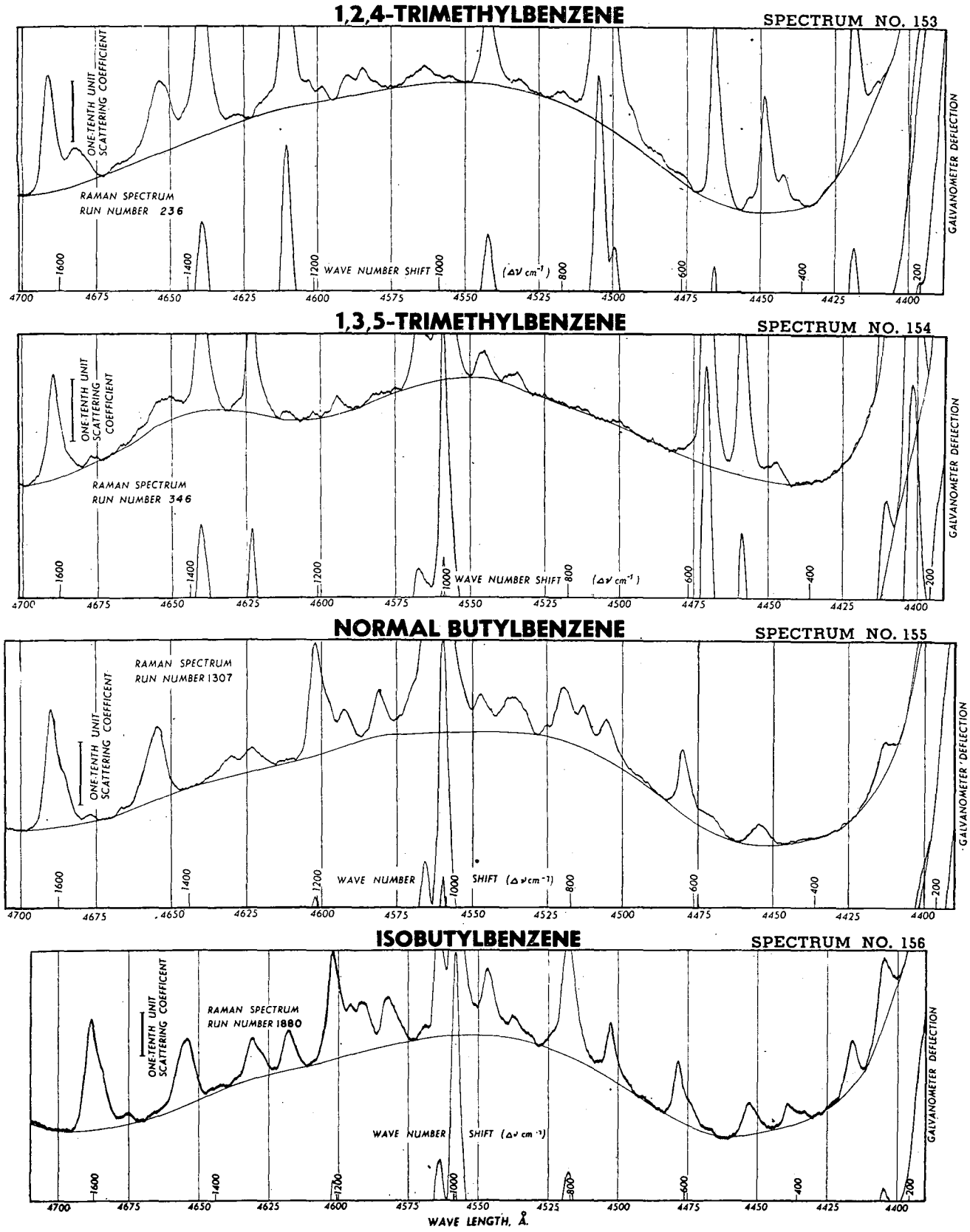
CYCLOHEXENE SPECTRUM NO. 140




BENZENE
SPECTRUM NO. 141
RAMAN SPECTRUM
RUN NUMBER 301
ONE-TENTH UNIT
SCATTERING COEFFICIENT
GALVANOMETER DEFLECTION
WAVE NUMBER SHIFT (Δν cm⁻¹)
TOLUENE
SPECTRUM NO. 142
RAMAN SPECTRUM
RUN NUMBER 295
ETHYLBENZENE
SPECTRUM NO. 143
RAMAN SPECTRUM
RUN NUMBER 247
1,2-DIMETHYLBENZENE
SPECTRUM NO. 144
RAMAN SPECTRUM
RUN NUMBER 240
WAVE LENGTH, Å.

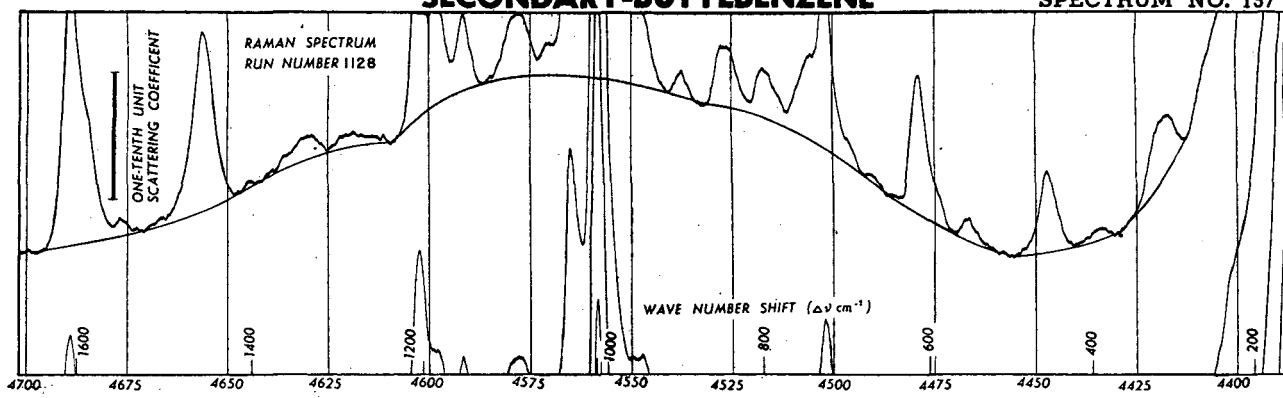

1,3-DIMETHYLBENZENE
SPECTRUM NO. 145
RAMAN SPECTRUM
RUN NUMBER 250
ONE-TENTH UNIT SCATTERING COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1,4-DIMETHYLBENZENE
SPECTRUM NO. 146
RAMAN SPECTRUM
RUN NUMBER 244
ONE-TENTH UNIT SCATTERING COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
NORMAL PROPYLBENZENE
SPECTRUM NO. 147
RAMAN SPECTRUM
RUN NUMBER 214
ONE-TENTH UNIT SCATTERING COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
ISOPROPYLBENZENE
SPECTRUM NO. 148
RAMAN SPECTRUM
RUN NUMBER 220
ONE-TENTH UNIT SCATTERING COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
WAVE LENGTH, Å.


1-METHYL-2-ETHYLBENZENE
SPECTRUM NO. 149
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 221
GALVANOMETER DEFLECTION
WAVE NUMBER SHIFT, (Δν cm⁻¹)
1600 1400 1200 1000 800 600 400 200
4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400
1-METHYL-3-ETHYLBENZENE
SPECTRUM NO. 150
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 234
GALVANOMETER DEFLECTION
WAVE NUMBER SHIFT (Δν cm⁻¹)
1600 1400 1200 1000 800 600 400 200
4700 4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400
1-METHYL-4-ETHYLBENZENE
SPECTRUM NO. 151
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 222
GALVANOMETER DEFLECTION
WAVE NUMBER SHIFT (Δν cm⁻¹)
1600 1400 1200 1000 800 600 400 200
4700 4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400
1,2,3-TRIMETHYLBENZENE
SPECTRUM NO. 152
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM
RUN NUMBER 235
GALVANOMETER DEFLECTION
WAVE NUMBER SHIFT (Δν cm⁻¹)
1600 1400 1200 1000 800 600 400 200
4700 4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400
WAVE LENGTH, Å.


1,2,4-TRIMETHYLBENZENE
SPECTRUM NO. 153
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM RUN NUMBER 236
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1,3,5-TRIMETHYLBENZENE
SPECTRUM NO. 154
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM RUN NUMBER 346
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
NORMAL BUTYLBENZENE
SPECTRUM NO. 155
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM RUN NUMBER 1307
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
ISOBUTYLBENZENE
SPECTRUM NO. 156
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM RUN NUMBER 1880
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1600 1400 1200 1000 800 600 400 200
4700 4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400
WAVE LENGTH, Å.

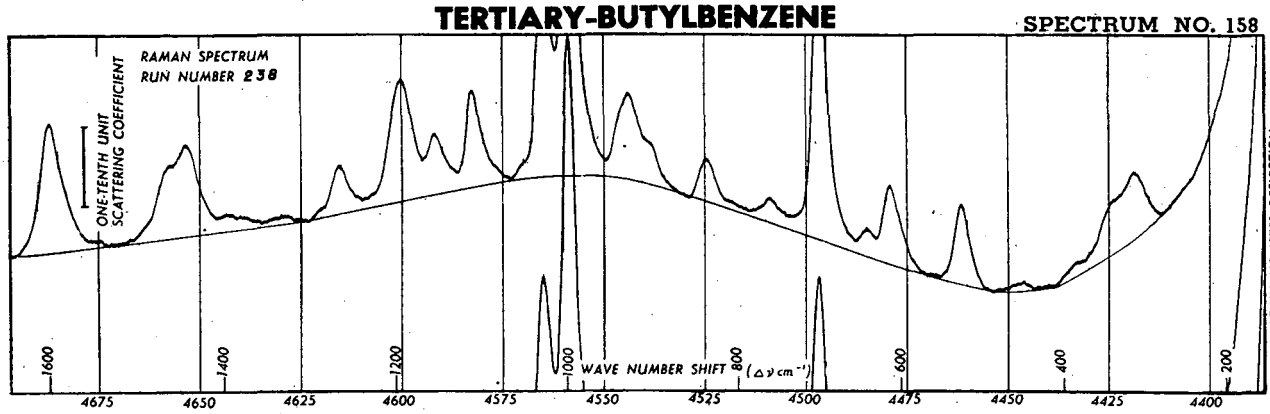
SECONDARY-BUTYLBENZENE

SPECTRUM NO. 157



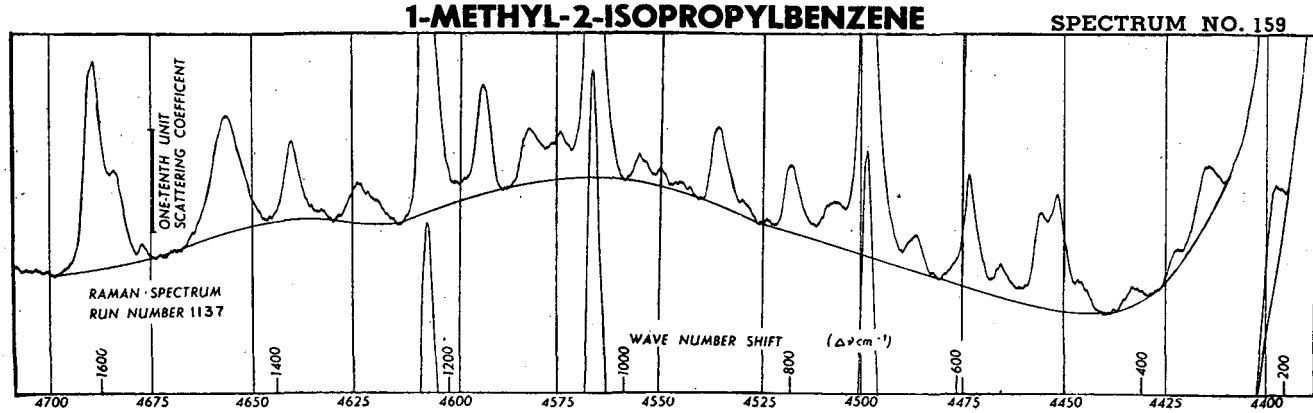
TERTIARY-BUTYLBENZENE

SPECTRUM NO. 158



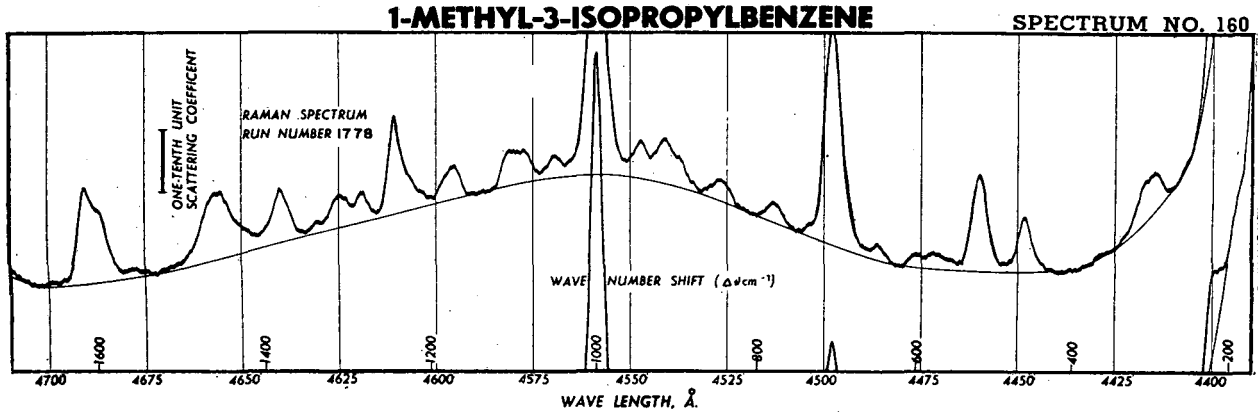
1-METHYL-2-ISOPROPYLBENZENE

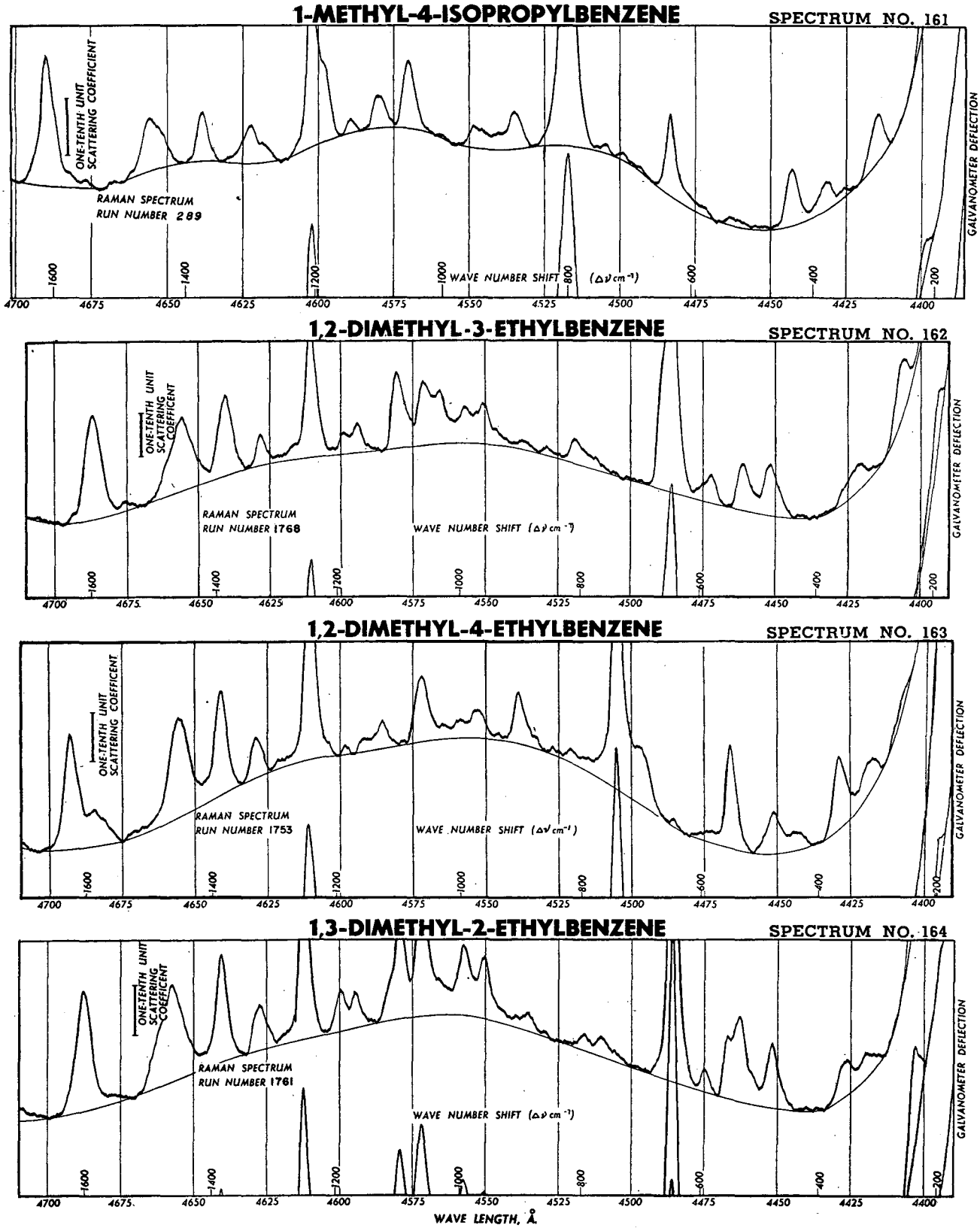
SPECTRUM NO. 159

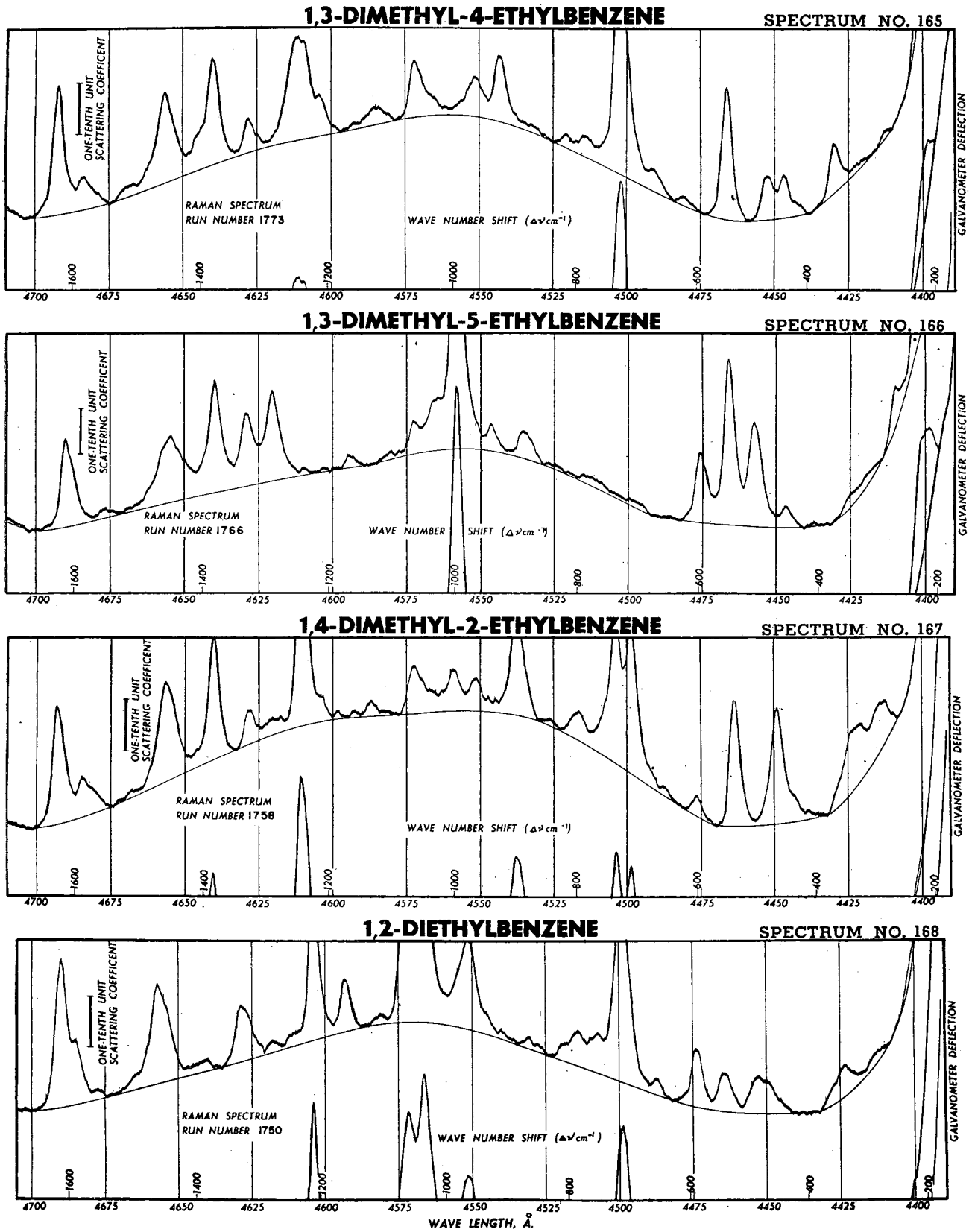


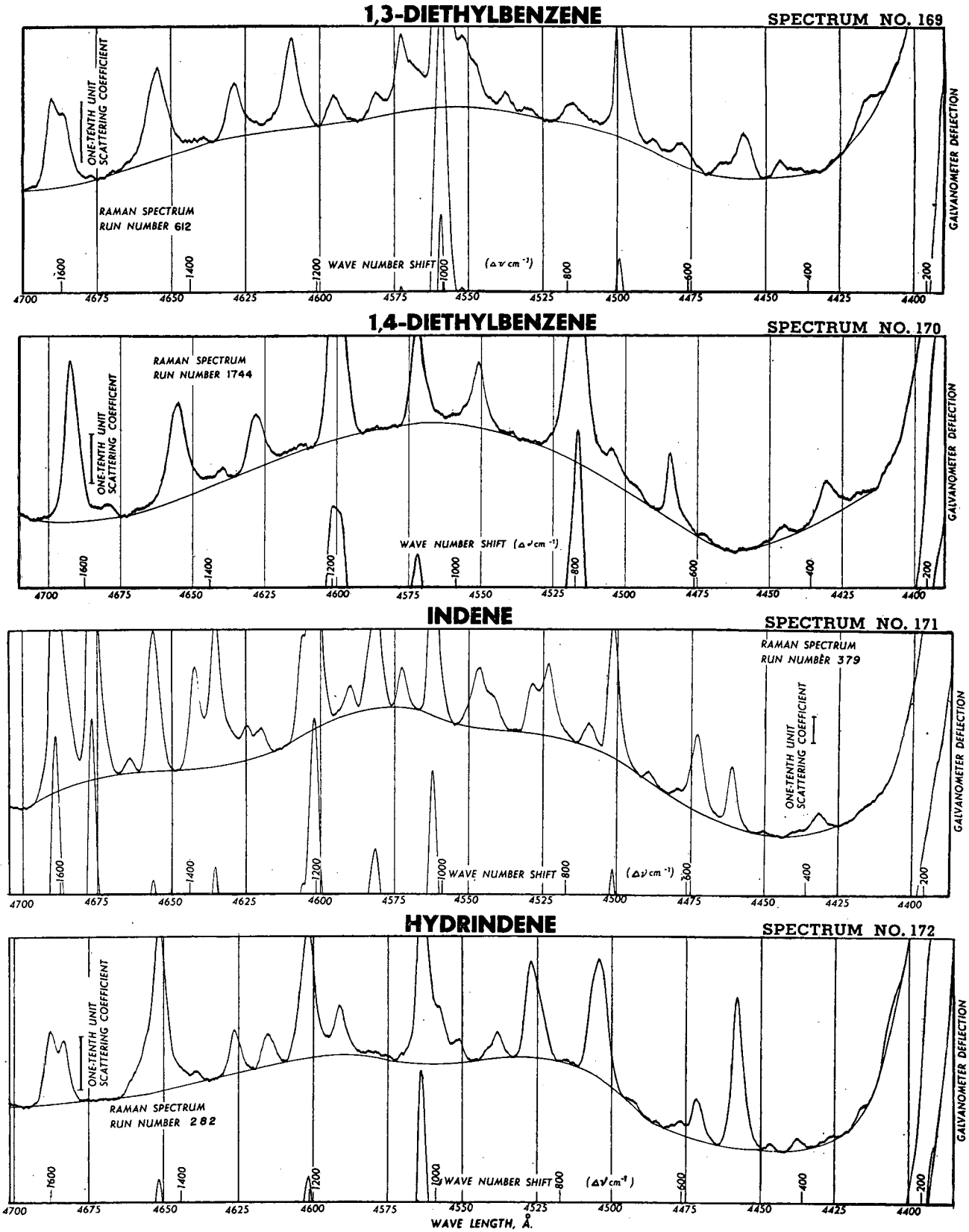
1-METHYL-3-ISOPROPYLBENZENE

SPECTRUM NO. 160




1-METHYL-4-ISOPROPYLBENZENE
SPECTRUM NO. 161
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM RUN NUMBER 289
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1,2-DIMETHYL-3-ETHYLBENZENE
SPECTRUM NO. 162
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM RUN NUMBER 1768
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1,2-DIMETHYL-4-ETHYLBENZENE
SPECTRUM NO. 163
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM RUN NUMBER 1753
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1,3-DIMETHYL-2-ETHYLBENZENE
SPECTRUM NO. 164
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM RUN NUMBER 1761
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1600 1400 1200 1000 800 600 400 200
4700 4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400
WAVE LENGTH, Å.


1,3-DIMETHYL-4-ETHYLBENZENE
SPECTRUM NO. 165
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM
RUN NUMBER 1773
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1,3-DIMETHYL-5-ETHYLBENZENE
SPECTRUM NO. 166
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM
RUN NUMBER 1766
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1,4-DIMETHYL-2-ETHYLBENZENE
SPECTRUM NO. 167
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM
RUN NUMBER 1758
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1,2-DIETHYLBENZENE
SPECTRUM NO. 168
ONE-TENTH UNIT SCATTERING COEFFICENT
RAMAN SPECTRUM
RUN NUMBER 1750
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1600 1400 1200 1000 800 600 400 200
4700 4675 4650 4625 4600 4575 4550 4525 4500 4475 4450 4425 4400
WAVE LENGTH, Å.


1,3-DIETHYLBENZENE
SPECTRUM NO. 169
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM RUN NUMBER 612
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
1,4-DIETHYLBENZENE
SPECTRUM NO. 170
RAMAN SPECTRUM RUN NUMBER 1744
ONE-TENTH UNIT SCATTERING COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
INDENE
SPECTRUM NO. 171
RAMAN SPECTRUM RUN NUMBER 379
ONE-TENTH UNIT SCATTERING COEFFICIENT
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
HYDRINDENE
SPECTRUM NO. 172
ONE-TENTH UNIT SCATTERING COEFFICIENT
RAMAN SPECTRUM RUN NUMBER 282
WAVE NUMBER SHIFT (Δν cm⁻¹)
GALVANOMETER DEFLECTION
WAVE LENGTH, Å.

Correlation of Intensity Measurements in Raman Spectra Obtained with Different Instruments

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The chief sources of error in intensity measurements in Raman spectra for analytical purposes are discussed. Three of the major causes of discrepancies between observations of different observers using different instruments are treated and suggestions are made for minimizing these errors. The variation in apparent intensity caused by variable polarization of Raman lines and widely different transmission factors for plane polarized light for different spectrographs is discussed in detail. Equations are derived to enable polarization corrections to be made to the "scattering coefficients" tabulated in the catalog of hydrocarbon spectra by Fenske and his collaborators. By means of curves given in the paper, scattering coefficients given in the catalog can be calculated approximately as they would be observed in other spectrographs if the transmission factor for the two kinds of plane polarized light is known.

ANOTHER paper (*1*) presents an outline of the method in use at The Pennsylvania State College for analysis of hydrocarbons by means of their Raman spectra and in addition, tabulates the scattering coefficients and depolarizations of many of the lines of 172 pure hydrocarbons. The aforementioned paper points out that the values obtained for the scattering coefficients are somewhat dependent on the instrument used for their determination. It is well known that in making quantitative analyses with infrared and ultraviolet absorption equipment, it is necessary to calibrate the particular instrument employed, making use of standard samples. Quantitative analysis by means of the Raman effect suffers essentially the same limitations with respect to standard samples as infrared and ultraviolet spectrophotometry.

The main reasons for the variation of scattering coefficients with different instruments are: variable polarization of raman lines, variable breadth of lines, and incomplete resolution of lines.

Data given in the preceding paper (*1*) represent work on many hydrocarbons which are rare, and difficult or almost impossible for many investigators to obtain. It is the purpose of this paper to acquaint other investigators with the possibilities of using the above data for crude quantitative work with their own instruments in cases where standard samples for calibration are not available.

Incomplete Resolution of Lines. With regard to incomplete resolution of lines, conformity of instruments can be obtained by employing a slit width so that sharp lines 15 cm.$^{-1}$ apart can just be resolved.

Variable Line Breadth. Conformity of variable line breadth cannot be achieved easily for a number of reasons. Because of the necessity of producing a large signal-to-noise ratio in the photoelectric spectrograph, a time constant of some seconds must be employed in the electrical circuit. It is, of course, necessary to scan the spectrum in a reasonable time. If the Raman lines all had the same breadth, the scattering coefficients would all be relatively correct, regardless of the percentage of full deflection obtained for the lines. However, this is not the case and, as a result, broad lines will have an apparent scattering coefficient which may be as much as 30% too great compared to sharp lines. If the scattering coefficients were measured photographically by means of the density produced on a photographic plate, the net effect would be to obtain "peak" deflections uniformly for all lines. The scattering coefficients given in (*1*) are correct as far as the variable breadth of the lines is concerned in the case of sharp, well-resolved lines, since the standard $\Delta\nu$ = 459 cm.$^{-1}$ carbon tetrachloride line is sharp and well resolved.

The difficulties enumerated in the discussion of variable line breadth above are not so serious as might be expected. In the particular photoelectric instrument used, no difficulty in quantitative work is experienced from this cause, since the line shape stays constant with concentration and thus cancels out of the analysis. When other workers use the above data in lieu of standards for quantitative work with other instruments, either photoelectric or photographic, little can be done with respect to errors arising from variable line breadth. Fortunately, the situation is not very serious in any event, since the broad lines are often weak and frequently, but not universally, are of no interest for quantitative analysis.

Variable Polarization of Raman Lines. As for variable polarization of Raman lines a considerable degree of conformity can be achieved with regard to data on scattering coefficients given in the preceding paper and those to be expected using other instruments.

It is well known that a spectrograph does not transmit the two kinds of plane polarized light with equal facility. Spectrographs

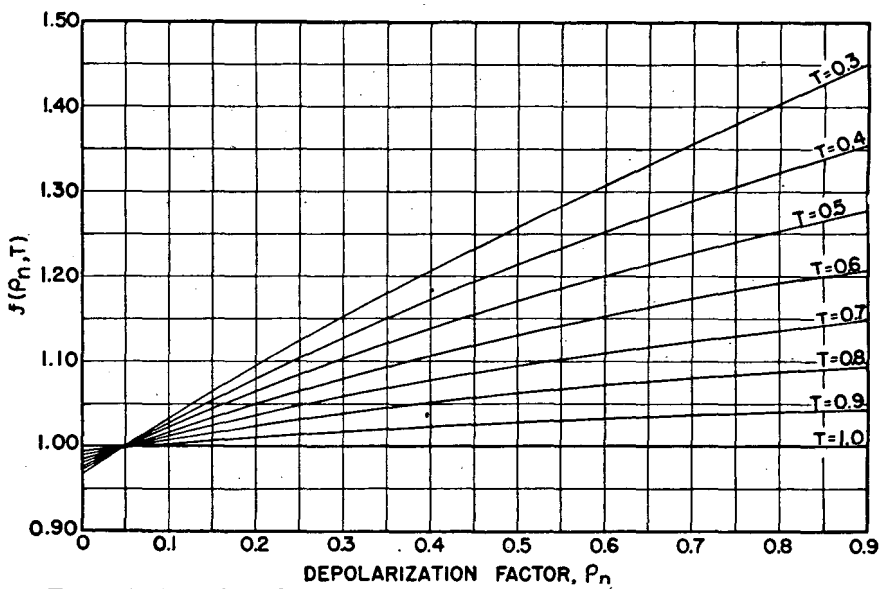

Figure 1. Family of Curves Representing Equation 7a Plotted for Various Values of *T*

of different design and manufacture, grating instruments as well as prism instruments, differ widely in their ability to transmit the two kinds of plane polarized light. These transmission characteristics of spectrographs for polarized light are largely responsible for much of the variation in intensity measurements quoted in the literature.

The author (*2*) has shown how true relative intensities can be measured in Raman spectra. For the convenience of the reader, the derivation of the equation for the true intensity in terms of ρ_n, the depolarization factor for natural unpolarized exciting light, and T, the transmission factor of the spectrograph for the two kinds of plane polarized light, are given below.

The transmission of an instrument, T, for natural unpolarized light is

$$T = S_0/P_0 \text{ [unpolarized]} \tag{1}$$

where S_0 is the intensity measured for the perpendicular ($\perp$) component, the electric vector vibrating in the vertical plane, and P_0 the intensity for the parallel ($\parallel$) component, or electric vector vibrating in the horizontal plane. Then ρ_n, the depolarization factor for a polarized line, will be given by

$$\rho_n = \frac{\perp}{\parallel} = \frac{S_0}{P_0 T} \tag{2}$$

If I_t represents the true intensity of the line in question and I_0 represents the observed natural intensity of the spectrum line, the following relationships result:

$$I_t = P_0 (1 + \rho_n) \tag{3}$$

$$I_0 = P_0 (1 + \rho_n T) \tag{4}$$

from which is obtained

$$I_t = I_0 \frac{(1 + \rho_n)}{(1 + \rho_n T)} \tag{5}$$

The scattering coefficient K_0 referred to in the previous paper is defined as

$$K_0 = \frac{I_0}{I_{0s}} \tag{6}$$

where I_0 is the observed intensity of the line in question and I_{0s} is the $\Delta\nu = 459$ cm.$^{-1}$ line of carbon tetrachloride—i.e., the standard line.

The true scattering coefficient, as would be observed by means of an instrument which did not preferentially transmit one kind of plane polarized light, we shall call K_t. K_0 is related to K_t by means of the following equation.

$$\frac{K_t}{K_0} = \frac{(1 + \rho_n^l)(1 + \rho_n^s T)}{(1 + \rho_n^l T)(1 + \rho_n^s)} \tag{7a}$$

where superscripts l and s on the ρ_n's refer to the line in question and the standard line, respectively. The part of the fraction involving only ρ_n^s and T is a constant for all lines observed under a given set of experimental conditions. Then Equation 7a becomes, for the purposes of transforming the data of the preceding paper (*1*):

$$\frac{K_t}{K_0} = 0.995 \frac{(1 + \rho_n^l)}{(1 + \rho_n^l T)} \tag{7b}$$

Let us call the right-hand side of Equation 7a $f(\rho_n, T)$. In Figure 1 $f(\rho_n, T)$ is plotted against ρ_n, using a value of $T = 0.90$ as was observed in ($\perp$). In order to find K_t it is only necessary to multiply the $f(\rho_n, T)$ value for a given ρ_n by the K_0 observed by Fenske and his collaborators. In Figure 1 $f(\rho_n, T)$ is also plotted against ρ_n for various values of T ranging from $T = 0.3$ to $T = 1.0$. If a K_t value is known from the data of Fenske *et al.* the K_0 value can be obtained for a given instrument by dividing the value of $f(\rho_n, T)$ (for a given T appropriate to the instrument in question) into K_t.

The treatment given above is applicable only to experimental conditions where true theoretical depolarization factors are experimentally achieved. The method of excitation used by the author and his collaborators (*3*, *4*) has been shown to fulfill these conditions. A recent paper of the author's has shown that the cylindrical lens method of excitation yields quantitatively theoretically correct values of ρ_n, ρ_s, and ρ_p.

Two additional observations concerning the excitation of Raman spectra might be pertinent. The cylindrical lens method of excitation, properly used, is the most powerful method of excitation with which the author is acquainted. The original Wood's light furnace method of excitation does not yield theoretically correct depolarization values when used in the ordinary manner.

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(3) Rank, D. H., Pfister, R. J., and Grimm, H. H., *Ibid.*, **33**, 31 (1943).
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System for Rapid Evaluation of Catalysts for Production of Butadiene from Ethanol

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THE great number of chemical combinations that must be investigated in a catalyst development program make the use of some type of screening test essential. This program was based on the testing of five hundred catalysts per year, with each material evaluated at five different conditions. In order to meet these requirements, it was necessary to be equipped to handle at least ten catalysts per week, plus a control; it was also desirable to be able to do special work on at least one material. Laboratory production of large batches of catalysts is a slow time-consuming procedure; it is very much easier and quicker to prepare a small quantity of most catalysts. These factors were the guides which led to the design of an apparatus to evaluate simultaneously twelve materials using only 20 cc. of each catalyst per test.

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SMALL-SCALE TESTING UNIT

A small-scale testing unit was designed, which consists essentially of the feed system, reactor, separation and collection system for C_4 and lighter hydrocarbons, and sampling system. The main requirements of such a unit are: (1) constant feed rate for very small rates of flow for the alcohol feed mixtures, (2) accurate control of reactor temperature, (3) continuous separation and collection of a C_4 and lighter fraction free from traces of acetaldehyde (and other oxygen-containing compounds which might

In order to evaluate in a short time a large number of new catalysts for the production of butadiene from alcohol, a multiple-test apparatus has been developed that appraises twelve catalysts simultaneously. As only 20 cc. of catalyst are required for each test, the apparatus permits the evaluation of catalysts which are difficult or time-consuming to prepare in large quantities. A feeder enables liquid addition at rates as low as 6 cc. per hour with an accuracy of ±10%. Gaseous products are scrubbed to remove soluble components and collected by displacing a salt solution in a constant-pressure system. Gas samples are taken by mercury displacement for analysis by chemical or physical methods. This apparatus is applicable to catalyst studies in which the feed is in a liquid state and of such a nature that it may be separated from the low-boiling products by countercurrent scrubbing. Soluble products may be separated by the use of appropriate solvents.

interfere with subsequent butadiene analysis), and (4) an accurate measure of the C_4 fraction collected.

A flow diagram for a single unit developed to fill these needs is shown in Figure 1.

Feed is supplied from a constant-rate buret, 1, to the reaction tube, 2, which consists of a 95-cm. (38-inch) length of 13-mm. outside diameter Pyrex tubing, including a preheat section packed with glass beads followed by the bed section containing 20 cc. of catalyst. The side arm at the top of the reaction tube is connected to a nitrogen supply, 5, and to a water manometer, 6. The nitrogen is used for flushing out the system at the beginning and end of each run. Manometer 6 measures the difference in pressure between the reactor and the atmosphere. It was found necessary to insert the trap, 4, in the side-arm connection in order to prevent the manometer liquid from being drawn into the reactor in case of a pressure drop in the system. The reactor, 2, is heated by an electric furnace, 3. Standard-taper 12/30 ground joints, 7, and 7-mm. Pyrex tubing are used to convey the product to the separation train.

Separation of the water-soluble and higher-boiling components is effected by means of a countercurrent scrubber 9, (*2*) and a fractionation column 360 mm. long and 15 mm. in diameter packed with 0.3-cm. (0.125-inch) Pyrex helices, 10. Water for scrubbing is supplied from a constant-head reservoir, 8. Liquid fractions are collected in a flask, 11, which is kept at a gentle boil by a heater, 12; the boiling drives absorbed or dissolved gases back up the fractionation column. Gaseous products come off the head of the scrubber and pass through a bubbler, 13, which contains a neutral solution of hydroxylamine hydrochloride and an indicator (bromophenol blue). If any acetaldehyde is present in the gas, the indicator changes color (from blue to yellow). The gas from the bubbler is collected in bottles, 14, by displacement of a sodium sulfate solution. The pressure of the whole system is controlled by adjusting the height of outlet *B* with respect to gas inlet *A*. At the conclusion of a run the volume of solution collected is equal to the volume of gas in the bottle. The difference in pressure from the atmosphere is measured by a mercury manometer, 16. The trap, 15, is used to prevent salt solution from entering the sampling system, which consists of a tower, 17, packed with calcium chloride to remove water and Ascarite to remove carbon dioxide. Gas samples are taken by displacement of mercury from a standard 250-cc. sample bottle, 18, to the reservoir, 19.

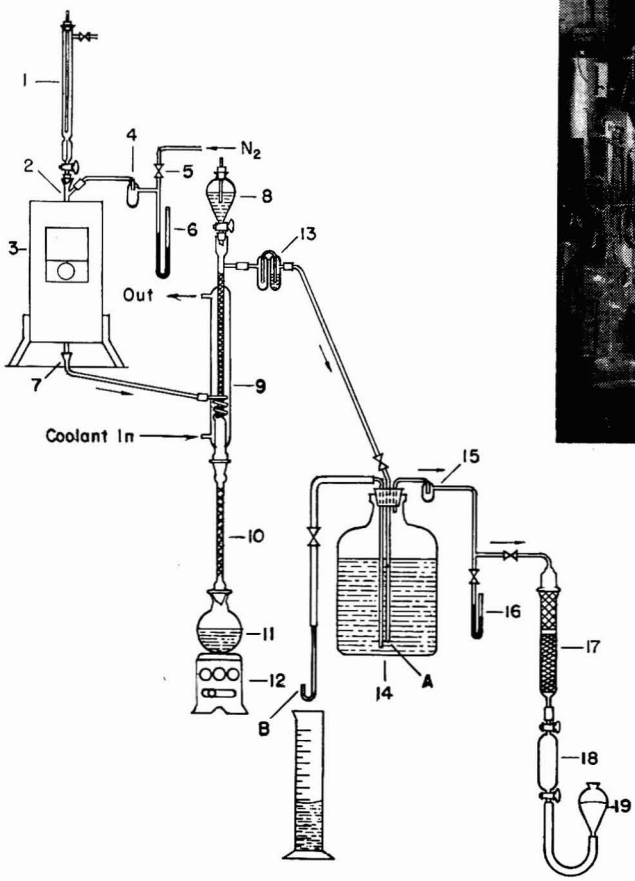

Figure 1. Flow Diagram of Single-Catalyst Test Unit

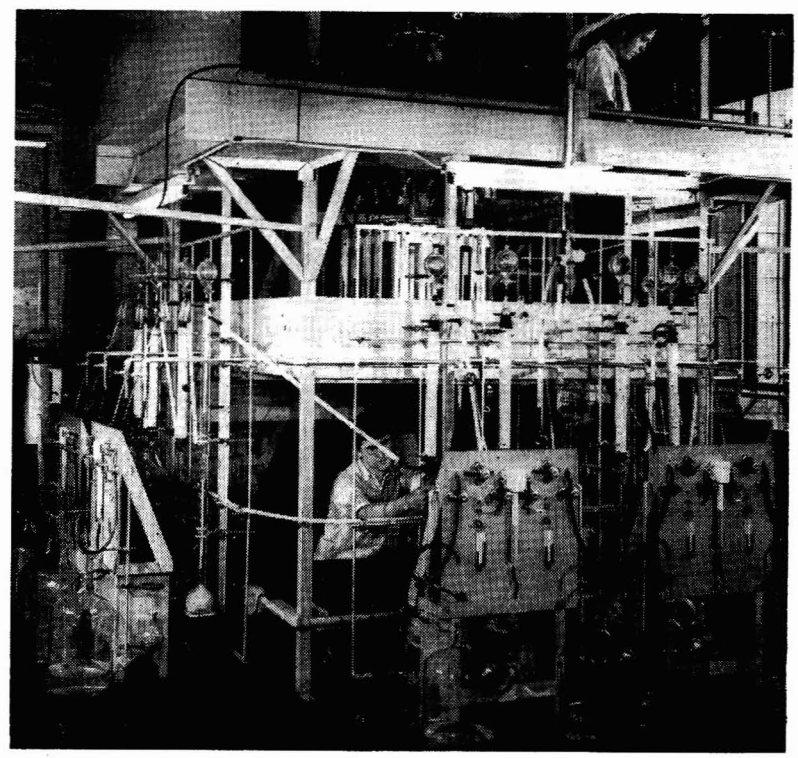

Figure 2. General View of Multiple-Test Assembly

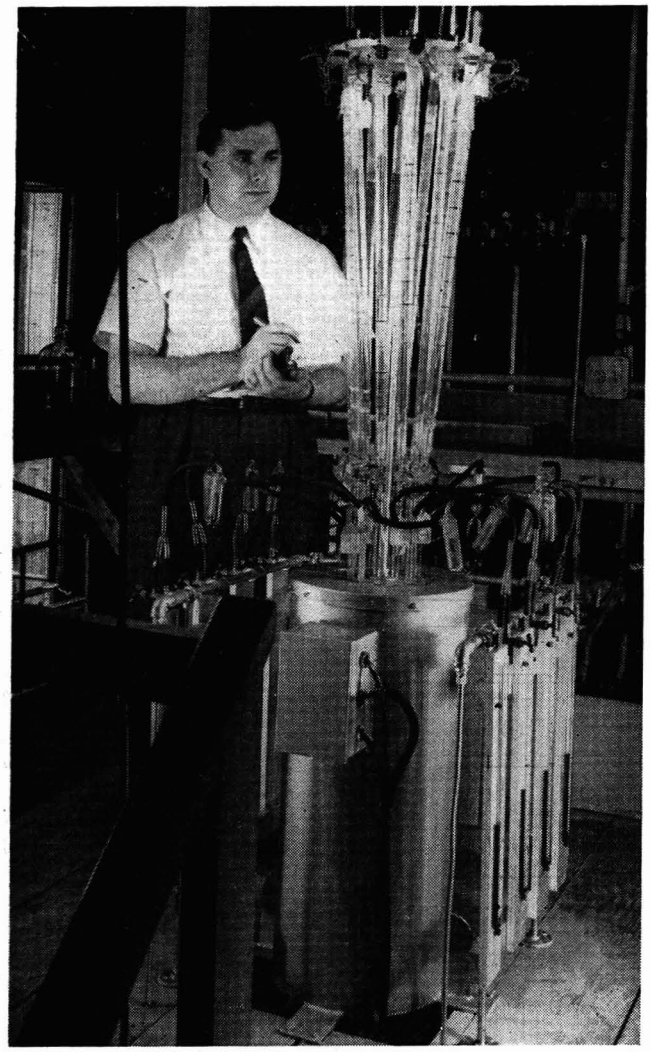

Figure 3. Feeders, Nitrogen Flushing System, Manometers, and Furnace of Multiple-Test Assembly

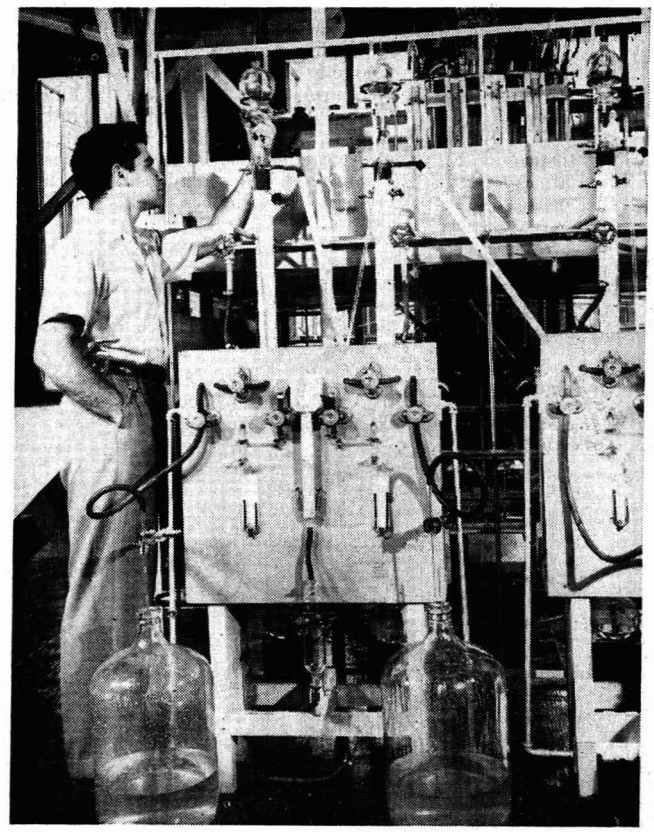

Figure 4. Scrubbers and Gas-Sampling System of a Pair of Test Units

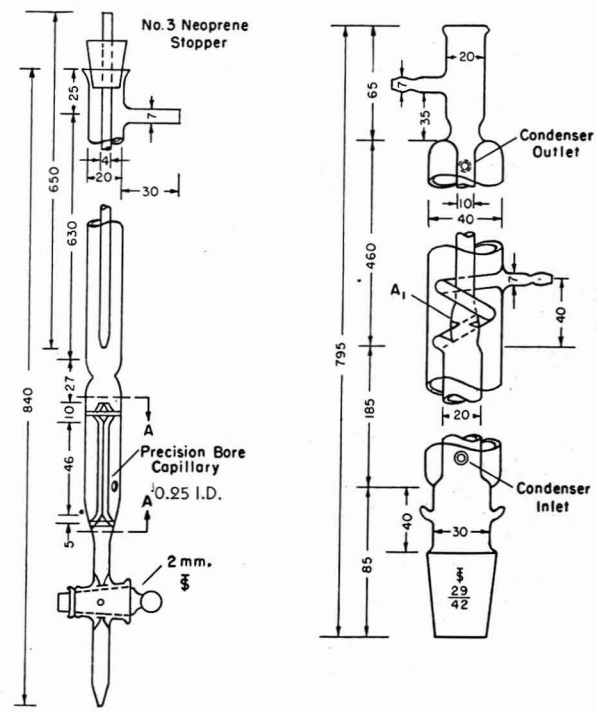

Figure 5. Structural Details of Countercurrent Scrubber Fractionating Column (Right) and Microfeeder (Left)

Dimensions in millimeters

MULTIPLE-TEST UNIT

The multiple-test unit comprises a centralized group of twelve single units with one furnace to heat all the reactor tubes. To eliminate the need for pumping or heated lines a gravity flow system is employed, the furnace being mounted on a platform 7 feet square raised 4.5 feet above the floor (this was found inconveniently low and should be made higher). The scrubbers, fractionating columns, and heaters are mounted on racks at three sides of the platform. The general layout of the unit can be seen in Figure 2. The constant-rate burets are mounted in a circle above the furnace and deliver directly into the top of the reactor tubes. The traps, manometers, and nitrogen flushing system are mounted around the furnace. The details of the upper portion of the multiple-test unit are clearly shown in Figure 3. The furnace contains twelve vertical chambers, one for each tube. Before the start of each run the bottles (14, Figure 1) are filled with salt solution from an overhead storage tank. For efficiency in operation the units are grouped in pairs, two gas-collection bottles being placed on a bench. The gas-sampling system is shown in Figure 4. One drying tower and one mercury displacement system are used for each pair of units. All flexible connections are made of neoprene tubing.

SPECIAL CONSTRUCTIONAL DETAILS

Figure 5 gives the structural details of the special glassware used in these units.

The heart of the microfeeder (constant-rate buret) is the section marked A-A, which is made from a 5-cm. (2-inch) length of precision-bore capillary tubing having an inside diameter of 0.25-mm. (0.010 inch) (*1*). The side arm on the feeder is closed by rubber tubing and a pinchclamp. A cotton filter is placed at the constriction above the capillary. In the scrubber A_1 indicates supports for the packing. The tube should be enlarged at this point to provide an open area at least as large as the cross-sectional area of the packed section. The packing material in the scrubber is 0.3-cm. (0.125-inch) Pyrex helices.

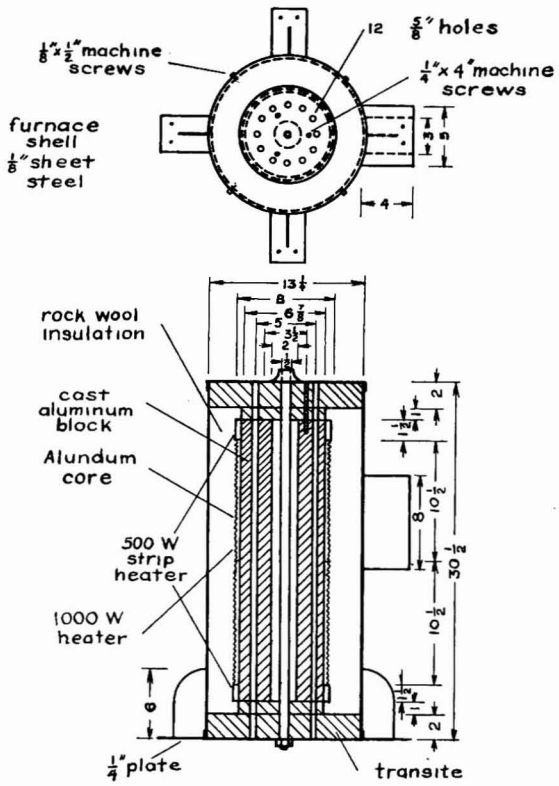

Figure 6. The Furnace

Dimensions in inches

Figure 6 shows the construction of the furnace. The wiring diagram for the controls and furnace is given in detail in Figure 7 because the excellent temperature control realized in the reactor tubes was due to the use of this circuit.

Table I. Mole Per Cent Conversion to Butadiene

(Temperature, 350° C.)

Run No.	Elapsed Time in Hours 0–6	6–12	12–18	18–24	24–30	30–36	Av.
A	26	29	24	25	27	25	26
C	30	31	28	27	30	30	29
E	30	28	29	27	28	26	28
F	29	28	29	28	..	..	28
J	31	28	30	30	..	..	30
L	29	26	26	27	..	..	27
							28

At the end of 4 hours (the usual length of a run) the feed is turned off and 2 liters of nitrogen are slowly flushed through. The feeders are then weighed. Three gas samples are taken from each unit. The catalyst is weighed out of the reactors and is stored in 1-ounce bottles. The reactor tubes are left overnight in cleaning solution. It takes approximately 16 hours to complete these tests, to service the units for the next runs, and to clean up the laboratory. Two operators are required, one to start the runs and the other (on the following shift) to close down and to take samples.

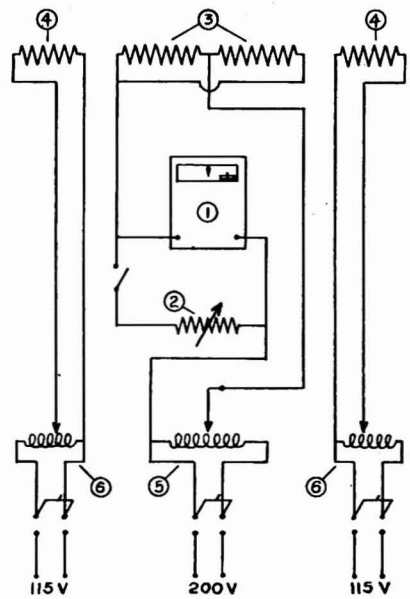

Figure 7. Wiring for Control Panel and Furnace

1. Wheelco Potentiotrol Model 3244
2. Ward Leonard rheostat, 32-ohm 600-volt
3. 1000-watt heater, 100 feet of No. 18 Chromel A
4. 500-watt strip heater
5. Variac Type 100-R, 230-volt
6. Variac Type 200-CM, 115-volt

EXPERIMENTAL RESULTS

Typical data obtainable with this system are shown in Table I. Six runs were made, three of 24-hour duration and three of 36-hour duration. Two sets of collection bottles were used, one for 6 hours, then the other for the next 6 hours, and so on. These results show that with the analytical method used the test is reproducible to within ±3% conversion.

The equation used to obtain these figures is:

$$\frac{2 \times \text{moles of butadiene produced} \times 100}{\text{moles of ethanol used}} = \text{mole \% conversion}$$

METHOD OF OPERATION

It is advantageous to run the unit once per day. The catalyst is measured into the reaction tubes and the glass beads are added to form a preheater. The packed tubes are then placed in the furnace, connected to the separation train, and flushed with nitrogen for 2 hours. The burets are filled with feed and are weighed. The water to the scrubber is started and the rate adjusted to about one drop in 4 seconds. The gas-collection bottles are filled with solution. Fresh hydroxylamine hydrochloride solution is placed in the bubbler. The feeders are connected to the reactor tubes but are not turned on. Each unit is pressure-tested for leaks; if any are found, they are corrected. The boilers (containing 100 cc. of water) are started and the nitrogen is turned off. When the conditions in the units have reached equilibrium, the runs are started by turning on the feeder. It is convenient to start the units at 5-minute intervals; in this way all twelve are running within one hour after the first is started. The feed rates are checked from time to time and adjustment is made by varying the pressure of the system (as indicated by manometer 6 in Figure 1). The pressure adjustment is made by raising or lowering the point of liquid overflow from the gas-collection bottle.

ACKNOWLEDGMENTS

The authors wish to acknowledge the aid of J. A. Hinckley in designing the extractive distillation column, of J. F. Miller and L. J. Lohr for analysis of gas samples, of A. L. Marston for development of spectroscopic analytical techniques, of E. C. Kovacic and J. Smarsh for operational assistance, of G. H. Young and B. B. Corson for advice and guidance, and of the Office of Rubber Reserve for permission to publish an account of this development.

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New Method for Testing Catalysts

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A new type of catalyst testing system employs a device for continuously separating the reaction products from a catalyst testing furnace. These fractions are more readily analyzed than the converter-make collected as a whole. This new system has resulted in improved accuracy in testing catalysts used for making butadiene from ethyl alcohol.

CATALYST testing in the laboratory usually consists of determining the change in composition of a feed stock that takes place under given conditions in the presence of the catalyst. The accuracy of the testing depends on the accuracy of the analysis of the reaction mixture for unreacted feed and main product. The main problems involved in the analysis usually arise from the presence of the inevitable profusion of by-products caused by the severe conditions imposed upon the feed stock, and from the difficulty of obtaining a proper sample of a mixture containing components ranging from gases to heavy tars.

An improvement in accuracy obtained by modifying the usual method of recovering the reaction products is described here. The modification consists essentially in separating the products continuously and precisely, during the test, into two fractions containing constituents boiling below and above room temperature.

The reaction under consideration is that of a mixture of ethyl alcohol and acetaldehyde to form 1,3-butadiene. In addition, hydrogen, carbon monoxide and dioxide, light hydrocarbons, aldehydes, alcohols, esters, heavy hydrocarbons, oils, etc., are recovered.

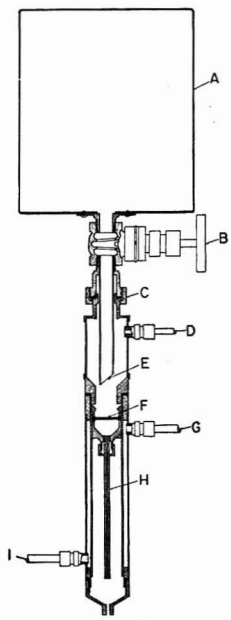

Figure 1. Orifice Feeder

A. Reservoir
B. Valve
C. Union
D. Nitrogen pressure inlet
E. Constant head device
F. Filter disk
G. Constant - temperature liquid exit
H. Constant - bore capillary
I. Constant - temperature liquid entrance

The reaction product is separated into a butadiene and lighter fraction and an acetaldehyde and heavier fraction. The light hydrocarbon fraction is collected in its entirety in a steel cylinder previously evacuated, from which a representative sample can be drawn for analysis by low-temperature distillation or other means. The acetaldehyde or heavier fraction is recovered in aqueous solutions, which may be analyzed for acetaldehyde and alcohol by distillation and chemical means. The butadiene is contained entirely in the gas fraction and the acetaldehyde and alcohol are entirely in the aqueous solution.

SPECIAL CATALYST TESTING EQUIPMENT

Feeders. Orifice-type feeders (Figure 1) are used to admit feed stock to the catalyst and water to the product separator. They continuously supply a well-regulated feed by employing a constant-bore glass capillary as a metering orifice. The temperature of the capillary is held constant by a jacket through which a liquid is circulated at controlled temperature. Nitrogen gas pressure, controlled by a diaphragm valve and mercury bubbler, pushes the feed through the orifice. The feeder is designed so that the weight of material fed in each test can be measured accurately. A reservoir, detachable from the metering orifice, holds the feed. The reservoir is weighed before and after each test to measure the amount of material fed into the system. The feeder is designed to prevent holdup of feed within the metering orifice. A constant-head device within the feeder assures constant feeding as the liquid level drops within the reservoir.

Reactor. The catalyst is tested in a 1-inch stainless steel reactor held at constant temperature by an electric resistance furnace. The pressure over the catalyst bed is constantly atmospheric. Feed stock is vaporized over a steam coil before entering the reactor. The reaction products are separated immediately after leaving the catalyst.

Product Separator. An extractive distillation column (Figure 2), which separates the reaction products, consists of a scrubbing column integral with a fractionating column.

The reaction products enter this separator through a glass tubing coil concentric with the scrubbing column. Ice water is circulated in a jacket about the scrubber and coil. Liquid reaction products are condensed and a fog form of entrainment is eliminated in the coil. Scrub with water uncondensed materials in the packed scrubbing section to remove acetaldehyde from the gas. The scrubbing section is cooled to 0° C. by the ice water jacket, greatly lowering the vapor pressure of acetaldehyde and thereby increasing efficiency of the scrubber many fold. The scrubbing water picks up a small amount of butadiene in addition to acetaldehyde. This butadiene is continuously fractionated out of solution by means of an integral fractionating column located just below the scrubbing section. An unpacked jacketed section between the fractionating column and the scrubbing column serves as a reflux condenser for the fractionating column. The reflux temperature is controlled at the boiling point of acetaldehyde, assuring complete removal of butadiene from the scrubbing water. The unreacted feed and liquid products are collected in the still pot with the scrubbing water. Scrubbed gas flows from the top of the product separator into the gas-collection system.

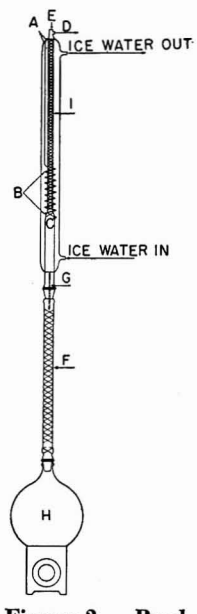

Figure 2. Product Separator

A. Product entrance to jacket
B. Entrainment removal coil
C. Product entrance to column
D. Product gas exit
E. Scrubbing water entrance
F. Fractionating column
G. Thermometer
H. Still pot
I. Scrubbing column

Gas-Collection System. The gas flows from the product separator and is immediately and continuously tested for complete acetaldehyde removal.

Acetaldehyde is detected by means of a concurrent scrubber in which the gas is washed with a water solution of hydroxylamine hydrochloride containing bromophenol blue indicator.

[1] Present address, Podbielniak, Inc., Chicago, Ill.

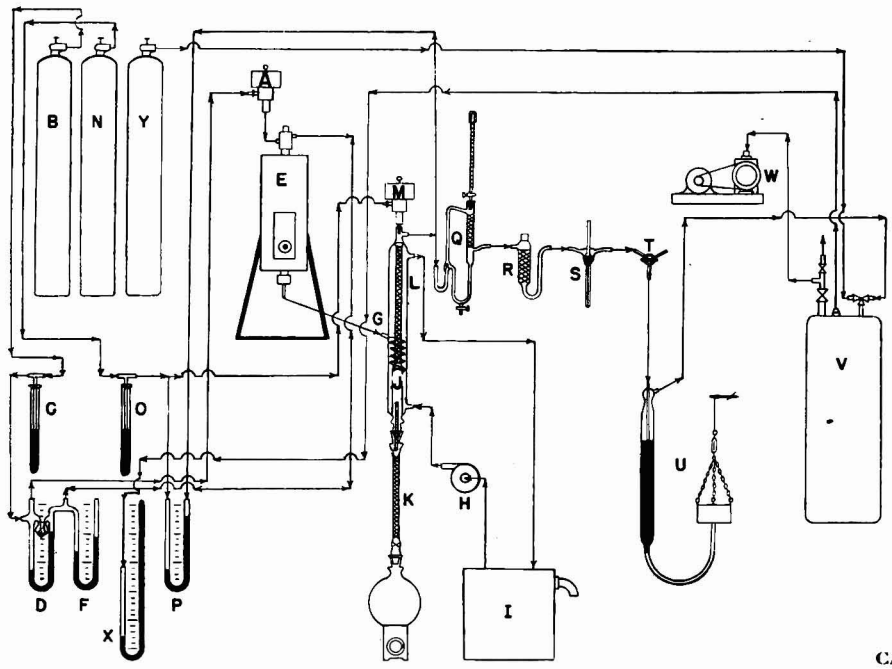

Figure 3. Catalyst Testing Unit

The hydroxylamine hydrochloride solution is placed in the scrubber at a pH of 4.6, so that a trace of acetaldehyde in the scrubber gas will react with the hydroxylamine hydrochloride and cause the color of the solution to change from a blue-pink to yellow. If any acetaldehyde is detected, it can be determined directly by titrating it with the buret filled with 0.5 *N* sodium hydroxide attached to the top of the scrubber. In this way good operation of the separation unit is assured, for poor operation is detected and can be corrected immediately. This hydroxylamine scrubber is operated by an air-lift principle which circulates the gas with the reagent solution concurrently down over a section packed with glass helices. The gas is dried with Ascarite, which removes traces of carbon dioxide in addition to water. It flows through a pressure regulator into an evacuated storage cylinder.

The gas is admitted to a pressure regulator through a long capillary tube that extends nearly to the bottom of the enclosing glass cylinder shown in Figure 3. An evacuated tank, *V*, is connected to the top of the enclosing cylinder while the bottom of the cylinder is connected by means of a rubber hose to a cylindrical wooden pot suspended by chain from a spring scale. The wooden pot is filled with mercury and the pot-scale assembly is suspended by a linen cord from an adjusting rod that is used to raise and lower it. Before evacuating, the height of the mercury reservoir is adjusted so that mercury covers the tip of the glass capillary that admits gases from the system to the regulator. As the tank is evacuated, mercury flows from the reservoir into the cylinder, so that the pressure in the tank is equal to atmospheric pressure minus the height of the column of mercury it suspends. The height of the column is the distance between the top of the mercury in the cylinder and the top of the mercury in the reservoir. The actual pressure in the tank is measured by means of a closed-end manometer, *X*.

When the collection tank is evacuated and the system is ready for operation, the gas stream is directed into the mercury pressure regulator. The gas flows in through the capillary tube and bubbles up through the mercury, leaving the regulator and flowing into the collection tank. When the gas flows into the regulator, however, the pressure as it leaves the capillary must be atmospheric; otherwise, a back pressure is transmitted to the system as indicated by manometer *S*. If there is a back pressure it means that the height of the column of mercury above the entering point of the gas (as it leaves the capillary) is greater than the column of mercury which the vacuum in the tank will suspend. With such back pressure, the mercury reservoir must be lowered so that the column of mercury above the entering point of the gas is just equal to the column of mercury which the vacuum in the tank will hold up. Actually if it were not for the resistance across the capillary, this adjustment would bring the level of the mercury in the reservoir just opposite the tip of the capillary where the gas flows into the mercury. Owing to gas flow resistance in the capillary, however, the level of mercury in the reservoir is just slightly below the entering point of the gas to the mercury column. This means that the tank is pulling a vacuum at that point just sufficient to overcome the pressure drop in the capillary. It is readily seen that a vacuum could be pulled on the entire system by making the column of mercury above the point of gas entrance into the regulator too small. Changes of this sort are all indicated on manometer *S*.

During the run, the pressure in the gas-collection tank increases, so that it will no longer suspend so great a column of mercury. The mercury flows back out of the cylinder into the reservoir. As the reservoir fills, it becomes heavier and elongates the spring in the scale from which it is suspended. The diameter of the mercury reservoir was calculated so that, in view of linear elongation of the spring, the level of mercury in the reservoir does not change with respect to the tip of the capillary where the gas enters the regulator. In this way the device is completely automatic throughout an entire run.

CATALYST TESTING UNIT

A flow sheet of the catalyst testing unit is presented as Figure 3.

The feed is supplied at a constant rate to the unit from an orifice feeder, *A*, operated by maintaining a constant differential pressure across the feeder orifice by means of nitrogen pressure in cylinder *B*, which is controlled by mercury bubbler *C* and differential pressure manometer *D*. The feed is admitted to a vertical reactor tube containing the test catalyst, which tube is

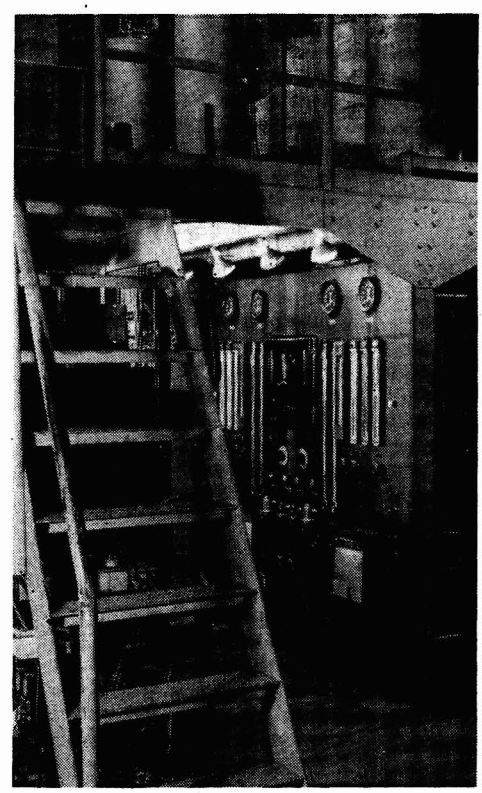

Figure 4. Catalyst Testing Unit

At top, furnaces and gas-collection tanks on steel platform. Instrument board located directly below gas-collection tanks. Constant-temperature machine at left, underneath stairway. Product-separation train directly in front of instrument board, obscured by constant-temperature machine

Table I. Experimental Results

	Probable Value, %	Average Deviation, %
Mole conversion to butadiene	34	±2
Ultimate efficiency	63	±1
Alcohol efficiency	54	±2
Aldehyde efficiency	83	±2

$$\text{Mole percentage conversion to butadiene} = \frac{\text{moles of butadiene formed} \times 200}{\text{moles of feed}}$$

$$\text{Ultimate efficiency} = \frac{\text{moles of butadiene formed} \times 200}{\text{moles of ethanol reacted} + \frac{\text{moles of acetaldehyde reacted}}{0.92}}$$

$$\text{Alcohol efficiency percentage} = \frac{\text{moles of butadiene formed}}{\text{moles of ethanol reacted}} \times 100$$

$$\text{Aldehyde efficiency percentage} = \frac{\text{moles of butadiene formed}}{\text{moles of acetaldehyde reacted}} \times 100$$

maintained at the desired temperature by means of furnace *E*. The temperature of the furnace is controlled by means of a microswitch operated in conjunction with a mercury relay. The back pressure caused by material flow across the unit is indicated by manometer *F*. Directional flow arrows on the line connecting *F* with the catalyst tube are in both directions, since the line serves two purposes. First, the back pressure from the unit is exerted through the line to *F* during operation, and secondly, the line carries nitrogen gas that is used to purge the unit before and after each test run. The nitrogen is by-passed across manometer *D* through this dual-purpose line to the reactor.

The converter-make flows from the reactor in furnace *E* into the separation unit at point *G*. Here the converter-make enters a cooling coil immersed in ice water that is circulated by a centrifugal pump, *H*, from the ice water reservoir, *I*. All the condensable materials from the converter are condensed in this coil and flow into an unpacked section of the separation column at point *J*. At this point the liquid materials flow down into the fractionating column, *K*, while the uncondensed gases flow up into the water scrubber, *L*. Water is admitted to *L* by means of an orifice feeder, *M*, operated by maintaining a constant differential pressure across the feeder orifice by means of nitrogen pressure in cylinder *N*, which is controlled by mercury bubbler *O* and differential pressure manometer *P*. A thermometer placed at the top of *K* serves to show that the butadiene is fractionated out of the lower section. The butadiene and other gases flow from the top of the water scrubber into a hydroxylamine hydrochloride solution scrubber, *Q*. From *Q* the gas flows through drying tube *R* and then over a mercury-filled manometer, *S*, which shows the pressure in the system at that point. From the manometer the gases flow through a three-way stopcock, *T*. This stopcock normally connects the system with the gas-product collecting tank, but it can also be used for diverting the gas stream at any instant into a gas-sampling bottle so that the catalyst performance can be checked at any time.

After flowing through the three-way stopcock, the gas is conducted to an automatic mercury pressure regulator, *U*, that allows the gas to flow from the system at atmospheric pressure into an evacuated tank, *V*. The gases, as they are collected in the tank, are sampled by means of a Toepler pump and analyzed. The tank is then brought up to atmospheric pressure by means of nitrogen from cylinder *Y* and is purged for some time into a hood before re-evacuating by means of pump *A*.

A photograph of the unit is shown as Figure 4.

EXPERIMENTAL RESULTS

Results from forty runs of 8 hours' duration used to standardize the first catalyst testing unit are shown in Table I.

In the calculation of the ultimate efficiency percentage, the moles of reacted acetaldehyde are divided by 0.92 because, in plant operation, ethanol is converted to acetaldehyde by a separate reaction which is approximately 92% efficient. The ultimate efficiency is therefore expressed on the basis of ethanol.

ACKNOWLEDGMENTS

The authors wish to acknowledge the aid of Albert Roth in designing and building many of the devices used in the catalyst-testing units, of Gilbert Kivenson for aptly handling the product gases in a reduced pressure system while obtaining analytical and physical data, and of G. H. Young and E. E. Stahly for administrative guidance.

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Quantitative Analysis with the X-Ray Spectrometer

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The x-ray spectrometer has greatly reduced the time and difficulties involved in carrying out diffraction analyses. The methods used in the author's laboratory for specimen preparation and preparation of quantitative curves are described. Also shown are the results of semiquantitative and quantitative methods applied to mixtures of heavy metal carbides. Excellent agreement has been obtained on known mixtures; results are obtained in as little as 10 minutes once the necessary working curves have been established.

IN present-day problems, the analyst is frequently presented with the problem of determining the presence of a compound or given state of combination as opposed to the presence of an element or radical. In rarer cases the quantitative determination is very important. X-ray diffraction is a well established method of doing this (*3*) but it has not been used for many problems where it was applicable because the available methods were time-consuming and capable of only semiquantitative results. Aside from the exposure time and the time involved in processing the film, the interpretation of patterns on films requires measurement of line location and measurement of line intensities by densitometry. The latter is not entirely satisfactory in the case of x-ray diffraction films. The advent of the Norelco direct-reading x-ray diffraction spectrometer made by North American Philips Company (*2*) has made quantitative diffraction methods very much more practical and worthy of consideration as an everyday aid in the solution of problems and in control.

With the spectrometer, the film is replaced by a Geiger counter tube, the output of which is amplified and fed to a strip chart recorder. A plot of the x-ray intensity versus the angle is obtained. The speed of scanning may be varied over a wide range from 0.25° to 4° per minute. Most of the work done in this laboratory has been at 2° per minute, which has been found satisfactory. At this rate the x-ray pattern may be recorded in as little as 1 minute if the intensity of only one reflection is required. The angular location of the reflection and the intensity are read directly from the recorder chart. An entire determination, including preparation of the specimen and calculation of

the results, may be made in 10 to 15 minutes. While training is required to set up the determination, an untrained operator may be taught in a short time to prepare specimens, record the patterns, read the charts, and calculate the results.

In studying heavy metal carbides and compositions of these carbides made by sintering them with auxiliary metals (commonly known as cemented carbide compositions), several semiquantitative and quantitative methods have been found useful. Some of these are described below to illustrate the method of use of the spectrometer and the type and accuracy of the results obtainable.

SAMPLE AND SPECIMEN PREPARATION

The most important consideration in specimen preparation is the avoidance of orientation. The method depends upon obtaining random orientation of the crystal planes in the specimen as examined with the spectrometer. For most materials a sample passing a 200-mesh sieve has been found satisfactory, but the elimination of orientation effects may require reduction to a very fine particle size well below 325-mesh. The material must not be so fine as to result in the broadening of the reflections which occurs at a particle size of about 0.1 micron and smaller. In the case of carbides requiring reduction to a fine size, ball milling in a steel ball mill with cemented carbide balls has been found satisfactory. The determination of the proper state of division for a given material is empirical and is based upon the reproducibility of the results.

The preparation of the actual specimen for x-ray exposure likewise must obviate orientation effects. As in the case of the sample preparation, the attainment of a satisfactory result is largely determined by the reproducibility of the results.

In this laboratory, two specimen preparations have been used. The first is a paraffin-casting technique in which about 1 gram of the powdered sample material is mixed with molten paraffin in a small porcelain crucible. The powder is permitted to settle and the crucible is immediately cooled in water. The button is then tapped from the crucible and the face containing the powder is flattened by very light pressure on a glass slide. The button is cooled rapidly in water. This specimen is then mounted on the specimen post of the spectrometer by pressing it powder side up with a glass slide into modeling clay in a small steel block with a recess milled into it. This method has been largely discarded because although satisfactory for some materials, orientation effects make it unsatisfactory with others and it is more time-consuming than the method described below.

The method now largely used consists of preparing a slurry of the powder sample and ethylcellulose dissolved in toluene by grinding with a small porcelain mortar and pestle. The slurry

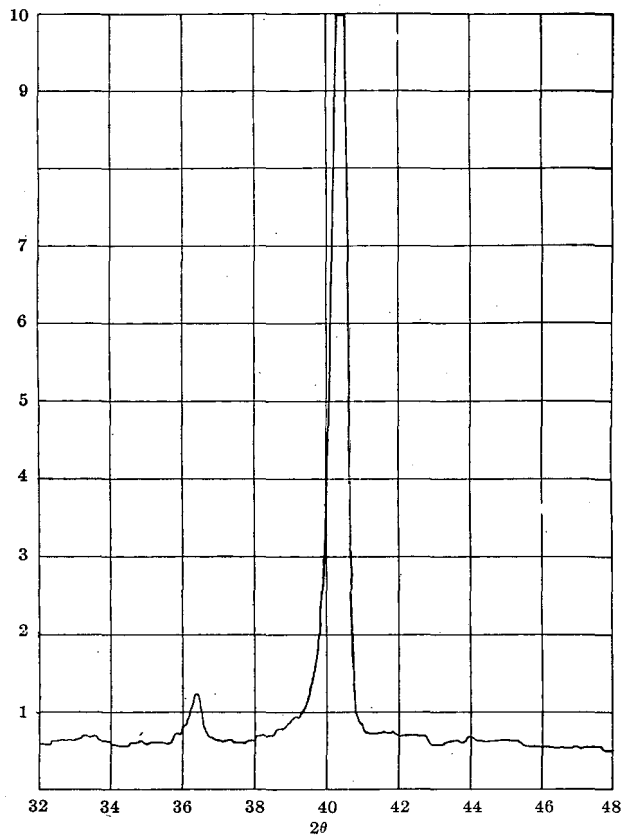

Figure 1. 100% Tungsten

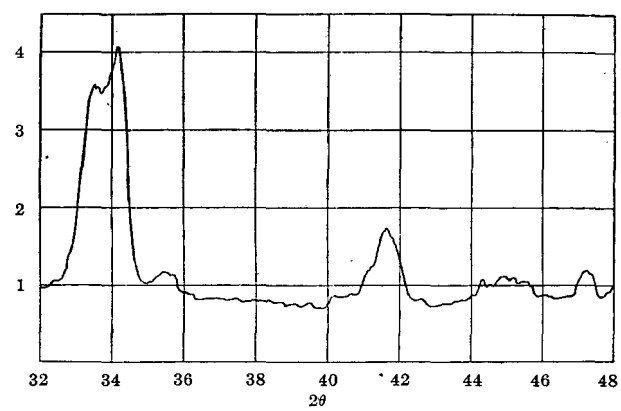

Figure 2. Tungstic Oxide

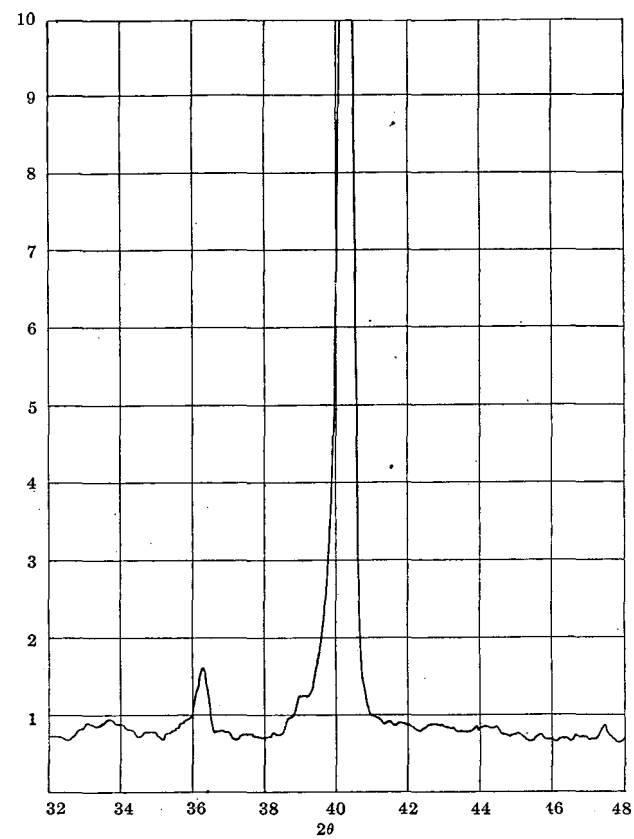

Figure 3. 90% Tungsten–10% Tungstic Oxide

is then thinned with ethyl acetate and poured onto a clean glass slide. The slurry must be of just the proper consistency, so that an even film of the proper thickness will result. The slide is manipulated continuously while the solvents are evaporating until a uniform smooth film is obtained. It is then dried a few minutes and is ready to be placed on the specimen post of the spectrometer (*1*). The entire process need take no more than 5 minutes.

No universally applicable method is known to the author and the preparation of specimens for the use of this method requires continued investigation.

RECORDING OF THE PATTERNS

The specimen on the glass slide is mounted on the specimen post and the pattern recorded in accordance with the instructions furnished by the manufacturers of the Norelco. The adjustments of the instrument, slit widths and heights, and the amplitude control are determined by trial to give the maximum height of recording on the Brown electronic recorder chart for the reflections which are to be used. In general, the strongest reflection of the structure being analyzed for should be used, provided that it is within the range for which the spectrometer is adjusted. When two or more substances are being determined from one recording, a weaker reflection of one or more of them may be preferable to reducing the amplitude of the entire recording. Some reflections may thus be off the chart, but this does no harm.

When the reflections which are to be used have been selected as indicated above, synthetic mixtures covering the range to be determined are next prepared, being certain that there are no orientation effects and that the chemical composition is identical with that which will be encountered in the unknowns. The spectrometer must also be standardized—that is, the output to the recorder may vary from day to day according to line voltage

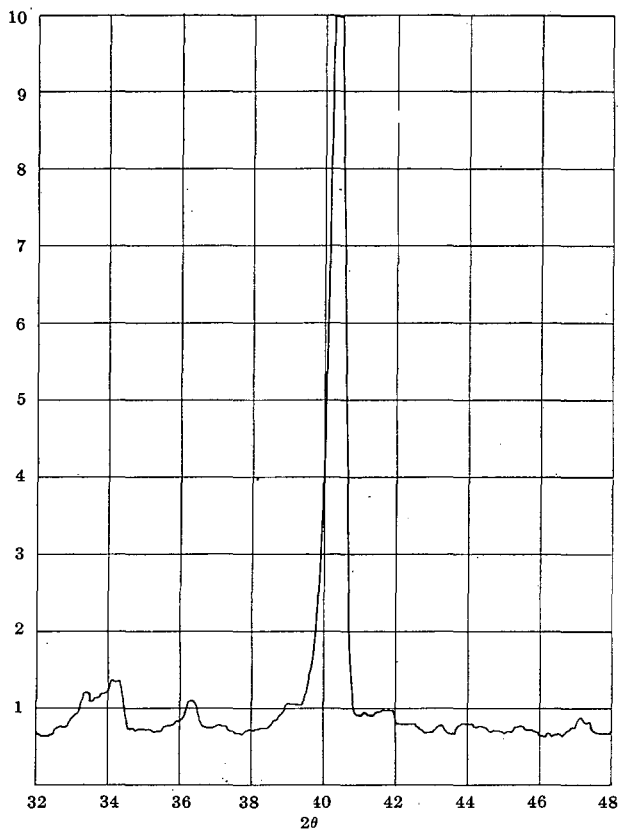

Figure 4. 75% Tungsten–25% Tungstic Oxide

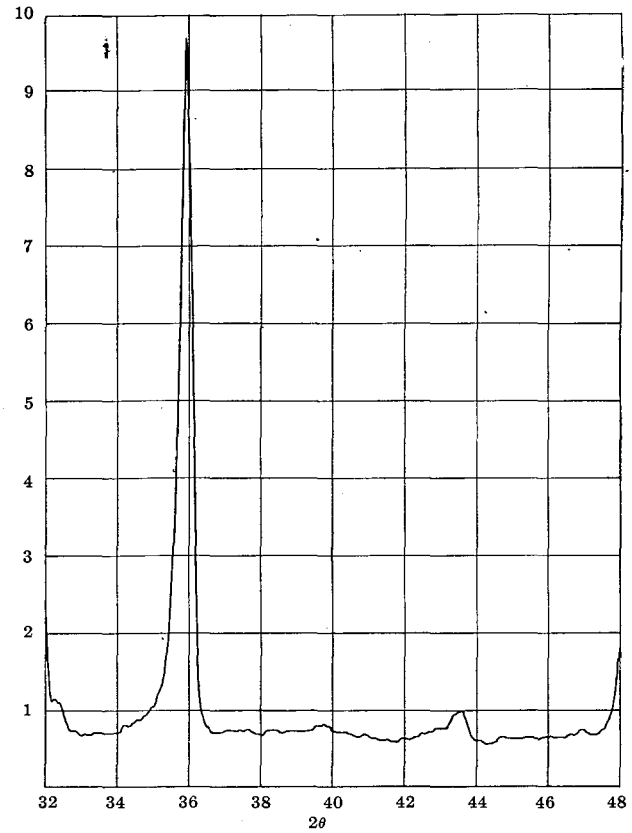

Figure 5. Pure Tungsten Carbide

variation and a check is desirable on the correct functioning of the equipment.

This standardization is carried out by obtaining the pattern of a standard material such as dry powdered rock salt or quartz with the adjustments of the instrument which it is desired to use for the determination being undertaken. Thereafter, the output of the instrument may be checked and adjusted by comparing the pattern with the original standardization. In this laboratory it has been found convenient to use as a secondary working standard a cemented tungsten carbide blank, which is used every day. The heights of the three major reflections of tungsten carbide obtained from the daily recording of the pattern of this standard blank are adjusted to within ±2% of the desired heights by means of the slit height wedge. In practice very little day-to-day adjustment has been required.

The patterns of the known mixtures are recorded over the desired angular range. Next, the heights of the selected reflections are read from the recordings, correction being made for the average height of the background at either side of the base of the reflection. While the area under the peak is more strictly the true value of the intensity of reflection, the author has found in his work that measurement of the height is satisfactory. From the values read from the recordings and the known compositions of the mixtures, working curves are then constructed. The response is very nearly linear, but falls off somewhat at higher intensities because of lag in the amplifier and recorder. The amount of the departure from a straight-line relationship will depend on the speed at which the scanning is carried out, the width of the reflections, and the height of the reflections.

Unknowns may now be analyzed using the working curve; it is necessary to use the same precautions with regard to preparation of the specimen, standardization of the spectrometer, and so on. It will be found that the angular locations of the peaks of the reflections vary somewhat (the author's experience

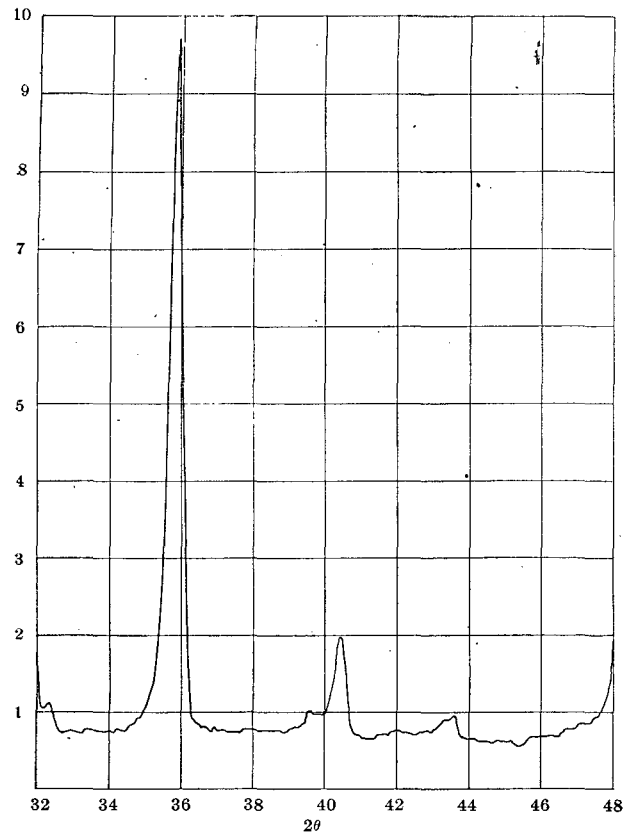

Figure 6. Tungsten Carbide Deficient in Carbon

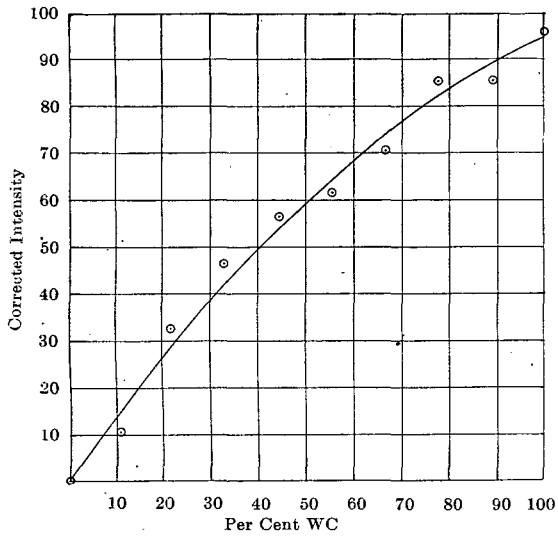

Figure 7. Working Curve for Unheated Mixtures of Tungsten Carbide and Molybdenum Carbide

is ±0.2°) and this is the reason for using recordings rather than the more time-consuming counting which would be more accurate and for which the spectrometer is equipped.

RESULTS

An example of the semiquantitative use of the spectrometer is the examination of tungsten powder for residual tungstic oxide. Figures 1, 2, 3, and 4 show recordings for pure tungsten, pure tungstic oxide, and tungsten powder containing 10.0 and 25.0% of tungstic oxide, WO_3. The differences are very evident and

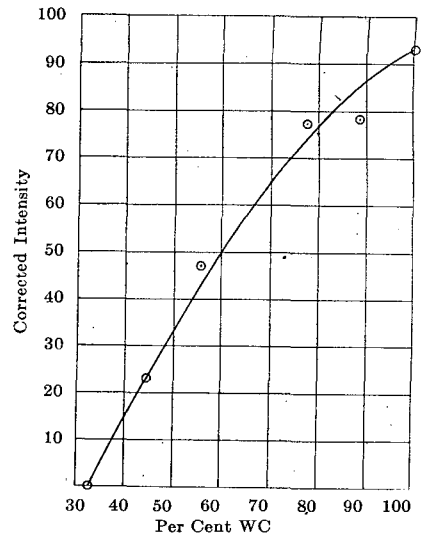

Figure 8. Working Curve for Heated Mixtures of Tungsten Carbide and Molybdenum Carbide

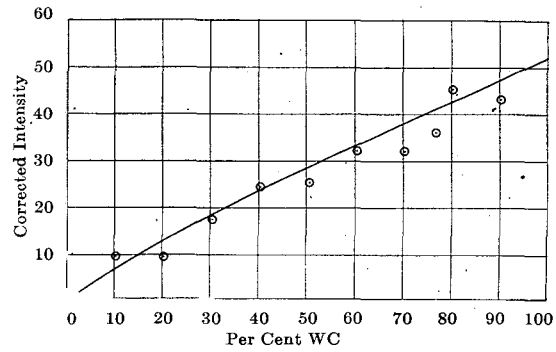

Figure 9. Working Curve for Unheated Mixtures of Tungsten Carbide and Titanium Carbide

Table I. Determination of Tungsten Carbide in Mixtures of Tungsten Carbide and Molybdenum Carbide

WC Present %	WC Found %		Deviation %
18.0	18.5		±0.5
33.6	33.4		−0.2
46.8	52.5		+5.7
58.4	60.5		+2.1
68.6	69.0		+0.4
78.0	77.0		−1.0
86.0	86.0		0.0
		Av.	±1.4

may be estimated by inspection. The average particle size of the powders was 0.5 to 2.5 microns measured by the air permeability method and glass slides were used. Filtered copper radiation was used.

Another example of semiquantitative work is shown by Figures 5 and 6 for pure tungsten carbide, WC, and tungsten carbide deficient 0.90% in carbon from the theoretical 6.12%. The carbon deficiency is evidenced clearly by the reflections at $2\theta = 39.5°$ of tungsten carbide, W_2C, and at $2\theta = 40.3°$ of tungsten, W. The average particle size of the samples was 2.5 microns and paraffin castings were used. The author has detected as little as 0.16% carbon deficiency by this method. Filtered copper radiation was used.

An example of the quantitative use of the instrument is the study of mixtures of tungsten carbide, WC, and molybdenum car-

bide, Mo_2C, and the effect of heating such mixtures. In this study, a working curve for tungsten carbide in ball-milled mixtures of the two carbides (average particle size, 2μ) was constructed using paraffin cast specimens. Figure 7 is the working curve for tungsten carbide. A second set of mixtures was then made up covering the same range in somewhat different increments and the percentages of tungsten carbide were read from the curve. The results are shown in Table I.

The average deviation obtained is seen to be excellent for many purposes. The deviations do not appear to improve with the lower percentages.

With the aid of Figure 7, the effect of heating these mixtures at 2000° C. was readily determined (Figure 8). The agreement of the points with the line is poorer than in the case of Figure 7. This is due, not to the method, but to the fact that solid solution of tungsten carbide in molybdenum carbide takes place during the heating, and since this action is one of solid diffusion, the results are affected by intimacy of mixture and small variations in the state of division. A confirmation of the excellent average accuracy even in this case is the fact that the point of complete solid solution was determined on a second set of samples and was found to be 68.5% as against the 67.0% obtained from Figure 7.

Similar working curves are shown for heated and unheated mixtures of tungsten carbide and titanium carbide in Figures 9 and 10. The deviation of the points from the lines are about as in the case of the tungsten carbide–molybdenum carbide mixtures. Here a different tungsten carbide reflection—namely, that at 2θ = 31—was used to make the intensities more comparable with those for titanium carbide.

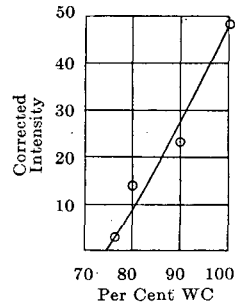

Figure 10. Working Curve for Unheated Mixtures of Tungsten Carbide and Titanium Carbide

The inability to eliminate the effects of orientation may make it impossible in some cases to obtain as good results as in the examples discussed above. However, for many problems, the Norelco spectrometer makes possible x-ray diffraction methods comparable to chemical and spectrographic methods in speed and accuracy.

ACKNOWLEDGMENT

Appreciation is expressed to Leona Gerst and Hertha R. Freche, formerly of this laboratory, and others of the staff for their assistance in this work.

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Pore Size in Protective Films by Electrographic Printing

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A satisfactory technique for the electrographic printing of pores in protective films involves the use of a sandwich consisting of metal pressure platens, a sheet of imbibition paper in contact with the area of coated metal to be studied, and the proper electrolyte. The pressure, voltage, and time, as well as the developing agent necessary, are important for proper printing.

THE method of determining porosity in protective coatings, described in this paper, should provide a simplified instrumental procedure that permits recording of porosity data of quantitative significance.

Many tests of protective coatings depend, for their ultimate results, somewhat on the porosity of the protective film. Measurements of the ohmic resistance of films such as paint coatings may not be comparable if the films under test have wide variance in porosity. Thus, a need for evaluating the porosity of a protective film is highly desirable. In this paper, no attempt has been made to arrive at a system of numerical evaluation of the porosity of tested films.

Glazunov's electrographic method for testing coats of varnish (*1*, *2*, *3*) brought forth a powerful analytical tool for the determination of porosity in coatings. There has been considerable interest in the use of this technique for the porosity evaluation of protective coatings such as those provided by paint films.

Essentially, the method involves anodic solution of the metal underlying the protective film, transmission of the cation through the pores of the film, and retention of the metal ions on a paper in contact with the film and the cathode. Subsequent development of the paper in the proper reagents results in the formation of a colored metal salt, permitting the determination of location and approximate size of the pores and cracks through which the metal ions have passed. For the work reported here, the base metal used was iron, but with proper choice of developer any other structural metal could be used.

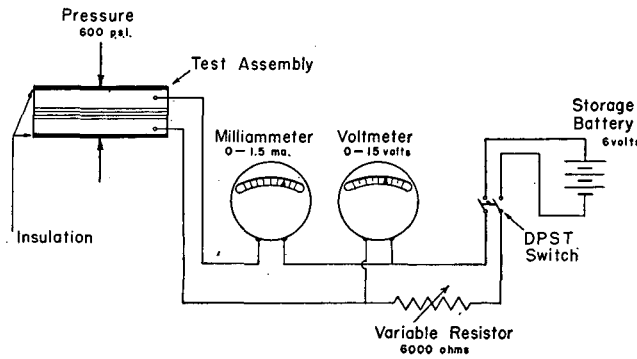

Figure 1. Complete Assembly of Test Equipment

The equipment used in this study consists of a 20-ton Elmes press, a suitable current supply and measuring source, and two sets of pressure platens. Figure 1 shows the electrical setup. Figure 2 is a detailed, sectional view of the platens.

To ascertain the proper conditions for performing the test, the following variables have been considered: (1) pressure, (2) time, (3) voltage, (4) recording paper, (5) electrolyte, (6) developing agent, and (7) interfering ions.

PRESSURE

Sufficient pressure must be obtained for intimate contact; however, too much pressure could destroy the film or possibly seal over

Table I. Tests on Recording Paper

Paper	Results
Whatman's filter No. 5 Whatman's filter No. 42 Mounting paper	Wet strength of paper is low. Falls apart on handling in solutions. Severe bleeding occurs
Drawing paper High-grade index Bristol	Do not separate from blotting paper after excess electrolyte is removed by squeezing
91 index Bristol	Useful for rough work. Gives a fairly clear print
Kodak imbibition paper	Best and most satisfactory results obtained

small cracks and pores. It is considered important, therefore, to use the minimum pressure conducive to obtaining a satisfactory print.

An investigation of the effect of pressure upon the suitability of the print showed that in a range of 120 to 2400 pounds per square inch prints made at values less than 600 pounds per square inch lacked the sharpness of those made at 600 pounds per square inch or better. Investigations as to time under pressure and voltage showed this value to be satisfactory. No injury to film, as regards slippage, thickness, or breakage, could be observed. Many prints could be made from a single test panel and still show the same pattern, provided the pores were cleaned cathodically in a 10% ammonium citrate solution before each printing. It was decided, therefore, that the working pressure should be maintained at 600 pounds per square inch.

Very thick coatings, such as those produced with paints of the linseed oil or bituminous type, which are inherently soft, may be badly distorted. Any coating suspected of being in this category should be given a preliminary test on a separate specimen.

TIME

The length of time for which the film and paper must be maintained under pressure and with an applied potential, to give good prints, was next investigated. If too much time is allowed for the migration of the iron ions into the imbibition paper under a definite voltage gradient, these ions may migrate laterally on the test sheet and exaggerate the indicated size of the pore. Further, sharpness as related to the true pore size can suffer because of this migration.

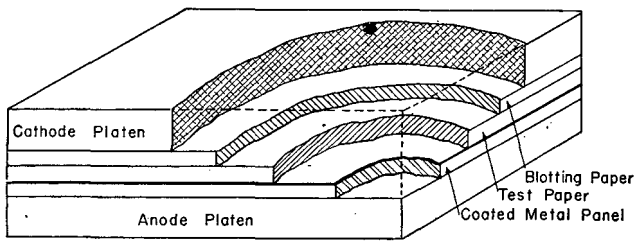

Figure 2. Test Assembly

It was found, upon varying the time of pressure and voltage application over a range of 5 to 60 seconds, that the most satisfactory time of contact was 15 to 20 seconds. Prints made at less than 15 seconds were light and of poor detail; prints made at contact times greater than 20 seconds showed exaggerated pore size. The period of pressure and voltage application was standardized at 15 to 20 seconds.

VOLTAGE

The voltage gradient was next investigated. It was felt that the higher voltage might be of advantage in getting a sharper pore or line reproduction. The investigation, however, showed that diffusion became more pronounced at high voltage. Over an investigated range of 1.5 to 15 volts, the most satisfactory prints, within the agreed time limit, were obtained at 6 volts. The extremely high electrical resistance of pore-free paint films indicated that some picture of the porosity of the film would be given by current density measurements. However, no appreciable variation could be measured. The size of the panel tested, more than the porosity, seemed to govern the current flow.

RECORDING PAPER

The kind of paper used for the printing is important. Coarse or rough-grained paper does not give suitable clarity. Papers containing large quantities of sizing or coloring agents can cause unevenness in printing. Table I shows the results of tests made with six different papers which were thought to be usable.

As these tests showed, Kodak's imbibition paper, double weight, F, to be the most satisfactory, it was therefore used for the tests.

Table II. Developers

Solution	Results
Cupferron	Light in color, unsatisfactory
α-Nitroso-β-naphthol	Not sensitive enough, unsatisfactory
α-Dipyridyl	Too light in color, unsatisfactory
Potassium ferrocyanide	Satisfactory prints
50% potassium ferrocyanide and 50% potassium ferricyanide mixture (5% solution)	Clear and satisfactory prints. Best results obtained

ELECTROLYTES

Possible salts for the electrolyte were considered on the basis of reported ionic conductances (7). The cations considered were ammonium, potassium, and sodium; the anions were bromides, chlorides, iodides, nitrates, and sulfates. Tests were performed using various combinations of these ions at different concentrations and a 5% solution of potassium nitrate was found to be most satisfactory. The effect was judged by the clarity and depth of color obtained under standardized conditions.

DEVELOPER

The requirements for a "developing agent" for the ferrous and ferric ions that are retained on the paper are simple. The agent must produce a visually observable insoluble compound with these ions. Subsequent development—that is, development of the precipitate after the paper is removed from the assembly—is preferred. It was found in preliminary work that if the developer was imbibed into the paper before the current was passed through the paper, the resultant "spot" was not so clearly defined as when the subsequent development procedure was followed. Table II lists compounds that were used as developers and results that were obtained under fixed conditions.

The mixed solution of potassium ferro- and ferricyanide undoubtedly gave the best results. This indicated that the ions in the paper were a mixture of ferrous and ferric. The intensity of color developed was definitely greater with the mixed salt than with the potassium ferrocyanide itself.

Some difficulty in washing was occasioned by the use of the mixture. Its removal from the paper by washing was slow. As this factor does not cause much trouble, the mixture of the two salts is proposed as the standard developer.

INTERFERING IONS

The effect of other ions, commonly found in paint or paint films, on this printing technique was next studied. Many paint films, pigmented with different common pigments, were examined by this proposed procedure and no difficulty has been encountered in obtaining good prints.

PROCEDURE

Blotting paper and imbibition paper are cut to size desired for final print; these pieces must be of exactly the same size. The papers are soaked in 5% solution of potassium nitrate for 0.5 hr.

Both blotting and print papers are removed from the soaking bath and, together, squeezed between two dry pieces of blotting paper which must overlap the soaked papers by 0.75 inch on all sides. The pressure used should be approximately 550 pounds per square inch. The wider border of the dry papers will take up the excess solution squeezed out of the soaked papers.

The coated metal panel is then laid on the anode platen with the metal of the panel in contact with the metal of the anode and the imbibition papers placed emulsion side in contact with the [illegible] of which the desired porosity study is to be made. The [illegible]ed and squeezed blotting paper is laid congruently on the imbibition paper. The cathode platen is then placed over the blotting paper. This entire "sandwich" is centered in the press and necessary pressure applied. The current is switched on as soon as the pressure required is obtained. After 20 seconds current is switched off and pressure immediately released.

The imbibition paper is placed in a developing bath of 2.5 grams of potassium ferrocyanide and 2.5 grams of potassium ferricyanide per 100 ml. of distilled water. The prints are left in this bath for 0.5 hour, washed in warm water until the yellow color of the ferricyanide is removed, and then dried between blotting papers or on ferrotype tins.

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Infrared Spectroscopic Analysis of Five Isomers of 1,2,3,4,5,6-Hexachlorocyclohexane

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The methods of infrared spectroscopy have been applied to the analysis of the insecticide hexachlorocyclohexane. The spectra of five pure isomers of 1,2,3,4,5,6-hexachlorocyclohexane and of a mixture of heptachlorocyclohexane impurities have been determined in the 2- to 25-micron range. A relatively simple infrared method for the quantitative determination of each of the five isomers has been developed, which is satisfactory for the analysis of nearly pure samples and relatively free of interference from the usual type of impurities. The possible structures of the isomers are discussed.

RECENT advances in the use of the insecticide hexachlorocyclohexane and the inauguration of its commercial production forecast the widespread use of this material. It is, of course, important that both the insecticidal and the toxicological properties be thoroughly investigated and this has been hampered by the fact that the commercial insecticide, frequently designated as HCH (hexachlorocyclohexane) or BHC (benzene hexachloride), is not a pure compound but consists of a mixture of compounds, the concentration and identity of which are not easily determined. Thus, it is important that a method of assay be developed for use both in the evaluation of the insecticide and in the formulation of specifications for its purchase and application.

The industrial preparation of this compound by the chlorination of benzene to form 1,2,3,4,5,6-hexachlorocyclohexane results in a mixture of stereoisomers (alpha, beta, gamma, delta, and epsilon) as well as small quantities of hepta- and octachlorocyclohexane. These isomers differ only in the orientation of the chlorine atoms about the cyclohexane ring. This stereoisomerism induces a difference in insecticidal effectiveness, the gamma isomer, whatever its form, being the one especially endowed with insecticidal value. The toxicity of the isomers toward warm-blooded animals also varies, the gamma isomer being reported more toxic than DDT (*8*). In many cases—for example, where only the insecticidal effectiveness is concerned—it may be sufficient to know only the gamma isomer content of the product but in other cases, especially in the complete evaluation of the toxicological properties, it is important to know the complete composition.

It was the purpose of the present investigation to apply the methods of infrared spectroscopy to the analysis of the insecticide hexachlorocyclohexane. Since impurities such as hepta- and octachlorocyclohexanes exist in only very small quantities in the commercial insecticide, and the manufacturers believe that these impurities can be reduced to a negligible quantity (*7*), only the five stereoisomers are considered in the analysis. In addition to the development and evaluation of an analytical method it was desired to obtain any information relative to the structure of the isomers and its effect upon insecticidal or toxicological properties.

PREVIOUS WORK

Slade (*16*) and Jenkins (*8*) have prepared comprehensive reviews of the literature on hexachlorocyclohexane, and for the biological and toxicological aspects of this compound one is referred to these reviews. Although the compound was first prepared by Michael Faraday in 1825, it was not until 1912 that Van der Linden established the fact that the product was a mixture of at least four isomers (*16*). In 1943 the insecticidal value of one of these, the gamma isomer, was discovered by F. J. D. Thomas (*16*). For this reason concentrated efforts to investigate this compound have been recent and the results are probably unpublished. A new isomer has been reported by Kauer, DuVall, and Alquist (*9*), bringing the number of known isomers to five.

From Slade's article it appears that up to 1945 the methods of determining the composition of a crude preparation consisted of fractional solution and recrystallization of the crude with appropriate solvents. A more recent article by Ramsey and Patterson (*13*) on partition chromatography offers an alternate means of analysis. Kauer *et al.* mention that infrared spectroscopic techniques were used to determine the five isomers in hexachlorocyclohexane crudes. The spectra of Kauer *et al.*, which extend from 2 to 15 mu, are in substantial agreement with the present work.

SPECTROSCOPIC EQUIPMENT

All spectral measurements were made with a research-type prism spectrometer of high resolving power (*10*). Experimental records were made by recording, as a function of wave length, the energy transmitted by a blank and that transmitted by the sample as corresponding ink traces on the recorder chart. Slit widths were changed periodically by manual control.

The wave-length measurements of the transmission curves are accurate to ±0.01 micron or better and the per cent transmittance

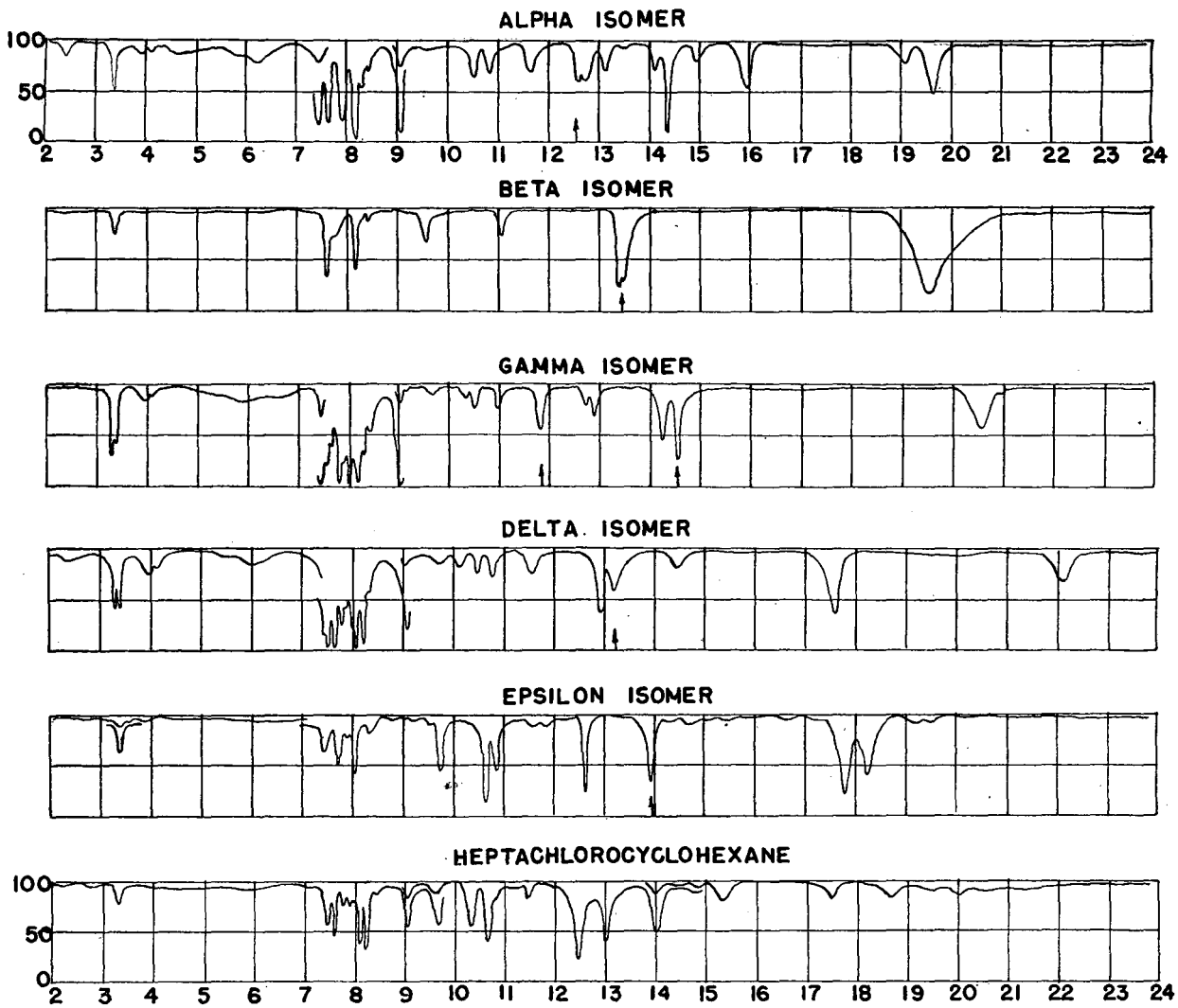

Figure 1. Spectra of Hexachlorocyclohexane Isomers and Heptachlorocyclohexane

measurements are accurate to about ±1 to 2% over the range 20 to 80% transmittance. Quantitative spot measurements were made by setting on a particular wave length instead of by scanning through a band. By taking the average of several deflections the spot measurements can be made accurate to ±0.5% transmittance.

Samples studied in solution were placed in amalgam-sealed absorption cells constructed and calibrated by the method of Smith and Miller (*17*). Samples studied in the solid state were prepared by grinding with mortar and pestle and mixing with petrolatum to form a paste which was placed between potassium bromide plates with an appropriate spacer. The blank for the solid samples was made in a similar manner using a potassium bromide and petrolatum paste.

BASIS OF ANALYTICAL METHOD

Infrared spectroscopy can be used both for analytical purposes and for investigation of molecular structure. The bands in the infrared spectrum are produced by preferential absorption of various wave lengths of infrared energy, the energies absorbed corresponding to the energies of certain molecular vibrations. Thus, each compound possesses a unique spectrum characterized by its atomic composition and arrangement. The spectra of geometrical isomers, although they may have several bands which coincide, will, in general, be sufficiently different at other wave lengths to be distinguishable.

The spectra of the five known isomers of hexachlorocyclohexane are shown in Figure 1. Discontinuities are due to different concentrations. Each isomer has at least one absorption band in a spectral region where the others are relatively transparent. These differences in spectral absorption constitute a basis for spectroscopic identification of an isomer, either alone or in a mixture with other isomers. The presence of the various isomers in a mixture can be recognized by absorption maxima at the following wave lengths:

Isomer	Wave Length, mu
Alpha	12.58
Beta	13.46
Delta	13.22
Gamma	11.81 and 14.53
Epsilon	13.96

If the region beyond 15 mu is overlooked, for reasons discussed later, a consideration of the intensities of the absorptions shows that the magnitudes of the spectral differences at these wave lengths are greater than at any other set of wave lengths which might be chosen.

This basis for qualitative analysis of a mixture is sufficient for quantitative analysis if the intensity of absorption at each wave length is measured under controlled conditions.

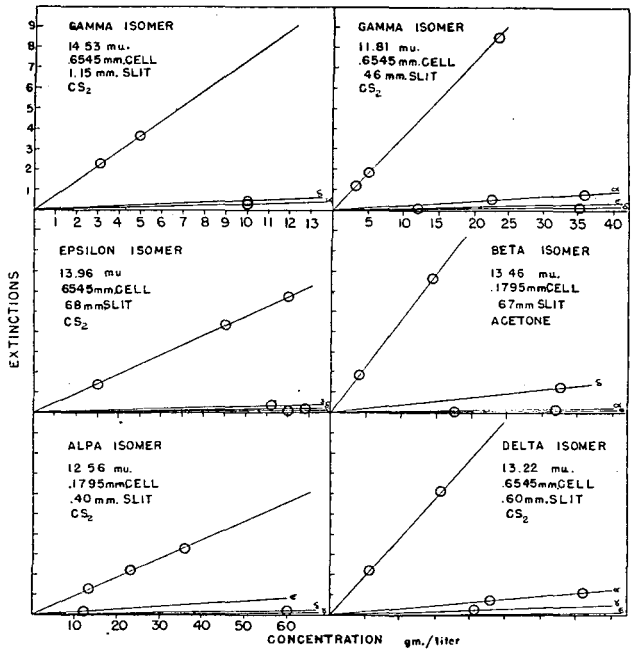

Figure 2. Working Curves

In the absence of molecular interaction, the law of Beer and Lambert states that for a solution of an absorbing material in a transparent solvent $E = \log I_0/I = Kcl$, where E = extinction, I_0 = light transmitted by a blank (pure solvent), I = light transmitted by the solution, K = extinction coefficient of absorbing material, c = concentration in grams per liter, and l = length of solution path in centimeters. If the absorbing material is a pure compound its extinction coefficient, K, for a given wave length can be determined by measuring the extinction for a solution of concentration c in a cell of length l. For a material containing several components, this equation may be written:

$$E = K_1c_1l + K_2C_2l + K_3c_3l + \ldots\ldots\ldots \quad (1)$$

$$K_1c_1l = E - K_2c_2l - K_3c_3l - \ldots\ldots\ldots \quad (2)$$

where the subscripts refer to components 1, 2, 3, etc. The K's can be determined from measurements on the pure components and if the above equation for a mixture of n components is applied to a sample at n wave lengths the n simultaneous equations obtained determine the concentrations of the n components in the mixture. These equations can be solved exactly by any of several methods—for example, by the use of special computing machines, or by a graphical method of successive approximations described below.

In the application of this method to mixtures of the five isomers of hexachlorocyclohexane Equation 1 is applied at each of the selected analytical wave lengths. At each wave length only one component absorbs strongly and therefore all but one of the right-hand terms of equations will be small. By neglecting these small correction terms it is possible to obtain an approximate value of the concentration of the main absorbing components from the extinctions of the sample measured at the various wave lengths. These approximate concentrations can then be used to calculate the magnitude of the correction terms and thus to determine more accurate values of the concentrations.

To obtain the experimental measurements required in the application of the method to hexachlorocyclohexane a solvent which is transparent at each of the analytical wave lengths is required. Carbon disulfide appeared to be the only sufficiently transparent solvent and an investigation of solubilities has shown that satisfactory concentrations of all the isomers except beta can be obtained in this solvent (Table I).

Since the beta isomer is nearly insoluble, the use of carbon disulfide effects a simplification in the analysis by limiting the number of variable components to four. The beta isomer, then, may be determined by total insolubles (assuming no foreign matter in the sample) or by difference, using the measured values of the other four isomers. A superior approach, however, is to determine the beta isomer directly by a separate spectroscopic analysis, using an acetone solution for measurement of the extinction at the beta wave length.

ANALYTICAL PROCEDURE

Calibration of the method is based upon absorption measurements on solutions of the pure isomers at the various analytical wave lengths. The absorption measurements (calculated as per cent transmittance) are converted to extinctions by Beer's law and plotted against concentration to give the working curves of Figure 2. The curves appear to be linear and straight lines have been drawn. The exact analytical wave-length setting of the spectrograph is best determined by slowly scanning the band and plotting the record obtained. This is an especially necessary procedure at the 11.81 mu gamma band which is on the side of a carbon disulfide (solvent) band. Since it can be shown that the optimum accuracy for a measurement is obtained for a sample that transmits 37.5% of the light, a procedure of analysis specifying certain cell thicknesses and sample concentrations will yield most accurate results for only a certain small range of sample composition. The procedure presented here is devised for samples containing approximately 70% alpha, 5% beta, 15% gamma, 10% delta, and less than 5% epsilon. This corresponds closely with the composition of the commercial products at the present time; for samples having appreciably different composition the results will be somewhat less accurate unless cell thicknesses and sample concentrations are properly adjusted. However, reasonable accuracy is obtained for transmittance measurements between 20 and 80%, so that even high gamma preparations such as that reported by Gunther (*3*) could be analyzed with only small changes of the analytical procedures.

Table I. Solubility of Hexachlorocyclohexane in Carbon Disulfide[a]

	G./cc.
Gamma	0.1995
Alpha	0.0590
Delta	0.0950
Beta	0.0007
Epsilon	0.0125

[a] Solubilities determined by weighing residue upon evaporation of solvent from 1 cc. of saturated solution at room temperature (approximately 25° C.).

There are several additional considerations in the choice of cell thickness, concentrations, and slit widths. If the solvent absorption is high, as at 11.81 mu, a larger slit and/or a thinner cell is necessary to obtain full-scale deflections, and if the absorption band is very strong, as in the 13.46 mu beta band, the thinner cell enables an appreciable concentration range to be covered.

An unknown mixture should be sampled by some adequate procedure and about 0.3 gram weighed into each of two 10-ml. volumetric flasks and made up to volume with carbon disulfide and acetone, respectively. The appropriate solution is used at the various analytical wave lengths under the same conditions used to determine the working curves. The transmittance measurements are converted to extinctions and the approximate concentrations are then determined by the working curves. The approximate concentrations for alpha, delta, gamma, and epsilon (all too high) now enable the extinctions at each wave length to be corrected for the absorption of the interfering components at that wave length. These corrections are also determined graphically from the correction curves and are evaluations of the small negative terms of Equation 2. The new values are overcorrected, but a second evaluation using the new values will usually give results that are within the experimental error. The

beta isomer is then determined in the acetone solution and corrections are applied using the now known percentages of alpha, gamma, delta, and epsilon.

EXPERIMENTAL RESULTS

The necessary calibration curves, shown in Figure 2, were constructed from measurements on samples of the pure isomers. Absence of impurity absorption in the spectra (Figure 1) and narrow melting point ranges, as determined by the usual capillary method, indicated that the samples were of suitable purity for this work:

Isomer	Melting Point, ° C.
Gamma	111.8–112.2
Delta	136.0–136.2
Alpha	155.3–155.8
Epsilon	202–227 (sublimed
Beta	196–210 (sublimed)

The calibration curves were then used in the analysis of several synthetic solutions of pure isomers (Table II). For one solution detailed results which indicate the method of successive approximations are presented. Separate solutions were used for the beta isomer determinations, since this required a different solvent. Most of the data in Table II were obtained before the new epsilon isomer was reported, but a quantity of this isomer sufficient for making one five-component mixture was later obtained and the results are included as the last analysis.

Table III contains the results of several analyses of two crude samples from the commercial production of the insecticide. The presence of epsilon isomer was neglected in these analyses, and consequently the results for all other isomers are uncorrected for the epsilon isomer content. This does not affect the usefulness of the data, since the corrections introduced by the small amount of epsilon in these crude samples are of negligible size in all but the most accurate analytical attempts. At a later date the epsilon content of these samples was determined by a separate analysis and found to be 2 and 1% for products 1 and 2, respectively. It has been determined that the presence of 2% of epsilon found for product 1 would cause errors of only 0.30, 0.02, and 0.06%, respectively, in the original experimentally determined concentrations of alpha, beta, delta, and gamma. These combined errors are well within the experimental error of the analysis.

The totaled percentages, including epsilon, are 104.2 and 101.2% for products 1 and 2, respectively. The high values obtained for the total concentrations in these analyses are discussed below after the inherent accuracy of the method itself has been considered. The spectra of products 1 and 2, as well as a third product, No. 3, are presented in Figure 3. Although the complete analysis for the latter product is not included, it was found to have substantially more epsilon isomer (4%) than the other products.

DISCUSSION

Since this method, like any method employing working curves, is empirical, its inherent errors are negligible, the ultimate accuracy being limited chiefly by the accuracy of the calibration data (working curves). If the analyses are performed under the same conditions used for the calibration, the latter need not be absolute but only experimentally reproducible. Thus, the accuracy of the method is determined almost entirely by the experimental reproducibility realized in the laboratory.

If care is used in sampling, making standard solutions, handling sample, etc., the most important errors affecting reproducibility are probably those in the percentage transmittance measurements. However, for any given reproducibility a high degree of accuracy may be obtained by averaging a sufficiently large number of measurements. Hence it may be assumed that the calibration data (working curves) can be determined as accurately as desired.

Table II. Analysis of Known Solutions

(Alpha, gamma, delta determinations. Known concentrations: gamma = 7.18 grams per liter, delta = 8.11 grams per liter, alpha = 5.99 grams per liter. Total sample = 21.28 grams per liter)

Wave Length	Substance	% Transmittance	Extinction Total	Extinction Sample	Experimental Concentration, G./Liter
14.53	Gamma	21.80	0.6611	0.5621	7.63
	CS_2	79.50	0.0990		
13.22	Delta	38.82	0.4109	0.3650	9.10
	CS_2	89.90	0.0459		
12.58	Alpha	81.50	0.0882	0.0641	7.00
	CS_2	94.55	0.0241		
11.81	Gamma	51.25	....	0.2900	7.90
	CS_2	...	....		

Corrections (First Approximation)

Wave Length	Substance	Extinction	Corrections Alpha	Gamma	Delta	Total	Corrected Extinction	Corrected Concentrated
14.53	Gamma	0.5621	0.023	....	0.038	0.061	0.5011	6.80
13.22	Delta	0.3650	0.023	0.0075	....	0.0395	0.3345	8.30
12.58	Alpha	0.0641	...	0.0025	0.0040	0.0065	0.0575	6.00
11.81	Gamma	0.2900	0.014	....	0.004	0.018	0.2720	7.40

Second Approximation

14.53	Gamma	0.5621	0.020	....	0.027	0.047	0.5151	6.95
13.22	Delta	0.3650	0.020	0.0075	....	0.0275	0.3375	8.40
12.58	Alpha	0.0641	...	0.0025	0.004	0.0065	0.0576	6.00
11.81	Gamma	0.2900	0.013	....	0.004	0.017	0.2730	(7.50)
								21.35

Other Solutions

Wave Length	Isomer	Known Concentration	Experimental Concentration
14.53	Gamma	6.07	5.60
13.22	Delta	3.87	3.94
12.58	Alpha	32.41	32.40
(11.81)	(Gamma)	(6.07)	(6.10)
		42.35	42.14
14.53	Gamma	6.48	6.11
13.22	Delta	4.54	4.70
12.58	Alpha	35.59	35.81
(11.81)	(Gamma)	(6.48)	(6.90)
		45.61	46.62
	Beta Isomer Determinations		
13.46	Beta	4.41	4.40
13.46	Beta	6.21	6.20
13.46	Beta	5.71	5.50
13.46	Beta	7.89	7.85
	Five-Component Determination		
14.53	Gamma	4.37	4.20
13.96	Epsilon	2.05	1.95
13.22	Delta	7.77	7.55
12.58	Alpha	10.98	11.50
	(Beta)	(2.51)	....
(11.81)	(Gamma)	(4.37)	(4.35)
		25.17	25.20

Table III. Analysis of Crude Hexachlorocyclohexane Industrial Products

	Gamma, 14.53 mu	Gamma, 11.81 mu	Alpha, 12.53 mu	Delta, 13.22 mu	Beta, 13.46 mu
Product 1[a]	14.29 ± 0.83	15.15 ± 0.70	70.29 ± 2.5	8.83 ± 0.39	10.85 ± 0.36
Product 2	12.14	13.08	75.55	6.70	6.77

[a] Average of 10 determinations.

The accuracy of an analysis, then, will be limited chiefly by the reproducibility of the transmittance measurements on the unknown sample and can be calculated for any given reproducibility of transmittance measurement.

Assuming, for example, that the measurements are made at the optimum value of 37.5% transmission, an experimental uncertainty of 0.5% transmittance corresponds to ±0.0055 in optical density or to ±1.34% in the extinction determination. Neglecting, for the moment, the absorption of interfering components, this uncertainty in the optical density determination at each analytical wave length leads to the following uncertainties in the concentrations of the various isomers:

Wave Length	Isomer	Uncertainty[a] Concentration, Grams/Liter	Uncertainty[a] Percentage (on Total Sample)[b]
14.53	Gamma	±0.074	±0.25
11.91	Gamma	±0.151	±0.50
12.58	Alpha	±0.583	±1.95
13.22	Delta	±1.35	±0.45
13.96	Epsilon	±0.114	±0.38
13.46	Beta	±0.120	±0.40

[a] Analytical uncertainty resulting from an experimental uncertainty of 0.5% in transmittance measurement.
[b] Total sample concentration = 30 grams per liter.

The figures in the right-hand column represent the analytical precision which can be obtained under the conditions given. Greater precision in transmittance measurement and the use of average values would lead to correspondingly less uncertainty in the analytical results.

It was assumed in the previous paragraph that the correction for the absorption of interfering isomers at each analytical wave length could be determined precisely and that introduction of this correction, therefore, would not contribute to the uncertainty of the analytical results. The validity of this assumption may be shown in the following manner. By computing (from Figure 2) the quantities of the various isomers which have equal absorption at each of the analytical wave lengths as given in Table IV, it is seen that the absorption at each analytical wave length is relatively insensitive to the presence of other components, and therefore errors resulting from inaccuracies in the corrections for interfering absorptions are negligible.

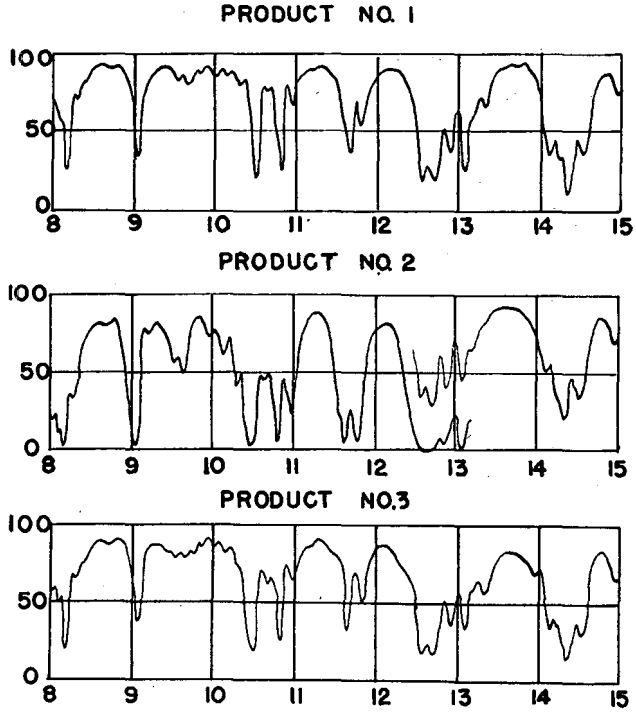

Figure 3. Spectra of Hexachlorocyclohexane (Commercial Crudes)

It is concluded, therefore, that if the per cent transmittance is measured to within ±0.5, it is possible by a careful application of the method to obtain analytical results which are correct to within ±0.5% for the beta, gamma, delta, and epsilon isomers and to within ±2% for the alpha isomer, the values based on total sample. This theoretical accuracy (or reproducibility) agrees well with the experimental reproducibility obtained in Table III.

Table IV. Parts of Interfering Isomer Equivalent to One Part of Absorbing Isomer

Microns	Gamma	Alpha	Delta	Epsilon	Beta
11.81	1	17	578	35	.
14.53	1	23	18	400	.
12.58	42	1	28	6.7	.
13.22	35	12.4	1	125	.
13.96	23	73	443	1	.
13.46	..	91	11	135	1

In addition to these factors the over-all accuracy (as distinguished from precision or reproducibility) of the analyses for the crude samples in Table III will also be determined by the accuracy of the working curves and by the possible presence of interfering impurities, such as hepta- and octachlorocyclohexanes. The high values of total concentration are very probably due to errors in the working curves, since it has been observed that in general all analyses made in this investigation are consistently high, and in the particular case of the gamma determination the values obtained in the "check" determination at 11.81 mu are consistently higher than those determined at 14.53 mu. It is clear that these small calibration errors could be eliminated in routine work and should not be considered in evaluating the method. The presence of isomeric hepta- and octachlorocyclohexane impurities may cause errors in the results. However, comparison of the spectra of the crudes (Figure 3) with the spectra shown in Figure 1 substantiates the manufacturer's claim that very little impurity is present. Hence, it is believed that the results have been unimpaired and that future products will likewise have negligible corrections from such sources of error. In addition, the error caused by loss of solvent in filling the absorption cells would tend to give high results. This error could be avoided by using special absorption cell and procedures, the devising of which would be feasible in routine applications.

It has been indicated that both 14.53 and 11.81 mu seem to be suitable for gamma isomer analysis and since a two-band check for the active component would be appropriate, analyses at both bands have been included in the present scheme. Nevertheless, the recommendation of the longer wave length must be stressed. The set of working curves at 14.53 mu is more sensitive to the presence of gamma isomer and provides a more accurate determination. In addition, the 11.81 mu band has the disadvantage of being on the side of a strong carbon disulfide absorption band, making it difficult to locate or check the position of the center of this band. Greater accuracy in the epsilon determination may be had by using an absorption cell of greater thickness than was used in this investigation.

In the analytical work described here no correction was made for the small amount of beta isomer which will dissolve in the carbon disulfide solutions. Some finite interference in the analysis for the other isomers will exist, although under the conditions of the analysis this interference was too small to be measured. However, if the method is to be applied to sample solutions containing at least 2% of beta (the quantity required to saturate the sample solution), then any interference, however small, arising from the presence of beta in the sample may be completely eliminated by using in place of the "solvent" blank one which is saturated with pure beta isomer.

In the application of the method to routine analysis it might be desirable to measure directly the transmittance of the sample-

filled cell relative to the solvent-filled cell instead of measuring separately the transmittance of each cell relative to a blank rock-salt or potassium bromide plate. This can be done by employing cells of known and approximately equal thicknesses, one filled with solvent (or beta-saturated solvent) and the other with sample solution.

There are other combinations of bands that could be used in this analysis but those chosen appear to be the best available from 2 to 15 mu. Beyond 15 mu where the vibrations become more characteristic of the molecule as a whole one would expect the bands for different isomers to be more isolated. Such was found to be the case. They are strong and there is no interference between isomers if beta is first eliminated by using carbon disulfide solutions. This is necessary because beta has one band at 19.55 mu which overlaps the alpha band at 19.64 mu (see Figure 1). The equations then would be simplified to one term and any isomer could be determined without knowing the concentration of the other isomers, experimentally or otherwise. However, since many laboratories are not equipped to investigate the region beyond 15 mu, advantage has not been taken of these great spectral differences. Instead, analysis has been confined to the region below 15 mu in order that the analytical method might be used in any infrared laboratory.

It appears possible with the set of chosen wave lengths to use only one solution in acetone to determine all five isomers. One would then have to obtain correction curves for all isomers (including beta), for they are all soluble in acetone. This solvent has strong absorption at about 14.35 and 12.75 mu but is relatively transparent at all the analytical wave lengths. Since it is a polar solvent there might be some nonlinearity in working curves caused by molecular interaction. However, in using this solvent for beta determination no such interaction was noticed.

Finally, since the analytical bands are relatively broad, the quality of the spectrographic equipment used for this analysis is well above the minimum requirement. This instrument has a resoltuion of approximately 0.7 cm.$^{-1}$ at 10 mu when an estimated 3 or 4 cm.$^{-1}$ would be satisfactory. The resolutions claimed for most commercial instruments by their manufacturers are usually within this range.

STRUCTURE OF THE ISOMERS

The alicyclic compounds have not been too thoroughly investigated and their stereochemistry is not well understood. Sachse (*15*) in his theory of strainless rings postulated that a ring such as cyclohexane would be able to take two configurations now commonly designated the C or "boat" form and the Z or "chair" form. Such an idea (for cyclohexane) is supported by the work of Hassel (*4*) who investigated monochlorinated cyclohexane and came to the conclusion that within one of these forms (the Z form) the chlorine in a monochloro derivative was able to assume two positions in the molecule, making two forms that were interconvertible. The two positions of the chlorine are on valence bonds parallel and perpendicular to the axis of the molecule, there being six equivalent bonds of each type in the Z form of cyclohexane. In an earlier article by Hassel and Ottar (*5*) it is stated that the possibility of other less symmetrical forms is not excluded. These other less symmetrical forms would be the C form and the planar form. The word "planar" is used here in its strictest sense—that is, all the carbon atoms are contained in one plane, the plane of the ring. It is apparent from the literature that this term has been loosely used. For example, Parodi (*11*) states that cyclohexane is a planar molecule. Likewise, the hexahydroxy derivative, inosital, is discussed by R. L. Shriner and R. Adams (*2*) as a planar ring. The connotation of "planar" meaning a molecule whose atoms determine several planes which are parallel to one plane simplifies the discussion, but oversimplifies when one is discussing the number of likely isomers in a derivative. Thus, inositol is stated to have eight possible isomers and one would assume that 1,2,3,4,5,6-hexachlorocyclohexane would have the same number. However, if one builds Fischer models of 1,2,3,4,5,6-hexachlorocyclohexane *in the Z and C forms* the following facts become apparent.

For the Z or Chair Form. 1. There are sixteen possible configurations if one assumes only one chair form is possible.
2. Of these sixteen, five are relatively strainless and one of the five is the mirror image of another.
3. There are eight different possible configurations assuming all chairs are interconvertible and strained bonds such as in the eleven strained configurations of statement 2 are stable.

For the C or Boat Form. 1. There are eight possible isomers if the two chlorines on the bow and stern of the boat are directed to the outside of the boat (it is too strained in the other position).
2. Of these eight only two are relatively strainless and they are mirror images.

Patterson and White (*12*) discuss the Z form in much the same manner. If the logical assumption is made that those forms which are strainless are the ones which will probably form in the preparation of an isomeric mixture, it is evident that there should be seven isomers of 1,2,3,4,5,6-hexachlorocyclohexane, of which two pairs are mirror images (see Figure 4). This leaves five isomers whose infrared spectra would be unique (the mirror images being spectroscopically identical).

It should be relatively easy to identify the optically active pairs by their activity but none of the pure isomers investigated appeared to be optically active. A saturated solution of the crude insecticide in a 20-cm. cell showed no activity, which would seem to substantiate the fact that the optically active isomers, if present, are racemates.

Actual structural determinations have been confined to the beta isomer (*1, 6*). X-ray analysis easily characterizes it to be in the cubic system. It therefore has a centrosymmetric structure and has been assigned the 1,3,5, configuration in the chair form. The other structures must await further investigation of their x-ray diagrams which is being attempted at the present time. X-ray data for the new epsilon isomer are said to be included in the report of its separation (*9*).

The external crystal structure of these isomers may be informative on their internal molecular arrangement and may be helpful in distinguishing between isomeric crystals (Table V).

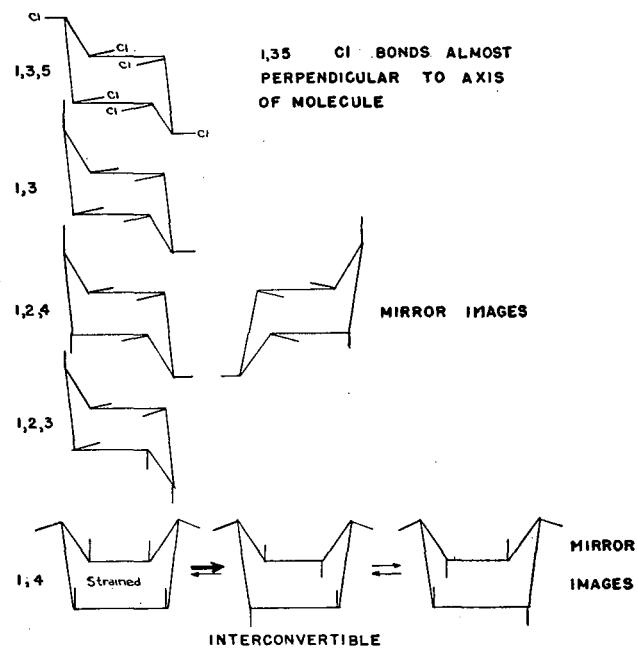

Figure 4. Sketches of Seven Strainless Configurations of 1,2,3,4,5,6-Hexachlorocyclohexane

Table V. Crystallographic Data

Isomer	Type	Sign	Approximate 2V	Birefringence	Range of Indices
Beta				None	1.630
Alpha	Biaxial	+	30°	Medium	1.60–1.626
Gamma	Biaxial	+	65°	Medium	1.60–1.635
Delta	Biaxial	+	...	Very high	1.576–1.674
Epsilon	Biaxial	+	75°	Medium	1.60–1.635

The beta isomer was found to be isometric, which checks the cubic classification by x-ray analysis. Its index of refraction, by the immersion method and Becke line, was determined to be 1.630. The solubility of the compounds in the usual organic immersion oils necessitated the use of potassium mercuric iodide–water solutions which were found to change index rapidly. As a universal stage was not used, the orientation of the small crystals was unknown. The data are therefore offered as a preliminary set of measurements. However, the other four isomers are known to belong to the orthorhombic or monoclinic crystal classes. The very high birefringence of the delta isomer and the low 2V angle for alpha distinguish these crystals from the rest. To distinguish gamma from epsilon would require more exact information on their three refractive indices, alpha, beta, and gamma. These data were obtained in conjunction with O. S. Tuttle of the Crystal Section at the Naval Research Laboratory, to whom the author is indebted.

The similarity of gamma and delta goes further than crystal structure. Their infrared absorption spectra have some peculiar correspondences. The doublet structure of these two isomers at the C—H vibration frequencies of 3.34 and 3.39 mu is contrasted with the singlet structure of the other three isomers. In the region from 7.5 to 8.5 mu there is a definite similarity of shape and intensity between bands for gamma and delta, as well as alpha. At larger wave lengths where the total molecular configuration is more important, the similarity disappears.

Beta and epsilon isomers are also spectrally similar in the shorter wave-length regions (2 to 10 mu). The most striking feature of these two spectra is their simplicity when compared with those of the other isomers. Simplicity or symmetry of structure is the usual cause for simplified absorption spectra and therefore one might look for a more or less symmetrical molecule for the epsilon isomer. Of the remaining four configurations (1,3,5 = beta) the 1,2,3, chair form and the 1,4 boat form are the most symmetrical (see Figure 4). The former has a plane of symmetry and a center of symmetry and the latter has two planes of symmetry. Since the epsilon concentration is the lowest in the preparation of the insecticide, the structure of higher energy content would probably be epsilon. This corresponds to the 1,4 boat form (*4*). Validity of this designation rests on rather slender evidence and it is offered as a suggested structure to assume when matching future data with possible structures.

Another spectral peculiarity, which must also be dealt with in general terms at the present time, is the apparent doubling of the beta bands at 7.6 and 8.12 mu in the alpha, delta, and gamma isomers. The single beta band at 7.60 mu splits into two at 7.42 to 7.62 mu for alpha, 7.52 to 7.67 mu for delta, and 7.45 to 7.82 mu for gamma. Similarly, with the beta band at 8.12 mu the two bands for alpha are at 7.92 to 8.18 mu at 8.09 to 8.24 mu for delta, and at 8.05 to 8.21 mu for gamma. According to Rasmussen (*14*), who investigated cyclohexane by infrared methods, the bands in the range 700 to 1350 cm.$^{-1}$ (7.5 to 14 mu) are due to CH_2 rocking and twisting vibrations or C—C stretching vibrations. The apparent splitting of the beta bands could be due to the two kinds of —CHCl— groups, depending upon which bond of each carbon the chlorine had added. The two types of bonds would correspond to those mentioned by Hassel in his monochloro derivatives. The chlorine atoms in the beta structure are attached by only one of the types of bonds (perpendicular to the axis of the molecule). This might explain the doublet C—H vibrations mentioned previously but the singlet C—H vibration for the alpha isomer contradicts the hypothesis. Further work along these lines will be reported at a later date.

SUMMARY AND CONCLUSIONS

The spectra of five pure isomers of the insecticide 1,2,3,4,5,6-hexachlorocyclohexane and of a mixture of heptachlorocyclohexane impurities have been determined in the 2- to 25-micron range. The differences in the spectral absorption of the isomers are sufficiently great to permit the qualitative and quantitative analysis of mixtures by infrared methods.

An infrared method for the quantitative determination of each of the five isomers in the insecticide has been developed and a recommended procedure is described in detail. The method is relatively simple for a five-component analysis and could be applied either to control or to research determinations. It has been successfully applied to the analysis of a few synthetic mixtures of pure isomers and to crude samples from the commercial production of the insecticide. For all but one of the isomers the precision of the method is numerically equal to the precision of the per cent transmittance measurements, and the over-all accuracy of the method is limited only by its precision.

It is concluded that the method is entirely satisfactory for the analysis of nearly pure samples of the insecticide and is relatively free of interference from the usual type of impurities encountered. It is estimated that ±0.5% accuracy in analytical results can readily be obtained in most infrared laboratories by a careful application of the method.

The possible structures of the isomers are discussed; seven are relatively strainless forms and of these two pairs are optical isomers. Preliminary crystallographic data for the five known isomers are given which distinguish all but two by optical properties. The accepted cubic classification for the structure of the beta isomer is checked by x-ray and crystallographic data.

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Color Reactions of Amine Antioxidants

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Several color reactions of the amine antioxidants are useful for the detection and identification of the most important classes of these materials used commercially. The principal tests are based on coupling and oxidation reactions in organic solution in the presence of anhydrous stannic chloride. They may be applied to isolated materials or to solvent extracts of vulcanized rubber samples.

AN ANALYTICAL problem frequently encountered by the rubber chemist is to identify or confirm the presence of the amine antioxidants either in rubber samples or as chemical compounds. The task may be the relatively simple one of establishing whether a rubber batch has been mixed correctly, or it may involve more extensive testing to determine the type of stabilizer used in a vulcanized compound of unknown source. To identify the isolated materials, standard procedures, such as the determination of melting point and ultimate analysis, are frequently used. However, it is helpful to have available methods by which a preliminary idea of the nature of the sample can be obtained.

Endô (*2*) has described tests for the detection of the arylamines by the colors formed on oxidation in the presence of sulfuric acid. In the case of the diarylamines, it is probable that a benzidine rearrangement occurs, followed by a partial oxidation of the intermediate product. The mechanism of this reaction has been investigated in detail by Kehrmann (*4*). While it is useful in some applications, the colors formed are difficult to reproduce, and the test suffers from a technical disadvantage in that it must be carried out in the presence of aqueous sulfuric acid.

This paper describes several new color reactions suitable for the detection of a wide variety of antioxidants, which can be carried out in the organic solvent used to extract the rubber sample. In addition to the obvious advantages inherent in the use of a medium in which the reactants are easily soluble, a much wider variety of reaction conditions can be employed. This allows for a sharper distinction between the various classes of antioxidants.

Several of the tests described are variations of familiar procedures, such as the coupling of diazonium salts with amines and the indamine reaction with *p*-phenylenediamine in the presence of ferric chloride (*10*). However, the reactions of greatest interest are several new coupling and oxidation procedures which are carried out in the presence of anhydrous stannic chloride. This reagent is colorless and soluble in most organic solvents. It can increase its covalence to 6 and thus acts as a powerful electron acceptor, which leads to the ready formation of intermediate complexes that can rearrange or react further to give the desired products. The colors formed are reproducible and relatively stable. In a number of specific cases they have been made the basis for quantitative methods of analysis.

As the composition of many commercial antioxidants is indefinite, they are generally referred to by their trade names. A list of the materials discussed is given in Table I.

Table I. Approximate Compositions of Commercial Antioxidants

AgeRite Resin	Aldol 1-naphthylamine
AgeRite Resin D, AgeRite Syrup	Acetone-aniline condensation products containing 2,2,4-trimethyl-1,2-dihydroquinoline and polymers
AgeRite White	*N,N'*-bis(2-naphthyl)-*p*-phenylenediamine
Aminox	Diphenylamine-acetone condensation product
Aranox	*p*-(*p*-Tolylsulfonylamido)-diphenylamine
Betanox	Phenyl-2-naphthylamine–acetone condensation product
BLE	Diphenylamine-acetone condensation product
Flectol A, Flectol B, Flectol H	Acetone-aniline condensation products
Neozone A	Phenyl-1-naphthylamine
Neozone D, AgeRite Powder	Phenyl-2-naphthylamine
Santoflex B	Acetone-*p*-aminodiphenyl condensation product
Stabilite	*N,N'*-diphenylethylenediamine
Stabilite Alba	*N,N'*-di-*o*-tolylethylenediamine
Stalite	Alkyl-substituted diphenylamines
VGB	Aniline-acetaldehyde condensation product

DESCRIPTION OF METHODS

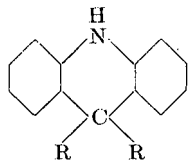
I. Stannic Chloride–Amyl Nitrite Reaction. Diaryl amines and naphthyl aryl amines unsubstituted in at least one of the para positions are readily oxidized to intensely colored products by nitrous acid in the presence of anhydrous stannic chloride. Amyl nitrite is used as the source of acid and benzene as the solvent. The reaction is similar to the condensation and subsequent oxidation of diphenylamine in strong sulfuric acid; however, here the reaction proceeds readily in 0.1 *M* stannic chloride solution. The mechanism is demonstrated by the fact that the product obtained from diphenylamine is optically identical with that obtained by the oxidation of diphenylbenzidine. It is of interest to note that *N*-nitrosodiphenylamine will react in the absence of amyl nitrite.

The complex formed is an intermediate oxidation product, and the color fades on the addition of a large excess of reagent. When the reaction is carried out in glacial acetic acid, in which the intermediate product is more stable, it can be used for the quantitative estimation of diphenylamine and related materials. It is necessary to maintain the amyl nitrite concentration at 0.0005 molar or less to avoid excessive fading. The transmission is measured at 590 mμ at a concentration of 2.5×10^{-5} mole per liter of diphenylamine. The color formation follows the Beer-Lambert law except at concentration ranges below 1.0×10^{-5} mole per liter where fading occurs. As the *N*-acetyl derivatives do not react, it is necessary to avoid long standing or refluxing in acetic acid solution. In making both the qualitative and quantitative tests, the stannic chloride must be added before the amyl nitrite.

In a qualitative test intense colors ranging from blue-violet to blue-green are obtained from the diaryl amines, while the products formed from the naphthyl aryl amines are green. This permits the detection of these materials in many types of rubber compounds. Typical antioxidants which give strong positive tests are phenyl-2-naphthylamine, phenyl-1-naphthylamine, AgeRite Stalite, and *N,N'*-diphenyl-*p*-phenylenediamine. Stabilite and Stabilite Alba form brilliant red precipitates. Thus, the test serves to detect both the diaryl amines and the aryl-substituted ethylenediamines and to distinguish them from one another. Acetone-aniline antioxidants and aldehyde-amine accelerators give yellow to orange colors, which are not sufficiently intense or characteristic to serve as criteria of identity.

II. Stannic Chloride–Benzotrichloride Reaction. A very intense color test semispecific for the diarylamine-ketone conden-

sation products is obtained by reacting the antioxidant with benzotrichloride in the presence of anhydrous stannic chloride. Ethylene dichloride is used as the solvent. The reaction is believed to proceed through the formation of carbonium ions by the interaction of the reagent and the stannic chloride, which results in coupling at the para position of the amine to form highly colored arylmethane chlorostannates. Stannic chloride is particularly efficient in this reaction because of its ability to abstract chlorine from the reagent and product to form the stable $SnCl_6^{--}$ anion (*3*). The reactive constituents in the antioxidants are the alkyl-substituted acridans produced in the condensation reaction:



The selectivity of the reaction is evidently dependent on the basic properties of the amines. Those which can donate the unshared electron pair on the nitrogen to the tin to form stable coordination complexes are deactivated at the ortho and para positions, while those of low basicity such as triphenylamine and 5,5-dimethylacridan react readily. This is to be expected in view of the difference in reactivity between aryl amines and aryl amine hydrochlorides. The use of ethylene dichloride as a solvent partially satisfies the electron-accepting powers of the tin and greatly increases the rate at which the reaction can take place when compared to its speed in benzene. Traces of polar solvents which form stable complexes with stannic chloride completely inhibit the reaction. When carried out under strictly anhydrous conditions the colors are sufficiently stable and reproducible for accurate photometric estimation.

Caution must be used in the choice of the solvent, for some types of commercially available ethylene dichloride contain unsaturated impurities which modify the results of the test. BLE, Aminox, and other diphenylamine-ketone condensation products normally produce violet colorations, while Betanox forms a green, and triphenylamine a red product. Most of the other aryl amines react slowly to form pale yellow to orange colorations which are unimportant analytically. In the presence of the contaminated solvent the reactions of Betanox and triphenylamine are unaltered; however, the products obtained from materials of the BLE type are a deep blue violet, while phenyl-1-naphthylamine which normally does not react at all yields an intense scarlet coloration. This is the most specific reaction described. It can be used for the detection of the diaryl amine–ketone condensation products either alone or in the presence of accelerators and other antioxidants.

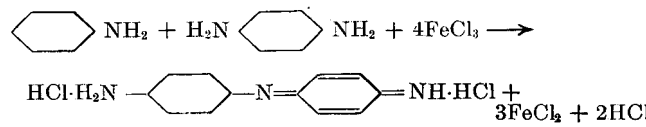
III. Coupling Reaction. A familiar reaction, and one which has probably found use in many rubber laboratories, is the coupling of diazonium salts with amines to form azo dyes. As all aromatic amines react, the distinction is one of degree rather than kind. The reagent chosen for this work because of its stability and activity in coupling reactions is *p*-nitrobenzenediazonium chloride. Many other compounds will serve equally well, if the reactions with amines of known composition are observed and classified. The reagent is added to an acetone solution of the amine, and the color develops immediately. Phenyl-1-naphthylamine gives a violet coloration, while phenyl-2-naphthylamine and acetone-aniline condensation products such as Flectol B and AgeRite Resin D yield red solutions. Most other antioxidants give colors ranging from orange to pale yellow. While many of them can be distinguished by direct comparison, the differences in color are slight, which precludes the use of the test in many applications.

IV. Benzoyl Peroxide Oxidation. In benzene solution *N,N'*-diphenyl-*p*-phenylenediamine is oxidized quantitatively to quinone dianil by benzoyl peroxide (*9*). The intense orange-yellow color produced in this reaction is useful for the detection of the aryl-substituted *p*-phenylenediamines and several other easily oxidized materials, as most of the antioxidants react slowly, if at all. In some cases the color is deepened to red-violet or blue by the addition of anhydrous stannic chloride. This is a valuable aid, as it allows the operator to distinguish between a number of additional types, and produces a color more easily recognized in the extract from a rubber sample.

The reactions obtained on several materials of this class on solutions containing 0.05 gram per liter are tabulated below. The Mulliken system of color notation is used (*7*):

Antioxidant	Bz_2O_2	$Bz_2O_2 + SnCl_4$
N,N'-diphenyl-*p*-phenylenediamine	OY–N	RV–N
AgeRite White	O–S1	B–N
Aranox	OY–T2	V–T2

V. Indamine Reaction. The reaction of aniline with *p*-phenylenediamine in aqueous ferric chloride solution to form a green indamine dye has been widely used in the analysis of both primary amines and diamines (*10*):



If an acetone solution of an amine antioxidant is diluted with two volumes of water and *p*-phenylenediamine and ferric chloride are added, a characteristic color is produced. The reaction takes place with diaryl amine and aryl naphthylamines as well as with primary amines. In some cases an oxidation product is formed in the presence of ferric chloride alone.

Many of the antioxidants react to give brilliant green colors similar to that obtained from aniline. However, phenyl-1-naphthylamine produces only faint yellow color, while phenyl-2-naphthylamine forms a bright red. Thus diaryl amines may be detected in the presence of the former and a characteristic color reaction is available for the latter. Acetone-aniline condensation products, which give tests difficult to distinguish from those of phenyl-2-naphthylamine in some previous reactions, form green products similar in appearance to those of the primary amines. These materials frequently produce intense blue-green colors on the addition of ferric chloride alone.

Aldehyde-amine antioxidants give reactions similar to those of the primary amines. The applicability of the test is limited, as a relatively high concentration of antioxidant is required to produce a color sufficiently intense for analytical purposes. If the sample does not contain large amounts of asphaltic softeners or extenders, this disadvantage may be partly overcome by extracting a large sample and reducing the volume of solvent on a steam bath.

VI. Stannic Chloride–Bromine Test. Stannic chloride and bromine react with aniline–acetone condensation products in ethylene dichloride solution to give orange-red insoluble addition complexes, the formation of which is specific for materials of this class. Excess bromine is removed by the addition of an unsaturated compound such as allyl chloride. The test is not sufficiently sensitive to be applied to the analysis of rubber samples. *N,N'*-diphenyl-*p*-phenylenediamine and other easily oxidized materials produce dark green-blue solutions which interfere. Antioxidants which give positive tests include Flectols A, B, and H, AgeRite Resin D, and AgeRite Syrup, all of which are described as acetone-aniline condensation products containing 2,2,4-trimethyl-1,2-dihydroquinoline and polymers.

Table II. Classification of Reaction Colors According to Mulliken[a]

Test	I	II	III	IV	V
Phenyl-1-naphthylamine	G–S1	yo–n	VR–N	...	Y–n
Phenyl-2-naphthylamine	G–S1	cy–n	R–N	...	R–N
AgeRite Stalite	BG–S1	y–n	yo–n	...	BG–N
BLE	BG–S1	V–N	yo–n	yo–t2	BG–N
Betanox	GY–N	G–S1	OR–N	y–t1	V–T1
N,N'-diphenyl-*p*-phenylenediamine	BV–S2	y–n	yo–n	OY–N–RV–N	OR–N
AgeRite White	B–S1	y–n	RO–N	O–S1–B–N	O–t1
Flectol A	oy–n	y–n	R–N	...	BG–N
Stabilite	Red precipitate	y–n	RO–N	...	VR–S1
Santoflex B	oy–n	y–n	yo–n	RV–N	RV–T2
VGB	oy–t1	gy–t1	yo–n	...	G–S1

[a] BG–S1 = blue-green shade one, RV–N = red-violet normal, etc.

REAGENTS

Stannic Chloride Solution. Dissolve 14.7 ml. of fuming stannic chloride in anhydrous analytical reagent grade benzene and make the volume up to 250 ml.

Amyl Nitrite Solution. Dilute 5 ml. of amyl nitrite to 100 ml. with benzene.

p-Nitroaniline Solution. Dissolve 1.0 gram of *p*-nitroaniline in a mixture of 25 ml. of concentrated hydrochloric acid and 25 ml. of water and make the volume up to 100 ml. with water.

Sodium Nitrite Solution. Dissolve 2.5 grams of sodium nitrite in water and make the volume up to 100 ml.

Benzoyl Peroxide Solution. Dissolve 5.0 grams of benzoyl peroxide in a mixture of 10 ml. of glacial acetic acid and 40 ml. of benzene. Prepare fresh daily.

Ferric Chloride Solution. Dissolve 10 grams of ferric chloride hexahydrate in a mixture of 10 ml. of concentrated hydrochloric acid and 90 ml. of water.

p-Phenylenediamine Reagent. Dissolve 0.1 gram of recrystallized *p*-phenylenediamine in 10 ml. of acetone. Prepare fresh daily.

Bromine Solution. Dilute 5 ml. of bromine to 100 ml. with carbon tetrachloride.

Benzotrichloride, allyl chloride, ethylene dichloride, benzene, and acetone.

SAMPLE PREPARATION

Weigh out 0.05 gram of the antioxidant and dilute to 20 ml. with the solvent specified in the procedure. Dilute 1.0 ml. to 50 ml. for tests I, II, III, or IV. This solution will contain approximately 0.05 gram per liter. Prepare a solution containing 0.25 gram per liter by diluting 1.0 ml. of the original solution to 10 ml. Use this for tests V and VI.

The following procedures have been found satisfactory for testing tread stocks containing 1.0 part of antioxidant on 100 parts of rubber. Prepare the sample by breaking it down on a rubber mill. Place 0.5 gram in a test tube and add 5 ml. of the specified solvent. Heat gently in water bath for 4 to 5 minutes. Cool to room temperature and proceed with test I, II, III, or IV. Under some circumstances test V may be used by refluxing 5.0 grams of sample with 20 ml. of solvent for 30 minutes and testing the extract. The sample should not contain intensely colored materials.

PROCEDURE

I. Stannic Chloride–Amyl Nitrite Reaction. To 5 ml. of a benzene solution of the antioxidant containing approximately 0.05 gram per liter, add 1 ml. of stannic chloride solution and 3 drops of amyl nitrite solution. Note the color which develops.

II. Stannic Chloride–Benzotrichloride Reaction. To 5 ml. of an ethylene dichloride solution of the antioxidant containing approximately 0.05 gram per liter, add 1 ml. of stannic chloride solution and 2 drops of benzotrichloride. The color develops in a few seconds.

III. Coupling Reaction. Add 5 ml. of sodium nitrite solution to 25 ml. of *p*-nitroaniline solution and permit the mixture to stand for 15 minutes. Add 3 drops of reagent to an acetone solution of the antioxidant containing 0.05 gram per liter. The color develops immediately. The reagent should be prepared fresh daily.

IV. Benzoyl Peroxide Oxidation. To 5 ml. of a benzene solution of the antioxidant containing 0.05 gram per liter add 3 drops of benzoyl peroxide solution. Record the color which develops after 1 minute. Add 1 ml. of stannic chloride solution and record the modified color.

V. Indamine Reaction. Place 5 ml. of the acetone solution of antioxidant in a test tube and add 5 drops of *p*-phenylenediamine solution. Add 10 ml. of water and 3 drops of ferric chloride solution. The color requires several minutes to develop. The optimum concentration of antioxidant is about 0.25 gram per liter.

VI. Stannic Chloride–Bromine Test. To 5 ml. of an ethylene dichloride solution of the antioxidant add 1 ml. of stannic chloride solution. Mix and add 3 drops of bromine solution. After 30 seconds add 2 drops of allyl chloride to remove the excess bromine. The formation of a red precipitate indicates the presence of an acetone-aniline condensation product. Many easily oxidized amines produce green to blue-green colors under these conditions and obscure the test. The optimum concentration of antioxidant is 0.25 gram per liter. The test cannot be applied to the analysis of rubber samples.

DISCUSSION

The purpose of this paper is to present a detailed description of a number of specific reactions with only broad general indications of how they can be used. This is in part necessary because of the large number of amine antioxidants now available and the many more which may be marketed in the future. To include information on all the materials in use would be impractical; furthermore, many commercial products are mixtures of several chemical types. On these, the color tests may be intermediate, or in some cases give evidence of the presence of several components.

The principal values of these reactions are (1) to establish whether or not an amine antioxidant is present in a given stock, and (2) to determine the broad general class to which it belongs. Minor variations in structure or composition cannot be detected unless they influence the reactivity of the material toward a given reagent. None of the tests described will distinguish Flectol A from Flectol B, or BLE from Aminox. The most we can say is that the former materials are acetone-aniline condensation products, while the latter belong to the diaryl amine–ketone group.

A convenient approach to a systematic identification of the isolated compounds is to examine the reactions of materials expected to be of interest and classify the colors produced in the various tests by comparison with standards such as those provided by Mulliken (7). A summary of the reactions obtained on some typical commercial products at the concentrations specified in the analytical procedures is shown in Table II.

The notation is an abbreviated form of the one described by Mulliken. The reactions which can be used to detect or characterize the antioxidants are printed in capitals while those which yield faint colors or are not sufficiently specific are printed in lower case letters. In choosing the reactions and classifying the tests emphasis was placed on those yielding strong red, blue, and green colorations which can be perceived at high dilution. The orange and yellow colors are not so useful, as they are less characteristic and more difficult to detect in solvent extracts.

The use of the Mulliken notation is of limited value for the detection of antioxidants in rubber, as the concentration is not known and the depth of the color may vary considerably from the standard. Judgment, therefore, must be based on hue alone. While this is usually reproducible, it may sometimes be altered by the presence of other materials in the extract. Thus, a strong yellow background may cause a blue to appear green-blue.

The tests described were evaluated on a series of tread stocks containing 5 parts of softener and 1 part of antioxidant, and were found to give results in agreement with those obtained on solutions of pure materials. Samples may occasionally be encountered, however, where this is not the case. In such instances it is

frequently possible to concentrate or isolate the material sought by auxiliary physical methods such as steam-distillation (*1*), chromatographic adsorption, or selective solubilities of the amines or their hydrochlorides in various solvents. The materials most likely to interfere are softeners and extenders which produce dark colored extracts. Dithiocarbamate and thiazole accelerators do not react. Diphenylguanidine and aldehyde-amine accelerators give colors similar to those of the antioxidants in test V but do not interfere in other tests. Many of the phenolic antioxidants couple with *p*-nitrobenzene diazonium chloride in test III to yield pale yellow reaction products. Aged samples in which the antioxidant has deteriorated may fail to give satisfactory results. This is to be expected, however, as the reactions described are characteristic of the amines but not of their oxidation or decomposition products.

There are many color tests other than those described above which can be used to characterize the antioxidants. Primary amines such as aniline can be diazotized and coupled with 2-naphthol, or reacted with *p*-dimethylaminobenzaldehyde to form yellow Schiff's bases (*8*). Diphenylamine can be detected by a modification of the Zerewitinoff reaction in which benzoyl chloride is added to the product obtained on treating the amine with methyl magnesium iodide in the presence of anisole (*6*). Aldol 1-naphthylamine gives a red-violet color in the presence of cupric chloride (*5*). Further investigations in this laboratory on reactions carried out in the presence of anhydrous stannic chloride indicate that phenyl-2-naphthylamine can be oxidized by *tert*-butylhydroperoxide to an orange-red complex useful for its quantitative determination, while the tetraaryl hydrazines produced by lead peroxide oxidation of the diarylamines yield the highly colored tetraaryl hydrazinium chlorostannates (*11*).

These, and other methods may be of value in some applications. However, the six procedures described above appear to be the most useful of those investigated. The colors produced are brilliant and reproducible and sufficiently selective to allow the operator to distinguish among a large number of antioxidants.

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Fluorometric Method for Estimating Small Amounts of Chlorophyll a

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In purified preparations of chlorophyll a and b in acetone, chlorophyll a fluoresces more than chlorophyll b, when excited by the monochromatic ultraviolet, violet, and blue bands of the mercury arc spectrum. There is about a tenfold difference in fluorescent activity of the two chlorophyll components when irradiated with violet light (4047 Å.); a threefold difference when irradiated with blue light (4358 Å.). Chlorophylls a and b fluoresce independently of one another in mixtures. The composition of a mixture of pure chlorophylls a and b can be estimated by determining its fluorescence when irradiated by violet and by blue light, since the fluorescence ratio, violet/blue, is characteristic for each percentage mixture of a and b. The presence of carotenoids does not interfere appreciably with the fluorescence of very low concentrations of chlorophyll a unless the carotenoid concentration becomes greater than that of the chlorophyll. Chlorophyll a can be estimated in a mixture of a and b by determining the fluorescence of the mixture when excited by violet light and by assuming that all the fluorescence is due to chlorophyll a. Under these conditions, errors in the estimate due to the presence of b will be constant for any given percentage and will be less than 6% for any mixture containing less than 40% chlorophyll b. Crude acetone extracts of less than 1 mg. of green tissue can be assayed for chlorophyll directly and rapidly by the fluorescent method. Absolute values of less than 2 micrograms of chlorophyll a can be obtained with a standard deviation between a series of similar samples of less than 10%.

THE present paper reports an investigation of fluorometric methods for the quantitative measurement of chlorophyll. Kavanagh (*8*), in describing a new photoelectric fluorometer, suggested its use in the determination of the chlorophylls. His data indicate that concentratations as low as 1 microgram per liter could be determined, if a weaker quinine standard (0.25 mg. of quinine sulfate per liter) were used.

The fluorometric method has a certain number of advantages: (1) It is very sensitive. Much smaller quantities of chlorophyll can be determined in this way than by the usual spectrophotometric and colorimetric methods using standard equipment (*1, 4, 11*), although special colorimeters (*7*) and spectrophotometers (*13*) have been devised which allow measurements of comparable sensitivity to be made. (2) Purification of extracts may be omitted under certain conditions, since the red chlorophyll fluorescence can be measured at such great dilutions and other pigments present have little or no effect, and since chlorophylls are the only substances, naturally occurring in most plants in appre-

ciable amounts, which give a red fluorescence. Even a small amount of turbidity in an extract, a serious source of error in colorimetric work, has little effect upon a fluorometric determination. (3) It is rapid. (4) The equipment required is standard and relatively inexpensive.

The absorption spectra of chlorophylls a and b in the visible and ultraviolet are distinct (*6*, *16*), as are also their fluorescent spectra (*18*). If the relative fluorescence of the two chlorophyll components is different for each exciting wave length, quantitative methods for total chlorophyll in a mixture will give different results for different ratios of chlorophylls a and b. The study of differences in fluorescent behavior of chlorophylls a and b has been one of the objectives in this investigation.

PREPARATION OF PURIFIED CHLOROPHYLLS a AND b

The chlorophylls were extracted and purified by the procedures described by Zscheile and Comar (*16*), and the organic solvents were purified as recommended by Zscheile (*15*). Their directions were followed explicitly with the exception of some minor departures.

Eight hundred grams of fresh spinach leaves were ground in a mortar in cold acetone in 100-gram lots. The acetone extracts were filtered, and the pigment from each batch was transferred to petroleum ether. The petroleum ether solution was washed with water, methyl alcohol, and again with water, until the chlorophyll precipitated. The precipitated suspension was dried over anhydrous sodium sulfate and filtered on a 3-cm. layer of powdered sucrose. The precipitate was washed with petroleum ether to remove carotenoids and was then extracted from the sucrose with ether.

This crude chlorophyll solution was made up to contain 70% petroleum ether and 30% ether, and was adsorbed on a sucrose column 5 cm. in diameter and 35 cm. in length. The chromatogram was developed for about 1.5 hours, during which time 500 ml. of fresh solvent (70% petroleum ether, 30% ether) were added. The central portion of the upper green zone and the lower three quarters of the lower blue zone were mechanically removed from opposite ends of the column and the pigment from each zone was separately eluted from the sucrose with ether. The blue ether solution of chlorophyll a was washed thoroughly with distilled water, dried over sodium sulfate, filtered, made up to 100 ml., and stored on solid carbon dioxide until just before spectroscopic observations had been made.

The green fraction was further purified. The ether eluate was again made up to 70% petroleum ether and 30% ether and was readsorbed on another sucrose column. After 2 hours the central portion of the green zone was again removed, and the pigment eluted. This process was repeated once more with a third column. Spectroscopic study of the ether eluate from the third chromatogram revealed the presence of an appreciable amount of chlorophyll a. Since this preparation was made during very humid weather, the failure to separate the two chlorophylls completely may have been due to moisture entering the absorption columns after their removal from the desiccator. The still impure chlorophyll b preparation was stored in ether on solid carbon dioxide until a fourth column could be prepared. The fourth chromatogram was developed 3 days later, and a clear separation between chlorophyll b and the remaining chlorophyll a occurred. The green band was eluted with ether, and the ether solution was then washed, dried, filtered, made up to volume, and stored on solid carbon dioxide, as in the case of the chlorophyll a preparation. All the foregoing procedure was carried out in a dimly lighted room.

Immediately following completion of the preparations, aliquots in tared volumetric flasks were evaporated in a vacuum desiccator, dried for an hour at 103° C., cooled for 0.5 hour in a desiccator, and weighed. Meanwhile, fluorometric determinations were made on other portions of the solutions.

Absorption spectra were obtained in each case on the following day at the Massachusetts Institute of Technology on an automatic recording spectrophotometer (*5*) made available through the courtesy of Arthur C. Hardy and the department of physics. The width of the spectral band was maintained at 100 Å. throughout the range of wave lengths studied. The data were given in terms of percentage transmission or as $(I/I_0) \times 100$, where I is the intensity of the light transmitted by the solution containing the pigment and I_0 is the intensity of the light transmitted by the solvent alone. The specific absorption coefficients (α) for chlorophylls a and b were calculated from the data as follows:

$$\alpha = \frac{\log_{10} \frac{I_0}{I}}{cx} = \frac{\log_{10} \left(\frac{100}{(I/I_0) \times 100} \right)}{cx}$$

where c = concentration of chlorophyll in grams per liter, and x = thickness of absorption cell in centimeters (1.00 cm.).

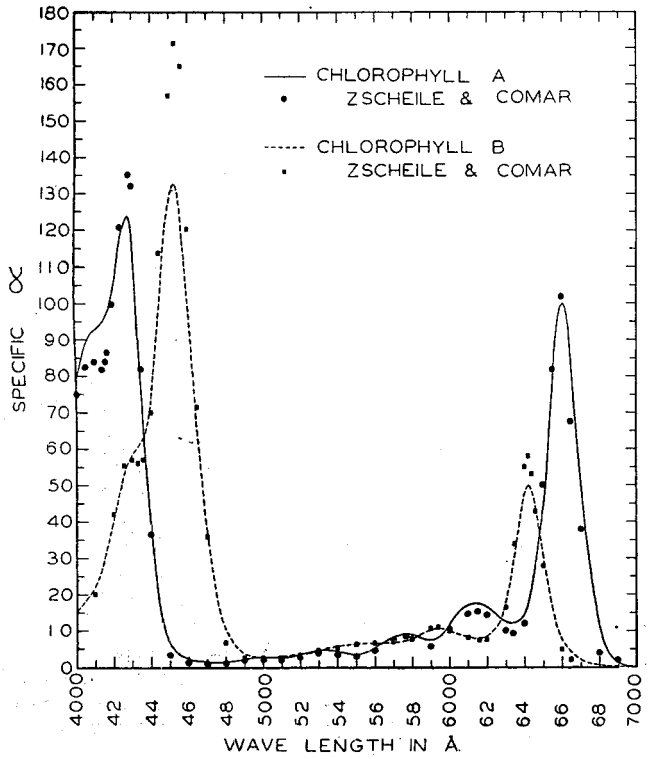

Figure 1. Absorption Spectra of Chlorophyll a and b Preparations in Ether

Specific absorption coefficients obtained for these pigments by Zscheile and Comar (*16*) shown for comparison

The values of α obtained for chlorophylls a and b are shown in Figure 1. The discrepancies between the author's values and those of Zscheile and Comar (*16*), also shown in Figure 1, are due at least in part to the fact that Zscheile and Comar isolated narrower spectral regions with their monochromator, which would tend to give sharper and higher absorption maxima. The absence of pheophytin absorption peaks between 5000 and 5350 Å.—the presence of which would indicate chlorophyll decomposition (*16*)—the close agreement in the position of all the chlorophyll absorption maxima, and the similar absorption coefficient ratios of blue to red absorption maxima (see *9*), all point to a comparable purity for the two sets of preparations.

FLUOROMETRIC METHODS

The fluorometric determinations were made with a Klett fluorometer-colorimeter originally designed and described by Kavanagh (*8*). In this instrument two optical paths lead from the same light source, one to the "standard," a cuvette containing a known solution of some stable fluorescing substance, and the other to the "unknown," a cuvette containing a solution of the compound, the fluorescence of which is to be determined. Photocells placed facing these cuvettes, and at right angles to the incident beams, receive the fluorescent light. The ratio of the fluorescence of the unknown to that of the standard is then measured by a two-photocell balanced circuit, a high-sensitivity galvanometer being used as a null instrument. The ratio is indicated by a built-in potentiometer with a 300-division linear scale. In the work reported here, a Leeds & Northrup Type R galvanometer was used at a sensitivity of 0.0005 microampere per millimeter. The design of the fluorometer eliminates uncer-

Table I. Fluorescence in Acetone of Four Different Chlorophyll Preparations

Date of extraction of each preparation is given. Values represent potentiometer readings calculated as equivalent to concentrations of 10 micrograms per liter. Standard, 1 mg. of quinine sulfate per liter of 0.1 N, H_2SO_4. Unknown, lamp filter 5850 (which transmits 3650, 4047, and 4358 Å. lines)

Age of Preparation, Days	Chlorophyll a 6/14	Chlorophyll a 8/30	Chlorophyll a 10/12	Chlorophyll b 6/14
0	26.4[a]	17.2	...	...
1	...	19.4	15.9	...
3	25.2[a]	...	14.2	4.13[a]
4	...	19.7	...	...
7	20.4[a]	...	...	4.38[a]
8	20.4[a]	...	...	...
14	...	...	15.3	...
71	18.4	...	...	4.11
72	18.4	...	...	3.97
81	...	...	...	4.42
89	18.3	...	...	4.31
Av.	21.1	18.8	15.1	4.22

[a] Values obtained before certain improvements had been made in optics and electrical circuit of fluorometer. These values corrected by factor determined by difference between fluorescence of a standard quinine solution before and after alterations.

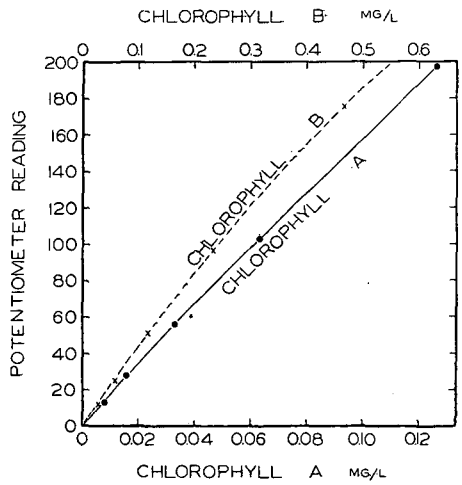

Figure 2. Calibration Curves for Chlorophylls a and b

Standard, 1 mg. of quinine sulfate per liter of 0.1 N sulfuric acid. Unknown, lamp filter 5850

tainties caused by fluctuations and drifts of lamp intensity, nonlinear galvanometer scale, and inconstancy of galvanometer response.

The light source was a 100-watt, A-H 4 Mazda mercury arc lamp, screened with suitable Corning glass filters (lamp filters) of standard thickness to isolate certain lines in the mercury arc spectrum. The cuvettes were 1 × 5 × 5 cm. internal dimensions. Quinine sulfate solutions (1 or 0.2 mg. of quinine sulfate per liter of 0.1 N sulfuric acid), shielded by a 5970 lamp filter, were used as standards. The standard photocell was shielded by a Corning 3389 photocell filter.

Solutions of chlorophyll in pure acetone (*15*) were used as unknowns. It was found that the addition of 5% by volume of water to the acetone made no detectable difference in the fluorescence of chlorophyll. In this investigation, the maximum amount of water derived from plant material in crude acetone extracts never exceeded 1.5%. Various Corning lamp filters were used to isolate the following wave lengths of the incident beam: 5850 for the 3650, 4047, and 4358 Å. lines; 5113 (1/2 standard thickness) and 3389 for the 4358 Å. line; 4308, 3060, and 5970 for the 4047 Å. line; 5860 and 738 for the 3650 Å. line. A red Corning filter, 2408, which has a high transmission for the red chlorophyll fluorescence, was used as the photocell filter. Two mirrors, one at the end and the other facing the broad side of the unknown cuvette opposite the photocell, were used to increase the fluorescent light reaching the photocell. These mirrors doubled the sensitivity of the instrument.

Fluorometric measurements were made at room temperature, 22° to 26° C. Zscheile and Harris (*18*) have shown that chlorophyll fluorescence decreases with an increase in temperature, but the errors involved due to temperature fluctuations within this range would be less than 3%. Readings were made as rapidly as possible to reduce photodecomposition to a minimum. Fifteen to 20 seconds were required to balance the circuit after opening the shutter shielding the solutions. Decay of fluorescence was most pronounced when filters transmitting ultraviolet light were used, but was negligible with the blue and violet filters.

FLUOROMETRIC DATA

Fluorescence of Pure Chlorophylls a and b. The relationship between concentration of chlorophyll and fluorescence, as measured by the potentiometer of the fluorometer, is shown in Figures 2, 5,*A*, and 6,*A*. The potentiometer readings are proportional to the chlorophyll present, when the concentrations are low.

Data on the fluorescence of three chlorophyll a preparations and one chlorophyll b preparation, when excited by the blue, violet, and ultraviolet lines, as transmitted by the 5850 lamp filter, are given in Table I. The average value for the chlorophyll b solution (4.22) showed a standard deviation of ±0.16. This is a percentage standard deviation of ±3.8%, and is a fair measure of the magnitude of the various errors involved, when repeated samples have been taken over a period of several weeks. Differences between the average values obtained for the three chlorophyll a preparations are larger than ±3.8%, and are probably due chiefly to errors in weight determinations. There is some indication of decay of the first chlorophyll a extract with age, and the average of determinations for this extract is in error for this reason.

Chlorophyll a is a much more fluorescent pigment than chlorophyll b; and it also may be somewhat less stable upon storage in ether in the dark at 0° C., conditions recommended by Zscheile and Harris (*17*). The fluorescence of the a and b components when excited by different monochromatic spectral lines is compared in Table II. The difference between the fluorescence of a and b is greatest when excited by the violet line (4047 Å.).

Table II. Fluorescence of Chlorophylls a and b in Acetone Excited by Radiation of Various Wave Lengths

(Standard, 0.2 mg. of quinine sulfate per liter of 0.1 N H_2SO_4)

Exciting Wave Length, Å.	Estimated Potentiometer Reading for Concentration of 0.1 Mg. per liter Chlorophyll a	Chlorophyll b	Relative Fluorescence, a/b
3650, 4047, 4358	800	188	4.25
3650	42.4	11.9	3.56
4047	12.7	1.25	10.16
4358	70.9	24.1	2.94

Fluorescence of Mixtures of Chlorophylls a and b. Knowing the fluorescence of the two separate chlorophyll components and assuming that they fluoresce independently of one another in mixtures, it is possible to compute the fluorescence of various mixtures containing a constant total amount of chlorophyll. These theoretical calculations were made and then checked experimentally. The results are shown in Figure 3 (broken line). The agreement between the theoretical and observed values is very close, justifying the original assumption that the two chlorophylls do fluoresce independently.

Pure chlorophyll a can be distinguished from chlorophyll b by the ratio:

$$R = F_{(4047)}/F_{(4358)}$$

where $F_{(4047)}$ is the fluorescence excited by the 4047 Å. line and $F_{(4358)}$ is the fluorescence excited by the 4358 Å. line, in the same solution. This ratio can be determined with considerable precision without knowing the concentration of the preparation, since the relative fluorescence at these wave lengths is the deter-

mining factor. For a mixture of chlorophyll a and b, the following relationship should hold:

$$R = \frac{F_{(4047)}}{F_{(4358)}} = \frac{Fa_{(4047)}(X)}{Fa_{(4358)}(X)} + \frac{Fb_{(4047)}(1 - X)}{Fb_{(4358)}(1 - X)}$$

where Fa is the fluorescence of a given concentration of chlorophyll a, Fb is the fluorescence of an equal concentration of chlorophyll b, when excited by light of the wave lengths indicated, and X is the proportion by weight of chlorophyll a in the mixture.

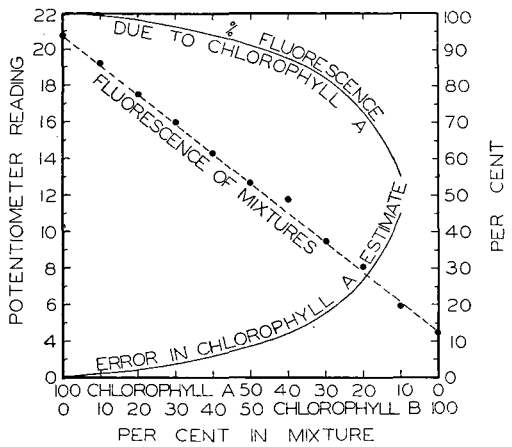

Figure 3. Fluorescence of Mixtures of Chlorophylls a and b

Broken line. Theoretical values derived on assumption that two pigments fluoresce independently of one another in mixtures. Points were experimentally determined. Standard, 1 mg. of quinine sulfate per liter of 0.1 *N* sulfuric acid. Unknown, lamp filter 5850 Unbroken line. Per cent of fluorescence of mixture due to chlorophyll a when excited by violet (4047 Å.) line, and corresponding percentage errors in chlorophyll a estimates if assumption is made that all fluorescence is due to chlorophyll a

The curve in Figure 4 shows the theoretical relationship between R and X for the fluorometer setup used in this investigation; and the individual points on this graph are experimentally determined values of R for known mixtures of chlorophyll a and b. An estimate of the proportion of a and b in an unknown mixture can be made by determining R, and finding this value on the calibration curve in Figure 4. The curve is rather flat for high percentages of chlorophyll a, and the accuracy of the estimate is, therefore, low when using this portion of the curve. Spectrophotometric methods (*1*, *4*) for obtaining the a/b ratios are preferable where the quantity of material and the equipment permit. Since values of R for chlorophylls a and b will vary somewhat, depending upon the filter transmissions, the spectral sensitivity of the photocells, and other experimental conditions, a calibration curve would have to be computed for each new setup.

This method is not applicable to crude extracts, since the value of the ratio, R, is altered somewhat by the presence of other pigments. In one experiment R was found to be 0.179 for pure chlorophyll a, and 0.177, 0.172, and 0.166 for chlorophyll a/β-carotene ratios of 2, 1, and 0.5, respectively. A chromatographic separation of chlorophylls from the carotenoids can be carried out on a rather small amount of material, however (*3*).

The pigments in an acetone extract of the shoots of 270 etiolated oat seedlings, irradiated for 3 hours with monochromatic blue light (4358 Å.), were transferred to petroleum ether, and the petroleum ether solution was washed repeatedly with distilled water to which a trace of calcium carbonate had been added, dried over anhydrous sodium sulfate, and filtered onto a small column of powdered sucrose 2 cm. in diameter and 15 cm. high. When the carotenoids had separated from the chlorophylls,

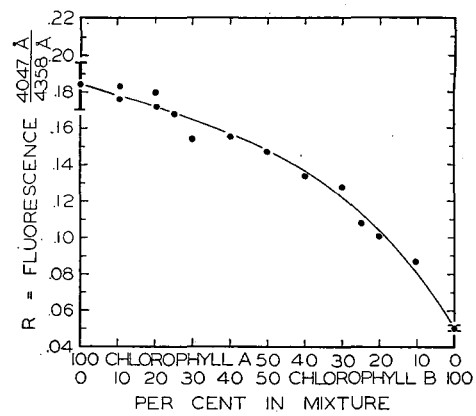

Figure 4. Ratio of Fluorescence Excited by Radiation from 4047 Å. Mercury Line to That Excited by 4358 Å. Line for Chlorophylls a and b and Mixtures of Two

Standard deviations of determinations of ratio for pure chlorophylls a and b indicated by vertical lines. Curve shows theoretical values of R for mixtures; points were experimentally determined

the green layer was mechanically removed, and eluted with ethyl ether, and the pigments were transferred to acetone. The ratio, R, was then determined on the fluorometer. It was found to be 0.175, very close to that of pure chlorophyll a. Spectrophotometric data on the pigments separated from a similar crude acetone extract by shaking with ethyl ether (*3*), and on the pigments extracted from similar material with ethanol (*2*), indicate a complete or nearly complete absence of chlorophyll b in such material.

Zscheile and Harris (*18*) have reported differences in the fluorescent spectra of chlorophylls a and b in ethyl ether, a having a maximum at about 6645 Å. (6700 Å. in acetone) and b, at about 6480 Å. An attempt was made to distinguish between the fluorescence of these components in acetone by using photocell filters with different short-wave cutoffs. The results of this experiment are shown in Table III. The fluorescent spectrum of chlorophyll b is reduced to a greater extent than that of chlorophyll a by Corning 2408 and 2403 filters, but the differences seem scarcely large enough to be serviceable in determining the ratio of a/b in mixtures.

Table III. Reduction in Fluorescence of Chlorophylls a and b by Various Photocell Filters with Sharp Short-Wave Cutoffs

Corning Filter Nos.	Approximate Wave Length of Cutoff, Å.	Percentage Reduction in Fluorescence Chlorophyll a	Chlorophyll b
2418	5850	0	0
2408	6050	2.0	8.7
2403	6250	13.2	25.2

Estimation of Chlorophyll a. Since chlorophyll a fluoresces about ten times as much as b (see Table II) when excited by the violet line (4047 Å.), the assumption can be made that all the fluorescence emitted by mixtures of the two components under these conditions is due to the fluorescence of a. The theoretical errors in chlorophyll a determinations made by such an assumption for various mixtures of chlorophylls a and b are shown in Figure 3.

For extracts of green tissue, usually containing about 70% chlorophyll a (*1*, *14*), the theoretical error should be around 4%. If enough material is available, a determination may be made of the a/b ratio, either fluorometrically (see above) or spectrophotometrically (*1*, *4*). Then, assuming constancy of this ratio for

Table IV. Chlorophyll Determinations on Four Series of Leaf Samples

[Each sample a single disk 5 mm. in diameter. Values in columns 5 to 11 as % of fresh weight. Standard, 0.2 mg. of quinine sulfate per liter of 0.1 *N* H_2SO_4. Unknown, lamp filters 4308, 3060, and 5970 (fluorescence excited by violet, 4047 Å., line)]

			Assuming 100% Chlorophyll a		Assuming Ratio a/b = 4			Assuming Ratio a/b = 2.33		
1	2	3	4	5	6	7	8	9	10	11
Species	No. of Samples	Av. Fresh Weight of Samples, Mg.[a]	Mg. of chlorophyll a per sample	Chlorophyll a as % fresh weight[a]	80% a (0.98 × column 5)	20% b (0.25 × column 6)	a + b (columns 6 + 7)	70% a (0.96 × column 5)	30% b (0.43 × column 9)	a + b (columns 9 + 10)
Lactuca sativa unboiled	5	2.53 ± 0.11	1.49	0.059 ± 0.003	0.058	0.014	0.072	0.057	0.024	0.081
Lactuca sativa boiled	5	2.47 ± 0.11	1.70	0.069 ± 0.007	0.068	0.017	0.085	0.066	0.028	0.094
Ailanthus glandulosus	5	2.48 ± 0.07	4.39	0.177 ± 0.004	0.174	0.044	0.218	0.170	0.073	0.243
Magnolia tripetala	5	2.65 ± 0.07	4.03	0.152 ± 0.011	0.149	0.037	0.186	0.146	0.063	0.209
Lycopersicon esculentum	5[b]	0.96 ± 0.08	1.83	0.191 ± 0.006	0.187	0.047	0.234	0.183	0.079	0.262

[a] Standard deviations of averages of each series of tests given.
[b] Sample disks cut 3.5 mm. in diameter.

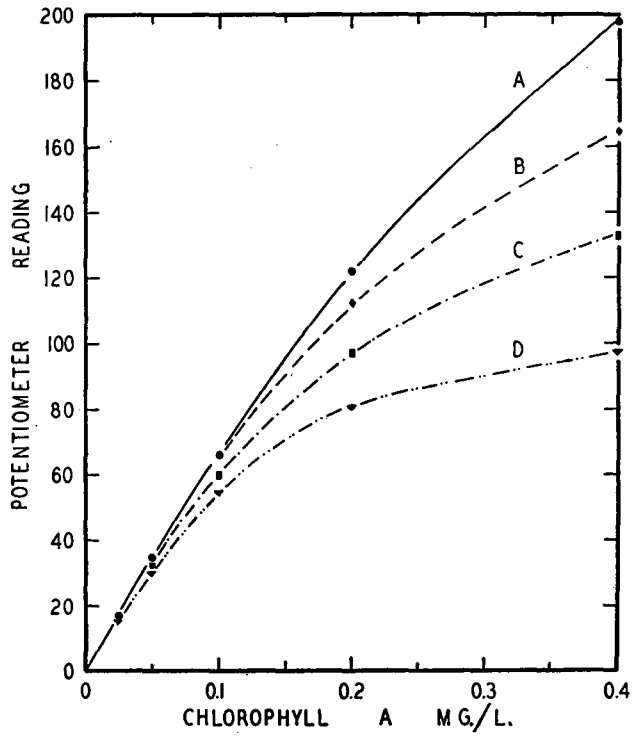

Figure 5. Effect of β-Carotene on Fluorescence of Chlorophyll a Irradiated with Blue Light

A. Pure chlorophyll a
B. β-carotene concentration half that of chlorophyll a
C. β-carotene concentration equal to that of chlorophyll a
D. β-carotene concentration twice that of chlorophyll a
Standard, 0.2 mg. of quinine sulfate per liter of 0.1 *N* sulfuric acid
Unknown, lamp filters 5113 and 3389

subsequent samples, the chlorophyll a estimate can be corrected, and a computation of the total chlorophyll content of the extract can also be made (see Table IV).

If only the relative concentrations are required, and if the ratio of a/b can be assumed to remain nearly constant among the samples to be tested, greater sensitivity will be attained by using ultraviolet or blue light as the exciting wave lengths. When using ultraviolet, however, readings must be made as rapidly as possible, to reduce the photodecomposition of chlorophyll (particularly the more labile a component) to a minimum.

Fluorescence of Chlorophyll in Presence of Carotenoids and Flavones. If quantitative determinations of chlorophyll are to be made upon unpurified acetone extracts of plant material, the presence of other pigments may interfere with the determinations. The following experiment was carried out to ascertain the effect of carotenoids upon the fluorescence of chlorophyll a.

A sample of pure β-carotene (General Biochemicals, Inc.) was dissolved in ether. The ether solution was then diluted with acetone, and added to three chlorophyll a solutions in such amounts that the ratio (on a weight basis) of chlorophyll a to β-carotene was equal to 2, 1, and 0.5. The fluorescence of dilution series of pure chlorophyll a and of each of these three mixtures, when irradiated with blue, violet, and ultraviolet light, was then measured on the fluorometer. The fluorescence was least affected by the presence of β-carotene when the solutions were irradiated with ultraviolet light, which is not strongly absorbed by the carotene, and most affected when irradiated with violet light.

The relations between chlorophyll a concentration and potentiometer response when irradiated with blue and violet light are shown in Figures 5 and 6, respectively. The reduction in fluorescence due to the presence of carotene becomes progressively more pronounced, the higher the concentration. At the lowest chlorophyll concentrations the carotene does not appreciably reduce the fluorescence, even when present in larger amounts than chlorophyll a.

In normal green tissues of higher plants the ratio (on a weight basis) of chlorophylls to carotenoids has values falling between 1.6 and 6.2 (*12*, *14*). The chlorophyll-carotene ratio for tobacco tissues has been reported as being around 20 (*4*). It would appear, therefore, that carotenoids will not appreciably interfere with chlorophyll determinations in very dilute solutions, unless they occur in concentrations considerably higher than that found in normal green tissues.

In an experiment to determine the effect of flavones on chlorophyll a fluorescence, 3.95 grams of the shoots of dark-grown oat seedlings were extracted with 100 ml. of acetone. The acetone extract was then shaken with 50 ml. of petroleum ether and 20 ml. of distilled water. The aqueous acetone fraction, containing the flavones, was drawn off. It was found that amounts of this

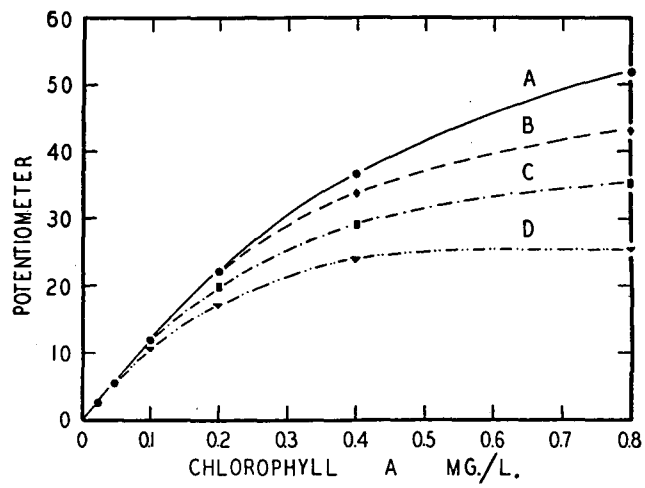

Figure 6. Effect of β-Carotene on Fluorescence of Chlorophyll a Irradiated with Violet Light

A to *D*. Same as in Figure 5
Standard, 0.2 mg. of quinine sulfate per liter of 0.1 *N* sulfuric acid
Unknown, lamp filters 4308, 3060, and 5970

Table V. Effect of Adding Pure Chlorophyll a to Crude Chlorophyll Extracts

Source of Extract	Estimated Chlorophyll a in Extract	Pure Chlorophyll a Added	Chlorophyll a Theoretically in Mixture, Column 1 + 2	Chlorophyll a Estimated from Fluorescence of Mixture
	Micrograms per liter			
Dark-grown Avena seedlings exposed to violet light for 2 hours	6.7	42.9	49.6	49.0
Dark-grown Avena seedlings exposed to sunlight for 2 hours	5.9	42.9	48.8	50.4
Piece of grass leaf	39.2	42.9	82.1	86.4

flavone-containing fraction equivalent to 100-mg. fresh weight of tissue could be added to chlorophyll a solutions without causing a decrease in the fluorescence of the chlorophyll. Only a small fraction of this weight of green tissue is needed for chlorophyll determinations. It is very possible, however, that crude extracts of certain types of plant material may contain sufficient amounts of flavones or other pigments to interfere with the chlorophyll fluorescence.

Chlorophyll a Determinations in Crude Extracts. Crude extracts of chlorophyll for fluorometric determinations were prepared as follows.

The fresh tissue to be extracted was weighed to the nearest 0.1 mg on a Roller-Smith torsion balance, dipped for 30 seconds in boiling water in certain cases, and then finely ground up with acetone in a special homogenizer constructed from a heavy-duty, conical centrifuge tube fitted with a tapered, ground-glass plunger. Mackinney states (*10*) that chlorophyll may be hydrolyzed by chlorophyllase during extraction, but that this process is stopped as soon as the pigment has been separated from the cellular debris. The cellular debris was immediately thrown down by centrifugation, and the clear supernatant liquid was decanted. This crude extract was then made up to 20-ml. volume. The fluorescence of the extract or a suitable dilution thereof was tested immediately in the fluorometer, using the violet (4047 Å.) line, and the amount of chlorophyll a estimated from a calibration curve (see Figure 6,*A*).

The results of determinations on series of samples cut from leaves with a cork borer are given in Table IV. Standard deviations for individual values in each series of similar samples are not greater than 10%. The amount of chlorophyll a per fresh weight of tissue is in good agreement with the data of other investigators (*1*, *14*). If the exact ratio of a/b is known, a correction can be made in the chlorophyll a estimate, and the amount of chlorophyll b can also be computed, as shown in Table IV.

The effect of adding pure chlorophyll a to crude chlorophyll extracts is shown in Table V. There is reasonably good agreement between the theoretical chlorophyll a content and the fluorescence of the mixtures.

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Continuous Recording Ultraviolet Spectrophotometer

Application to Butadiene Analysis

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WITHIN recent years the utility of ultraviolet spectrophotometry as a method of quantitative analysis of certain systems has become generally recognized. When the system to be analyzed contains only one component which absorbs in the ultraviolet region, the analytical problem is particularly simple because the other components act merely as inert diluents. This favorable situation exists for the spectrophotometric analysis of butadiene in the presence of other C_4 hydrocarbons because butadiene has a strong absorption band with a peak near 2150 Å., while paraffins and olefins do not absorb in this region. Acetylenes with the exception of vinyl acetylene have negligible absorption. The presence of appreciable concentrations of vinyl acetylene causes high apparent butadiene analyses but a suitable correction can be applied if necessary. 1,2-Butadiene absorbs weakly and can usually be neglected. Conjugated pentadienes interfere seriously and must be absent for reliable results.

It is most convenient to carry out this analysis in the gas phase. When a definite sample pressure and an absorption cell of definite length are used and the spectrophotometer is set at a suitable wave length, the fraction of ultraviolet radiation transmitted depends only on the concentration of butadiene in the sample. When the spectrophotometer has been calibrated with known concentrations of butadiene, the measured transmittance gives the percentage of butadiene directly. Thus, the ultraviolet spectrophotometric method replaces lengthy and difficult distillations and chemical procedures with a rapid and simple measurement.

A continuous recording ultraviolet spectrophotometer is described with particular reference to its application to the analysis of a plant stream for butadiene in the range 0 to 20%. The problem of measuring small photocell currents under refinery conditions is discussed and a solution to the problem is given in the form of a null system employing a high-impedance direct to alternating current conversion system. This recording spectrophotometer has adequate stability and accuracy and its maintenance is relatively simple.

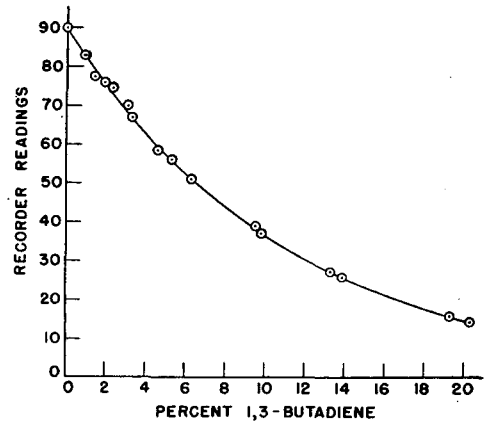

Figure 1. Calibration Curve Showing Recorder Reading *vs.* Per Cent Butadiene

The speed of measurement becomes of special importance in following the variations in the composition of a plant stream. For this purpose an instrument which yields a continuous record of the butadiene concentration in a flowing sample is very valuable. Such an instrument, described in this paper, was developed by the Brown Instrument Company and the Sun Oil Company for use in the Toledo butadiene plant of the Sun Oil Company. In this application it supplies an immediate indication of unusual conditions and has greatly facilitated the study of process improvement. The plant personnel have been relieved of frequent manual analyses, and the human error factor has thus been minimized. Although automatic control of butadiene plant operations was not attempted on this installation, it appears to be a definite possibility for the future. The instrument described here was developed for butadiene analysis, but can be applied to other systems for which the spectral location of absorption bands is favorable. A similar instrument which was developed during the same period by National Technical Laboratories is partially described by Beckman (*1*).

ANALYTICAL SYSTEM

The recording spectrophotometer is based on the Beckman quartz photoelectric spectrophotometer (*2*) equipped with a hydrogen arc lamp and lamp current regulator. The lamp used has a reservoir bulb to hold additional hydrogen. It is supplied by the National Technical Laboratories and is designated by catalog number 2230A. The modifications made in this instrument to adapt it for continuous recording are described below. The butadiene range required to be covered extends up to 20%, at which concentration the absorption of radiation whose wave length is near that at the absorption peak is too great for accurate results to be obtained. For this reason, the spectrophotometer is set at a wave length of 2350Å. which is on the long wave-length side of the absorption maximum. The slit width used is 1 mm.

The essentially monochromatic beam of radiation passes to a phototube through a vitreous silica gas absorption cell 1 cm. long, through which the sample for analysis flows continuously. The cell is vented to the atmosphere through a small flowmeter; the effect of a variation in atmospheric pressure is so small that it is neglected. (If in some particular application this is undesirable, it would not be difficult to use a manostat on the exit side of the absorption cell.) Provision is made for stopping the sample flow and flushing the cell with pure nitrogen when it is desired to check the reading for zero butadiene percentage (100% transmittance).

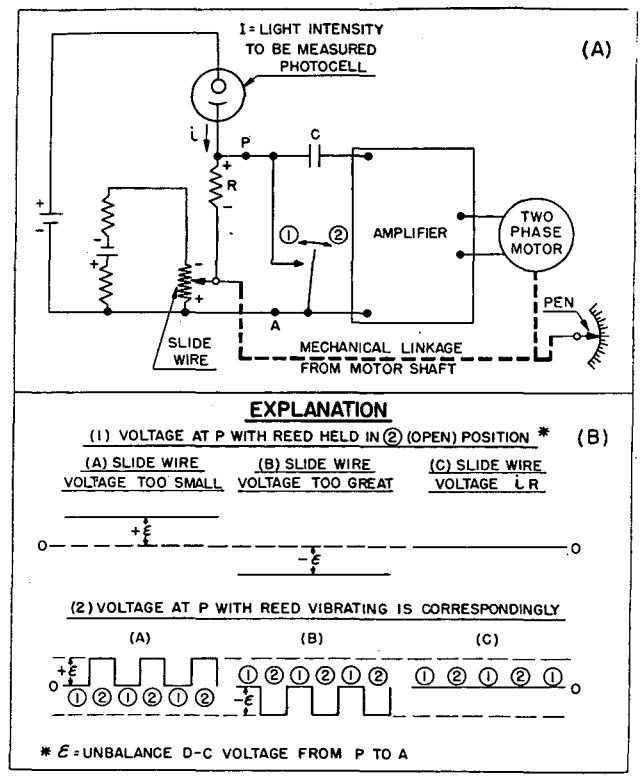

Figure 2. High-Impedance Self-Balancing System

Changes in temperature have a relatively marked effect on the absorption coefficient of butadiene. For this reason the incoming sample is passed through a copper coil immersed in a thermostated water bath, which holds the sample temperature constant to ±0.05° F.

The spectrophotometer is calibrated by admitting pure butadiene to the absorption cell and maintaining various measured pressures while readings are taken on the recording potentiometer. Because a nonabsorbing diluent has no effect on butadiene absorption, this procedure is equivalent to varying the partial pressure of butadiene in the presence of such a diluent. By considering the total pressure as one atmosphere, the results of the calibration are expressed as percentage of butadiene versus recorder reading. An example of such a calibration curve is shown in Figure 1. In this case the recorder reading for 0% butadiene was arbitrarily set at 90% of full scale to allow opportunity for a possible drift upscale.

MEASUREMENT AND RECORDING OF RADIATION INTENSITY

The intensity of the radiation transmitted through the absorption cell (which is a measure of butadiene concentration) is measured by a photocell, amplifier, and recorder. The dispersed radiation reaching the photocell produces a current which is directly proportional to the radiation intensity. Because this

photocell current is small (10^{-13} to 10^{-10} ampere), its accurate measurement under plant conditions presents several problems:

1. The frequent presence of contaminating vapors and high relative humidity in refinery applications make it necessary to use a low-value photocell resistor for adequate stability. Consequently, it was considered desirable in designing this instrument to reduce the value of the photocell resistor drastically from approximately 2000 megohms commonly used in laboratory-type, manually operated instruments to 50 megohms.
2. Vibration conditions are in general unfavorable.
3. Tube replacement or similar routine maintenance has to be very infrequent and easily and economically accomplished.
4. The use of storage cells or B-batteries is not desirable for maintenance reasons.
5. Voltage regulators in the amplifier are to be avoided in the interest of simplicity and cost reduction of the installation.

To assure accuracy of the photocell current measurement, a null system is employed. Such a system does not affect the current being measured, since at balance it theoretically draws no current. Moreover, strict proportionality between the pen reading and the current measured is theoretically attainable, since the voltage gain characteristics of the detector do not affect the balance point. However, the detector must not introduce its own variable potential or the system will drift in zero reading.

Galvanometers were not considered as null detectors, because of their inherent fragility and relative current insensitivity. Two types of nongalvanometer unbalance detectors exist which are sensitive enough for measuring currents considered in this paper: direct current amplifiers and direct to alternating current conversion systems.

The use of a direct current amplifier as a null detector in the photocell circuit was found to be undesirable in view of the requirements previously mentioned. Such amplifiers introduce excessive drifts in zero unless large battery or voltage regulator assemblies are employed. Moreover, for measurement of the low currents in this application rather expensive electrometer tubes and high value photocell resistors are needed to assure electrical stability. Such components require special maintenance and service, and are adversely affected by various vapors and high relative humidity, such as may be found in refinery applications.

Because of these considerations, a direct current amplifier was excluded as a final solution although temporarily employed as an emergency expedient. Instead, the unbalance voltage produced in the photocell circuit was converted into alternating voltage of power line frequency before amplification. As a result, drifts in gain and operating point of the amplifier tubes do not affect the system.

Various direct to alternating current conversion systems have been described in the literature, among them the standard Brown transformer-type conversion system (*3*). These have been used primarily for detecting minute voltages developed across low impedances, and are not normally recommended for detection of currents of less than 10^{-9} ampere. Since the measured currents in this application are as low as 10^{-13} ampere, these systems were not usable.

The present conversion system is designed for the measurement of small currents and is ideally adapted to photocell load resistances of 50 megohms. It is shown in Figure 2, which also illustrates the basic operation of the high-impedance self-balancing system.

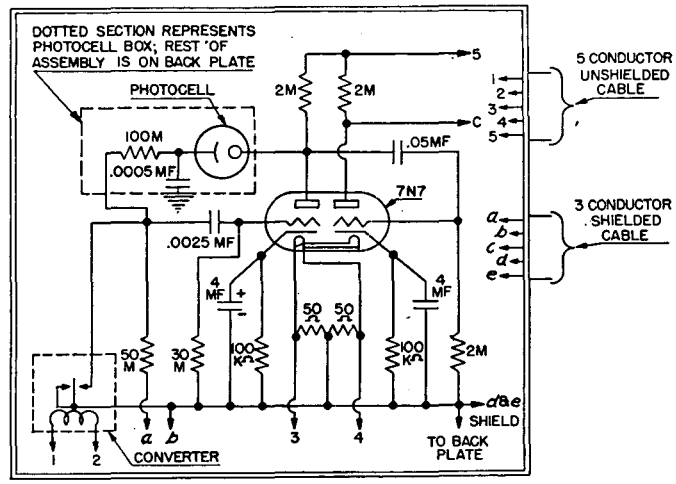

Figure 3. Schematic Wiring Diagram of Recording System. Preamplifier

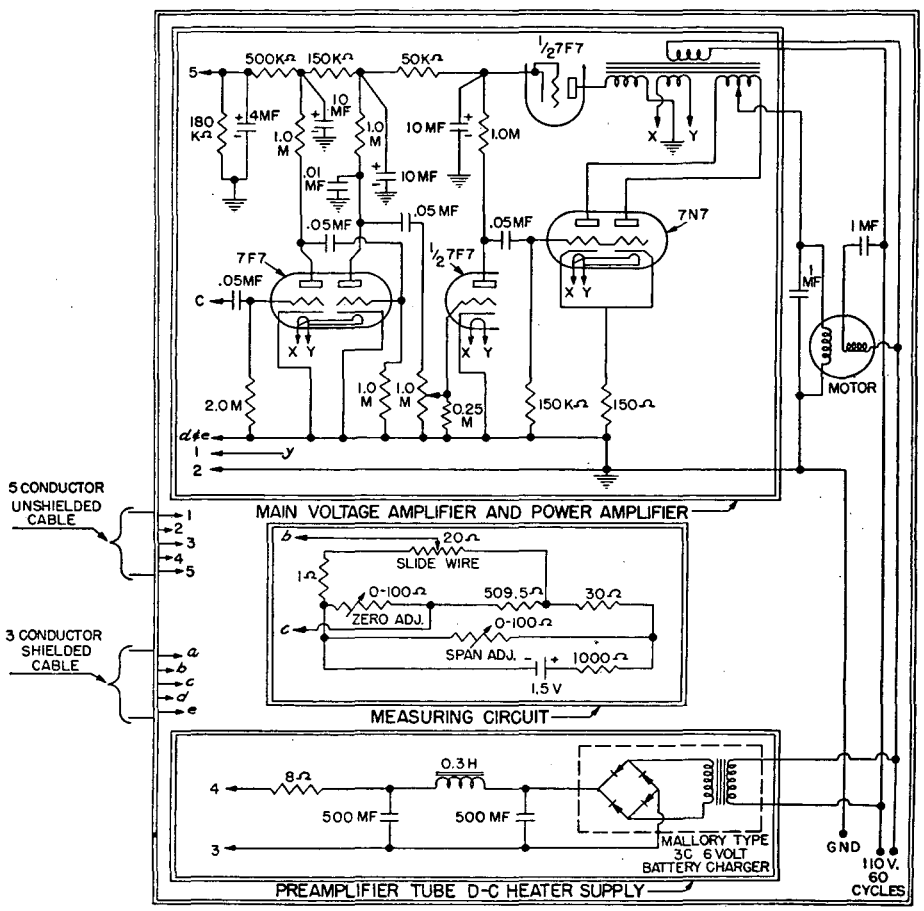

Figure 4. Schematic Wiring Diagram of Recording System. Recorder

Light striking the photocell results in a photocell signal current, i, proportional to the light intensity, I. The signal current, flowing through a resistor, R, yields a voltage drop, iR, of the polarity indicated. The latter voltage drop is opposed by the slide-wire voltage. When the two voltages are equal, there is no potential difference between points P and A. When the current rises from the balance value for the particular slide-wire position, P is positive with respect to A; if the current falls, P is negative with respect to A. An unbalance direct current voltage of reversible polarity is thereby produced. The converter reed shown at A is energized by a coil supplied with voltage of line frequency. This reed alternately makes and breaks the connection between points A and P.

By shorting P to A when the reed makes contact in the (1) position, the converter changes the unbalance direct current voltage into a 60-cycle alternating current voltage of one phase or of opposite phase, dependent upon the relative polarity of P and A. This alternating current voltage when amplified drives a two-phase motor in a direction determined only by the polarity of the unbalance direct current voltage impressed at the converter input terminals. The motor is coupled mechanically to both the pen and slide wire in such a manner that the motor drives the slide-wire contactor to produce the voltage required to balance the voltage drop, iR, and thereby yield zero input voltage to the converter. The pen reading at balance then is proportional to the photocell current and can be interpreted in terms of chemical composition.

The motor almost instantly responds to photocell current changes, so that the system continuously rebalances to record changes in sample concentration.

The schematic wiring diagram of the recording system is shown in Figures 3 and 4.

The two major units in the instrument are the preamplifier, mounted directly on the Beckman optical unit, and the modified circular chart electronic recorder (*3*). The preamplifier unit contains the photocell with its manually operated shutter control mechanism, a desiccator assembly, and a 7N7 twin electrometer conversion preamplifier tube, selected for low microphonics (see Figure 3). A three-conductor shielded cable and a five-conductor unshielded cable connect the preamplifier unit and the recorder. The recorder contains a special main amplifier, a measuring circuit with the associated conventional mechanical balancing mechanism, and a rectifier and filter providing direct current for the heaters of the preamplifier tube (see Figure 4).

Various design details incorporated in these units are of interest:

1. The photocell operating potential is obtained from the "B" supply of the amplifier. This eliminates the need of a separate photocell battery.
2. A filter in the photocell circuit effectively smoothes out any optical 60-cycle ripple (such as is produced when an alternating current arc is employed). In addition, the capacitor greatly reduces photocell noise.
3. The preamplifier and converter assembly which replaces the Beckman preamplifier unit is built on a steel cover plate $^3/_{16}$ inch thick, and the box itself is built of reinforced 0.125-mm. (0.050-inch) sheet steel. This heavy and rigid construction reduces the effects of vibration and shock to negligible proportions.
4. As shown in Figure 5, the entire converter and preamplifier tube assembly can be quickly removed from the instrument and transferred to a bench for service. The rear cover plate assembly of the preamplifier is easily detached from the unit and cable assembly without unsoldering any wires, since electrical connections are made by means of banana plugs. The relatively confined space of the unit itself contains only the photocell, filter, and banana plug assemblies; these are easily accessible.
5. To prevent excessive photocell leakage, desiccation of the preamplifier unit is provided. The desiccator is readily removed without disturbing any optical or electrical components. Moreover, the preamplifier box is sealed completely, so that desiccant replacement is not generally required more often than once every 3 or 4 months.
6. To permit compensation of the system for photocell dark current variations, an electrical zero adjustment is provided. This adjustment is accomplished by closing the shutter in the preamplifier unit by turning the knob on the preamplifier and adjusting the zero rheostat in the recorder until the pen reading is zero.
7. To permit electrical adjustment of recorder span, a rheostat is provided across the slide-wire circuit. The span adjust-

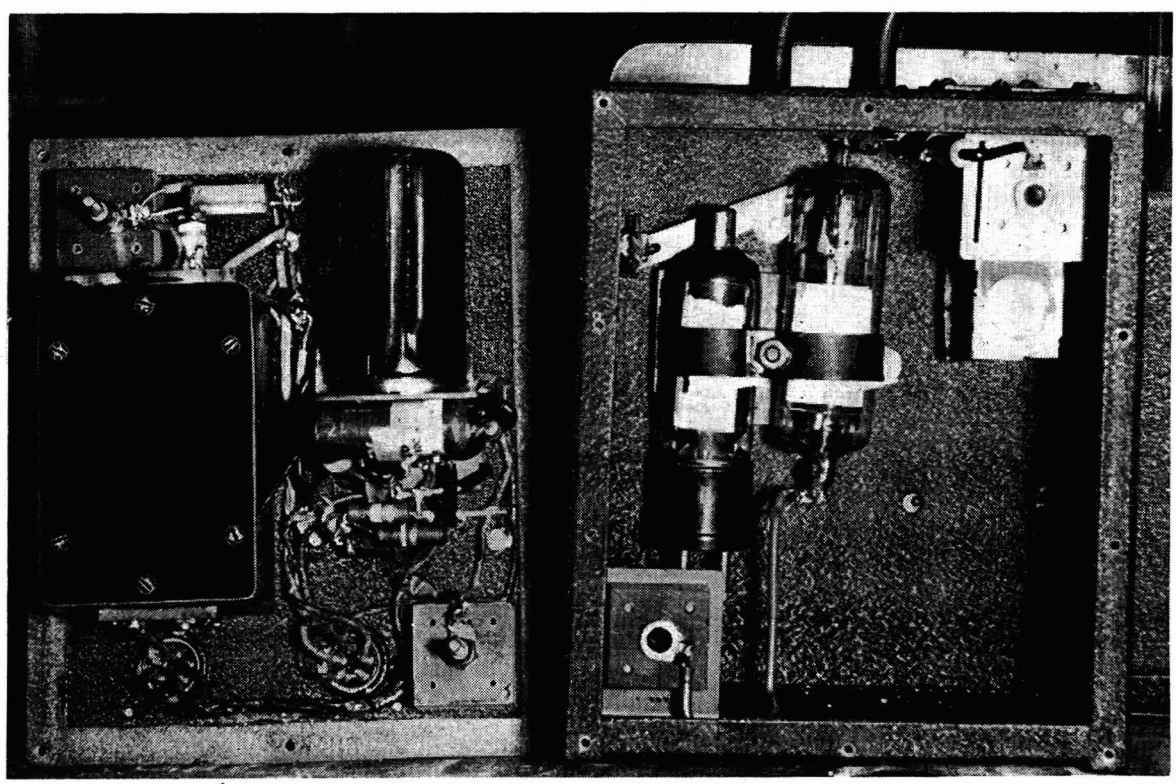

Figure 5. Photograph of Preamplifier Unit

Left. Rear cover plate assembly, showing 7N7 tube with shield and converter box
Right. Interior of photocell unit, shown mounted on spectrophotometer. Sampling cell leads at top. Photocell in upper central part of box is employed; other is not used

ment consists in flushing the absorption cell with nitrogen and then adjusting the recorder reading to the desired value for 100% optical transmission.

8. The recorder supplies four different voltages to the preamplifier:

(*a*) Direct current voltage to operate the 7N7 preamplifier heaters; (*b*) alternating current voltage to operate the converter; (*c*) direct current voltage for the 7N7 tube plates and the photocell anode; and (*d*) measuring circuit voltage to oppose the *iR* drop produced by the photocell current.

RECORDER PERFORMANCE

Figure 6 shows a six-day circular chart record in which the recorder drift is seen to be less than 10^{-12} ampere. Over 24-hour periods the high-impedance recording system described in this paper normally introduces drifts of less than 5×10^{-13} ampere. It can stably detect currents of less than 10^{-13} ampere for periods up to 0.5 hour.

It is clear that such a recording system has many applications beyond the present spectrophotometric one.

PERFORMANCE OF OVER-ALL SYSTEM

The quality of the record provided in actual service by the recording spectrophotometer can be judged from Figure 7. To check the accuracy of the recorded analyses, a sample is taken once a day from the same sampling point which supplies the recording spectrophotometer. This sample is analyzed by the standard Rubber Reserve Corp. volumetric maleic anhydride absorption method. A comparison of the two sets of data for two 7-day periods in January and February 1946 is given in Table I. The agreement must be considered good, when it is realized that the maleic anhydride method is not completely accurate. It is probable that most of the deviation between the spectroscopic and the chemical methods can be ascribed to the latter.

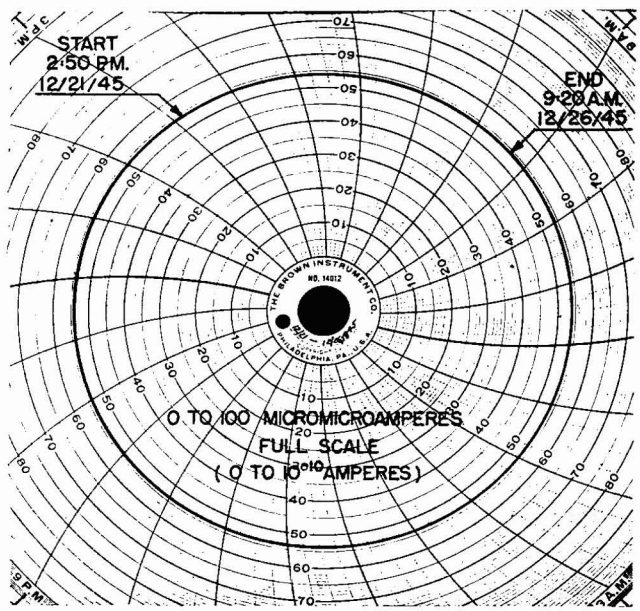

Figure 6. Six-Day Stability Test Record of Electrical Recording System

MAINTENANCE

Up to the present, the recording spectrophotometer herein described has been in continuous service under plant conditions for over a year. During that time its over-all stability has been excellent and it has been remarkably free from maintenance difficulties.

Table I. Comparison of Butadiene Analyses Read from Recording Spectrophotometer with Those Obtained by Maleic Absorption Method[a]

Spectrophotometric	Maleic Anhydride	Difference
10.5	10.0	0.5
11.5	11.4	0.1
13.4	12.9	0.5
13.6	13.2	0.4
12.6	11.7	0.9
11.2	10.5	0.7
11.5	11.4	0.1
13.2	13.1	0.1
13.8	13.8	0
13.4	13.1	0.3
14.7	14.1	0.6
13.0	13.0	0
12.0	12.1	0.1
12.4	11.7	0.7

[a] Data from Sun Oil Co., Toledo, Ohio.

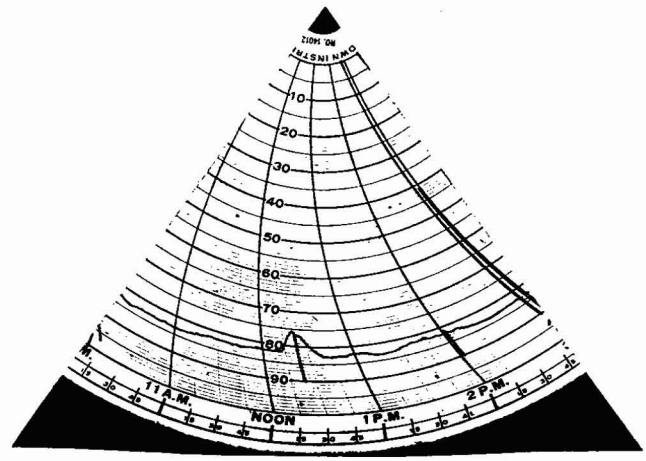

Figure 7. Typical Record of Analysis

When the recording spectrophotometer was first under consideration, it was anticipated that frequent automatic adjustment at both ends of the range would be necessary: that at the "no-illumination" end to take care of variations in the photocell dark current, and that at the empty cell end to take care of variations in the output of the radiation source and the photocurrent amplifier. However, this has not been the case. The dark current adjustment is stable for days, although it is checked routinely once a shift. The empty cell adjustment requires more attention, but even for this a check once a shift is adequate.

All the power required for the recording spectrophotometer is obtained from a 115-volt alternating current line; consequently, there is no problem of battery deterioration and replacement.

ACKNOWLEDGMENT

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Microdetermination of Molecular Weight by a Vapor Pressure Comparison Method

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A method for the microdetermination of molecular weight, based upon the vapor pressure lowering produced in a determinate solution of the sample, is described. The vapor pressure data are secured through the use of two dynamic isoteniscopes of slightly modified design. A weight of 2 to 8 mg. of the sample is ordinarily adequate for a nonvolatile material whose molecular weight does not exceed 700, and the sample is easily recovered at the end of the experiment. There is no theoretical limitation to the choice of solvent. The probable error does not exceed 2%, the measurements are essentially simple, and the time expended in one of a series of determinations is about 2 hours.

A SURVEY of a representative recent text on microtechniques (*5*) provides a view of some of the shortcomings of the four methods most commonly applied to the microdetermination of molecular weights of organic compounds.

The vaporimetric method is limited in its applicability to substances which can be vaporized without decomposition, and so cannot be used for the considerable range of compounds which combine relatively low volatility with thermal instability.

The cryoscopic method, based upon the observed freezing point depression of a determinate solution of the unknown in solvents like camphor or borneol, is not applicable to the considerable variety of materials which either do not dissolve in camphor, borneol, etc., or do not form approximately ideal solutions in these solvents.

Ebullioscopic methods yield results of an order of accuracy which Friedrich (*2*) avers is poor, and which is seldom claimed to be better than 5%. The method is restricted in its applicability to those solvents which show a satisfactorily large molar boiling point depression, and a rather large sample, varying from 10 to 25 mg., must be used.

Methods which rely on isothermic distillation to produce solutions of equal molarity are of considerable generality and accuracy, but as much as one or two weeks are often required for the solutions to come to equilibrium concentration. Certain semimicro adaptations of this method (*1*) are said to produce equilibrium within 3 days, but a rather large sample is required.

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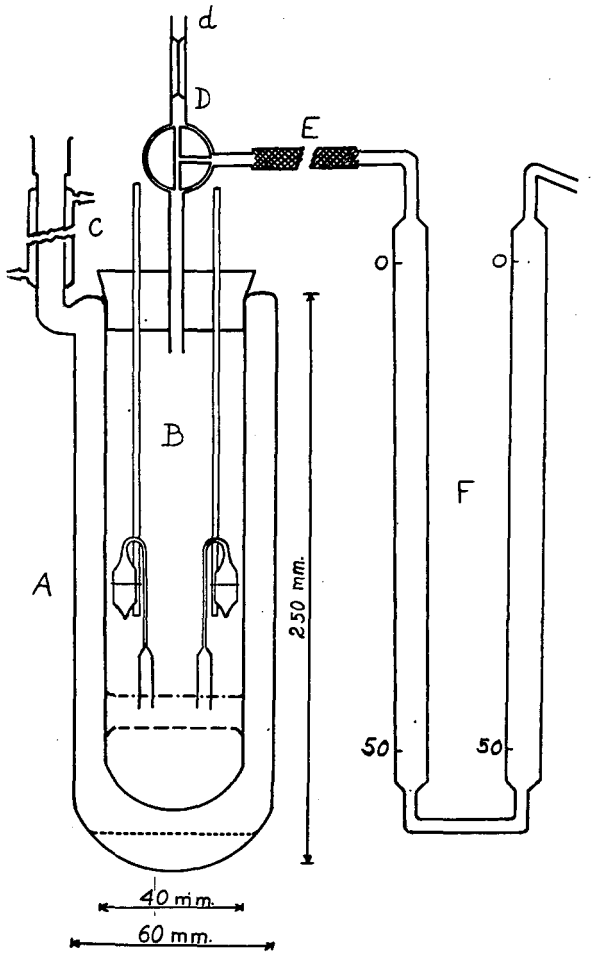

Figure 1. Apparatus

An isothermic method in which, instead of allowing time for two solutions to come to equal molar concentration, there is a direct, immediate measurement of the vapor pressure lowering produced by solution of a known weight of solute in a known weight of solvent appears to possess certain advantages. The solute so studied must not be appreciably volatile at the boiling point of the solvent, but there is no restriction on the nature of the solvent, as in cryoscopic and ebullioscopic methods, since, at low concentrations, solutions in any solvent tend to obey Raoult's law equally well. This relatively unrestricted range of applicability is accompanied by a high potential accuracy. Menzies has indicated (*4*) that a benzene solution showing a boiling point depression of but 0.1° C. would show a vapor pressure lowering (at the boiling point of pure benzene) of 32 mm.

Menzies and others have described molecular weight determinations based upon measurement of vapor pressure depression, but it does not appear that any microdetermination based on this plan has been attempted. Modification of the Smith and Menzies submerged bulblet method for vapor pressure determination (*6*) might, however, be expected to provide the requisite vapor pressure data for the microdetermination of molecular weights.

APPARATUS

The apparatus designed for these studies is illustrated in Figure 1. *A* represents a constant-temperature jacket, wound with several layers of sheet asbestos, in which windows are cut to allow observation of the lower ends of the bulbs shown. The bulbs are supported by glass rods inserted through holes in the stopper. Application of glycerol to the rods at the points at which they pass through the stopper makes it possible to raise or lower them at will. About 20 cc. of the solvent to be used in the determination are placed in *A*, together with some glass beads to promote even boiling. When the solvent boils under the reflux condenser, *C*, the inner tube, *B*, and its contents soon come to a uniform constant temperature close to the boiling point of the solvent. A guard tube containing calcium chloride is inserted in the top of *C*, to prevent contamination of the solvent with water vapor.

The inner chamber, *B*, which contains the bulbs in which measurements are to be made, contains a 3-cm. layer of mercury on

which is floated a layer of 85% phosphoric acid about 1 cm. deep. *B* is connected through the rubber stopper and a three-way stopcock, as shown, with the butyl phthalate manometer, *F*. A length of rubber tubing, *E*, gives this connection flexibility. To facilitate easy and accurate reading of the manometer the arms of the latter may be fabricated from two 50-cc. burets whose scales are of equal length. The length of the scales may be measured in centimeters, so that each cc. reading can be converted to a linear measurement. The conversion factor may be combined with that used to transpose the butyl phthalate readings to millimeters of mercury.

The third branch of the three-way stopcock can be connected, via *d*, with a water aspirator or a source of compressed air, so that any desired pressure may be produced within the system. A short length of thermometer capillary is inserted in this branch to facilitate precise adjustment of the pressure by restricting the rate of pressure change in the system to a rather low value.

PROCEDURE

Two bulbs of the general shape shown in Figure 2, *a*, are required. The body of the bulb, of a capacity of ca. 0.7 cc., is made of 10-mm. Pyrex tubing. The heavy-walled capillary section is about 8 cm. in length, with interior diameter of ca. 0.3 mm. The lower portion, or shank, of the tube is roughly 3 cm. in length and is made of 8-mm. Pyrex tubing. The two bulbs are thoroughly cleaned and dried, and the bottom tips are then sealed off to give vessels of the shape shown in Figure 2, *b*. Care should be taken to prevent condensation within the bulbs of moisture from the flame.

About 0.5 cc. of the pure solvent is now conveyed into one bulb by alternately introducing a few drops of the solvent into the open end of the tube and then immersing the lower part of the bulb in a dry ice bath.

In preparing the solution bulb, the empty bulb is weighed with an accuracy of a few tenths of a milligram against a counterpoise of like design. Then some 2 to 8 mg. of the sample are introduced into the open end of the bulb from a weighing tube of suitable shape—for example, that shown in Figure 2, *c*. The loss of weight of the weighing tube is determined with an accuracy of a few hundredths of a milligram. Using 0.5 cc. or less of the solvent, the sample is transferred quantitatively into the bulb by adding the solvent to the sample one or two small drops at a time, and then immersing the bulb in the dry ice bath.

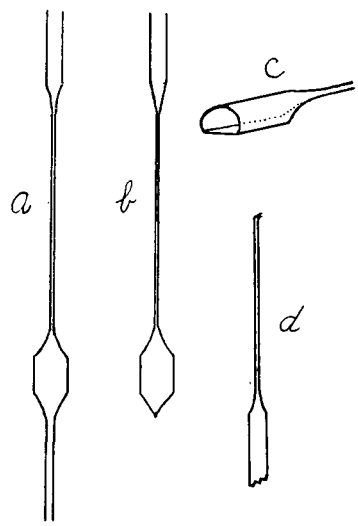

Figure 2. Bulbs

The solvent and solution are now frozen by brief immersion of their respective bulbs in a dry-ice bath. Using a microburner flame, held well away from the open ends of the bulbs, the capillaries are bent so that the containers assume the form shown in Figure 1. The two bulbs are now attached to the glass rods with loops of wire, and the rubber stopper is set in place, so that the configuration shown in Figure 1 is obtained.

The bottom of jacket *A* is heated with a microburner, so that the solvent in the jacket boils briskly under reflux. The positions of the glass rods are adjusted so that the open ends of the bulbs are just immersed in the phosphoric acid layer. With the stopcock in the position shown in the diagram, a weak source of evacuation is connected at *d*. The pressure is slowly diminished until it is lower than atmospheric pressure by a quantity corresponding to about a 55-cm. column of butyl phthalate. At this point, as the right branch of the manometer is drained, bubbles of air are drawn into the system, preventing the pressure from going lower. Thus the manometer is made to serve as a barostat.

Under the reduced pressure the solvent is vaporized, without boiling, from both bulbs. About 8 bubbles a minute emerge from each tube, and within 0.5 hour all the air is swept from the isoteniscopes. During this period the last stages of the preceding run may be completed.

When sweeping is completed both bulbs are lowered by the attached glass rods so that the open ends are immersed to a depth of about 1.5 cm. in the mercury layer. The aspirator is disconnected and the pressure in the system is allowed to revert (slowly) to atmospheric. A pause of 0.5 hour must now ensue, with bubbling prevented by immersion of the open ends in the pool of mercury, to allow both bulbs to come to the temperature of the inner jacket, since both will have been cooled (unequally) by vaporization of the solvent. During this period the samples for the next run may be prepared.

At the close of this equilibration period the level of the mercury inside the solution bulb is brought to approximate coincidence with the mercury level outside. The pressures inside and outside the bulb must then be approximately equal, and the bulb may be raised so that its open end projects a few millimeters into the phosphoric acid layer. Now the pressure within chamber *B* is brought to exact equality with the pressure in the bulb, so that the phosphoric acid levels inside and outside the shank are even. The pressure setting can be made with great sensitivity because the lower edge of the meniscus is picked out as a sharp light line by illumination from behind and slightly below the phosphoric acid level. When matching has been achieved, the stopcock is turned so that *B* is connected only with the manometer. After a pause of about 5 minutes to ensure a true rather than a transient equilibrium the equilibrium pressure is read from the butyl phthalate manometer.

The open end of the solution bulb is now thrust back into the pool of mercury, and, after a preliminary pressure adjustment, the solvent bulb is drawn up to project into the phosphoric acid layer and the pressure balanced, and then read as before. Following this another measurement is made of the pressure in the solution bulb, and then another of the solvent pressure. This completes the pressure readings.

The solution bulb must now be removed from the system without loss of solvent vapor and without allowing any phosphoric acid to suck back into the bulb. To this end the pressures are first balanced roughly, and the solution bulb is raised until its tip is clear of the phosphoric acid layer. The tip should still be sealed with a layer of phosphoric acid not exceeding 2 mm. in thickness. The stopper is then immediately removed, carrying the bulbs with it. As the solution bulb emerges the sealing film at the end of the tube begins to travel upward; but, if it is not too thick, it ruptures almost immediately, so that air is free to enter the bulb. No appreciable quantity of solvent vapor can escape at this point because there is a steady inward flow of air when the sealing film is broken.

Provided that the next run is to be made with the same solvent, it may be started at this point.

When the solution bulb has cooled to room temperature the outside is rinsed with water, and the inner wall of the shank tube is washed out by inserting in the open end of the tube a vertical wash-bottle tip like that shown in Figure 2, *d*. The shank tube is then placed over another tube, shaped like the wash-bottle tip, and by warming the shank with a tiny flame and drawing through a very slow stream of air with an aspirator the tube is dried rapidly. This procedure, when carefully performed, has been shown to yield weights which are reproducible to 0.1 or 0.2 mg.

The bulb is now wiped, and after standing for a few minutes in the balance case, it is weighed with accuracy of a few tenths of a milligram. This completes the determination.

The method of pressure measurement described above would obviously be more nearly ideal if the pressure measurements could be made simultaneously. However, the low density of the phosphoric acid, which makes it ideal as an auxiliary manometer fluid, effectively prevents both bulbs from being held in the phosphoric acid layer at the same time, since the acid would be driven back into the solution bulb by a pressure sufficient to balance the pressure in the solvent bulb, while a pressure that balanced the pressure over the solution would allow bubbles to escape from the solvent vessel. Thus solution and solvent must be studied separately, the tip of the bulb not in use being immersed in the mercury pool which, by its high density, prevents the difficulties listed above.

It has been observed, however, that for a long time after completion of the sweeping-out process there is a slow rise in the vapor pressure in a given bulb, so that it is not possible to compare directly pressure measurements made at different times in the present system. Fortunately, within 0.5 hour after sweeping is completed a plot of observed pressure against time becomes linear—i.e., the rate of pressure rise is substantially constant. Thus if

two measurements are made for each bulb a simple interpolation provides values for the pressures that would have been manifested had they been measured simultaneously.

CALCULATIONS

A standard statement (*3*) of Raoult's law is:

$$\frac{p^0 - p}{p^0} = \frac{\frac{W_2}{M_2}}{\frac{W_1}{M_1} + \frac{W_2}{M_2}}$$

where p^0 is the vapor pressure of the pure solvent and p (measured at the same temperature) is the solvent vapor pressure over a solution prepared by dissolving W_2 grams of material of molecular weight M_2 in W_1 grams of solvent of molecular weight M_1. Denoting $p^0 - p$ as Δp, the above equation may be written as:

$$M_2 = \frac{W_2 M_1 (p^0 - \Delta p)}{\Delta p W_1}$$

whence M_2 may be calculated if the other parameters are determined. M_1 is known at the outset and W_2 is determined directly. p^0 is equal to atmospheric pressure (as read from a neighboring barometer) plus or minus the pressure equivalent of the butyl phthalate column that represented the difference between atmospheric pressure and the pressure in the system which was in equilibrium with the vapor pressure over the pure solvent.

The value of Δp is computed from the vapor pressures of the solvent and the solution calculated for the same time. For example:

Bulb Measured	Time	Time Interval, Min.	Manometer Readings h_1	h_2	Δh
Solution	4:27		37.0	27.1	−9.9
		20			
Solvent	4:47		32.05	32.1	+0.05
		12			
Solution	4:59		36.35	27.7	−8.65
		14			
Solvent	5:13		31.55	32.55	+1.0

The pressures in the bulbs are barometric pressure plus or minus the mercury equivalent of the butyl phthalate columns indicated in the column headed Δh. By linear interpolation Δh values are calculated for solvent and solution at the same moment.

$$\text{Solution at } 4{:}47 = -9.9 + \frac{20}{32}(1.25) = -9.9 + 0.8 = -9.1$$

Comparing this with the Δh value for the solvent at 4:47 we find

$$L = 0.05 - (-9.1) = 9.15$$

where the pressure difference between solution and solvent is represented by a butyl phthalate column of length L. A second value of L, for 4:59, is calculated similarly. The average value for L is converted to the equivalent pressure in centimeters of mercury and substituted as Δp in the above formula.

For W_1 we have:

W_1 = final weight of bulb + solution − initial weight of empty bulb − weight of solute

but this figure for W_1, while accurately reflecting the weight of solvent present at the end of the experiment, is greater than the weight present at the time of the pressure measurement by the weight of the solvent vapor then present in the free space of the bulb. To determine this correction factor the free volume in the bulb must be estimated. This estimate is most conveniently secured after the final weighing of the experiment, by roughly determining the gain of weight that ensues when the solution bulb is completely filled with the solvent employed. From this weight gain and the density of the solvent the volume of the free space is computed. The subtractive correction for the weight of the solvent may then be deduced from the gas-space volume and the temperature and pressure prevailing during the experiment.

The correction factor in the weight of the solvent is a marginal one, of the order of 1 mg., and may generally be ignored. However, in cases in which less than 0.050 gram of solvent is present (because a particularly small sample or one of rather high molecular weight was used) the correction may be used. After some experience it may be estimated with sufficient accuracy by inspection.

Table I. Molecular Weight Determinations

Solute	Solvent	Formula of Solute	Molecular Weight of Solute Calculated	Molecular Weight of Solute Experimental
Tri-triacontane	Benzene	$C_{39}H_{72}$	542.0	526 552 543
Naphthalene	Chloroform	$C_{10}H_8$	128.2	130.7 131.3
2-Methyl-β-naphthoflavone	Chloroform	$C_{20}H_{14}O_2$	286.3	288.5
10-Phenyl-perhydroquinoline	Toluene	$C_{15}H_{21}N$	215.3	218.0
2-Phenyl-2-(2 cyanoethyl)-cyclohexanone	Carbon tetrachloride	$C_{15}H_{17}NO$	227.3	223.5
n-Hexacosane	Hexane	$C_{26}H_{54}$	366.7	369 360
sym-Triphenyl benzene	Benzene	$C_{24}H_{18}$	306.4	302

All the other terms now being known, M_2 may be computed from Raoult's law. The results of some determinations by this method are shown in Table I. Where several values are given for one compound they represent the results of duplicate determinations.

DISCUSSION

The probable error of a determination by this method is seen to be about 2%. Any attempt to secure still greater accuracy appears unpromising since the nonideality of actual solutions would become a disturbing factor of increasing importance. It is notable, however, that the solutions used in this method are only about 0.01 *M* in concentration, and so provide a closer approach to ideal behavior than the much more concentrated solutions required in ebullioscopic and cryoscopic methods. The vapor pressure lowering in a 0.01 *M* solution, at the boiling point of the solvent, corresponds to approximately 10 cm. of butyl phthalate, and can easily be measured with adequate accuracy.

Ordinary reagent grade solvents were used throughout, without further purification, since any errors due to small amounts of impurity in the solvent are largely cancelled in this essentially comparative method. All the solvents used appear to be equally satisfactory, as was anticipated. To make a change from one solvent to another it is necessary merely to replace the old solvent in the constant-temperature jacket with the new one, so that the measured vapor pressures will be close to atmospheric pressure, and the balancing pressures will fall within the range of pressures measurable with a small butyl phthalate manometer with reference arm open to the atmosphere.

Alcohols, ethers, acetone, etc., react with phosphoric acid, and so cannot be used with this sealing fluid. However, other sealing media suitable for use with these solvents may be found. A satisfactory sealing medium (1) must be transparent; (2) must have moderate viscosity and density close to 1; (3) must have low volatility at the temperature of the boiling solvent; and (4) the sealing medium must neither dissolve nor react with the vapor of the solvent in use. For use with most of the common solvents 85% phosphoric acid meets these conditions fairly. Some recent trials indicate that somewhat more reproducible results may be obtained with 95% phosphoric acid (prepared by adding an appropriate quantity of phosphorus pentoxide to 85% phosphoric acid), presumably because of the lower aqueous tension over the more concentrated reagent.

Although the solutes treated by this method should be of relatively low volatility, even a material as volatile as naphthalene can be handled satisfactorily if the sweeping-out period is held to the bare minimum. Determinations have been made by this method with materials of molecular weight as high as 1100, but in this extreme range the accuracy is no better than 5%, and the

experimental difficulties are considerable. Practically speaking this method is primarily useful for materials of molecular weight under 700.

The *conditio sine qua non* for success in this method is that both bulbs be treated as closely alike as possible to take full advantage of the tendency toward cancellation of errors characteristic of a comparative method. In particular, small changes of barometric pressure produce no significant aberrations in the results. No hydrostatic effects can occur, since the measurement is made with the menisci inside and outside the bulb's shank at the same level. Capillarity effects must be rather small because of the rather large diameter of the shank tubes and, in any case, would alter solvent and solution values to the same extent, and so cancel. The condensation of water within the bulbs during their preliminary immersions in the dry-ice bath has been shown to be of negligible extent, provided that cooling is not unduly prolonged. Similarly, the loss of vapor from the bulb before the final weighing is not an appreciable factor. Because of the long capillary through which the vapor must diffuse when escaping, the bulb's loss of weight amounts to only about 0.1 mg. per hour. Consequently a weighing made within 0.5 hour of the end of the run, and with an accuracy of but 0.2 to 0.3 mg., will not be significantly affected.

ACKNOWLEDGMENT

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Fluorometric Determination of Microgram Quantities of Boron

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A new, highly sensitive method for the quantitative determination of boron is based on the intensity of greenish-white fluorescence obtained upon addition of benzoin, in slightly alkaline 85% ethanol solution. Studies have been made of the effects of such variables as time of standing, type of alcohol, and concentrations of benzoin, alkali, and water. It is essential for the success of the method that these variables be carefully controlled. Intensity of fluorescence is shown to be a linear function of boron concentration in the range from 0 to 10 micrograms, in a volume of 50 ml. Excellent results were obtained in determining such amounts of boron in pure solution, the accuracy being 1 or 2 parts per hundred. This method has been applied successfully to determining a few thousandths of 1% of boron in steel. The highly specific separation by distillation of methyl borate serves as a preliminary removal of interfering elements. The method serves for the qualitative as well as quantitative analysis of boron.

VERY small amounts of boron have been found significant in soils and plant nutrition, and a few thousandths of 1% is of importance in steel manufacture (*3*, *4*). Conventional gravimetric (*13*) and distillation-titration methods (*2*, *8*) are not suited for the determination of microgram quantities of boron.

A variety of colorimetric reagents have been proposed. Quinalizarin (*1*, *12*, *16*) is representative of the polyhydroxy aromatics, which form chelation compounds with boric acid in concentrated sulfuric acid. Other such reagents are Chromotrop 2B (*14*) and alizarin S (*5*); for all these, the use of concentrated sulfuric acid as solvent involves a loss in convenience. The highly sensitive turmeric reaction (*7*, *9*) does not suffer from this disadvantage, but requires a more lengthy procedure.

A few fluorescence reactions have been described for the detection of boron, but not for its quantitative determination. Among the reagents used are flavonols (*15*), 1-amino-4-hydroxyanthraquinone (*11*), and *o*-hydroxycarbonyl compounds such as resacetophenone (*10*). Again, the latter two require the use of concentrated acid solutions.

In describing benzoin, C_6H_5-CO-CHOH-C_6H_5, as a fluorescence reagent for zinc, White and Neustadt (*17*) noted that in alkaline solution it also gave a fluorescence with boron, antimony, and beryllium. Further work showed that the intensity in alcohol solution was great enough to detect small traces of boric acid, so that the present procedure was evolved as a new quantitative method for the determination of boron in microgram amounts. Distillation of methyl borate was used as a separation from possible interferences.

APPARATUS AND REAGENTS

Measurements of fluorescence intensity were made with the Lumetron fluorescence meter, model 402EF, using a 4.77-mm. thickness of Corning violet ultra No. 5860 as the primary filter, and sheets of Wratten 2A gelatin as the secondary filters. The relation of the transmissions of these filters to the boron-benzoin greenish white fluorescence band at 4400 to 6300 Å. is shown in Figure 1. Turbidity in the solution causes no error, because light which is passed by the primary filter cannot get through

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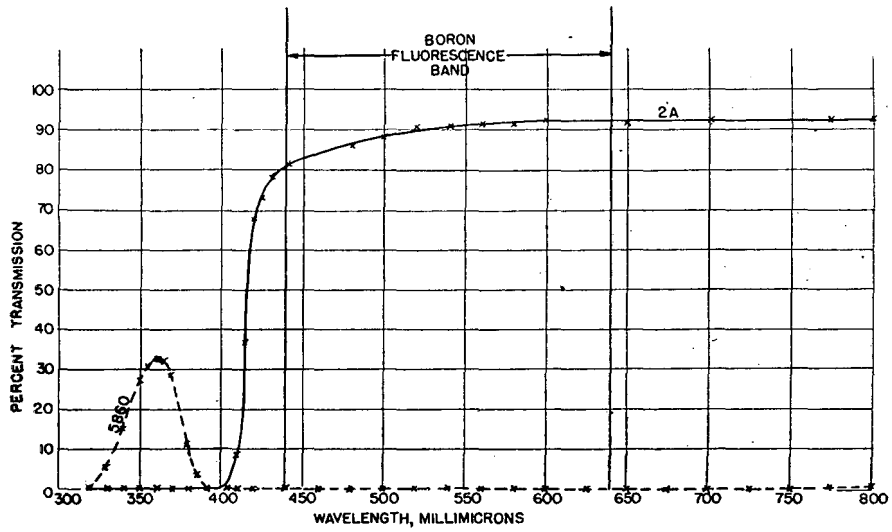

Figure 1. Transmittance of Primary (5860) and Secondary (2A) Filters

the secondary filters to the photocells. The scale of the instrument was readjusted arbitrarily for each experiment.

In order to avoid boron contamination from glassware, vessels of platinum or quartz were used wherever possible. An all-silica distilling apparatus, used in the analysis of steels, consisted of a 100-ml. distilling flask closed at the top by a ground joint, and connected by another ground joint to a condenser tube about 50 cm. long and 10 mm. in diameter, which was cooled by a water jacket.

Benzoin solution, 0.5%, was prepared by dissolving 2.50 grams of benzoin (recrystallized twice from alcohol) in 500 ml. of redistilled 95% ethyl alcohol. All ethyl alcohol was redistilled before use, in order to eliminate fluorescent impurities. Absolute methyl alcohol, C.P., and isopropyl alcohol were used without further purification.

Standard boron solution A, 1.00 ml. = 0.100 mg. of boron, was prepared by dissolving 0.5716 gram of analytical reagent boric acid in water and diluting to 1 liter. A weaker solution, B, containing 0.010 mg. of boron per ml., was prepared by tenfold dilution of A. By fivefold dilution of B, a still weaker solution, C, was prepared, having 2.0 micrograms of boron per ml.

Sodium hydroxide solution, 0.6 *N*, was prepared by dissolving 24 grams of C.P. sodium hydroxide in water in a platinum dish, transferring to a quartz flask, and diluting to 1 liter.

EXPERIMENTAL WORK

Preliminary investigations showed that in approximately 85% alcohol solution containing about 0.02% of benzoin and a little sodium hydroxide, the intensity of fluorescence increased when the boric acid concentration was increased. But the intensity was also greatly affected by time of standing, concentration of benzoin and of alkali, and the order in which the reagents were added. Therefore it was necessary first to study the influence of each variable individually, holding the others constant. The temperature was 25° ± 2° C. in all these experiments.

Time of Standing. In a 50-ml. volumetric flask, 1.0 ml. of standard solution B (containing 0.010 mg. of boron) was mixed with 1.0 ml. of 0.6 *N* sodium hydroxide, and diluted immediately to about 45 ml. with ethyl alcohol. Then as rapidly as possible 4.0 ml. of 0.5% benzoin solution were added, a stop watch was started, and the mixture was diluted to the mark with alcohol and shaken vigorously. Half of this was poured into the 25-ml. cell and placed in the instrument. Readings of fluorescence intensity were taken at 1-minute intervals, under continuous irradiation. After 10 minutes, the solution in the cell was discarded and replaced by the other half of the original mixture. Readings were again taken at 1-minute intervals.

As shown in Figure 2, the fluorescence increased at first, reached a maximum after about 4 minutes, and then dropped off smoothly. The portion of the same solution which was not exposed to ultraviolet rays showed a relatively high intensity at first, but then decreased rapidly. The graph suggests two antagonistic influences: the gradual formation of the fluorescent compound or colloid by a slow reaction, and its destruction by oxidation, photochemical processes, or the formation of larger particles which settle from the solution.

The experiment was repeated using 0.100 mg. of boron, ten times as much as before; very similar results were obtained.

Because of the usefulness of the methyl borate distillation, methyl alcohol was tried as the solvent instead of ethyl alcohol. The boron content was 0.010 mg. and the other conditions were kept the same. The rise and decay of fluorescence were found to be more gradual than before. When 0.100 mg. of boron was used, in still another methanol run, the readings became fairly constant, but the intensity was very much less than in ethanol solution; consequently, the use of methanol was abandoned.

Concentration of Sodium Hydroxide. A series of ten solutions was prepared and mixed in the manner previously described; each contained 4.0 ml. of benzoin, varying amounts of 0.6 *N* sodium hydroxide solution up to 4.0 ml., and 5.0 ml. of solution C equivalent to 0.010 mg. of boron. Maximum fluorescence was obtained by the use of about 0 25 ml. of 0.6 *N* sodium hydroxide in the 50-ml. volume, as is seen in Figure 3. It was found in this and subsequent experiments that satisfactory and reproducible readings could be obtained 2 minutes after mixing, but the interval must be timed accurately and the technique carefully standardized.

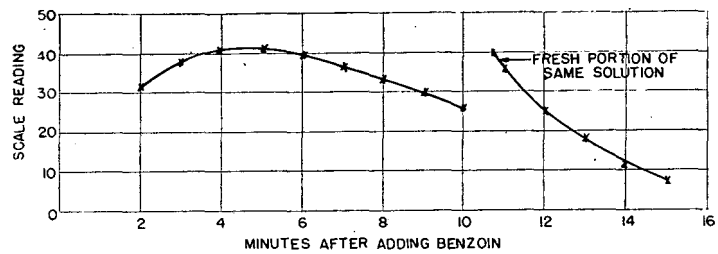

Figure 2. Change of Fluorescence with Time

0.010 mg. of boron in ethanol

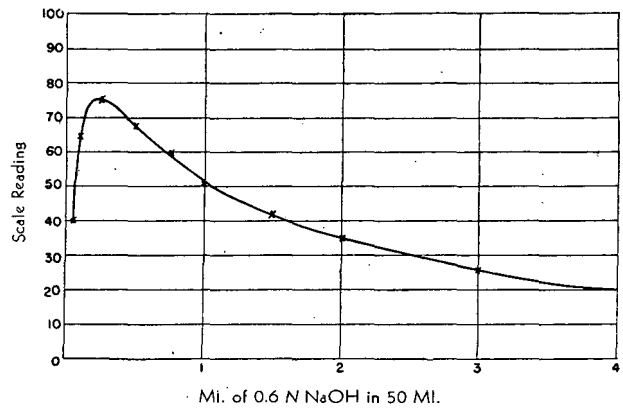

Figure 3. Effect of Sodium Hydroxide Concentration on Fluorescence

The experiment was repeated at the higher concentration of 0.100 mg. of boron. A curve of the same general shape was obtained, with the maximum again at about 0.25 ml. of sodium hydroxide.

Concentration of Benzoin. A series of solutions was prepared in the usual manner, each containing 0.50 ml. of 0.6 *N* sodium hydroxide, 5.0 ml. of boron solution C, and various amounts of 0.5% benzoin solution up to 7.0 ml. Readings taken 2 minutes after mixing gave the results depicted in Figure 4. The curve is approximately parabolic, which means that the intensity is proportional to the square root of the concentration of benzoin.

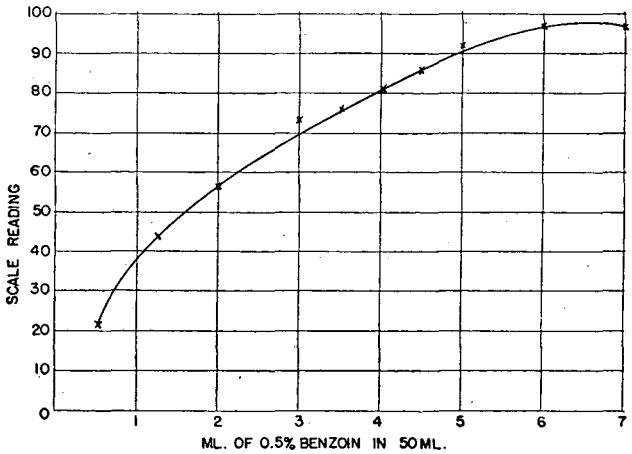

Figure 4. Effect of Benzoin Concentration on Fluorescence

Concentration of Water. Inasmuch as the reaction takes place in alcohol solution, it was not surprising to find that the amount of water present affected the intensity. Ten solutions were prepared as usual, each containing 1.0 ml. of solution A equal to 0.100 mg. of boron, 1.0 ml. of 0.6 *N* sodium hydroxide, 4.0 ml. of 0.5% benzoin, and various amounts of added water up to 10 ml. Figure 5 shows that the intensity measured 5 minutes after mixing decreased considerably as the water content increased, so that it was necessary to control closely the amount of water, as well as of sodium hydroxide and benzoin, in the later quantitative determinations.

Concentration of Boron. Next it was necessary to find out whether the fluorescence increased uniformly with the boron content. A set of solutions was prepared in the customary fashion, containing various quantities of standard solution A plus sufficient water to make the sum equal 5.0 ml. As seen in Figure 6, the intensity increased in a fairly uniform manner up to about 0.350 mg. of boron, and then leveled off.

A smaller range of concentration was investigated more thoroughly, from 0 up to 0.050 mg. of boron in the 50-ml. volume. In this region the graph was found to be nearly a straight line. When the region from 0 to 0.010 mg. was studied more intensively, an almost perfectly linear relation was obtained (Figure 7). Consequently, all the analyses performed later were within this lowest range of concentrations. An additional advantage was the smaller sample weight of steel required, which facilitated the solution and distillation of the sample.

Other alcohols than ethyl were tried as solvents. Isopropyl alcohol gave a linear relation up to about 0.050 mg. of boron, but methyl alcohol under the given conditions showed a rather irregular increase of intensity with boron concentration up to 0.100 mg. The fluorescence was strongest by far in ethanol, however.

In all these experiments the solutions had to be shielded from bright sunlight, which caused the fluorescence to decrease greatly.

Determination of Boron in Pure Solution. The above findings were applied to the determination of boron by fluorometry.

Known amounts of boron (as boric acid) dissolved in 5.0 ml. of water were mixed with 0.50 ml. of 0.6 *N* sodium hydroxide in a 50-ml. glass-stoppered volumetric flask, and diluted to about 45 ml. with ethyl alcohol. Then 4.0 ml. of 0.50% benzoin were added, a stop watch was started simultaneously, and the solution diluted to the mark with ethanol. It was shaken vigorously, the requisite amount was poured into the cell, and the fluorescence intensity measured exactly 2 minutes after the addition of the benzoin. The amount of boron present was determined by reference to a standardization graph, constructed by drawing a straight line through two points given by standard solutions containing 0.000 and 0.010 mg. of boron, respectively. The standard solutions were prepared in the same manner and at the same time as the "unknowns."

Excellent results were obtained by the above procedure, the average error for these microgram quantities of boron being only 1.5%, as shown in Table I.

Table I. Determination of Boron in Pure Solution

Boron Added *Micrograms*	Boron Found *Micrograms*	Error %
0.0	0.00	...
	0.02	...
	0.05	...
2.0	2.00	0.0
	2.06	3.0
	2.10	5.0
4.0	3.88	3.0
	3.94	1.5
	4.10	2.5
5.0	4.90	2.0
6.0	5.97	0.5
	5.99	0.2
	6.01	0.2
8.0	7.83	2.1
	7.88	1.5
	7.82	2.3
9.0	8.92	0.9
10.0	10.02	0.2
	9.98	0.2
	9.95	0.5
	Av.	1.5

Determination of Boron in Steels. Finally, it was desired to apply the procedure to the analysis of the industrially important material steel, in which the presence of 0.002 or 0.003% of boron may or may not affect the mechanical properties. It is obvious that in this method for the determination of boron, ions which are precipitated by dilute sodium hydroxide, as well as salts which are insoluble in alcohol, must be removed. In addition, beryllium and antimony give a fluorescence under similar conditions to boron and cannot be tolerated.

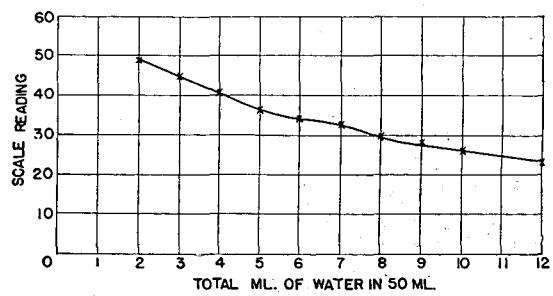

Figure 5. Effect of Water Concentration on Fluorescence

Preliminary experiments showed that mercury cathode electrolysis was not a suitable separation, because of the alcohol-insoluble salts produced by neutralization of the acid electrolyzate. Since filtrations of heavy precipitates are objectionable in the determination of the microquantities desired, the separation of boron by distillation as methyl borate was decided upon.

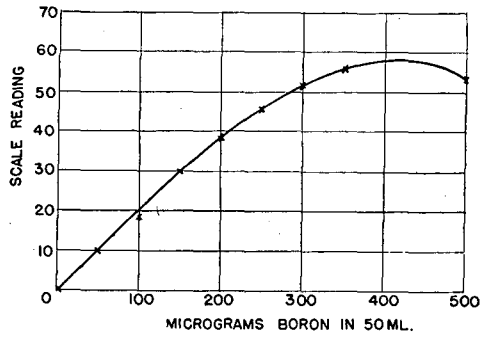

Figure 6. Relation of Fluorescence to Boron Concentration, High Range

The method finally evolved for the determination of acid-soluble and acid-insoluble boron in steel was as follows:

A 0.100-gram sample of steel was transferred to the 100-ml. flask of the all-silica distilling apparatus, 5 ml. of 1 to 4 sulfuric acid were added, and the apparatus was connected up as for a distillation, the receiver being a 300-ml. platinum dish containing 0.50 ml. of 0.6 *N* sodium hydroxide. The flask was warmed until the steel dissolved completely; usually a drop or two of liquid distilled over. Then a silica boiling chip and 40 ml. of methanol were added to the flask, and the contents were distilled down to a few milliliters, where salts started to separate out. The flask was cooled in ice water, 30 ml. of methanol and another boiling chip were added, and the contents were distilled down to the separation of salts again, the distillate being collected in the same receiver. The well-mixed distillate was evaporated to dryness, and the residue dissolved in 5.50 ml. of water. Then about 20 ml. of ethanol were added, and the slightly turbid mixture was transferred to a 50-ml. volumetric flask and diluted to about 45 ml. with alcohol. Simultaneously with the starting of a stop watch, 4.0 ml. of 0.50% benzoin were added, and the solution was diluted to the mark with ethanol and shaken well. The required volume was poured into the cell, and the fluorescence measured exactly 2 minutes after the addition of the benzoin. Standards prepared similarly, except for distillation, were used to construct a standardization graph of scale reading against boron concentration, from which the percentage of boron present could be determined. This gave the amount of acid-soluble boron in the steel.

In order to determine the acid-insoluble boron, the residue remaining in the flask after the second distillation was dissolved in 15 ml. of hot water and filtered through the retentive No. 42 Whatman paper. The filtrate and washings were discarded, and the filter paper was sprinkled with about 100 mg. of anhydrous sodium carbonate and ignited in a platinum crucible until most of the carbon had disappeared. The residue was fused for a minute or two, allowed to cool, dissolved in 5 ml. of 1 to 4 sulfuric acid, and transferred to the distilling flask with 40 ml. of methanol. From this point on, the procedure was exactly the same as for the acid-soluble portion: double methanol distillation into 0.50 ml. of alkali, evaporation of the distillate to dryness, solution in 5.50 ml. of water, and addition of reagents and measurement of fluorescence in the usual manner. The blank was determined by running a boron-free steel through the entire procedure; it amounted to about 0.0015% of boron. This is admittedly a relatively high blank; however, it must be considered that it involves only 1.5 micrograms of boron.

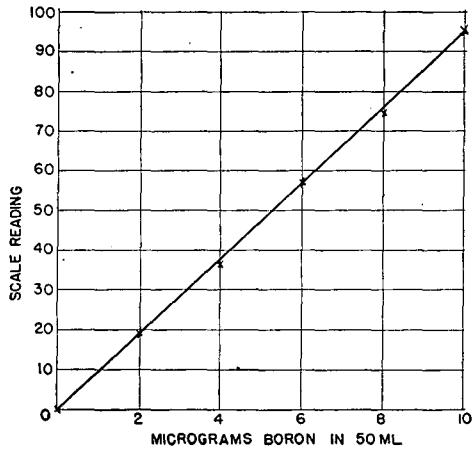

Figure 7. Relation of Fluorescence to Boron Concentration, Low Range

Analyses of some Bureau of Standards steels by the above method are listed in Table II. The sums of the acid-soluble and acid-insoluble boron contents found, minus the blank, were close to the certified values. However, low results were obtained on steels of higher boron content, presumably because of losses during the distillation or evaporation. It was nevertheless felt that the new method is fundamentally sound, because the distillation is a standard method and the validity of the fluorometric determination in pure solution was proved beyond question.

SENSITIVITY

Using the relative quantities of reagents and alcohol indicated above it is easy to detect both visually and on the instrument as little as 0.2 microgram of boron. With a simple visual comparator (*6*) one can distinguish without difficulty 0.2, 0.5, and 0.8 microgram in 10 ml. of solution. The range on the photoelectric instrument is indicated in Figure 7. This is more sensitive than the visual method and differences of 0.1 microgram can be distinguished.

Table II. Determination of Boron in Bureau of Standards Steels

Steel	Certified Value %	Found %
825	0.0006	0.0007
		0.0005
		0.0005
826	0.0011	0.0013
		0.0011
		0.0009
		0.0010
151	0.0027	0.0028
		0.0028
		0.0025
		0.0027

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Detection of Drugs in Horse Saliva

Comparison of Sensitivities of a Chemical and a Biological Method

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Comparison of a chemical and a biological method for detecting drugs in horse saliva shows that the chemical method is both more sensitive and more reliable.

THE examination of horse saliva and urine for the possible presence of drugs is a routine procedure in states in which horse racing has been legalized. Standard chemical toxicological methods adapted to the recovery and identification of drugs in such materials have ordinarily been used. Biological methods have been used extensively in toxicological investigation (*5*) and in the standardization of certain crude drugs, a number of such procedures being official in the United States Pharmacopoeia.

A biological method for the "screening" of saliva and urine samples from race horses has recently been recommended to racing authorities and is being used in several states. It (*4*) consists of injecting intraperitoneally into male white mice weighing 15 to 20 grams an aliquot of a sample of urine or saliva and observing the reactions of the mice for a period of 15 minutes. If the responses of the mice are abnormal, the remainder of the sample is chemically analyzed; if no abnormal responses are noted, the sample is discarded without further investigation.

If the biological screening procedure were reliable, the elimination of negative samples and the segregation of suspicious samples would be of real value. Its use would greatly accelerate the reporting of negative samples, which constitute the large majority of samples examined. The necessity for chemical analysis would be limited to suspicious samples, and a considerable financial saving would be made.

Because results of experiments comparing the sensitivities of the biological and chemical methods in the detection of drugs in horse saliva and urine have not been published, the present investigation was undertaken. Except for certain experiments with drug-free horse urine, its scope was limited to horse saliva. (Saliva, as referred to herein, consisted of a mixture of saliva and the water used in its collection by the routine technique employed at New York race tracks.)

EXPERIMENTAL

Biological Method. In the evaluation of the biological method 730 male white mice were used. The mean weight for the group was 17.6 grams with a standard deviation of 3.4 grams. The mice were obtained from three sources: Carworth Farms (C.F.W. strain), Animal Supply and Research Co., Brooklyn, and College of Physicians and Surgeons, New York.

Samples of horse saliva and of horse urine were obtained by official veterinarians of the New York State Racing Commission from thoroughbred race horses owned by reputable stables, after the reason for securing the samples had been explained to the horses' trainers. These precautions were taken to preclude the possibility of having in the control group a sample from a horse which had received medication.

To determine the sensitivity of the biological method for the detection of drugs in horse saliva, eight samples of horse saliva were pooled and 1 ml. of this pooled saliva containing a known concentration of a drug in solution was injected intraperitoneally into each of six mice. The mice were observed for 15 minutes, and changes in the character of the gait, hair, respiration, tail, posture, and reaction to mechanical stimuli, such as sudden noise, a blast of air, a touch with a rod, etc., were noted for each animal. Control mice were injected with drug-free saliva. The concentration of drug in the saliva was increased until two end points were reached. The first was the smallest quantity of drug (threshold dose) required to produce abnormal responses in a majority of the mice but equivocal or no responses in the remainder. The second end point was the smallest quantity of drug (positive dose) required to produce unmistakable effects in each of the injected mice.

The diagnosis of abnormal responses in the mice is largely subjective, and, therefore, the determination of the positive and threshold doses is approximate. They are, however, useful quantitative expressions of the order of magnitude of dosage required to produce overt biological effects in mice.

Chemical Method. The chemical method used was the routine one employed by the New York State Racing Commission Laboratory, which is an adaptation of well-known toxicological procedures. It comprises a preliminary purification and reduction in bulk, a semimicro modification of the Stas-Otto extraction technique as described by Autenrieth (*1*), and an identification procedure similar to that suggested by Stephenson (*6*), using a selected group of chemical reagents to produce crystalline test forms and colored reaction products. Test forms or colors thus obtained are compared with controls prepared from known drugs.

The sensitivity of the procedure was determined by adding progressively decreasing amounts of drugs to 100-ml. portions of saliva sample composites. When these solutions were analyzed, the smallest amount of each drug which could be definitely identified was noted. At least two positive tests were the minimum required for definite identification. In the course of this and previous similar work more than 400 such analyses were made. The quantity of a drug which could be definitely identified in a majority of samples but not necessarily in all was termed the "threshold" amount of that drug. The quantity which was adequate for definite identification in all samples was called the "positive" amount. These two quantities indicated the practical sensitivity of the method toward each drug.

Table I. Incidence of Abnormal Responses and 48-Hour Mortality in Mice Following Injection of Normal Horse Saliva

No. of Normal Horse Saliva Samples Investigated	Time between Collection and Injection	No. of Mice Injected	Mice Showing Abnormal Responses	48-Hour Mortality
	Hours		%	%
10	48, room temperature	60	70	88
9	24, refrigerated	54	22	69
10	Less than 1	60	30	65

Results. The threshold doses of 12 drugs were compared in mice obtained from the three sources mentioned above. There was no detectable difference in the sensitivities of the mice to the action of these drugs, and it was therefore concluded that the mice from these sources could be mingled for this investigation.

Twenty-nine samples of drug-free horse saliva, arbitrarily divided into three groups as indicated in Table I, were examined to determine whether they had any detectable effect when injected into mice. The effect of injection of horse saliva was compared with that of intraperitoneal injection of isotonic saline in a control group of mice. Even fresh saliva or saliva which had been refrigerated for 24 hours produced detectable signs in an appreciable fraction of the experimental animals. The high 48-hour

mortality rate, observed following the injection of all saliva samples, is not surprising in view of the well-known contamination of saliva with a large variety of microorganisms.

Drug-free horse urine was injected into mice to determine whether any abnormal responses would occur. Of ten samples investigated, six produced striking effects consisting of labored respiration followed by convulsions and death. All the specimens which had this biological effect, as well as two samples which failed to produce reactions in the mice, were carried through the chemical procedure; none of them revealed the presence of a drug. As it was considered possible that the pH of the urine might be a factor in the production of the toxic manifestations in mice, two of the urine samples which had had no biological effect were pooled, and the pH was progressively decreased from 8 to 3 by the addition of sulfuric acid. (In a series of 307 official urine samples, 28% had a pH of 4, indicating that horse urine is frequently quite acid.) At a urine pH of 8 no deaths occurred within 15 minutes following injection in ten mice; when the pH was adjusted to 3, 60% of the injected mice died in convulsions within 10 minutes. At intervening pH levels the mortality averaged 40%.

The results of determinations of the positive and threshold doses by the two methods are summarized in Table II. The 20 drugs chosen for these experiments were pharmacological agents either known to have been administered to race horses or suspect because of their pharmacological effect in other species.

In examining the experimental results presented in Table II, it should be kept in mind that the drugs were detected in 1 ml. by the biological method and in 100 ml. by the chemical procedure. The volume of solution which can be administered intraperitoneally to a mouse is sharply limited, whereas there is no such limitation of volume in the chemical method. As can be seen from Table II, seven of the drugs at the positive dose level and six at the threshold level can be detected in smaller absolute quantities by the biological than by the chemical procedure. However, in evaluating the relative sensitivities of the two procedures from a practical standpoint, the volumes of solution used for analysis must be considered. When these are taken into account, it is apparent that in no instance is the sensitivity of the biological method equal to that of the chemical one at either dose level.

To test the reliability of the values obtained by each method, this table was given to an impartial referee who prepared two series of unknown saliva solutions which either contained drugs in the dosages specified by the biological or chemical method or were blank. Because the work was necessarily done at a time when the chemical staff had other demands, chemical threshold quantities were not included in the series of unknowns. The unknown solutions were submitted to the chemist and pharmacologist, who evaluated them by their respective procedures. The total number of unknown solutions to be analyzed, the number of blanks to be included in the series, and the number of drugs which would be used in the experiment were not known to the examining participants. The results obtained by each method were not compared until examination of all the unknown samples had been completed (Table III).

Table III shows that each drug in the samples containing them was detected and correctly identified by the chemical method and that each blank was correctly reported. Atropine and hyoscyamine were not differentiated, because, being optical isomers, they give identical tests with the reagents used. Diacetylmorphine was hydrolyzed to morphine during analysis and was accordingly isolated as such. Photomicrographs were made of all crystalline test forms obtained.

The error of the biological method was not inconsiderable. However, statistical analysis of the results obtained by this method showed that the success of detection could not occur by chance alone. The largest proportion of errors occurred in the recognition of the blanks. This was to be expected in view of the appreciable incidence of abnormal responses which occurred in mice following the injection of drug-free horse saliva. It is evident from this experiment that the values recorded in Table II are in the main reasonable. Comparable values given in the literature for brucine and strychnine (*2*) and for morphine, dilaudid, and heroin (*3*) are in substantial agreement with those here reported. Munch (*3*) gives a lower value for codeine.

DISCUSSION

The control experiments with 29 samples of drug-free horse saliva indicate that the age of the samples and the conditions under which they are kept is an important factor in determining the type of responses in mice following injection. Were the biological method to be used for the detection of drugs in horse saliva, the tests should be run as soon as possible after the collection of the saliva samples. Even if saliva is injected very shortly after collection, a certain proportion of mice will respond in an abnormal manner, leading to a postive diagnosis.

The incidence of toxic effects following injection of drug-free horse urine into mice makes it likely that a considerable percentage of false positives would eventuate if this medium were used in a biological screening program. Certainly the pH of each urine sample should be determined as a possible aid in the interpretation of positive effects.

The comparison of the absolute sensitivities of the biological and chemical methods at the positive dose level reveals that the biological is more sensitive than the chemical method in the detection of 35% of the drugs, less sensitive for 55%, and equally

Table II. Comparison of Absolute Sensitivities

Drug	Threshold Amount		Positive Amount	
	Biological	Chemical	Biological	Chemical
	Mg.	*Mg.*	*Mg.*	*Mg.*
2-Aminoheptane sulfate (tuamine sulfate)	0.10	0.10	0.50	0.50
Amphetamine, racemic (benzedrine)	0.03	0.10	0.10	0.20
Atropine	0.75	0.05	2.00	0.25
Brucine	0.50	0.025	1.00	0.25
Caffeine	1.50	0.10	3.00	0.20
Cocaine	0.35	0.075	0.50	0.10
Codeine	0.75	0.05	1.00	0.25
Diacetylmorphine (heroin)	0.001	0.05	0.01	0.10
Dihydromorphinone (dilaudid)	0.02	0.10	0.06	0.25
Ephedrine	2.00	0.25	3.30	0.25
Hyoscyamine	1.00	0.10	2.00	0.25
Isonipecaine (demerol)	0.10	0.10	0.18	0.25
Morphine	0.10	0.02	0.25	0.05
Nicotine	0.005	0.05	0.025	0.25
Nicotinic acid diethylamide (coramine)	1.00	1.00	2.00	2.00
Pentamethylenetetrazole (metrazole)	0.50	1.00	0.75	2.00
Procaine	1.00	0.25	1.50	1.00
Quinine	3.50	0.05	5.00	0.25
Strychnine	0.005	0.02	0.02	0.05
Theophylline	2.00	0.50	4.00	0.50

Table III. Results of Analyses of Unknown Solutions

Total No. of Unknown Saliva Solutions	No. of Saliva Solutions Containing Drugs		No. of Drug-Saliva Solutions Detected		No. of Blanks	No. of Blanks Recognized	Total No. of Errors in Detection
	In threshold amounts	In positive amounts	Threshold	Positive			
			Biological Method				
48	20	20	14	18	8	5	11
			Chemical Method				
			Drug Correctly Identified				
26	..	20	20	20	6	6	0

sensitive for 10%. In a consideration of the usefulness of the biological method as a screening device for the elimination of negative saliva samples from race horses, however, it must be clearly kept in mind that the values in Table II are amounts per mouse for the biological method and amounts per sample for the chemical method. In these experiments 1.0 ml. of drug-saliva solution was injected into each mouse. It would not be physiologically permissible to increase this volume by more than 100%. The amount of drug-saliva solution chemically analyzed was 100 ml., which is the minimum size of the average, routine, saliva sample collected at race tracks. The significance of these volumes is immediately apparent. If 1.0 or even 2.0 ml. of any of the drug-saliva solutions containing the "positive" amount of drug for the chemical method were injected into mice, in only two instances, diacetylmorphine and nicotine, would even threshold responses be detectable.

Saliva is produced by a secretory process by the salivary glands. It is not known to what extent drugs may be concentrated in this secretion if they are eliminated from the body by this route. It is conceivable that small doses of drugs administered to a horse may be sufficiently concentrated in the salivary secretion to be detected by the biological method and correspondingly more readily by the chemical method. However, the experience of the laboratory in the analysis of a large number of saliva samples, both official and experimental, which were found to contain drugs, indicates that drugs are seldom present in such amounts. It is also possible that the breakdown products of drugs may be eliminated in the saliva and that these may have apparent effects on mice and yet not be detectable by the chemical methods employed. Until such time, however, as these possibilities have been demonstrated experimentally, the biological method does not seem justifiable for the detection of drugs in horse saliva.

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NOTES ON ANALYTICAL PROCEDURES . . .

Efficient Apparatus for Leaching Samples with Water

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IN connection with the analysis of guayule shrub for rubber, it is necessary to leach great numbers of samples in hot water before extracting with acetone and benzene. The samples are held in glazed porcelain thimbles, 28 × 75 mm., with a slight taper toward the bottom. Glass wool pads are placed over the perforated bottoms of these thimbles and glass wool plugs are inserted above the samples to keep particles from floating out. Figure 1 shows an apparatus that has worked very satisfactorily for this leaching. In addition to ease of manipulation and rapidity of leaching, an advantage is that the entire thimble is surrounded by hot water, which is important when leaching is slow.

A two-compartment water- and air-tight box, made of wood that does not warp in contact with water, is built with the top compartment open. The partition between the top and bottom compartments is 2 inches thick. In this partition, holes of a little greater diameter than the thimbles (depending upon the thickness of the gaskets to be used) are drilled 1.25 inches deep with the bottoms sloping toward the centers of the bottoms. In the centers of the larger holes 0.125-inch holes are drilled the rest of the way through the partition. The sides of the larger holes are then lined with rubber gaskets. Boxes can be made to hold any number of thimbles. Those used by the authors have a capacity of 20 thimbles each.

The box is connected with a vacuum line leading from the top and with a tail pipe leading from the bottom of the lower compartment. Water is admitted to the upper compartment by means of an inlet provided with a float valve. (If hot water is used it is desirable to have an automatic water heater.) The tail pipe should extend at least 5 feet below the bottom of box into a sump when vacuum of not more than 5 inches is used, and its lower end must be immersed in water.

If now the thimbles whose contents are to be leached are placed in the box, and water is turned on in the top compartment and vacuum in the lower, water will be sucked through the thimbles. (For some types of material, gravity flow might be sufficient without vacuum.) Some method must be provided to keep the vacuum from going above the equivalent head between the water level in the sump and the bottom of the box; otherwise water will be sucked back into the box and into the vacuum system. The authors use an automatic vacuum system set so as to shut off just before the vacuum reaches this equivalent head, but an ordinary aspirator filter pump could be used with a mercury trap that would not allow the vacuum to go above the equivalent head.

To check whether water is passing through thimbles or not, water is shut off and vacuum left on. As soon as the water reaches

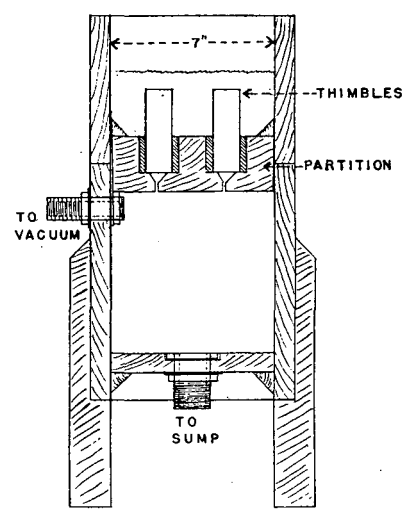

Figure 1. General Construction of Leaching Box

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the level of the top of a thimble, the water level within that thimble should drop faster than that without. If the water used for leaching contains enough mineral matter to interfere with later steps, it can be removed by cutting off the water at the end of leaching and pouring distilled water through the thimbles as many times as necessary.

If water pours into the box from above, it is best to have it pour into a compartment at one end, which also contains the leveling device and is separated from the rest of the box by a partition which extends within a fraction of an inch of the partition between upper and lower compartments. This is to prevent the turbulence of the entering water from dislodging glass plugs or particles of samples from thimbles.

Between the acetone and benzene extractions it is necessary to free the thimbles of acetone. At this stage the samples are very sensitive to heat and it has been found best to remove the acetone by sucking air through them at room temperature. By cutting the water supply off, the same equipment can be used for freeing the thimbles of acetone. For this purpose the vacuum system will have to have a greater capacity than is needed for leaching, and the tail pipe and vacuum regulator are not necessary.

ACKNOWLEDGMENT

Credit is due to E. A. Meldrum of the Emergency Rubber Project for perfecting the details of construction and for constructing the apparatus used.

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Routine Method for Determining Selenium in Horticultural Materials

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PERCHLORIC acid and a vanadium catalyst are used with nitric acid and sulfuric acid to destroy seleniferous organic matter. Selenium is distilled with hydrobromic acid from the digested sample into the vessel wherein it is titrated by a modified Norris-Fay procedure. Greater recovery and less working time per analysis have been observed with this than with previous methods.

Numerous investigators have written (*1, 3, 4, 7, 8, 11*) and reviewed (*6*) papers on various means of converting organic to inorganic selenium, isolating it, and determining the quantity present. The first of these steps was improved in this laboratory, by devising a continuous digestion which required less attention than digestions in common use. Smith (*12*) has described his own and Kahanes' extensive work with perchloric, nitric, and sulfuric acids and various catalysts to destroy organic matter rapidly and retain inorganic constituents. Hoffman and Lundell (*2*) showed that selenium was incompletely distilled, with 15 ml. of hydrobromic acid, from mixtures in which perchloric acid predominated.

DISCUSSION

It was found in this laboratory that, after 10 grams or less of vegetation were digested with 5 ml. of 60% perchloric, 50 ml. of concentrated sulfuric, and 75 ml. of concentrated nitric acids at a temperature not exceeding 210° C., the perchloric acid remaining permitted complete recovery of added selenium on distillation with 15 ml. of 48% hydrobromic acid (Table I).

The high concentration of organic matter in pot soils (one part manure, one part peat, two parts native soil, and one part sand) interfered with the recovery of added selenium by the Robinson *et al.* (*8*) procedure. A vanadium-catalyzed sulfuric-nitric-perchloric acid digestion, however, enabled the recoveries shown in Table I. Using these same investigators' (*8*) method for evaporating solutions, the present distillation and titration were adapted to nutrient salt solutions.

Table I. Recovery of Selenium Added to Organic Matter

Type of Organic Matter	Selenium Added, P.p.m.	Net Selenium Recovered, P.p.m.
Alfalfa meal	50	50.8
	100	101
	250	250
	250	250
	250	248
	330	330
Pot soil	2.0	1.9
	4.0	3.5
	5.0	5.1
	8.0	7.9
	15.0	15.1
	50.0	49.4
	50.0	50.1

The proposed distillation procedure resembles Hoffman and Lundell's (*2*). A hydrazine sulfate solution, in which the distillate is received, serves to suppress bromine and selenious acid until bromide and hydrogen attain sufficient magnitude to keep $HSeO_4^-$ insignificantly small in the system (*10*):

$$\frac{(HSeO_4^-)(Br^-)^2(H^+)^3\gamma^6}{(H_2SeO_3)(Br_2)} = 0.88$$

Coleman and McCrosky (*1*) discussed the application of this relationship in preventing the conversion of selenium to the hexavalent state, preceding a Norris-Fay titration.

In the present method, the Norris-Fay reaction

$$4Na_2S_2O_3 + H_2SeO_3 + 4HBr \longrightarrow Na_2SeS_4O_6 + Na_2S_4O_6 + 3H_2O + 4NaBr$$

proceeds simultaneously with the reaction

$$32HI + 8H_2SeO_3 \longrightarrow 32I + Se_8 + 24H_2O$$

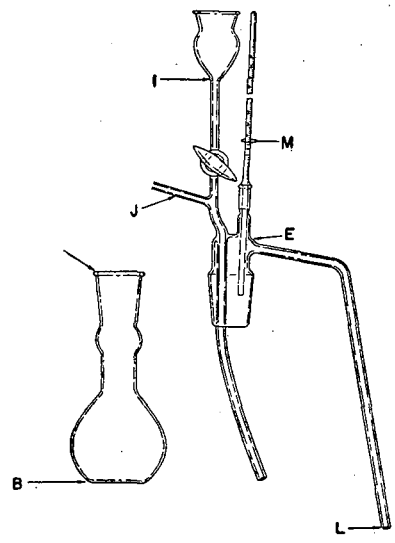

Figure 1. Digestion Flask and Distillation Head

The small quantity of potassium iodide recommended in the present procedure favors a sharp starch-iodine end point but limits the second reaction. As a result, only a tint of suspended selenium and a trace of elemental iodine are produced. The iodine eliminates the usual back-titration.

The elimination of transfers between the distillation and the titration, the hydrolysis of selenium tetrabromide before contact with the atmosphere, and the degradation of natural selenium compounds (*6*) incompletely oxidized by nitric acid are factors which largely account for the higher selenium values frequently obtained with the present method than with methods now in general use.

The apparatus, shown in Figure 1, combines features of Scherrer's (*9*) and Pavlish and Silverthorn's (*7*) apparatus. The

flask (19 cm. from *A* to *B*) is made by attaching a 34/45 female standard-taper joint to the bulb of a 275-ml. Johnson flask. The thermometer, *M* (Fisher Scientific Co., Catalog No. 15-002), has a range of 0° to 250° C.

PROCEDURE

Digestion. TISSUES. Quickly moisten 10 grams of prepared sample, contained in a digestion flask, with 30 ml. of "starting solution" and 5 ml. of water. To prepare the starting solution, dissolve 1.6 grams of ammonium metavanadate in 300 ml. of water mixed with 1500 ml. of concentrated nitric acid. After seething stops, add 75 ml. of concentrated nitric, 5 ml. of 60% perchloric, and (carefully) 50 ml. of concentrated sulfuric acids. Place a thermometer in the flask and slowly heat to 140° to 150° C. When nitrogen dioxide no longer is in evidence, slowly increase the temperature to 210° C., then cool. Wash the thermometer with 10 ml. of water.

If the solution becomes green during digestion, add 1 ml. of perchloric and 10 ml. of nitric acids, then decrease the heating rate.

SOILS. Heat 50 grams of soil with 30 ml. of starting solution, until the foam breaks. Then add 75 ml. of nitric, 7 ml. of perchloric, and 100 ml. of sulfuric acids. Incline the flask in a 600-ml. Moroney antibumping cup and digest as for tissues.

NUTRIENT SOLUTION. Evaporate an appropriate volume of solution to 30 or 40 ml., with 0.5 gram of sodium peroxide (*8*) in a digestion flask. Add 50 ml. of concentrated sulfuric and 1 ml. of 60% perchloric acids and 5 to 10 mg. of ammonium metavanadate. Add nitric acid only if the color due to vanadium changes from yellow to green. Heat to 210° C.

Distillation. TISSUES AND SOLUTIONS. Apply silicone grease to the joints and assemble the distillation apparatus on a ring stand. Start air flowing into the tube, *J*, at a rate such that 2 or 3 bubbles per second rise from outlet *L*, which is immersed in 50 ml. of 0.1% aqueous hydrazine sulfate solution, contained in a cooled 250-ml. Berzelius beaker. Run 5 ml. of 48% hydrobromic acid into the sample through the funnel, *I*. Heat the flask until most of the bromine is driven from it, then allow 10 ml. more of hydrobromic acid to drain into it, at the rate of 1 ml. per minute, while a vapor temperature of 125° to 135° C. is maintained. Heat the thermometer hole, *E*, as required to remove condensate.

SOILS. Distill as above, but thoroughly mix 10 ml. of hydrobromic acid with the sample before heating. Add only 5 ml. of hydrobromic acid at the rate of 0.5 ml. per minute while heating.

Titration. Add about 3 grams of urea and 2.5 ml. of 90% formic acid to the receiving beaker and heat until the bromine is reduced. Neutralize to phenolphthalein with 45% sodium hydroxide solution. Add 13 ml. of 18 *N* sulfuric acid and cool. Dissolve 1.0 gram of potassium iodide in 100 ml. of 0.1% wheat starch paste. Add 5 ml. of this reagent to the sample and immediately titrate with 0.005 to 0.01 *N* sodium thiosulfate. When the change from purple to pink is stable for more than 7 seconds, the titration is complete.

Standardize the sodium thiosulfate by carrying a pure selenite or selenium dioxide through the appropriate steps of the above titration.

A reagent blank should accompany a series of samples.

After this paper had been completed, attention was called to an improved van der Meulen titration developed by McCullough, Campbell, and Krilanovich (*5*). In the present method, which employs hydrobromic acid and about 1/200 as much potassium iodide as McCullough *et al.* use, only a fraction of the selenium being titrated appears as the element. The remainder combines as a colorless compound in the Norris-Fay reaction.

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Saturated Potassium Hydrogen Tartrate Solution as a pH Standard

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A SATURATED aqueous solution of potassium hydrogen tartrate is a more convenient secondary standard for the calibration of pH-measuring instruments than any of the buffer solutions generally used for this purpose. The preparation of the solution is extremely simple; it is only necessary to shake an excess of the pure salt with distilled water of good quality for 2 or 3 minutes at room temperature to obtain a solution whose pH is reproducible to ±0.02 unit.

Potassium hydrogen tartrate is available commercially in a high state of purity, and further purification is achieved easily by simple recrystallization from water. A sample of the C.P. commercial salt was recrystallized twice, and the pH values of saturated solutions of the original material and the two recrystallizates agreed to ± 0.005 unit. Since the pH of potassium hydrogen tartrate solutions is about 0.4 unit smaller than that of water saturated with carbon dioxide at one atmosphere, the small amount of carbon dioxide dissolved from a normal atmosphere has no significant effect on the pH.

Solutions of potassium hydrogen tartrate appear to be more stable than the commonly used potassium hydrogen phthalate solutions; a saturated solution showed an increase of only 0.03 pH unit after standing for a year in a stoppered Pyrex bottle. However, since the preparation of the solution is so simple, it should be prepared freshly as needed, and not stored, so that the possibility of accidental contamination is avoided.

Hitchcock and Taylor (*2*) determined the pH of an exactly 0.03 *M* potassium hydrogen tartrate solution by means of the hydrogen electrode and obtained a value of 3.567 at 25° C. on the same empirical but thermodynamically consistent scale recently recommended by MacInnes, Belcher, and Shedlovsky (*3*, *4*) and Bates, Hamer, Manov, and Acree (*1*). The writer found that the pH of a saturated solution of the salt (0.034 *M* at 25°) does not differ significantly from the foregoing value. For all practical purposes the value 3.57 ± 0.02 for the pH of the saturated solution may be used.

The influence of dilution on the pH of a solution of potassium hydrogen tartrate, originally saturated at 25°, was determined with the result shown by curve 1 in Figure 1. For comparison the dilution effect observed with 0.05 *M* potassium hydrogen phthalate is also included (curve 2). In this figure Δ pH is the apparent difference in pH between the original and diluted solutions and it includes any effect resulting from changes in the liquid-junction potential between the saturated calomel reference electrode and the glass electrode half-cell. The dilution factor,

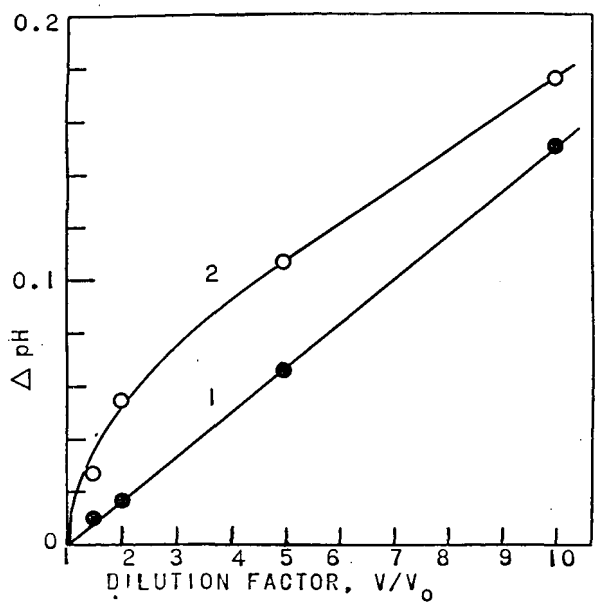

Figure 1. Influence of Dilution on pH

V/V_0, is the ratio of the diluted to the original volumes. In both cases the apparent pH increases on dilution, but the effect is much smaller with the potassium hydrogen tartrate than with the potassium hydrogen phthalate.

From data given by Seidell (*5*) the following values of the molar solubility, S, of potassium hydrogen tartrate at various temperatures have been computed:

Temperature, ° C.	0	10	15	20	25	30
S, molar	0.0123	0.0190	0.0231	0.0283	0.0341	0.0405

On comparing these data with curve 1 in Figure 1 it is evident that a solution saturated at any temperature above 10°, and then brought to 25° for measurement, will exhibit a pH within 0.02 unit of a solution saturated at 25°, so that no special care is necessary in preparing the saturated solution.

The temperature coefficient of the pH of a saturated potassium hydrogen tartrate solution has not been precisely determined, but it is probably very nearly the same as that of 0.05 M potassium hydrogen phthalate (+0.0014 unit per degree at 25°, *1*), and hence negligible for all practical purposes.

Since the ionization constants of tartaric acid are much closer together than those of *o*-phthalic acid, a potassium hydrogen tartrate solution has a greater buffer capacity, and therefore is less sensitive to adventitious acidic or basic impurities, than an equiconcentrated solution of potassium hydrogen phthalate.

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RECEIVED October 7, 1946.

Improved Trap for Analytical Distillations

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STEAM leaving a distilling flask is supposed to contain only those components of the boiling liquid which are volatile under boiling conditions—for example, ammonia but no sodium hydroxide in a Kjeldahl distillation, or arsenious chloride but no antimonious chloride in a strong hydrochloric acid solution containing these elements. However, the outgoing vapor always contains dispersed liquid.

To remove from the vapor stream these liquid droplets, formed by the bursting steam bubbles, connecting bulbs are used which, although varied in some details of their design, are all based on the same principle: They impose a directional change on the vapor stream, projecting it against wet surfaces so that the droplets may be absorbed and carried back to the distilling flask by the condensed liquid. There may be one or more bulbs, round or oblong, connected by curved or T-shaped tubes, but in all cases these bulbs add to the air-filled volume which must be washed out by the passing stream, and they act as reflux condensers. Both factors prolong the distillation time, while the active surface and consequently the efficiency of these devices are limited. In Kjeldahl distillations, when the generation of hydrogen is used to avoid bumping of the solution, or in the reduction of nitrate by Devarda metal, etc., microscopic gas bubbles are projected through the surface of the boiling liquid and are not washed out completely by the connecting bulbs. When the inner active surface is increased for the purpose of improving the efficiency of the bulbs, the outer cooling surface and consequently the distilling time increase at the same rate.

Because of these limitations of the external connecting bulbs it would be useless to suggest any new form, but the aspect changes if the trap is installed inside instead of on the distilling flask neck. In the droplet catcher here described, the total air-filled volume of flask and trap is less than that of the empty flask alone. Furthermore the active inner surface can be increased a hundredfold, while the outer surface (the cylindrical neck of the flask) always remains the same.

CONSTRUCTION AND OPERATION

The construction of the new droplet catcher is shown in Figure 1. (This apparatus is available from Scientific Glass Apparatus Co., Inc., Bloomfield, N. J. Specify joint and flask sizes when ordering.) The material used is Pyrex. Dimensions depend on the size of the distilling flask used. The three concentric tubes—i.e., the neck of the flask and the two tubes of the droplet catcher—ought to be as close as possible to speed the passing of vapors and leave the maximum space to the most important part, C, which is filled with helices. The outer tube of the droplet catcher is equipped with two 4-mm. or three 3-mm. openings as vapor inlets and a small tip with a 1-mm. opening at the bottom for the return of collected droplets into the flask.

In use, the steam rises in the exterior passage, A, passes through the openings at O down the middle tube, B, and at last rises through the helices filling the wide central tube, C. The very small quantity of condensate containing all the washed-out droplets of bubbles drops back through the capillary point, P.

The efficiency of this device in separating liquids from gases (vapors) in which they are dispersed has been confirmed in practice for many years. In addition, it has proved very useful in the separation of the real vapors of a higher and lower boiling liquid. The separation of arsenic and antimony by distillation of a strong hydrochloric acid solution of the trivalent forms of these elements is a very old analytical method which, however, presents a very difficult problem. It can be demonstrated that codistillation of antimony in this analytical operation is due to the fact that parts of the boiling liquid are projected to the upper

part of the distilling flask and evaporated to dryness on its overheated surface. Consequently, in spite of the fact that antimonious chloride does not volatilize in an aqueous hydrochloric acid solution, its real vapor is formed and carried with the outgoing vapor stream. The liquid condensed in the interior of the droplet catcher is sufficient to dissolve this antimonious chloride and carry it back to the boiling solution. The passing of a stream of hydrochloric acid through the liquid and the use of any of the other precautions formerly suggested for this purpose are thus eliminated and a sharp separation of arsenic and antimony can be performed in a single distillation.

A former model of the device described (*1*) had an inner steam conducting tube which did not affect the efficiency of the droplet catcher, but caused difficulty in filling it with the small glass rings. So, although highly appreciated by the chemists who used it, the device has not been fabricated in quantity. The new modification overcomes these technical difficulties in the fabrication.

TESTING EFFICIENCY OF DROPLET CATCHER

In a 1-liter flask provided with a connecting bulb 500 ml. of 1 *N* sodium hydroxide and a small quantity of zinc powder (to generate hydrogen) were boiled. The pH of the distillate was found to be 8 to 9, proving that one part of dispersed liquid was carried along with 100,000 to 1,000,000 parts of distilling liquid. When the assay was repeated, the interior droplet catcher replacing the exterior bulb, the pH of the distillate was 7.0 to 7.2. At the same time, if the position of the distilling flask and the height of the gas flame were maintained exactly, the distilling rate, in milliliters per minute, increased 50%. It could have been further improved up to 100% by increasing the intensity of heating. On the other hand, when the connecting bulb was used, it was not possible to speed the distillation by more intense boiling because in this case the condensed liquid closed the inner tube, so that the passing steam threw quantities of it towards the condenser.

Exactly the same relations were observed in the distillation of an acid ammonium chloride solution with zinc powder and measurement of the ammonia in the distillate with Nessler reagent; no coloration at all was found with the droplet catcher, while 10^{-6} to 10^{-5} part of the ammonia content of the boiling liquid was observed in the distillate when the conventional connecting bulb was used.

An example may be cited as nonanalytical proof of the efficiency of the droplet catcher. In 1942, while in charge of an agricultural institute, where it was not possible to acquire a modern still, the author was in immediate need of relatively large quantities of distilled water, pure enough to be used in soil analysis. An old still of some 30-liter capacity, regarded as unserviceable, was found in storage. A droplet catcher was installed in the interior of the retort and the still was fed with tap water to which potassium permanganate and sodium hydroxide were added continuously. During two years, the outgoing distilled water was always colorless and practically neutral. In this case the use of the droplet catcher proved that it is possible to obtain water with the purity of "redistilled" water in a single distillation.

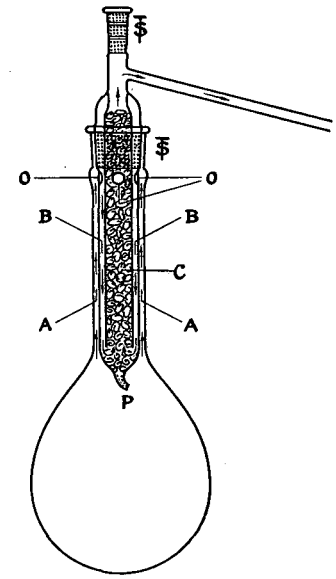

Figure 1. Droplet Catcher

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Apparatus for Rapid Electrometric Titration of Acid

Determination of pH and Measurement of Turbidity in Microbiological Assays

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THE apparatus shown in Figure 1 has been employed more than a year in the writers' laboratory for the determination of turbidity, pH, and titratable acid of solutions in the microbiological assay of amino acids and vitamins. These measurements may be made simultaneously by an experienced worker with the aid of a technician at the rate of about 90 per hour and independently at rates of about 150, 300, and 200 per hour for turbidity, pH, and titratable acid, respectively.

Reeves (*2*) has described an apparatus for multiple pH determinations and Silber and Mushett (*5*) have pointed out the convenience, speed, objectivity, and applicability of the pH procedure in the determination of pantothenic acid with *Lactobacillus casei*. A spread of about 2 pH units was obtained over a working range of 0.02 to 0.10 microgram of pantothenic acid per tube. The precision and accuracy attained by the present authors in microbiological assays of histidine with *Leuconostoc mesenteroides* P-60 have been reported (*1*). It has been found that the acid production of organisms in microbiological assays may be determined more rapidly, conveniently, and accurately by means of the described apparatus than by titration using bromothymol blue indicator to determine the end point. Some of the shortcomings which are eliminated or minimized include eyestrain, general fatigue, and end-point errors caused by indicator fading, turbidity, and colorations.

APPARATUS

The titration cup is a Pyrex funnel, *A* (Corning 6140, ESPGY), and 2- to 3-mm. bore Pyrex stopcock, *b*. The outlet, *a*, of the cup under stopcock *b* is clamped to a ringstand and is connected to a water aspirator with rubber pressure tubing.

A 25-ml. automatic zero Kimble Blue Line Exax buret, *B*, with a three-way stopcock is clamped to the ringstand in such a manner that the buret is just above and in the center of the titration cup.

The buret is filled through the stem of the stopcock by gravity flow from a 5-gallon bottle of standard carbon dioxide–free base.

An Aero-Mix (Precision Scientific Company) stirrer, *C*, is clamped to the ringstand. The chuck of the stirrer is fastened to a 25-mm. length of 6-mm. glass tubing with fire-polished ends. The glass stem of the stirrer is connected to the 150 × 4.5 mm. solid-glass stirring rod, *e*, with an 80-mm. length of 7-mm. outside diameter Tygon tubing. The bearing, *f*, consists of a 45-mm. length of 7-mm. outside diameter glass tubing fitted into a rubber stopper and clamped to the ringstand. The end of stirring rod *e* is flattened and bent slightly to effect rapid mixing of the liquids in the titration cup. The air inlet, *d*, is connected to a compressed-air line.

The rinsing cup, blown from Pyrex, is clamped to the ringstand adjacent to the buret. Rinse water enters the rinsing cup through the inlet, *g*, at the orifice, *h*. A 150-mm. length of 10-mm. outside diameter transparent Tygon tubing, *j*, is attached to the outlet, *i*, of the rinsing cup and the tubing is clamped with a Fisher (5-849B) Castaloy pinchclamp, *k*.

The glass electrodes (Beckman 4990-A and 1170) are connected to the pH meter, *G*, by means of 30-inch leads. The glass electrode is supported by means of a piece of glass tubing, *o*, which is fitted into a rubber stopper and clamped to the ringstand. The pH meter switch is at *p* and the operating button at *q*.

A Brewer automatic pipetting machine (Baltimore Biological Laboratory) is set beside the titration cup and is connected to inlet *g* of the rinsing cup, *D*, by means of the rubber tubing, *n*. The rinse water enters the pipet at *m* and the switch operating the pipet is at *l*.

A Beckman industrial pH meter, Model M, is placed on its side at eye level on a shelf back of the titration assembly.

The bacterial cell suspension is made homogeneous by inserting the test tube in the rubber-tubing holder of the vibrator-stirrer (*S*) and rotating and wobbling the tube by means of the motor-driven attachment.

The photoelectric colorimeter is a Lumetron (Photovolt Corporation, Model 400-A). The neutral gray filter plate with wire screen is placed in the space provided between the light source and the test-tube holder. Pyrex 18 × 150 mm. test tubes of uniform outside diameter are employed for the determination of the optical density or the per cent transmission of the cell suspensions. With the blank tube (distilled water or zero level test solution) in position, the pointer on the dial is adjusted to 0.0 on the optical density scale (equivalent to 100% on the transmission scale), the test sample tube is placed in position, and the optical density or per cent transmission value for the sample is read on the dial. The blank setting of the pointer is made prior to the turbidimetric analysis of each sample, since the blank readings vary slightly even with the use of the constant-voltage transformer, *J*. Usually, 8 to 10 ml. of cell suspension are employed for turbidimetric analyses.

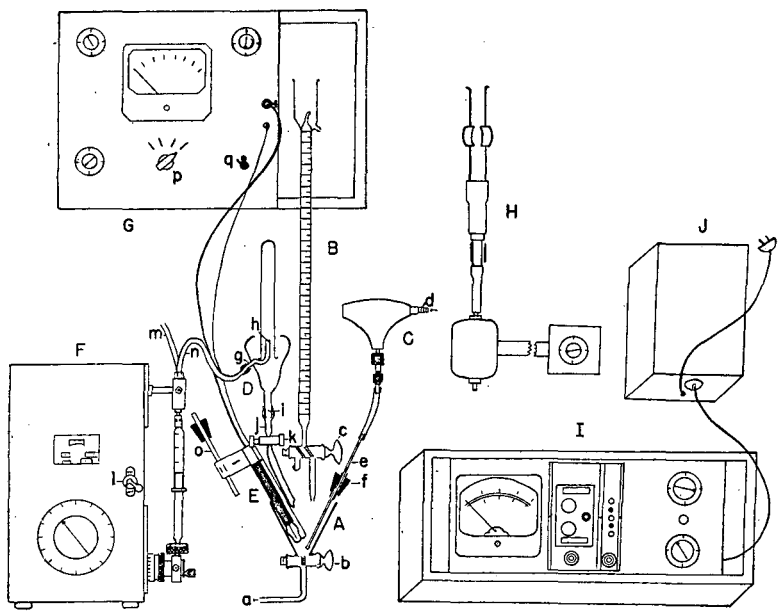

Figure 1. Assembly for Determination of Turbidity, pH, and Titratable Acid

A. Titration cup
B. Buret
C. Stirrer
D. Rinsing cup
E. Glass electrodes
F. Automatic pipetting machine
G. pH meter
H. Vibrator-stirrer
I. Photoelectric colorimeter
J. Constant-voltage transformer

PROCEDURE

The first determination made is the turbidimetric analysis of the cell suspension. If matched tubes are employed in the assay, the contents of one of the sample tubes are thoroughly mixed by the vibrator-stirrer, and the tube is dipped in a cleansing solution (mixture of equal parts of water, acetone, and ethanol) and wiped clean and dry. The tube is placed in position in the instrument and the reading is taken. If unmatched tubes are used in the assay, the mixed contents of each tube are transferred to a clean, dry matched tube for the turbidimetric analysis.

The pH of the cell suspension is next determined. The automatic pipet is set to give the desired operating speed and size of wash-water aliquot. The pH meter is checked against standard buffer solution placed in the titration cup and stirred vigorously without splashing by adjusting the air pressure driving the Aero-Mix stirrer. An electric stirrer, unless well grounded, would interfere with the operation of the pH meter. Stopcock *b* is opened to permit the buffer solution to be aspirated from the funnel at *a*. The funnel is rinsed by placing a test tube over *h* and pumping water into the system by means of the automatic pipet. Pinchclamp *k* is opened to allow the rinse water to drain into the funnel and stopcock *b* is opened to permit rinsing of the funnel. Rinsing is continued until the pH of distilled water is reached. The rate of drainage may be observed by noting the flow of liquid through the transparent Tygon tubing. That complete rinsing has been effected may be determined by noting the change in color of bromothymol blue indicator added to the wash water.

The buret is filled with the standard base (usually approximately 0.1 *N* sodium hydroxide solution) and the pH meter is adjusted to give readings of pH 0 to 7. Stopcock *b* is closed, the tube containing the sample is inverted over the injector arm, *h*, and the pH of the solution in the titration cup is determined. The predetermined number of aliquots of wash water are delivered into the system by means of the automatic pipet, pinchclamp *k* is closed, and another sample is transferred to the rinsing cup by the described technique while the first sample in the titration cup is being titrated.

The sample in the titration cup is titrated with standard base delivered at a uniform rapid rate from the buret until the pH, read on the dial of the pH meter, is 6.0 to 6.5. The buret stopcock is closed, the mixture is allowed to stand (a few seconds) until the pH is constant, and the titration is completed to pH 7.00 by rotating the stopcock of the buret rapidly in order that only 0.01- to 0.02-ml. aliquots of base may be delivered. The accuracy and the speed of the titrations are increased by this means greatly beyond those attainable when drop-size aliquots are delivered. The titrated solution is drained completely from the titration cup in 2 or 3 seconds by opening stopcock *b* and applying suction at *a*. It is unnecessary to rinse the titration cup, since the pH of the titrated solution is 7.00. The volume of base used is read and the buret is refilled to the zero mark. Buret and temperature corrections are unnecessary, since only relative titration values of standard and unknown are required.

ACKNOWLEDGMENT

This work was aided by grants from the National Institute of Health of the U. S. Public Health Service and the University of California.

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Nomographs for Distillation of Low-Boiling Hydrocarbons

Conversion of Distillation Temperatures and Pressures to Boiling Point at One Atmosphere

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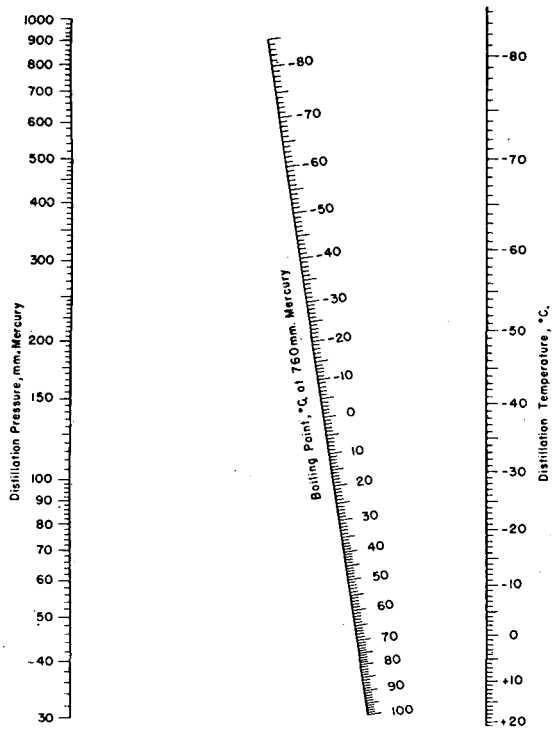

Figure 1. Conversion of Distillation Temperatures and Pressures to Boiling Point at 1 Atmosphere from −85° to 20° C.

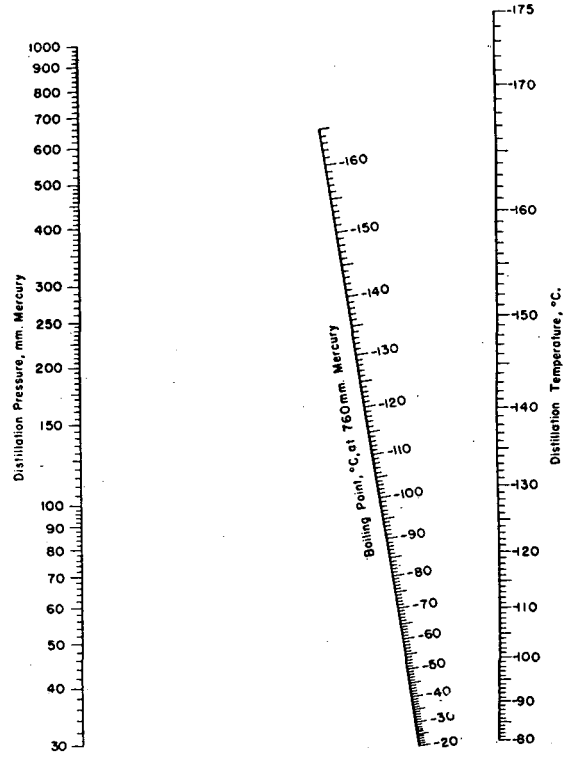

Figure 2. Conversion of Distillation Temperatures and Pressures to Boiling Point at 1 Atmosphere from −175° to −80° C.

IN THE fractionation of a liquefied gaseous sample by means of low-temperature distillation, it is usually necessary to carry out at least part of the distillation at reduced pressures. Inasmuch as the distillate is conveniently identified by its boiling point, by means of a thermocouple located in the condenser section of the column, it is desirable to have a rapid and simple means for converting distillation temperatures and pressures to the more familiar boiling points at 760-mm. pressure. This conversion can be closely approximated for the aliphatic hydrocarbons by means of nomographs.

Such nomographs have been used in these laboratories for some time. To cover the full temperature range encountered in distillation of low-boiling hydrocarbons, it was found most convenient to construct two nomographs, one covering a distilling range +21° to −85° C. and the other from −80° to −175° C. (Figures 1 and 2). These nomographs have been constructed empirically from vapor pressure data taken from the tables of selected values of properties of hydrocarbons issued by the American Petroleum Institute (*1*).

In constructing the nomographs, the distillation pressure was plotted in millimeters of mercury, from 30 to 1000 mm., on a vertical two-cycle logarithmic scale. Then a parallel line of nearly the same height was drawn for the distillation temperature scale. A hydrocarbon for which vapor pressure data were available throughout most of the desired temperature range was selected. The highest temperature for which the vapor pressure of the reference hydrocarbon was known was then arbitrarily established near the bottom of the distillation temperature scale and the lowest temperature for which the vapor pressure was available was established near the top of the scale. Intersecting lines were then drawn between the two values on the distillation temperature scale and the corresponding vapor pressures on the distillation pressure scale for the reference hydrocarbon. A straightedge placed on the intersection point of these two lines and any given value on the distillation pressure scale was used to determine the proper location of the corresponding temperature on the distillation temperature scale. In this manner a number of values were located on the distillation temperature scale and the scale was further subdivided by interpolation and by similarly using vapor pressure data of other hydrocarbons. *n*-Butane was used as the principal reference hydrocarbon for Figure 1 and ethane for Figure 2.

From the determined distillation temperature and pressure scales, intersection points were established for various hydrocarbons using available vapor pressure *vs.* temperature data. It was found that these intersection points lay very nearly on a straight line, which was then drawn in for the 760-mm. boiling point scale. The values for this scale were filled in as much as possible by laying a straightedge from the 760-mm. point on the distillation pressure scale to various temperature values on the distillation temperature scale (at 760-mm. mercury pressure the readings on the distillation temperature scale and those on the 760-mm. boiling point scale should be identical). The scale was then further extended by interpolation.

It has been found simple, with the aid of these nomographs, to follow the course of a distillation performed at reduced pressure in terms of the boiling point at atmospheric pressure. The nomographs have been used for the distillation of a large number of low-boiling paraffins, olefins, and diolefins and have proved accurate to within ±1° C. throughout their working range with all hydrocarbons through C_5 thus far encountered except acetylene. The anomalous behavior of acetylene is not surprising, however, because its vapor pressure curve rises more sharply than do those of the other hydrocarbons.

ACKNOWLEDGMENT

The present nomographs are an outgrowth of one developed by Ritchie R. Ward of these laboratories.

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RECEIVED September 27, 1946.

Simplified Still Head with Automatic Control of Reflux Ratio

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THE literature contains numerous designs of still heads with provision for automatic control of reflux ratio, independent of boil-up rate. One principle much used is the intermittent take-off, in which the entire condensate is directed alternately to the receiver and to the column as reflux (*1–4*). The valve controlling this flow is operated by a commercial electric cycle timer. The still head described here is of this type, but has some advantages over each of the previously published designs. It is compact, rugged, and relatively easily constructed. The take-off valve is readily removed, facilitating cleaning. No lubricant is required on the valves exposed to the condensate. No stopcocks are required on the head when used at atmospheric pressure, while with vacuum, only one stopcock, exposed only to cold vapor, need be manipulated to withdraw condensate from the receiver.

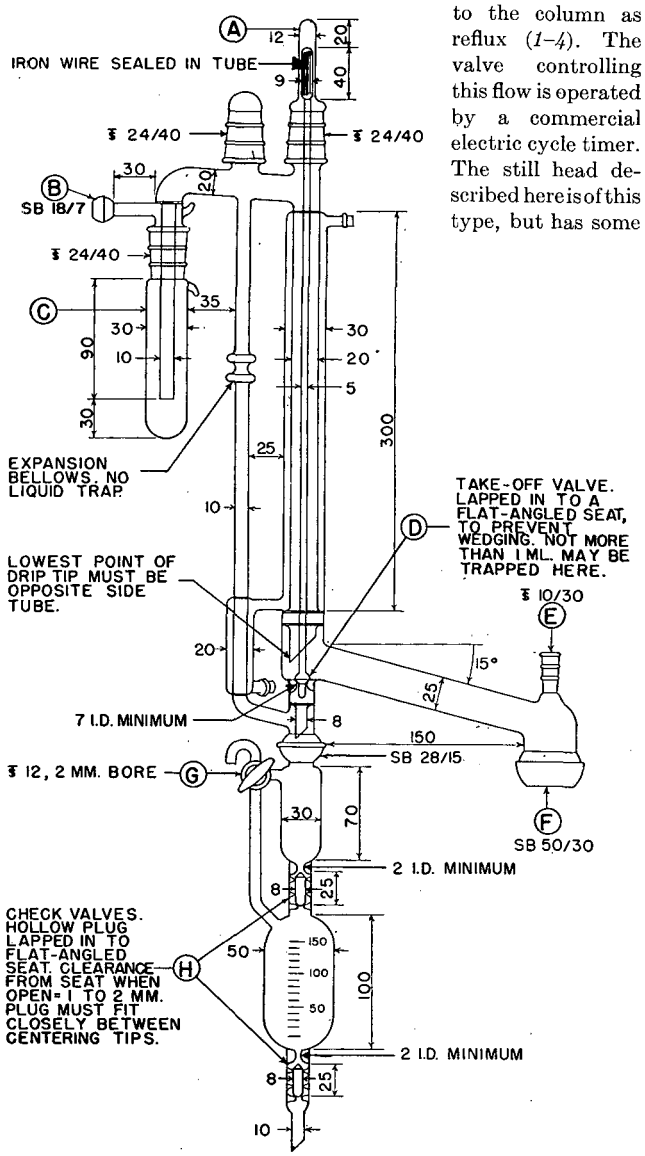

Figure 1. Still Head

All dimensions in millimeters. Tubing sizes outside diameter

The still head is shown in Figure 1. A 110-volt alternating current relay coil, such as Struthers-Dunn type D, slipped over the 12-mm. tube, *A*, projecting from the top of the head, operates the take-off valve. Vapor temperature may be measured with a standard-taper thermometer fitted in the 10/30 joint, *E*, at the right. The spherical joint, *F*, connects to the column.

No provision has been made for cooling the condensate coming from the take-off valve, *D*. This is unnecessary with the high-boiling materials for which the head was designed. For use with lower-boiling compounds, the addition of a water jacket below the take-off valve would be desirable.

The still head is constructed in two parts, to facilitate cleaning, and to permit its convenient use for either vacuum or atmospheric pressure. The spherical joint, *B*, connects to the pressure regulator and vacuum pump. The trap, *C*, to which it connects may be immersed in a dry-ice bath, if desirable. In normal operation, the 3-way stopcock, *G*, is turned to connect the upper and lower sections of the receiver. Atmospheric pressure then closes the lower check valve, *H*, and condensate collects in the lower section. To remove the condensate, the stopcock is turned to admit air into the lower section, thereby closing the upper check valve, *H*, and opening the lower one. Condensate then collects in the upper section until the stopcock is returned to its original position.

Lubrication of stopcock *G* is no problem, since it is not exposed to the condensate. When slightly viscous liquids are distilled, the check valves tend to stick closed. Although they may be loosened by tapping, a more convenient arrangement is to keep them warm with a few turns of B&S 32 Nichrome wire wrapped over asbestos paper, operated from a bell-ringing transformer.

A slight amount of air leakage inevitably occurs at the check valves of this still head, since unlubricated ground joints cannot be perfectly airtight. However, if the valves are carefully lapped in, and assembled so as to prevent imperfect seating, the amount of leakage at 10-mm. pressure is insignificant. Dirt lodging in the valve seats will, of course, cause leakage. Such dirt usually can be dislodged by one or two operations of the valve. In practice, this occasional inconvenience has been found far less troublesome than the many ills afflicting lubricated stopcocks, particularly when distilling high-boiling organic materials.

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RECEIVED July 16, 1946.

Determination of Halates in Sodium Hypochlorite

SYDNEY ATKIN[1], *Analytical Section, Process Development Department, General Aniline & Film Corporation, Grasselli, N. J.*

SODIUM hypochlorite can be determined quantitatively by reaction with a standard solution of sodium benzene sulfinate. The resultant sodium benzene sulfonate solution in the presence of sodium chloride can be treated with concentrated hydrochloric acid, potassium bromide, and potassium iodide and the total halates (as sodium chlorate) determined. Using this procedure both components can be determined in one sample, and the analysis completed in approximately 0.5 hour.

Several methods for the quantitative determination of chlorates in hypochlorite have been described.

Gaukhman and Stefanovski (*2*) determined chlorates in hypochlorite by using the catalyst osmium tetroxide. Results were usually low.

Hernandez (*3*) recommended determining chlorates in hypochlorite by decomposing with hydrochloric acid and distilling the solution into potassium iodide solution. The arsenite method was used for the determination of the hypochlorite.

Kolthoff (*4*) determined chlorates in hypochlorite by boiling gently with hydrochloric acid and a known amount of 0.1 *N* sodium arsenite and then titrating the excess arsenite with 0.1 *N* potassium bromate, using indigo as the indicator.

Ackerman (*1*) found that sodium benzene sulfinate reacts quantitatively with sodium hypochlorite according to the following reaction

$$C_6H_5SO_2Na + NaOCl \longrightarrow C_6H_5SO_3Na + NaCl$$

and does not affect the chlorate present. This has been verified by the author, who used this reaction for the determination of the hypochlorite. The total halates (as sodium chlorate) were then determined in the presence of the sulfonate, as prescribed by Kolthoff and Furman (*5*), with slight modification for existing conditions.

The latter procedure is recommended because (1) the possibility of low results obtained in an acid solution is eliminated by titrating in a neutral or alkaline solution, (2) no distillation is required, reducing possible sources of error due to loss of vapors, (3) both chlorate and hypochlorite can be determined on the same sample, and (4) the method is rapid and accurate.

Table I. Effect of Sodium Benzene Sulfinate

$NaClO_3$ Added	$NaClO_3$ Found
Mg.	*Mg.*
10	11.0
	10.3
	10.2
20	21.3
	19.8
	20.2
25	25.0
	24.8
	24.9
50	50.0
	49.1
	49.7

REAGENTS

Sodium benzene sulfinate, 0.1 *N*. A good technical grade can be used. Dissolve 8.5 grams in 500 ml. of water, add 50 ml. of barium chloride (10%), and digest on a steam bath for one hour (the sulfites and the sulfates are precipitated). Filter the solution, wash with water, cool the filtrate, and dilute to 1 liter with water.

Sulfuric acid, 50%.
Potassium iodide solution, 10%.
Sodium arsenite solution, 0.1 *N*.
Sodium thiosulfate solution, 0.1 *N*.
Sodium hypochlorite solution, about 6.0%.
Starch-iodide test paper (*1*).

STANDARDIZATION OF SODIUM BENZENE ULFINATE

Pipet two 25-ml. aliquots of the sodium hypochlorite solution into 200 ml. of water. Titrate one aliquot with 0.1 *N* sodium arsenite solution, using starch iodide test paper. Titrate a second aliquot with the sodium benzene sulfinate solution, using the starch-iodide test paper. Calculate normality of the sodium benzene sulfinate.

Procedure. Dilute about 10 grams of the sodium hypochlorite to be analyzed to 250 ml. in a volumetric flask. Pipet a 25-ml. aliquot into a 300-ml. Erlenmeyer flask with a ground-glass stopper. Titrate with 0.1 *N* sodium benzene sulfinate, until a blue spot no longer appears on starch-iodide test paper, taking care not to add an excess of the reagent. A = ml. of 0.1 *N* sodium benzene sulfinate. Then add 3 grams of potassium bromide and concentrated hydrochloric acid, so that the resultant acid solution is approximately 8 *N* (20 ml. of concentrated hydrochloric acid for each 10 ml. of solution). Place stopper in flask and let stand for 5 minutes. Add 10 ml. of potassium iodide (10%) and titrate the liberated iodine with 0.1 *N* sodium thiosulfate.

B = ml. of 0.1 *N* sodium thiosulfate

$$\text{Weight of sample} = \frac{3.725\ A}{} = \%NaOCl$$

$$\text{Weight of sample} = \frac{1.775\ B}{} = \%\text{ total halates as } NaClO_3$$

Table II. Comparison of Methods

Samples	NaOCl by Sodium Arsenite	NaOCl by Sodium Benzene Sulfinate
	%	%
1	15.44	15.48
2	14.56	14.70
3	14.23	14.24
4	14.28	14.24
5	13.83	13.88

EXPERIMENTAL

The standard sodium benzene sulfinate was found to be very stable.

Tests were run to determine whether any chlorate was affected by the sodium benzene sulfinate. Known amounts of sodium chlorate were added to a hypochlorite solution containing 0.5% sodium chlorate as determined by the proposed procedure. The sodium chlorate found in Table I represents the chlorate after 0.5% in the sample was deducted.

A comparison of the sodium benzene sulfinate and the arsenite methods for determining sodium hypochlorite is shown in Table II.

ACKNOWLEDGMENTS

Appreciation is expressed to Leo Ackerman, whose suggestions and advice resulted in the completion of this work. The author also thanks P. Nawiasky, F. Ebersole, W. C. Wilhelm, and L. T. Hallett for cooperation and proofreading.

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RECEIVED December 23, 1946.

Instrument Society of America Conference

Abstract of Analytical Papers

The second National Conference of the Instrument Society of America was held in Chicago, September 8 to 12, 1947. Both the exhibits and technical papers contained information of interest to analysts. Inquiries concerning preprints of these papers may be made to the Instrument Society of America, 1117 Wolfendale St., Pittsburgh 12, Pa.

Officers announced for 1947–48 are as follows: president, Paul G. Exline, section engineer, Gulf Research Corp., Pittsburgh, Pa; vice president, Carl P. Kayan, Department of Mechanical Engineering, Columbia University, New York, N. Y.; vice president, Herbert H. Barnum, H. H. Barnum Co., Detroit, Mich.; vice president, H. C. Frost, assistant director of engineering, Chemical Division, Corn Products Refining Co., Argo, Ill.; vice president, F. H. Trapnell, instruments engineer, E. I. du Pont de Nemours & Co., Wilmington, Del.; treasurer, Hugh E. Ferguson, Peoples Gas Light & Coke Co., Chicago, Ill.; executive secretary, Richard Rimbach, Instruments Publishing Co., Pittsburgh, Pa.

The next convention will be held at Convention Hall, Philadelphia, Pa., Sept. 13 to 17, 1948.

Among the topics which were discussed, the paper by R. H. Kienle and E. I. Stearns of Calco Chemical Division, American Cyanamid Co., Bound Brook, N. J., on the "Adaptation of the Automatic Spectrophotometer for Special Measurements" afforded an interesting example of the flexibility of a modern tool when it is in capable hands. Numerous modifications and attachments to the G.E. recording spectrophotometer were described for extending its use beyond that of defining color. These included determinations of chemical identity, quantitative chemical analysis, reaction rates, refractive index, extinction coefficients, rotatory dispersion, and dichroism. This strikes us as an excellent example of instrumentation, wherein a complete understanding of the design, construction, and function of a complex instrument at once suggests minor modifications which will greatly expand its usefulness. In its intended role, we imagine that the color analyzer will continue to be fed with additional thousands of colored compounds, but now its future does not seem to be limited to such prosaic tasks.

"Some Problems of Application of Conductivity Equipment" were discussed by Allen L. Chaplin of the Askania Regulator Co., Chicago, Ill. These dealt with applications of conductance to the regulation of chemical processes, for which it has some advantages as well as limitations over other methods. Techniques involving the use of external electrodes were also described. These are particularly attractive and the newer electronic techniques offer many advantages over the classical methods.

"The Design and Application of a New Metals Comparator" was described by D. E. Bovey of the General Electric Co., Schenectady, N. Y. Although this device is primarily suited to differentiate between specimens on the basis of annealing, heat treatment, and hardness, it is, under suitable conditions, susceptible to composition differences and analysts will at once recall the Carbometer as an instantaneous means of determining the carbon content of steels. The comparator consists of a solenoid which forms one arm of a bridge circuit, the adjacent arm of which is a variable resistor. The bridge is driven by a variable-frequency oscillator and the output after rectification and filtering is fed to a balanced push-pull direct current amplifier and output microammeter. If the system is balanced initially with a standard sample inserted in the solenoid, then subsequent samples will reveal their identity or difference from the standard in terms of the microammeter deflection. The test is nondestructive and the samples to be tested need not be wiped, cleaned, or otherwise specially prepared. In many cases, two samples, obviously different, may show identical readings, but at another exciting frequency will be quite different. For this reason, test frequencies of 50, 250, 500, 1000, 2500, 4000, and 10,000 cycles are provided. In general, low frequencies penetrate the sample and are more characteristic of the composition; the higher frequencies reveal surface differences and are particularly suited to case-hardening criteria. The simple meter readings are ideal for nontechnical operators and scales can be calibrated in tolerance units as a basis of acceptability. It is obvious that the technique, under suitable standardization, is ideally adapted to automatic inspection and sorting.

"Moisture Measurement with an Electronic Dew Point Indicator" was described by V. E. Suomi of the Department of Meteorology of the University of Chicago. After developing an elementary treatment of moisture relationships in the atmosphere, he showed that the dew point method of moisture measurement has a definite advantage over others in that its percentage accuracy is nearly constant over a wide range of temperatures. In common with previous instruments, his dew point indicator depends upon the photoelectric scanning of a refrigerated mirror and initiation of mirror heating as soon as the mirror is fogged. The important innovation lies in the use of r.f. induction heating for fast response and elimination of lags which ordinarily reduce the precision of the method. The accuracy and performance of this instrument were described along with possible industrial applications.

R. D. Evans, Massachusetts Institute of Technology, Cambridge, Mass., in his paper, "The Application of Radioactive Indicators to Industrial Problems," stated that most of the published work in this field is in biochemistry and medicine and that, although considerable work is in progress on the industrial and analytical applications, little can be released at the present time for publication. After citing some published work—for example, "Measuring Concentration and Film Thickness of Printing Ink and Paint Films" by Buchdahl and Polglase [ANAL. CHEM., 18, 115 (1946)]—he described the determination of the uniformity and amount of sodium oleate on rayon yarn. After the unsuccessful use of fluorescent dyes for this determination, Na 24 was mixed with oil and sodium oleate before application. The quantity of sodium oleate, 17 mg. per meter, must be uniform, and the uniformity and amount were determined by the Geiger counter with an accuracy of 2% on a length of 1 mm. Other applications were mentioned, such as measuring the thickness of enamel coatings on manufactured products. Usefulness of the method in industrial hygiene problems was shown in tracing dust and smoke fumes and in determination of mercury in air inhaled by operators in plants or laboratories. This method is far more sensitive for the estimation of mercury than the use of ultraviolet light. It was pointed out that some consideration has been given to identification of manufactured articles by the addition of isotopes. This method of marking a product may find wide-scale use to protect both the consumer and the manufacturer against substitution and fraud. By tracer techniques one industrial plant is following the elimination of a deleterious impurity in a 12-ton batch process. There is no preprint of this paper available.

"Instrument Servicing and Maintenance in an Educational and Research Electrical Laboratory" was the subject of the paper by H. N. Hayward, University of Illinois, Urbana, Ill., who outlined the practice in checking new instruments when received and preparing them for use. He reviewed identification marking and modifications or additions found desirable in adapting commercial instruments and other laboratory items to meet storage, handling, and usage conditions in a particular laboratory. He also described a combination instrument and apparatus requisition and service record system, and an instrument damage, repair, and calibration data file, and gave procedures for testing and inspection that have been effective in detecting damage and other conditions requiring attention. The paper included an account of organization and operation of a calibration and standards laboratory to service and maintain several hundred instruments and provide other essential services.

Lynn D. Wilson of the Corn Products Refining Co., Argo, Ill., discussed "Polarographic Analysis—Principles, Techniques and Applications," in which he reviewed the basic theory leading to the Ilcovič equation and its practical applications. The principal recording polarographs were described and also the simpler manual devices. The qualitative and quantitative aspects of polarography were explained with typical examples of industrial applications, particularly for trace constituents in alloys and major constituents in plating solutions.

These were but a few of the many topics discussed at this important conference. There were the customary discussions on servomechanisms, computers, and many examples of industrial control applications, none of them without indirect interest for the analyst. It is becoming an endless and arduous task to keep track of the developments which command the attention of the modern analyst. One can no longer trust labels—the radio engineer or aeronautical expert may have an analytical problem—or in its absence he may have a solution for which the analyst has been waiting.

CORRESPONDENCE

Formation of Explosive Derivatives in Determination of Cobalt as Potassium Cobaltinitrite

SIR: In a note on explosion in determination of cobalt as potassium cobaltinitrite, Broughton and associates (*1*) state that the explosion always took place when they concentrated the solution coming from the filtration of cobaltinitrite. They also observed that the explosion took place soon after the formation of a purple compound, which they suggest is a new complex of nitro or nitritocobalt which may have been responsible for the explosion.

This is very interesting to those who work with this kind of cobalt complex.

Observing the medium in which the reaction and explosion take place, the following suggestions based on bibliographic sources may be of some interest.

Would it not be reasonable to admit the formation of derivatives of fulminic acid?

Wieland (*5*) states, "Nach meiner Theorie geht die Knallsäure-Bildung vom Alkohol über Acetaldehyd, Isonitrosoacetaldehyd, Isonitrosoessigsäure, Methylnitrolsäure zur Knallsäure. Acetaldehyd ist von Wöhler selbst als erstes Produkt erkannt worden. Da Ponzio schon früher die Isonitrosoessigsäure durch Stickstoffdioxyd in Methylnitrolsäure übergeführt hat, die ihrerseits nach meiner Beobachtung in Knallsäure und salpetrige Säure zerfällt," and gives the following chemical equations:

$$\begin{matrix} HC.COOH \\ \| \\ N.OH \end{matrix} \longrightarrow \begin{matrix} O_2H.CH + CO_2 \\ \| \\ N.OH \end{matrix}$$

$$\begin{matrix} O_2N.CH \\ \| \\ N.OH \end{matrix} \longrightarrow C{=}N.OH + HNO_2$$

The cobalt would act catalytically in the formation of fulminic acid.

Once this acid is formed, in all probability the complex $K_5[Co^{III}(OCN)_{11}] + 22H_2O$ would be built. This is a very explosive fulminate according to Wöhler and Berthmann (*6*).

It is also possible that another explosive compound is formed as the ethylnitrolic acid, because the erythro salts of this acid are red and very explosive (*2*, *3*, *4*).

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BOOK REVIEWS

Micro-Diffusion Analysis and Volumetric Error. *Edward J. Conway.* 2nd edition. xix + 357 pages. Crosby Lockwood & Son, Ltd., 20 Tudor St., London E.C. 4, England, 1947. Price, 21s.

In 1940, the reviewer stated of the first edition, "This book appears to be a valuable if not actually indispensable addition to the library of any microchemist interested in biochemical methods, and a valuable possession as well for the general analyst . . ." Of the second edition, certainly as much can be said, with the additional statement that the revision has not only brought the material reasonably well up to date but considerably improved the presentation.

From 32 chapters in the first edition, the text has been expanded to 43, most of which increase represents new material, largely the description of the numerous new analytical diffusion techniques that have been published by a number of authors. The simplicity and accuracy of diffusion analysis have appealed to many investigators, who have extended the range of analysis and developed new applications. Basically, the diffusion technique described is most readily applicable to volatile nitrogen compounds, or compounds which can be transformed into them, and to the halogen group. For this reason, the new edition, like the old, is largely concerned with the analysis of ammonia, total nitrogen, urea, and a few related nitrogen compounds; the halogens; and carbon dioxide or compounds which liberate this gas under suitable conditions. The second edition includes also diffusion procedures for quantitative analysis of nitrate and nitrite, amide nitrogen, blood glucose and fermentable sugar, carbonic anhydrase, oxidation rate of organic substances, acetone, acetaldehyde, lactic acid, threonine, ethyl alcohol, carbon monoxide in blood, and total molecular concentration in small fluid samples.

The general organization of the book remains essentially unchanged from the first edition. Part I deals with apparatus and principles of diffusion analysis; Part II, methods of analysis; and Part III, the error of volumetric titration. Of Part III it can be stated that few if any treatments of volumetric errors in texts examined by the reviewer are as practical and complete as that given in this book. Concerned primarily as it is with matters of drainage, holdup at pipet tips, and similar sources of error, it is supplementary to, rather than duplication of, such excellent treatments of volumetric errors as that of Kolthoff and Stenger's "Volumetric Analysis," Vol. I. The treatment of chemical errors is, on the whole definitely less practical than that of the latter authors. Aside from some deficiencies, the section on errors is valuable to any analytical chemist who is concerned with maintenance of accuracy and an understanding of his basic operations.

The paper and typography of this volume are of good quality.

It is probably unfortunate that in America the difficult availability of proper diffusion analysis equipment and the limited access to this useful volume on the subject of diffusion analysis have retarded the adoption of these methods. It is to be hoped that wider attention will be given to a technique which is inherently simple, capable of high accuracy, and wide in its application. PAUL L. KIRK

Semimicro Qualitative Organic Analysis. *Nicholas D. Cheronis* and *John B. Entrikin.* xiv + 498 pages. Thomas Y. Crowell Co., 432 Fourth Ave., New York 16, N. Y., 1947. Price, $3.75.

The main novelty of this text is an emphasis on the use of 1 or 2 decigrams of sample for class reactions and preparation of derivatives, whereas older texts, Kamm, Shriner and Fuson, and McElvain, specify five to ten times this amount of material. The apparatus and manipulations described by Cheronis and Entrikin are conventional and involve a reduction of the previously overlarge scale of operations in test tubes, flasks, beakers, filters, etc., to a minimum of about 50 mg. of sample, which the student can handle conveniently. There is no attempt to teach manipulation in capillary tubes or chemical microscopy.

The approach of the text is essentially that of the sound Kamm (1922) system which later authors have followed in large outline

The chapters discuss in order: purification and determination of physical constants; detection of elements other than carbon, hydrogen, and oxygen; solubility tests with water, dilute acid and base, ether, and sulfuric acid; class reactions for detection of functional groups; and preparation of derivatives. A valuble innovation is an introduction to chromatographic adsorption, Chapter XV, by A. L. LeRosen.

The authors assert in the preface (page v) that three groups were considered as users of their book: industrial chemists and workers in related fields, students in college courses in qualitative organic analysis, and students in first-year organic chemistry. The last group is ordinarily not considered in a manual of this type; authors generally assume at least a year of organic chemistry as the student background. This text, in the reviewer's opinion, would be of little use to first-year organic students. To college seniors and graduate students, who can get along with the somewhat sketchy exposition of the theoretical material, the text should be useful for its excellent bibliographies, clear and (sometimes overly) detailed procedures, and good selection of class tests. In connection with class tests, the reviewer was pleased to see reference to Davidson's use of mixed indicators for detecting weak acids and bases, and to note extensive use of the ferric hydroxamate test for esters, amides, etc.

It is to the professional group that the text should be the most useful. The number of entries in the derivative tables is greater than in other manuals, as is the number of types of derivatives (many of the tables have a width of two pages). There seems to be a good effort to indicate the reliability of reported melting points, and there is considerable discussion of the best derivatives to make for specific types of unknowns. Many of the entries are compounds interesting to the industrial chemist—e.g., sulfonic acids—and to toxicologists (Table 42 of physiologically active compounds). C. W. GOULD

Sequential Analysis. *Abraham Wald.* Wiley Mathematical Statistics Series. Walter A. Shewhart, editor. xii + 212 pages. John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y., 1947. Price, $4.

This is a technical book, an exposition in mathematical terms of the theory of sequential tests. This theory was developed by the author during the war, and until now has been available in less complete form, only in a restricted pamphlet and a few journal articles. The companion restricted pamphlet on applications has already appeared as a book of pamphlets (SRG-255) published by the Columbia University Press in 1945, which is still the reference for those who wish to apply sequential analysis to a standard case.

Sequential analysis was foreshadowed by Dodge and Romig's double sampling plans, where the results of testing a first sample were classified as satisfactory, unsatisfactory, or inconclusive, and in the third case another sample was taken and tested. At the urging of Friedman and Wallis, the development of a general theory of such step-by-step procedures was undertaken by Wald, who solved the basic problems in an amazingly short time. Sampling plans and testing procedures based on this theory were then rapidly put into use in both government procurement and private industry.

This book can be recommended to scientists who feel at home with mathematical notation and who are familar, as the preface suggests, with college algebra and one course of calculus. They will be able to work slowly but surely through the body of the book, greatly enhancing their background in statistical theory.

Any scientist who is willing to read a sentence, stop and ask himself what it means, draw a sketch or two, and then go on, can learn much of the best current approaches to the testing of hypotheses from the 70 pages spread through the book which concern this subject. Since testing hypotheses is one of the principal functions of a scientist, the time will be well spent.

Those scientists or engineers fortunate enough to have a mathematician in their organization will do well to see that this book is available to such collaborators and that substantial parts of it are read.

In general, the author gives a precise and concise account, in mathematical language, without extended exposition. The one annoying feature of the book, to this reviewer, was the style of the the figures, where quantities known to range between 0 and 1 are represented on coordinate axes which extend to 2 or to 3, and then have an arrow pointing onwards! The paper and binding seem adequate. JOHN W. TUKEY

Mikro-Methoden zur Kennzeichnung organischer Stoffe und Stoffgemische. *Adelheid Kofler.* Vol. 1, 242 pages. Vol. 2, 135 pages. Mimeographed. Novitas, Innsbruck, Austria, 1947. Arthur H. Thomas Co., West Washington Square, Philadelphia 5, Pa. Price per set, $8.

Volume 1 includes a literature review up to the end of 1946, with subject index, and chapters on micromelting point determination, refractive index of fused substances, behavior of mixtures, mixed melting points, eutectic diagrams, testing for purity, qualitative and quantitative analysis of two-component mixtures, molecular weight determination, and extensive treatment of microthermal analysis for observation of polymorphism, isomorphism, and liquid crystals.

Volume 2 gives tables covering over 1000 organic compounds, arranged according to micromelting points, with eutectic temperatures, refractive index of the fused substance, and information on special behavior of compounds during the melting process.

The book is based on the work by Ludwig and Adelheid Kofler and co-workers and is an extended version of the monograph by Ludwig Kofler on micromethods for the identification of organic substances, published in 1942 in the *Zeitschrift des Vereines Deutscher Chemiker.*

First-Year Qualitative Analysis. *Carl J. Likes* and *Aubrey E. Harvey, Jr.* 134 pages. Thomas Y. Crowell Co., New York, N. Y., 1947. Price, $1.25.

The volume is an attempt to fill the need for a brief text on qualitative analysis, written on the freshman level, but designed for a fairly complete study of both cations and anions, judged from both experimental and theoretical standpoints. Instead of beginning with studies on group separations, the student is issued a composite solution of the ions being considered and the groups are removed one at a time from this solution as each is studied. Calculations based on the equilibrium law are spaced throughout the text to be considered only as they dovetail with the experimental procedures.

Fisher Award in Analytical Chemistry

C. G. Fisher, president of the Fisher Scientific Co., has offered to finance an award to recognize and encourage outstanding contributions to analytical chemistry. The Board of Directors of the AMERICAN CHEMICAL SOCIETY has accepted administrative responsibility.

It is hoped to present the first award in 1948. As nominations must be received not later than January 1, prompt action must be taken by all those who wish to propose recipients. To accelerate action, President Noyes has appointed a Canvassing Committee: C. M. Alter, chairman, G. E. F. Lundell, and M. G. Mellon. Rules for the award contain the following statements:

1. **Purpose.** To recognize and encourage outstanding contributions to the science of analytical chemistry, pure or applied, carried out in the United States or Canada.
2. **Nature.** The award consists of $1000 and a medallion. An additional allowance of not more than $150 is provided for actual traveling expenses to the meeting at which the award will be presented.
3. **Rules of Eligibility.** A nominee must be a resident of the United States or Canada and must have made an outstanding contribution to analytical chemistry. Special consideration will be given to the independence of thought and the originality shown, or to the importance of the work when applied to public welfare, economics, or the needs and desires of humanity.
4. **Award Lecture.** The recipient of the Fisher Award may be asked by the Award Committee to deliver a paper or lecture upon the subject of his scientific work at the time the award is presented.

Any member of the SOCIETY (except a member of the Award Committee) may submit one nomination. Such proposal must be accompanied by a biographical sketch of the nominee, including date of birth, a list of his publications, and specific identification of the work on which the nomination is based. Eight copies of this material must be sent to the Executive Secretary of the SOCIETY, 1155 Sixteenth St., N. W., Washington 6, D. C, and must be received before January 1, 1948.

AIDS FOR THE ANALYST . . . .

Determination of Total Solids in Sulfate Pulp Mill Evaporator Feed Liquor. B. B. Edmonds, Jr., The Chesapeake Corporation of Virginia, West Point, Va.

ALTHOUGH the determination of total solids by refluxing with xylene is less time-consuming than the overnight oven drying method, it requires upwards of 2 hours as performed in this laboratory. With the control laboratory primarily in mind, an attempt has been made to devise a method of reasonable accuracy which would require less time.

Experiment I. Rectangles of 0.022-inch caliper bleached blotting paper, cut to 2 × 4 inches, were dried in an oven maintained at approximately 230° F., and cooled in a desiccator. One milliliter of sulfate pulp mill evaporator feed liquor was transferred to each of seven such blotters, which were returned to the oven. At the end of 15 minutes the blotters were removed, cooled again in the desiccator, and rapidly weighed. The weight of the dry solids was calculated.

The Baumé of the liquor was determined at 80° F. and the weight of the sample read from a pipet calibration curve shown.

Division of the dry solids weight by the weight of the sample, multiplied by 100, gave the per cent total solids

Blotter	Total Solids %
1	15.4
2	15.9
3	15.2
4	15.4
5	15.6
6	15.6
7	15.2

Experiment II. An analytical balance accurate to ±1 mg. was placed on the oven in such a manner that the left weighing pan was suspended by a wire which led through holes in the top of the oven and the bottom of the balance case to the left arm of the balance. Thus the steps involving cooling in the desiccator were eliminated.

Ten solutions of sulfate pulp mill evaporator feed liquor were prepared, which ranged in specific gravity from 1.047 to 1.087. Total solids were determined on each solution by three different methods: (1) blotter method as described but modified according to the preceding paragraph; (2) refluxing with xylene; and (3) overnight oven drying.

Specific Gravity	Per Cent Total Solids		
	Blotter	Xylene	Oven
1.047	9.5	10.5	9.4
1.050	10.3	11.2	10.6
1.054	11.2	11.5	11.2
1.062	12.1	12.7	12.3
1.063	13.0	13.0	13.0
1.065	13.5	13.8	13.4
1.073	14.8	14.5	14.9
1.081	16.2	16.0	16.4
1.084	16.9	16.6	17.0
1.087	17.1	17.5	17.6

Preventing Extension of Cracks in Repairing Glass Apparatus. Ernest R. Kline, Department of Chemistry, University of Connecticut, Storrs, Conn.

MOST glass blowers are aware that moistening a file scratch facilitates breaking a length of glass tubing. The moistening agent may be either water or saliva and the exact nature of the action is obscure. The author has observed that unless the finger with which the saliva or water is applied is free from grease, the scratch will become more resistant to fracture upon application of pressure. It seemed logical that this operation could be used in reverse to check the extension of a crack or to prevent its starting.

The procedure used in this laboratory consists of applying an approximately 1 to 1 mixture of No. 10 motor oil and vaseline to the glass with a camel's-hair brush. The article to be repaired is then presented to the flame in the usual way and with reasonable care. By the time the grease has been burned away the glass will have reached the softening point and all danger of cracking will be past.

The only failures experienced in the use of this procedure have been encountered in cases where a crack started in an inner seal and extended into the inner tube where the grease could not be applied. One particularly gratifying use is found in the replacing of tips on burets where the break is within a half inch of the stopcock. "Ringing off" is prevented by the use of the grease and more rapid heating of the region to be repaired is permissible.

A Modified Atomizer for the Flame Photometer. Vincent Toscani, Russell Sage Institute of Pathology, New York, N. Y.

THE need for a rapid method for the quantitative estimation of sodium and potassium has led to the development of the flame photometer [Barnes, R. B., Richardson, D., Berry, J. W., and Hood, R. L., IND. ENG. CHEM., ANAL. ED., **17**, 605 (1945)].

One of the difficulties encountered was the inability of the atomizer to produce a constant spray after several weeks' use. The internal surface of the metal needles became rusted and altered the characteristics of the spray. This necessitated the making of a new atomizer unit after a short period of time.

To overcome this trouble a new atomizer was constructed of glass as shown in Figure 1. The unit was made by E. Machlett & Son, New York.

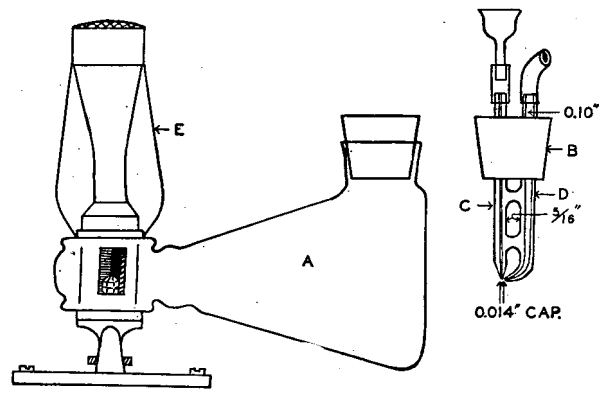

Figure 1

Flask *A* is the medium through which the spray from the atomizer is carried to the burner, *EC* is a capillary tube of 0.014-inch bore through which the unknown solution is fed. *D* is a capillary tube of 0.10-inch bore drawn to a tip having a bore of 0.014 inch. *C* and *D* are joined together with two solid glass rods. The distance between the two capillaries is $^5/_{16}$ inch.

The all-glass atomizer has the following advantages: The glass unit can be easily duplicated, the spray is always constant, and in case of clogging of the capillaries, another unit can be quickly substituted while the clogged unit is being cleared in cleaning solution. The atomizer operates efficiently using 10 pounds air pressure, while a pressure of 2.5 pounds is used for the burner gas.

Several all-metal atomizers manufactured by the Spraying Systems Co. of Chicago have been used by other laboratories and appear to work satisfactorily.

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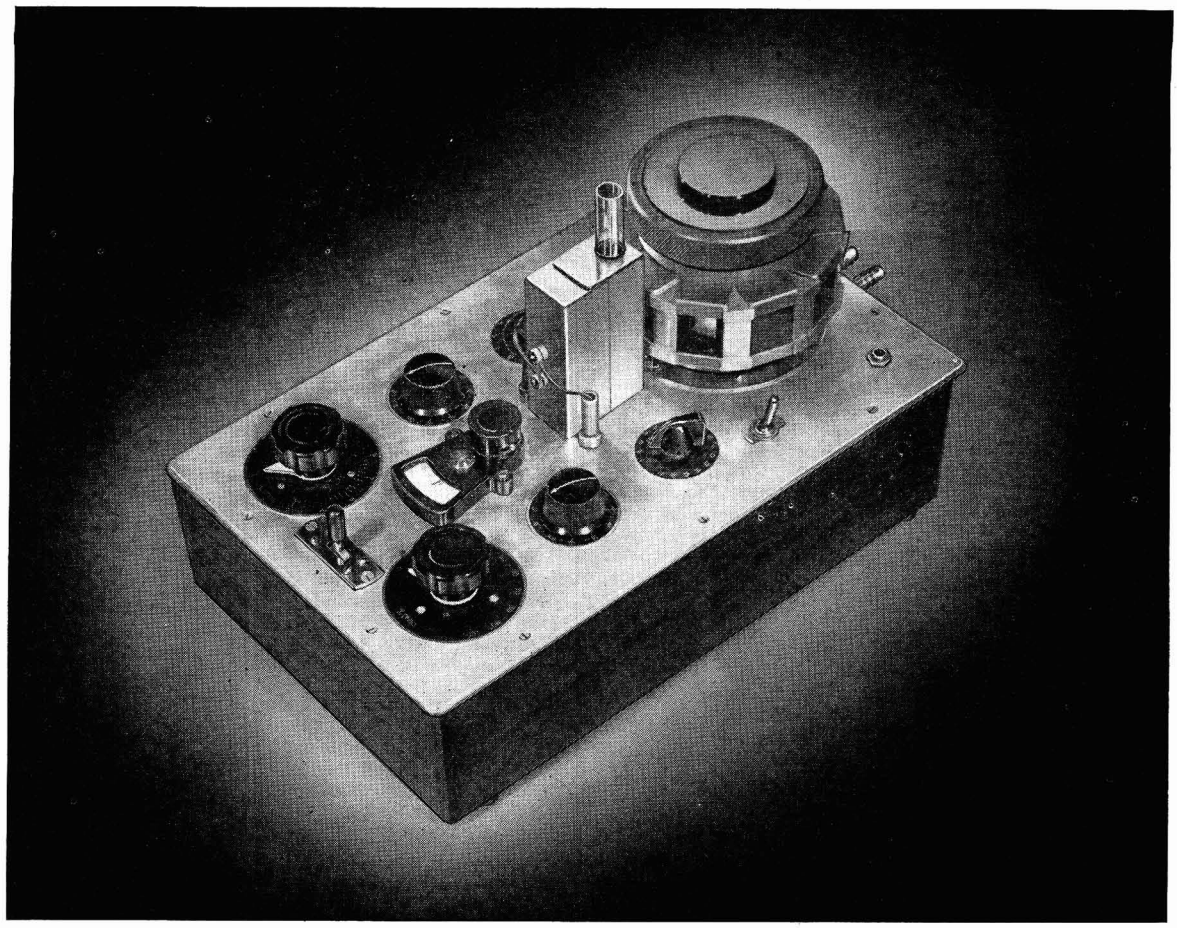

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LABORATORY APPARATUS AND CHEMICALS

INSTRUMENTATION

A versatile capacity-sensitive circuit, recently become commercially available, is suitable for a variety of control problems in the laboratory and plant

by Ralph H. Müller

SIMPLE control equipment has been a necessary adjunct to laboratory instruments for a long time and there are few laboratories which do not require thermostats, pressure regulators, and the like. The first use of electronics in thermostat control is more than a quarter of a century old, for in 1921 D. J. and J. J. Beaver of Columbia described a line-operated tube circuit for use in conjunction with mercury-toluene regulators. In most of the better, commercially available thermostats, electronic control is a standard feature.

An extremely versatile circuit has recently become commercially available, known as the Thermocap relay, manufactured by the Niagara Electron Laboratories of Andover, N. Y. It is furnished in a "laboratory" and in a "plant" model. A general view of this control is shown in Figure 1.

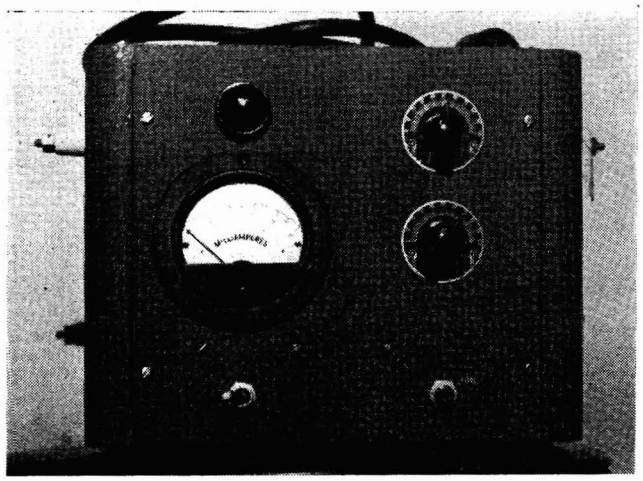


Figure 1

The circuit is a.c. line-operated and is based on a capacity-relay scheme of Shepard. This relay was originally developed for burglar alarm service, using the variable capacity to ground created by persons moving in the vicinity of an "antenna." A 6B8G tube is used as an r.f. oscillator with an RC network in the grid lead. If the distributed capacity between this lead and ground is changed by a very small amount, the amplitude of oscillation is changed by large amounts. The resulting amplitude change is fed through the diode elements of the 6B8G to the control grid of a 25A6G power pentode, the plate circuit of which includes a relay and milliammeter. The reversible relay contacts connect the power line to the load which is to be controlled.

The control function is achieved by producing a capacitance change between the control grid and ground. The simplest example is illustrated by Figure 2, *A*, in which a thermostat is to be controlled by an ordinary mercury-in-glass thermometer.

The grid connection is made to a metal clip which is fastened at the appropriate point on the thermometer stem. The capacity of the mercury to ground is large and will increase as the meniscus approaches the plane of the metal clip. At a certain critical position the Thermocap will operate. In practice, it is not necessary, indeed not feasible, to move the clip until positive relay action is secured. The clip is adjusted to the desired point and an adjustable trimmer condenser which is part of the "grid-leak" network is adjusted until the circuit is brought to the control point. Small changes in temperature will now exert on or off control. If the control point is not quite correct, it may be changed by an appropriate shift of the clip and readjustment of the trimmer. An alternative control element is shown in Figure 2, *B*, as a split clip, one section of which is connected to ground directly. This arrangement is suitable for the control of liquid level in manometers, burets, flowmeters, etc., and operates with conducting or nonconducting liquids.

It has been found that with a thermometer with 1° C. calibrations, an average of ±0.1° C. control may be achieved; one calibrated to 0.1° C. will control to ±0.02° C., and with special thermometers of large bulb and fine capillary as little as ±0.001° C. will effect control.

Minute pressure changes are readily used for control by the Thermocap. The pressure change is communicated to a thin metal foil diaphragm, the motion of which changes the capacitance between diaphragm and a metal electrode placed a few thousandths of an inch away from it. Differential pressures are similarly accommodated by exerting the pressure on either side of the diaphragm. In a related technique, radiation effects are detected and controlled by using a blackened diaphragm as a receiver and depending upon its flexure on heating. In this case the diaphragm casing is open on both sides to eliminate ambient pressure fluctuations.

As a typical example of a useful application, laboratory distillation control may be cited.

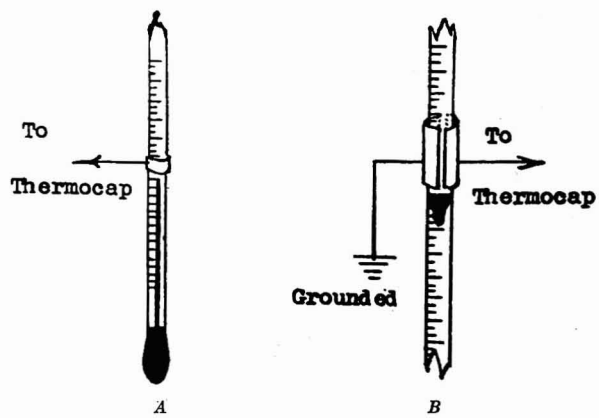


Figure 2. Simple Clip (*A*) and Split Clip (*B*)

It was desired to control the boiler heat input by the head temperature, to retard boiler heating if the reflux went too high in the column, and to turn off the heat when the receiver was filled to a predetermined level. All these functions were performed by one Thermocap by connecting one wire to the head thermometer, a longer wire to a clip on the reflux column, and a third wire to a clip on the receiver. The heater was plugged into the output of the Thermocap. If the reflux and distillate were below the predetermined level, the boiler heat was continuously controlled in accordance with the head temperature. Should the reflux rise too high and threaten carry-over, the heat was turned off until it quieted down. When the receiver had filled with a

INSTRUMENTATION

distillate to the desired level, the heat was cut off until the material was removed. In addition, higher boiling fractions could not contaminate the distillate, as the head temperature was prevented from rising by the Thermocap until its control point was purposely reset.

Obviously, any small displacement can be converted into a capacitance change and serve to control the Thermocap. On this basis, the motion of a pointer on a gage, meter, or galvanometer can be used without any physical contact with the moving element. In a typical installation shown in Figure 3, Thermocaps are controlling the temperature of furnaces. In this case, small metal vanes are located in proximity to the galvanometer needle of a potentiometric pyrometer. Any deflection of the galvanometer from the preset value operates the Thermocap. There is nothing particularly critical about the setting of these vanes or in their fabrication. The manufacturers of the Thermocap are in a position to devise and install control vanes or meters, galvanometers, etc., for special problems or applications.

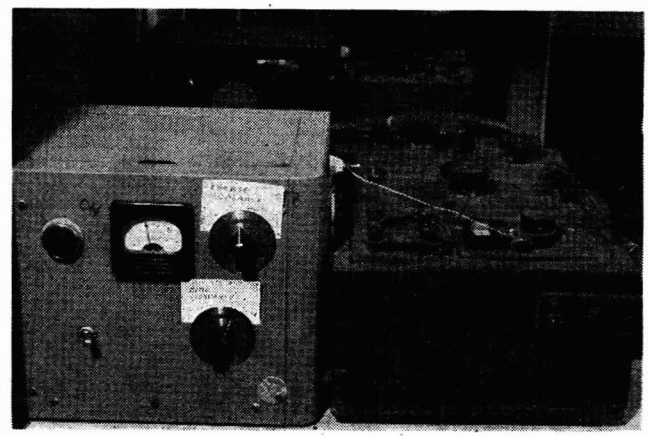


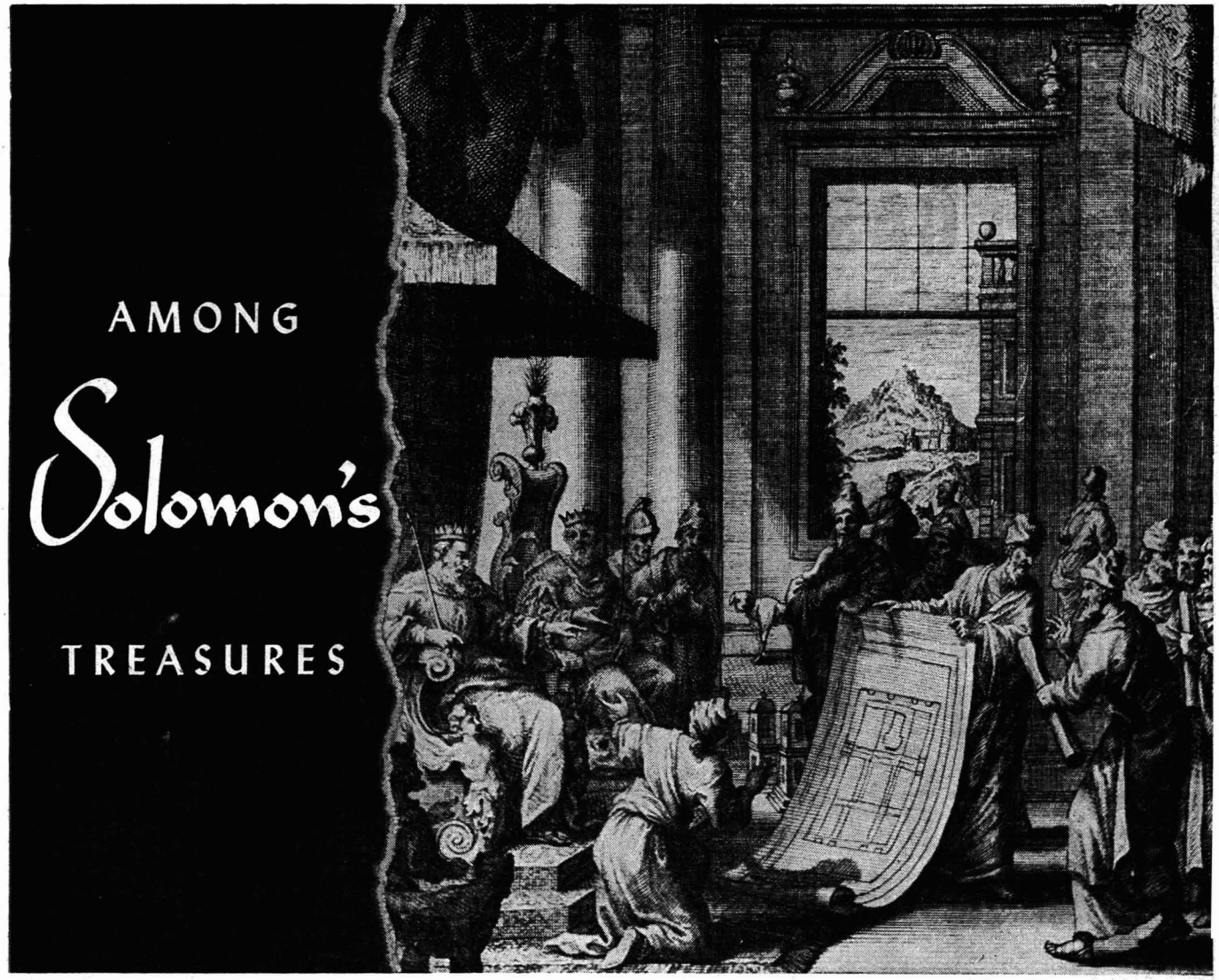
Figure 3

This method of control is analogous to another scheme which finds wide use in industrial controls in which two small coils are placed in the tank circuit of an oscillator. If a moving vane is caused to enter the plane of the coils, oscillation will cease abruptly. This action is usually transferred to a trigger tube which actuates a relay. The Thermocap is adaptable to the smooth control of large amounts of power in addition to its "on-off" action. This arises from the fact that the plate current in the output stage increases uniformly as the input-controlling capacitance changes. The output tube therefore acts as a varying resistor and may be used to phase-shift a large thyratron.

Interesting uses have been made of the Thermocap in conductivity measurements. If two ring electrodes are fastened to the outside of a glass tube and one of them is grounded and the other connected to the control grid of the Thermocap, control may be effected by a change in the conductance of the solution in the tube. The electrodes are external to the system, do not have to be made of noble metals, and can be crude, as long as their locations are stable and secure. There is no one-to-one correspondence between the true conductance and the equivalent capacitance changes, although they are quite similar. Presumably, this is of little importance in many applications and is outweighed by the very great sensitivity to conductance changes.

In all probability the Thermocap could be used as a very simple element in servo-mechanisms in which the initiation of control by the primary element would start a compensating element to oppose the change in the original variable. On this basis, one has the opportunity of eliminating all arbitrary or empirical factors in the control or measuring operation.

We were amused and startled recently in the laboratory of one of our gifted organic friends. Along with a number of important operations which were proceeding simultaneously, he had fitted a distillation assembly with the Thermocap control, essentially as described above. Most of us would be satisfied with a simple alarm or trouble lamp as an indicator, but this chemist is also a music lover and had connected a broadcast receiver in the relay circuit; consequently when Beethoven went "off the air" he knew that his attention was required.



Lead, the low-melting-point metal of many uses, is mentioned in the Old Testament as being found among Solomon's treasures. In ancient times, the Romans mined lead when they controlled Wales. Today, the British Isles still produce a large percentage of the world's supply of this essential element.

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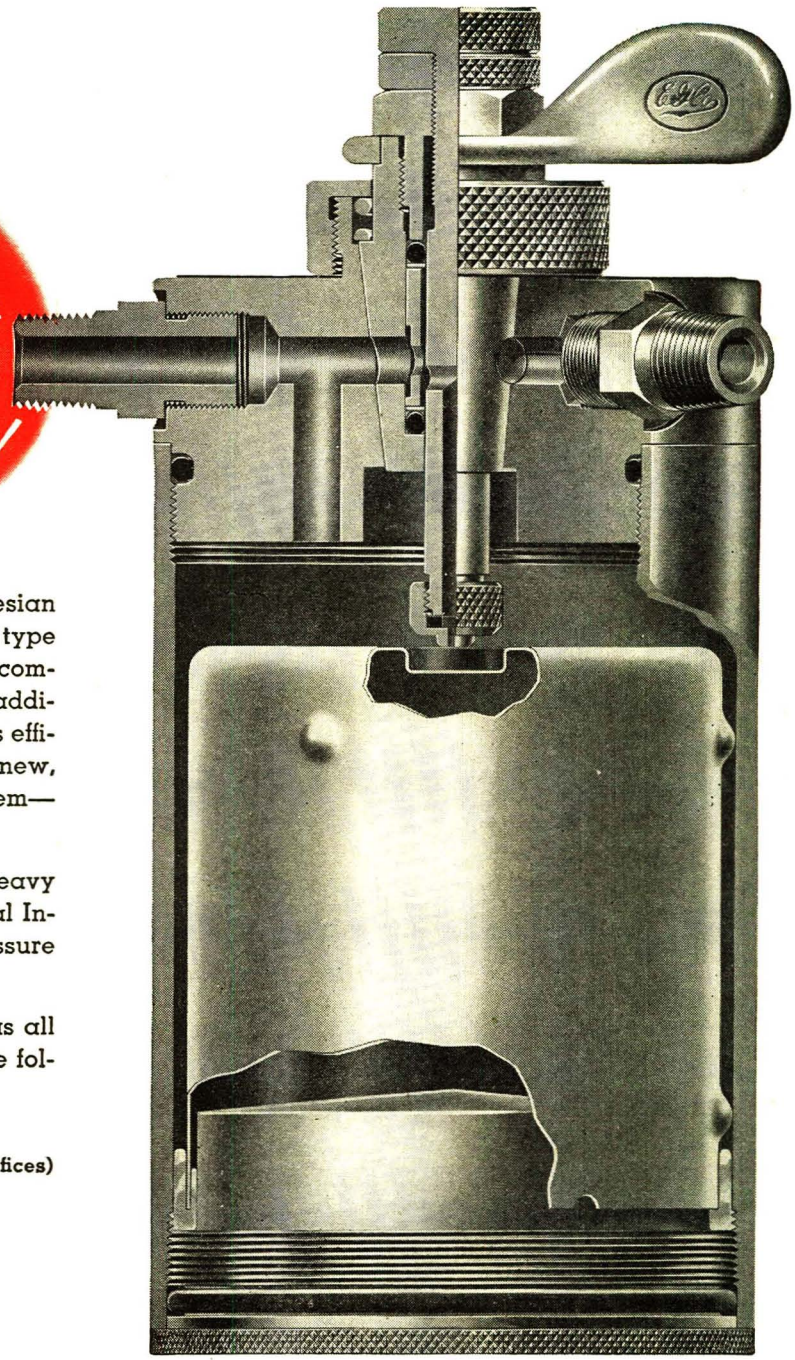

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VISKON—radically different new filtering material recently developed by Visking Research—now points the way to improved methods of filtering many types of industrial liquids.

Exhaustive tests with VISKON indicate economies and other important advantages far beyond the limitations of other filtering materials.

PROPERTIES OF VISKON

Not a paper, VISKON is an unwoven cotton or rayon cloth—strongly bonded with an *insoluble agent*. The two different types of VISKON are available in a wide variety of weights and sizes—and the principal properties that recommend VISKON for many different filtering applications are:

1. High wet strength
2. Unusually high flow rate
3. Ability to support standard filter aids such as diatomaceous earth and similar filtering material
4. Re-usable when carefully washed
5. Cuts cost because it is re-usable
6. Chemically pure and non-toxic
7. Durable—doesn't fall apart in use
8. Insoluble—fibers bonded with insoluble agent
9. Lint-free—as compared to woven cloth or paper
10. Porous yet absorbent
11. Will not ravel. No threads to contaminate flow lines.

TYPICAL SUCCESSFUL APPLICATIONS

Recent tests indicate decided advantages in the use of VISKON for filtering of gelatinous products, edible oils, glucose, sugar liquors, varnishes, photographic emulsions, starches and air.

Used on plate and frame filter presses by one of America's largest food processors, VISKON gave substantial operating economies. While four complete uses of VISKON have been standardized on in this plant before discarding, tests indicate it could be used safely five to eight times. Very successfully used on certain applications in sparkler type filters.

Tested in a large sugar refinery, VISKON withstood an unprecedented number of filterings before being replaced with new VISKON.

TEST VISKON WITHOUT OBLIGATION

To enable you to determine how VISKON may fit in with your filtering requirements, and to give research men every opportunity to examine and test VISKON, samples will gladly be sent on request. Simply write us on your letterhead—or use the convenient coupon. Either way, no obligation to you.

VISKON...a product of VISKING Research

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NOW... temperatures to 3,000°f ... continuous operation to 2,500°f with the NEW Lindberg *one-unit* laboratory box furnace!

● You get this great temperature range in the new Lindberg Model G-10 laboratory furnace. This versatile box furnace can also be used as a muffle furnace, or with carbon blocks for non-oxidizing atmospheres. The furnace can be operated continuously up to 2,500° F. and its 3,000° F. top heat can be used intermittently.

COMPACT. This is a self-contained unit that's only two feet wide and three feet from front to back. All necessary instruments and accessories are mounted inside the supporting base.

The furnace is five feet high with door closed. Working chamber, door lever, and most-used controls are at easy operating level. Front and sides are full-enclosed; quick access to the working mechanism is through mesh guard plates on the back.

The work chamber is 12″ deep, 6½″ wide, 4½″ high. The furnace shell is insulated with 3,000° F. insulating brick backed up with magnesium block.

The work chamber door lifts vertically, so the hot side is always away from the operator. Counterbalanced, it opens at a touch of the lever mounted on the right side, and locks in open position.

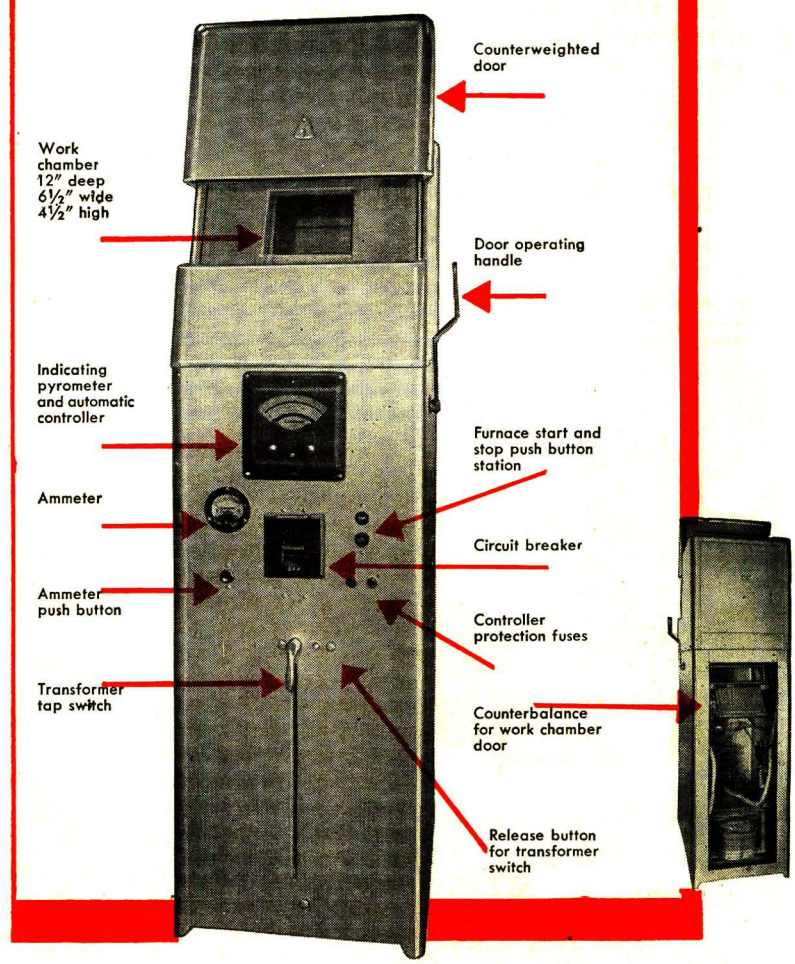
UNIFORM. Heating is even, with 10 silicon carbide *Globar* heating elements distributed equally at top and bottom of the work chamber.

FAST. The 3,000° F. top heat capacity provides heat at any lower level more quickly.

EXACT. Model G-10 reaches and *holds* exact temperatures. The indicating controller pyrometer is entirely automatic . . . operates electronically.

Model G-10 is designed for operation on 230 volts, 60 cycle, single phase A. C. Special voltages in A. C. to order. The variable voltage transformer has a capacity of 8 KW and is used in conjunction with the 11-point tap switch.

Ask your laboratory equipment dealer for complete information about this new Lindberg Model G-10.



This back view, with mesh guard plates removed, shows quick accessibility

LINDBERG

Lindberg Engineering Company, Chicago, Illinois. Manufacturers of furnaces, hot plates, and carbon determinators for the modern laboratory.

SOLD EXCLUSIVELY THROUGH LABORATORY EQUIPMENT DEALERS

CHLORINE TRIFLUORIDE, perhaps the most reactive chemical compound ever made, is the latest addition to the Harshaw Fluoride Line and takes its place beside Bromine Trifluoride as another Halogen Fluoride made available to industry by Harshaw. "That stuff is just fluorine which has been tricked into staying liquid," commented a visiting chemist after reviewing our accumulated information on Chlorine Trifluoride.

Chlorine Trifluoride does show so many of the reactions of fluorine, such as those listed above, that often it is a very acceptable alternate to the element itself. It constitutes a very valuable supplement to the fluorine cells in laboratories and pilot plants conducting investigations in fluorine chemistry. It is a great aid in the elimination of delays imposed on experimental schedules by limited fluorine generation capacity.

The use of Chlorine Trifluoride is so simple—just a cylinder containing a volatile liquid gives you the reactivity of fluorine held under perfect control. Where the reactive properties of fluorine in a very slightly modified form are desired, Chlorine Trifluoride is the answer.

CHEMICAL PROPERTIES

1. Converts CoF_2 to CoF_3
2. Converts AgCl or AgF to AgF_2
3. Reacts vigorously with water, organic materials, hydrogen, sulfur dioxide and a vast number of other elements and compounds.

PHYSICAL PROPERTIES

1. Boiling point . . . . . 11.3°C
2. Freezing point . . . . —83°C
3. Density . . . . . 1.8 g/ml

OTHER HARSHAW FLUORINATING AGENTS

Antimony Trifluoride, Anhydrous
Argentic Fluoride
Argentous Fluoride
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Hydrogen Fluoride, Anhydrous
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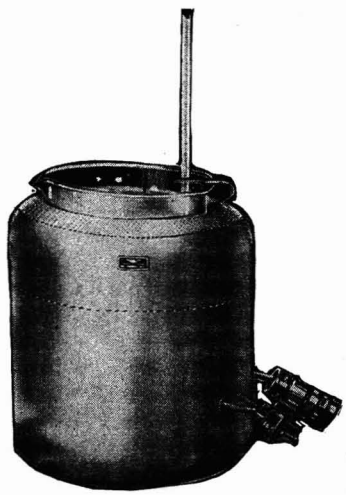
No glowing elements

No heat "build-up"

No exposed wires



A Gyco Jacket on a Griffin Beaker— one of many types now available.

Laboratory heating devices must be safe to use - and Gyco Heating Jackets (patent applied for) fully satisfy this requirement. Here's why:

The elements in Gyco Jackets *do not glow*, an essential quality when used in the presence of inflammable vapors. For a recent test a Gyco Jacket taken from stock was fitted with a flask filled with pure acetone. Under full power this volatile solvent boiled violently, splashing over the top without igniting. The flask was then removed and the elements were allowed to heat to over 600° F., as shown by a pyrometer. The flask filled with acetone was poured directly onto the operating elements, completely flooding them. The inflammable solvent evaporated safely—without flash or flame!

A second important safety factor found only in Gyco Heating Jackets results from placing the fully-insulated elements at the inner surface. There is *no heat "build-up"* requiring a cutback in power. Elements buried in insulation have a tendency to overheat because of a lag in heat transfer. The close contact of the elements in Gyco Jackets overcomes this danger by transferring heat rapidly and more efficiently.

You can also depend on Gyco Jackets for long life. They *are now guaranteed* against all material or construction defects for one year. Enjoy, too, the convenience of lightness and flexibility. All sizes are immediately available from stock, for flasks, jars, beakers, bottles, funnels, Buchner funnels, columns, and resin flasks.

Specify Gyco Heating Jackets on your next order. You can be sure they're safe! Descriptive literature sent on request.

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BAKER & ADAMSON *Announces*

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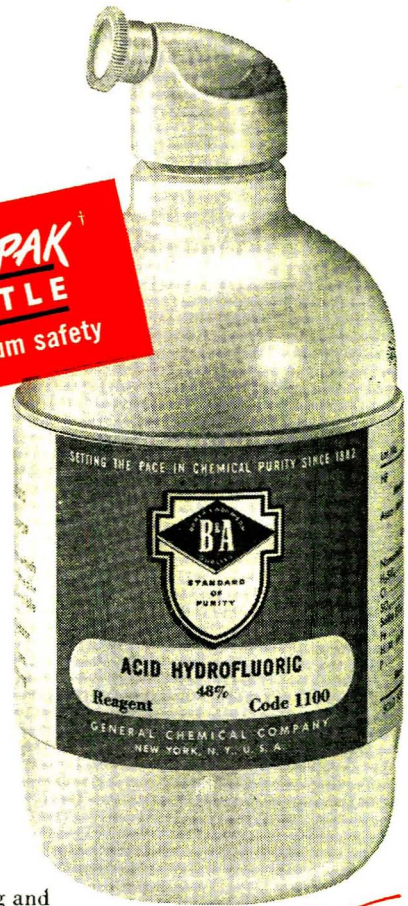
Exclusive SAFTEPAK† PLASTIC BOTTLE
maximum utility • maximum safety



Two years ago, Baker & Adamson pioneered plastic containers for its Reagent A. C. S. Hydrofluoric Acid. Thus, it eliminated for all time the hazardous old-fashioned wax bottle for HF so long in use by the chemical industry. This package met with immediate success and widespread acceptance, for it answered a long-felt need of laboratory chemists.

Now, with new advancements in plastics themselves, Baker & Adamson has developed a still finer container—its exclusive new *Saftepak* bottle. This offers the combination of special pouring and sealing features outlined, which provide maximum utility and protection in laboratory use. Study them carefully, then order your Reagent HF requirements from B&A today . . . and be among the first to enjoy the advantages of the exclusive *Saftepak*. It is readily available from convenient shipping points, coast to coast.

† Trade Mark, General Chemical Co.

1 Outstanding Pouring Control

Now pours drops, needle stream, or full flow, depending on your requirements.

Accurate measure . . . "siphon-action" pour-out draws back into bottle any drops clinging to lip when pouring stops.

Translucent . . . acid level always visible.

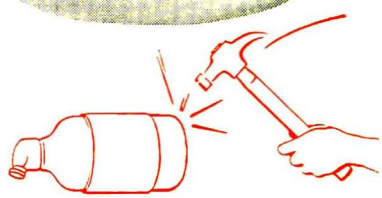
Easy to handle . . . the *Saftepak* with its sturdy encircling label band fits conveniently into your hand for easy pouring.

2 Acid Resistant

Entire unit made of special plastic highly resistant to aqueous HF.

3 Shatter-Proof

Bottle is pressure molded of shatter-proof plastic . . . does not become brittle, crack or break as do ordinary wax containers. Will not shatter or smash even under heavy impact.



4 Screw-Tight Cap

Provides easy reclosure; safeguards against possible spillage or leakage; protects Reagent A. C. S. purity of the acid.

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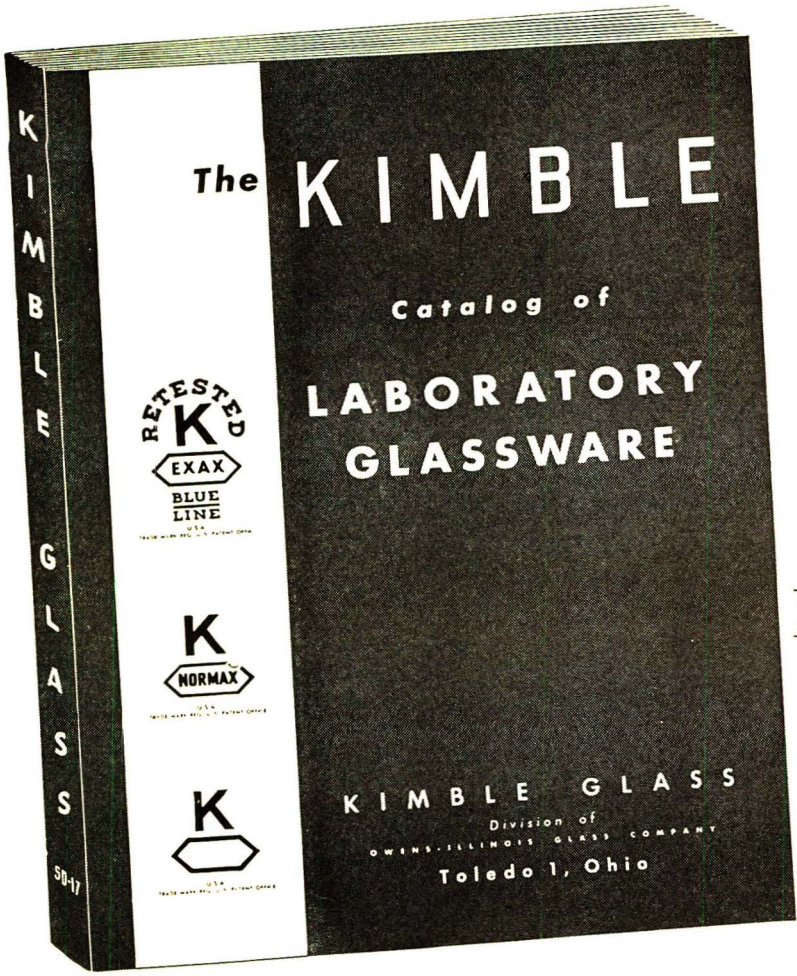

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A complete line of glassware for general and special uses in the research, analytical and control laboratories of science and industry.

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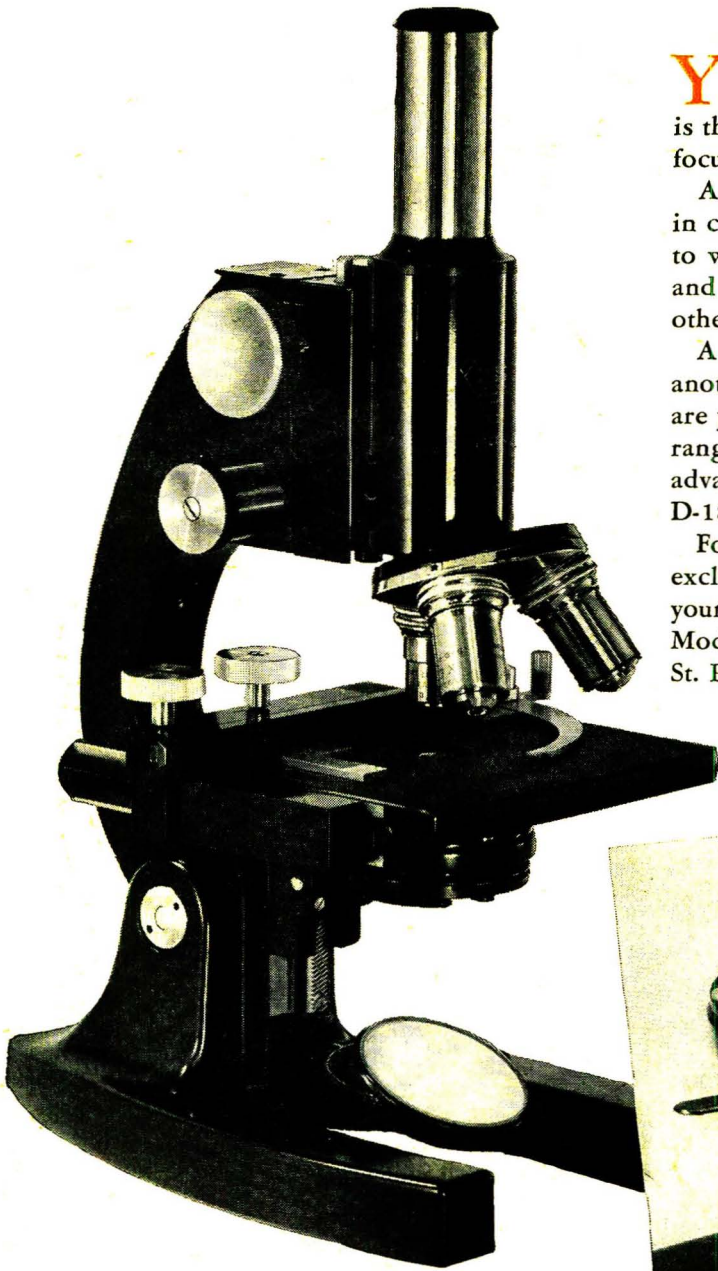
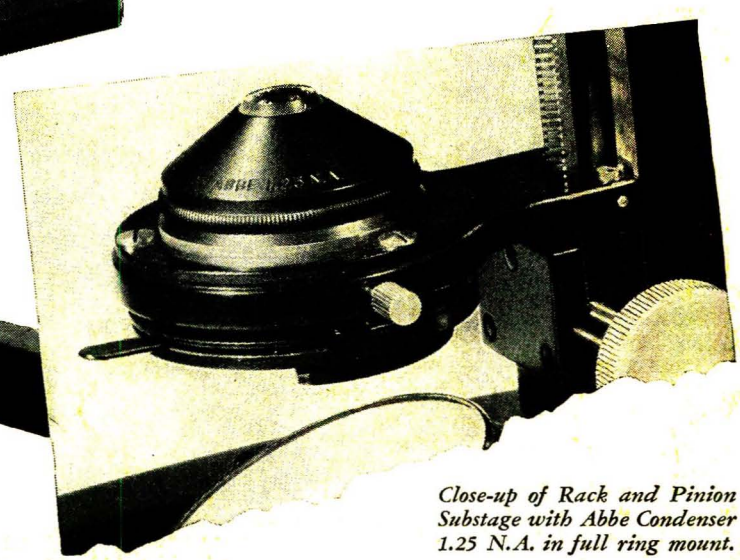


YOU'LL prefer the Bausch & Lomb Model BA-8 Microscope for basic laboratory work. One reason is the exclusive design of rack and pinion substage for focusing the condenser.

A full 360° ring mount gives you high initial accuracy in centration *for the full life of the instrument.* No arms to wear, bend, or break. *And,* the condenser is easily and quickly removed for substitution of dark field and other accessories.

A revolving nosepiece with roller-bearing stops is another exclusive Bausch & Lomb feature. Objectives are parfocalized and centered accurately. Magnification range of standard unit is from 20X to 970X. Other advantages and specifications are listed in Catalog D-185, available on request.

For superior performance, built by Bausch & Lomb exclusive design features, quality, and precision, be sure your new laboratory microscope is a Bausch & Lomb Model BA-8. Bausch & Lomb Optical Company, 609-J St. Paul St., Rochester 2, N. Y.



Close-up of Rack and Pinion Substage with Abbe Condenser 1.25 N.A. in full ring mount.

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