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THE THERMAL DEGRADATION OF POLYVINYL ALCOHOL

BY

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A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

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AT

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ABSTRACT

The thermal degradation of polyvinyl alcohol has been investigated using mass spectrometry, differential thermal analysis, and infrared spectroscopy unlike previous investigators, formaldehyde and acrolein were not observed volatiles. In addition, acetic acid was observed, a product not reported previously.

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INTRODUCTION

The application of polymers at ever increasing temperatures has given impetus to research on the chemistry of thermal decomposition. In recent years polymers have been used for a variety of high temperature applications, such as cooking vessels, motor insulation, and reentry vehicle heat shields.

In this study the thermal decomposition of polyvinyl alcohol (PVA) is going to be investigated. The current methods of analysis for thermal degradation are : mass spectrometry, gas chromatography, optical spectrometry, and differential thermal analysis.

For pyrolytic reactions a form of mass spectroscopy called mass spectrometric thermal analysis (MTA) will be used. In MTA the pyrolysis gases are analyzed continually with a fast scanning mass spectrometer as polymer samples are heated through linear rates of temperature rise. MTA results will supply information about the nature of the volatile products of decomposition of PVA, the temperature at which they appear, and more importantly, the relative amount of each product formed at each temperature.

The published data on the volatile products of thermal decomposition of PVA are not only limited, but are also conflicting. The thermal decomposition of PVA

is known to occur in two stages⁽¹⁾. The products of decomposition of the first stage which starts at around 200 C have been analyzed by a number of authors. Yamaguchi and Amagasa⁽²⁾ analyzed these products by chemical methods and found acetaldehyde, crotonaldehyde, benzaldehyde and acetophenone. Kaesche-Krischer and Heinrich⁽³⁾ found formaldehyde, acetaldehyde and acrolein. Ettore and Veradi⁽⁴⁾ using a pyrolysis-gas chromatographic technique reported that the main organic products formed at a pyrolysis temperature of 500°C were acetaldehyde and acetic acid. They also found smaller amounts of ethanol, methyl acetate and some hydrocarbons. At this temperature the products of both stages of decomposition must have been collected. Tsuchiya and Sumi⁽⁵⁾ using the latest gas chromatographic techniques found water, aldehydes of the general formula

$$\text{HC} \begin{array}{c} | \\ \text{-(CH=CH)}_n \\ | \\ \text{O} \end{array} \text{CH}_3$$

and methyl ketones having the formula

$$\text{H}_3\text{C}-\text{C} \begin{array}{c} | \\ \text{-(CH=CH)}_n \\ | \\ \text{O} \end{array} \text{CH}_3.$$

In the second stage of the decomposition of PVA, the macromolecules having polyene structure are degraded to produce carbon, hydrocarbons and other gases. Gilbert and Kipling⁽⁶⁾ analyzed the gases formed in the second stage decomposition of vinyl polymers.

MTA, therefore, should prove to be a very powerful

tool for determining the nature of the volatile products of thermal decomposition.

Infrared spectroscopy (IR) and differential thermal analysis (DTA) are most powerful in detecting transformations in the polymer before extensive degradation takes place. From DTA the temperature at which degradation starts can be obtained.

From the results obtained by different methods of analysis a comprehensive picture will be given as to the transformation that occurs when PVA is heated to decomposition.

MTA, the determination of total ion current as a function of time and temperature has been extensively used for investigation of pyrolytic reactions^(7,8). MTA was first described by Langer and Gohlke⁽⁹⁾, and has since been applied to polymers by Friedman⁽¹⁰⁾, and Shulman⁽¹¹⁾. In MTA pyrolysis gases are analyzed continually with a time-of-flight mass spectrometer, as polymer samples are heated through linear rates of temperature rise.

Determination of total ion current alone is not particularly informative in most cases of polymer degradation, when several products may be formed simultaneously or sequentially. The usual procedure has been modified by repeatedly scanning spectra as the temperature is raised or a linear program and then plotting peak height as a function of temperature.

Once the mass peaks have been ascribed to specific degradation products, and based on the assumption that the equilibrium pressure in the vicinity of the ionizing filament (and hence, the ion intensity) depends on the rate of degradation products, height of an m/e peak is therefore proportional to the rates of production of any products in whose mass spectrum it occurs. For competitive first order reactions the amount of each product is proportional to the rates of production so that the composi-

tion of the product mixture at a particular temperature may be derived from a single spectrum.

Experimental

A mass spectrometer-Finnigan Quad 1015-was used for the MTA experiments. Two to fifteen mg. samples were placed in a crucible, a spectrum was scanned at the following temperatures: 100, 180, 210, 250, 300, 325, 350, 375 and 400^o C, while the sample was being heated at a linear rate.

In all experiments a commercial grade of PVA was used. The manufacturer⁽¹²⁾ specifies this product to be 99 to 100% hydrolyzed polyvinyl acetate with a molecular weight of 115,000. All samples were dried before thermal degradation.

Results

Treatment of Data. A mass spectrum was obtained at each of the specified temperatures and they are shown in a tabular form in Tables I to IX. As it can be seen there are numerous absorption peaks in each spectrum, to account for each absorption seems to be very difficult. However, in the spectra taken from 100^o C to 250^o C the spectra of the following compounds can be definitely be observed: water, acetaldehyde, crotonaldehyde, acetic acid, acetophenone acetone, benzene, methane and acetaldehyde. And in the spectra from 300^o C to 400^o C the following compounds are

definetely present: carbon monoxide, water, carbon dioxide benzene, methane and acetaldehyde. These compounds account for the great majority of absorption observed and for their relative abundances.

Because of the difference in the nature of products formed at temperatures below and above 300°C, this temperature is the dividing line between two groups of products of decomposition and they will be treated differently throughout this study.

The individual spectrum of each of the compounds formed in the lower temperature range are shown in Table X in the form of m/e peak and the particular abundance. These spectra were obtained from standard tables⁽¹³⁾.

As it can be seen one cannot in all cases plot the parent peak absorption of each compound and assume it represents the abundance of that compound. For example, the parent peak of acetaldehyde at $m/e = 29$ is also common to acetic acid, and crotonaldehyde. What has been done is select a particular m/e peak for each compound that is characteristic for that compound only. In some cases this is the parent peak as well, as is the case with benzene where a peak at $m/e = 78$ can only be ascribed to benzene.

These characteristic peaks are shown below.

<u>Compound</u>	<u>m/e peak</u>	<u>Compound</u>	<u>m/e peak</u>
Ethanol	31(parent)	Water	18 (also parent peak)
Acetone	58(37%parent)	Acetaldehyde	44 (77% abundance of parent)
Benzene	78(parent)	Crotonaldehyde	70 (83% abundance of parent)
Methane	66(parent)	Acetic Acid	45 (also parent)
CO	28(parent)	Benzaldehyde	77 (also parent)
CO ₂	44(parent)	Acetophenone	104 (also parent)

By plotting the peak height of each of these peaks the relative abundances of each compound will be known. To make sure that this is an accurate method for treating the data obtained we have double checked in the following manner.

From Table XI it can be seen that there are numerous ^m/e absorption peaks that are common to two, or sometimes more products proposed. Therefore, the relative abundance of this common peak observed in each spectrum where it occurs must agree with the relative amounts calculated for each of the compounds that originate such peaks. For example, in the spectrum taken at 100°C (Table I) the 43 ^m/e

peak shows an abundance of 122 units. This peak at m/e 43 is a common absorption peak for acetaldehyde and acetic acid. Now, acetic acid shows an abundance of 82 units taken from its characteristic peak at m/e 45, which in turn corresponds to an abundance of 81 units for the peak at m/e 43, since in a pure spectrum of acetic acid the peak at m/e 43 will show an abundance of 99% of the parent peak at m/e 45. The absorption at m/e 43 also originates from acetaldehyde. Following the same reasoning as before acetaldehyde shows an abundance of 28 units (from m/e 44) and this corresponds to an abundance of 12 units for the 43 peak (43 peak is 42% of 44 peak). Therefore, the abundance at m/e 43 originating from these two compounds amounts to 93 units which accounts for most of the 122 units obtained in the spectrum.

The abundance of each degradation product obtained from a spectrum was double checked this way and in most cases 80 to 90% of the peak height was accounted for. It seems therefore that this method of calculating the relative abundance of a compound is valid and accurate.

Results

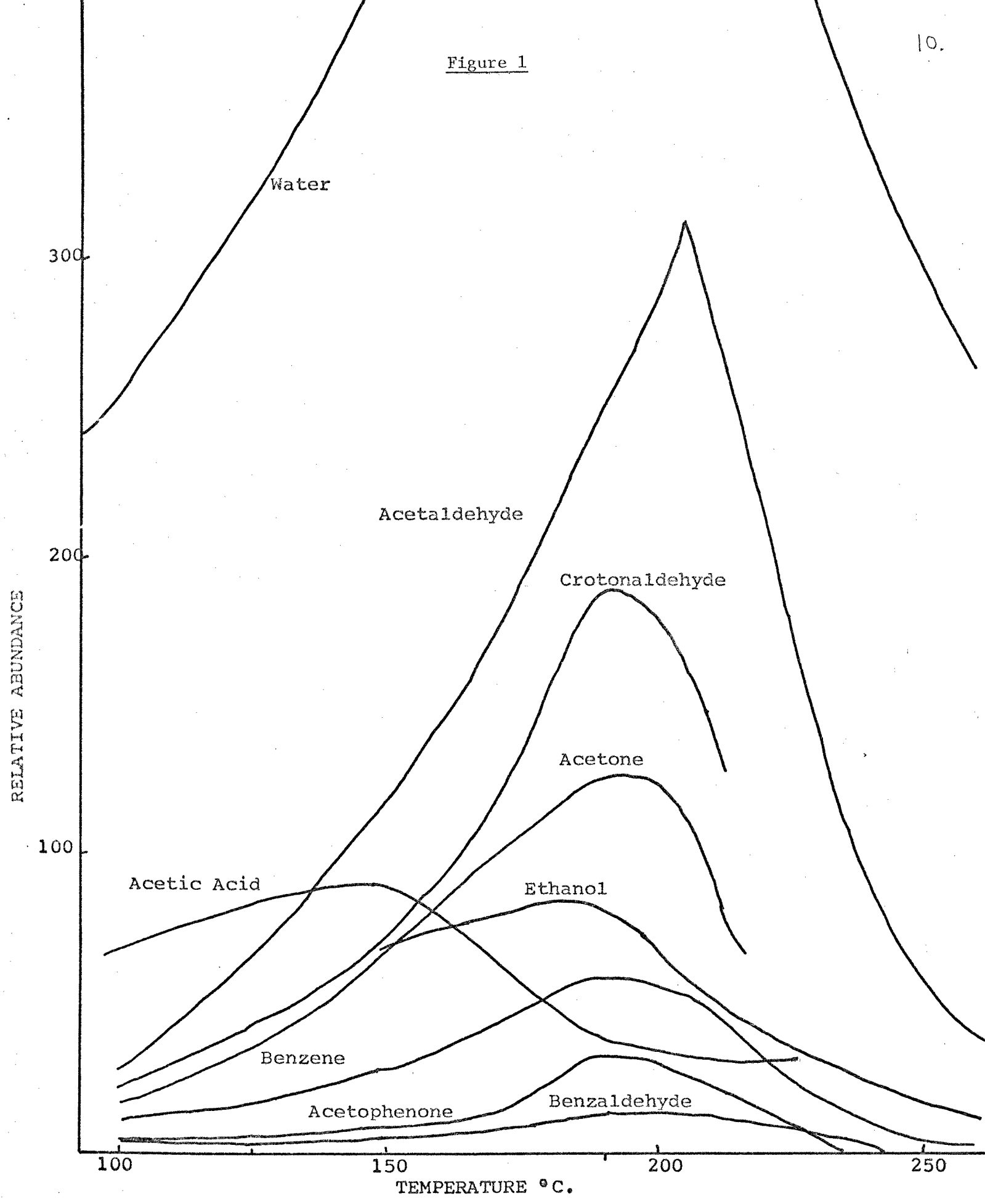
Following the method described above the relative amounts of each product of decomposition in each spectrum was obtained. A graph was constructed showing the relative

amounts of the decomposition products of PVA versus temperature.

Figure 1 shows the volatile products formed in the first stage and Figure 2 in the second stage of the thermal decomposition of PVA.

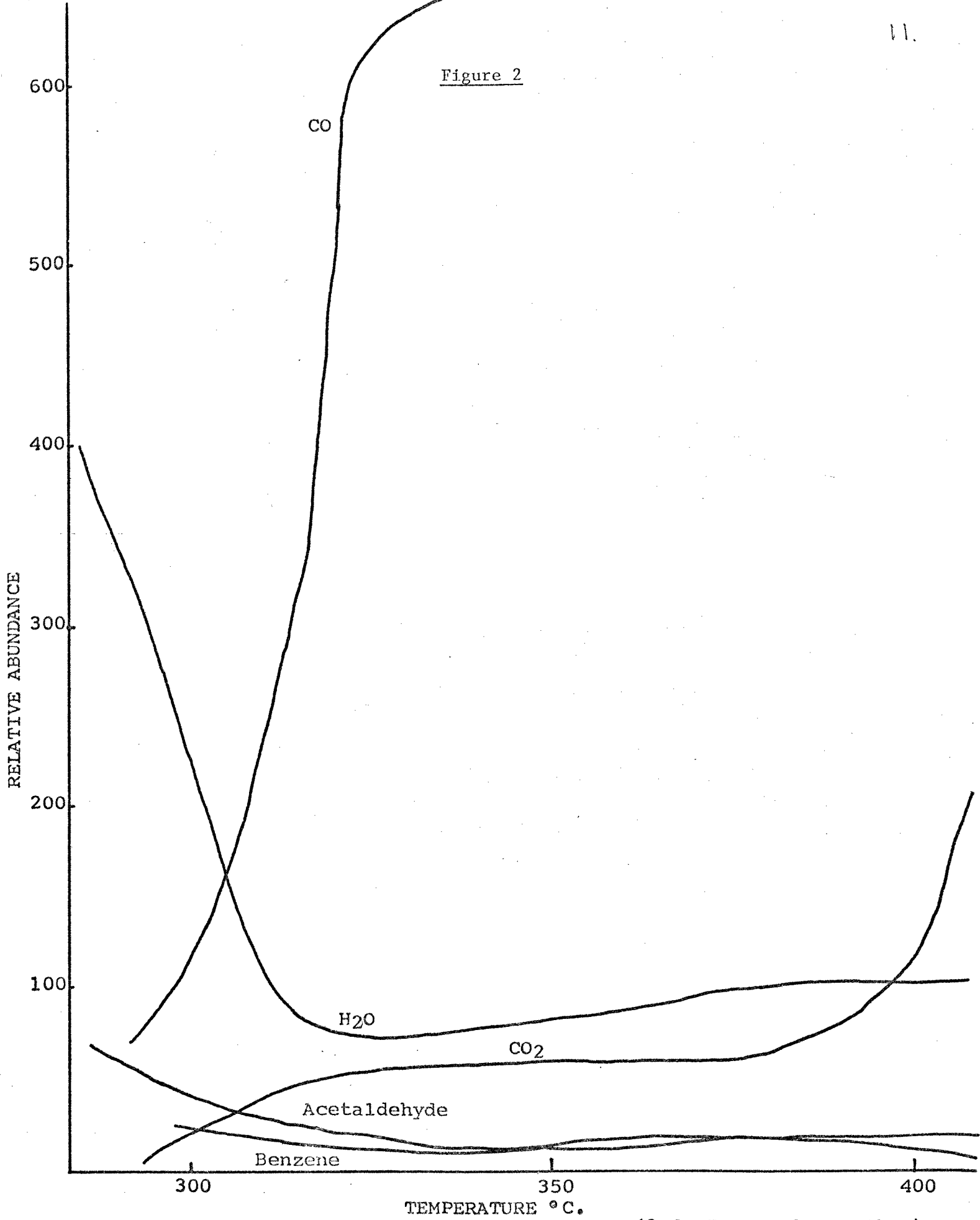
The first stage starts at about 100°C. Water is the main product formed throughout this stage. The exact amount of water could not be measured accurately because of overloading. Acetaldehyde and crotonaldehyde are major products of decomposition. The amount of acetaldehyde increases very rapidly starting at about 160°C so that in the range from 200 to 250°C it becomes together with water the two most abundant products. Acetic acid increases from 100 to 150°C and then it decreases abruptly to become after 180°C only a small contributor. Crotonaldehyde follows the general path of acetaldehyde but always in smaller amounts. Acetone shows a considerable amount but in a very narrow temperature range (150-210°C). Ethanol is formed throughout the first stage in small amounts, so is benzene which shows an increase around 180°C but then it decreases to a very small amount past 300°C. Acetophenone and benzaldehyde form only a very small part of the total of products evolved from PVA.

Figure 1



THERMAL DECOMPOSITION OF POLYVINYL ALCHOL (1st STAGE - 100-250°C.)

Figure 2



THERMAL DECOMPOSITION OF POLYVINYL ALCOHOL (2nd STAGE - 250-400°C.)

Starting at about 170°C the rate of decomposition of all products increases rapidly and at 200-210°C it becomes the fastest. Most of the curves show a maximum at this point. From 210 to 250°C a sudden decrease in the amounts of all products formed takes place. In most experiments performed little decomposition was observed in this range.

At about 300°C the second stage of decomposition starts to take place. In this stage carbon monoxide is formed in very large quantities and remains as the most abundant product. Water is formed in much lesser quantities than during the first stage, and remains very much constant from 300 to 400°C. Carbon dioxide appears at below 300°C but it is only when the temperature reaches 325°C when its amount becomes important. Acetaldehyde decreases to a very small level at 325°C and stays constant. All products formed during the first stage disappear at temperatures above 325°C, except benzene which remains constant in very small amounts. A minor component during the second stage is methane which shows a slight increase starting at 400°C.

A most interesting finding is the appearance of some unidentified products of high molecular weight starting at about 250°C. These high molecular weight species have m/e peaks of 180 and higher. The nature of these products cannot be investigated with the information we have avail-

able. However, the possibility of investigating their composition by MTA methods opens a new avenue for research. In most pyrolysis-gas chromatographic experiments one serious limitation is the inability to analyze products of decomposition that do not have sufficient vapor pressure at elevated temperatures. From this experiment it is shown that molecular species with high molecular weight are part of the products of thermal decomposition of PVA and that MTA may prove to be the method to investigate this phenomenon.

Discussion

In evaluating and comparing MTA data one point to keep in mind is that thermal degradation in MTA is carried out at a high vacuum and therefore the temperature at which a compound decomposes are always lower than the temperature of decomposition at atmospheric pressure. It has been observed that very little decomposition of PVA occurs at temperatures below 200°C ⁽⁵⁾ and from differential thermal analysis and experiments shown later on it is evident that at atmospheric pressure degradation starts to take place at about 230°C . Therefore, if in MTA experiment degradation of PVA is observable at temperatures between $100\text{-}150^{\circ}\text{C}$ it must be concluded that this is due to the high vacuum of the mass spectrometer. Further-

more, thermal analyses performed at higher pressures have shown that the lower decomposition temperatures obtained in MTA experiments are indeed due to pressure difference⁽¹³⁾.

In comparing the results presented earlier with published data on the volatile products of PVA decomposition several interesting points can be noted. First of all, contrary to the findings of Kaesche-Krischer and Heinrich⁽³⁾ we did not find formaldehyde or acrolein as part of the volatile products of decomposition of PVA. None of the spectra obtained showed a peak at m/e 56 which although not a parent peak for acrolein it should show as 83% of the parent peak at m/e 27. Some spectra show a peak at m/e 27 but they do not originate from acrolein. In the case of formaldehyde the parent peak is at m/e 18 and therefore can be observed by the presence of water but in the mass spectrum of pure formaldehyde there should be a peak at m/e 30 and its height should be 51% of its parent peak; this peak is not present in any spectrum. The difference in results may be due, to some extent, to differences in procedure. For example, if pyrolysis takes place in the presence of air, oxidation of volatile products will certainly occur. Also, differences in time span between sampling and analyzing can cause difference because of secondary reactions. However, the fact that

in all other studies reported in literature no formaldehyde or acrolein has been reported, insinuates that pyrolysis conditions may have quite different for obtaining such compounds.

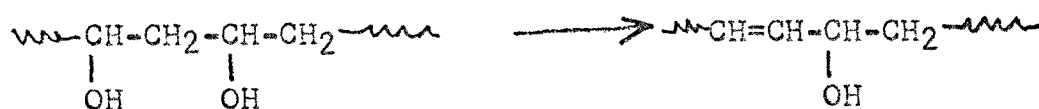
Ettre and Veradi⁽⁴⁾ pyrolyzed PVA under inert conditions and used a new device for minimizing secondary reactions. Their list of products however does not include crotonaldehyde, acetone, acetophenone, benzaldehyde which in the present study are present in considerable amount. On the other hand, we do not find ethane, ethylene and methyl acetate which although in small amounts (.6, .6 and 2.0% respectively) are present at temperatures up to 800 C. In their method, however, products of the first and second stage of decomposition are not differentiated which increases the possibility of secondary reactions. Also, their pyrolysis takes place at atmospheric pressure, whereas in MTA the sample is in a high vacuum.

The products of decomposition of PVA found by Tsuchiya and Sumi⁽⁵⁾ agrees to a great extent with the findings reported here. One compound found in this study and not reported by them is acetic acid. It is true that the amount of acetic acid should vary with different sources of PVA due to differences in percent hydrolysis, but nevertheless acetic acid must be present regardless of the source of PVA.

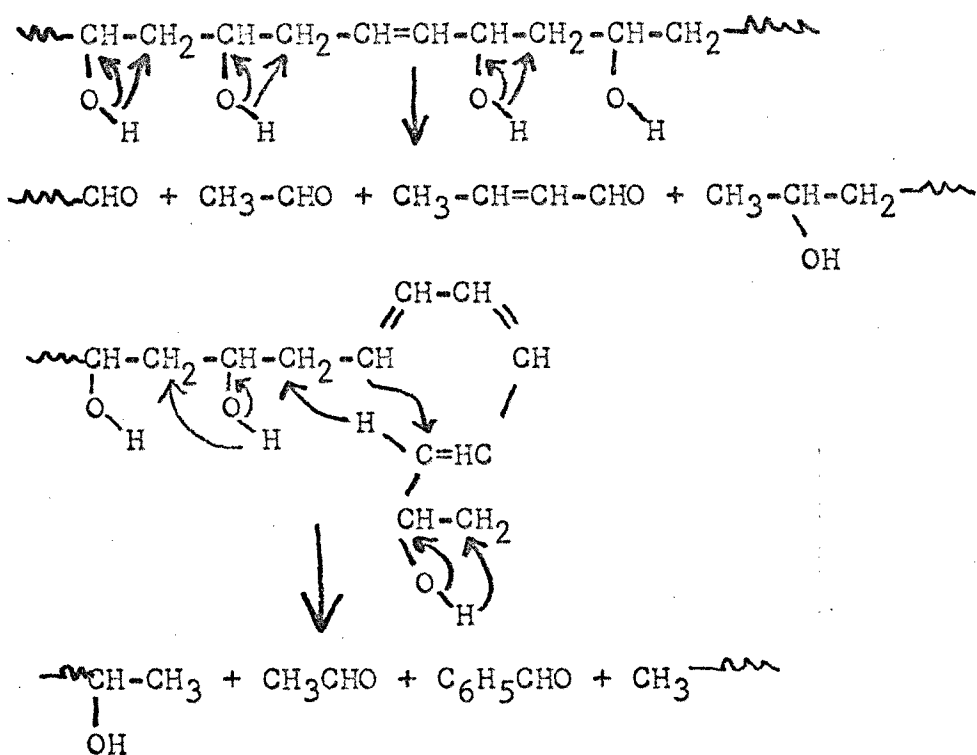
Compounds reported by Tsuchiya and Sumi not verified in this study are 3-pentene-2-one, 2,4-hexadiene-2-one, 2,4,6-octadiene-1-al and 3,5,7-nonatriene-2-one. The primary reason being the lack of pure mass spectra for these compounds. It should be added that some peaks have not been accounted for and therefore other compounds in lesser quantities must exist. Again, the conditions of thermal degradation between pyrolysis methods and MTA methods must be reemphasized. Even though in pyrolysis reactions the products of decomposition are swept by an inert gas flow as to minimize secondary reactions, this condition can not compare to the high vacuum that exists in MTA. Also, in MTA we analyze the instantaneous composition of the volatiles, whereas in pyrolysis studies the volatiles are collected over a period of several hours. For example, Tsuchiya and Sumi pyrolyzed their sample for 4 hrs. at 240°C. Also, when gas chromatographic techniques are used compounds that do not have sufficient vapor pressure cannot be analyzed. In this respect, Tsuchiya and Sumi, could not analyze a portion of their products of decomposition because of such a cause. In this experiment the existance of products of decomposition having high molecular weight has been verified.

Now, from a mechanistic point of view, the products

of decomposition can be accounted for in the following manner. Water is formed by a mechanism similar to that forming hydrogen chloride from poly (vinyl chloride) and acetic acid from poly (vinyl acetate), leaving a residue having conjugated polyene structure.



Acetaldehyde can possibly be produced simply by depolymerization of the PVA chain from the ends by a reaction like a noncatalyzed alcohol condensation, but elimination from within the polymer chain is more likely. The following types of rearrangements in the partly dehydrated polymer are no doubt mainly responsible for the decomposition of PVA.



Experimental

Infrared spectra can conveniently be obtained from films of PVA of thickness in the range 5-10 microns. Uniform films of PVA were formed by the slow evaporation of water from thin layers of aqueous solution on glass. The films were easily peeled off intact.

The free film was placed between salt crystals in a heating cell that attaches to a Perkin-Elmer spectrophotometer model No.457. The temperature of the cell was slowly raised from room temperature to 300°C and spectra were obtained at several temperatures. The temperature inside the cell was determined by using a thermocouple. The thermocouple leads were placed between the two salt plates, the heating cell has an opening that leads directly to the salt plates. The IR spectra obtained are shown in Figures 3-13.

Results and Discussion

IR Spectrum No. 1 (Figure 3) was taken at room temperature and when compared to published spectra of PVA⁽¹⁵⁾ very close agreement was found. Band assignments have been reviewed in detail by various authors^(16,17,18), but the table given by Liang and Pearson⁽¹⁹⁾ was used in this case. The infrared absorption bands of PVA are all quite broad and severely overlapped in the 600-1500 cm⁻¹ region. There are several reasons for this. About half of the bulk of

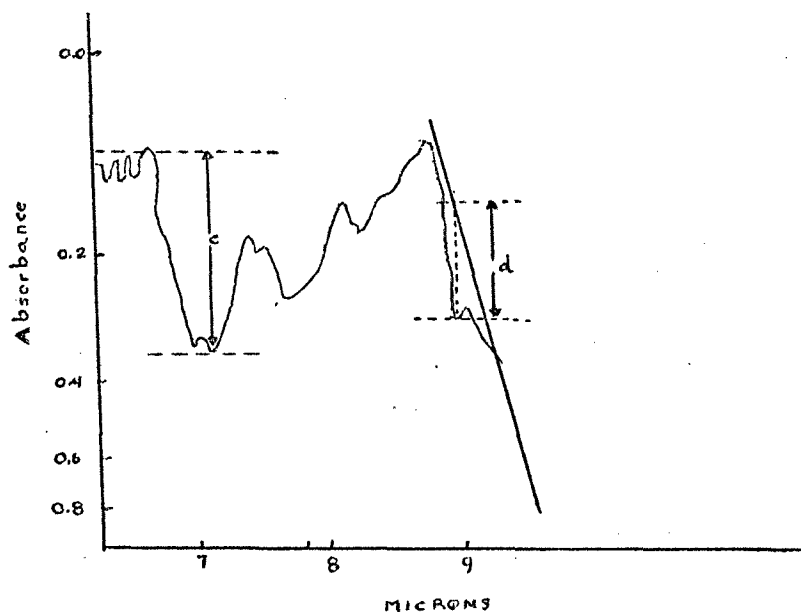
PVA consists of crystallites imbedded in a matrix of glassy material. The difference in symmetry between PVA molecules in the crystal and in the glass is expected to contribute two sets of frequencies to the infrared spectrum. Slight shifts between equivalent frequencies in the two phases no doubt contribute to the overlapping. As is well known, the hydroxy bands are always strongly broadened in hydrogen bonded alcohols, probably as a result of very pronounced anharmonicity of the vibrations, and the O-H in-plane bending motion is coupled strongly with other molecular motions that involve frequencies in the range 600 to 1500 cm^{-1} (15,19). The presence of isotactic and syndiotactic sequences introduces an additional duality of frequencies although gross effects from this cause are limited. The absorptions of most interest in this study are those at 3340, 1739, 1420 and 1141 cm^{-1} . First of all, from the band at 1739 cm^{-1} it can be determined that this commercial sample of PVA is almost fully hydrolyzed. The absorption at 1739 cm^{-1} belongs to the carbonyl band which is associated with the acetyl group. An infrared spectrum of a partially hydrolyzed PVA shows an intense peak in this region⁽²⁰⁾, whereas in spectrum No. 1 this band has almost disappeared.

The band at 1141 cm^{-1} has been associated with crystallinity of PVA. This band has been assigned to a

stretching motion of C-C stretching in the planar zig-zag backbone of the polymer chain in the crystal^(16,17,21), and this motion is almost certainly coupled with the C-O stretching motion, which is also coupled to the in-plane O-H bending motion⁽¹⁹⁾.

Sakurada⁽²²⁾ has measured the percent crystallinity based on the absorption at 1141 cm^{-1} and found good correlation to the percent crystallinity as measured by density determinations and by x-ray diffraction.

The basis for determining percent crystallinity in PVA is the crystalline sensitive band at 1141 cm^{-1} . The first step for this determination is to draw a line along the portion of the spectrum between 9.0 and $9.2\text{ }\mu$ extended far enough to intercept a vertical line through the 1141 cm^{-1} peak as shown in the following figure.



The vertical distance, 'd' between the 1141 cm^{-1} peak and the intercept point is then determined. Next, the vertical distance 'c' between the 7.1 micron peak and the base line is determined. The percent crystallinity is then calculated by using the following equation.

$$\text{Percent crystallinity} = 92 (d/e) - 18$$

The effect of temperature on crystallinity can readily be measured using this technique. The following table gives the figures calculated from spectra 1 to 6.

	<u>T°C</u>	<u>% Crystallinity</u>
Spectrum No. 1	25°C	27%
Spectrum No. 2	50°C	34%
Spectrum No. 3	100°C	37%
Spectrum No. 4	150°C	36%
Spectrum No. 5	175°C	28%
Spectrum No. 6	200°C	0%

The crystallinity at room temperature has been explained by Haerle⁽²³⁾ by means of the "fringed micelle" theory, which may be likened to microscopic cooked spaghetti in which crystallization has occurred in those adjacent parts that have well correlated direction and orientation of groups.

The amount of crystallinity of PVA at room temperature has been accurately measured by x-ray diffraction and it gives a pattern of reflections consisting of several

diffuse rings and a strong background due to general scattering.

Increasing the temperature results in a relaxation of intermolecular hydrogen bonds between the hydroxyl groups of PVA. The increased mobility should allow rapid crystallization of incompletely crystallized regions. From the figures obtain an increase from 27 to 36% crystallinity has occurred upon heating PVA film from 25°C to 175°C. Above 175°C the crystallinity decreases and as it will be shown later, melting occurs with the concurrent loss of crystallinity.

The effect of heating PVA from 25°C to 175°C results in a considerable increase in percent crystallinity. Above 175°C melting and decomposition takes place. By using IR some idea of the type of decomposition can be gained by following the 3340 cm^{-1} absorption by hydroxyl groups. The intensity of this band is seen to decrease as the temperature is raised. In order to gain some insight as to the content of loss in this absorption a table can be formed where the absorption at 3340 cm^{-1} can be compared to an absorption that remains constant such as the band at 2942 cm^{-1} due to C-H stretching. The ratio of these two absorptions at different temperatures is

shown below:

<u>IR Spectrum No.</u>	<u>T°C</u>	<u>Absorption 3340cm⁻¹ / Absorp. 2942cm⁻¹</u>
1	25	1.41
2	50	1.41
3	100	1.34
4	150	1.35
5	175	1.35
6	200	1.21
7	227	1.16
8	255	1.16
10	280	1.04
11	300	0.82

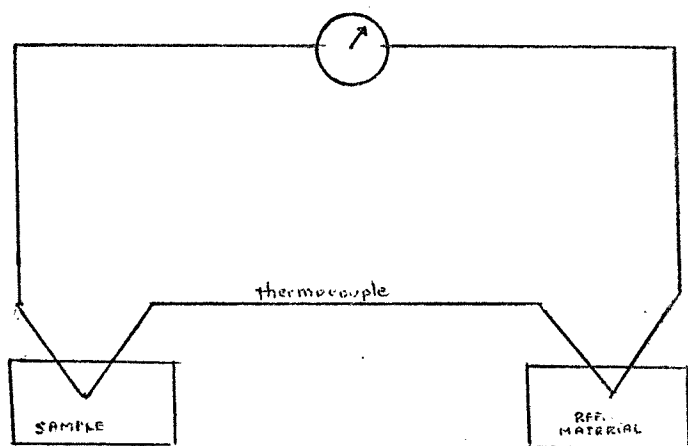
These results show that starting at about 175°C significant loss of hydroxyl groups can be evidenced, which in this case results in polymer degradation whose product is water^(4,2,24). Earlier MTA results agree with this fact as well as other studies performed using different methods. Above 255°C extensive decomposition is taking place as seen by the rapid decrease in the ratio of the two absorptions compared. It is also around this temperature where water shows the maximum rate of evolution in the MTA experiment. At temperatures higher than 280°C little hydroxyl functionality remains.

Other absorptions that show rapid decrease in intensity above 255°C are the peaks at 1446 cm⁻¹ (O-H and C-H bending) and 1096 cm⁻¹ (CO stretch and OH bend), which also indicate rapid deterioration.

The nature of the decomposition non-volatile products remaining can not be determined by IR analysis. The only clues as to their nature seems to be come weak absorptions in the range between 1580 and 1700 cm^{-1} that appear at temperatures above 255°C. Absorptions in this range can be due to carboxyl groups, alkene double bonds and possibly also carboxyl groups.

Introduction

Differential Thermal Analysis (DTA), or thermal spectroscopy measures the heat-energy change occurring in a substance as a function of temperature. Experimentally, the sample is heated side by side with an inert reference material at a uniform rate, and the temperature difference between them is measured as a function of temperature as shown in the following figure.



from the resulting curve or thermogram information on the temperature, heat, and rate of transformation can be derived.

DTA was first used by Chatelier in 1887 for the study of thermal transformations in days. Since then it has been

widely used in such fields as mineralogy, soil science, metallurgy and the chemistry of organic and unorganic compounds^(25,26). More recently DTA has been applied to the study of a wide variety of problems involving high polymers^(27,28,29)

In the present study DTA will be particularly helpful in detecting heat-energy transformations before degradation and most important it will tell us the temperature at which degradation begins.

More informative data concerning the thermal degradation of PVA can be obtained by thermogravimetry analysis (TGA). TGA is defined as a continuous process that involves the measurement of Sample weight as the temperature is changed by means of a programmed rate of heating.

Additional information concerning operation and principles of the apparatus can be found in the manufacturer's bulletin.

Again, a thermogram is obtained and from it the temperature of decomposition, the extent of degradation and kinetic parameters of degradation can be obtained.

Experimental

For DTA experiments the DuPont 900 differential thermal analyzer was used.

For DTA a heating rate of 15 and 20°C per minute were used. One experiment was run on air and another under vacuum.

Results and Discussion

DTA. Two DTA experiments were performed. The first experiment was run at a heating rate of 15°C per minute and the second one at 20°C per minute and they showed slightly different results which are presented below.

The thermogram of the first experiment is shown in Figure 14. This thermogram is characterized by a slight endotherm at about 40-45°C which is the glass temperature for this polymer. At higher temperatures there is a broad peak with a minimum at about 110°C. This transition temperature is not interpreted as a true endotherm but as the result of second order transition in the crystalline phase followed by further crystallization. It has recently been demonstrated that the PVA crystallite undergoes a transition at about 130°C⁽³⁰⁾. Also, from the previous

chapter on the infrared study during heating, it shows that at this temperature the percent crystallinity is the highest. This transition involves a change in the temperature coefficient of specific heat, as well as, a change in all the crystal lattice expansion coefficients. This is interpreted as a relaxation of intermolecular hydrogen bonds between the hydroxyl groups of PVA⁽³¹⁾. The increased mobility should allow rapid crystallization of incompletely crystallized samples, which was readily observed before.

From this gradual increase in crystallinity, a net gradual exotherm should be expected in the thermogram. The thermogram obtained in this study is consistent with this view.

The endotherm at 207°C is undoubtedly melting. The melting peak area is relatively large indicative of strong intermolecular forces, i.e. high crystallinity. Samples with small amounts of crystallinity show small area peaks⁽³²⁾. The melting temperature was taken as the minimum of the melting endotherm. Although this is not probably the temperature at which the last trace of crystallinity disappears, it is most easily identified.

This thermogram's melting curve doesn't quite return to the baseline but there is an overlap with the decom-

position deflection indicating that melting occurs with some degree of decomposition.

Past the melting point, degradation starts to take place. Extensive decomposition starts at about 250°C. Since this thermogram was run under air some questions may arise as to the exact melting and decomposition temperatures. Thermograms of PVA performed under an oxygen atmosphere differ markedly from thermograms under vacuum⁽³³⁾ since dehydration occurs even at the melting temperature and the polymer can take up oxygen to saturate the double bonds formed and this reaction is exothermic. For this reason a thermogram was also taken under vacuum.

Figure No. 15 shows the vacuum thermogram. The transition occurring before the melting point are hard to observe probably because of the higher heating rate (20°C per minute). The melting point occurs in this case at 224°C which agrees closely with results from other authors⁽³⁴⁾. The decomposition temperature appears at 277°C. Past 277°C there is little change in the polymer indicating that most degradation has taken place at lower temperatures than 277°C.

In the thermogram taken under air the shape of the curve after decomposition is different from the one taken

under vacuum. This difference is due to oxidative reactions that occur when the polymer is thermally degraded in the presence of air.

By using several methods of analysis a comprehensive picture of the thermal degradation of PVA has been gained. IR results indicate that heating PVA up to 50-100°C only small physical changes occur such as an increase in crystallinity. Using this technique the onset of chemical degradation is around 175°C where hydroxyl functionality is being lost. At 280°C little hydroxyl functionality remains, indicating extensive decomposition. The residue after heating to 300°C shows absorptions due to carbonyl groups, alkene double bonds and possibly carboxyl groups. We must emphasize that the IR experiment was run under air and the residue remaining must have oxidation products.

From DTA experiments the increase in percent crystallinity found by IR is verified by an endotherm observed at 110°C. At higher temperatures the melting point of PVA and the temperature of decomposition can be obtained. Experiments run on air and under vacuum are quite different, principally because of oxidative reactions occurring on experiments not run under vacuum.

IR and DTA therefore gives us information of changes occurring mainly before chemical decomposition of PVA. The MTA method on the other hand has given us a remarkable insight into the thermal degradation of PVA. Most products of decomposition have been determined temperature of their

appearance and more importantly their relative amounts. The fact that several products are formed together with water at low temperatures is very important. PVA is being used in an ever increasing number of applications, many of them include consumer products. Such products in the form of paper coatings or textile finishes could be exposed to temperatures high enough to evolve products such as acetaldehyde, acetic acid, ethanol and even benzene which are a hazard to human health.

In comparing MTA with other methods of analysis of thermal decomposition reactions we find several advantages. The precision of mass spectrometric measurements is usually higher than gas chromatography or other methods. Pyrolysis-gas chromatography does not give the instantaneous composition of the products formed at each temperature. And as noted previously MTA may be the preferred method for studying the nature of high molecular weight products of thermal decomposition of polymers.

- (1) J. B. Gilbert, J. J. Kipling, B. McEnaney and J. N. Sherwood, 3,1 (1962).
- (2) T. Yamaguchi and M. Amagasaka, Kobunshi Kagaku, 18, 645 (1961).
- (3) B. Kaesche-Krischer and H. J. Heinrich, Z. Physik. Chem., Frankfurt, 23, 292 (1960).
- (4) K. Ettore and P. F. Veradi, Anal. Chem., 35, 69 (1963).
- (5) Y. Tsuchiya and K. Sumi, J. of Polymer Sci., Part A-1, 7, 3151 (1969).
- (6) J. B. Gilbert and Kipling, Fuel, 41, 249 (1962).
- (7) H. G. Langer, R. S. Gohlke, and D. S. Smith, Anal. Chem., 37, 433 (1963).
- (8) R. S. Gohlke, and H. G. Langer, Anal. Chem., 37, No. 10, 25A (1965).
- (9) R. S. Gohlke, and H. G. Langer, Anal. Chem., 35, 1301 (1963).
- (10) H. L. Friedman, "The Relationship Between Structure and Thermal Stability of New High Temperature Polymers", ML-TDR-64-274. Air Force Materials Laboratory. Wright-Patterson Air Force Base, Dayton, Ohio, Aug. 1964.
- (11) G. P. Shulman, J. Macromol. Sci. (Chem.), A-1, (1), 107 (1967).
- (12) Monsanto Technical Bulletin No. 6082A.
- (13) G. P. Shulman, J. Macromol. Sci. (Chem.), A-1 (1), 107 (1967).
- (14) H. L. Friedman, J. Macromol. Sci. (Chem.), A-1 (1), 57 (1967).
- (15) H. Tadoroko, S. Seki, and I. Nitta, J. Chem. Phys., 23, 1351 (1955).
- (16) H. Tadoroko, H. Nagai, S. Seki and I. Nitta, Bull. Chem. Soc. Japan, 34, 1504 (1961).
- (17) H. Tadoroko, S. Seki, and I. Nitta, J. Polymer Sci., 22, 503 (1956).

- (18) K. Fujii, T. Mochizuki, S. Imoto, J. Ukida and M. Matsumoto, J. Polymer Sci., A-2, 2327 (1964).
- (19) C. Y. Liang, and F. G. Pearson, J. Polymer Sci., 25, 303 (1959).
- (20) J. G. Pritchard, Poly (vinyl Alcohol), Gordon and Breach Inc., N. Y. 1970.
- (21) H. Tadoroko, Bull. Chem. Soc. Japan, 32, 1334 (1959).
- (22) I. Sakurada, Poly (vinyl Alcohol), Kobunshi Gakkai, Tokyo, 1955.
- (23) J. W. S. Haerle, J. Polymer Sci., C, #20, 615 (1967).
- (24) Kaesche-Krischer, and H. Heinrich, Chem. Ing. Tech., 32, 598 (1960).
- (25) N. J. Smothers and Y. Chiang, OTA: Theory & Practice, Chem. Rubber Co., Cleveland, 1959.
- (26) W. W. Wendlot, Thermal Methods of Analysis, Interscience Publishers, Division of John Wiley & Sons, Inc., N.Y. 1964.
- (27) B. Ke, Organic Analysis, Vol. 4, Interscience Publishers Inc., N.Y. 1960.
- (28) B. Ke, Polymer Reviews Series, No. 6, Interscience Publishers, Inc., N.Y. 1964.
- (29) B. Ke, J. Polymer Sci., C, Polymer Symposie No. 6 Interscience Publishers, Inc., N.Y. 1964.
- (30) B. Ke, J. Polymer Sci., 42, 15 (1960).
- (31) R. K. Tubbs, J. Polymer Sci., A, 3, 4181 (195).
- (32) J. F. Kennedy, and G. W. Willcockson, J. Polymer. Sci., A-1, 4, 679 (1966).
- (33) B. Kaesche-Krischner, Chem. Ing. Tech., 37, 9 (1965).
- (34) R. K. Tubbs, J. Polymer Sci., A, 3, 4181 (1965).

TABLE ISpectrum #1 100°C

<u>m/e</u>	<u>Abundance</u>	<u>m/e</u>	<u>Abundance</u>
14	9	67	14
15	24	69	22
16	7	70	18
17	60	77	24
18	260	78	11
27	20	79	16
28	80	81	11
29	50	91	20
31	46	93	8
32	40	95	11
39	40	96	7
41	47	105	9
42	24	106	4
43	122	115	3
44	21	119	6
45	82	120	25
50	6	149	8
51	9		
52	6		
53	12		
55	14		
60	54		
65	11		

TABLE IISpectrum #2 150°C

<u>m/e</u>	<u>Abundance</u>	<u>m/e</u>	<u>Abundance</u>
14	16	57	20
15	52	58	24
17	160	60	56
18	01.	65	30
26	16	67	39
27	42	69	66
28	96	70	60
29	156	77	54
31	74	78	30
32	40	79	42
38	18	81	56
39	98	91	56
40	26	93	20
41	150	95	30
42	54	96	17
43	250	105	26
44	94	106	8
45	100	107	14
50	14	115	20
51	23	117	18
52	12	119	18
53	37		
55	36		

TABLE III

Spectrum #3 180°C

<u>m/e</u>	<u>Abundance</u>	<u>m/e</u>	<u>Abundance</u>	<u>m/e</u>	<u>Abundance</u>
14	24	53	100	107	32
15	76	55	88	115	41
16	25	57	42	117	39
17	88	58	48	119	38
18	01	60	32	120	16
19	14	63	30	121	30
26	32	65	100	122	33
27	100	66	32	128	12
28	120	67	110	129	28
29	260	69	170	131	31
31	80	70	157	132	20
32	24	71	14	133	26
37	24	77	144	141	16
38	40	78	61	143	22
39	270	79	110	145	26
40	16	81	204	147	18
41	230	91	150	148	16
42	110	93	48		
43	390	95	72		
44	200	96	14		
45	94	103	22		
50	31	104	24		
51	56	105	62		
52	12	106	12		

TABLE IVSpectrum #4 210° C

<u>m/e</u>	<u>Abundance</u>	<u>m/e</u>	<u>Abundance</u>	<u>m/e</u>	<u>Abundance</u>
14	24	55	62	119	28
15	76	57	28	121	20
17	139	58	42	122	20
18	01	60	14	127	20
26	30	63	22	128	29
27	72	65	48	130	24
28	108	67	76	132	18
29	274	69	144	140	14
31	48	70	138	142	18
32	20	71	24	144	20
37	18	77	88		
38	35	78	44		
39	217	79	68		
40	44	81	134		
41	300	91	98		
42	100	93	34		
43	325	95	50		
44	240	96	30		
45	44	105	42		
50	24	106	12		
51	40	107	22		
52	9	115	32		
53	64	117	30		

TABLE V

Spectrum #5 250°C

<u>m/e</u>	<u>Abundance</u>	<u>m/e</u>	<u>Abundance</u>
14	30	79	30
15	20	81	16
17	60	91	50
18	275	105	35
27	30	107	15
28	700	115	35
29	65	117	12
31	25	119	12
32	170	120	
39	45		
40	30		
41	60		
42	30		
43	80		
44	115		
45	25		
51	30		
53	25		
55	30		
67	20		
69	45		
77	40		
78	30		

TABLE VI

Spectrum #6 300°C

<u>m/e</u>	<u>Abundance</u>	<u>m/e</u>	<u>Abundance</u>
14	5	78	20
15	14	79	30
17	55	81	45
18	240	91	40
27	20	95	23
28	130	105	20
29	55	105	20
31	10	115	10
32	35	117	10
39	65	119	8
41	85	120	5
42	25		
43	70		
44	50		
45	16		
51	15		
53	25		
55	18		
65	17		
67	25		
69	35		
70	38		
77	35		

TABLE VII

Spectrum #7 320°C

<u>m/e</u>	<u>Abundance</u>
14	20
16	10
17	25
18	82
27	10
28	650
29	25
32	150
39	15
40	14
41	20
43	30
44	65
55	15
69	15
77	15
78	18
79	10
91	20

TABLE VIII

Spectrum #8 375°C

<u>m/e</u>	<u>Abundance</u>
14	20
16	10
17	20
18	85
28	650
29	20
32	145
36	10
39	15
40	20
41	20
43	25
44	85
77	15
78	15
91	15

TABLE IX

Spectrum #9 > 375 °C

<u>m/e</u>	<u>Abundance</u>
14	15
16	13
17	35
18	115
28	700
29	25
32	145
36	20
38	10
39	25
40	20
41	30
42	15
43	30
44	185
55	20
77	25
78	17
79	20
71	35
105	20

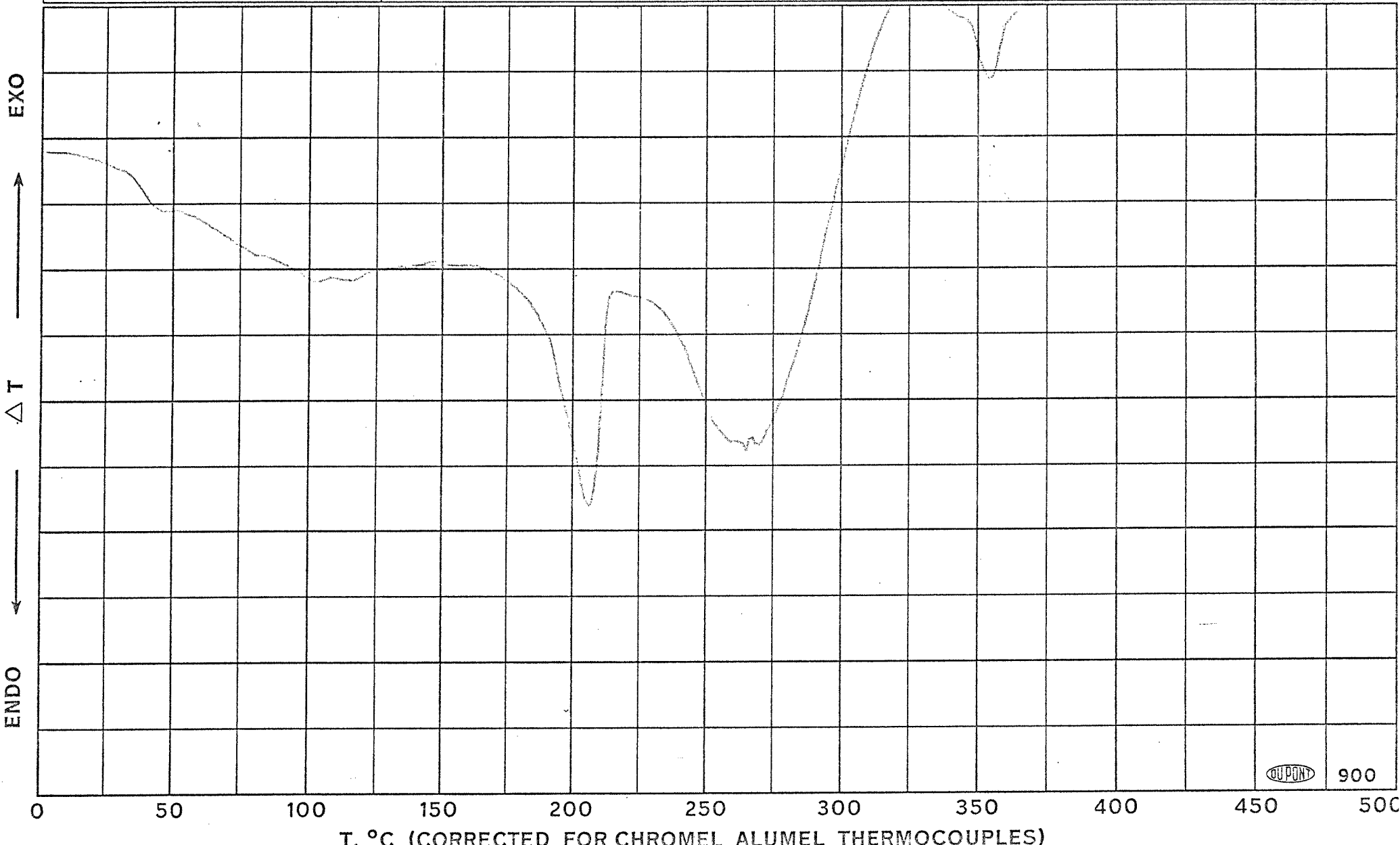
TABLE X

<u>Compound</u>	<u>m/e</u>	<u>Abundance</u>	<u>Compound</u>	<u>m/e</u>	<u>Abundance</u>
Water	18	100	Ethanol	31	100
	17	21		45	36
Acetalde- hyde	29	100		29	25
	44	77		27	23
	43	42		46	16
	15	32	26	9.3	
	42	12	Benzene	78	100
	14	10		52	19
	26	5		51	18
	41	5		50	16
		77		14	
Crotonal- dehyde	41	100	Aceto- phenone	105	100
	39	90		77	83
	70	83		51	30
	69	40		120	25
	28	34		43	18
	29	24		50	13
	27	24		78	9
	38	21		28	6
Acetone	43	100	Benzalde- hyde	77	100
	58	37		105	92
	15	14		106	90
	42	6.7		51	51
Acetic Acid	45	100			
	29	100			
	43	99			
	60	85			
	15	21			
	42	12			
	28	10			
14	6				

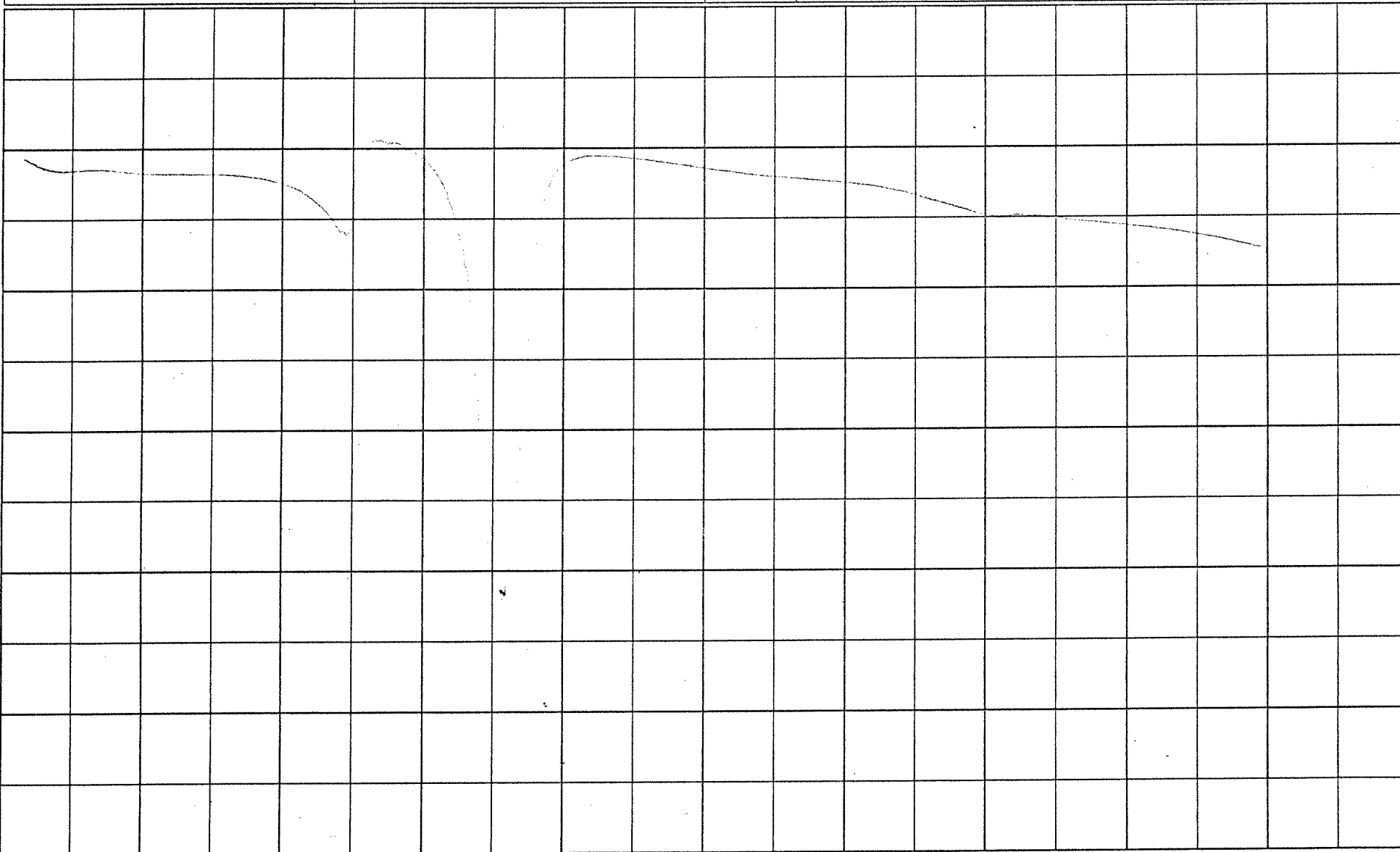
TABLE XI

<u>Compound</u>	<u>m/e</u>	<u>Abundance</u>
Carbon	28	100
Carbon Dioxide	44	100
	28	9.8
	16	9.6
	12	8.7
	22	1.9
Methane	16	100
	15	79
	14	8

SAMPLE: FIGURE No. 14	SIZE _____	ATM. <u>MR</u>		RUN NO. _____
	REF. _____	T _____	ΔT _____	DATE _____
ORIGIN:	PROGRAM MODE _____	SCALE SETTING 50 $\frac{^{\circ}\text{C}}{\text{IN.}}$ 0.2 $\frac{^{\circ}\text{C}}{\text{IN.}}$		OPERATOR _____
	RATE <u>15</u> $\frac{^{\circ}\text{C}}{\text{MIN}}$, START _____ $^{\circ}\text{C}$			



SAMPLE: RISURE No. 15	SIZE _____	ATM. <u>VACUUM</u> _____ MM	RUN NO. _____
	REF. _____		DATE _____
ORIGIN:	PROG. MODE _____	SCALE <u>50</u> $\frac{^{\circ}\text{C}}{\text{IN.}}$	OPERATOR _____
	RATE <u>20</u> $\frac{^{\circ}\text{C}}{\text{MIN.}}$, START <u>100</u> $^{\circ}\text{C}$	SHIFT <u>-2</u> IN.	BASE LINE SLOPE <u>0</u>

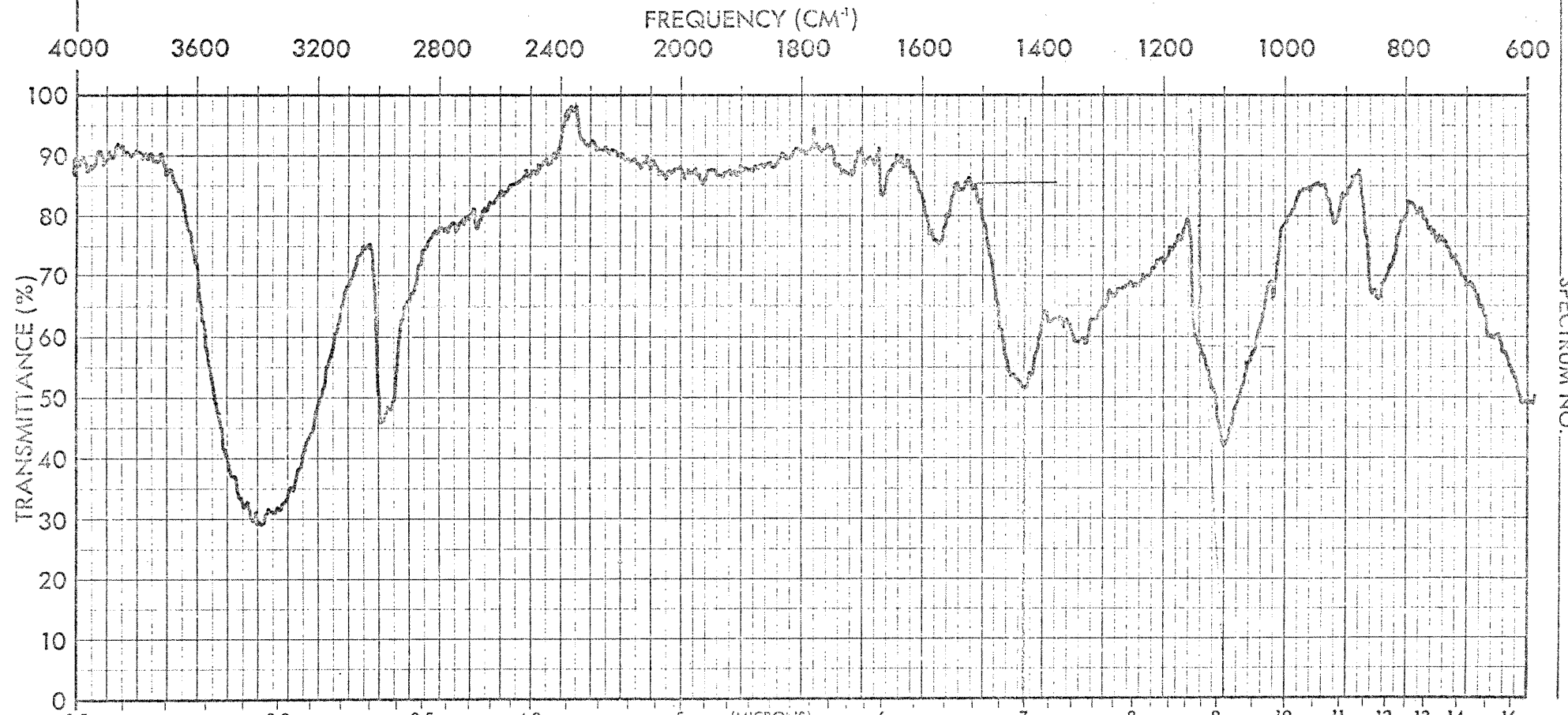


SAMPLE: _____
RUN NO.: _____

T °C (CHROMEL - ALUMEL)*

* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

REMARKS <u>R.T.</u>	ORIGIN _____	PERKIN-ELMER
	PURITY _____	
<u>FIGURE No. 3</u>	SPEED _____ NORMAL <u>X</u> FAST _____	SPECTRUM NO. <u>IR 51</u>
	SLITS _____ NORMAL <u>X</u> WIDE _____	SAMPLE 1 _____
<u>TEMP. 25°C</u>	PHASE <u>RT</u>	_____
<u>IR Spectrum No. 1</u>	CONCENTRATION _____	SAMPLE 2 _____
	THICKNESS _____	_____
	DATE _____	_____
	OPERATOR _____	_____
	_____	_____



SAMPLE _____
SPECTRUM NO. _____

REMARKS *2nd spectra* *t²⁵F*
50°C

FIGURE No. 4

TEMP 50°C

IR Spectrum No. 2

ORIGIN _____

PURITY _____

SPEED _____ NORMAL _____ FAST _____

SLITS _____ NORMAL _____ WIDE _____

PHASE _____

CONCENTRATION _____

THICKNESS _____

DATE _____

OPERATOR _____

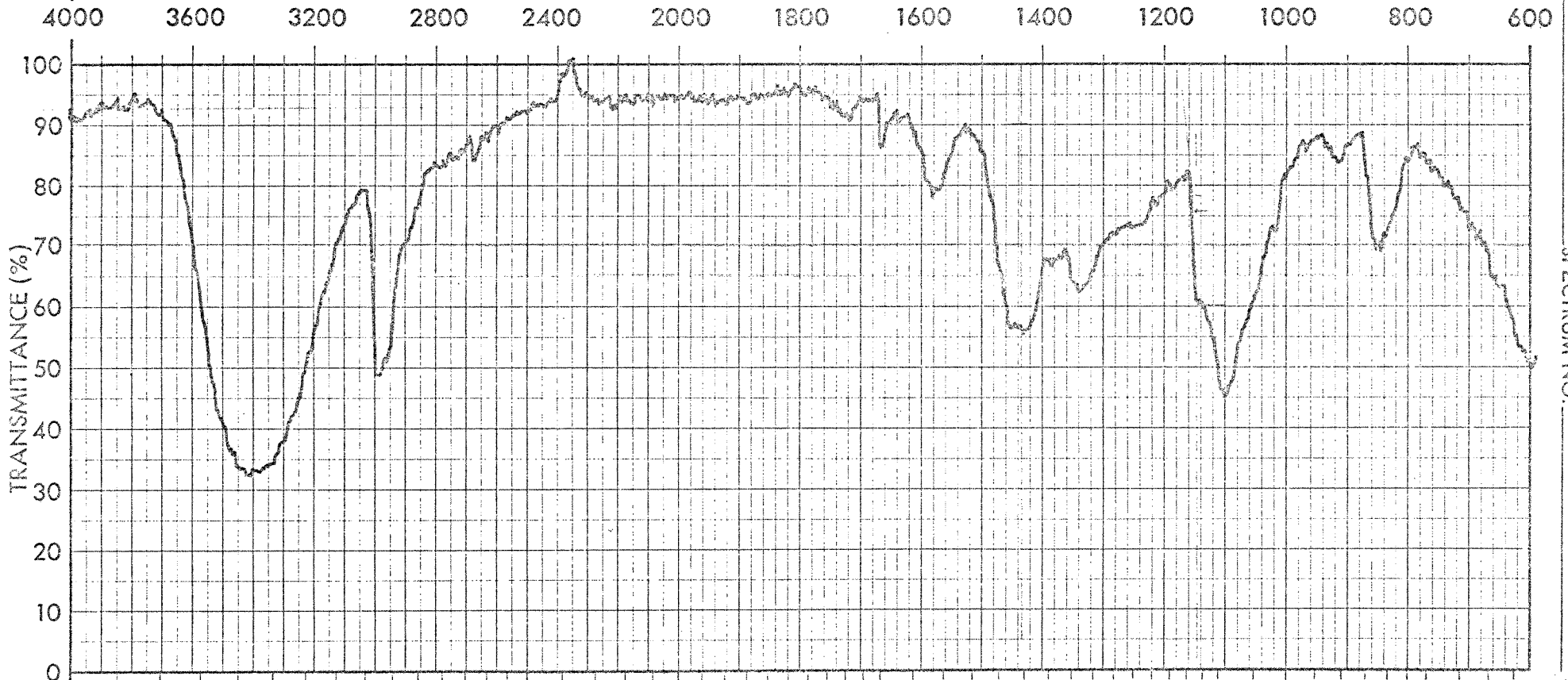
PERKIN-ELMER

SPECTRUM NO. _____

SAMPLE 1 _____

SAMPLE 2 _____

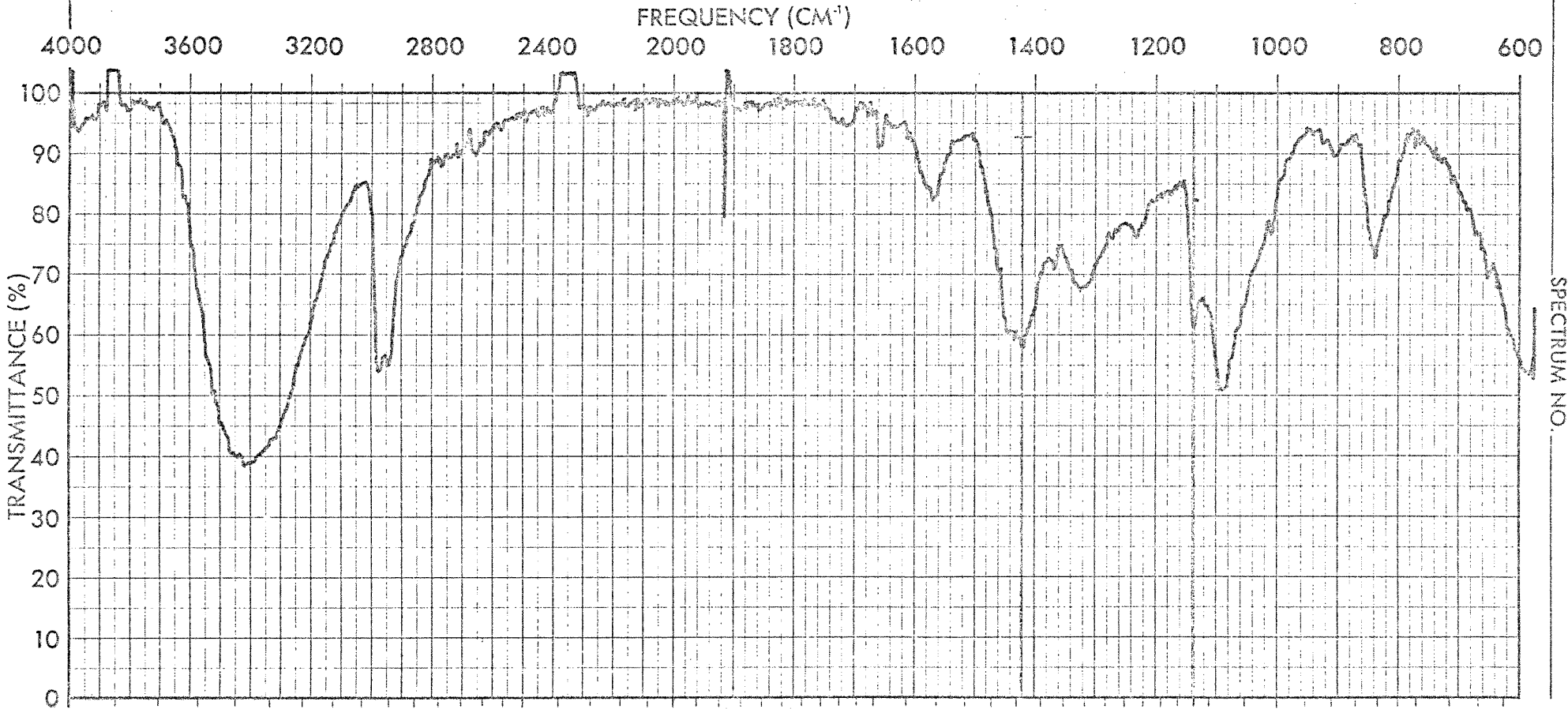
FREQUENCY (CM⁻¹)



SAMPLE

SPECTRUM NO.

REMARKS <i>IR spectra 2+off 100c</i> FIGURE No. 5 TEMP. 100°C IR Spectrum No. 3	ORIGIN _____	PERKIN-ELMER SPECTRUM NO. _____ SAMPLE 1 _____ _____ SAMPLE 2 _____ _____ _____
	PURITY _____	
	SPEED _____ NORMAL _____ FAST _____	
	SLITS _____ NORMAL _____ WIDE _____	
	PHASE _____	
	CONCENTRATION _____	
	THICKNESS _____	
DATE _____	OPERATOR _____	



SAMPLE _____
SPECTRUM NO. _____

REMARKS *4th spectrum 150°C*

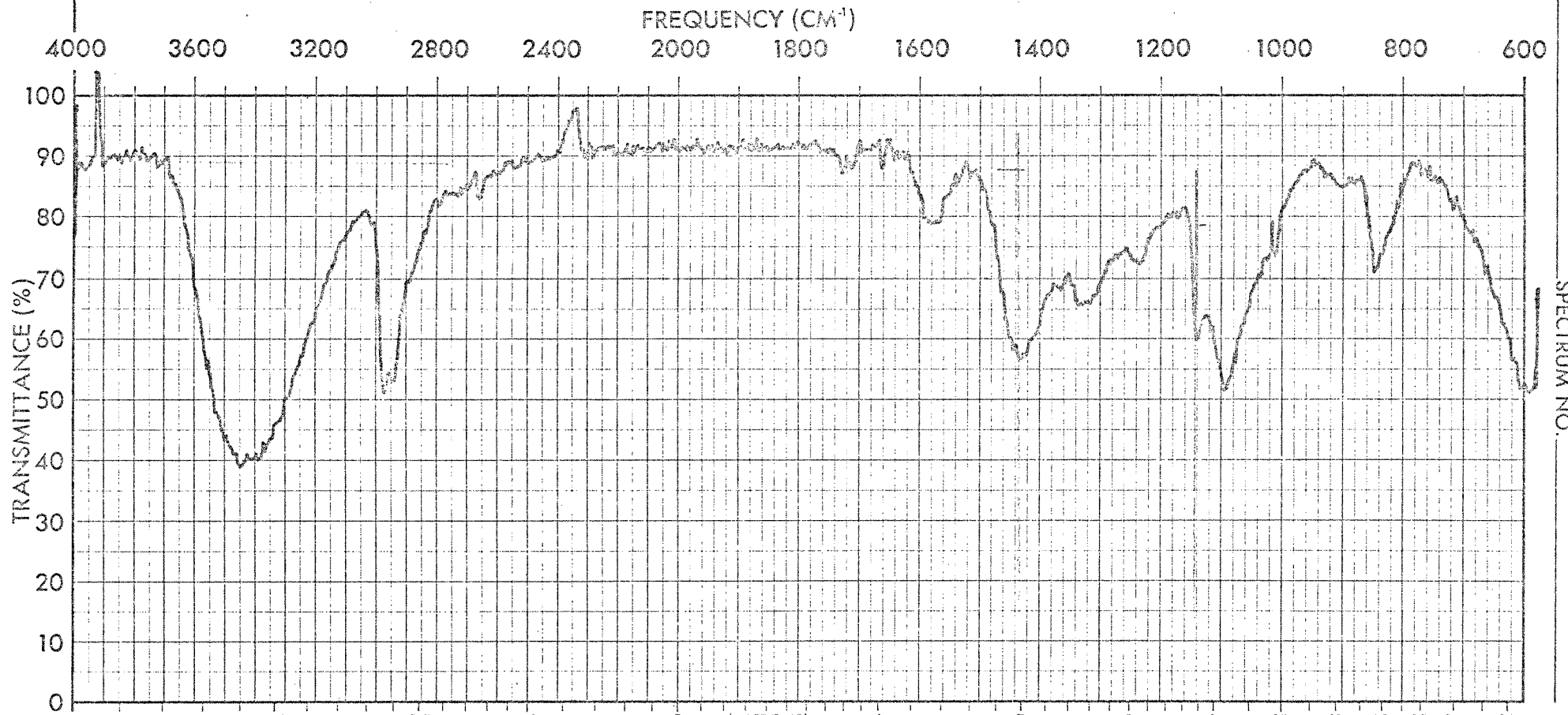
FIGURE No. 6
TEMP. 150°C

IR Spectrum No. 4

ORIGIN _____
PURITY _____
SPEED _____ NORMAL _____ FAST _____
SLITS _____ NORMAL _____ WIDE _____
PHASE _____
CONCENTRATION _____
THICKNESS _____
DATE _____
OPERATOR _____

PERKIN-ELMER

SPECTRUM NO. _____
SAMPLE 1 _____
SAMPLE 2 _____



SAMPLE
SPECTRUM NO.

REMARKS 5th sp 175°C

FIGURE No. 7

TEMP. 175°C

IR Spectrum No. 5

ORIGIN _____

PURITY _____

SPEED _____ NORMAL _____ FAST _____

SLITS _____ NORMAL _____ WIDE _____

PHASE _____

CONCENTRATION _____

THICKNESS _____

DATE _____

OPERATOR _____

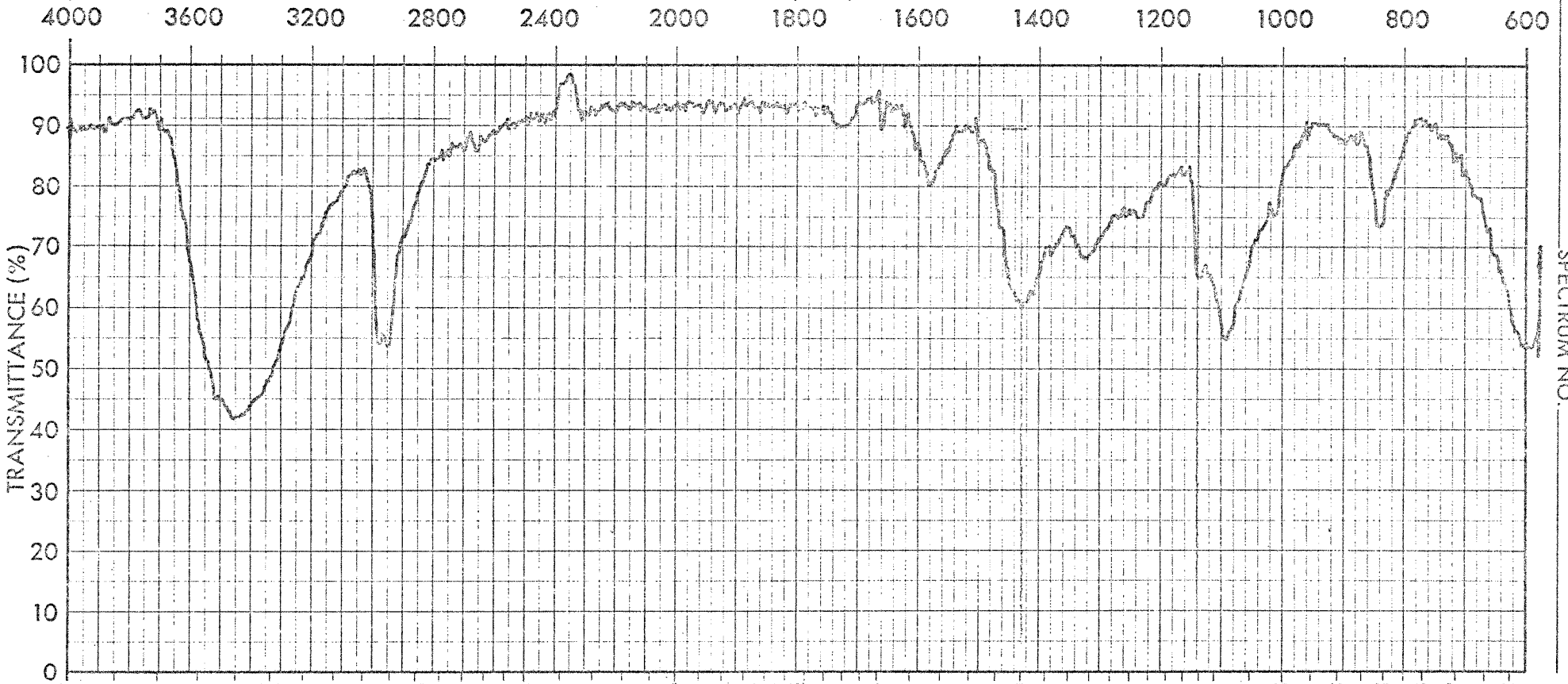
PERKIN-ELMER

SPECTRUM NO. _____

SAMPLE 1 _____

SAMPLE 2 _____

FREQUENCY (CM⁻¹)



SAMPLE

SPECTRUM NO.

REMARKS *6th spec. 200°C*

FIGURE No. 8

TEMP. 200°C

IR Spectrum No. 6

ORIGIN _____

PURITY _____

SPEED _____ NORMAL _____ FAST _____

SLITS _____ NORMAL _____ WIDE _____

PHASE _____

CONCENTRATION _____

THICKNESS _____

DATE _____

OPERATOR _____

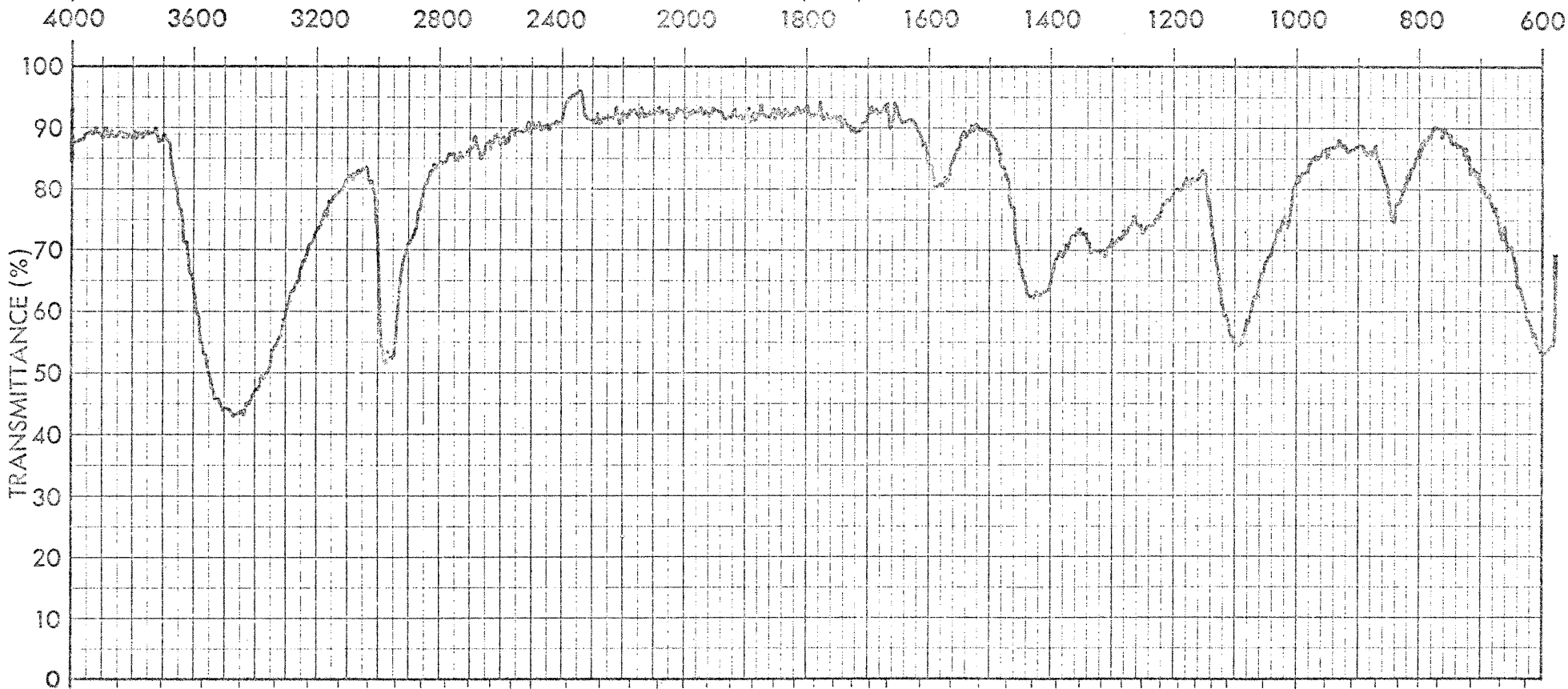
PERKIN-ELMER

SPECTRUM NO. _____

SAMPLE 1 _____

SAMPLE 2 _____

FREQUENCY (CM⁻¹)



SAMPLE

SPECTRUM NO.

REMARKS 7th 227°C

FIGURE No. 9

TEMP. 227°C

IR Spectrum No. 7

ORIGIN _____

PURITY _____

SPEED _____ NORMAL _____ FAST _____

SLITS _____ NORMAL _____ WIDE _____

PHASE _____

CONCENTRATION _____

THICKNESS _____

DATE _____

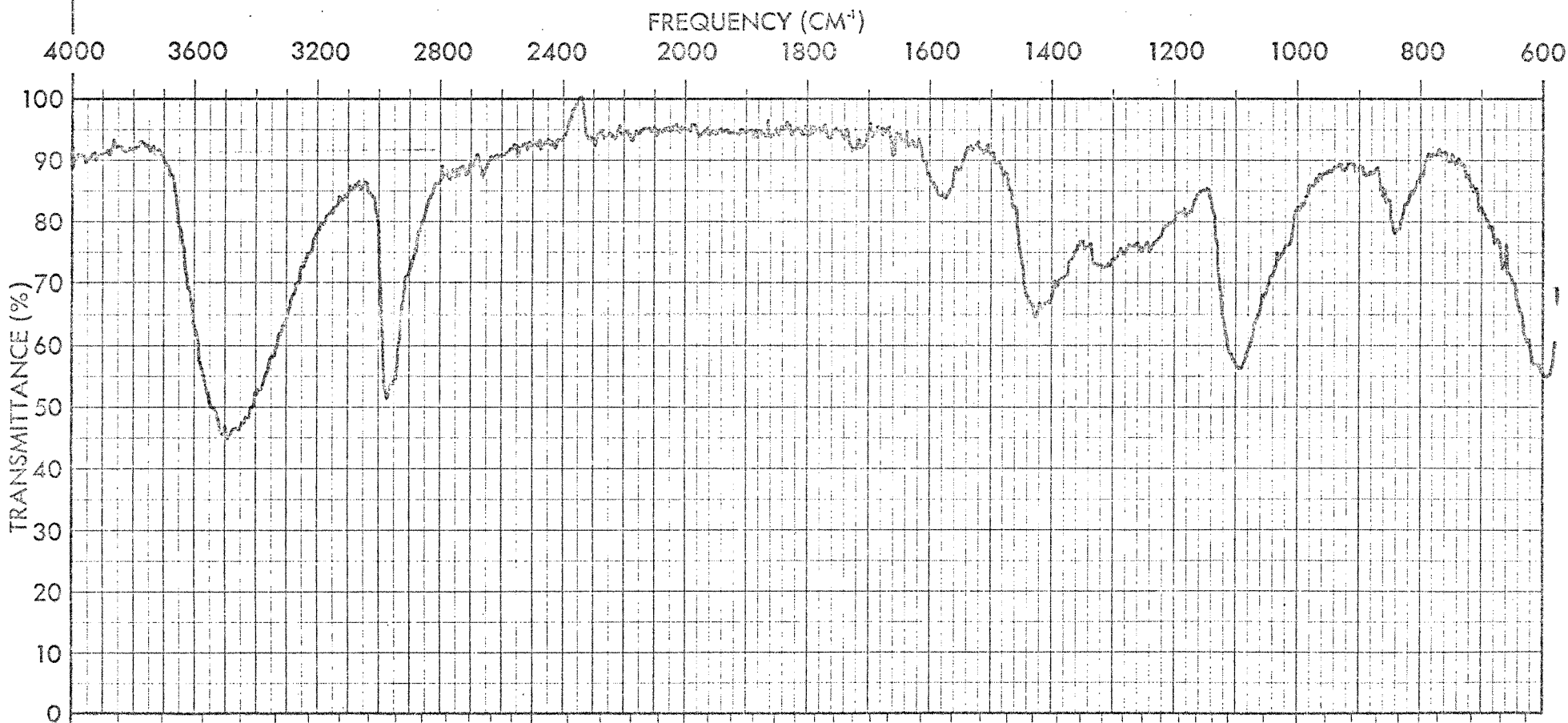
OPERATOR _____

PERKIN-ELMER

SPECTRUM NO. _____

SAMPLE 1 _____

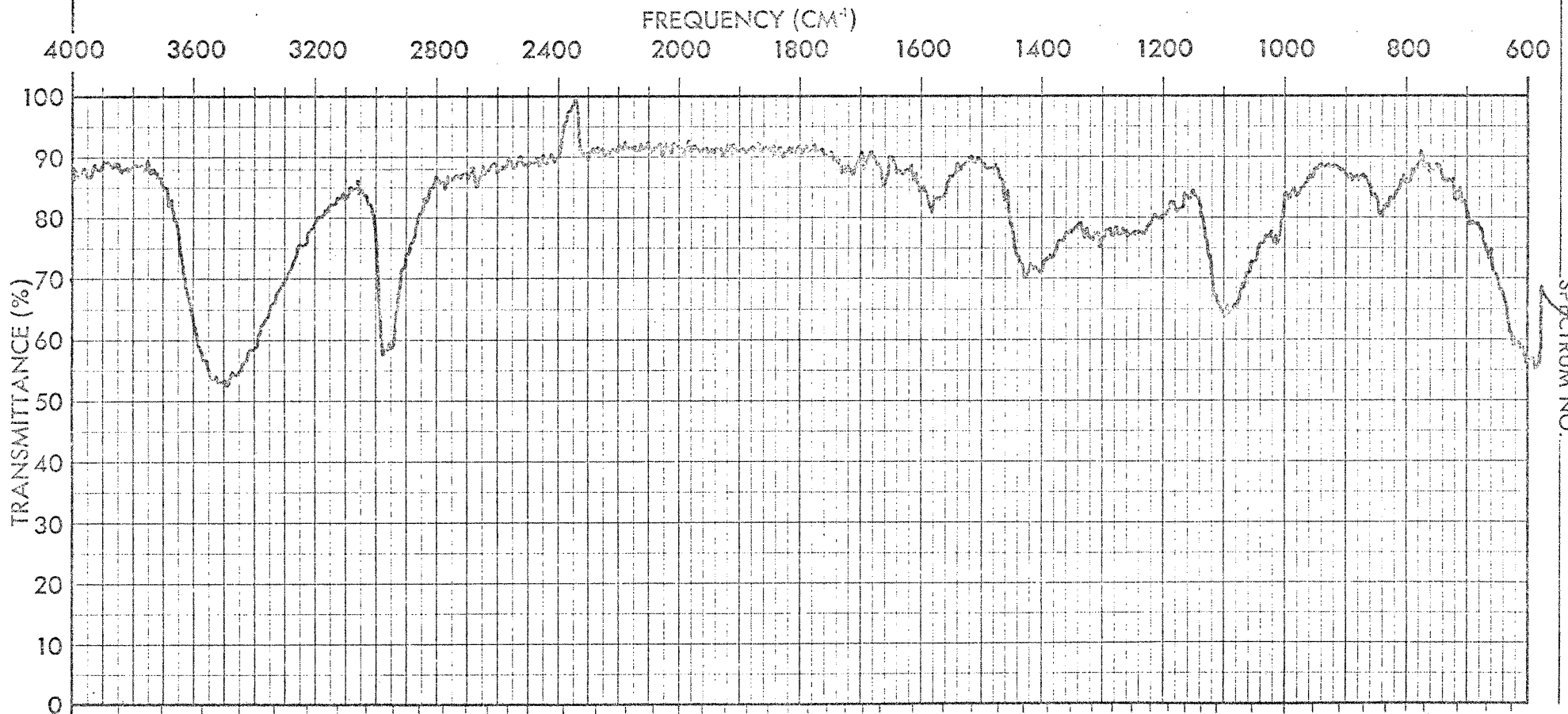
SAMPLE 2 _____



SAMPLE

SPECTRUM NO.

REMARKS <u>SL</u> <u>255°C</u> <u>FIGURE No. 10</u> <u>TEMP. 255°C</u> <u>IR Spectrum No. 7</u>	ORIGIN _____	PERKIN-ELMER SPECTRUM NO. _____ SAMPLE 1 _____ SAMPLE 2 _____
	PURITY _____	
	SPEED _____ NORMAL _____ FAST _____	
	SLITS _____ NORMAL _____ WIDE _____	
	PHASE _____	
	CONCENTRATION _____	
	THICKNESS _____	
DATE _____		
OPERATOR _____		



SAMPLE _____
SPECTRUM NO. _____

REMARKS *9th* 263°C

FIGURE No. 11

TEMP. 263°C

IR Spectrum No. 9

ORIGIN _____

PURITY _____

SPEED _____ NORMAL _____ FAST _____

SLITS _____ NORMAL _____ WIDE _____

PHASE _____

CONCENTRATION _____

THICKNESS _____

DATE _____

OPERATOR _____

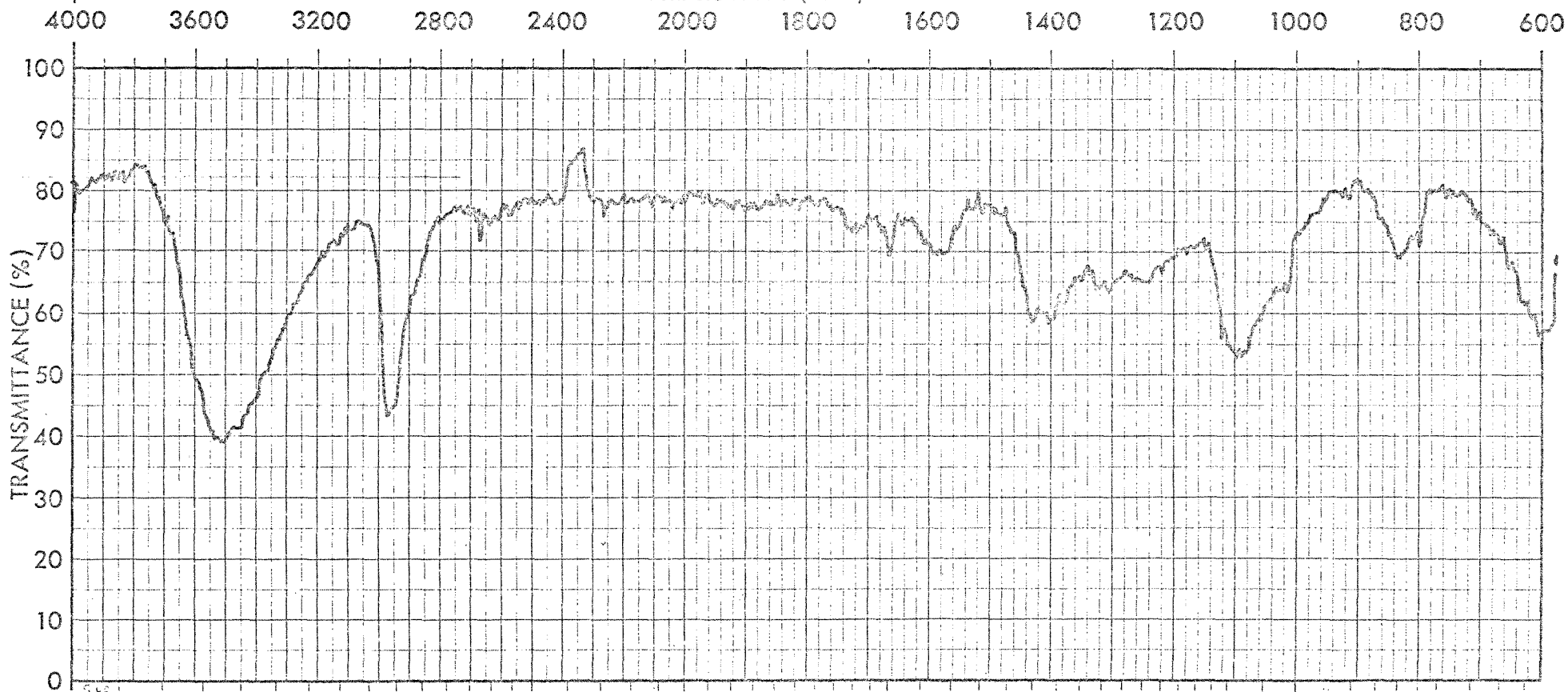
PERKIN-ELMER

SPECTRUM NO. _____

SAMPLE 1 _____

SAMPLE 2 _____

FREQUENCY (CM⁻¹)



SAMPLE

SPECTRUM NO.

REMARKS *10th 280*

FIGURE No. 12
TEMP. 280°C

IR Spectrum No. 12

ORIGIN _____
 PURITY _____

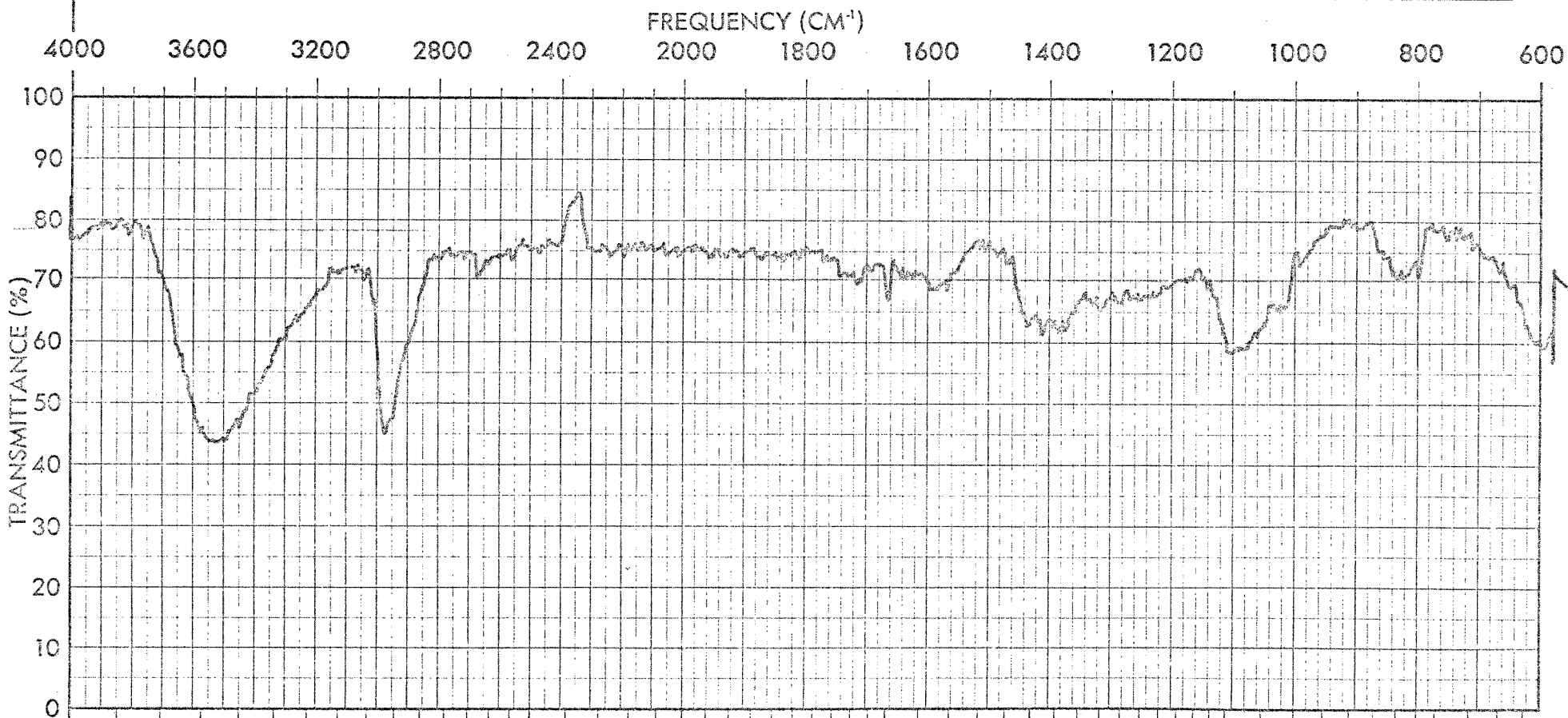
 SPEED _____ NORMAL _____ FAST _____
 SLITS _____ NORMAL _____ WIDE _____
 PHASE _____
 CONCENTRATION _____
 THICKNESS _____
 DATE _____
 OPERATOR _____

PERKIN-ELMER

SPECTRUM NO. _____

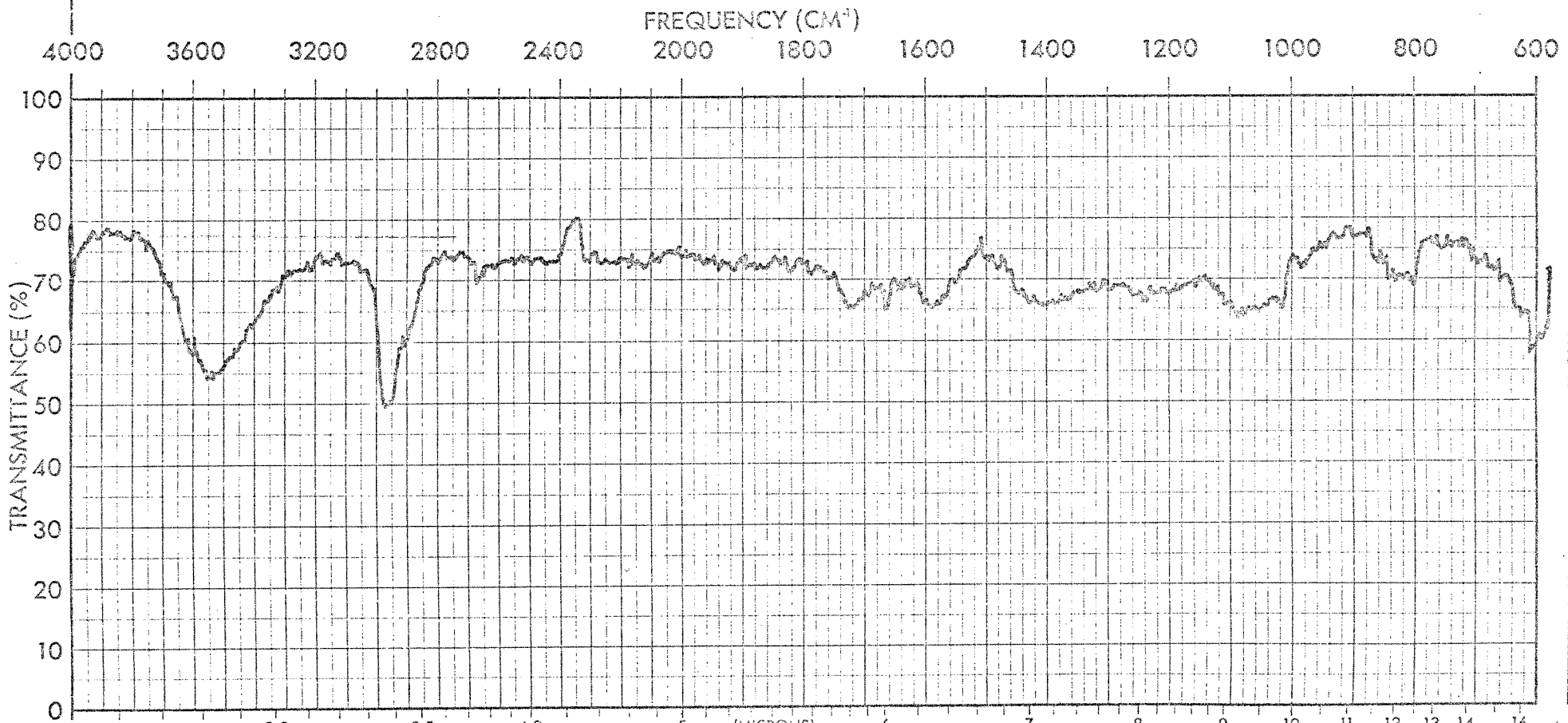
SAMPLE 1 _____

SAMPLE 2 _____



SAMPLE _____
SPECTRUM NO. _____

REMARKS 30°C FIGURE No 13 TEMP 300°C IR Spectrum No. 17	ORIGIN _____	PERKIN-ELMER SPECTRUM NO. _____ SAMPLE 1 _____ SAMPLE 2 _____
	PURITY _____	
	SPEED _____ NORMAL _____ FAST _____	
	SLITS _____ NORMAL _____ WIDE _____	
	PHASE _____	
	CONCENTRATION _____	
	THICKNESS _____	
	DATE _____	
OPERATOR _____		



SAMPLE _____ SPECTRUM NO. _____