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A study of the evaporation of organic liquids and mixtures of organic liquids

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A STUDY OF THE EVAPORATION OF ORGANIC LIQUIDS AND MIXTURES OF ORGANIC LIQUIDS

BY

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A

THESIS

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Professor of Chemistry

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INTRODUCTION

The purpose of this thesis is to make a study of the evaporation of organic solvents. The relative rates of evaporation of the single substances and binary and ternary mixtures are to be considered. A study of the changes in composition of binary and ternary mixtures that occur on evaporation are to be made. Information on the evaporation of organic liquids is important in relation to lacquers, and for that reason the solvents used in this work are liquids commonly used in making lacquers.

There are many factors which affect the evaporation rate of liquids, some of which are vapor pressure, latent heat of evaporation, specific heat, conductivity for heat, the viscosity, surface tension, and molecular weight. These factors are specific for the individual substances. General conditions which vary the rate are humidity, temperature, rate at which the vapor is removed, and direction of the air current over the surface of the liquid. These general conditions may be controlled by proper manipulation and selection of apparatus.

The presence of a non-volatile substance, such as are used in lacquers, affects the rate of evaporation of the volatile solvent, but this effect was not investigated.

Evaporation rates and the boiling points of liquids depend upon their vapor pressure, but the ratio of the volatility of two liquids at room temperature cannot be predicted by comparison of their boiling points, as has been pointed out by Brown and Begin (5)

Ind.Eng.Chem. 19:968 (1927)

and Hofmann(3)

Ind.Eng.Chem. 24:135 (1932)

To investigate the changes in composition that take place upon evaporation, a method for analysing the mixture should be available by which the analysis can be done rapidly and require only a small amount of liquid. To measure the refractive index and the specific gravity requires very little time and liquid. Since the refractive index and the specific gravity of mixtures of organic liquids vary with the composition of the mixtures, these physical constants were used to analyze the mixtures.

HISTORY

Quite a bit of work has been done on the determination of the relative rates of evaporation.

One method[(1)]

Ind. and Eng. Chem. 20:184 (1928)

is to evaporate one gram of solvent in a friction top can cover and weigh at intervals until the solvent has completely evaporated. If samples are run at different times, the results do not check very well.

Another method[(2)]

Ind.Eng.Chem. 21:592 (1929)

is to measure equal volumes of solvent into dishes which are placed in an air tunnel. At definite intervals, the air is stopped, and the dishes covered and weighed. The results check if the temperature is kept within .5°C.

Hofmann[(3)]

Ind.Eng. Chem. 24:135 (1932)

gives a good review of the different methods used for determining evaporation rates. The following methods are listed in his article:

1. Air is passed over the surface of the liquid contained in a flask immersed in a constant temperature bath. The humidity and velocity of the air is controlled, as well as the temperature of the entire apparatus. The number of liters of air necessary to evaporate 10 cc. of liquid is used as a

measure of the

Volatility (6)

Brennstoff-Chem. 5: 371 (1924)

2. A "seccmeter" for temperatures above room temperature and for high concentration of the

Vapor (7)

Chem. News 141, 120 (1930) Abstract.

3. A method of determining constant evaporating mixtures by the use of the Abbe refractometer, as described by

King and Smedley (8)

J. Phys. Chem. 28, 1265 (1924)

Hofmann used two methods in the determination of relative evaporation rates. One was the evaporation of the liquid in aluminum dishes in still air and weighing at one hour intervals. 25-30 cc. of the liquid were placed in the dishes, which were 7.0 cm. in diameter. The formula $\frac{V.\ P \times M.\ Wt.}{11}$ is given to predict the rate of evaporation of a liquid.

This formula gives a rate of 100 for n-butyl acetate as a standard of comparison. In the second method, the temperature of the liquid, and the temperature, humidity, and velocity of the air was controlled. A flowmeter measured the air velocity. The temperature of the bath was 25°C. and the air velocity was 1 liter/min. The liquid was placed in a 200 cc. round bottom flask and evaporated to dryness and the time recorded.

Another method of comparing evaporation rates utilizes the Jolo balance. An unknown solvent is evaporated in a celluloid chimney while a standard sample is being evaporated in another. This device gives an accurate comparison of evaporation rates of liquids.[(4)]

Chem. and Met. Eng. March (1933)

DeHeen[(12)]

J. A. C. S. 5: 24 (1928)

worked on the rate of vaporization of several liquids by passing a gas current parallel to the liquid surface in the evaporator, but action normal to the surface was not entirely eliminated. Evaporation of a liquid into a current of air projected normal to the surface, where the action of a stationary layer of gas resting on the liquid surface is negligible, is essentially a different phenomenon from evaporation into a current of air projected tangentially where a stationary layer resting on the liquid surface is allowed to exist. With an increase in temperature, the speed of evaporation increases more rapidly than the vapor pressure of the liquid. At a given temperature, the weight of the liquid which evaporates varies as the product of the vapor pressure and the molecular weight. This product varied from 3.4 for water to 423 for ethyl bromide, but checked the weight of the liquid evaporated to about 10% for the 8 liquids studied. If S is the weight of liquid evaporated, V the speed of gas current and H a constant, H equals $S/\sqrt{V}$

Campbell[(13)]

Trans. Faraday Society 10:197 (1914-15)

states that it has generally been assumed that failure to get satisfactory results of vapor pressure measurements in presence of a gas, almost always air, has been due to experimental error, and in cases in which a stream of gas was used, to incomplete saturation.

Regnault convinced himself that the differences which he found were due to actual differences of pressure. He suggested that the molecular attraction between the substance of the walls and the vapor particles caused condensation and that equilibrium is never reached, because the rate of evaporation of liquids in presence of gases is slow and because a film of liquid of the thickness requisite to saturate the wall cannot form on account of the force of gravitation. It is suggested than an explanation more in consonance with the facts recorded in this paper is that gases form films on the surfaces of liquids; in other words that liquids absorb gases. It has been proved by experiments carried out in a number of ways by Campbell and others that liquids exert greater or smaller vapor pressure in presence of gases than when in contact with their own saturated vapors only. It has been shown that, in the case of any one liquid, the lowering is greater the more soluble the gas, certain evidence has been adduced which indicates that, with any one gas, the lowering is related to the solvent power of the liquid.

APPARATUS

The apparatus used was designed to control as many conditions as possible. The conditions which are controlled are the velocity of the air, temperature of the liquid, and humidity of the air. The evaporating area was constant and the distance of the surface of the liquid from the air inlet was the same at the start of each evaporation.

Constant air pressure was obtained by means of an air pump driven by a 1725 r.p.m. D.C. shunt motor. Several large bottles acted as buffers for any slight change in pressure. The air after being dried by calcium chloride was divided by a T-tube, each elbow leading to an evaporating bottle. Preceding the evaporating bottles were an orifice, flowmeter, and a water-cooled condenser. The opening in the orifice was adjusted by means of a screw, and was set so that the flowmeter indicated a rate of flow of air of 1/2 liter/min. Copper inner tubes were substituted for the glass tubing to give better conduction. The air temperature was lowered approximately to 20°C. by the condenser.

Two sets of apparatus were made so that evaporation tests could be carried on at the same time. Besides having the same air velocity, the following conditions in each apparatus had to be the same to get check results:

1. Temperature of the liquid
2. Area of the liquid.
3. Distance of the surface of liquid from air inlet.
4. Diameter of the air inlet tube.

The temperature of the liquids was maintained at 20°C ±.1°C. by a constant temperature bath controlled by a toluene mercury thermo-regulator. Since the room temperature varied between 24-32°, cold water was constantly run into the bath. The temperature was raised to about 19.5°C. by one lamp, and another lamp connected to the thermo-regulator maintained the temperature at 20°C.

The liquids to be evaporated were placed in weighing bottles (fig.2) which, when put on the corks having the air inlet tubes from the condensers, are immersed about half of their height into the constant temperature bath. The corks were ground to fit the bottles perfectly and a copper wire was wound around each cork so that the bottles would always fit up to the same height on the cork. The inlet tubes in each cork were the same inside diameter. The end of the inlet tube was level with the bottom of the cork. The rate of evaporation was faster with a narrow inlet tube than with a large inlet tube with the same amount of air. Neither the length nor the diameter of the air outlet tube had an appreciable effect on the rates of evaporation of the liquids.

The weighing bottles were 6 cm. in height, and 2.8 cm. in diameter and area 6.15 sq.cm. The bottles were ground glass stoppered so that the volatile liquids could be weighed without appreciable loss due to evaporation. The bottles and liquids were weighed to the fourth place. The following are the weights of the bottles with their caps:

Bottle No.1 - 22.0791

Bottle No.2 - 20.6828

The distances of the surfaces of the liquids from the inlet tube with different volumes of liquids are:

Vol. of liquid	Distance from tube
10 cc.	3.0 cm.
5 cc.	3.9 cm.
2 cc.	4.4 cm.

The refractive indices of the liquids were measured by an Abbe refractometer. The temperature of the refractometer was maintained at 20°C. by siphoning water from the constant temperature bath.

The specific gravities were measured at 20°C. and compared to water at 20°C. Fig.1 shows the type of bottle used. The bottles were filled by means of a capillary tube and suspended in the constant temperature bath and the level adjusted after the liquid had come to the temperature of the bath.

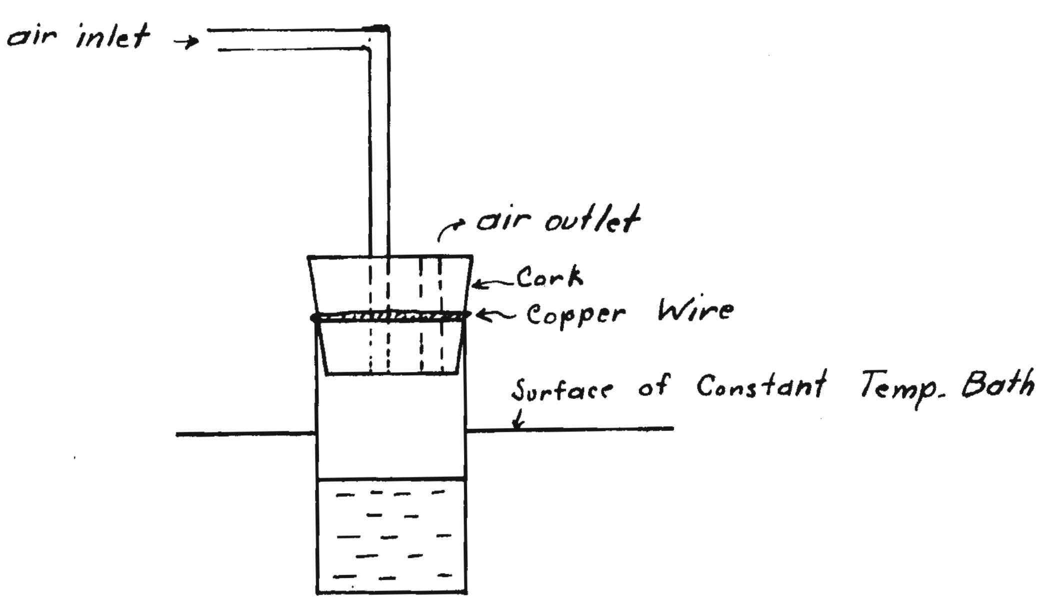
Calibration of the specific gravity bottles:

Bottle No.	1.	2.	3.	4
Weight of bottle	4.6132	4.7159	5.0635	5.1294
Weight of bottle plus water	5.1401	5.2756	5.6341	5.5904
Weight of water	.5269	.5597	.5706	.4646

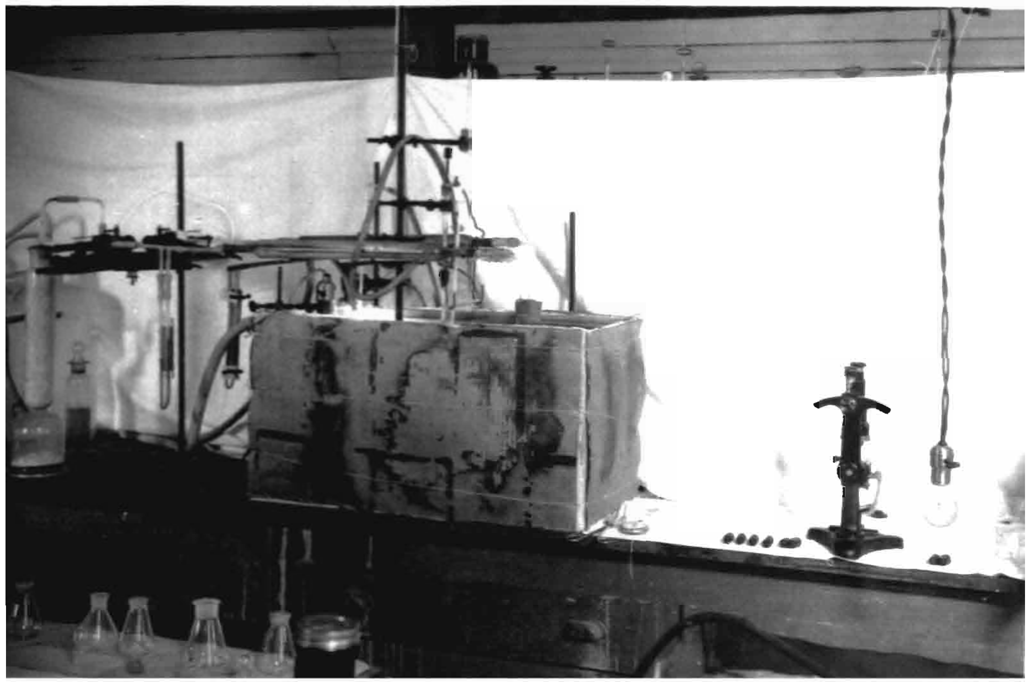
Fig. 1

Specific Gravity Bottle

Fig. 2



Evaporation Bottle



DATA AND RESULTS

Evaporation of pure solvents:

Table 1, 2, and 3 give the data obtained for the evaporation of the single solvents. The results in Table 1 give the loss in weight for 10 cc. of liquid.
The liquid was pipetted into the weighing bottles, care being taken not to let any liquid touch the sides of the bottle above the surface of the liquid. The bottles were covered and weighed, preventing as much as possible the splashing of the liquid. The covers were removed and the bottles placed on the corks. The air was started before the bottles were put in connection with the air inlet. The liquids were evaporated for 15 minutes, the time being checked by a stop watch. The bottles were removed from the apparatus, covered, dried and weighed.
Table 2 are results for 5 cc. of liquid, and Table 3 is for 2 cc. of liquid.

TABLE 1

Evaporation of single solvents using 10 cc. of sample.

(Time of Evap. = 15 min.)

Solvent	Loss in weight	Weight of sample
Acetone	1.660	7.6665
Ethyl Acetate	.950	8.6647
Benzene	.931	8.4154
Toluene	.375	8.3621
Iso-propyl alcohol	.350	7.7237
Iso-amyl acetate	.233	8.3249
n-propyl alcohol	.196	7.7566
n-amyl acetate	.192	8.4284
n-butyl acetate	.182	8.5884
Xylene	.138	8.4899
Iso-butyl alcohol	.134	7.7087
n-butyl alcohol	.100	7.8488
Amyl alcohol	.085	7.7907
Ethyl lactate	.081	9.9462
Cellosolve	.077	8.9963
DiButyl Phthalate	.017	9.8485

TABLE 2

Evaporation of single solvents using 5 cc. of sample.

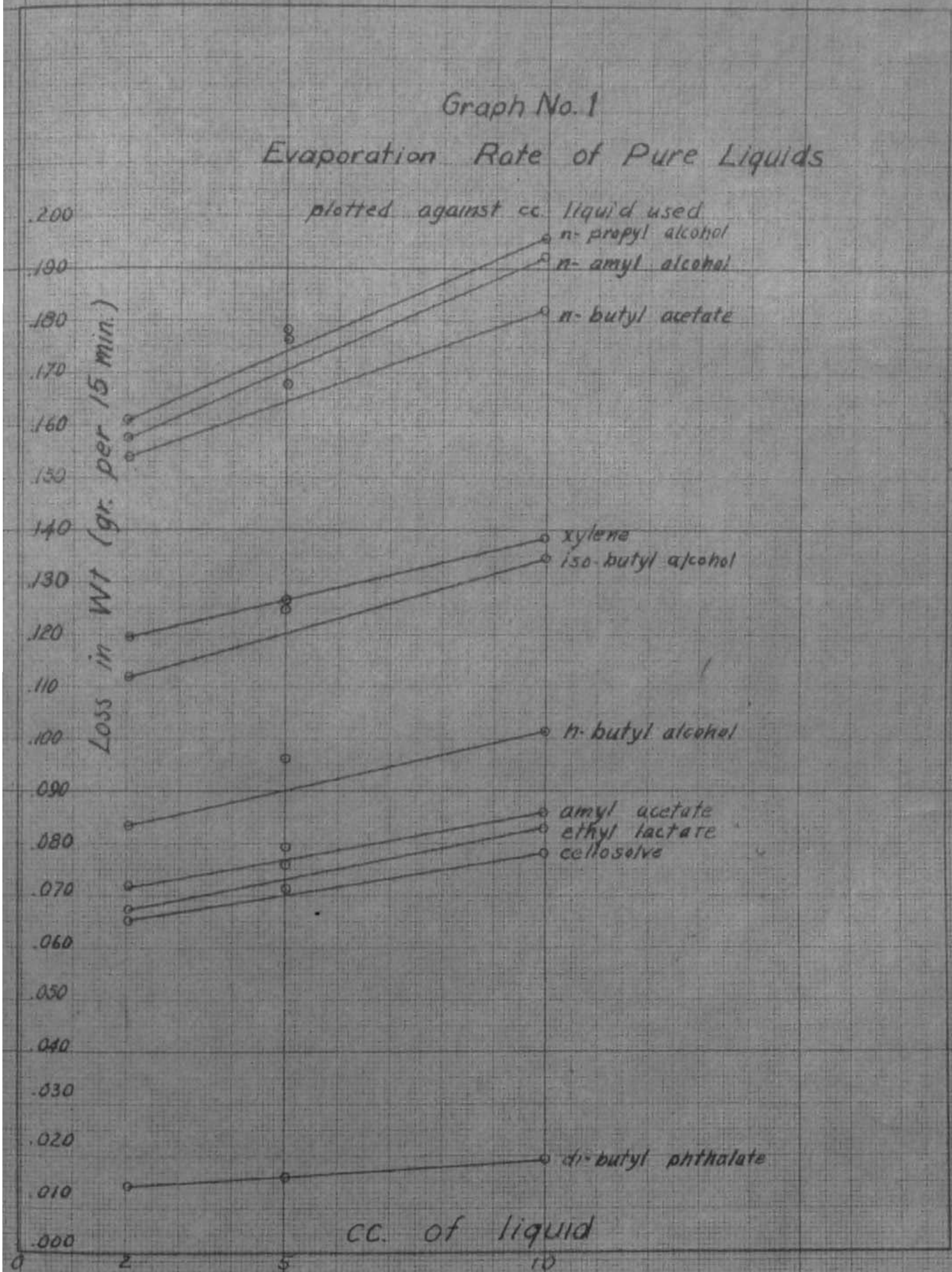
Solvent	Loss in weight	Weight of Sample
Acetone	1.372	3.8669
Ethyl acetate	.823	4.4220
Benzene	.824	4.2947
Toluene	.360	4.2260
Iso-propyl alcohol	.333	3.9202
Iso-amyl acetate	.212	4.2104
n-propyl alcohol	.179	3.9277
n-amyl acetate	.177	4.2543
n-butyl acetate	.168	4.3252
xylene	.126	4.2487
iso-butyl alcohol	.125	3.8831
n-butyl alcohol	.095	3.9582
amyl alcohol	.078	3.9421
ethyl lactate	.075	5.0136
cellosolve	.070	4.5598
dibutyl phthalate	.014	5.0182

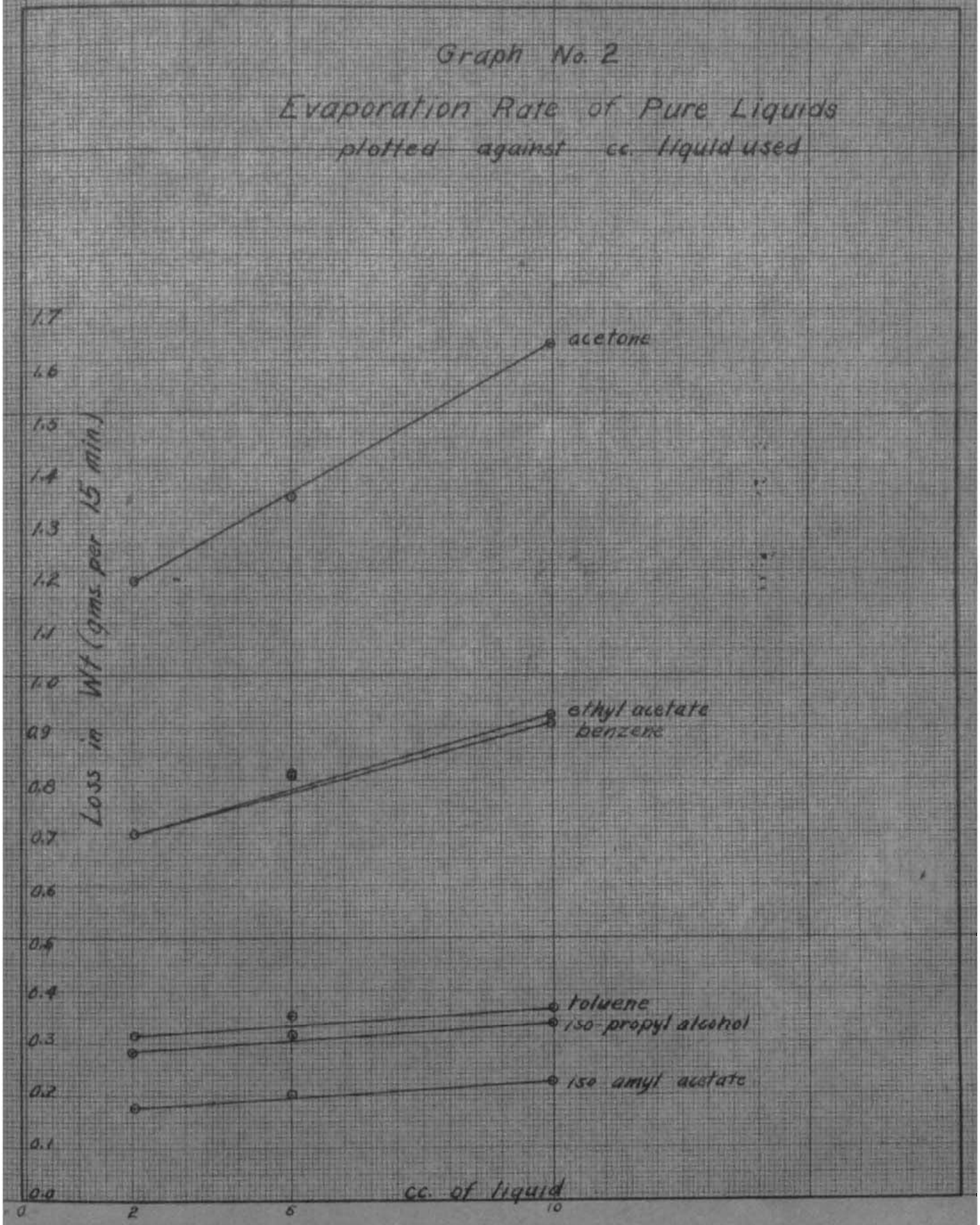
TABLE 3

Evaporation of single solvents using 2 cc. of sample

(Time = 15 min.)

Solvent	Loss in weight	Weight of sample
Acetone	1.204	1.4847
Ethyl acetate	.709	1.7082
Benzene	.710	1.6566
Toluene	.323	1.6467
iso-propyl alcohol	.299	1.5116
iso-amyl acetate	.186	1.6399
n-propyl alcohol	.161	1.5075
n-amyl acetate	.158	1.6469
butyl acetate	.154	1.6817
xylene	.119	1.6586
iso-butyl alcohol	.111	1.4847
n-butyl alcohol	.082	1.5123
amyl alcohol	.070	1.6032
ethyl lactate	.066	1.9086
cellosolve	.064	1.7533
Di butyl phthalate	.012	1.8943


Graph No. 1
Evaporation Rate of Pure Liquids
plotted against cc. liquid used
Loss in Wt (gr. per 15 min.)
cc. of liquid
n-propyl alcohol
n-amyl alcohol
n-butyl acetate
xylene
iso-butyl alcohol
n-butyl alcohol
amyl acetate
ethyl lactate
cellosolve
di-butyl phthalate
.200
.190
.180
.170
.160
.150
.140
.130
.120
.110
.100
.090
.080
.070
.060
.050
.040
.030
.020
.010
.000
0
2
5
10


Graph No. 2
Evaporation Rate of Pure Liquids
plotted against cc. liquid used
Loss in Wt (gms. per 15 min.)
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
acetone
ethyl acetate
benzene
toluene
iso-propyl alcohol
iso amyl acetate
cc. of liquid
0
2
6
10

Refractive indices and specific gravities of the liquids were determined, and the values given in Table No. 4. Binary mixtures were made and the refractive index and specific gravity for them given in Tables 5 - 10.
The liquids were weighed in glass stoppered weighing bottles and the percent by volume calculated from the weight and specific gravity. The ternary mixture butyl alcohol-toluene-ethyl acetate was examined in the same manner, and data is listed in Table 11. The graphs 3 - 8 are the curves obtained by plotting the refractive indices and specific gravities against the percent by volume composition of the binary mixtures. Graphs 9 and 10 show that the values of the refractive indices of the ternary mixture ethyl acetate-butyl alcohol-toluene fall on straight lines, which is very strange since the binary mixtures that make up the ternary mixture do not form straight curves. The values for the specific gravities do not all occur on a straight line connecting the values of the specific gravities of the binary mixtures, but the error resulting by assuming straight line curves is not very great.

TABLE 4

Refractive index and Specific Gravity of the solvents.

Solvent	Refractive index	Specific gravity 20/20
ethyl acetate	1.3713	.902
toluene	1.4922	.862
butyl alcohol	1.3981	.814
cellosolve	1.4065	.940
benzene	1.4981	.876
dibutyl phthalate	1.4913	1.049
n-propyl alcohol	1.3945	.808
n-butyl acetate	1.3937	.883

TABLE 5

Butyl alcohol-toluene mixtures.

butyl alcohol			toluene			ref.ind.	sp.gr.
weight	volume	% by vol.	weight	volume	% by vol.		
3.9346	4.85	50.0%	4.1596	4.83	50.0%	1.4440	.838
1.6768	2.07	30.0%	4.1538	4.82	70.0%	1.4650	.848
.7650	.94	8.7%	8.4592	9.81	91.3%	1.4832	.859
3.3414	4.10	38.3%	5.6595	6.58	61.7	1.4549	

TABLE 6

Ethyl acetate			toluene			ref.ind.	sp.gr
weight	volume	% by vol.	weight	volume	% by vol.		
4.4323	4.91	71.8%	1.6640	1.93	28.2%	1.4060	.891
4.4161	4.89	50.0%	4.2219	4.89	50.0%	1.4306	.883
1.6768	1.86	27.9%	4.1750	4.84	72.1%	1.4578	.875
.8683	.96	8.8%	8.4773	9.83	91.2%	1.4812	.867

TABLE 7

Ethyl acetate-butyl alcohol mixture

Butyl Alcohol			Ethyl Acetate			Ref.ind.	Sp.Gr.
Weight	volume	% by vol.	Weight	Volume	% by vol.		
4.3836	4.86	26.6	1.4387	1.76	73.4%	1.3775	.875
4.4146	4.99	50.0%	3.9134	4.80	50.0%	1.3836	.855
1.7063	1.89	71.8	3.9126	4.80	28.2%	1.3897	.837
1.8584	.95	91.2	7.9618	9.78	8.8%	1.3954	.821

TABLE 8

Ethyl acetate-butyl acetate mixtures

Ethyl acetate			Butyl acetate			Ref.ind.	Sp.Gr.
Weight	volume	% by vol.	Weight	volume	% by vol.		
4.3875	4.86	50.6%	4.1685	4.72	49.4%	1.3822	.891
4.4597	4.94	73.8%	1.5520	1.75	26.2%	1.3770	.894
1.6995	1.88	28.8%	4.1563	4.70	71.5%	1.3870	.889
.8540	.94	8.8%	8.7020	9.85	91.2%	1.3916	.884

TABLE 9

Ethyl acetate-n-propyl alcohol mixtures.

Ethyl acetate			n-propyl alcohol			Ref.ind.	Sp.Gr.
Weight	volume	% by vol.	Weight	volume	% by vol.		
4.4680	4.95	73.1%	1.4778	1.82	26.9%	1.3740	.874
4.3973	4.87	50.0%	3.9049	4.83	50.0%	1.3771	.853
1.7257	1.91	28.3%	3.9088	4.85	71.7%	1.3802	.834
.8863	.98	9.1%	7.8955	9.77	90.0%	1.3830	.818

TABLE 10

Ethyl acetate-cellosolve mixtures.

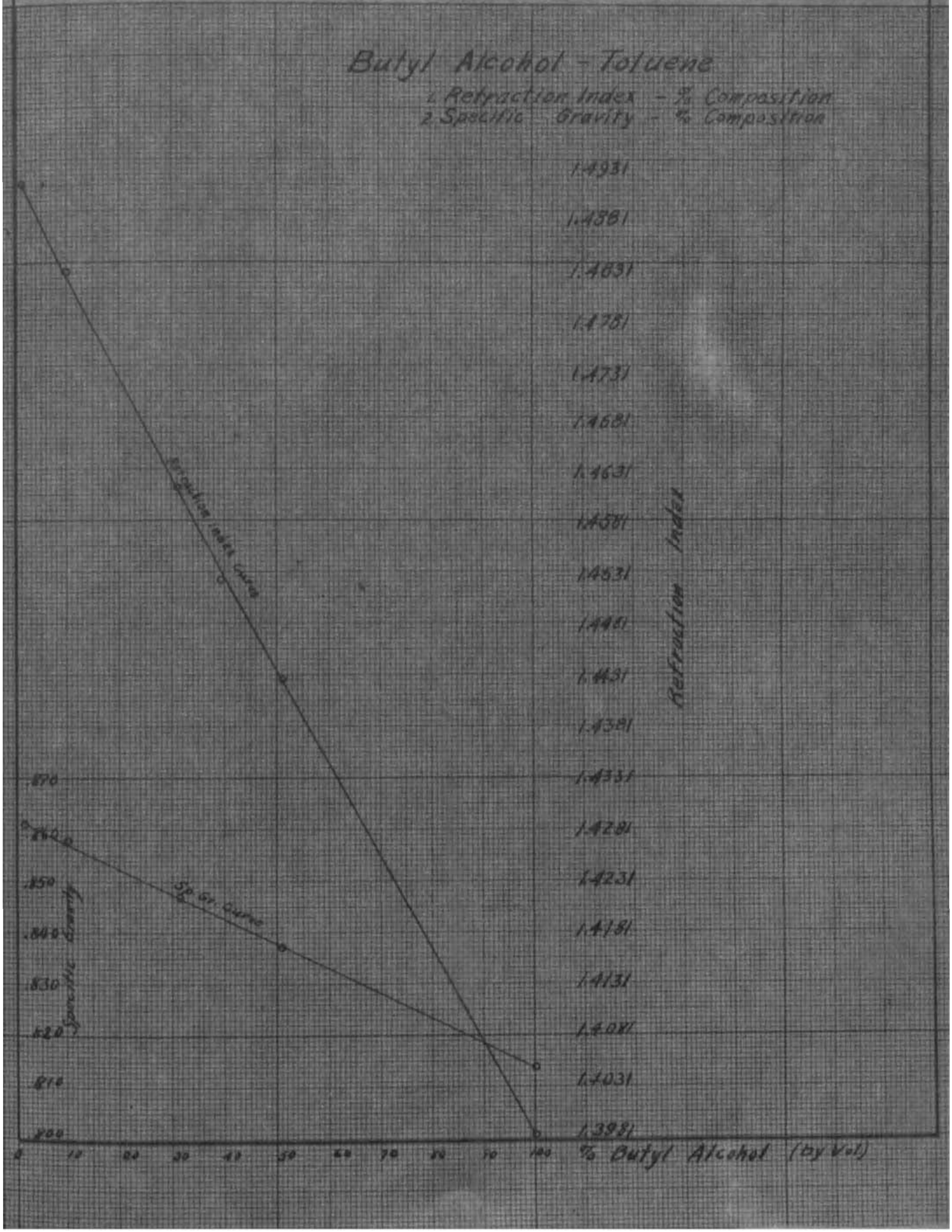
Ethyl acetate			Cellosolve			Ref.ind.	SpGr.
Weight	volume	% by vol.	Weight	volume	% by vol.		
4.3058	4.77	71.9%	1.7531	1.86	28.1%	1.3809	.910
4.4487	4.93	51.6%	4.3449	4.62	48.4%	1.3880	.917
1.66959	1.88	27.5%	4.5541	4.95	72.5%	1.3964	.926
.8592.	.95	8.8%	9.1316	9.72	91.2%	1.4050	.934

TABLE 11

Ethyl Acetate-Toluene-Butyl Alcohol

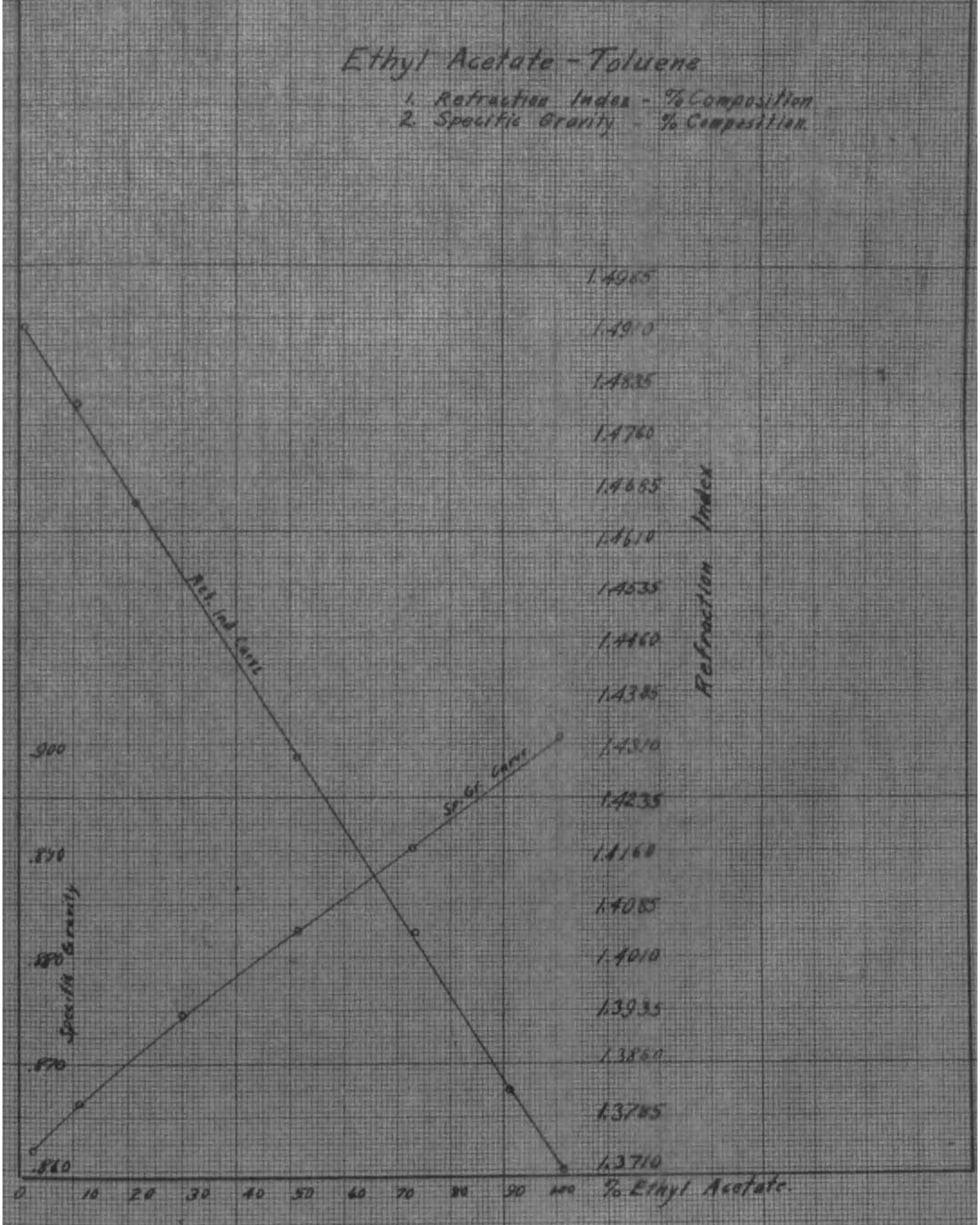
Butyl Alcohol % by vol.	Ethyl Acetate % by vol.	Toluene % by vol.	Ref. Ind.	Sp.Gr.
38.0	23.8	38.2	1.4268	.853
21.3	25.3	53.4	1.4403	.862
14.0	17.6	68.4	1.4565	.864
28.2	37.1	34.7	1.4193	.861
44.9	29.2	25.9	1.4132	.850
12.3	15.3	72.4	1.4610	.862
51.4	25.5	23.1	1.4123	.847
26.0	55.0	19.0	1.4003	.870
5.4	7.4	87.2	1.4778	.862
4.3	87.3	8.4	1.3821	.893

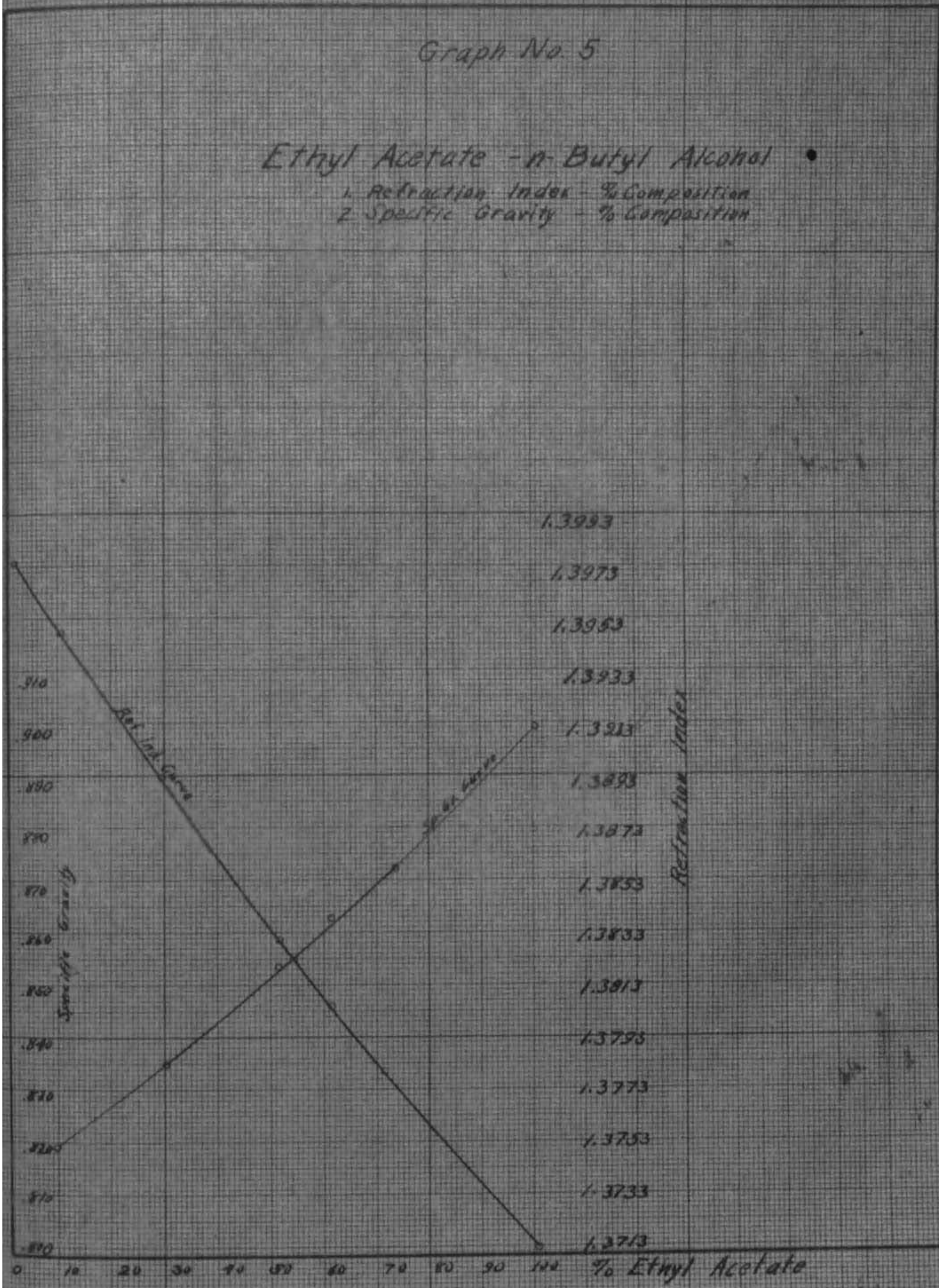
Graph No. 3



Butyl Alcohol - Toluene
1. Refraction Index - % Composition
2. Specific Gravity - % Composition
Refraction Index
1.4931
1.4881
1.4831
1.4781
1.4731
1.4681
1.4631
1.4581
1.4531
1.4481
1.4431
1.4381
1.4331
1.4281
1.4231
1.4181
1.4131
1.4081
1.4031
1.3981
Refraction Index Curve
Sp. Gr. Curve
Specific Gravity
.870
.860
.850
.840
.830
.820
.810
.800
0
10
20
30
40
50
60
70
80
90
100
% Butyl Alcohol (by Vol.)

Graph No. 4

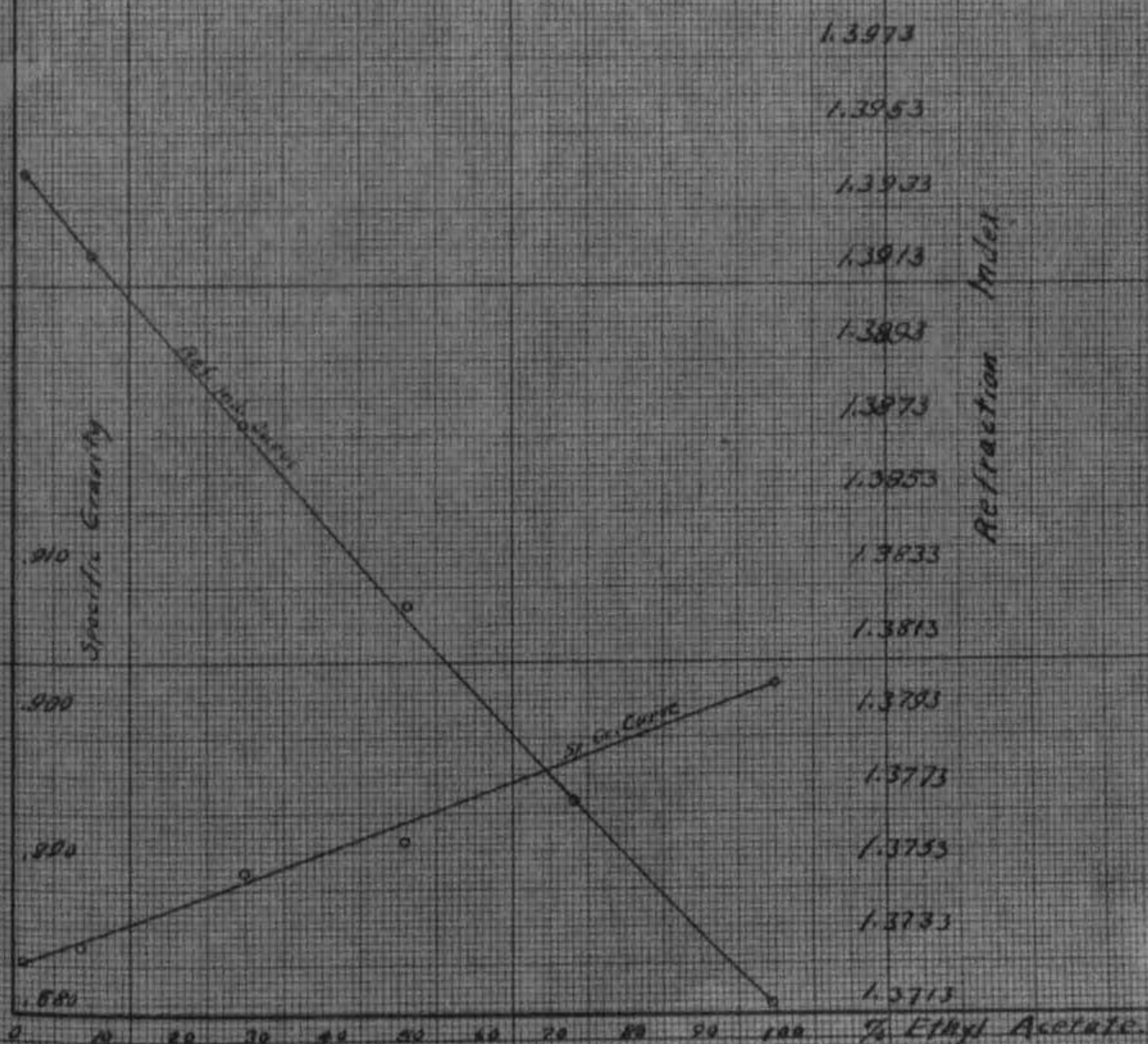

Ethyl Acetate - Toluene
1. Refraction Index - % Composition
2. Specific Gravity - % Composition
Ref. Ind. Curve
Sp. Gr. Curve
Refraction Index
Specific Gravity
% Ethyl Acetate
1.4985
1.4910
1.4835
1.4760
1.4685
1.4610
1.4535
1.4460
1.4385
1.4310
1.4235
1.4160
1.4085
1.4010
1.3935
1.3860
1.3785
1.3710
.900
.890
.880
.870
.860
0
10
20
30
40
50
60
70
80
90
100


Graph No. 5
Ethyl Acetate - n-Butyl Alcohol
1. Refraction Index - % Composition
2. Specific Gravity - % Composition
Ref. ind. Curve
Sp. Gr. Curve
Specific Gravity
Refraction Index
% Ethyl Acetate
1.3993
1.3973
1.3953
1.3933
1.3913
1.3893
1.3873
1.3853
1.3833
1.3813
1.3793
1.3773
1.3753
1.3733
1.3713
.910
.900
.890
.880
.870
.860
.850
.840
.830
.820
.810
.800
0
10
20
30
40
50
60
70
80
90
100

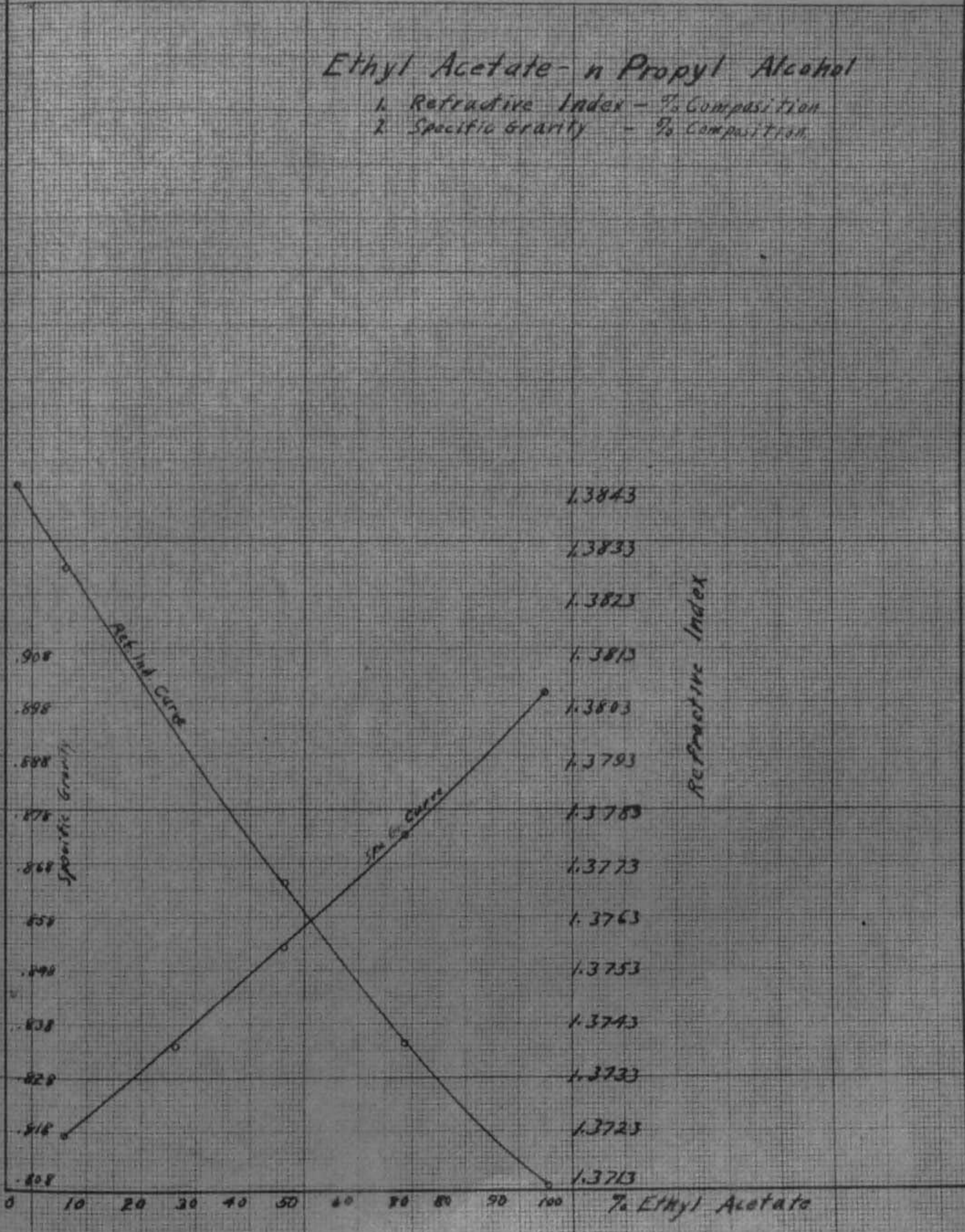
Graph No. 6

Ethyl Acetate - n- Butyl Acetate

1. Refraction Index % Composition
2. Specific Gravity - % Composition



Graph No. 7

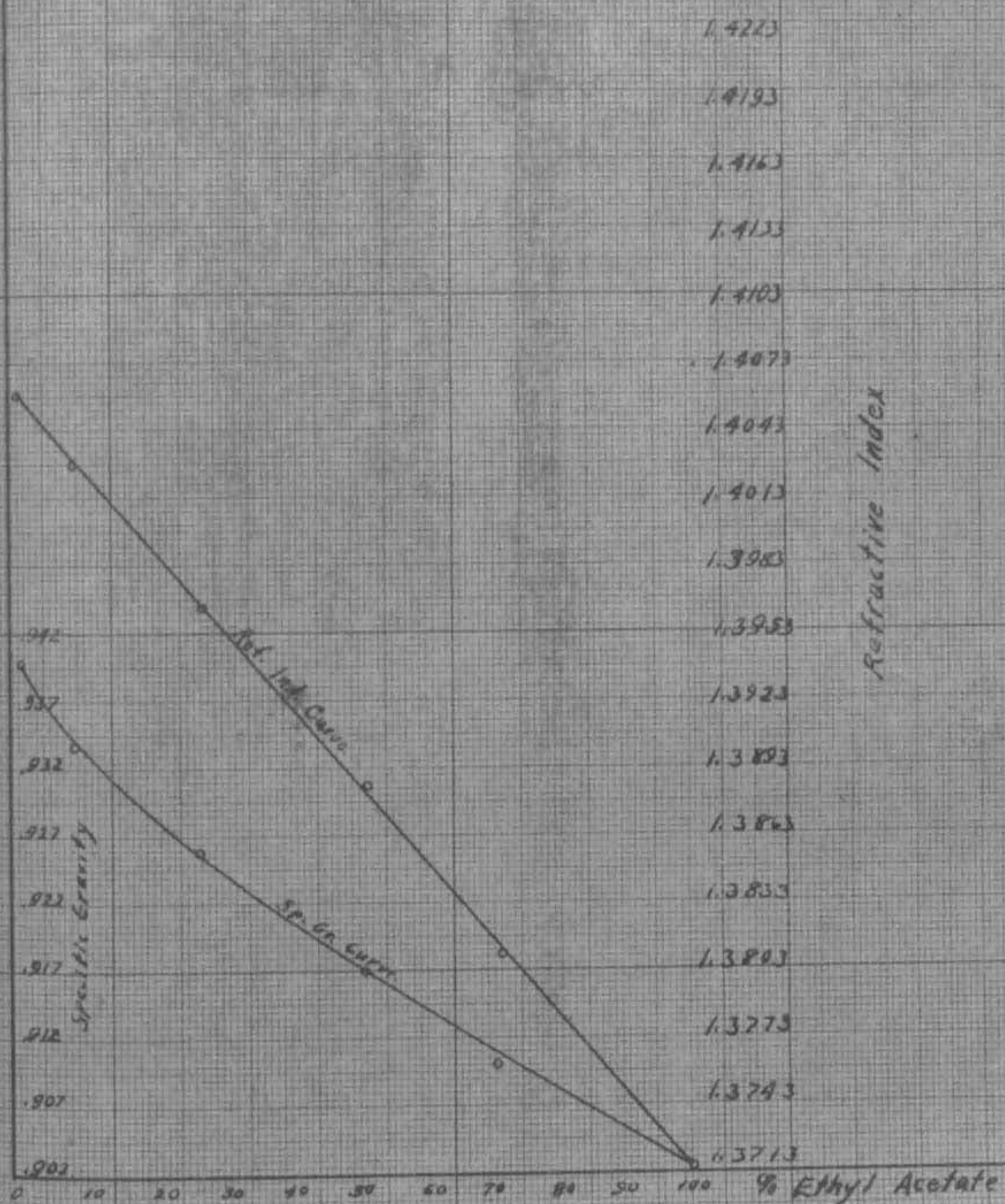


Ethyl Acetate - n Propyl Alcohol
1. Refractive Index - % Composition
2. Specific Gravity - % Composition
Ref. Ind. Curve
Sp. Gr. Curve
Specific Gravity
.908
.898
.888
.878
.868
.858
.848
.838
.828
.818
.808
Refractive Index
1.3843
1.3833
1.3823
1.3813
1.3803
1.3793
1.3783
1.3773
1.3763
1.3753
1.3743
1.3733
1.3723
1.3713
0
10
20
30
40
50
60
70
80
90
100
% Ethyl Acetate

Graph No. 8

Ethyl Acetate - Cellosolve

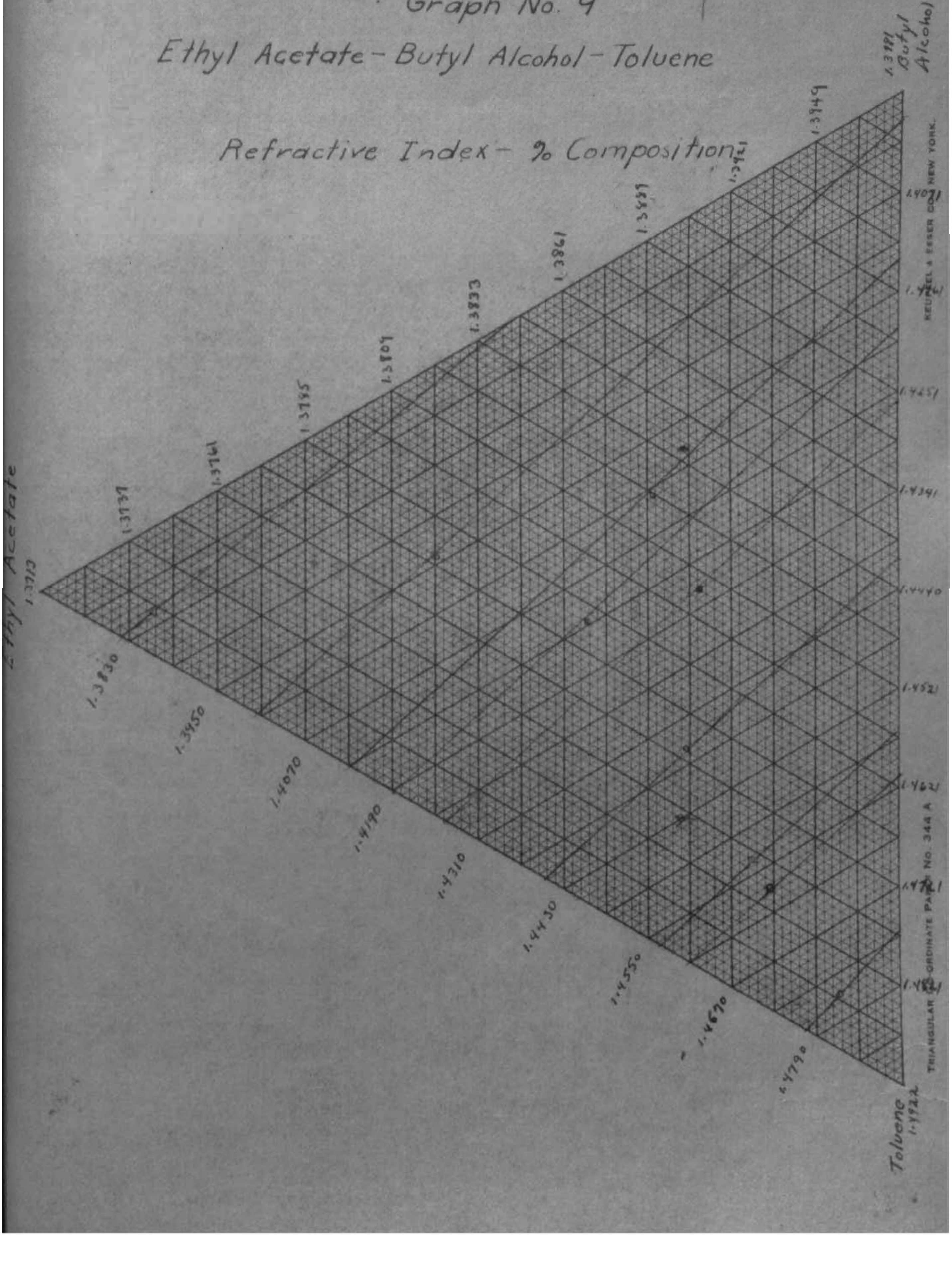
1. Refractive Index - % Composition
2. Specific Gravity - % Composition



Graph No. 9

Ethyl Acetate - Butyl Alcohol - Toluene

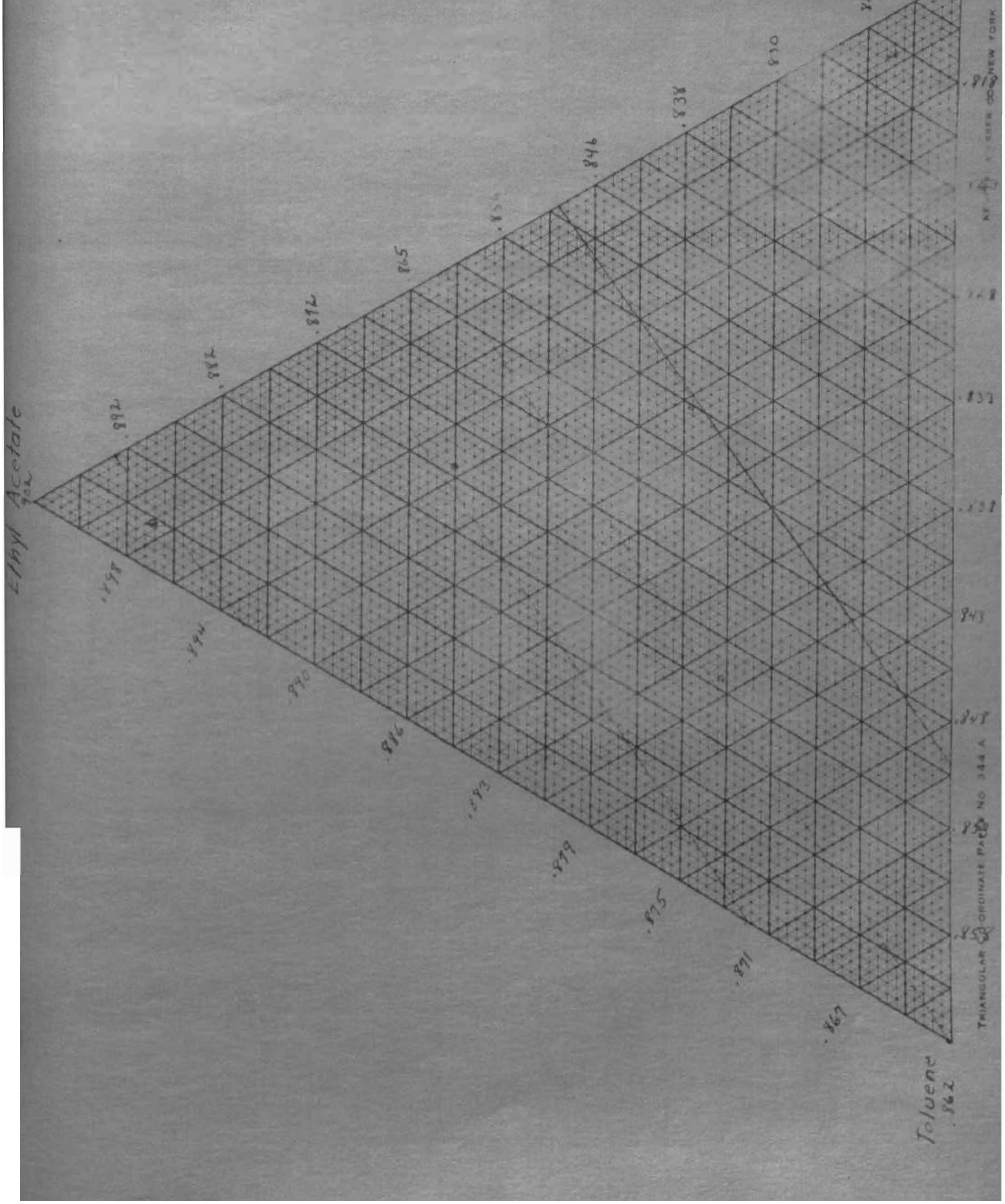
Refractive Index - % Composition



Graph No. 10

Ethyl Acetate - Toluene - Butyl Alcohol

Specific Gravity - % Composition.



Evaporation of binary mixtures:

Tables 12 - 15 give the results obtained by evaporating mixtures of the liquids. The refractive index of the mixtures were recorded before and after the evaporation, and the weight of the samples were taken before and after evaporation. 10 cc. of the mixture was used in all cases and evaporated for 15 minutes.

TABLE 12

Ethyl acetate-butyl acetate

Ref. Index before	after	Diff.	Loss in wt.
1.3903	1.3910	7	.3311
1.3878	1.3883	5	.4685
1.3854	1.3860	6	.5796
1.3827	1.3836	9	.6816
1.3809	1.3818	9	.7550
1.3793	1.3801	8	.7616
1.3780	1.3786	6	.8960
1.3773	1.3778	5	.8960

TABLE 13

Ethyl Acetate-Butyl alcohol mixtures.

(10 cc. evaporated for 15 min.)

Refractive Index Before evap.	Refractive Index After evap.	Diff. in Ref. Ind.	Loss in Wt.
1.3786	1.3773	5	.8548
1.3781	1.3787	6	.8379
1.3822	1.3832	10	.7470
1.3838	1.3850	12	.7077
1.3848	1.3861	13	.6757
1.3873	1.3888	15	.6243
1.3882	1.3889	7	.5782
1.3884	1.3889	5	.5711
1.3885	1.3892	7	.5680
1.3886	1.3889	3	.5656
1.3886	1.3892	6	.5633
1.3886	1.3894	8	.5560
1.3887	1.3900	13	.5666
1.3888	1.3890	2	.5518
1.3889	1.3889	0	.5405
1.3890	1.3896	6	.5352
1.3897	1.3912	15	.5230
1.3904	1.3919	15	.4946
1.3912	1.3926	14	.4564
1.3942	1.3952	10	.3098
1.3963	1.3969	6	.1982
1.3970	1.3975	5	.1658

TABLE 14

Toluene-Butyl alcohol mixtures

(10 cc. of mixture evaporated for 15 min.)

Refractive Index Before evap.	Refractive Index After evap.	Diff. in Ref. Ind.	Loss in Wt.
1.4906	1.4907	1	.3747
1.4893	1.4894	1	.3810
1.4890	1.4892	2	.3863
1.4866	1.4871	5	.3909
1.4851	1.4854	3	.3932
1.4820	1.4823	3	.3898
1.4805	1.4807	2	.3861
1.4770	1.4768	2	.3833
1.4757	1.4755	2	.3786
1.4723	1.4720	3	.3786
1.4696	1.4692	4	.3696
1.4660	1.4655	5	.3690
1.4647	1.4640	7	.3666
1.4619	1.4611	8	.3616
1.4598	1.4589	9	.3641
1.4570	1.4560	10	.3611
1.4549	1.4538	11	.3556
1.4436	1.4426	10	.3168
1.4418	1.4407	11	.3003
1.4407	1.4395	12	.3023
1.4393	1.4380	13	.2982

TABLE 14 (continued)

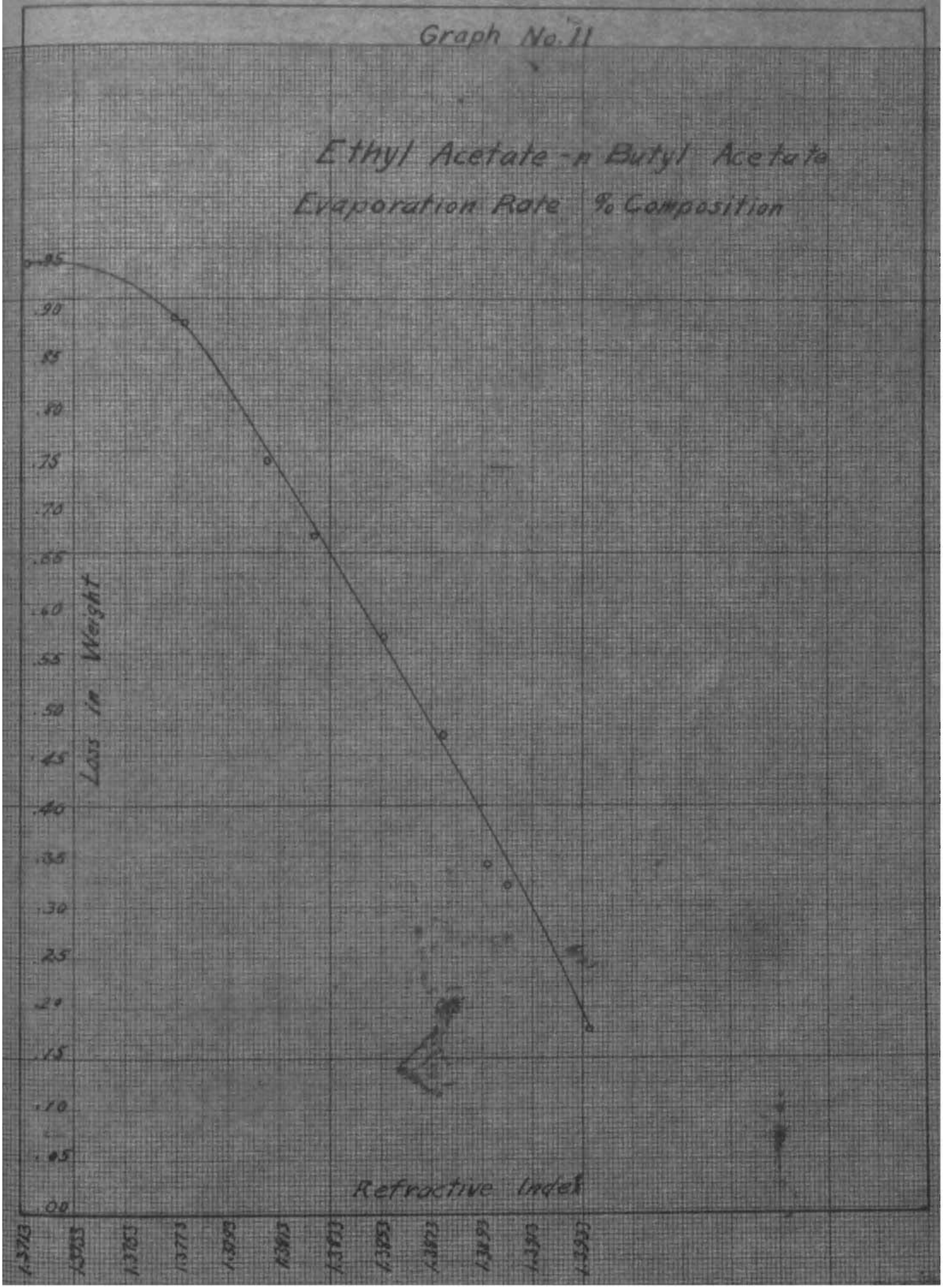
Refractive Index Before evap.	After evap.	Diff. in Ref. Ind.	Loss in Wt.
1.4378	1.4362	16	.2848
1.4307	1.4297	10	.2589
1.4300	1.4290	10	.2518
1.4260	1.4251	9	.2394
1.4237	1.4229	8	.2259
1.4207	1.4200	7	.2125
1.4159	1.4153	6	.1848
1.4108	1.4103	5	.1586
1.4075	1.4071	4	.1415

TABLE 15

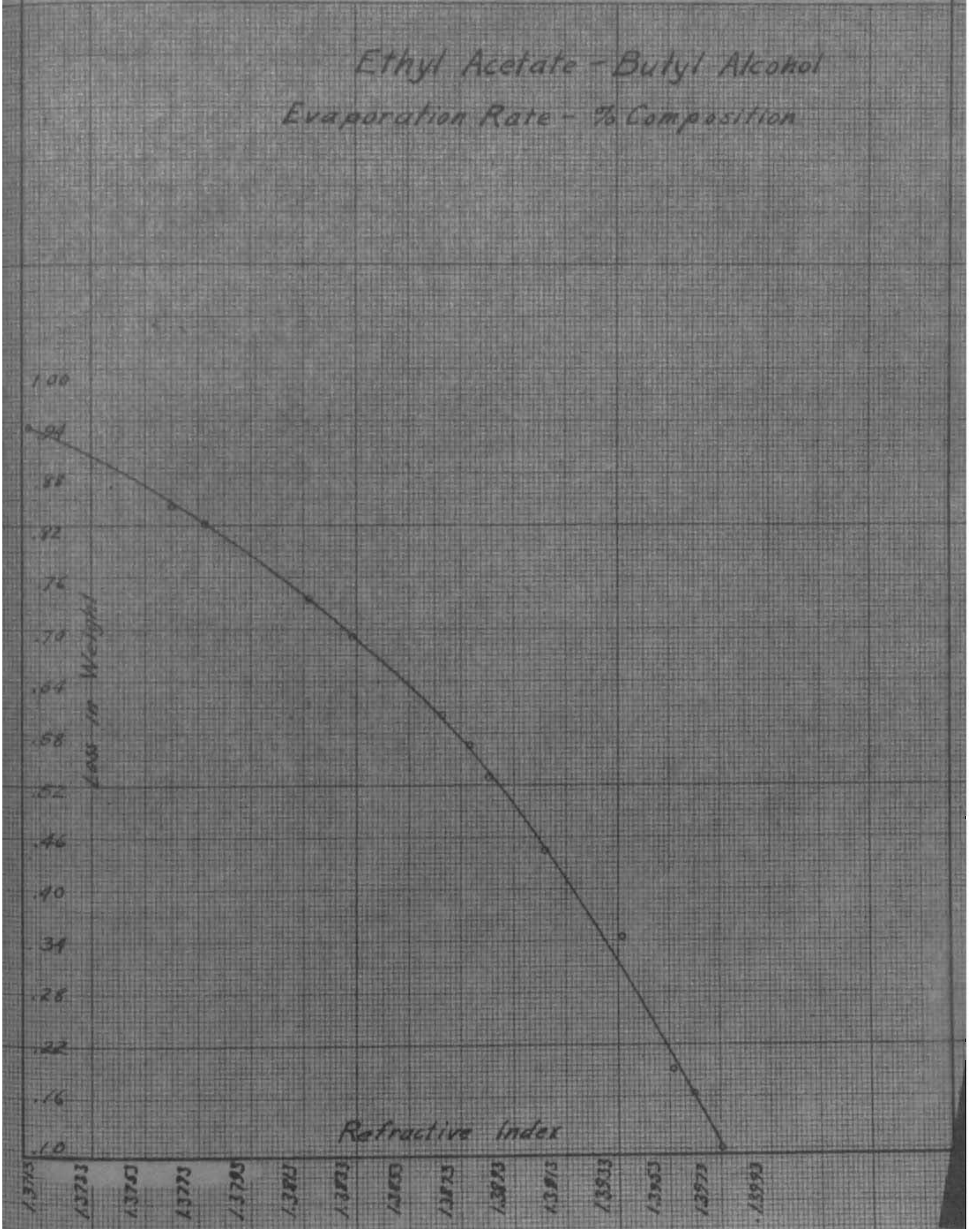
Toluene-Ethyl Acetate mixtures.

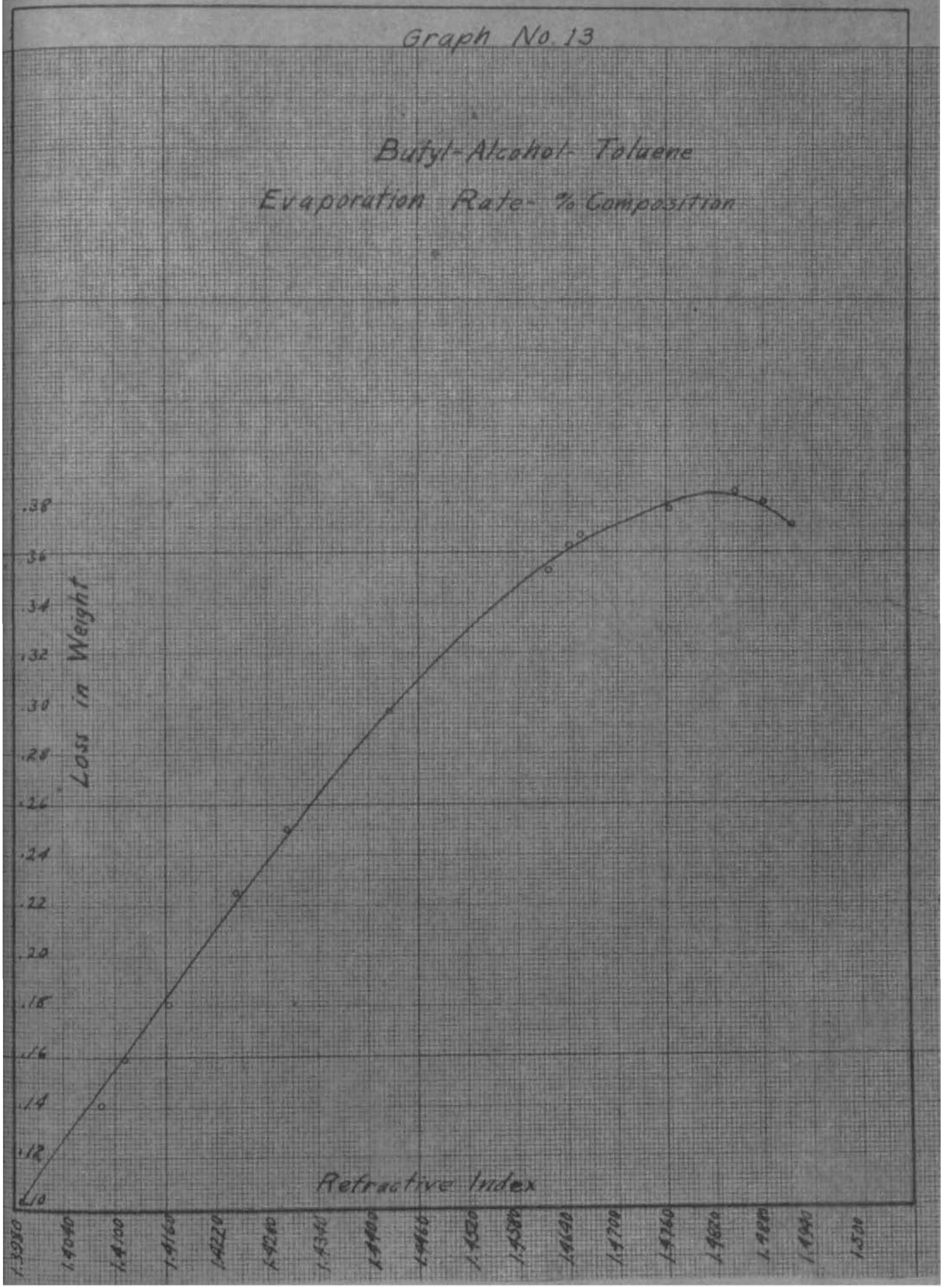
(10 cc. samples for 15 min.)

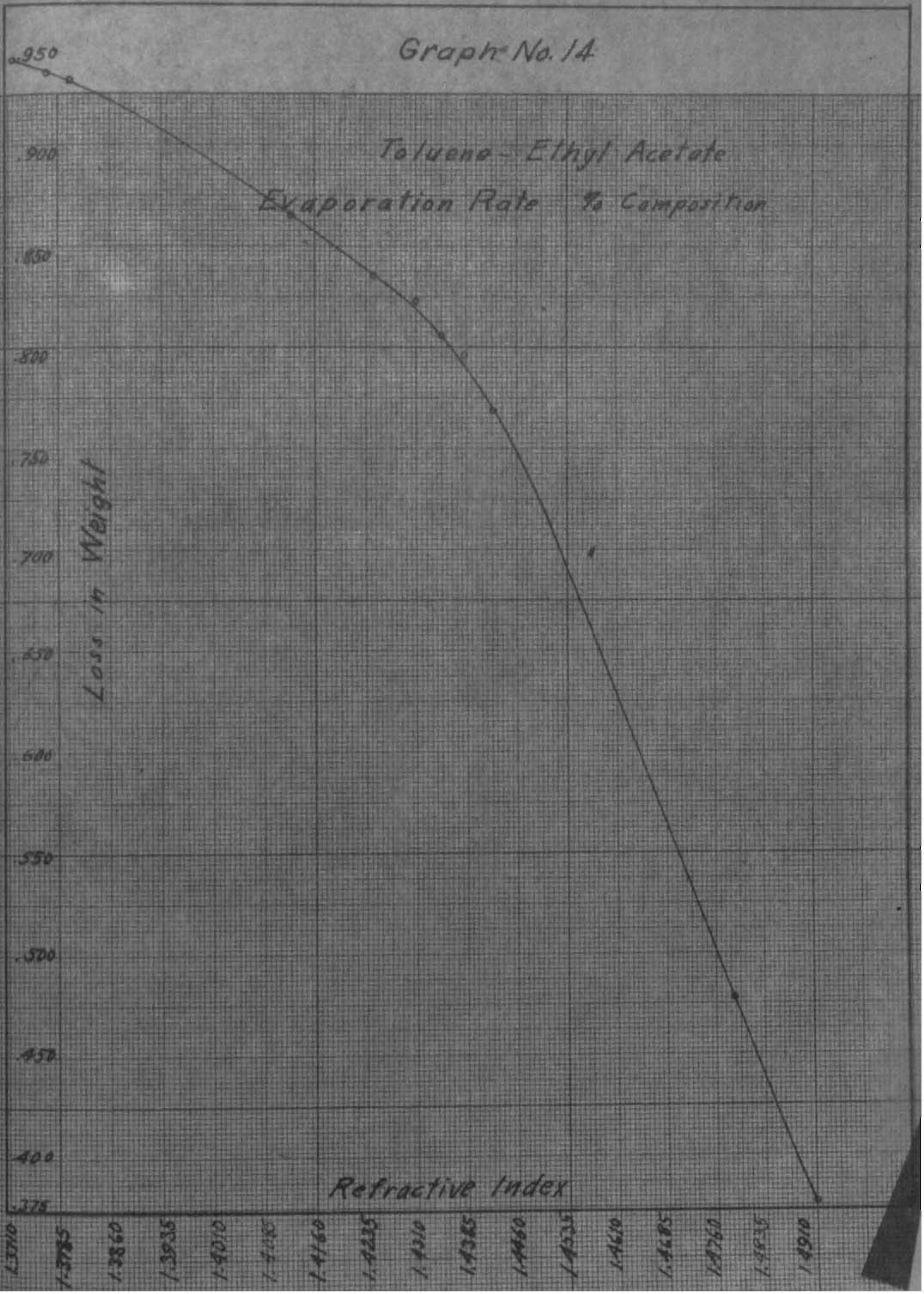
Refractive Index Before evap.	Refractive Index After evap.	Diff. in Ref.Ind.	Loss in Wt.
1.3745	1.3750	5	.9423
1.3795	1.3803	8	.9410
1.3863	1.3873	10	.9433
1.3866	1.3878	12	.9398
1.3957	1.3974	17	.9221
1.4120	1.4143	23	.8712
1.4200	1.4224	24	.8699
1.4248	1.4276	28	.8410
1.4310	1.4340	30	.8319
1.4341	1.4372	31	.8147
1.4356	1.4387	31	.8009
1.4382	1.4413	31	.8072
1.4400	1.4431	31	.7806
1.4431	1.4461	30	.7768
1.4464	1.4494	30	.7666
1.4493	1.4521	28	.7325
1.4793	1.4810	17	.4810


Graph No. 11
Ethyl Acetate - n Butyl Acetate
Evaporation Rate % Composition
Loss in Weight
Refractive Index
.95
.90
.85
.80
.75
.70
.65
.60
.55
.50
.45
.40
.35
.30
.25
.20
.15
.10
.05
.00
1.3713
1.3733
1.3753
1.3773
1.3793
1.3813
1.3833
1.3853
1.3873
1.3893
1.3913
1.3933

Graph No. 12


Ethyl Acetate - Butyl Alcohol
Evaporation Rate - % Composition
Loss in Weight
Refractive Index
1.00
.94
.88
.82
.76
.70
.64
.58
.52
.46
.40
.34
.28
.22
.16
.10


Graph No. 13
Butyl-Alcohol-Toluene
Evaporation Rate- % Composition
Loss in Weight
Refractive Index
.38
.36
.34
.32
.30
.28
.26
.24
.22
.20
.18
.16
.14
.12
.10
1.3980
1.4040
1.4100
1.4160
1.4220
1.4280
1.4340
1.4400
1.4460
1.4520
1.4580
1.4640
1.4700
1.4760
1.4820
1.4880
1.4940
1.500


Graph No. 14
Toluene - Ethyl Acetate
Evaporation Rate % Composition
Loss in Weight
Refractive Index
.950
.900
.850
.800
.750
.700
.650
.600
.550
.500
.450
.400
.375
1.3710
1.3785
1.3860
1.3935
1.4010
1.4160
1.4235
1.4310
1.4385
1.4460
1.4535
1.4610
1.4685
1.4760
1.4910

It was observed that the changes in refractive index of the binary mixture ethyl acetate-butyl alcohol gave a peculiar curve, so this mixture was investigated in another manner. 10 cc. of a mixture of ethyl acetate-butyl alcohol were pippetted into the evaporating bottles and placed on the corks for evaporation. Every 15 minutes, about 5-6 drops were removed from the bottles through the air outlet by means of a capillary tube. The results are shown in Table 16. When the evaporation was stopped, two layers were observed, but on shaking, these layers disappeared and a homogeneous mixture was formed.

TABLE 16

Ethyl acetate-Butyl alcohol

Time	Refractive Index	
Min.	Bottle No.1	Bottle No.2
0	1.3870	1.3834
15	1.3884	1.3843
30	1.3887	1.3858
45	1.3900	1.3880
60	1.3897	1.3860
75	1.3891	1.3850
90	1.3889	1.3860
105	1.3889	

The refractive indices in Table No.16 do not vary in any definite manner. The samples taken from the evaporating bottle seem to have a refractive index different for the upper and lower layers. This means that the two layers have a different composition. To investigate further the formation of these layers during evaporation, several binary and ternary mixtures were evaporated for one hour. The refractive index of the mixture before evaporation was recorded and the refractive index of the upper and lower portions of the liquid after evaporation was recorded and the liquid after evaporation was measured. The data is given in Table No. 17.

TABLE 17

Mixture	Ref.Ind before evap.	Refractive Index lower layer	upper layer
Ethyl acetate-butyl alcohol	1.3870	1.3872	1.3948
Toluene-butyl alcohol	1.4485	1.4435	1.4429
Ethyl acetate-propyl alcohol	1.3807	1.3811	1.3831
Ethyl acetate-cellosolve	1.3974	1.4020	1.4020
Ethyl acetate-toluene	1.4480	1.4607	1.4607
Ethyl acetate-butyl acetate	1.3885	1.3907	1.3907
Toluene-butyl acetate	1.4060	1.4038	1.4038
Benzene s-butyl alcohol	1.4260	1.4240	1.4108
Toluene-propyl alcohol	1.4019	1.3972	1.3972
" "	1.4080	1.4036	1.4036
" "	1.3920	1.3895	1.3895
" "	1.4290	1.4240	1.4240
" "	1.3880	1.3870	1.3870
Benzene-amyl alcohol	1.4200	1.4196	1.4060
Ethyl acetate-amyl alcohol	1.3940	1.3988	1.3948
Toluene-amyl alcohol	1.4227	1.4150	1.4220
Benzene-propyl alcohol	1.4147	1.4062	1.4001
Dibutyl phthalate-Ethyl acetate	1.4617	1.4802	1.4802

TABLE 17 (continued)

Mixture	Ref.Ind. before evap.	Refractive Index lower layer	upper layer
Ethyl Acetate-	1.3992	1.3990	1.3980
butyl alcohol		1.4020	1.3987
benzene	1.4030		
Ethyl Acetate-			
butyl alcohol	1.4085	1.4102	1.4096
toluene			
Ethyl Acetate-			
Amyl alcohol	1.4059	1.4054	1.4024
benzene	1.4092	1.4033	1.4069

DISCUSSION OF RESULTS

The solvents evaporated are given in Table 1 in the order of their spee of evaporation. Acetone is the most volatile liquid. Ethyl acetate and benzene have practically the same rate of evaporation, as do toluene and iso-propyl alcohol. Dibutyl phthalate has a very slow rate. The iso-compounds evaporate faster than the normal-compounds as shown by the data for propyl alcohol, amyl acetate, and butyl alcohol. The rate ofevaporation of the alcohols decreases with an increase of the number of CH_2 groups as illustrated by propyl alcohol, butyl alcohol, and amyl alcohol.

Graphs 1 and 2 show curves for the loss in weight of the liquids evaporated plotted against the number of cc. of liquid placed in the evaporating bottle. The curves are straight lines showing that the amount of liquid evaporated is directly proportional to the distance of the surface from the air inlet. The closer the surface is to the inlet, with the same amount of air, the faster will be the evaporation rate.

In the discussion of the history, several references are given which prove that the vapor pressure of a volatile liquid is lower when it is in the presence of an inert gas or when a stream of an inert gas is passed over the liquid. This was found to be the case in this work, as shown by the comparison of the vapor pressures of the liquids and the calculated values of vapor pressures from the experimental data in Table 18.
The liquids which have a very slow rate of evaporation give almost the same values of the theoretical vapor pressures at 20°C. whereas the more volatile liquids vary quite a bit from the true values. The amount of deviation from the correct value seems to be a function of the vapor pressure, in other words, the air passed over the more volatile liquids is less saturated than the liquids having a low vapor pressure. This effect may be partially caused by a thin air film over the surface of the liquid, and also by some absorption of the air by the liquids, and there may be a slight amount of water in some of the liquids which would cause a deviation in the vapor pressure.

TABLE 18

Solvent	Vap.press.	Calc.V.P.	Ratio
Acetone	184.8	63.6	.34
Ethyl Acetate	72.8	25.3	.34
Toluene	22.78	9.78	.44
n-propyl alcohol	14.5	8.0	.55
n-butyl acetate	9.5	3.8	.40
n-butyl alcohol	4.39	3.27	.74
amyl alcohol	2.8	2.4	.86

The data for the rate of evaporation of the binary mixtures ethyl acetate-butyl acetate, ethyl acetate-butyl alcohol, butyl alcohol-toluene, and ethyl acetate-toluene are plotted against the original refractive indices of the mixtures in graphs 11-14. The curves are smooth, but the one for butyl alcohol-toluene shows a peculiar rise near the pure toluene. Mixtures having a small amount of the butyl alcohol with the toluene have a faster rate of evaporation than pure toluene. This may be due to the presence of a small amount of water in the alcohol or toluene.

The change in refractiveindices of the two mixtures ethyl acetate-butyl alcohol and toluene-butyl alcohol during evaporation is not uniform change which is explained by later evaporation tests that show a formation of layers of these two mixtures. The mixtures ethyl acetate-butyl acetate and toluene-ethyl acetate and do not indicate a formation of a constant evaporating mixture that evaporates without change of composition. These two mixtures show a maximum change in composition.

The data in Table 17 shows a number of binary mixtures that form two layers during evaporation. In those mixtures in which the refractive indices are different for the upper and lower portions, two layers were definitely observed and which disappeared upon shaking to form a homogeneous mixture. The mixtures that formed two layers always contained an alcohol. Toluene-n-propyl alcohol wasthe only mixture containing an alcohol that did not form two layers. The three ternary systems in the table also show a formation of two layers. The lower layers in most cases did not differ in composition much from the original composition. The upper portion decreased in the amount of the more volatile liquid, becoming more concentrated with the least volatile liquid.

Several factors which may cause this formation of layers are:

1. The evaporation of the more volatile solvent from the surface, leaving the solution more concentrated at the surface with the less volatile liquid which does not very rapidly mix with the rest of the solution.

2. Presence of water in the liquids.

3. Absorption of air.

CONCLUSIONS

1. An apparatus is devised which gives evaporation rates that check within one percent.
2. Certain binary and ternary mixtures form two layers during evaporation when air is passed over the surface of the liquid.
3. The refractive index can be used to determine the percent by volume composition of binary mixtures of organic solvents.
4. The refractive index and specific gravity of mixtures of ethyl acetate-butyl alcohol-toluene can be used to determine their percent composition.
5. The binary mixtures toluene-ethyl acetate and ethyl acetate-butyl acetate show a maximum change in composition when there is about 50% of each component in the mixture.
6. The evaporation rate of a liquid varies indirectly with the distance from the air inlet.
7. The evaporation rates of binary mixtures of ethyl acetate-butyl alcohol, are between the evaporation rates of the two components.
8. Mixtures of butyl alcohol-toluene having a low percentage of butyl alcohol evaporate faster than either component.

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