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A study of methyl ethyl ketone and butanol-2 by gas-liquid partition chromatography

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A STUDY OF METHYL ETHYL KETONE AND BUTANOL-2 BY GAS-LIQUID PARTITION CHROMATOGRAPHY

by

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A thesis presented to the Department of Chemistry, Union College, in partial fulfillment of the requirements for the degree of Bachelor of Science with a Major in Chemistry.

By Ronald J. DuBois

Approved by Robert W Schaefer

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Table of Contents

Abstract

The problem of analysis of commercial and student preparations of butanol-2 from methyl ethyl ketone by gas-liquid partition chromatography is presented. The retention times of butanol-2 and methyl ethyl ketone are determined under varying conditions of temperature, flowrate, carrier gas, column packing and fixed phase concentrations. Optimum conditions are selected for the separation of butanol-2 and methyl ethyl ketone. Several methods are discussed for the quantitative interpretation of the data.

The presence of an unknown component in commercial methyl ethyl ketone and butanol-2 is found and possible identification is discussed.

A brief outline of the apparatus involved and of the theory of gas-liquid partition chromatography is included.

Introduction

Quality control in the preparation of organic material has always been a serious concern of the chemical industry. Organic preparations are usually marked by incomplete reaction of the starting materials and the presence of side products. Commercial organic compounds, therefore, require close control to provide pure products. The methods used to determine the purity of products are numerous.

In recent years, vapor phase chromatography has become a useful tool for both qualitative and quantitative analysis. Original vapor phase chromatography work dealt with adsorbent columns and is known as elution analysis (24). Later this method was modified and displacement analysis was introduced by Claesson in 1946 (2). Those above methods dealt almost exclusively with compounds that were in a gaseous state at room conditions.

In 1952, James and Martin (15) introduced the gas-liquid partition method of vapor chromatography. Their work depended on the absorption of readily volatile organic liquids in a fixed phase of a low volatility organic liquid or solid.

The work, here presented, deals with a gas-liquid partition study of methyl ethyl ketone and butanol-2. Butanol-2 is often prepared commercially and in the lab by the reduction of methyl ethyl ketone. Conversely, methyl ethyl ketone can be prepared by the oxidation of butanol-2. The resulting product always contains percentage amounts of impurity, mainly the unreacted starting products. Lower alcohols and condensation or dehydration side products are also possible. It is necessary to measure or control the purity of the final product by some quantitative analytical method.

Gas-liquid partition chromatography offers a relatively inexpensive, fast and accurate means of analysis.

Historical and Theoretical Development

The Russian botanist, Tswett (1), in the early 1900's, first developed and introduced liquid-solid phase chromatography. In the past fifty years, this type of chromatography has been refined and employed extensively in cooperation with the fields of both organic and inorganic chemistry.

Within the last several years, a new field of chromatography has been opened. A radical modification of the original liquid-solid chromatography is employed. The mobile liquid phase is replaced by a mobile gas phase, thus allowing analysis of not only liquids but also of vapors and volatile solids. This wider range of analysis is made possible by the greater freedom of operating conditions using vapor phase chromatography.

Gas Adsorption: Elution Analysis-

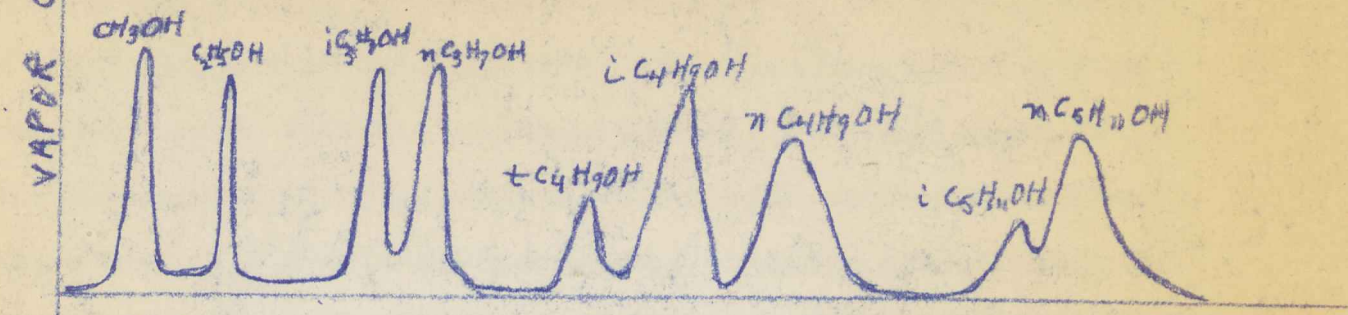
These first vapor phase chromatography experiments were carried out using columns filled with adsorbent materials such as charcoal, activated charcoal, silica gels, as the fixed phase. A sample to be analyzed is introduced at the head of the column and is carried through the column in a stream of inert carrier gas, the mobile phase. The resulting chromatograms consist of peaks of vapor concentrations corresponding to the individual components of the sample (Illustration 1a). The peaks from adsorption column analysis of this type usually have sharp fronts and diffuse tails.

This simple technique, first recognized and developed by Hesse in 1941 (13), is known as the elution analysis technique. Hesse was able to separate a number of volatile organic and inorganic compounds on a heated silica gel adsorption column. The separations, however, are not complete.

ILLUS. Ic.

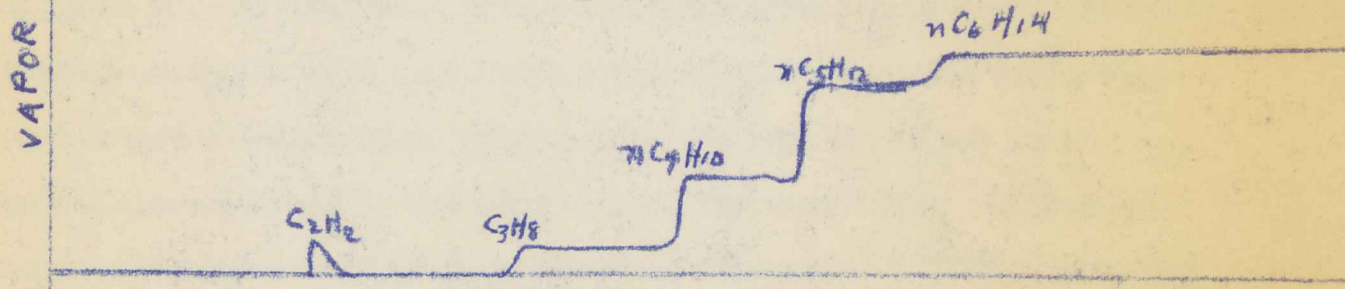
GAS-LIQUID PARTITION CHROMATOGRAM

SEP'N ON DINONYL PHTHALATE
NITROGEN MOBILE PHASE
(REF. 24)



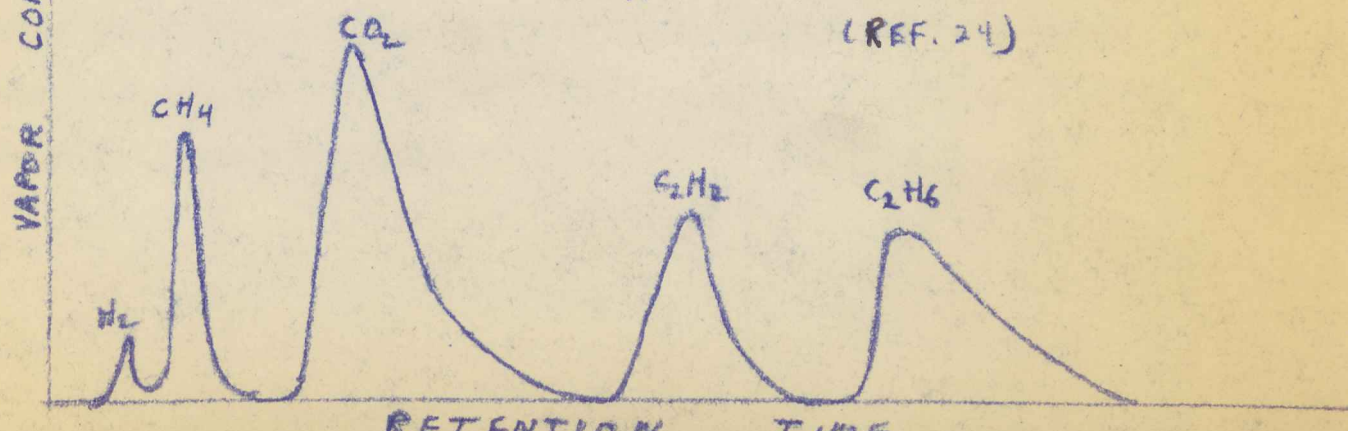
Ib DISPLACEMENT ANALYSIS CHROMATOGRAM

SEP'N ON ACTIVATED CHARCOAL
ETHYL ACETATE DISPLACER
(REF. 24)



Ia ELUTION ANALYSIS CHROMATOGRAM

SEP'N ON ACTIVATED CHARCOAL
NITROGEN MOBILE PHASE
(REF. 24)



Helium, nitrogen, hydrogen, carbon dioxide, nitrous oxide and ammonia are some of carrier gases used in the above and later work.

Turkeltaub (30, 31) further refined this method and used a chromatothermographic technique, in which the removal of the less volatile vapors is facilitated by a moving heater which produces an even thermal gradient along the column. Using gas adsorption methods and standard apparatus for this technique, Komissii (9) achieved a sensitivity enabling detection of the presence of .01% component by weight and a relative error of 2% in the separation of light saturated hydrocarbon gases on silica gels. The vapors eluted are detected and measured by a Thermal Conductivity cell.

Displacement Analysis-

Claesson (2) introduced a modification of the gas-adsorption method - displacement analysis. In this method, the sample vapors are displaced chemically from the adsorbent rather than being eluted by heat from the fixed adsorbent phase. A vapor more firmly adsorbed than any of the sample component vapors is continuously carried on to and over the column (at a constant concentration) by the carrier gas. The chromatograms consist of a series of steps corresponding to the vapor concentration of each component forced off the column (Illustration 1b) and measured by the indicating device.

Claesson separated and displaced many hydrocarbons from activated charcoal by using ethyl acetate as the displacer (2). Phillips and his coworkers (11, 12, 25, 17) extended this method and found that the use of weakly adsorbent glass beads in the column facilitated the separation of relatively high boiling (low volatility) substances (e.g. diethyl malonate-BP-199°C) at room temperature.

Qualitative analysis is accomplished by determination of the relative position of the individual steps produced in the displacement chromatogram. The results are checked by collection and analysis of the separated components as they are flush- from the column and through the indicating device.

Quantitative analysis is facilitated by measurement of step lengths. An accuracy of better than 0.5% is reported by Phillips (24).

Displacement analysis generally results in good separation and the particular components are recoverable in the pure state. However, with very similar substances, such as isomers, complete resolution is not always accomplished. The efficiency of the separations are increased by the use of finer adsorbent particles and longer, narrower columns.

Gas-Liquid Partition Chromatography-

The most important advance in recent vapor phase chromatographic work was the introduction of the gas-liquid partition method by James and Martin in 1952 (15). They suggested the separation of volatile substances in a column in which a non-volatile substance, the fixed phase, is impregnated on an inert solid support. If the samples added are small in comparison with the amount of fixed phase, the separation follows closely Raoult's Law (23). As in other vapor phase chromatographic methods, the sample is carried by an inert gas.

This gas-liquid partition method depends on the absorption rather than adsorption of sample vapors into the high molecular weight organic liquid or solid used as the fixed phase. This fixed phase has a materially lower vapor pressure and thus does not appreciably effect the vapor analysis.

In gas-liquid partition chromatography, the volatile sample may be

injected by a syringe through tygon tubing or some other suitable means. The injection is just prior to the column packing and vaporization occurs previous to being swept on to the packing. The components upon passing into the column are held to a greater or lesser extent in the fixed phase. The retention time of a particular vapor (the time between injection of a sample and the recorded maximum of its elution curve) depends on its volatility and its degree of solubility in the fixed phase. This equilibrium, once established, in turn determines the unique distribution coefficient of the particular vapor molecules between the gas and liquid phases.

This coefficient is dependent on the heat of solution of the particular component (24). The heat of solution is the result of four possible factors. The first two terms contribute relatively little to the sum. They are (1) dispersion forces (van der Waal forces), present in all cases, the only source of attraction between two non-polar substances: and (2) induced dipole association which results when a polar substance induces a dipole in an non-polar compound. More important effects are caused by (3) dipole association between two polar substances such as organic compounds with similar or electrically attractive functional groups, the familiar rule in organic chemistry specifies that "like substances dissolve like". The final factor: (4) specific interaction or chemical bonding, is also significant.

Generally, therefore, the use of a non-polar fixed phase results in sample components of the same homologous series being separated and eluted in order of decreasing volatility or rising boiling point (16). The use of a polar column packing causes separation of a sample to depend on a

combination of volatility and degree of absorption due to polar similarity. With increased column packing polarity, those components that are less polar would have shorter retention times than the more polar vapors (providing volatility is similar.)

Chromatograms obtained by gas-liquid partition consist of a series of peaks, each peak representing a pure component when complete separation is achieved. These peaks are very nearly symmetrical (Illustration 1c). The chromatograms are always obtained by the elution technique whereas either elution or displacement methods may be employed in gas-adsorption chromatography.

A method hybrid between gas-adsorption and gas-liquid partition chromatography has been recently developed. Eggersten, Knight and Groennings (8) found that tailing of curves in columns packed with an active solid can be reduced by adding a small percentage of a liquid solvent. They added up to 1.5% squalane on a column of paraffin wax and were able to greatly diminish tailing, thus facilitating the separations of C_5 and C_6 saturates. Care must be taken to avoid confusion caused by some peak inversion for quite similar vapors such as iso-pentanes and n-pentane.

Cremer (3) has found various suitable liquids for the gas-liquid partition chromatography fixed phase. Silicone oils, liquid paraffin, paraffin wax, high boiling aromatic hydrocarbons and esters, and ethylene oxide polymers have been used. There is a practically unlimited number of possible fixed phase compounds.

Keulemans, Kwantes, and Zaal (19) used diglycerol and dibutylphthalate for separation of oxygenated compounds.

Lichterfels, Fleck and Burow (21) have employed di-octylphthalate

held on "celite" in 4 foot and 10 foot columns for separations of a number of aliphatic ketones, aldehydes and alcohols. In general, high molecular weight phthalates have been especially popular fixed phase solvents.

Dijkstra, Keppler and Schols (6) were able to separate a series of oxygenated compounds including C_5-C_{16} alcohols. They used an inert "celite" support on which either silicone grease or paraffin was held as the fixed phase. It is of interest that these columns were able to remain workable at temperatures exceeding 230°C.

H. S. Knight (20), using the detergent Tide, was able to separate some hydrocarbons as well as a number of organic oxygen compounds, though the results were not outstanding. Knight also concludes that if a column contains enough solvent to nullify solid support surface effects, the data obtained is applicable to other columns of the same solvent. This is true even if solvent concentration, column diameter and length, particle size, pressure drop and flowrate are all varied.

As stated above, much of the gas-liquid partition work as well as subsequent experimentation was carried out by James and Martin. Therefore, a brief review of some of their work might be advantageous in relation to the general possibilities of gas-liquid partition chromatography with respect to organic compounds.

Their earliest work was somewhat limited by the means of detection employed; titration of the effluent vapors with an automatic recording burette. Later detecting devices such as Thermal Conductivity cells and gas density balances made it possible to apply gas-liquid partition chromatography to a very wide range of vapors.

The first work of James and Martin (15) with absorption columns was the separation of mixtures of volatile fatty acids. Glass columns of lengths varying from 4 feet to 11 feet and of a 4mm. inside diameter were used. A kieselguhr ("celite 545") support was employed, on which was fixed silicone fluid (DC 550) containing 10% by weight stearic acid. The researchers were able to separate C_2 through C_6 fatty acids.

With these volatile fatty acids, it was found that if silicone fluid is used alone, dimerization of the acids occurs, resulting in departure from linearity of the adsorption isotherm. Therefore a substance of low vapor concentration will move more rapidly through the column than a substance present in high vapor concentration. Phosphoric acid was also added to the fixed phase to prevent pre- and post-curve tailing due to dimerization effects.

The same technique was extended by James, Martin and Smith (14) to the separation and microestimation of volatile aliphatic amines, and the homologues of pyridine. James (15) also studied unsaturated, saturated, naphthenic and aromatic hydrocarbons. He found that by plotting the retention times of these substances on a non-polar paraffinic column versus retention times on a polar benzyldiphenyl column, the values obtained fell along four individual lines, each line composed of members of one particular type of hydrocarbon studied. This occurred because on the non-polar paraffin column, the retention time is determined by molecular weight of the component, and by length and configuration of the molecule. The only forces involved in the non-polar column between it and the component being analyzed are weak van der Waal forces and induced dipole association.

However, with a column containing a solvent compound similar to the

vapors being analyzed, additional forces dependent on the chemical nature of the groups in the molecules effect the results. The above phenomenon is not unique to hydrocarbons. Any organic compound, including oxygenated vapors, will have their retention times relatively and absolutely effected by varying the column fixed phase solvent.

In general, vapor phase chromatography compares very favorably with liquid-solid chromatography and other analytical methods. Several advantages over liquid-solid chromatography are (1) due to the low viscosity of gas. It is possible to use longer columns thus obtaining higher efficiencies. (2) Columns may be operated at high gas flowrates, so that analyses may be more rapid while still remaining highly efficient. This is the result of both low gas viscosity and rapid diffusion of the sample vapors between the gas and fixed phase. (3) Gas molecules are generally smaller and less strongly absorbed or adsorbed than liquid molecules. Therefore the distribution of vapors between the fixed and mobile phase is largely independent of the "solvent" gas. (4) There are many sensitive methods available for detection of small vapor concentrations in a gas. Most of these are rapid and continuous. It is also easier to detect small amounts of a vapor in a gas than to detect small quantities of solute in a liquid solvent.

Vapor phase chromatography is similar though superior to analytical distillation. Both processes depend upon repeated distribution between two phases, one of which is vaporous. However, vapor phase chromatography is more effective, as any phase overlap is avoided. Also a good fractionating column will have an efficiency of a few hundred plates, while vapor phase chromatography columns may have efficiencies as great as a few

thousand plates depending on the particular column dimensions (24). Vapor phase chromatography obviously can be made more versatile by varying the fixed phase. It is much more rapid than distillation and vapor phase chromatography utilizes much smaller quantities of sample. It is possible, however, to increase sample size sufficiently for preparative work.

While infra-red, mass spectra and chemical analysis are essentially identification methods, vapor phase chromatography is both a separation and identification technique. Vapor phase chromatography set-ups are relatively inexpensive and simple to construct. It is automatic in operation and applicable to as wide a range of molecules as the detector sensitivity permits.

Just as there are advantages of vapor phase chromatography over other analytical methods, gas-liquid partition has a number of advantages over gas-adsorption techniques. Adsorption columns give rise to more asymmetrical peaks which are not as suitable for qualitative and quantitative measurements, as the relatively symmetrical curves obtained from absorption columns. The partition method is also more ideally suited for separation and analysis of very similar vapors. Displacement analysis requires longer operating times and columns may have to be regenerated or repacked after every analysis, whereas an absorption column may be used repeatedly without great loss of efficiency. The partition method requires a faster, more sensitive detector and rapid introduction of the whole sample is necessary.

There are limits to gas-liquid partition chromatography. For instance, the peaks will remain symmetrical only as long as relatively small amounts of sample are dissolved in the column liquid. An advantage of adsorption

columns over partition packing is the fact that gas-liquid partition columns have no self-sharpening properties as do the adsorption materials. In fact, vapor curves will tend to spread slightly with increase of retention time. Those higher molecular weight components will tend to have increasingly lower, longer bands of vapor concentration (17).

While quantitative accuracy is relatively unaffected by temperature change, qualitatively a 1°C variance in column temperature will cause a retention time change of approximately 5%. Ray (26, 27), by using an internal standard, reduced flowrate and temperature change effects so that retention times are reproduceable within 1%. In this method, retention times of sample vapors are relative or in proportion to the retention time of the internal standard.

The range of gas-liquid partition chromatography is limited only in that the vapors to be analyzed must be stable, unreactive with the carrier gas or fixed phase at the column temperature, and they must be sufficiently volatile to be detected on emergence. The technique can be extended to higher molecular weight materials by use of a highly sensitive detector or a means to increase volatility; e.g., high temperature columns and/or a pressure reducer (4, 5) such as that used by Heymond for the separation of methyl esters of C_{12}-C_{22} fatty acids.

Extremely small quantities of vapor sample can be analyzed by gas-liquid partition chromatography. The lower limits being set by the sensitivity of the detector. The upper limit depends on the column size and the resolution required, as larger samples can cause broad, overlapping peaks. However, an increase in column diameter can circumvent this difficulty.

Analysis time can be maintained relatively low because temperature and flowrate can be increased without loss in efficiency up to certain limits. Another benefit of gas-liquid partition chromatography is the ability to recover pure sample components, frequently by means of very simple equipment.

Methods of Quantitative Analysis of Curves-

While it is necessary for quantitative analysis, to find the best conditions for separation (e.g., temperature, flowrate, carrier gas, column packing, concentration and dimensions), it depends on the chosen means of quantitative interpretation of the component curves, whether it is necessary to hold these conditions absolutely constant.

There are two general methods of quantitative measurement. One depends on determination of peak area and the other is based on the relation of peak heights.

Methods which depend on peak area appear less convenient. They require, when a paper recorder is used, either a means for integrating the curve areas or an even less accurate method of cutting out and weighing the curve areas in relation to the total weight of the areas of all the curves obtained in the sample chromatogram.

These methods require indicator device linearity for at least a certain component percentage range. James and Martin (18) found that a plot of percentage component composition versus peak area was linear for vapors of approximately the same thermal conductivity coefficient. Keulemans, Kwantes and Zaal (19) concluded that for vapors of quite different thermal conductivity coefficients, a similar plot was linear

only below 10% component concentrations.

Both of the above mentioned methods depending on peak area determination, require keeping all factors (temperature, flowrate), constant unless an internal standard is employed.

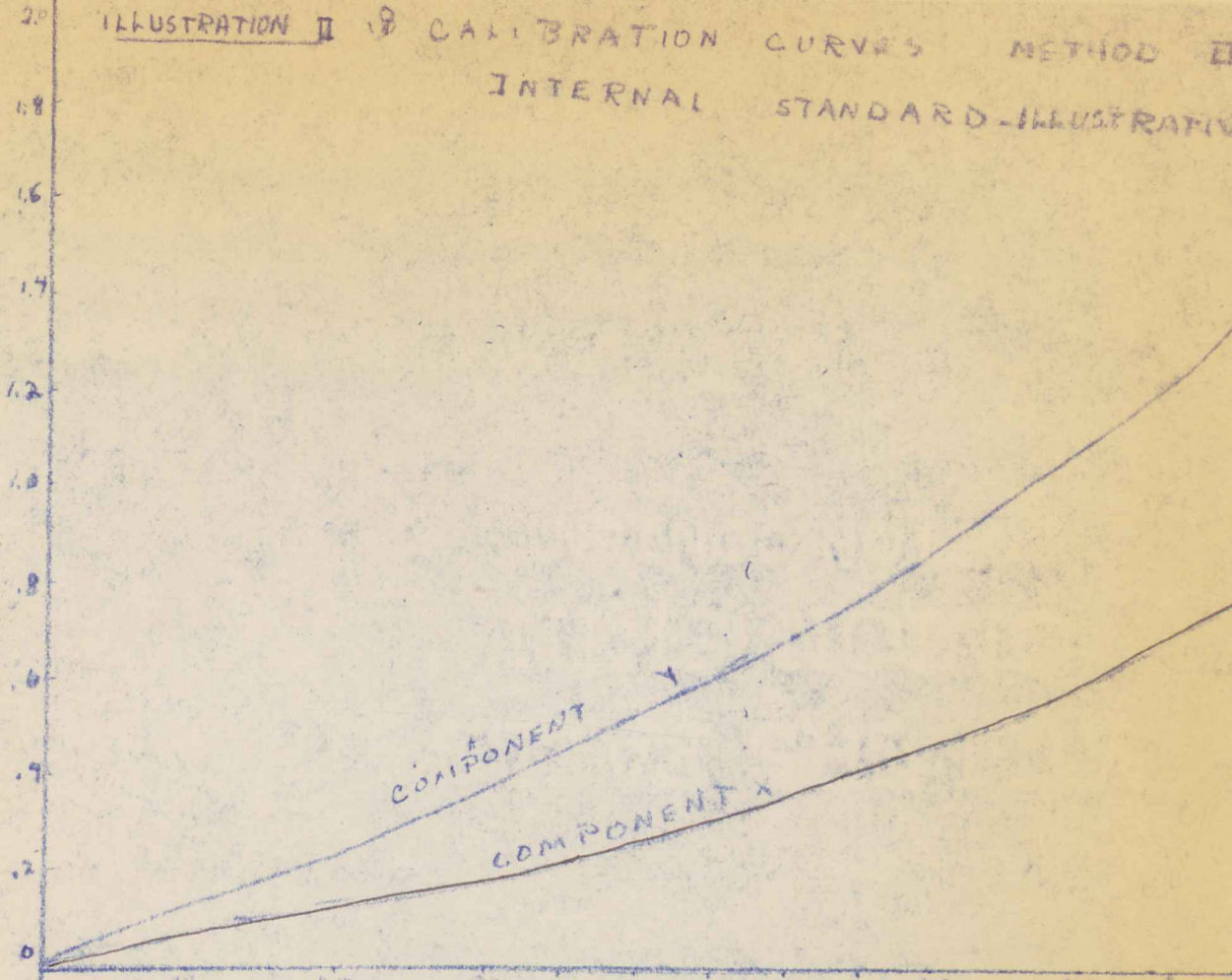
Measurements of peak heights seem to offer a more convenient technique. Use of peak heights require preparation of standard calibration curves. These curves can be prepared (Illus. II - Method I) by plotting percentage component versus component peak height of sample for each vapor present (curves for all but one component can be prepared and subtracting their total from 100% gives the amount of the last vapor). The objection to this method is that all variables, including sample size and fixed phase concentration, must be accurately reproduced for each analysis.

A more suitable quantitative technique in the opinion of the researcher, requires the use of an internal standard (Illus. II - Method II). All peak heights are then proportional or relative to the peak height of the internal standard. Calibration curves are made for each component by plotting percentage component composition versus ratio of component peak height to internal standard peak height. The use of an internal standard for quantitative measurements corrects each analysis for any temperature, flowrate, or other change of sensitivity. Sample volumes do not have to be maintained equal. Any elution of column solvent is corrected. (However, if a considerable loss occurs, in any method mentioned, the decrease in curve separation, if great enough, will tend to seriously impair the accuracy of the peak height or peak area measurements).

The use of peak height relations seem to have only one disadvantage

ILLUSTRATION II — CALIBRATION CURVES METHOD II

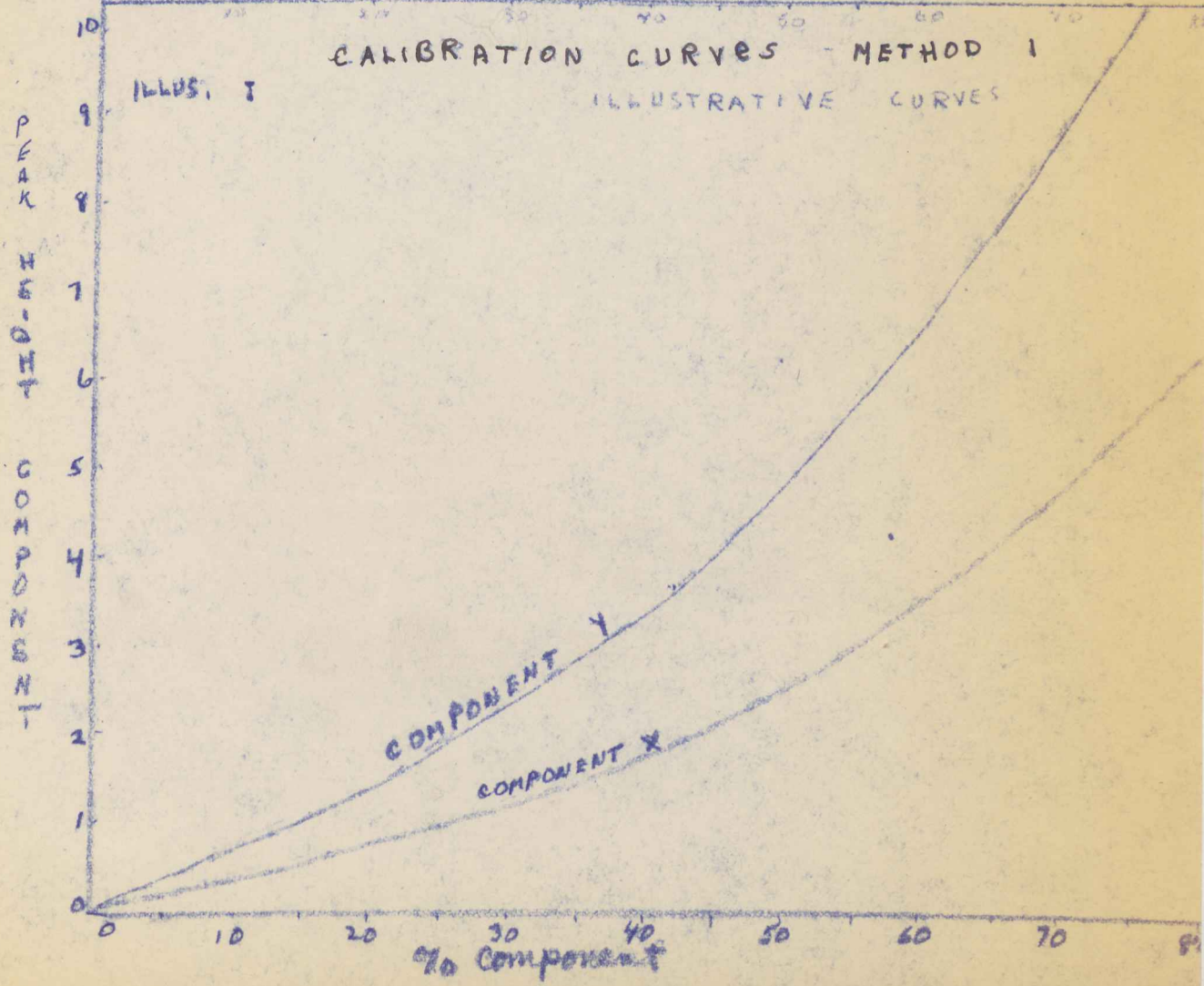
INTERNAL STANDARD - ILLUSTRATIVE



CALIBRATION CURVES - METHOD I

ILLUS. I

ILLUSTRATIVE CURVES



in relation to the peak area methods. It is necessary to prepare as many calibration curves as there are components. The peak area methods do not require calibration curves. Therefore, peak height methods would be time consuming in this respect.

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Apparatus

The vapor phase chromatography equipment is student assembled. The apparatus (Illus. 3) consists of a source of carrier gas, pressure regulator, flowmeter, a system for sample injection, a variable heat source, a column packed with the desired material and an indicating device which analyzes the sample vapors as they are eluted from the column.

The flowmeter (#091438) is made by the Manostat Corporation of New York City. The heat source is a simple oven, 150°C maximum, controlled by a rheostat. Inside this oven are placed the columns of 7 mm inside diameter, coiled glass tubing of 4 foot or 8 foot lengths. Samples, preferably under .25 ml, are injected by a macro-scale syringe through tygon tubing. The point of injection is placed immediately before the column packing but outside the oven to facilitate addition. The vaporization of the sample is aided by the insertion of a small quantity of glass wool in the column prior to the packing.

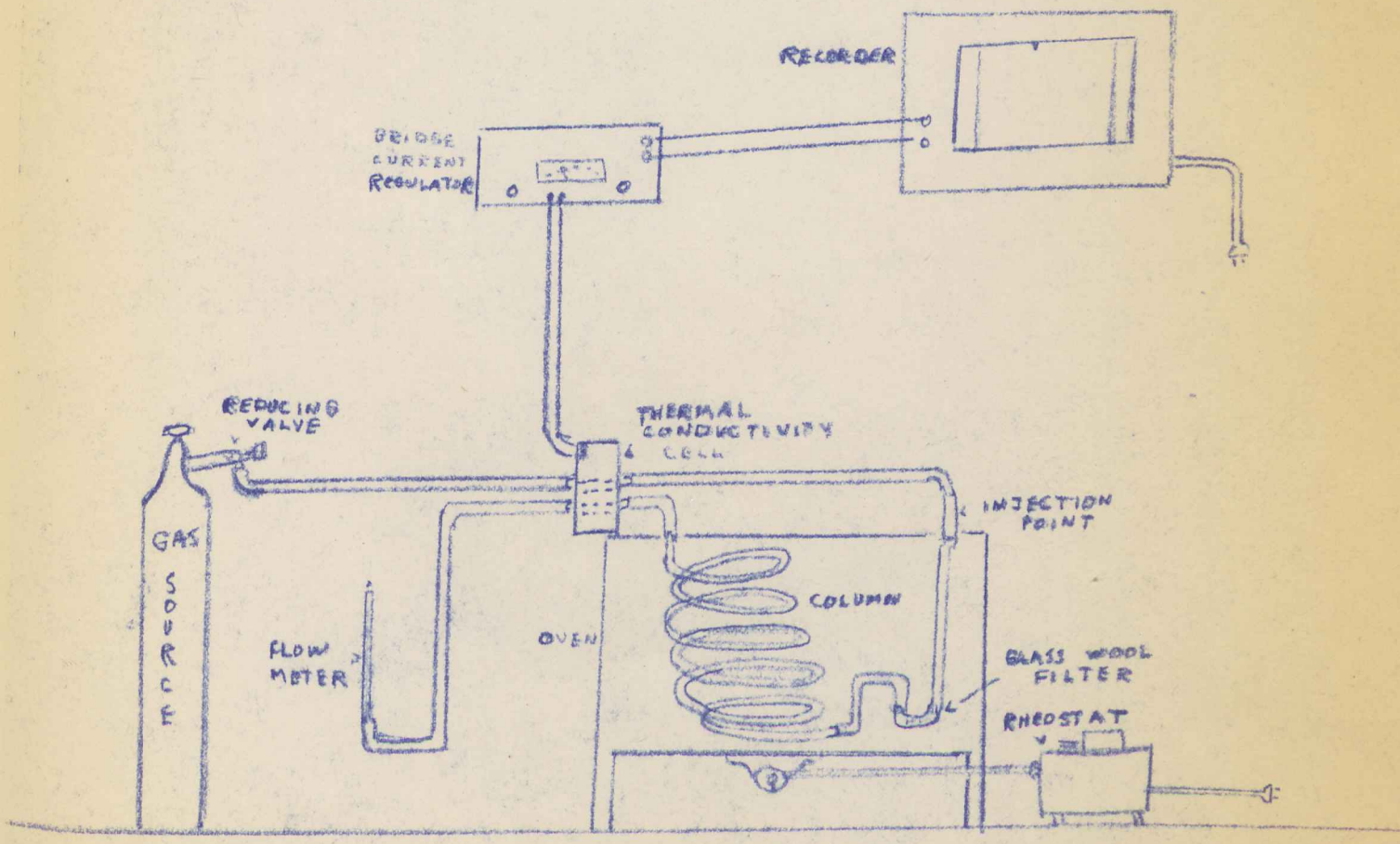
The indicating device (Illus. 4) is a combination of a Thermal Conductivity cell (Gow-Mac #77) in connection with a Weston Recorder (#6701,0-10 mvs). Variations in carrier gas composition caused by elution of sample vapor passing through the Thermal Conductivity cell, are measured and recorded as a change of potential by the Weston Recorder.

The Thermal Conductivity cell is basically a Wheatstone bridge (10, 22) which operates on the principle that "the resistance of a wire is proportional to the temperature of the wire". The carrier gas passes from its source, over one resistor (R_1), then through the sample chamber. It enters the column where the components of the sample are separated,

ILLUS. 3

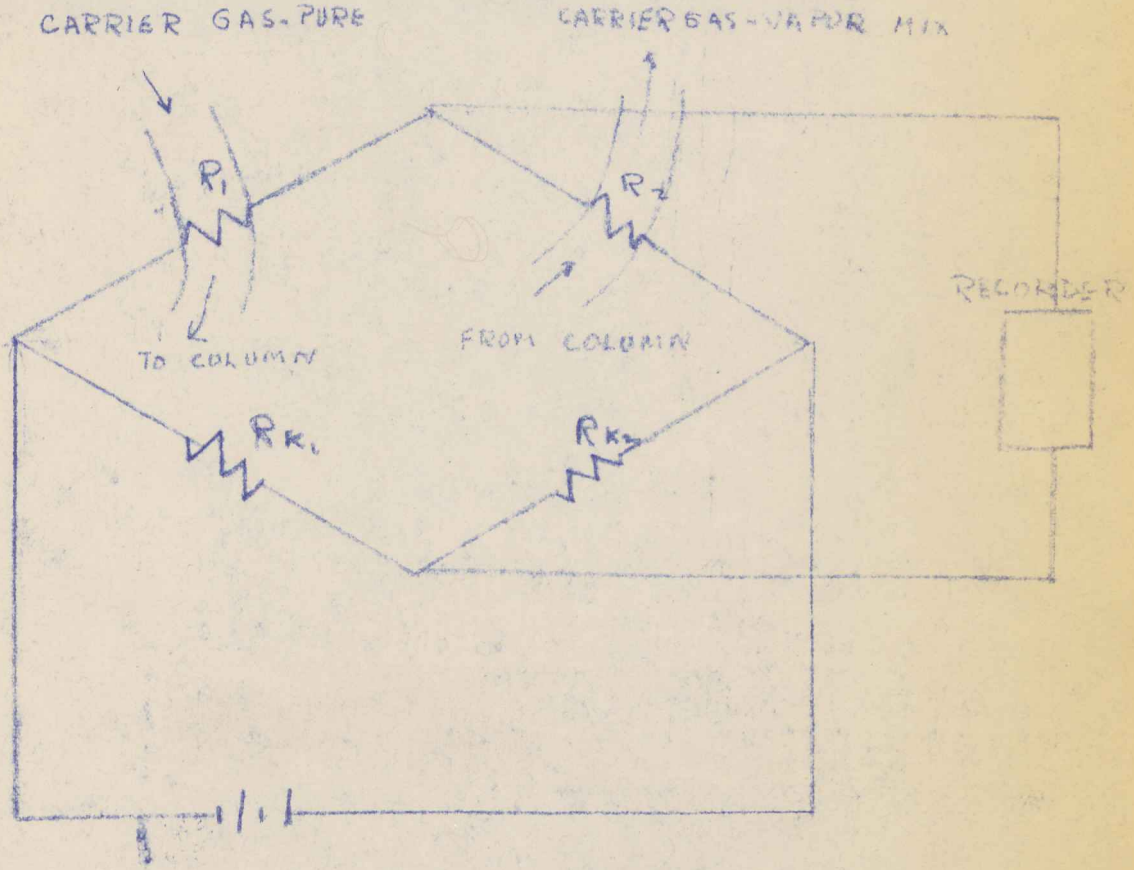
SCHEMATIC DIAGRAM: APPARATUS -

GAS-LIQUID PARTITION CHROMATOGRAPHY



(ILLUS. 4)

THERMAL CONDUCTIVITY APPARATUS



and finally over a second resistor (R_2).

When pure carrier gas flows over both resistors, the bridge is balanced. When a component vapor is present in the carrier gas passing through the Thermal Conductivity cell, this balance is upset and a potential change is registered by the recorder. This bridge imbalance is caused because of the difference in the thermal conductivity coefficients of the various vapors and carrier gas used. Due to this thermal conductivity coefficient difference, the ability to conduct heat away from the source, varies for pure carrier gas and for a mixture of sample vapor and carrier gas, thus upsetting the Wheatstone bridge balance.

Chemicals

Butanol-2 - prepared by reducing methyl ethyl ketone with sodium.

$CH_3COC_2H_5$ ------ $CH_3CH(OH)C_2H_5$

.50M of methyl ethyl ketone is added to .50M sodium, 200ml of ether, and 40ml of water. The mixture is continuously agitated until the reaction ceases. The ether-butanol-2 layer is separated, dried and distilled. Fractions are collected; distilling 1) up to 70°C; 2) between 78-84°C; 3) 84-96°C; 4) over 97°C. The boiling point of ether is 72°C; methyl ethyl ketone, 79.6°C; and butanol-2, 99°C.

Butene-2 - prepared by dehydrating butanol-2 with sulfuric acid.

$CH_3CH(OH)C_2H_5$ ------ $CH_3CHCHCH_3$ H_2O

2.5M of sulfuric acid diluted to 70% with water and cooled below 60°C is added to 1.0M of butanol-2. 4g. of kaolin is added to facilitate the reaction. The mixture is heated to boiling. The gas produced, is passed through solutions of 50% by weight sulfuric acid and then 5M sodium hydroxide. Finally, it is passed through drying tubes of calcium chloride and then soda lime. The gas is collected in an ampoule cooled by an acetone-dry ice mixture.

Di-sec-butyl ether - prepared by the dehydration and condensation of butanol-2 with sulfuric acid.

$CH_3CH(OH)C_2H_5$ ------ $(CH_3CHCH_2CH_3)_2O$

.4M of sulfuric acid is mixed with 3M of butanol-2. The solution is slowly heated to the boiling point. A two phase distillate of 1) di-sec-butyl ether and 2) water is collected. The desired phase is separated and

washed with sodium hydroxide and then water. Sodium sulfate is used to dry this phase. This di-sec-butyl ether (BP 121°C) phase is redistilled over a 117°C-121°C range to remove any traces of butanol-2.

Methyl Ethyl Ketone - Eastman-Kodak Chemicals (commercial grade - White Label)

Butanol-2 - Eastman-Kodak Chemicals (commercial grade- White Label)

Dipropylene glycol - Schenectady Varnish Company

Dibutylphthalate - Schenectady Varnish Company

Dioctylphthalate - Schenectady Varnish Company

Experimentation and Results

The experimentation for this paper is divided in two sections. The original work for this paper is primarily concerned with obtaining data for developing a suitable quantitative technique to measure the purity of butanol-2 and/or methyl ethyl ketone (Eastman-Kodak-commercial grade). Before this work was completed, the appearance of an unidentified impurity led to subsequent attempts to identify this unknown.

For the quantitative separation of methyl ethyl ketone and butanol-2, it is necessary to determine those conditions which give sufficient component curve resolution while minimizing run time.

The apparatus provides a means of varying temperature and flowrate of the carrier gas chosen, as well as the column size, packing ratio, and concentration. Changing any of these factors varies the retention time and curve parameters for the respective components. Sample size is an involuntary variable, but for experimental work this is not objectionable if kept within reasonable bounds (approximately less than .60 ml).

It is found that the current impressed across the Thermal Conductivity cell bridge effects the sensitivity of the equipment for a particular sample (Graph 1). The increase in peak height for identical size samples is proportional to the increase in bridge current. The best current selected is 200ma. At higher currents, an unsteady reading and thus curve distortion and baseline drift is encountered.

In experimentation, much consideration is given the column solvent for the separation of butanol-2 and methyl ethyl ketone. Some column fixed phases used are common detergents: Dreft, Fab, and Tide. Other

solvents employed are dipropylene glycol, dioctylphthalate and dibutylphthalate.

Retention time data for Dreft and dioctylphthalate under varying conditions are tabulated below.

1. Retention times for 4 foot Dreft columns using helium at 60ml/min.

Methyl Ethyl Ketone		Butanol-2	
Temp., °C	Rt., sec.	Temp., °C	Rt., sec.
93	80	50	675
90	90	45	915
85	105	40	1145
80	140		
70	165		
60	180		
50	200		
45	220		
40	255		
35	275		
30	330		
28	355		
25	425		

2. Retention times for 4 foot dioctylphthalate columns (.4M) on 40-60 mesh Johns-Manville crushed firebrick at 1:5 ratio.

Temp., °C	Methyl Ethyl Ketone Nitrogen Flow, ml/min.	Rt., sec.
80	170	125
70	170	140
60	170	210
50	170	300
38	170	420
27	170	690

Temp., °C	Methyl Ethyl Ketone Nitrogen Flow, ml/min.	Rt., sec.
80	120	170
70	120	215
60	120	280
50	120	420

Temp., °C	Methyl Ethyl Ketone He-Flow, ml/min.	Rt., sec.
80	155	80
70	155	110
60	155	165
48	155	205
43	155	300
30	155	435

Methyl Ethyl Ketone

Temp., °C	He-Flow, ml/min.	Rt., sec.
80	60	265
70	60	320
60	60	525
48	60	715
40	60	1020
30	60	(sample dependent)

Butanol-2

Temp., °C	Nitrogen-Flow, ml/min.	Rt., sec.
80	170	185
70	170	240
60	170	350
50	170	435
40	170	675
30	170	1080

Butanol-2

Temp., °C	N-Flow, ml/min.	Rt., sec.
80	120	240
70	120	310
60	120	470
50	120	660
40	120	1020

Temp., °C	Butanol-2 He-Flow, ml/min.	Rt., sec.
80	155	140
70	155	160
60	155	205
48	155	310
43	155	1140
30	155	--

Temp., °C	Butanol-2 He-Flow, ml/min.	Rt., sec.
80	60	420
70	60	530
60	60	790
48	60	1380

Discovery and Attempted Identification of Impurity-

It is noted during the above experimentation, that as flowrate and temperature are lowered, a small peak begins to separate from both methyl ethyl ketone and butanol-2 (Graph 2). This impurity is present in percentage amounts and its retention time is apparently identical when separated, under like conditions, from either of the two vapors. It is assumed that the impurity, therefore, is the same in both butanol-2 and methyl ethyl ketone.

In an attempt to identify the impurity, the retention time is determined at specific, measured rates. At 50°C, using helium at a 100ml/min. flowrate, over 4 foot dioctylphthalate columns, the impurity retention time for a series of runs average to 100 sec.

Likely simple contaminants are measured for their retention times at these conditions. The average retention time of acetone is 140 sec.; ethyl alcohol, 160 sec.; propyl alcohol, 225 sec.; isopropyl alcohol, 210 sec.; and t-butyl alcohol, 180 sec.

The difficulty of adding similar size samples and the resulting effects of sample volume on retention time, makes this means of identification doubtful. This is especially true in the cases of methyl alcohol and ether. Over a series of runs for each, the average retention time of diethyl ether is 85 sec. and methyl alcohol is 110 sec.

Two samples, one a 16g. sample of methyl ethyl ketone, and one a 32g. sample of butanol-2, hydrogenated, using a platinum oxide catalyst, at room temperature and slightly higher than room pressure, take up .004M and .0025M of hydrogen, resp. Chromatograms of both hydrogenated samples of methyl ethyl ketone and butanol-2 show that the impurity is uneffected by hydrogenation and no new peaks appear, to account for the hydrogen consumed.

Butene-2 chromatograms result in a retention time of 40 sec., thus ruling out this dehydration product. Another possible dehydration and condensation product is di-sec-butyl ether which shows a retention time of 870 sec. under similar conditions. This is somewhat near the retention time of butanol-2 (780 sec.).

It is found possible to separate (by use of the chromatographic column) the impurity from butanol-2 at a lower temperature and flowrate (40°C and 40ml/min.). The flowmeter is removed from its position after the Thermal Conductivity cell and is placed between the source of carrier gas and the point of sample injection. Its place is taken by a finely

drawn capillary tube attached close to the Thermal Conductivity cell. When the vapors are separated on the gas-liquid partition column and the impurity is eluted as indicated by the recorder, this capillary tube is immersed in a small amount of chloroform held in a 4 mm centrifuging tube. The impurity vapor-helium gas mixture is bubbled through the chloroform as long as the detector indicates the sole presence of the impurity. Several samples are required to collect a suitable amount of the impurity.

Infra-red absorption curves of the combined sample in chloroform, methyl ethyl ketone in chloroform and butanol-2 in chloroform, using pure chloroform for the reference cell are shown in Graphs 3, 4, 5. Dissimilarities in the curves show the presence of something other than butanol-2 or methyl ethyl ketone. The difference between the methyl ethyl ketone absorption curve and that for the impurity is readily seen. However, the difference between the butanol-2 and the impurity infra-red curve is less obvious, though on a larger scale. There are a number of visible discrepancies in their absorption spectra. For example: at a wavelength of 2.8-2.9u, there is a peak in butanol-2 which the impurity lacks; at 6.0u, butanol-2 has a peak not present in the impurity; from 8.0-8.5u there is a depression in the butanol-2 curve while the impurity shows a large hump; between 9.0-10.0u there are a number of peaks present in butanol-2 that are absent in the impurity; the butanol-2 peak at 10.9u is at 11.1u in the impurity; between 13-14u there is a large impurity hump, missing in the butanol-2 curve; and the butanol-2 curve tails up from 14-15u while the impurity goes steadily down.

Carbide and Carbon Chemical Company, producers of the commercial grade methyl ethyl ketone and butanol-2 for Eastman-Kodak, ran samples of both

chemicals by gas-liquid partition chromatography after the impurity was brought to their attention through correspondence. They discovered peaks corresponding in retention times to t-butyl alcohol and possibly isopropyl alcohol. These vapors, upon collection, were positively identified by mass spectroscopy. Butanol-2 was also found present in the methyl ethyl ketone and methyl ethyl ketone was present in the butanol-2. Unfortunately the relative positions of the t-butyl alcohol and isopropyl alcohol, with respect to the butanol-2 and the methyl ethyl ketone peaks were not disclosed.

The conditions for the chromatograms by Carbide and Carbon are similar to those used in the above experimentation. A 6½ foot column of didecyl-phthalate is used at 60°C with helium gas at a flow of 100ml/min. The fixed phase (28.5% by weight) is held on GC-22 "super Support" of 40-60 mesh.

Discussions and Conclusions

Helium gas is selected as the most suitable for the mobile phase. It is inert, free from impurities, easy to obtain and handle, and is advantageous due to the great difference of its thermal coefficient from those of the vapors being analyzed. This difference increases the sensitivity or ability of the indicator to detect sample vapors. At normal temperatures, smaller molecules, such as helium, have higher coefficients and are, therefore, more sensitive and preferred over nitrogen.

Helium, because its coefficient is higher than any samples analyzed, has the advantage that all vapor peaks are in the same direction from the baseline when a Thermal Conductivity cell-potential recorder device is used. All mixtures of component vapor-helium produce lower coefficients than pure helium, while vapor-nitrogen mixture coefficients may be higher or lower than pure nitrogen depending on the coefficient of the vapor analyzed.

All fixed phase solvents used in this work are polar and contain functional groups similar to those present in the organic liquids being tested thus facilitating resolution.

Using Dreft, retention times for the chemicals investigated increases slowly with temperature drop. At 50°C, the retention time for methyl ethyl ketone is 170sec. while butanol-2 is 730sec. However, even at this retention time difference, a mixture of the two vapors can not be separated. The result is one large curve of an intermediate retention time. Other detergents; Fab and Tide, show similar difficulties of resolution. Because of this and the fact that experimentation shows very close retention time similarity to Dreft, extensive data is not obtained for Fab and Tide.

All three detergents displayed other chemical and mechanical problems. Acetone, for example, cannot be eluted from Dreft or Fab columns, probably due to chemical interaction. The Dreft coloring agent forms a band and is slowly eluted through the column. All three show tendencies on use, to grow sticky at higher temperatures (70°C-90°C) and cause clogging.

Dipropylene glycol shows the same difficulty in the separation of a mixture of the methyl ethyl ketone and butanol-2 vapors. A further disadvantage of this column is the relatively rapid elution of this fixed phase solvent from the column. This causes a gradual decrease in retention time which must remain constant for any useful study or qualitative identification.

The most successful solvents used as the fixed phase are dioctylphthalate and dibutylphthalate. Both 4 foot columns of dioctylphthalate and dibutylphthalate give satisfactory curves for individual runs of methyl ethyl ketone and butanol-2. Dibutylphthalate, due to its greater volatility, is noticeably eluted. Therefore, extensive data is obtained only for dioctylphthalate.

In connection with the solvents, a number of references (19, 7, 30) recommend a 2:5 ratio of fixed phase to inert. However, when the proportion of the solvent to the support for any of these solvents, much exceeds a 1:5 ratio, temperatures roughly above 70°C cause the solvent to come off the solid support and collect in the column and condense in the indicating cell and flowmeter.

It is interesting to note that unless approximately identical volumes of sample are injected and vaporized, the retention times are noticeably effected. Retention time is proportional to sample size. These effects

are more noticeable at lower temperatures, with effects increasing with temperature drop. For example, at 55°C, t-butyl alcohol, for a sample of approximately .40ml, has a retention time of 210 sec. while a sample of .20ml has a retention time of 150sec. At 40°C, the retention time of butanol-2 doubles from 23 min. to 46 min. for roughly double sample size.

Temperature change effects are also important in relation to curve separation. Experimentation on temperature variation reveals that curve separation increases with temperature drop. However, the sensitivity of the Thermal Conductivity cell used also decreases at lower temperatures and broad, long bands result for the vapors being analyzed.

The effects of variable flowrates, when a Thermal Conductivity cell is employed, are important. The resolution retention times, and peak area decrease as flowrates are increased. If the quantitative method used depends on measurements of curve areas, the flow must be kept constant since peak areas do depend on flowrates. As with temperature, the optimum flowrate cannot be realized with the equipment at hand. James and Phillips (17) found that a drop in flowrate increases Thermal Conductivity cell quantitative accuracy down to a certain minimum flowrate, at which this accuracy levels off.

It is possible by regulation of flowrate to speed analysis. If some vapors of sample being analyzed have excessive retention times, the flowrate is increased after the elution of the vapors of shorter run time. When the later curves begin to appear, the flowrate is returned to its original value. It is also possible after increasing the flow to add another quantity of the internal standard, thus eliminating the reduction of the flowrate when later components are eluted.

From the data obtained the optimum conditions for a quantitative separations of methyl ethyl ketone and butanol-2 are determined. With dioctylphthalate columns of 4 foot length, at conditions approximating a temperature of 55°C and a flowrate of 60ml/min. using helium as the carrier gas, quantitative separations are theoretically possible (Graph 6a). Under these conditions, the retention time of methyl ethyl ketone is 420sec. and that of butanol-2 is 965sec. for individual runs. The conditions need not be faithfully reproduced if an internal standard is employed. However, too high temperatures or flowrates cause the curves to merge.

While theoretically possible, mixtures of methyl ethyl ketone and butanol-2 under these above conditions, provide poor separation (Graph 6b). With the 4 foot columns, no distinct curve resolution results, but rather with varying weight percentage compositions of the two chemicals, one curve is dominant and the other vapor curve is represented by an insignificant change of slope or a rough leveling of the tail of the dominant curve. 8 foot columns are more successful but still not satisfactory. Sufficient flowrate cannot be attained with columns much longer than 8 feet.

The difficulty of the above resolution may be caused by a chemical reaction or may result from a combination of physical factors thus causing simultaneous elution of the butanol-2 and methyl ethyl ketone vapors. However, the most likely factor in the lack of separation is the inability of the Thermal Conductivity cell used, to resolve the vapors present.

Advantage is taken of the information obtained in the previous experimentation and a variety of time versus temperature curves are plotted.

Graphs (7) and (8) show the similarity of the effects of the carrier gas at various flowrates as applied to both butanol-2 and methyl ethyl

ketone retention times over a temperature range from 30°C to 90°C. At all flowrates, the slopes of the curves are quite similar, though the curves rise somewhat faster for lower flowrates. For both vapors, it appears that helium gas provides more rapid elution of the respective vapors than does nitrogen. Butanol-2 is prohibitively non-volatile at lower temperatures and effects of varied sample sizes cause uncertain retention measurements.

Graphs (9) and (10) are comparisons of methyl ethyl ketone and butanol-2. Graph (9) uses helium at 60ml/min. and 155ml/min. and (10), nitrogen at 170ml/min. and 120ml/min. The curves are all very similar. The times for butanol-2 and methyl ethyl ketone separate slowly at high temperatures, but much more rapidly as the temperature drops. As mentioned indirectly above, low flowrate curves rise more steeply at lower temperatures, though this effect is not so apparent for nitrogen as higher flows are used.

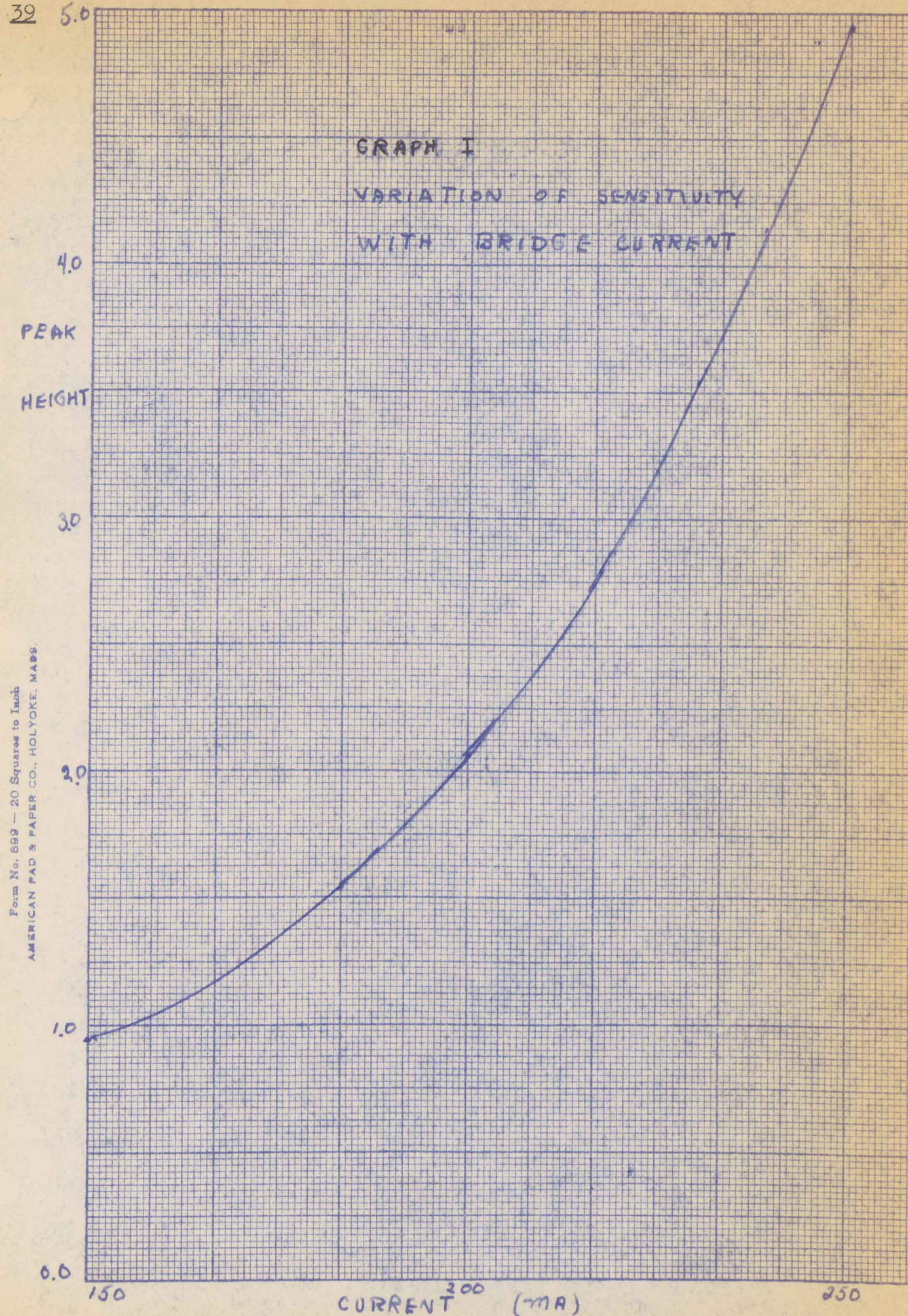
Attempts to identify the similar impurity present in butanol-2 and methyl ethyl ketone have resulted in the elimination of a number of possibilities. However, no definite conclusion can be made as to the identification of the unknown.

By direct measurements of retention times, a number of simple possibilities are eliminated. The presence of a reduceable $>C=O<$ is eliminated by hydrogenation and the resulting chromatograms. The presence of this bond or certain other potential condensation and/or dehydration products present in the butanol-2 or some starting material in its preparation are also ruled out by the preparation of specific chemicals and their resulting chromatograms.

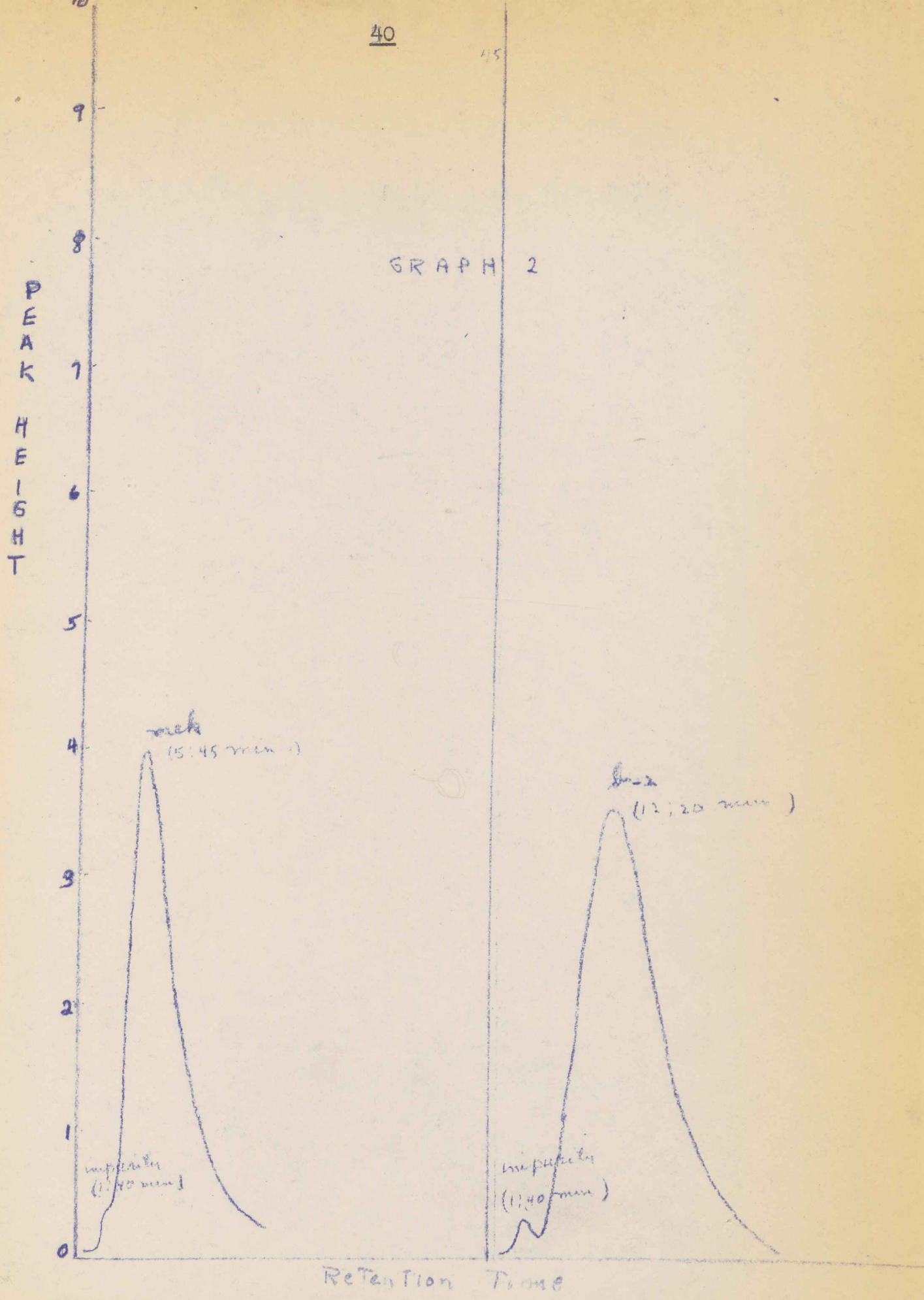
Infra-red curves of the impurity and the gas-liquid partition analyses by Carbide and Carbon suggest t-butyl alcohol but retention time measure-

ments are in disagreement.

Literature sources (28) disclose that ultraviolet light can cause photochemical decomposition of methyl ethyl ketone. Possible products are methane, ethane, propane, and butane. All, however, have prohibitively short retention times.



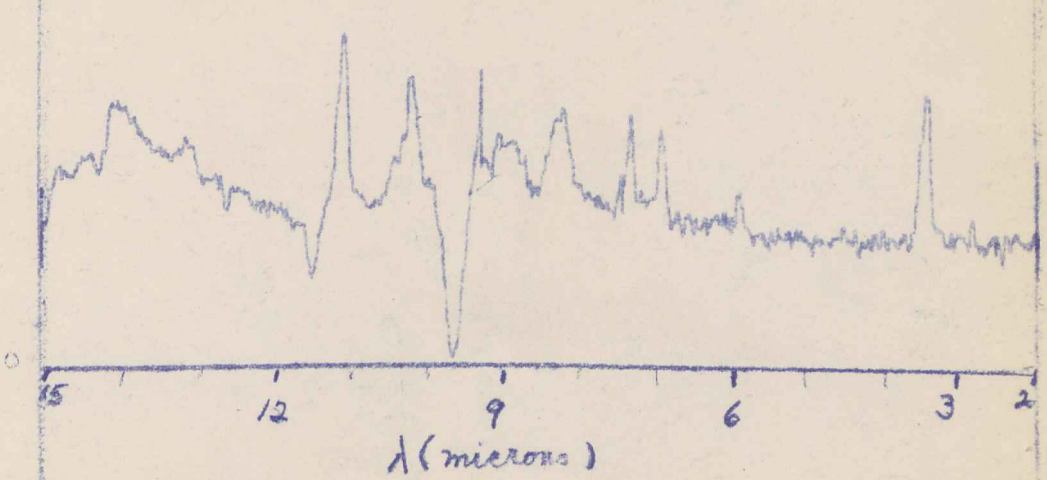
GRAPH 2

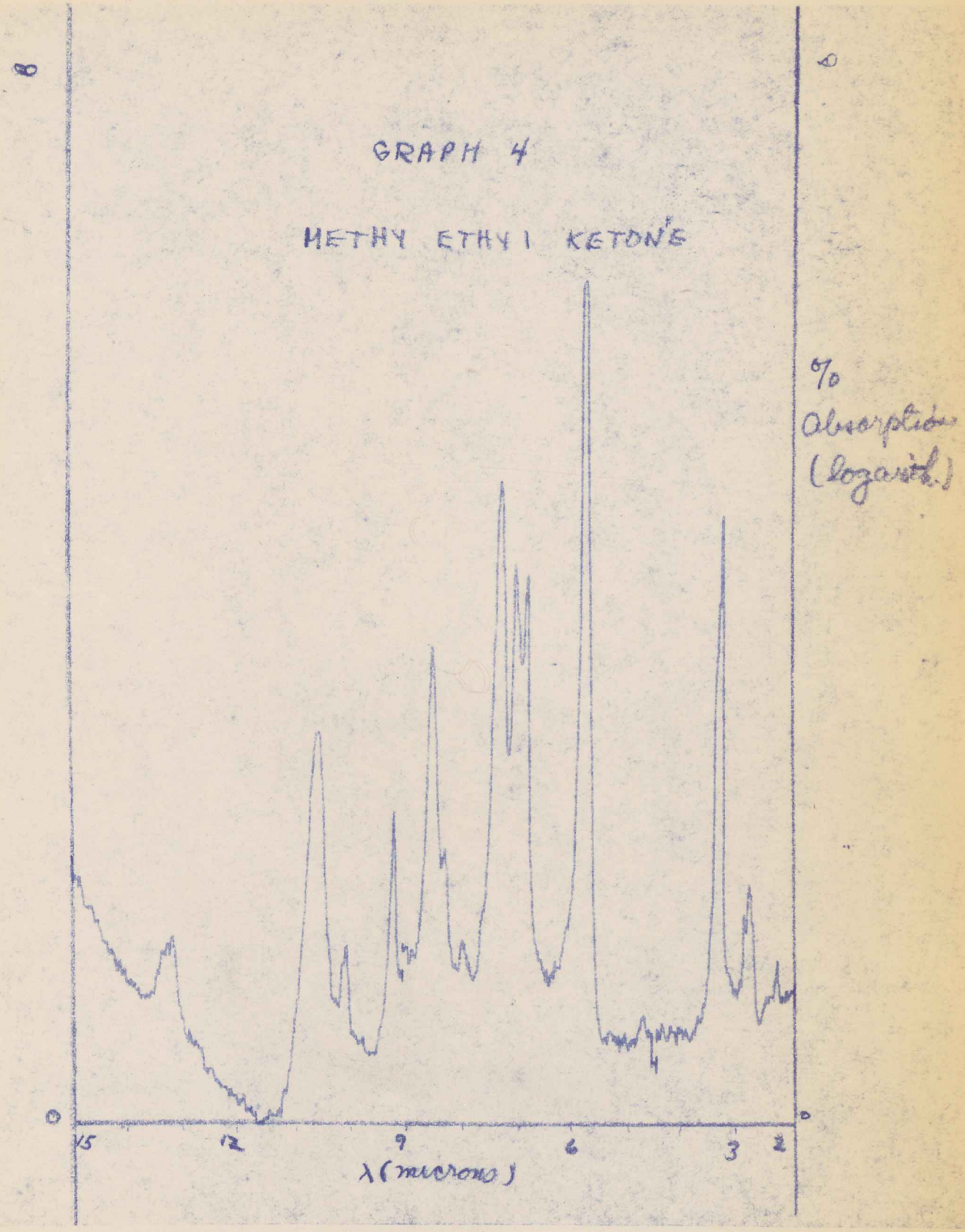

PEAK HEIGHT
9
8
7
6
5
4
3
2
1
0
mek
(15:45 min)
impurity
(1:40 min)
Retention Time

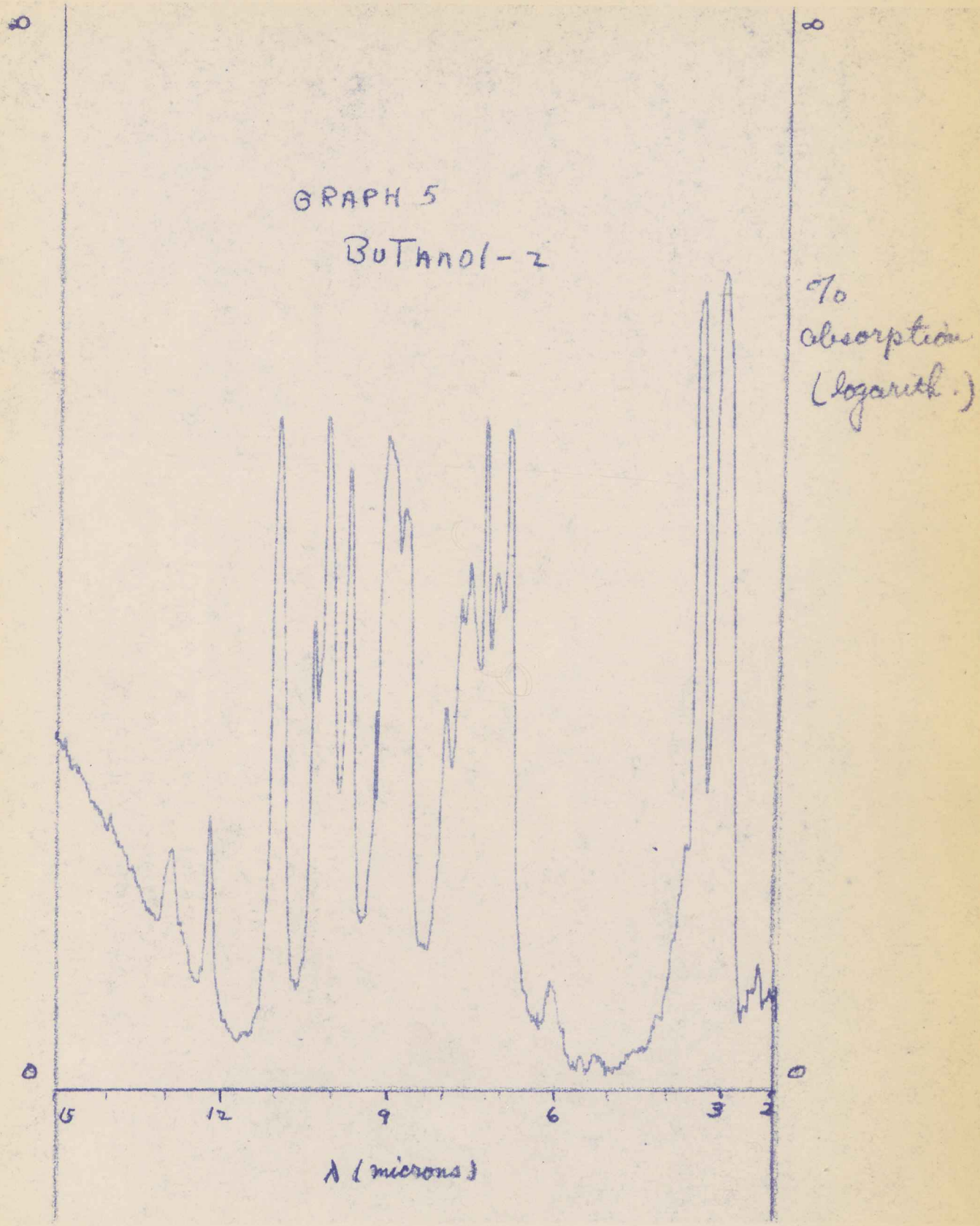
GRAPH 3

IMPURITY IN $CHCl_3$
(BALANCED TO $CHCl_3$ CELL)

% absorbance (logarithmic)

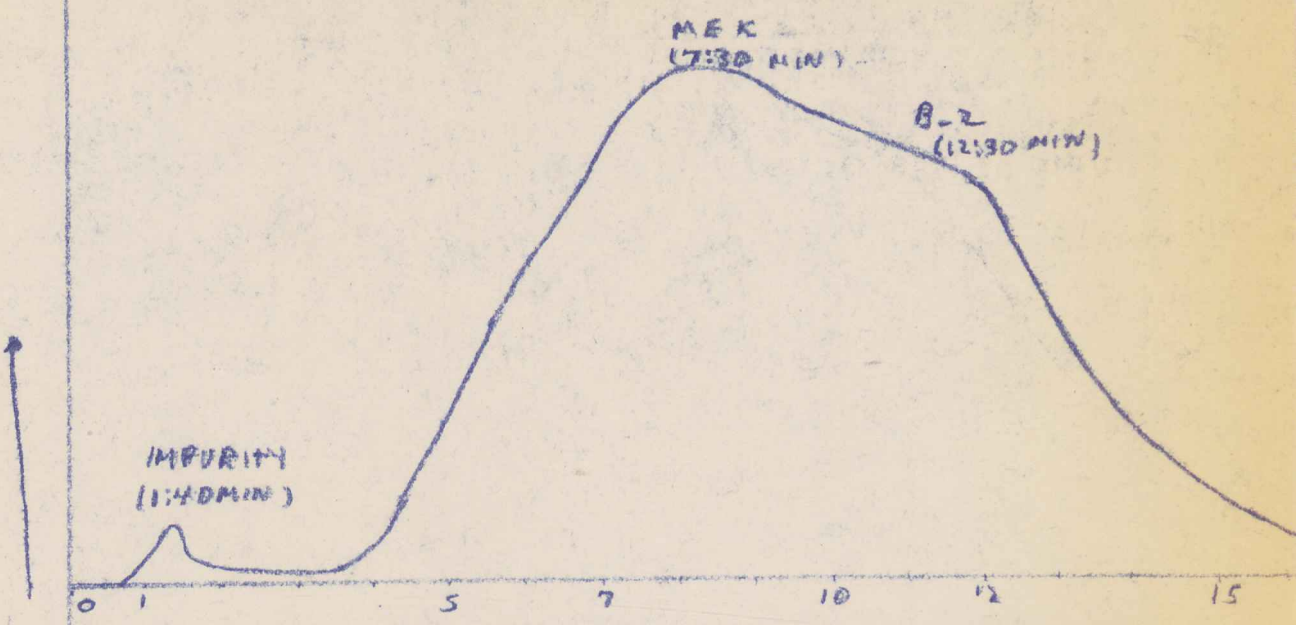



GRAPH 4
METHY ETHYl KETONE
% Absorption (logarith.)
0
15
12
9
6
3
2
λ (microns)


GRAPH 5
BUTANOL-2
% absorption (logarith.)
∞
0
15
12
9
6
3
λ (microns)

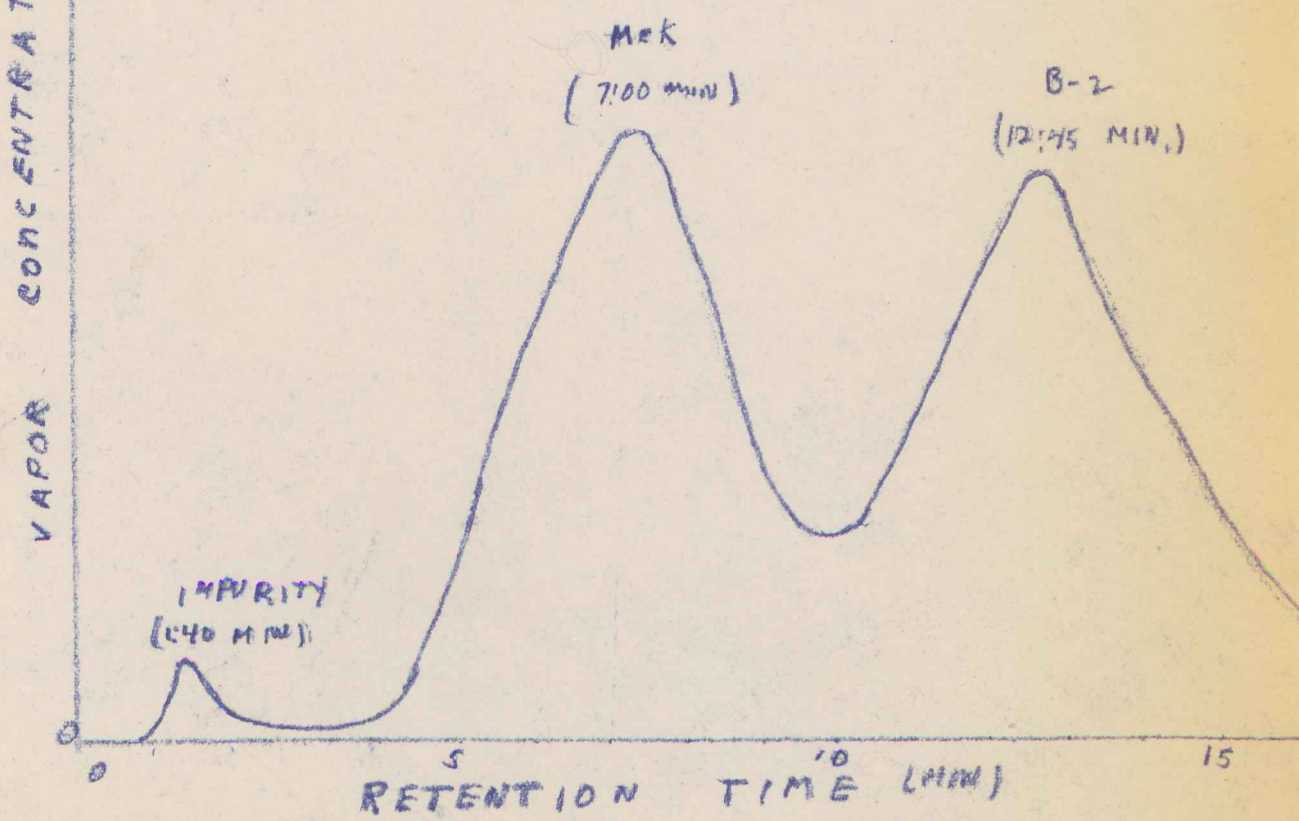
GRAPH 6 b

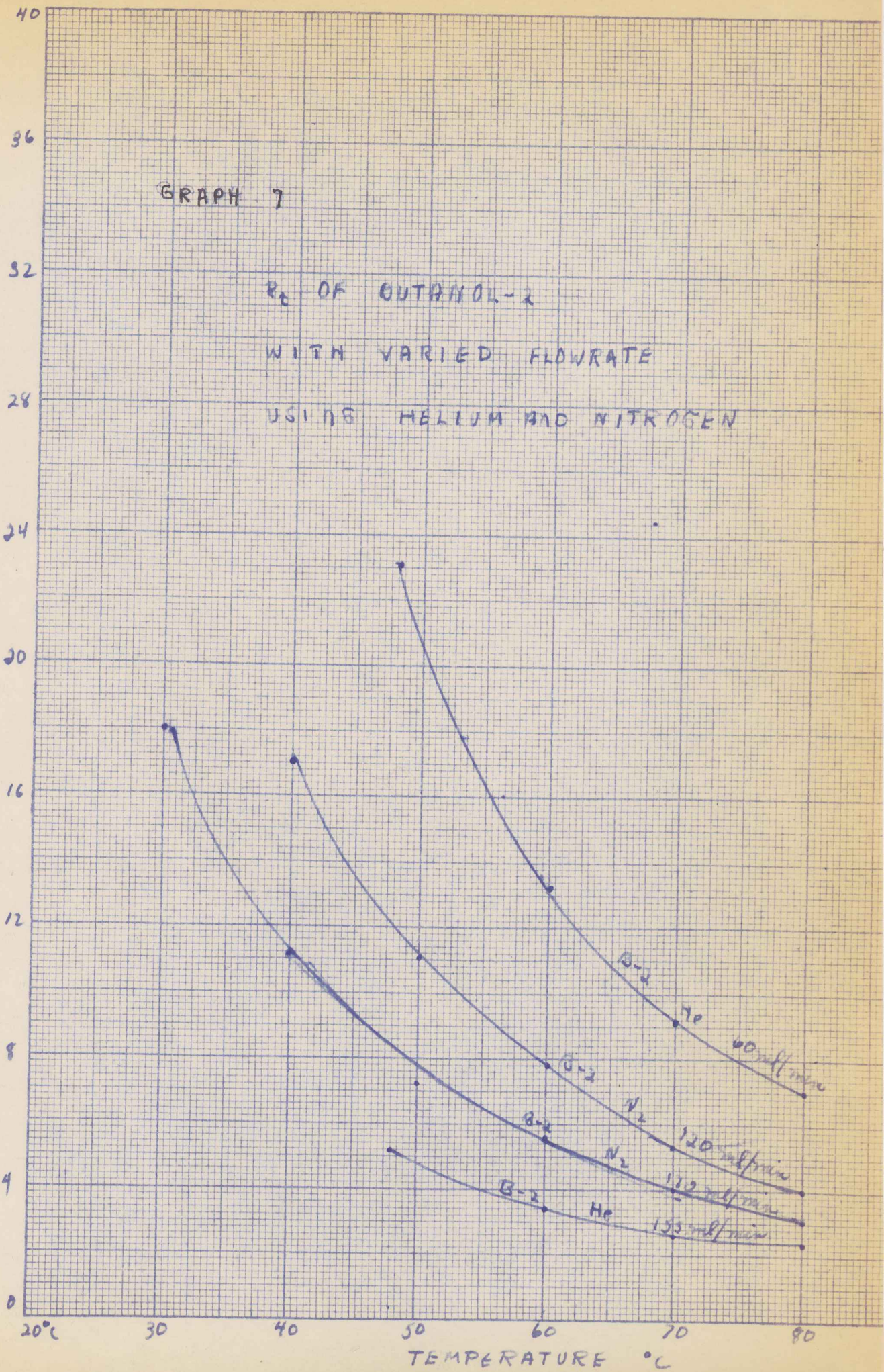
ACTUAL SEP'N OF B-2 AND MEK
(AT SELECTED CONDITIONS)



GRAPH 6a

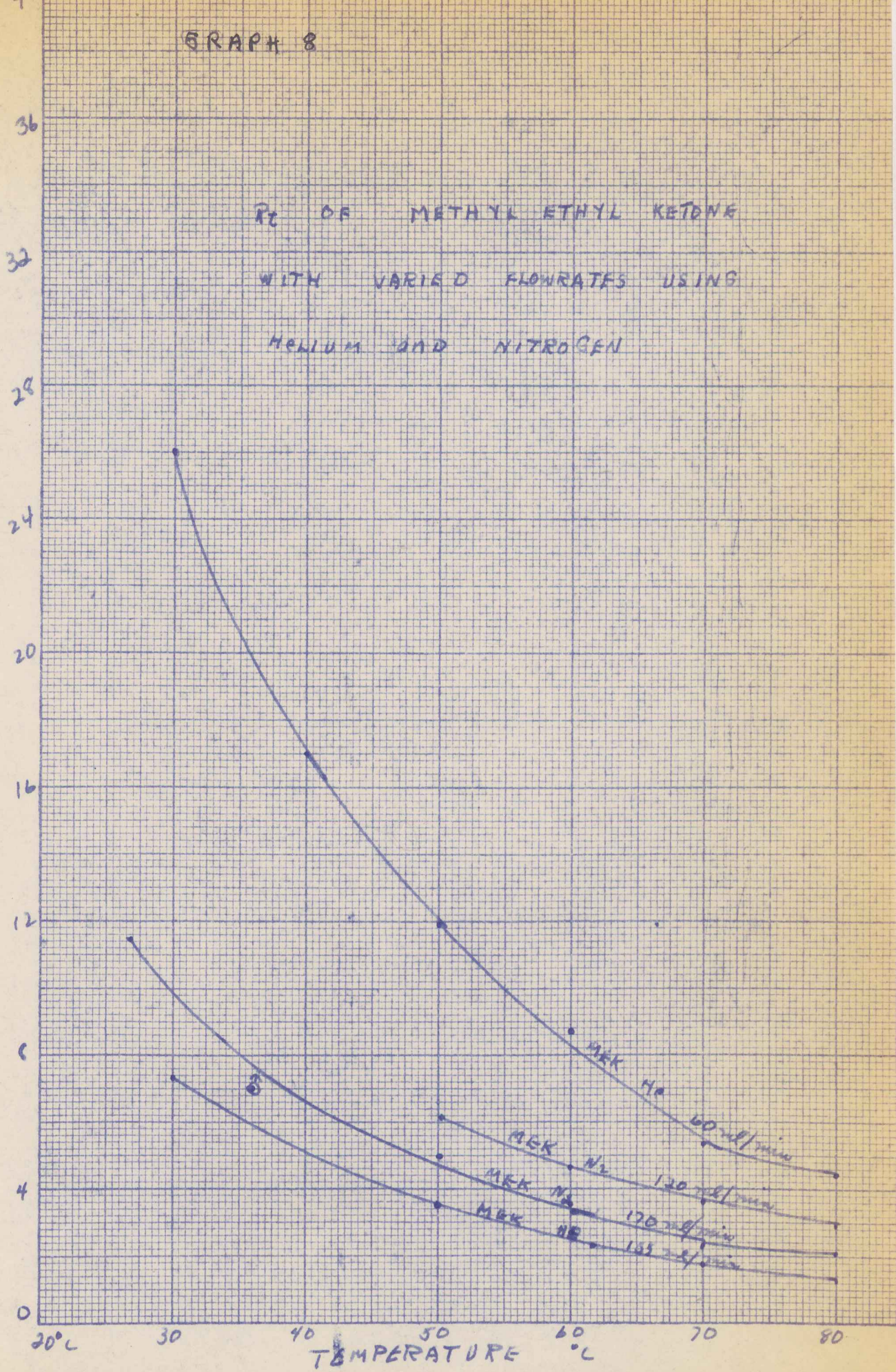
THEORETICAL SEP'N OF B-2 + MEK
(AT SELECTED CONDITIONS)





GRAPH 8

R_f OF METHYL ETHYL KETONE WITH VARIED FLOWRATES USING HELIUM AND NITROGEN

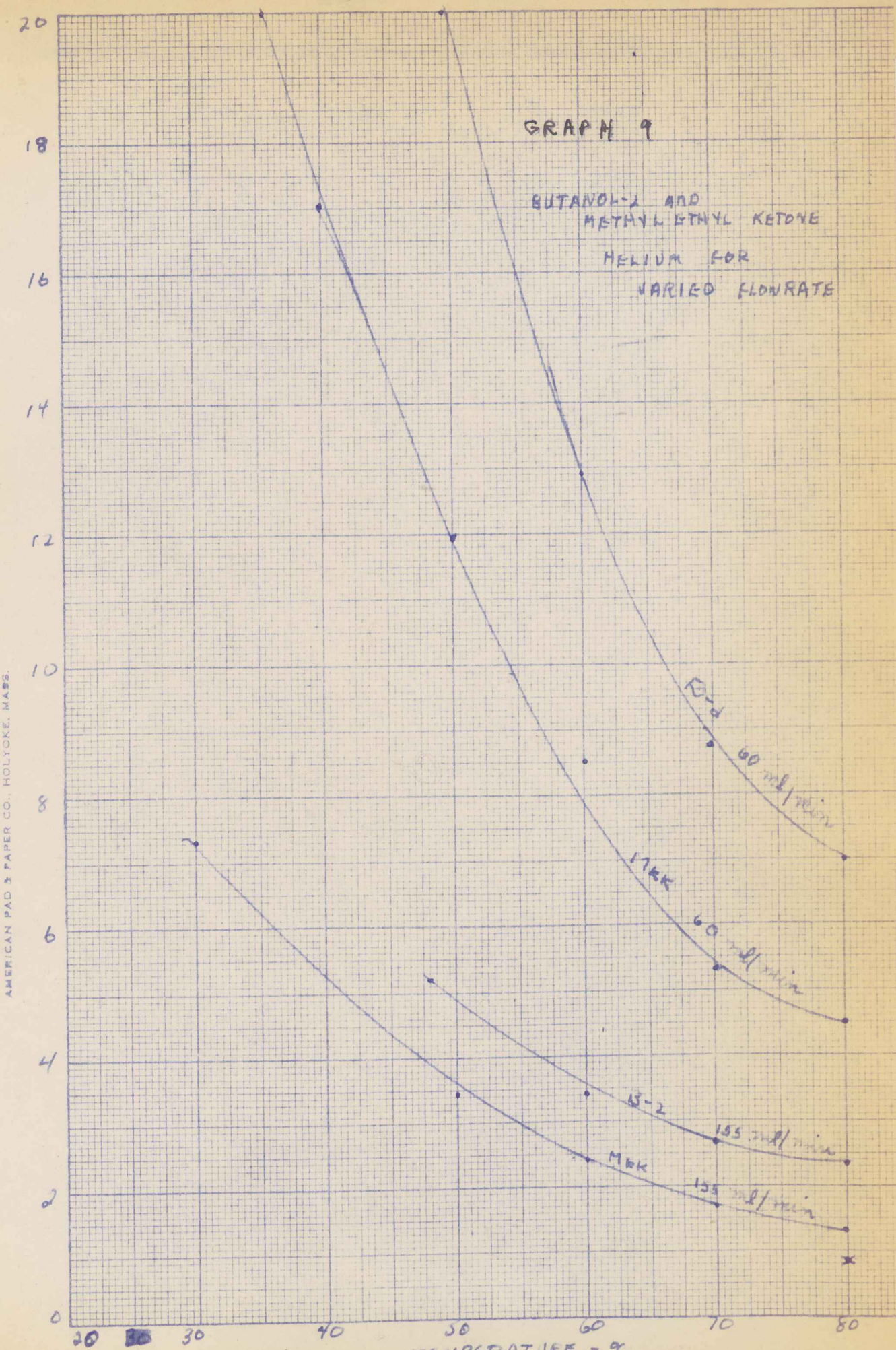


EM-1

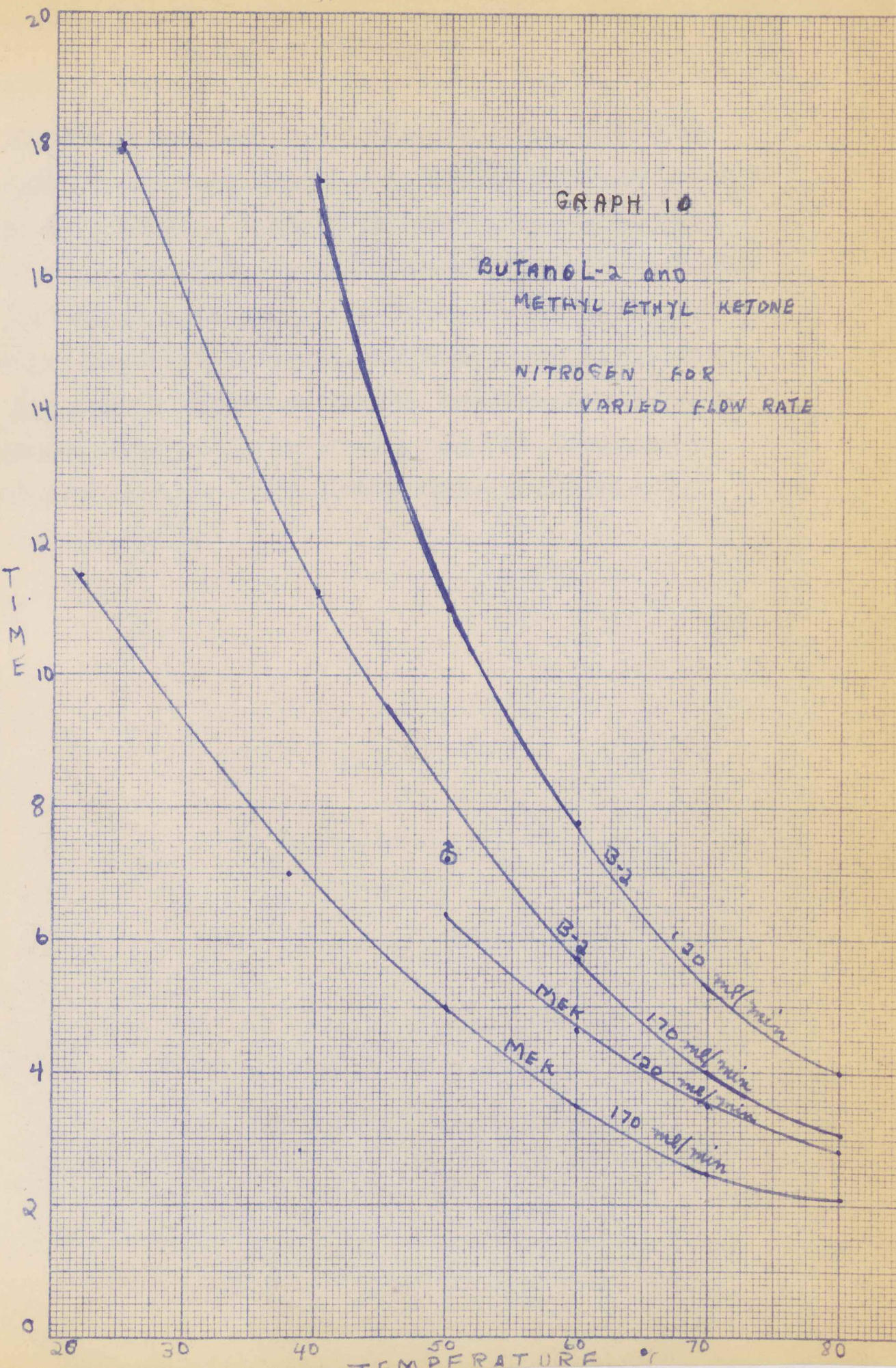
52

GRAPH 9

BUTANOL-2 AND
METHYL ETHYL KETONE
HELIUM FOR
VARIED FLOWRATE



E3-1



Suggestions for Further Work

A more sensitive Thermal Conductivity cell and/or longer columns in conjunction with a more accurate sample injection system will facilitate quantitative separation. Therefore, calibration curves for the vapors present can be prepared using a suitable internal standard to be selected.

The potential solvents used in the fixed phase are limitless and investigation of some of these possible absorbents could be continued.

More sensitive equipment and different techniques could be used in further attempts to identify the impurity found. Also with superior apparatus new impurities such as found by Carbide and Carbon may be found and investigated.

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