A STUDY OF THE MECHANISM OF LIQUID - LIQUID EXTRACTION FROM FORMING DROPS IN A STAGNANT CONTINUOUS PHASE

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ABSTRACT

A STUDY OF THE MECHANISM OF LIQUID - LIQUID
EXTRACTION FROM FORMING DROPS IN
A STAGNANT CONTINUOUS PHASE

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This thesis is concerned with a study of the mechanism of liquid-liquid extraction from single drops forming in a stagnant continuous phase. Photographic absorption photometry was used to determine the amount of solute transferred at any instant during formation.

The system consisted of the solute picric acid with toluene as the dispersed phase and distilled water as the continuous phase. Water and toluene were mutually saturated. With this system most of the mass transfer resistance was in the continuous phase.

Experimental data were obtained from motion picture films of the drop. The optical density of the film was related to the amount of solute extracted.

Extraction during drop formation was determined by two methods: by optical density measurements directly through the image of the forming drop, and by drawing the drop into the nozzle before break-off and taking optical density measurements through the image of the residual picric acid. The second method was used to check the results of the first.

In a range of drop formation time of 0.2 to 10 seconds, per cent extraction across the interface was 0.1 to 0.2 during drop formation. From 0 to 12 second formation times, mass transfer to the bulk of the continuous phase was essentially zero. Above the 12 second formation time some extracted material moved into the bulk of the continuous phase and remained behind when the drop rose.

Runs at six different formation rates showed that the rate of mass transfer increased with an increase in the formation rate.

The per cent extraction was higher during the early life of a drop.

For a fixed volume, per cent extraction decreased as formation time decreased at long formation times. At shorter times, this phenomenon was reversed.

An attempt was made to determine the effect of rate of mass transfer on liquid-drop coalescence time after rising to the main water-toluene interface. However, in most cases coalescence was practically instantaneous.

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APPROVED: Major Professor

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INTRODUCTION

Liquid-liquid extraction consists of the contacting of two immiscible liquid phases in order to transfer a solute from one phase to the other phase. The contacting devices usually disperse one phase in the form of droplets. Therefore, solute transfer occurs during the periods of drop formation, drop rise or fall, and drop coalescence.

This thesis is concerned with the mechanism of extraction during drop formation. The amount of a colored solute extracted at any time during drop formation was determined by the aid of photographic absorption photometry. To determine the amount of the absorbing substance in the light path, photographic films were used as calibrated responders to a light beam incident upon and transmitted by the absorbing substance, at the wave length range of 3800 to 5500°A.

The absorbing substance was picric acid, which was introduced into the beam of light in two ways and photographed in each case: in an absorption cell with a solution of known concentration; in a column while picric acid was transferred from a toluene drop into a continuous water phase.

One of the advantages of working with the picric acid-toluene-water system was that very small amounts of picric acid in the water phase blocked out more light than large amounts of picric acid in the toluene phase. For example, in a cell of the same thickness, a solution of 0.09 grams of picric acid per liter of water produced the same density on the film as a solution of 100 grams of picric acid per

liter of toluene. Therefore, a small amount of picric acid transferred from a toluene drop into the water adjacent to the drop surface blocked out extra light and produced a higher density on the film than the toluene-picric acid drop would produce by itself.

The density produced on the film was related to the amount of picric acid present in the path of the light beam passing through each solution. Therefore, from a plot of film density versus concentration it was possible to determine the concentration if the density produced on the film due to the solution was known.

This investigation is the continuation of work done by Tambo (22), with modifications in the light source, drop forming device, experimental procedure, and methods of calculation. Tambo obtained movies of the transfer of picric acid from a toluene drop into the stagnant water phase. The films showed that the extracted picric acid surrounded the drop and stayed adjacent to the drop surface, and that more than 0.1% of the total solute in the drop was extracted during coalescence. He attempted to determine the amount of picric acid extracted during drop formation by measurement of optical density around the edges of the drop profile through the image of the extracted material. This method was not successful because the extracted acid appeared as a very thin layer around the drop, and it was difficult to distinguish between the extracted material and the profile of the drop itself. Also, refraction at the extreme edges of the drop profile influenced the readings in this region.

In the present work the amount of extracted picric acid was determined by two methods: by forming a drop, drawing it back into the nozzle

before break-off, and obtaining film densities through the image of the picric acid that was left behind; by obtaining film density measurements directly through the image of the drop and determining the amount of picric acid extracted per unit area of drop surface and thus the total amount surrounding the drop.

LITERATURE SURVEY

Previous Work on Extraction in Drop Systems

Among the early investigators on mass transfer from single drops into a continuous liquid phase are Sherwood, Evans, and Longcor (21) who transferred acetic acid from benzene and methyl isobutyl ketone drops into water. Using different column heights, they plotted the amount of unextracted solute versus column height. Intersection of this line with the coordinate at zero column height showed a 40 to 45 per cent extraction during drop formation; comparison between experimental and theoretical amounts transferred indicated that drops had internal circulation. Later, West and co-workers (24) attempted to duplicate Sherwood's work on the acetic acid-benzene-water system, and obtained approximately 14 to 20 per cent extraction. The discrepancy between the results of these investigations was attributed to contamination of the acetic acid-benzene solution by the Tygon tubing feed line (25).

Licht and Conway (14) studied solute transfer in spray towers in which acetic acid was transferred from water drops into methyl isobutyl ketone. By using different column heights and extrapolating to zero height they found eight per cent extraction during drop formation, and postulated that the difference between their result and Sherwood's result might have been due to the direction of solute transfer.

During the work of the investigators (14, 21, 24, 25) on aqueous extraction of acetic acid from benzene or isobutyl ketone system, the

results obtained during drop formation varied from 8 to 45 per cent solute extracted. The variation in these results motivated Licht and Pansing (15) to make a study of solute transfer from single drops by studying each stage separately. They showed that, in general, straight line extrapolation of the fraction of solute not extracted versus column height was not valid down to zero height. Licht and Pansing also derived an expression relating fraction extracted, formation time, and molecular diffusivity in the continuous phase. They assumed a negligible transfer resistance inside the drop, transport by molecular diffusion outside the drop, and a plane area for transfer equivalent to the area of a sphere.

$$E_2 = 2.9 \frac{\sqrt{D_c t}}{H d} \qquad (1)$$

where,

E_2 = fraction solute extracted

D_c = molecular diffusivity in the continuous phase

t = formation time

H = distribution coefficient $\left(\frac{C_d}{C_c}\right)$

d = drop diameter

C_d = solute concentration in the dispersed phase

C_c = solute concentration in the continuous phase

Garner and Hale (4) derived the following formula for the over-all mass transfer coefficient during drop formation.

$$M = K \int_0^{t_f} A \, \Delta C \, dt \qquad (2)$$

where,

M = total material transferred during the growth of the drop

K = over-all mass transfer coefficient (a constant)

A = surface area of the drop at time t

t_f = formation time

ΔC = concentration driving force

For a feed rate of V cm^3/sec, the area at time t is given by,

$$A = 4\pi \left(\frac{3V}{4\pi}\right)^{\frac{2}{3}} t^{\frac{2}{3}} \qquad (3)$$

Substituting Equation 3 into Equation 2,

$$M = 0.6\, K A_f t_f \Delta C \qquad (4)$$

In order to determine coefficients for the formation and the rise periods, a total time of $(t_r + 0.6t_f)$ was used in Equation 4 where t_r is the time of rise through the water phase.

Coulson and Skinner (3), in their study of the mechanism of liquid-liquid extraction across stationary and moving interfaces, determined the amount of mass transfer during drop formation and rise. They transferred benzoic acid and propionic acid from water to benzene drops and measured the solute transferred when a drop was formed and then ejected from the system. Figure 1 is a sketch of the device that was used in these experiments.

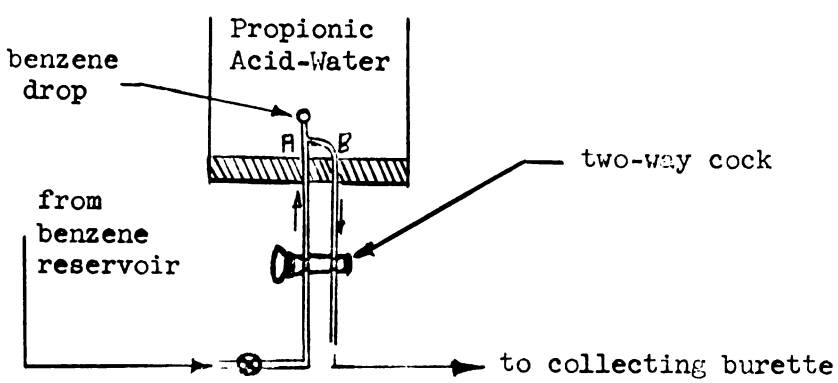


Figure 1

When the two-way cock was opened, benzene flowed from a small reservoir through a needle valve to form a drop at the end of the glass nozzle (A). A side tube (B) was sealed just below the tip of the nozzle and led to a collecting burette. Upon closing the two-way cock, the flow of benzene to the nozzle was stopped and the hydrostatic head in the column pushed the drop through the side tube. After a number of drops were formed, ejected, and collected, the sample was analyzed. It was found that: mass transfer during formation was almost independent of the formation time for a range of 1/2 to 1 second; the over-all transfer coefficient, K, based on the average area exposed during drop formation decreased with an increase in time of formation, but was independent of the drop size; smaller drops approached more closely to equilibrium because of the increased area of interface per unit volume.

Gregory (11) used an apparatus similar to that of Coulson and Skinner, but modified the design and experimental procedure. Systems were selected in which the distribution coefficient strongly favored the continuous phase so that resistance to mass transfer in the dispersed phase could be measured. Transfer was from the dispersed phase to the continuous phase. Data from the smallest drops showed that per cent extraction decreased as formation time decreased until a formation time was reached at which per cent extraction began to increase in spite of the shorter time. This was explained by the spread of turbulence from the jet of incoming fresh liquid.

The following are several different mechanisms of mass transfer during drop formation which were discussed and compared to the experimental data by Gregory:

1. Turbulence throughout the whole drop may be so great that the bulk concentration of dispersed phase is the same as the interface concentration, and there is no dispersed phase resistance.

2. Mass transfer may take place by molecular or eddy diffusion throughout the entire forming drop with the fresh liquid entering at the center and pushing the older portions of the liquid uniformly and without mixing toward the surface.

3. Mass transfer may take place by diffusion throughout the entire forming drop with the entering liquid distributing itself uniformly so that none of the older liquid is displaced from its position relative to the surface.

4. Circulation within the drop may cause constant renewal of the elements of liquid next to the surface. Mass transfer is by diffusion within these surface elements, which, in turn, mix with the bulk.

5. The film theory mechanism depends on the presence of a resistance which consists of a laminar film next to the interface and an inner turbulent film. The film must be thin enough so that any change in the quantity of solute present in the film is negligible compared to the change undergone by the bulk.

When the drop phase was lighter than the continuous phase the data was best correlated by the following equation, obtained from film theory.

$$\frac{K_d}{V} = 3.74 \left(\frac{dV\rho}{\mu}\right)^{-0.2} \left(\frac{\mu}{\rho D}\right)^{-1} \qquad (5)$$

where,

$V = \frac{\pi d^3}{6 A_n t}$ = jet velocity at the orifice of the nozzle, cm/sec

d = drop diameter, cm

D = molecular diffusivity in the dispersed phase, cm^2/sec

K_d = mass transfer coefficient in the dispersed phase, cm/sec

A_n = cross sectional area of nozzle, cm^2

t_f = time of formation of the drop, sec

ρ = density in dispersed phase, gm/cm^3

μ = viscosity in dispersed phase, gm/cm-sec

This equation was valid only when the following condition was fulfilled:

$$K_d > 1.52 \sqrt{\frac{D}{t_f}} \qquad (6)$$

When relation 6 was not satisfied, mass transfer by Mechanism 2 best described the experimental result.

Other attempts to study the mechanism of extraction from single drops have been made by Christenson and Terjesen (2), Garner and Skelland (5, 6, 7, 8), Treybal (23), and Johnson and Hamielec (13).

Investigations on liquid drop coalescence have been made by Gillespie and Rideal (10), Nielson et al (17), Linton and Sutherland (16), and Charles and Mason (1).

THEORY

I. Extraction in the Picric Acid-Toluene-Water System

The picric acid-toluene-water system was chosen because the extracted material could be determined photographically and, unlike most dyes, picric acid was not colloidal in water or toluene solutions (25).

Distribution coefficient data plotted in Figure 2 show that picric acid strongly favors the toluene phase at high concentrations. Therefore it was expected that the resistance to mass transfer in the toluene phase would be negligible compared to the resistance in the water phase.

The fact that picric acid has a more intense color in water than in toluene indicates that it exists in a different molecular form in each phase (20). Transition from one form to the other at the interface may result in an interfacial resistance to mass transfer. However this resistance was considered to be negligible.

In the stagnant continuous water phase, mass transfer probably occurs primarily by molecular diffusion. Therefore the expression developed by Licht and Pansing (15) should be applicable to the system studied. From Equation 1 the per cent extraction was given by

$$\% \text{ extraction} = 2.34 \frac{\sqrt{D_c t}}{H V^{\frac{1}{3}}} \qquad (7)$$

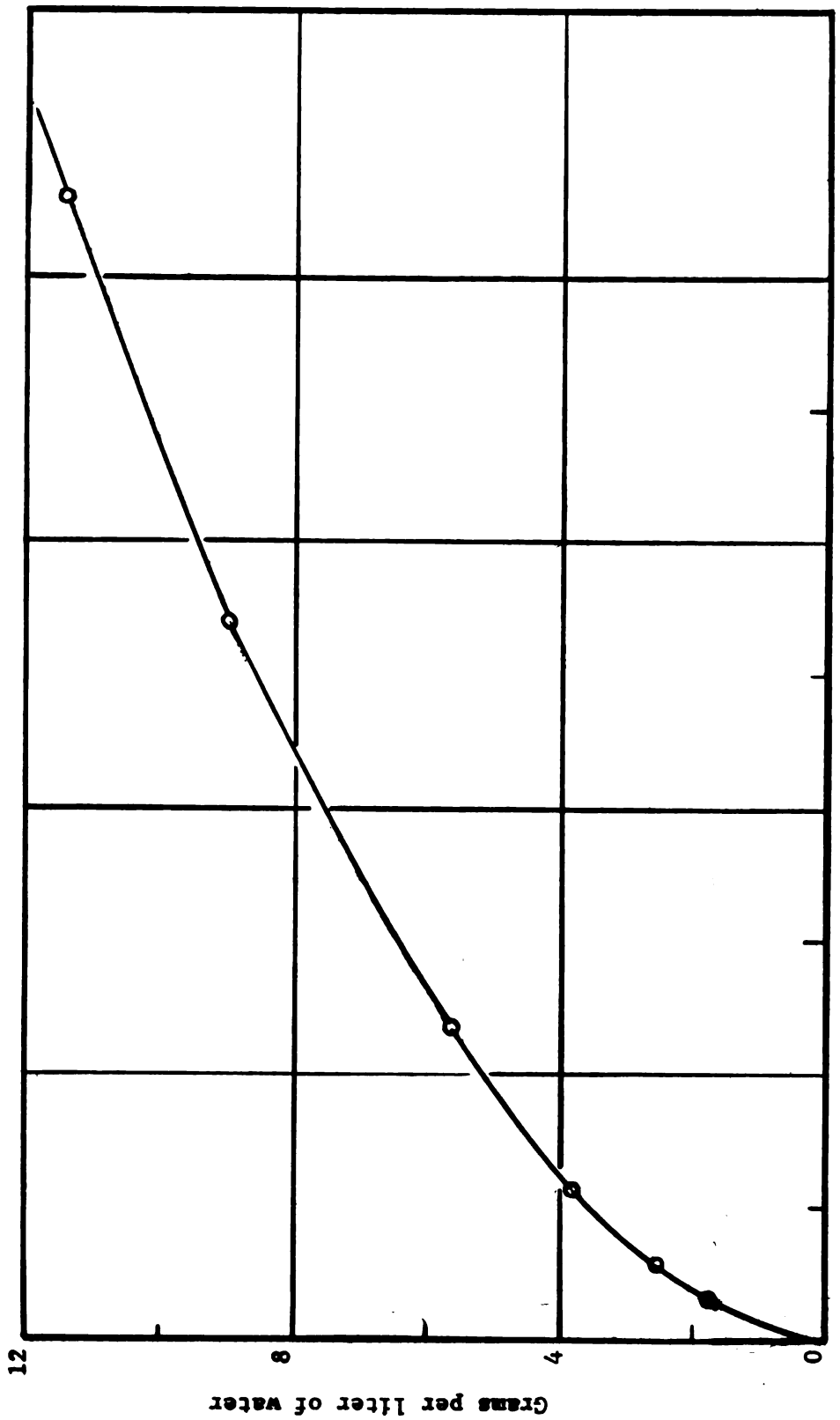


Figure 2 - Plot of distribution data of picric acid at 25° between water and toluene, Seidell (20).

where

D_c = molecular diffusivity in the continuous phase, 6.9×10^{-6} cm^2/sec

t = formation time, seconds

H = distribution coefficient, 10

V = drop volume, cm^3

Substituting the values of D_c and H into Equation 7,

$$\% \text{ extraction} = 6.12 \times 10^{-2} \frac{\sqrt{t}}{V^{\frac{1}{3}}} \tag{8}$$

Equation 8 was compared to the results of this investigation.

II. Photographic Absorption Photometry

Photographic absorption photometry involves photography of a beam of light after its attenuation by an absorbing medium. Application of this technique requires a suitable light source, an absorption cell for introducing the specimen into the beam of light, and photographic films.

In this study the absorbing substance was picric acid in water and toluene solutions. The optical density of a photographic film of these solutions depended upon the amount of picric acid in the path of the light beam and on which of the two solvents was used. When the optical density of a film of a solution of known concentration was equal to the density of a film of unknown concentration, the following equation was used to relate the solution concentrations.

$$K C_s L = \int_0^L K C \, dl \tag{9}$$

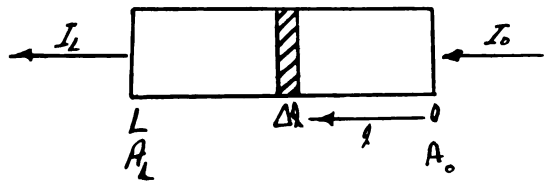
where,

K = extinction coefficient, a constant dependent upon the phase

C_s = known concentration in a standard cell of thickness L

C = unknown concentration in a cell of thickness L. The concentration may be a function of the solution depth.

In the following derivation of Equation 9 a light energy balance was made about a volume increment of thickness $\Delta\ell$ in the path of a light beam that passed through a cell. The cross sectional area of a light beam that fell on a fixed film area varied with the cell thickness. In the following sketch, I equals light intensity, A equals cross sectional area, and ℓ equals distance along the cell depth.



Energy balance:

(Energy in) - (Energy out) = Energy absorbed in volume A $\Delta\ell$.

Since intensity equals light energy per unit area,

$(IA)_\ell$ = input at position ℓ

$(IA)_{\ell + \Delta\ell}$ = output at position $\ell + \Delta\ell$

According to Beer's and Lambert's Laws of absorption, the light absorbed at a particular light wave length is proportional to the amount of picric acid in volume A $\Delta\ell$ and the light intensity.

$$K\ I\ (C\ A\ \Delta\ell\ ) = \text{Energy absorbed}$$

where

K equals the proportionality constant.

Combining these terms,

$$(IA)_{\ell} - (IA)_{\ell+\Delta\ell} = K\,C\,I\,A\,\Delta\ell \tag{10}$$

Dividing by $\Delta\ell$ and taking the limit as $\Delta\ell \longrightarrow 0$,

$$-\frac{d(IA)}{IA} = K\,C\,d\ell \tag{11}$$

Integrating from zero to L gives

$$I_L = \frac{I_0 A_0}{A_L}\; e^{-\int_0^L KC\,d\ell} \tag{12}$$

For a standard cell of concentration C_s,

$$I_{LS} = \frac{I_0 A_0}{A_L}\; e^{-KC_s(L-0)} \tag{13}$$

For a solution of unknown concentration

$$I_L = \frac{I_0 A_0}{A_L}\; e^{-\int_0^L KC\,d\ell} \tag{14}$$

Equations 13 and 14 are equal when the optical densities on the film produced by I_L and I_{LS} are equal.

Therefore

$$K C_s L = \int_0^L KC\,d\ell \tag{9}$$

If the solution of unknown concentration consists of only one phase which is the same as the standard cell phase,

$$C_s = C_{Average} = \frac{\int_0^L C\,d\ell}{L} \tag{9a}$$

Applying Equation 9 to water and toluene phases in series,

$$K_w C_{sw} L = K_w \int_0^{L_1} C_w dl + K_t \int_{L_1}^{L} C_t dl \qquad (15)$$

where w refers to the water phase of thickness L_1 and t to the toluene phase of thickness $(L - L_1)$.

In the extraction of picric acid from toluene drops, the concentration in the drop was approximately constant and equal to the initial concentration. Thickness $(L-L_1)$ equaled the drop diameter at the position of optical density measurement. In this case Equation 15 was solved for $\int_0^{L_1} C_w dl$ by the following procedure. From Equation 9,

$$\int_{L_1}^{L} C_t dl = C_t (L - L_1) = C'_{st} L \qquad (16)$$

where,

C'_{st} = concentration of a standard toluene cell that will block out as much light as the toluene drop.

By applying Equation 9 to standard solutions of toluene and water,

$$K_t C'_{st} L = K_w C'_{sw} L \qquad (17)$$

where,

C'_{sw} = concentration of a standard water solution that will block out as much light as the standard toluene solution of concentration C'_{st}.

Combining Equations 15, 16, and 17 and solving,

$$C_{w\ ave} = \frac{1}{L_1} \int_0^{L_1} C_w dl = \frac{1}{L_1} (C_{sw} - C'_{sw}) L \ , \qquad (18)$$

where,

$C_{w\ ave}$ = average concentration in the water phase of thickness L_1 (this includes the water phase in front and in back of the toluene drop).

The derivation of Equations 9 and 18 depended upon Beer's and Lambert's Laws of light absorption. These laws apply to solutions of picric acid in water and toluene over a narrow wave length range. This is illustrated by the straight line plots of solution optical density versus concentration at fixed wave lengths in Figures 3 and 4. A plot of the water concentration from Figure 3 versus toluene concentration of the same solution optical density from Figure 4 will result in a straight line as predicted by Equation 17.

In the extraction experiments the light filter did not sufficiently restrict the wave length range so that Beer's and Lambert's Laws were not strictly applicable. This was illustrated by the plot of water concentration versus toluene concentration at the same film optical density, Figure 5. Since solutions of equal film densities have equal solution optical densities, a straight line should have resulted. However, the error introduced by use of Equations 9 and 18 was not greater than the experimental error in the film optical density measurements. This fact was determined experimentally by obtaining film optical density measurements from a cell of three compartments of thickness L_1, L_2, and L_3 with known concentrations C_1, C_2, and C_3, and determining the numerical value of C_{ave} of Equation 9 or 18 directly from the optical density - concentration curve which is for standard solutions in a cell of thickness $L = L_1 + L_2 + L_3$. Using the numerical value of C_{ave} in Equation 9

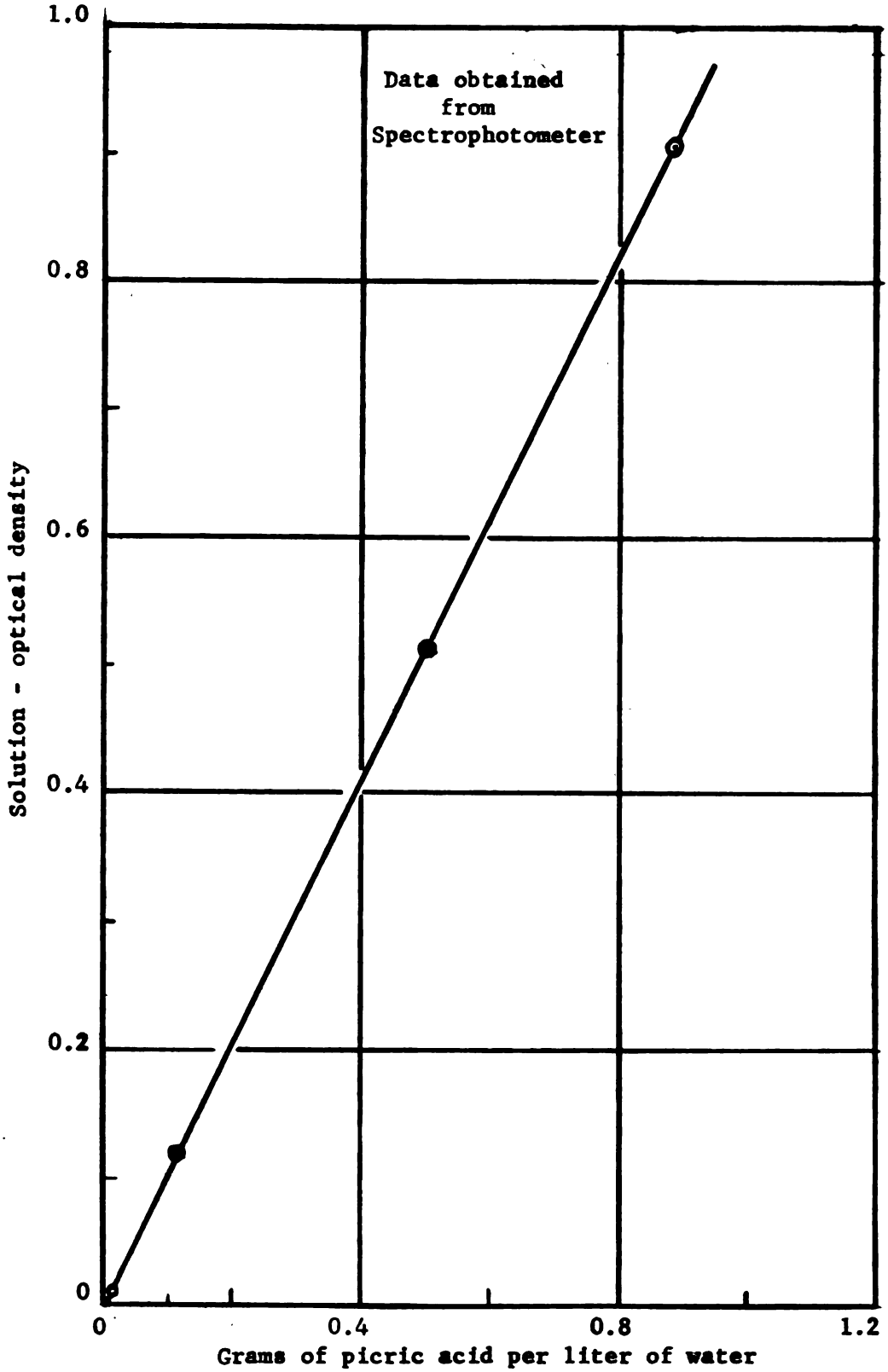


Figure 3 - Graph of solution - optical density versus concentration at 4800°A for a one centimeter cell.

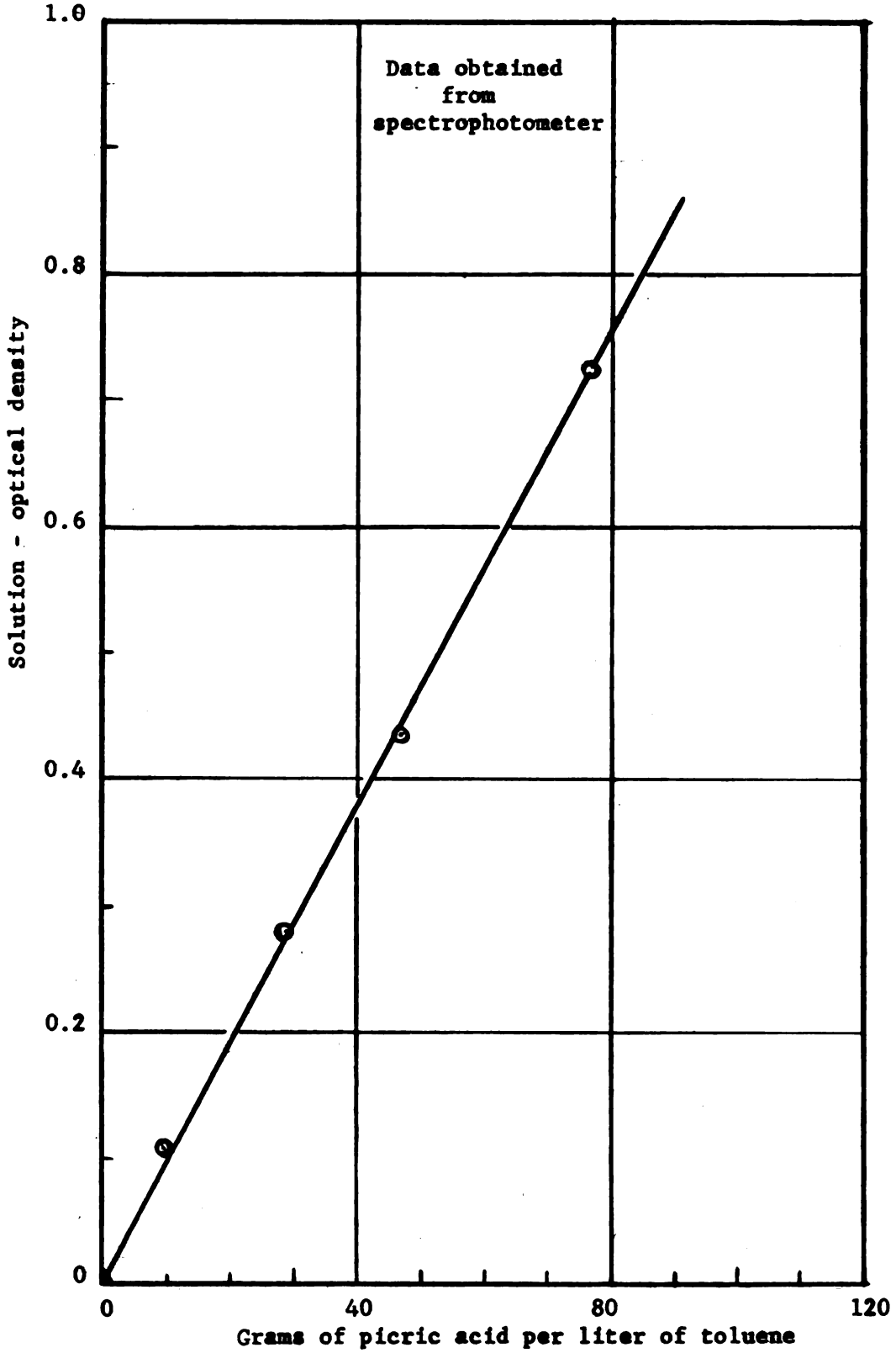


Figure 4 - Graph of solution-optical density versus concentration at 4500°A for a one cm cell.

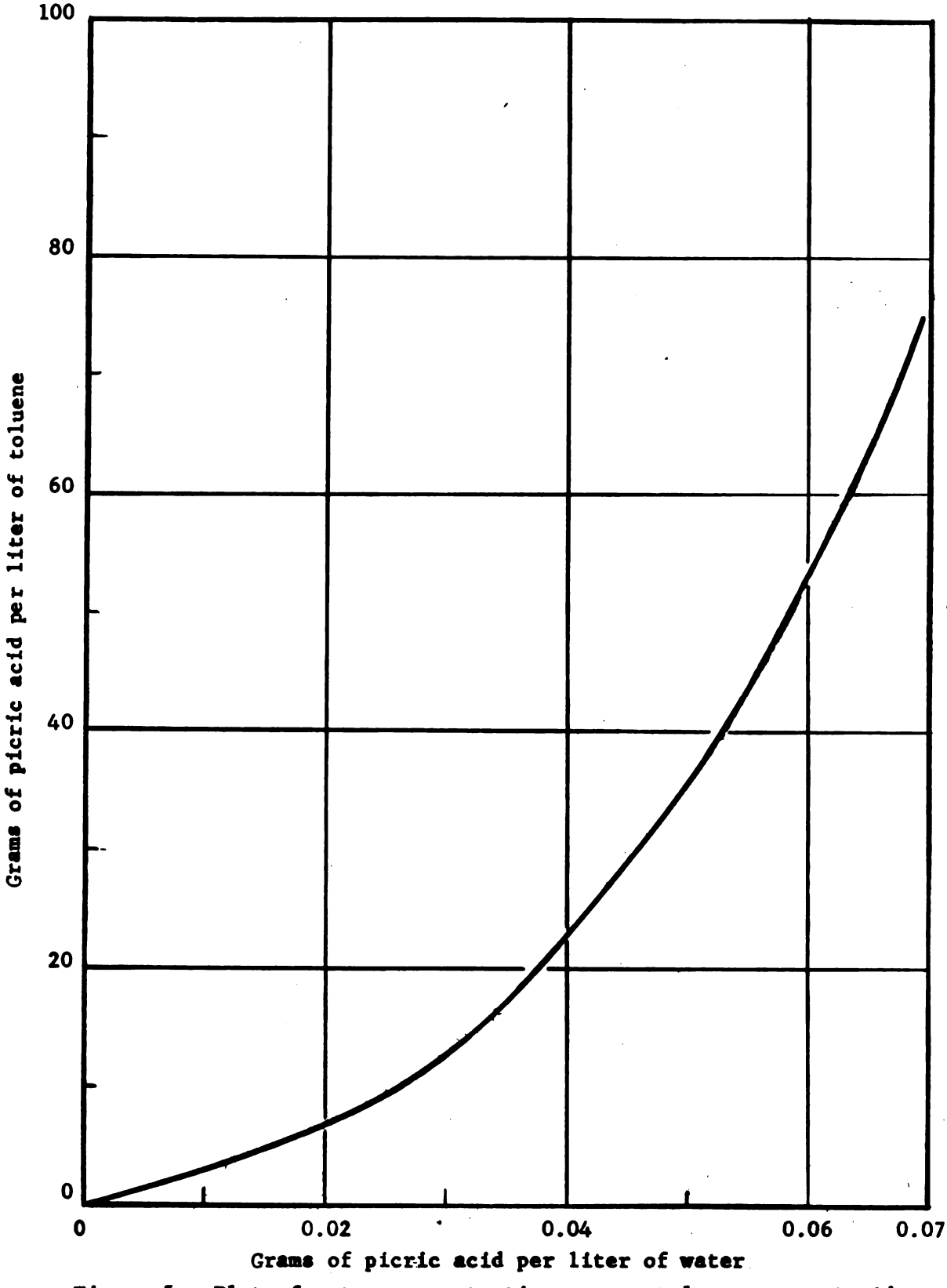


Figure 5 - Plot of water concentration versus toluene concentration at the same film density.

the concentration of the solution in the first compartment was determined and compared to the actual value in that compartment. For the case where both water and toluene phases were present the concentration C_{sw} corresponding to the measured optical density was substituted in Equation 18 and solved for C_{wAve}. The value of C_{wAve} was compared to the actual value of the concentration in the first compartment. The results of a number of experiments are presented in Table I and sample calculations are given in Appendix A. The calculated and actual concentrations agree within experimental error.

TABLE I - Comparison of the Actual and Calculated Concentrations of Solutions in a Standard Cell of Three Compartments

Run	Concentration in Grams of Acid/Liter* C_1	C_2	C_3	Measured Optical Density	Calculated Conc. in grams of Acid/Liter*
28	0.0145w	0.0000w	0.0145w	0.150	C_1 = 0.0141w
5	0.0242w	0.0000w	0.0242w	0.301	C_1 = 0.0235w
30	0.0340w	0.0000w	0.0340w	0.602	C_1 = 0.0356w
76	0.0000w	109t	0.0000w	1.076	C_2 = 112t
77	0.0000t	109t	0.0000t	1.076	C_2 = 112t
78	0.0235w	109t	0.0235w	1.347	C_1 = 0.0184w
79	0.0325w	109t	0.0325w	1.620	C_1 = 0.0324w
80	0.1762w	33t	0.1762w	2.699	----------

In Runs 28, 5, and 30, L_1 = 0.4985", L_2 = 0.1800", L_3 = 0.4985", and calculated concentrations were from Figure 16.

In Runs 76, 77, 78, 79, 80, L_1 = 0.3670", L_2 = 0.4430", L_3 = 0.3670", and calculated concentrations from Figures 18 and 19.

*w designates the water phase
t designates the toluene phase

METHODS OF DETERMINING THE AMOUNT OF EXTRACTION DURING DROP FORMATION

I. Method of Calculation of the Amount of Extracted Picric Acid from Density Measurements Directly Through the Image of the Drop

The extracted picric acid was determined from density measurements through the image of the drop. As an illustration consider the drop in Figure 6. The shaded area around the drop represents the extracted acid which surrounded the entire surface of the drop as a thin film. Symmetry was assumed about the vertical axis of the drop. Since the amount of extracted acid was always less than 0.3 per cent, the concentration in the drop was approximately constant and uniform throughout the drop. Therefore, Equations 15 through 18 can be used to determine the average water phase concentration in front and in back of the drop.

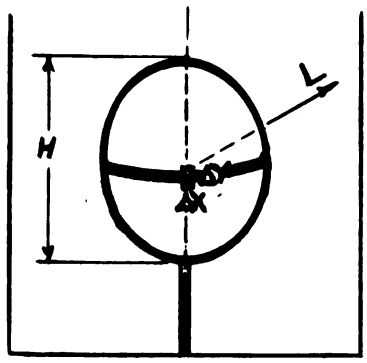


Figure 6

$$C'_{w\ ave} = \frac{\int_0^{L_1} C_w\, dl}{L_1} = \frac{(C_{sw} - C'_{sw})\,L}{L_1} \qquad (18)$$

where

C_{sw} = concentration corresponding to each density measurement along the vertical axis of the drop (C_{sw} was determined from the density measurement and the density-concentration calibration curve for the water phase).

C'_{sw} = concentration of a water cell of thickness L (the column thickness) which blocks out as much light as the toluene drop of

concentration C_t and thickness equal to the drop diameter at the position of density measurement. In order to determine C'_{sw}, the value of C'_{st} was first determined from Equation 16,

$$C'_{st} = \frac{(L-L_1)C_t}{L}$$

where $L-L_1$ equals the drop diameter. Using the film density equivalent to C'_{st} from the density--toluene concentration curve, and applying it to the density-water concentration curve, the value of C'_{sw} was obtained.

$C'_{w\ ave}$ = the average concentration in the water phase at the position of density measurement. It includes extracted acid both in front and in back of the drop (L_1 = L-drop diameter).

The area of film density measurement was equivalent to an area $\Delta X\ \Delta Y$ in the extractor as shown in Figure 6. Therefore the acid in the volume element $L_1\ \Delta X\ \Delta Y$ was $C'_{w\ ave}\ L_1\ \Delta X\ \Delta Y$. Since the extracted acid was present in a thin layer around the drop, the total amount of acid around the drop in height ΔY was,

$$\int_0^{\pi D} \frac{C'_{w\,Ave}}{2}\, L_1\, \Delta Y\, dx = \frac{1}{2} C'_{w\,Ave}\, L_1\, \pi D\, \Delta Y\ .$$

The group ($\frac{C'_{w\ ave}}{2}$ $L_1 \Delta Y\ \Delta X$) equals the amount of extracted acid either in front or in back of the drop over area $\Delta X\ \Delta Y$, and D is the drop diameter at each point of density measurement. The amount of acid over the entire drop was given by

$$A = \int_0^H \frac{1}{2} C'_{w\,Ave}\, L_1\, \pi D\, dy \quad , \tag{19}$$

where H is the height along the vertical axis and $C'_{w\ ave}$ is given by Equation 18.

Since light refraction or reflection due to the shape of the drop would influence the film density measurements, this effect was

investigated experimentally. Film density measurements of drops in equilibrium with the continuous phase were obtained. The measured densities agreed with values calculated from Equation 9. The results are presented in Table II and sample calculations are given in Appendix A.

During the experiments conducted on the effect of light refraction, the effects of camera focusing and distance of the camera from the column were also studied. The camera was focused at the center of a stationary drop. Photographs were obtained by moving the camera without refocusing. Film density measurements through the center of the drop showed that the density did not vary with camera position. Thus any error in density readings caused by inaccurate camera focusing were negligible.

II. Method of Calculation of the Amount of Picric Acid Left Behind in Water Phase When Drop was Withdrawn into the Nozzle

When the drop was withdrawn into the nozzle, the extracted acid was left behind in the water phase. The image of the extracted acid on the negative or on a photographic plate appeared as an irregular geometric shape as shown in Photograph 11 and sketched in Figure 7. The total amount of acid in the image was calculated from optical density measurements over areas $\Delta X\ \Delta Y$ which accounted for the acid in volume $L\ \Delta X\ \Delta Y$. Therefore,

$$A = \iint L\ C_{ave}\ dx\ dy, \tag{20}$$

where

A = total amount of extracted acid

L = column thickness or depth in the L direction in Figure 2.

TABLE II - Optical Density Measurements Through the Image of the Drops at Equilibrium with the Continuous Phase

	DROP 42+			DROP 43+			DROP 44+		
	Diameter	Optical Density		Diameter	Optical Density		Diameter	Optical Density	
H*,mm	D,mm	Measured	Calculated	D,mm	Measured	Calculated	D,mm	Measured	Calculated
0.1	0.55	-----	-----	0.40	0.468	0.436	0.40	0.710	0.745
0.3	0.90	-----	-----	0.70	0.456	0.425	0.85	0.699	0.728
0.5	1.15	-----	-----	1.00	0.432	0.412	1.20	0.674	0.710
0.7	1.57	0.208	0.195	1.40	0.421	0.398	1.60	0.658	0.688
0.9	2.00	0.214	0.192	1.80	0.404	0.382	1.90	0.653	0.674
1.1	2.25	0.225	0.189	2.10	0.404	0.377	2.15	0.620	0.658
1.3	2.60	0.225	0.187	2.30	0.398	0.377	2.40	0.602	0.647
1.5	2.80	0.200	0.184	2.55	0.398	0.367	2.60	0.602	0.638
1.7	3.00	0.194	0.184	2.77	0.382	0.361	2.80	0.599	0.624
1.9	3.15	0.194	0.181	2.90	0.352	0.360	2.92	0.594	0.628
2.1	3.32	0.187	0.177	3.10	0.352	0.352	3.05	0.592	0.612
2.3	3.40	0.194	0.177	3.15	0.354	0.348	3.08	0.586	0.612
2.5	3.45	0.187	0.178	3.25	0.350	0.347	3.05	0.599	0.612
2.7	3.45	0.194	0.178	3.30	0.333	0.347	3.04	0.602	0.602
2.9	3.45	0.194	0.178	3.30	0.347	0.347	2.95	0.599	0.612
3.1	3.34	0.187	0.180	3.24	0.338	0.347	2.82	0.602	0.625
3.3	3.30	0.200	0.180	3.15	0.314	0.348	2.67	0.599	0.625
3.5	3.17	0.194	0.180	3.10	0.328	0.348	2.34	0.602	0.625
3.7	2.98	0.180	0.180	2.92	0.382	0.352	2.05	0.599	0.625
3.9	2.70	0.187	0.187	2.70	0.377	0.366	1.60	-----	-----
4.1	2.40	0.200	0.187	2.43	0.377	0.377	0.90	-----	-----
4.3	1.95	0.208	0.194	2.00	-----	-----			
4.5	1.25	-----	-----	1.30	-----	-----			

*Position along the vertical axis of the drop. Calculated optical densities were from Figures 16 and 17.

+Drop No.	Continuous Phase Conc., gm/L	Dispersed Phase Conc., gm/L
42	0.0145	0.0160
43	0.0242	0.0260
44	0.0340	0.0380

C_{ave} = Average concentration in volume L ΔX ΔY. The numerical value of C_{ave} was determined directly from the optical density-concentration calibration plot and optical density measurement.

The integral in Equation 20 covers the entire area of the image, and was determined by first integrating along the X-axis with ΔY equal to the slit length of the densitometer. Values of $\int C_{ave}\, dx$ were obtained by graphical integration. These values were added in the Y direction and multiplied by L to give A, the total amount of extracted acid.

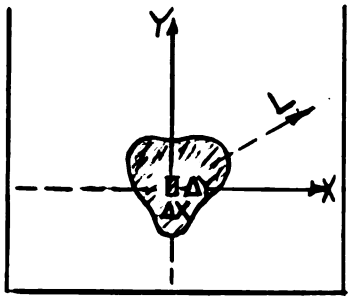


Figure 7

Drop volumes were determined by graphical integration of the following equation which was derived by Tambo (22).

$$V = \int_0^H \frac{\pi}{4} D^2 \, dh \qquad (21)$$

where,

V = volume of the drop

D = diameter of the drop as a function of H

H = height along the vertical axis of the drop.

The linear velocity of the jet entering the drop was determined by dividing the volumetric flow rate by the cross sectional area of the nozzle.

APPARATUS

The apparatus, illustrated in Figures 8 through 11, consisted of a vertical extraction column, a water tank and pump, a drop feeder device, a light source, absorption cells, light filters, and a camera mounted on an adjustable platform.

The extractor was fabricated from four brass plates 30 inches long and 3/8 inch thick, soldered together to form a column with a square inside cross section one inch on a side. Grooved openings were cut into the front and back sides of the extractor to accommodate two 1/4 inch thick plate glass windows one inch wide by eighteen inches long. The windows were held in place with epoxy resin with the inner surfaces of the windows 1.25 inches apart.

Piping was arranged so that distilled water saturated with toluene could be pumped from the storage tank to the bottom of the column. The column outlets at the top and bottom led to a drain.

Toluene-picric acid drops were formed at the end of a glass capillary which was joined to a 20-gage hypodermic needle with epoxy-resin (insoluble in water or toluene). A rubber stopper around the needle enabled the capillary to be inserted into the extractor from a side-hole. The needle was bent so the glass nozzle was vertical when inserted in the extractor. The inside diameter of the nozzle tip was 0.037 inches, and the outside diameter was 0.072 inches. A one milliliter syringe (A) held in place by platform (B) was used to form the drop. A spindle (C) placed behind the syringe plunger controlled the rate of drop

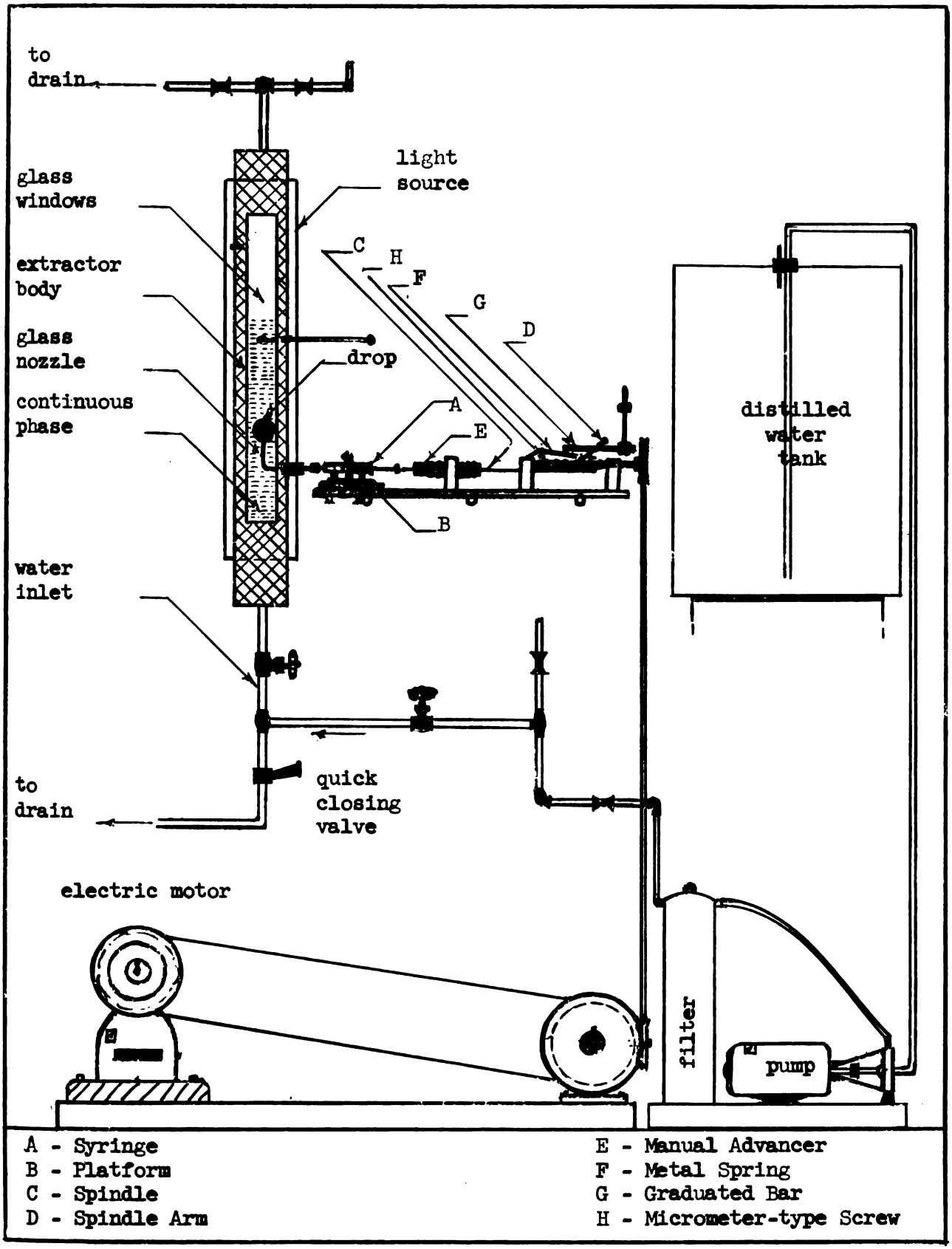


Figure 8 - DIAGRAM OF THE APPARATUS

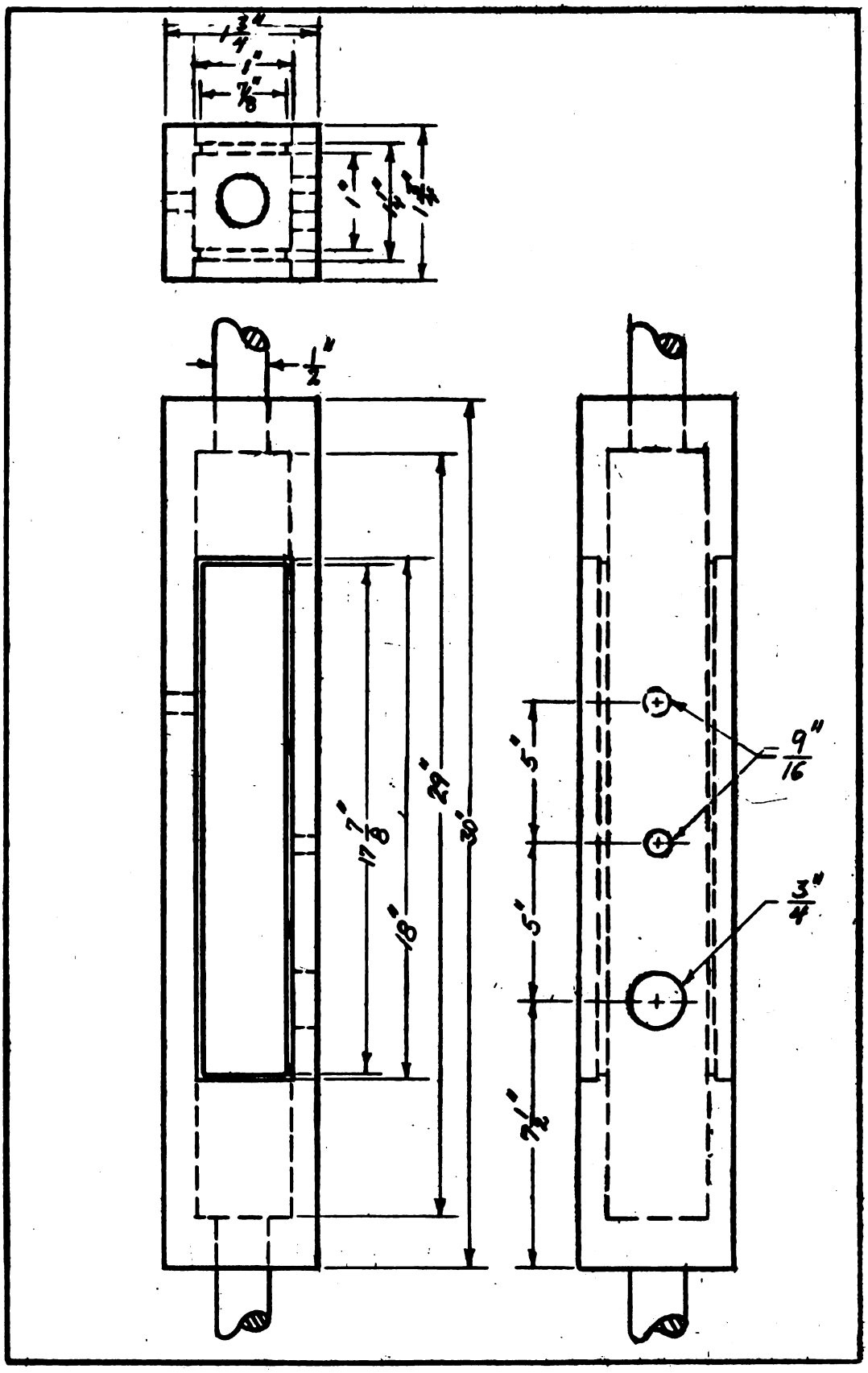


Figure 9 - Extractor Detail

formation. An arm (D) soldered to the spindle at a 90-degree angle was placed in the grooves of a micrometer-type screw. When the screw was turned, the arm, spindle, and plunger all moved parallel to the screw axis. The screw was turned by a combination of pulleys, cone sheaves, sash cord belts, and a gear reducer that was connected to a 1/50 horsepower variable speed electric motor. This arrangement provided drop formation times ranging from 0.2 to 25 seconds.

The initial plunger position was adjusted by a horizontal cylinder (E) which was screwed into the base of the feeder, and the spindle slid through the cylinder.

The arm (D) pressed against a flat metal-spring (F) while moving forward under a rigid, adjustable, graduated bar (G). When the arm (D) moved a linear preset distance (which would form one drop) and reached the end of bar (G), the spring (F) pushed the arm up, freed it from the grooves of the micrometer screw and thus stopped the advancement of the plunger.

Three 20-watt blue fluorescent tubes each 1 1/2 inches in diameter and 23 inches long served as light source. Blue tubes were used because they produced a high light intensity in the desired 3800 to 5500°A wave length range (26). The tubes were placed vertically with their axes forming an isosceles triangle with sides of about 1 5/8, 1 5/8, and 3 inches. The bulb at the tip of the triangle was 7/8 inch from the column.

During the preliminary experiments, the light source was operated on 60 cycle current. The film densities of a number of frames taken from one solution varied $\pm$ 8 units or more. A plot of per cent transmission versus number of frames showed an almost sinusoidal variation in readings.

This was caused by the nonuniform light output resulting from the cyclic variation in 60-cycle current. The nonuniform light output could have been also due to the "flicker" (per cent deviation from mean light output) of the fluorescent lamp, which is particularly higher for blue fluorescent tubes (9). To diminish the nonuniformity of light output, the light source was operated on a 1000-cycle circuit.

The arrangements for 1000 cycle circuit are illustrated in Figure 10. The bulb fixture carried a 60-cycle ballast (0.38A, 118V) in series with each bulb. The ballasts limit the current and raise or lower the circuit voltage to provide the wattage required by the lamp. In order to operate the bulbs at a frequency of 1000 cycles and voltage of about 110 volts, rheostats of 136-ohm resistance were connected in parallel to the ballast of each bulb.

The 1000 cycle alternating current was produced by a three-phase induction-motor and generator combination with a syncronous speed of 3450 R.P.M. The combination was connected to two electrical systems: A D. C. source or field exciter connected to the generator and an A. C. system connected to the motor.

The D. C. source was produced by connecting a 110-volt A. C. line through a variable voltage transformer (powerstat) and a 60-cycle rectifier to convert the alternating current to direct current.

The 440-volt, 60-cycle A. C. motor was on the same shaft as the 220-volt, 1035-cycle A. C. generator. The two were General Electric models 5K79BC4 and 5LYGGAIB, respectively.

Photographs of standard solutions were taken through standard cells. The cells were positioned on a wood column which replaced the extractor. The standard cells shown in Figure 11 had the same cross

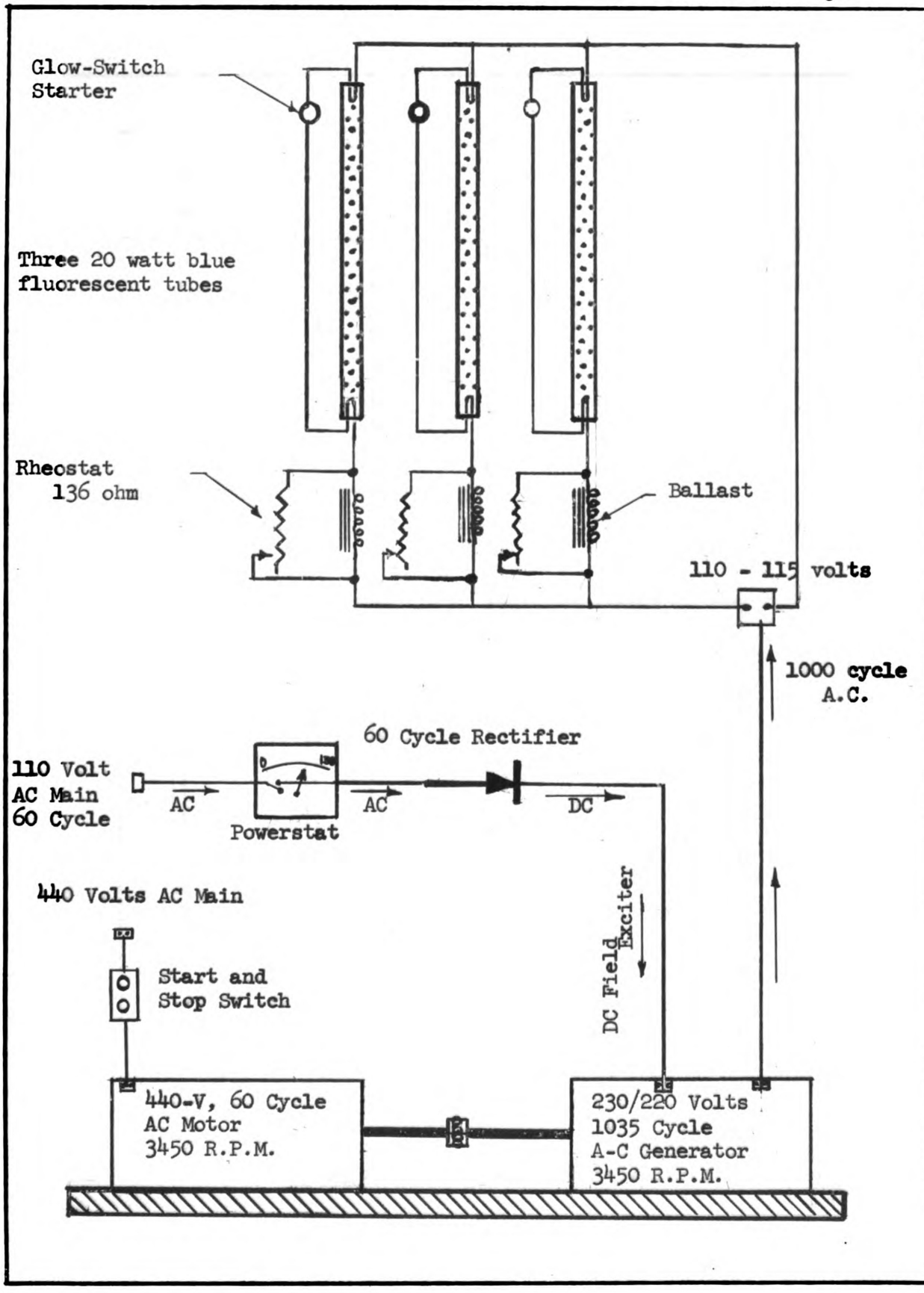
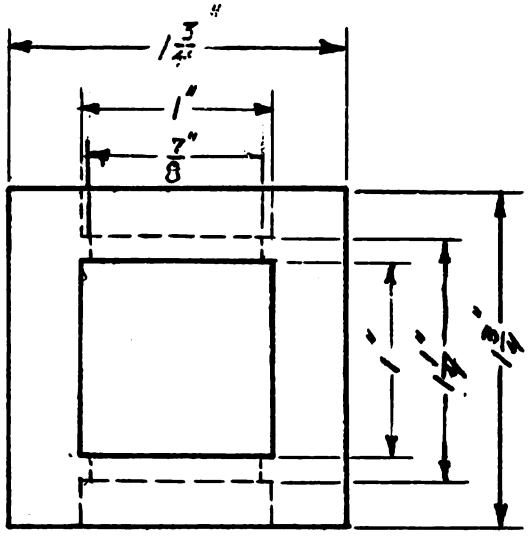
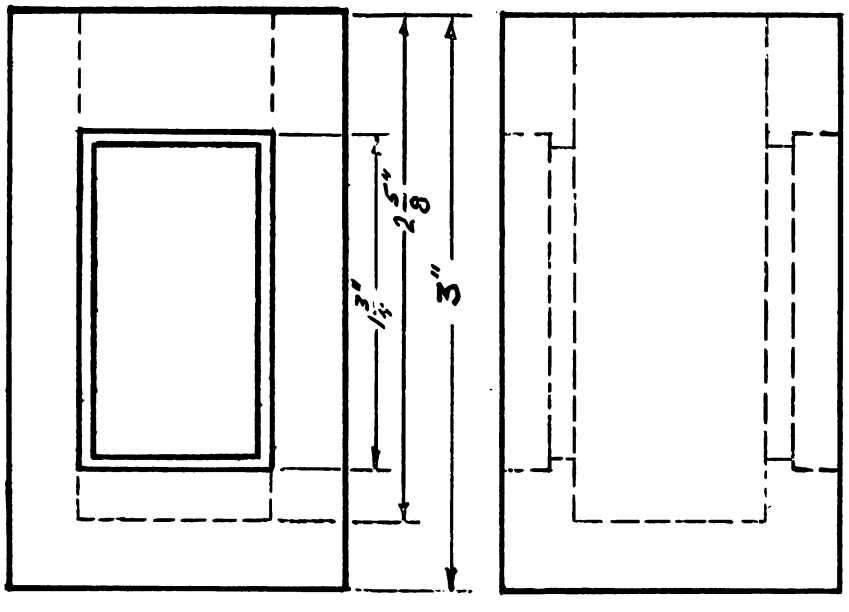


Figure 10 - Diagram of the light source.



Top View



Front View

Side View

STANDARD CELL DETAIL

Figure 11

section as the extractor, and a height of three inches. The bottom was closed and the top open; the glass windows were 1 3/4 inches high.

A rectangular glass cell (glass thickness 0.0365 inches) was positioned inside the standard cell to separate one layer of a solution from the rest of the cell contents when this arrangement was desired.

Pictures of the drops and standard solutions were taken at 32 frames per second at f/3.5 opening by a 16-millimeter CINE-Kodak Special movie camera. The film used was 16-millimeter, Plux-X reversal safety film (type 7276) made by Eastman Kodak Company. Kodak Wratten Filter Number 34 was placed between the camera and the column.

EXPERIMENTAL PROCEDURE

Standard Cell Pictures

The wooden column used to hold a standard cell was positioned and leveled in front of the light source. A standard cell containing distilled water was placed in the column, with a pin located at the center of the cell. The camera was clamped to the adjustable platform and was focused on the pin. Standard solutions of water-picric acid and toluene-picric acid were placed in the cell and pictures were taken for at least one second for each cell.

Movies of Forming Drops

After the syringe was filled with the toluene-picric acid solution, the glass capillary section was connected to the syringe. Care was taken to avoid air bubbles in the syringe. The needle section was then inserted into the column and the rubber stopper was tightened in the side-hole with the capillary in a vertical position at the center of the column. The body of the syringe was tightened in the saddle-type platform so the plunger was lined up with the moveable spindle. Using the manual advancer, the plunger was pushed forward until the solution in the syringe reached a point about 3/4 inch from the tip of the capillary. Next the plunger was held against the manual advancer while the spindle was pushed forward to reach the plunger. The arm of the spindle was positioned under the graduated bar at a point five millimeters from the end of the bar. The inlet valve to the column was

opened until the continuous phase reached above the capillary tip, and then the valve was closed. Finally, the electric motor was turned on and the spindle pushed the plunger forward. After the spindle traveled the preset distance of five millimeters, one air bubble and one toluene drop had been formed, and the spindle arm was automatically released from the micrometer screw. The movie camera was started as soon as the air-toluene interface began moving. After pictures of one drop were obtained, the column was flushed and rinsed with distilled water and the same operation was repeated. All the experiments were conducted at room temperature with water and toluene phases at 25 $\pm$ 2°C.

When a drop was withdrawn into the capillary, the manual advancer was pushed forward until the air bubble in the capillary was almost ready to detach. The spindle arm was held manually against the micrometer screw until the drop reached the desired size. Then the plunger was pulled back to the manual advancer. By this procedure only the drop itself was withdrawn.

Movies of Coalescing Drops

Experiments were conducted to study the effect of rate of mass transfer on stability of the drop at the toluene-water interface. The operation for drop formation was the same as for the regular drops except that before forming a drop, pure toluene was placed on top of the water above the capillary nozzle to form an interface. The interface was free of air bubbles and dirt which could promote coalescence. In order to prevent the drops at the interface from moving toward the sidewalls, the interface was shaped slightly concave downward by injecting additional water after the toluene was added. The level of the interface was

maintained 1/8 inch above the forming drop to eliminate extraction during the drop rise. Movies of the drops were taken with different rates of formation.

Film Processing and Recording on the Densitometer

The 16-millimeter Plux-X reversal type movie film was developed to a negative stage for five minutes in Eastman Kodak DK-60A Developer. Each roll of film contained both the standard solutions and the drop, so both were processed under the same conditions.

The negative film was enlarged and developed to a positive stage on 4" X 10" Kodak No. 33 photographic plates. The desired frames of the negative film were cut out in small rectangular sizes and placed between two clear glass plates in a rectangular area of 7/8 X 2 1/8 inches. A 4" X 10" black cardboard with an opening at the center was placed on top of the glass plates, leaving the area of the films open for exposure. The glass plates with the films between were placed on a Wollensak 135-millimeter enlarger, and projected to a magnification of about five times. The enlarger lens opening was at f/32, and the exposure times ranged from eight to ten seconds. The plates were processed as follows: developed in D-11 Kodak Developer for eight minutes, rinsed in 5% acetic acid solution for 40 seconds, fixed in Kodak acid fixer for 15 minutes, washed in running water for 20 minutes, rinsed in distilled water, and dried.

Optical density measurements along the axis of the drop were obtained by first placing a piece of graph paper on the densitometer screen along the slit length. By this arrangement it was possible to move the plate holder one slit length at a time. Readings were taken for each position along the vertical axis of the drop. The densitometer projected the drop from the plate to the screen with a magnification of 10

times, so that it was possible to move the plateholder and thus the frame containing the drop to the desired position along the vertical axis.

The diameters of a drop along its vertical axis were determined by projecting the plate on a graph paper to a magnification of 10 times.

In order to obtain optical densities across the image of the extracted material in the water phase, the recorder and synchronous motor drive were used to plot transmission values versus distance automatically. From the rate of plate movement and the recorder graph movement the distance along the image corresponding to optical density at each point was found and plotted versus concentration at that point.

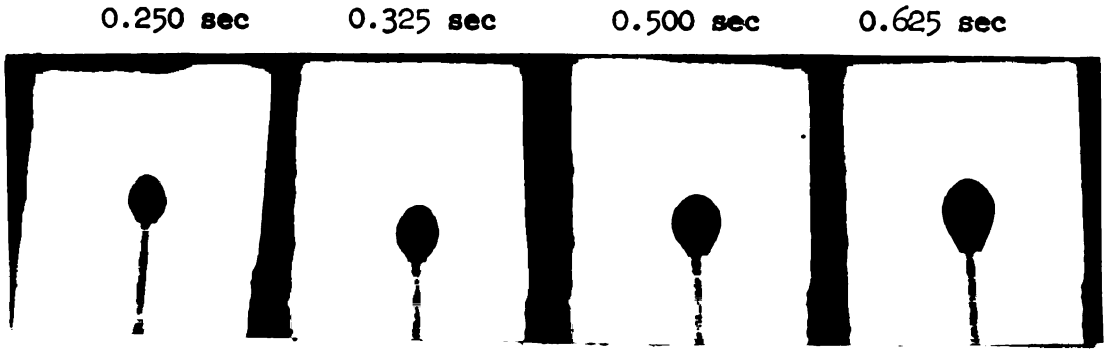
SUMMARY OF RESULTS

The experimental results are summarized in Table III, and plotted in Figure 12 as amount extracted versus time for each individual set of drops. Drop volume versus formation time is plotted in Figure 13.

The drops were not completely spherical in shape. As reported by Poutanan and Johnson (19), before break-off each drop had an elongated neck by which it was attached to the capillary.

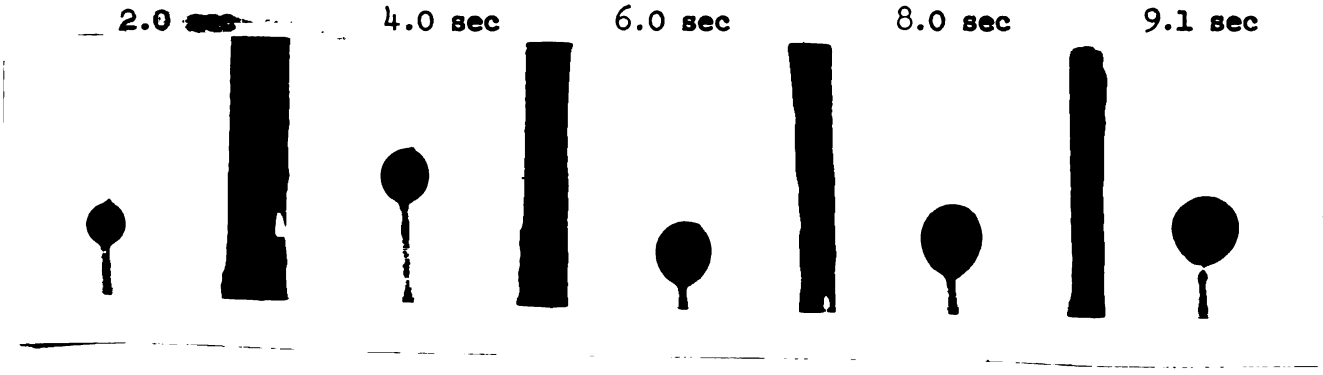
The results of one experiment in which a drop was withdrawn into the capillary is presented in Table IV.

Photographs of Drop Sets 53 and 56 appear on the following page.



DROP 53 DURING FORMATION

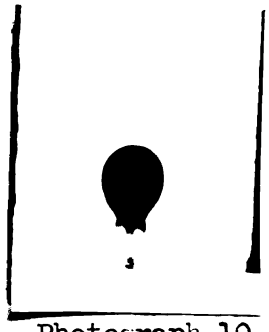
Photographs 1 - 4



DROP 56 DURING FORMATION

Photographs 5 - 9

No mass transfer into bulk of the continuous phase below 12 second formation time.



Photograph 10
Typical drop, formation time over 12 seconds Extracted picric acid diffusing into bulk of the continuous phase.

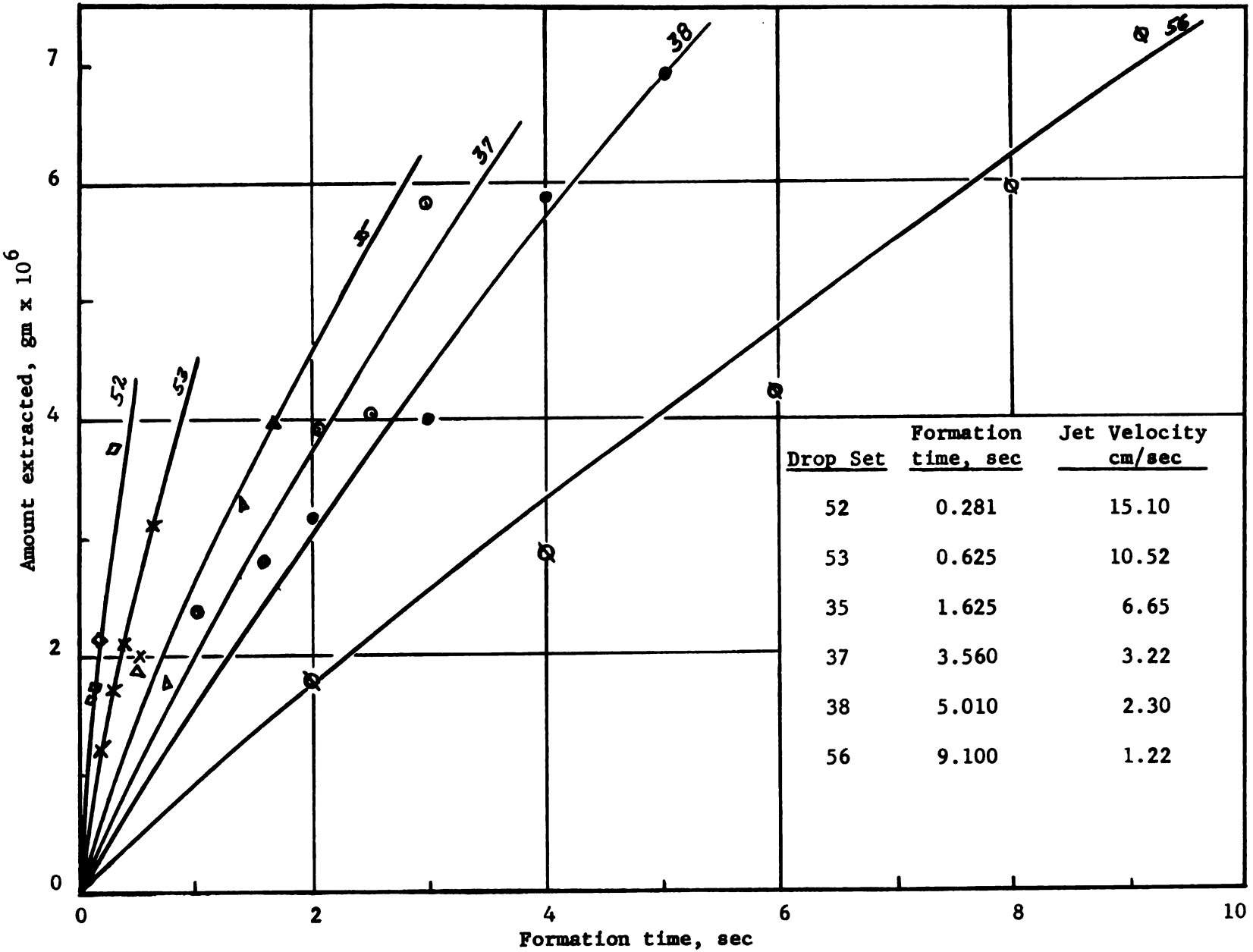
Photograph 11
Extracted picric acid remaining in the continuous phase after the drop has been withdrawn into the capillary.

TABLE III - Experimental Results

Drop Set and No.	Formation Time, Sec.	Volume cm^3	Amount Extracted grams x 10^6	Jet Velocity cm/sec
52-1	0.0625	0.00380	1.650	15.1
2	0.1250	0.00984	1.742	15.1
3	0.1875	0.01848	2.163	15.1
4	0.2810	0.01960	3.790	15.1
53-1	0.125	0.00845	1.268	10.52
2	0.250	0.01868	1.726	10.52
3	0.375	0.02790	2.075	10.52
4	0.500	0.03480	2.032	10.52
5	0.625	0.04570	3.100	10.52
35-1	0.468	0.01950	1.93	6.65
2	0.780	0.04065	1.79	6.65
3	1.406	0.06640	3.29	6.65
4	1.625	0.07460	4.02	6.65
37-1	1.00	0.01717	2.430	3.22
2	1.56	0.03365	2.825	3.22
3	2.03	0.04370	3.940	3.22
4	2.50	0.05210	4.020	3.22
5	2.94	0.06600	5.894	3.22
38-1	2.00	0.03130	3.22	2.30
2	3.00	0.04500	4.05	2.30
3	4.00	0.06410	5.95	2.30
4	5.01	0.08200	6.95	2.30
56-1	2.0	0.0168	1.83	1.22
2	4.0	0.0292	2.88	1.22
3	6.0	0.0513	4.42	1.22
4	8.0	0.0704	5.98	1.22
5	9.1	0.0726	7.27	1.22

TABLE IV - Results of Drop 60 Before and After it was Withdrawn into the Capillary

Time at which drop was withdrawn	5.62 seconds
Drop volume	0.0259 cm^3
Time it took to withdraw the drop	3.36 seconds
Amount of acid extracted during 5.62 seconds	3.24×10^{-6} gm
Amount of acid left behind after drop was withdrawn	4.86×10^{-6} gm



Drop Set	Formation time, sec	Jet Velocity cm/sec
52	0.281	15.10
53	0.625	10.52
35	1.625	6.65
37	3.560	3.22
38	5.010	2.30
56	9.100	1.22

Figure 12 - Plot of the amount of picric acid extracted versus drop formation time.

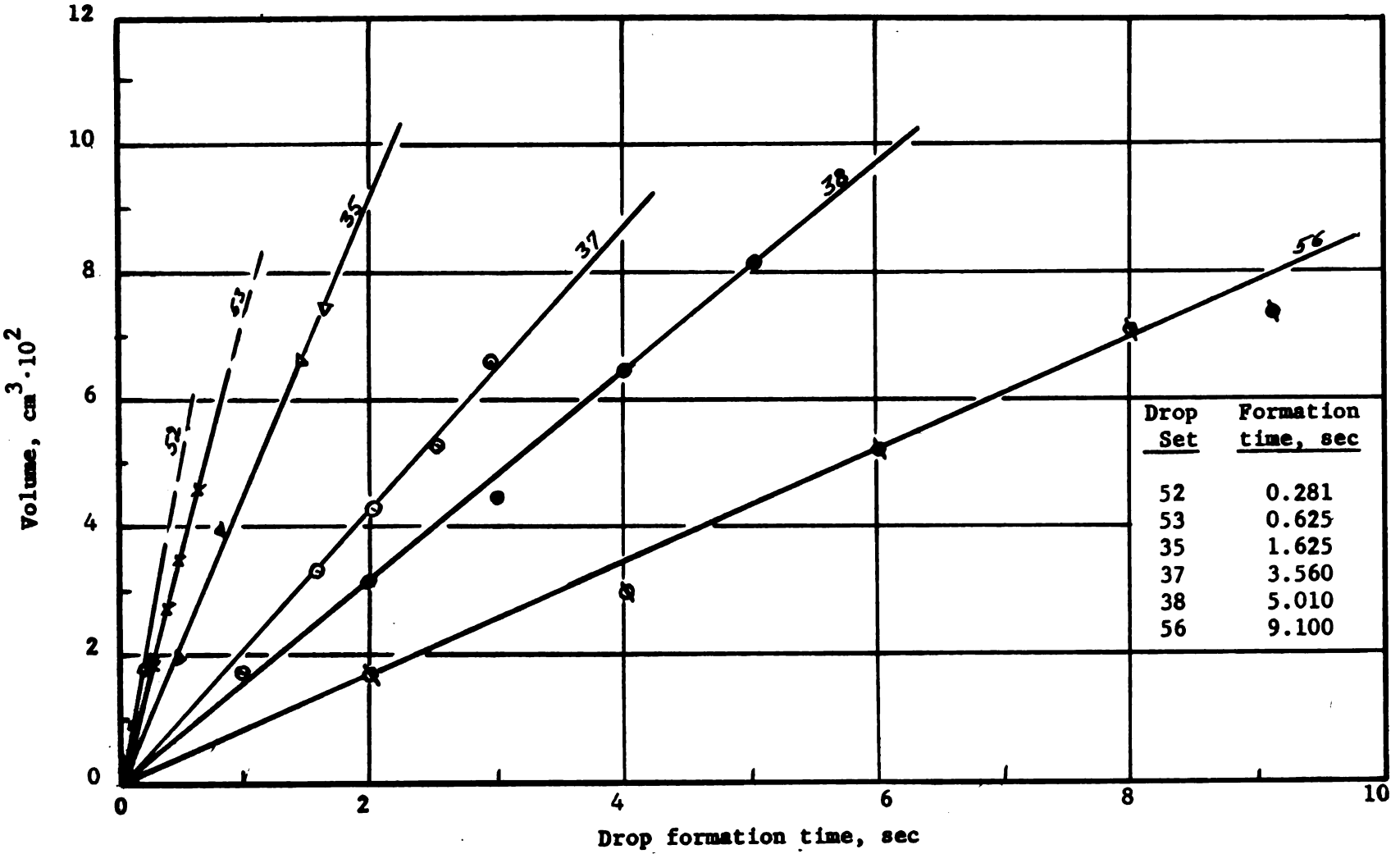


Figure 13 - Plot of drop volume versus drop formation time.

DISCUSSION OF RESULTS

Three methods were used to compare the results with the theoretical equation given in the theory section as,

$$\% \text{ extraction} = 6.12 \times 10^{-2} \frac{\sqrt{t}}{V^{1/3}} \qquad (8)$$

In the derivation it was assumed that mass transfer resistance inside the drop was negligible and that transport outside the drop occurred primarily by molecular diffusion. The per cent extraction from Equation 8 was 0.3 per cent for a drop of 0.082 cm^3 volume formed in five seconds. The experimental value was only 0.08 per cent. If the molecular diffusion assumption was not valid, transport by convection in the continuous phase would have increased the per cent extraction and the experimental value would be greater than the calculated value. Since the reverse was true, the assumption of negligible resistance inside the drop was not valid despite the 10 to 1 distribution ratio favoring the dispersed phase.

Inspection of Equation 8 shows that a log-log plot of per cent extraction versus time, for drops of a fixed volume, should result in a straight line of slope 0.5. However, the experimental data plotted in Figure 14 show that a curve exhibiting a minimum per cent extraction was obtained. A similar result was found by Gregory (11) with systems in which the dispersed phase resistance controlled the extraction rate. His results are included in Figure 14 for comparison. At formation times less than one second, apparently

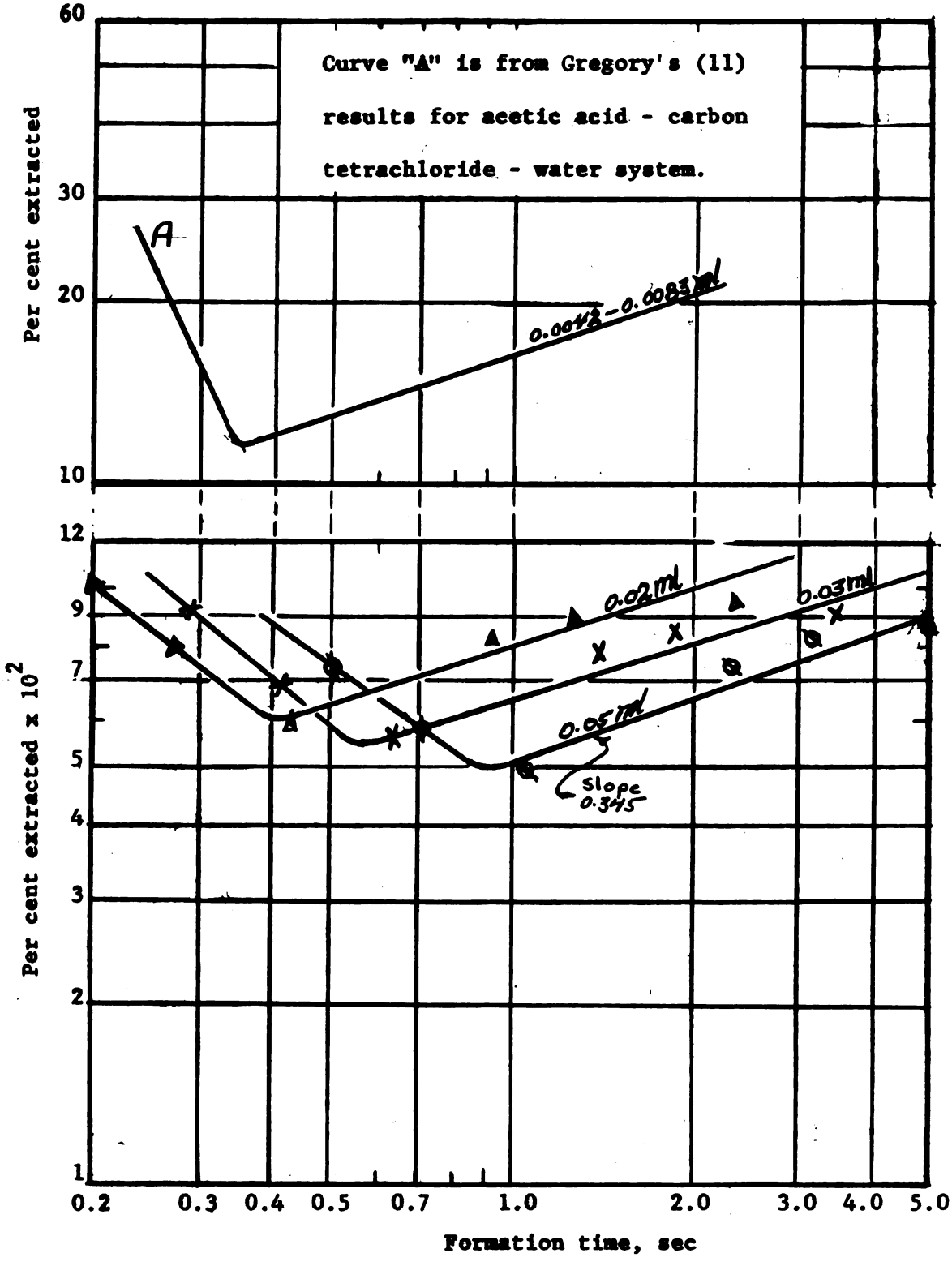


Figure 14 - Per cent extracted versus formation time.

the dispersed phase transfer coefficient increased rapidly due to the increase in formation rate.

Equation 8 was solved for the amount extracted as a function of the rate of formation and time,

$$\text{amount extracted} = 0.67\, U^{2/3}\, t^{7/6} \quad . \qquad (22)$$

Figure 15 is a log-log plot of amount of acid extracted versus time, for a constant formation rate. Inspection of Equation 22 shows that, for a constant value of U, a log-log plot of amount extracted versus time should result in a straight line of slope 1.17. It was found that the slope increased as the formation rate decreased. At the slowest formation rate of 8.45×10^{-2} cm^3/sec, the exponent of t was 0.95 compared to the theoretical value of 1.17. At lower formation rates, transport by molecular diffusion within the drop would increase in importance. In addition if the continuous phase resistance was negligible, an equation of the form of Equation 22 would be applicable. Therefore, it was expected that the time exponent would approach 1.17 at low formation rates.

The per cent of solute extracted was higher during the early life of each drop.

Inspection of the photographs of Drop Set 53 shows that in drops of less than one second formation time, extraction took place mostly around the bottom half of the drop. This is illustrated by the increase in darkness near the bottom of the drops. For drops that formed at a slower rate, extraction was uniform all around the drop. This was probably due to the increase in mass transfer coefficient inside the drop near the capillary tip at high formation rates.

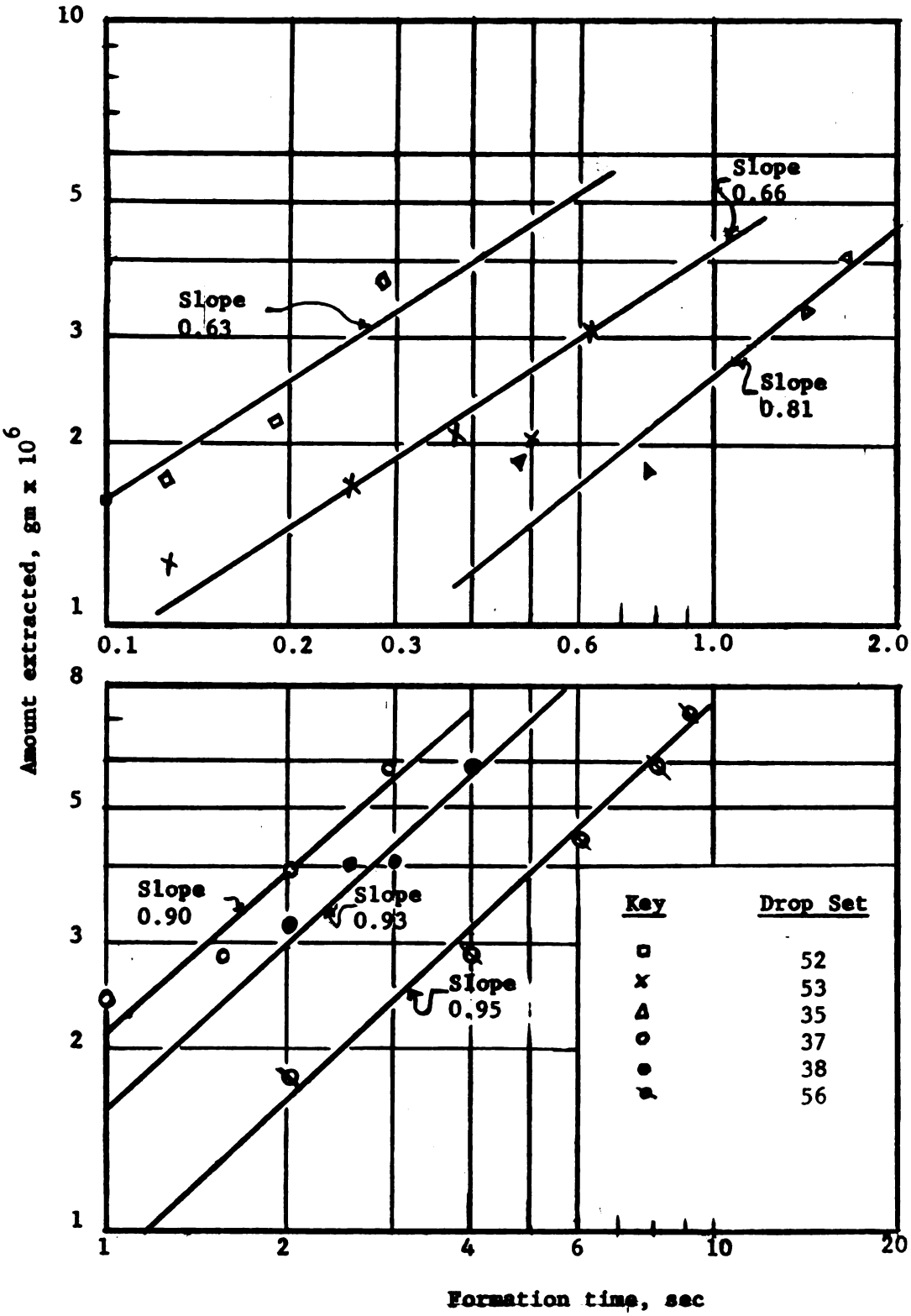


Figure 15 - Plot of amount extracted versus drop formation time in accordance with Equation 22.

Figure 12 of the results is a plot of the amount extracted versus drop formation time with formation rate as a parameter. At a fixed formation time the amount of extraction was lower for drops that formed at a slower rate.

When drops were formed in less than 12 seconds, none of the extracted acid was left behind as the drop broke away and rose. Therefore, in these experiments, transfer to the bulk of the continuous phase did not occur. This effect has not been previously reported in the literature.

Table IV of the results presents the amount of extraction from Drop 60 which was withdrawn into the capillary. The variation obtained in the amount of extraction by two methods, namely by taking optical density measurements directly through the image of the drop and by taking optical density measurements through the image of the extracted material, was due to: extra mass transfer during the time it took to draw the drop into the capillary and possible higher mass transfer from the unsteady motion of the plunger when withdrawing the drop manually.

Sufficient data on coalescence of the drops was not obtained; however, from the few experiments conducted, coalescence of the drops at the toluene-water-interface seemed to be instantaneous. The experiments conducted with drops forming at different rates of formation revealed that higher rates of mass transfer decrease the stability of the drops at the interface, as reported by Charles and Mason (14) for other systems. In the preliminary investigations it was found that for picric acid-water-toluene system , the coalescence was not complete; that is, the primary drop was succeeded by a smaller secondary drop of the dispersed phase.

CONCLUSIONS

It was possible to study the mechanism, rate, and amount of extraction at any time during drop formation period by photographic absorption photometry.

For the system picric acid-toluene-water, with toluene as the dispersed phase, and for drop formation times below 12 seconds, mass transfer to the continuous phase was essentially zero, and extraction across the interface was about 0.1 per cent.

The per cent of picric acid extracted was higher during the early life of a drop.

For a fixed drop volume, per cent extraction decreased as formation time decreased at long formation times. At shorter times, this phenomenon was reversed.

The rate of mass transfer increased with increase in the formation rate.

For drops with high rates of formation, extraction took place mostly around the bottom half of the drop. For slow rates of formation, extracted material was more uniformly distributed all around the drop.

The dispersed phase resistance was important and not at all negligible.

The coalescence of drops at the water-toluene interface was instantaneous in most cases, but it was not complete; that is, the primary drop was succeeded by a smaller secondary drop of the dispersed phase.

APPENDIX

APPENDIX A

SAMPLE CALCULATIONS

I. Sample Calculation of the Concentration of Different Layers of Solutions as Presented in Table I

Table I presents data obtained from a cell containing different solutions in each compartment of the standard cell.

Sample Calculation for Runs 28 and 79

Calculated concentrations were determined from Figures 16 and 17 and Equation 9,

$$K_w C_{sw} L = K_w \int_0^{L_1} C_1 dl + K_w \int_{L_1}^{L_2+L_1} C_2 dl + \int_{L_2+L_1}^{L} C_3 dl \qquad (9)$$

where,

$$L = L_1 + L_2 + L_3 .$$

For water phase, the values of K_w were constant and equal. Integrating Equation 9,

$$C_{sw} = \frac{1}{L} (C_1L_1 + C_2L_2 + C_3L_3) \qquad (23)$$

For Run 28

L_1 = 0.4985 inches	C_1 = 0.0145 gm/L
L_2 = 0.1880 inches	C_2 = 0.0000 gm/L
L_3 = 0.4985 inches	C_3 = 0.0145 gm/L
L = 1.2500 inches	measured optical density = 0.15

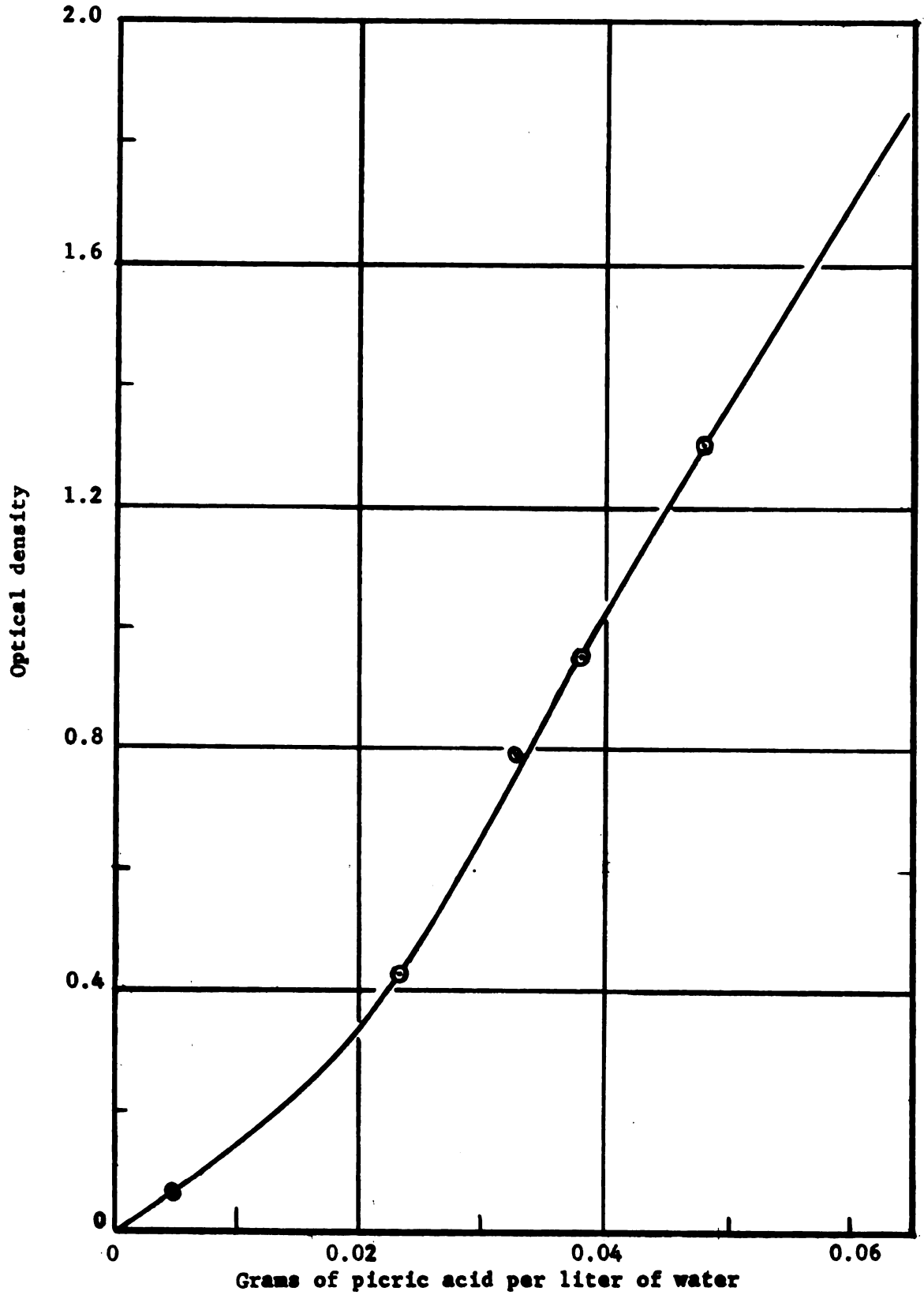


Figure 16 - Plot of optical density on the plage versus concentration of the standard solutions (calibration curve for Drops 35, 37, and 38).

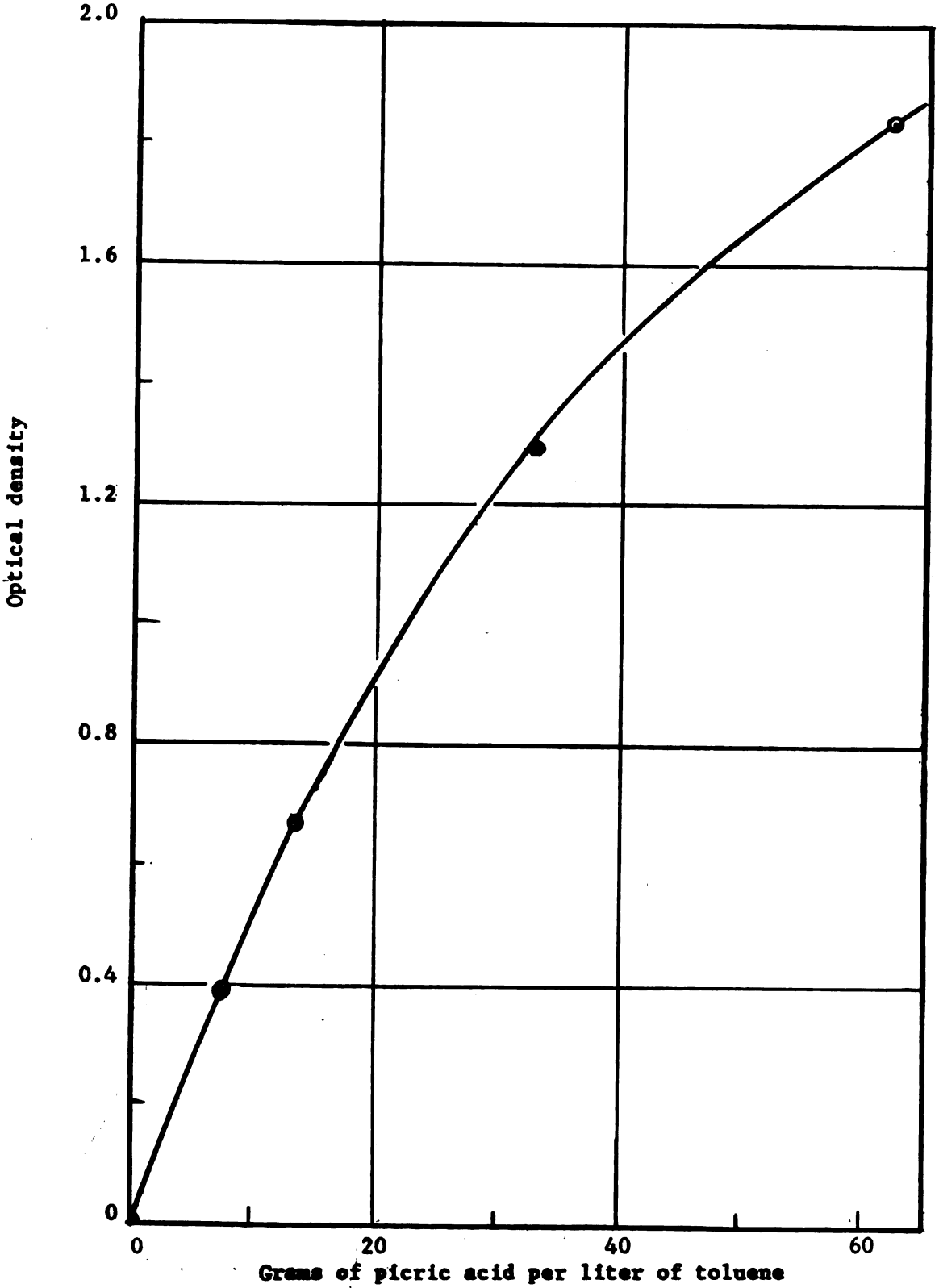


Figure 17 - Plot of optical density on the plate versus concentration of the standard solutions (calibration curve for Drops 35, 37, and 38).

The thickness of two glass pieces separating the compartments was 0.073 inches. Light absorption due to the glass was assumed zero. From Figure 16 for a measured density of 0.15,

$$C_{sw} = 0.0113 \text{ gm/L}$$

Substitution of C_{sw} and $L = L_1 + L_2 + L_3 + 0.073$ in Equation 23 gives $C_1 = C_3 = 0.0141$ gm/L.

For Run 79

$L_1 = L_3 = 0.367$ inches — $C_3 = C_1 = 0.0325$ gm/L water phase

$L_2 = 0.443$ inches — $C_2 = 109$ gm/liter of toluene

$L = 1.25$ inches — measured density = 1.62

Thickness of the glass separating the compartments was 0.073 inches.

In this case Equation 23 becomes

$$K_w L C_{sw} = K_w L_1 C_1 + K_t L_2 C_2 + K_w L_3 C_3 \qquad (24)$$

Then by application of Equation 9 to toluene phase,

$$C'_t = \frac{C_2 L_2}{L} = \frac{109 \times 0.443}{1.25} = 38.62 \text{ gm/L in toluene phase}$$

From Figure 19 - a plot of concentration in the toluene phase versus optical density - for a concentration of 38.62 gm/L, d = 1.065. In turn from Figure 18 - a plot of concentration in the water phase versus optical density - the water phase concentration equivalent to an optical density of 1.065 for a cell 1.25 inches thick was $C'_w = 0.0516$ gm/L.

Therefore,

$$K_w C'_w L = K_t C'_t L = K_2 C_2 L_2$$

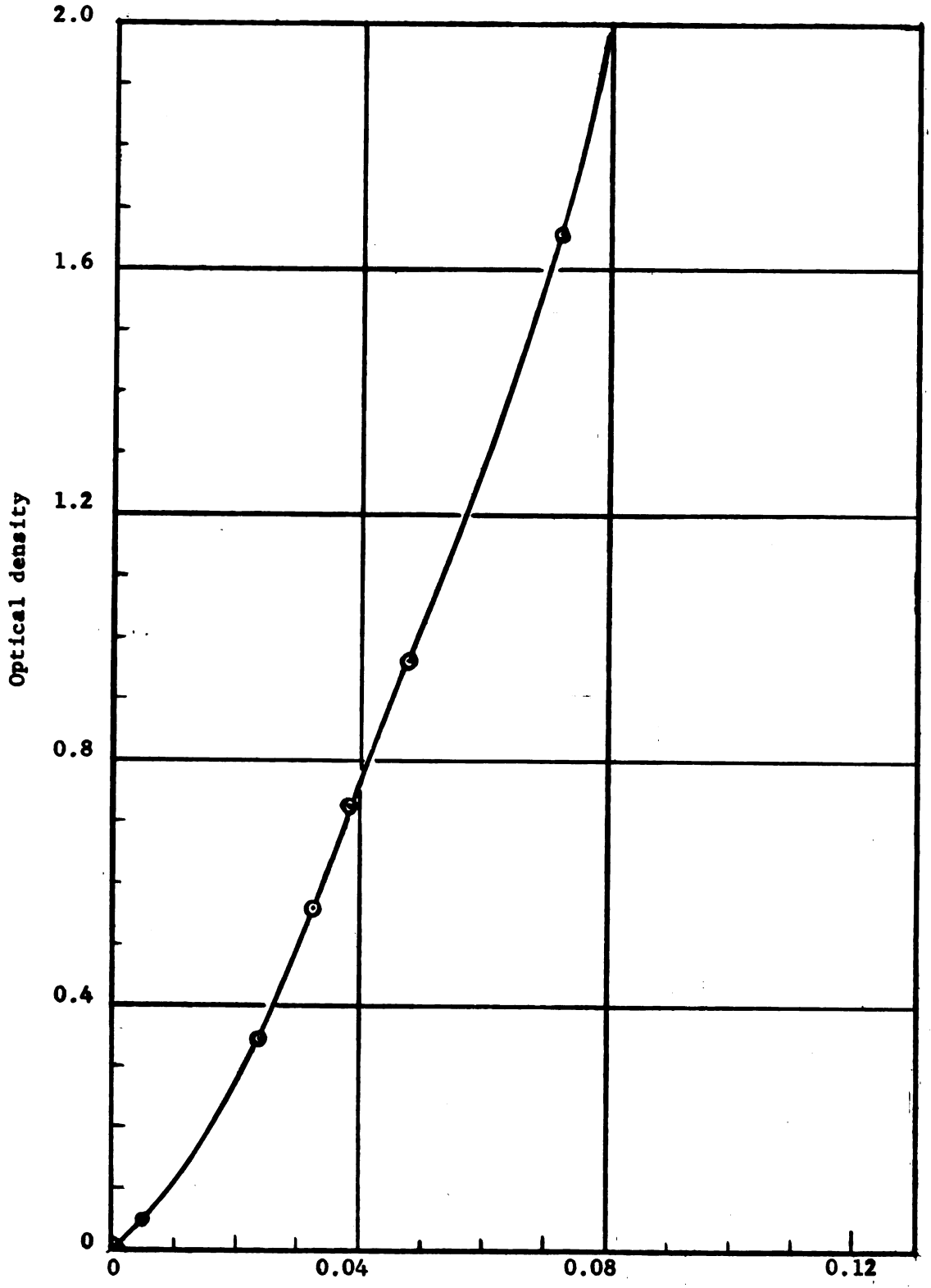


Figure 18 - Plot of optical density on the plate versus concentration of standard solutions.

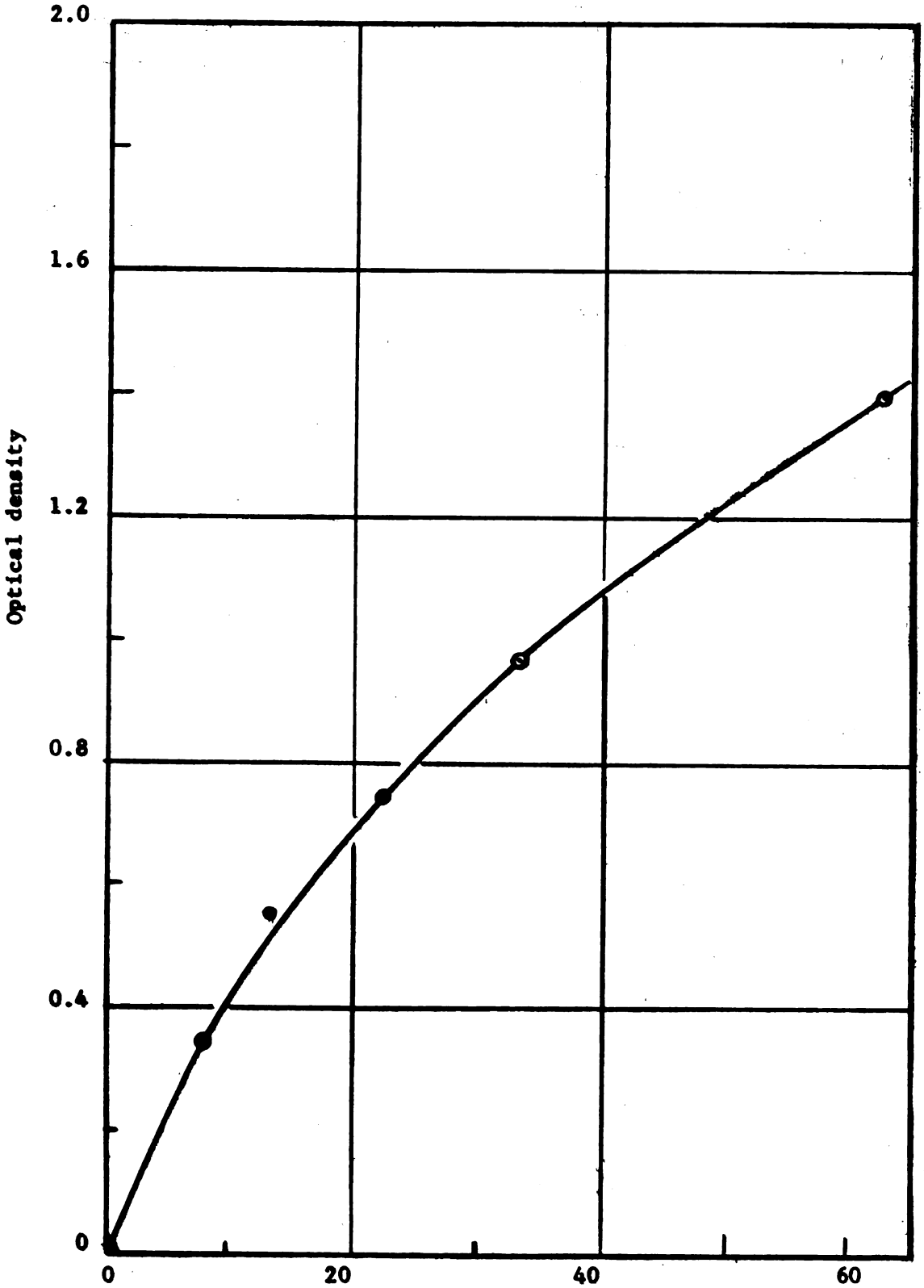


Figure 19 - Plot of optical density on the plate versus concentration of the standard solutions.

Or,

$$K_w\ (0.0516)\ (1.25) = K_2C_2L_2$$

From the measured density at 1.62 and the water calibration curve, Figure 18, $C_{sw} = 0.0706$. Substituting into Equation 24,

$$0.0706 \times 1.25 = 0.367 \times C_1 + 0.0516 \times 1.25 + 0.367 \times C_3$$

Since $C_1 = C_3$,

$$C_1 = 0.0324 \text{ gm/L}$$

This figure was compared to the actual value of 0.0325 gm/L.

II. Sample Calculation of the Optical Density for Drops at Equilibrium with Continuous Phase as Presented in Table II

The expected optical density through drops at equilibrium was calculated by a method similar to that of the previous section for Runs 75 through 80. Distance L_2, the drop diameter, equaled the thickness of the toluene phase.

For Drop 42,

$C_1 = C_3 = 0.0145$ gm/L in water phase

$C_2 = 0.016$ gm/L in toluene phase

At a point where the drop thickness was 1.57 mm on the image,

$L = (1.57 \times 0.0531) = 0.0835$ inches, where 0.0531 equaled inches in the extractor per mm of the image.

From Equation 16,

$$C'_t = \frac{C_2L_2}{L} = \frac{0.016 \times 0.0835}{1.25} = 10.7 \times 10^{-4} \text{ gm/L in toluene phase}$$

From Figure 17,

Optical density = 6.4×10^{-6} for C'_t (by interpolation)

From Figure 16,

$$C'_w = 7.5 \times 10^{-6} \text{ gm/L for optical density of } 6.4 \times 10^{-6}$$
(by interpolation)

Therefore,

$$K_t C_t L_2 = K_w C'_w L$$

Substituting into Equation 24,

$$C_{sw} = \frac{(L-L_2)\, C_3 + C'_w L}{L}$$

$$= \frac{(1.25-0.0835) \times 0.0145 + 7.5 \times 10^{-6} \times 1.25}{1.25}$$

$$= 0.0135 \text{ gm/L in water phase}$$

From Figure 16 for a concentration of 0.0135 gm/L the optical density was 0.195.

III. Calculation of the Amount of Extraction when Optical Density Measurements were made Directly Through the Drops

Sample Calculation for Drop 1 of Set 53

The amount of extraction was determined from Equation 25.

$$A = \int_0^H \pi D \, \frac{(C_{sw} - C'_{sw})}{2} \, \frac{L}{1000} \, dh \qquad (25)$$

where,

A = total amount of extraction, grams

D = thickness of the drop at each point of transmission measurement, cm

L = effective depth of the extractor or standard cell (L = 1.25 inches x 2.54 cm/in = 3.175 cm)

C_{sw} = concentration in water phase corresponding to the transmission read at each point of the drop, gm/L

C'_{sw} = concentration in water phase which gives the same transmission as a concentration C_{st} in toluene phase, gm/L (where $C_{st} = C_t \cdot D/L$)

H = position of diameter and transmission measurement along the vertical axis of the drop, cm

1000 = conversion from liters to cm^3

2 = a factor taking into account that $\Delta C = C_{sw} - C'_{sw}$ is twice the actual value.

Conversion factor from the plate to actual size in the extractor was equal to 1.35 (to convert from the plate to actual size in the extractor multiply by 1.35).

From Drop 1 of Set 53 the values for one point of optical density measurement are:

L . . . . . 3.175 cm

π 3.14

H, on the plate . . . . . 0.1 mm

D, on the plate . . . . . 0.6 mm

(The values of H and D were converted into cm in the extractor by multiplying by 0.135.)

T, per cent transmission 20%

C_{sw}, for a transmission of 20% (or $d = \log \frac{1}{0.20} = 0.699$) from Figure 21 . . . . . 0.0307 gm/L

C_t . . . . . 109 gm/L

$$C_{st} = \frac{Ct \cdot D}{L} = \frac{Ct \cdot (0.135\ D\ plate)}{L}$$

$$= 109\ gm/L \times \frac{(0.6 \times 0.135)\ cm}{3.175\ cm} = \ldots\ldots 2.78\ gm/L$$

C'_{sw}, for a concentration $C_{st} = 2.78$ gm/L from Figure 22, d = 0.16 and in turn from Figure 21 for an optical density of 0.16 . . . . 0.0108 gm/L

$\Delta C = C_{sw} - C'_{sw} = 0.0307 - 0.0108$ . . . . . 0.0199 gm/L

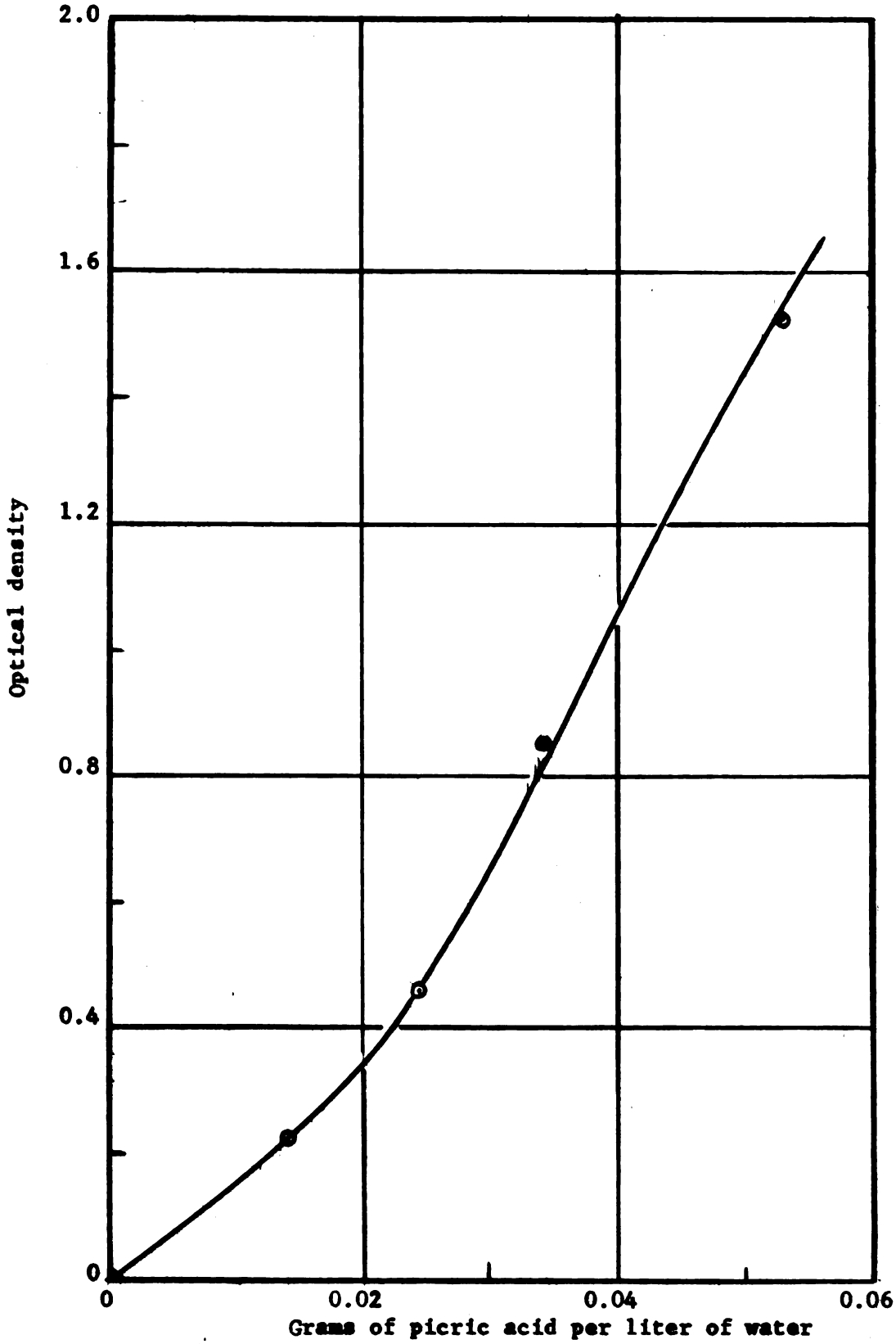


Figure 21 - Plot of optical density on the plate versus concentration of standard solutions (calibration curve for Drops 52, 53, and 56).

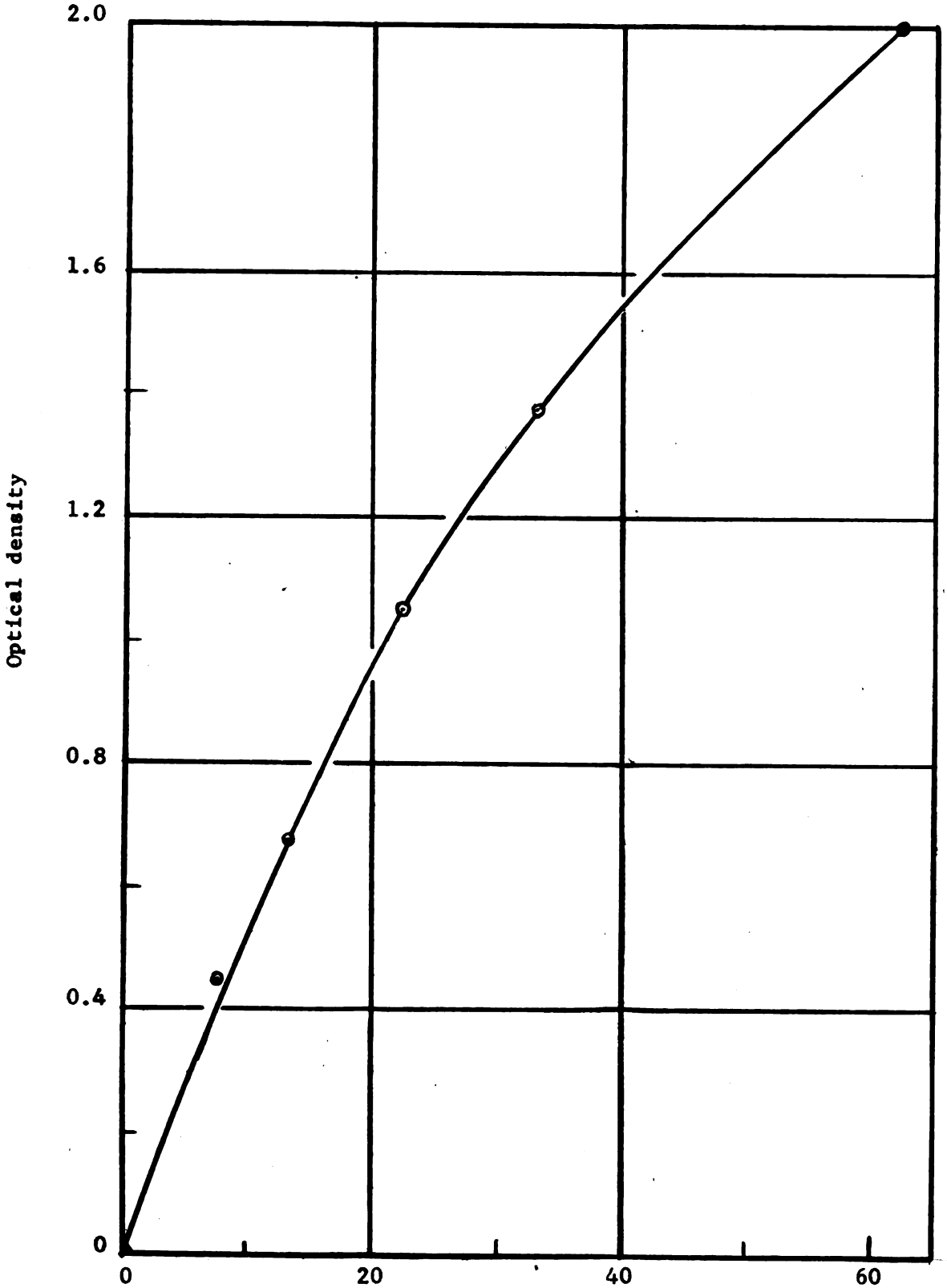


Figure 22 - Plot of optical density on the plate versus concentration of standard solutions (calibration curve for Drops 52, 53, and 56).

Substituting into Equation 25,

$$A = (0.135)^2 \int_0^H \left(\frac{\Delta C}{2}\right) \; 3.175 \times 10^{-3} \times 3.14 \times D \, dh \qquad (25_a)$$

or,

$$A = 9.08 \times 10^{-5} \int_0^H D \, \Delta C \, dh \qquad (25_b)$$

For the first point of optical density measurement,

$$D \, \Delta C = 0.6 \times 0.0199$$
$$= 11.94 \times 10^{-3} \text{ gm-mm/L}$$

Equation 25_b was evaluated graphically by plotting values of $D \, \Delta C$ versus H in Figure 20_a. The area under the curve was 0.14×10^{-1} gm-mm^2/L.

Total extracted acid, $A = 9.08 \times 10^{-5} \times 0.14 \times 10^{-1}$

$$= 1.27 \times 10^{-6} \text{ gm}$$

The drop volumes were determined by the following equation:

$$V = \int_0^H \frac{\pi}{4} D^2 \, dh \qquad (21)$$

where,

H = position along the vertical axis of the drop, cm

D = diameter of the drop at position H, cm

V = volume of the drop, cm^3

Since the values of H and D were in millimeters on the plate, the right side of Equation 21 was multiplied by the conversion factor $(0.135)^3 \left(\frac{\text{cm in extractor}}{\text{mm on plate}}\right)^3$ to obtain the actual volume. Then,

$$V = 1.93 \times 10^{-3} \int_0^H D^2 \, dh \qquad (21_a)$$

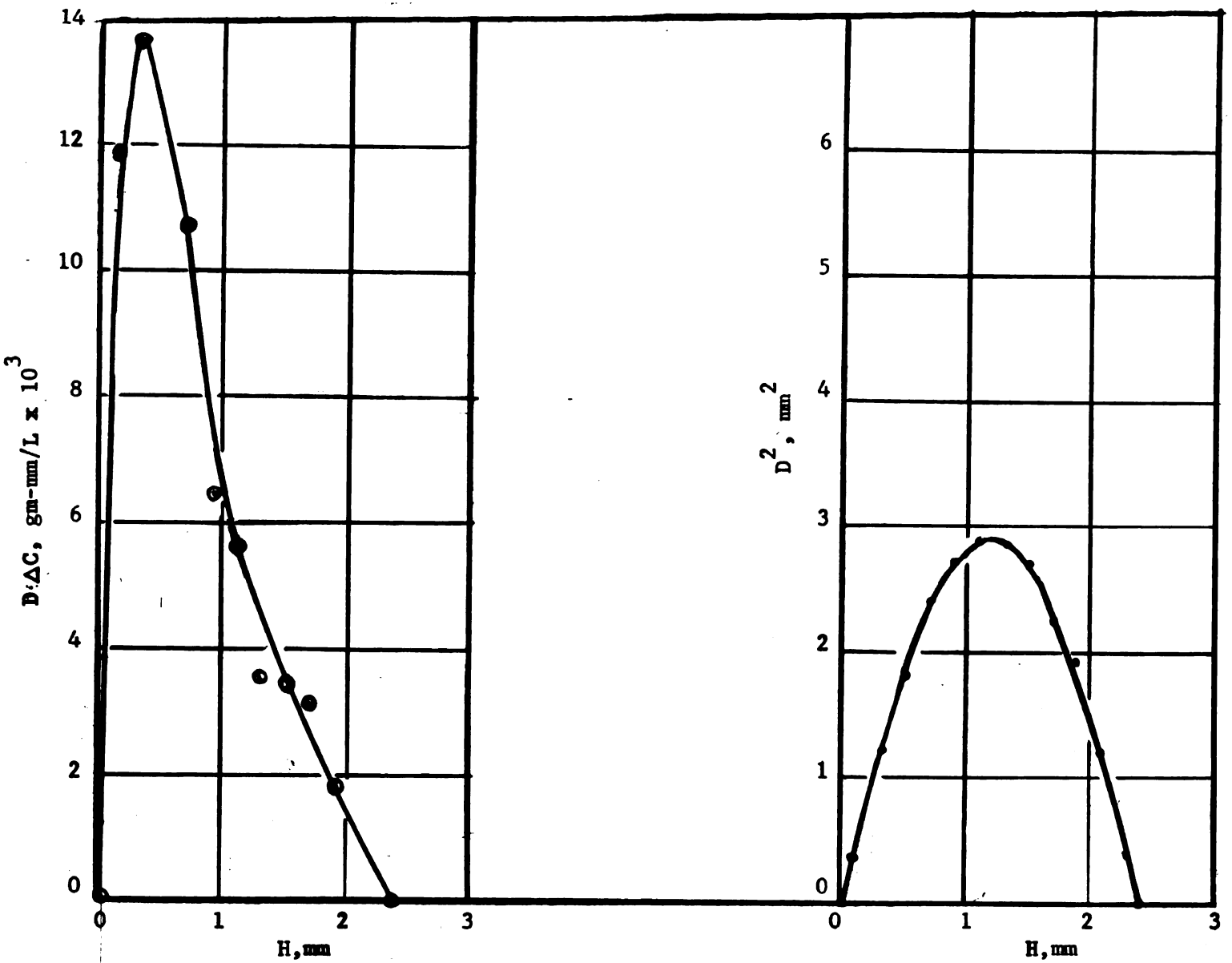


Figure 20_a - Typical plot of data in accordance with Equation 25_b.

Figure 20_b - Typical plot of data in accordance with Equation 21_a.

Equation 21_a was integrated graphically from a plot of D^2 versus H. Figure 20_b is a sample plot for Drop 1 of Set 53. The area under the curve was 4.38 mm^3. Substituting into Equation 21_a,

$$V = 8.45 \times 10^{-3} \text{ cm}^3$$

The linear velocity of the jet entering the drop was determined by dividing the volumetric flow rate by the cross sectional area of the nozzle.

Inside diameter of the nozzle at the tip was 0.037 inches. Then,

$$\text{cross sectional area} = \frac{\pi}{4}(0.037 \text{ in} \times 2.54 \text{ cm/in})^2$$
$$= 0.0694 \text{ cm}^2$$

Therefore, for Drop 56 with a volumetric flow rate of 8.45×10^{-2} cm^3/sec,

$$\text{Jet Velocity} = 8.45 \times 10^{-2} \text{ cm}^3/\text{ sec} \times \frac{1}{0.0694 \text{cm}^2}$$

$$= 1.22 \text{ cm/sec.}$$

IV. Calculation of the Amount of Extraction when Drops were Drawn into the Capillary

The amount of acid left behind the drop when drawn into the capillary was determined by the following equation:

$$A = \int_0^X C \cdot d' \cdot L \cdot dx \qquad (26)$$

where,

A = amount of picric acid in the volume covered by the slit along the X axis, grams

C = concentration in grams per cubic centimeters corresponding to the per cent transmission read

L = depth of standard cell or extractor = 3.175 cm

d' = slit length, cm. The slit length = 0.02 cm on the plate or 0.02 x 1.5 = 0.30 cm in the extractor (where 1.5 cm in the extractor = 1.0 cm on the plate)

X = distance in which picric acid was spread in X direction.

Then,

$$A = \int_0^X C \cdot 0.03 \cdot 3.175 \, dx$$

or,

$$A = 0.09525 \int_0^X C \, dx \qquad (26_a)$$

Equation 26_a was integrated by a plot of X versus concentration C in gm/L. The values of X were centimeters on the recorder graph. To convert X to centimeters in the extractor, let

recorder graph movement = N mm/min = 60 mm/min

plate movement = S mm/min = 2.5 mm/min

Then to convert centimeters on the recorder graph to centimeters in the extractor multiply by $\frac{1.5S}{N} = \frac{1.5 \times 2.5}{60}$. Therefore in Equation 26_a,

$$A = 0.09525 \times \frac{1.50 \times 2.5}{60} \int_0^X C \, dx$$

or,

$$A = 5.95 \times 10^{-3} \int_0^X C \, dx \qquad (26_b)$$

Figure 25 was a plot of X in centimeters on the recorder graph versus concentration C in grams per liter. The values of C for each

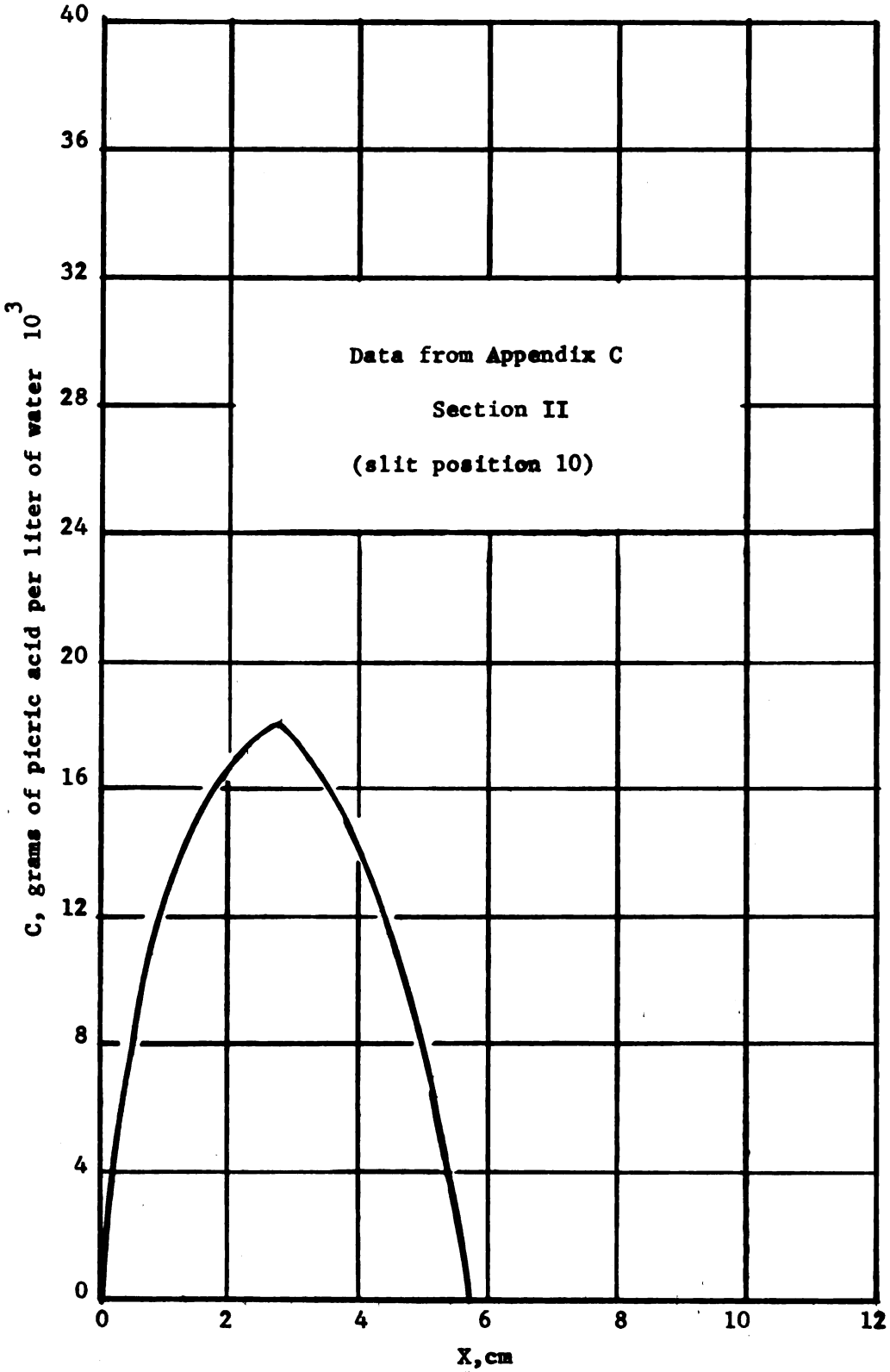


Figure 23 - Typical plot of data in accordance with Equation 26_b.

optical density measurement were read directly from Figure 24. The area under the curve of ten graphs similar to Figure 23 was 0.817×10^{-3} gm-cm/L. Thus, the total amount of acid left behind Drop 60 was,

$$A = 5.95 \times 10^{-3} \times 0.817 \times 10^{-3}$$
$$= 4.86 \times 10^{-3} \text{ grams.}$$

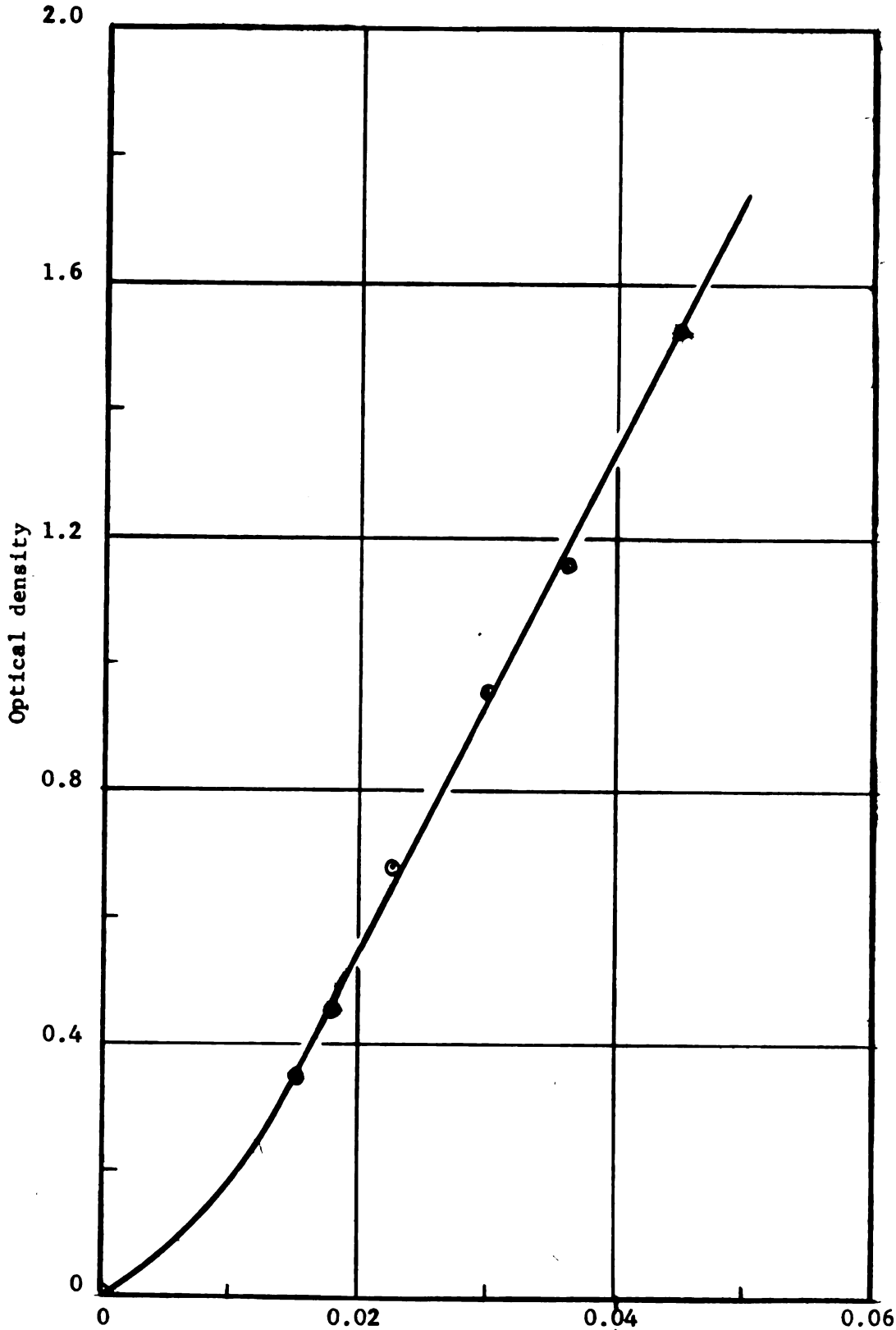


Figure 24 - Plot of optical density on the plate versus concentration of standard solutions of picric acid in water (calibration curve for Drop 60).

APPENDIX B

METHODS OF ANALYSIS AND PREPARATION OF STANDARD SOLUTIONS

The concentrations of picric acid in water and toluene were found by titration with a standard base solution to a faint orange phenolphthalein end point. A Beckman spectrophotometer was used to determine picric acid concentrations below 0.01 grams per liter.

Due to the different range of concentrations of picric acid in water and toluene, three standard solutions of sodium hydroxide with normalities of 0.0029, 0.035, and 0.57 were used. The hydroxide solutions were standardized against a standard solution of 0.02 N sulfuric acid.

Picric acid solutions were prepared from reagent grade crystals and distilled water or reagent grade toluene at room temperature. Solutions of low concentrations were obtained by dilution.

Analysis and Sample Calculation of Water-Picric Acid Solutions

Fifty milliliters of picric acid-water solution were transferred with a 50 ml pipette to a clean 250 ml Erlenmeyer flask. Two to three drops of phenolphthalein were added and the mixture was titrated against the standard base solution from a 50 ml burette. All the titrations of picric acid solutions were carried to a faint orange phenolphthalein end point.

Sample Data

Standard base normality, N_b	00.0029 N
Volume of picric acid-water solution, V_a	50.00 ml
Volume of the standard base consumed to reach the end point	22.30 ml
Volume of the standard base required for the blank test on 50 ml distilled water	00.04 ml
Actual volume of the base needed, by difference, V_b	22.26 ml

Then the concentration of the picric acid solution was,

$$22.26 \text{ ml of NaOH Sol.} \times \frac{0.0029 \text{ eq. of NaOH}}{1000 \text{ ml of NaOH Sol.}} \times \frac{1 \text{ eq. of picric acid}}{1 \text{ eq. of NaOH}} \times \frac{1}{50 \text{ ml of picric acid}} \times \frac{229.11 \text{ gm of picric acid}}{1 \text{ eq. of picric acid}} = 0.2965 \text{ gm/L}$$

Analysis and Sample Calculation of Picric Acid-Toluene Solutions

Ten milliliter portions of toluene-picric acid solutions were taken with a 10 ml pipette for titration against standard base solution. Equal amounts of pure ethyl alcohol were added to the samples before titration. A faint orange change of color was taken as the end point.

Sample Data

Standard base normality, N_b	00.35 N
Volume of the neutral ethyl alcohol	10.00 ml
Volume of the picric acid, V_a	10.00 ml
Volume of the standard base consumed to reach the end point, V_b	16.30 ml
Normality of the sample solution, N_a	?

$$Na = \frac{0.035 \times 16.3}{10} = 0.057 \quad \frac{\text{eq. picric acid}}{\text{liter toluene}}$$

Concentration of the same solution

$$= \frac{0.057 \text{ eq. of picric acid}}{\text{liter toluene}} \times \frac{229.11 \text{ gm picric acid}}{\text{eq. pciric acid}}$$

$$= 13.10 \text{ grams per liter.}$$

The concentrations of picric acid solutions analyzed by titration were checked by a plot of solution optical density versus concentration. Since both the water and toluene solutions obey Beer's Law, the plot resulted in a straight line. The refractive index data presented in Table V and VII were also measured.

TABLE V - Index of Refraction of Picric Acid in Water at 23.6° C

Concentration, gm/L	Refractive Index
0.0000	1.3320
0.0784	1.3320
0.2262	1.3321
0.8860	1.3323
1.6450	1.3325
12.5000	1.3355

TABLE VI - Index of Refraction of Picric Acid in Toluene at 23.6°C

Concentration, gm/L	Refractive Index
0.00	1.4940
12.30	1.4951
23.38	1.4960
34.60	1.4968
114.50	1.5037

APPENDIX C

DATA

I. Data from Optical Density Measurements Made Through the Image of the Drops

H = position of diameter and transmission measurement along the vertical axis of the drop image on the photographic plate, mm (transmission values were obtained starting at the tip of the capillary and going toward the top of the drop)

T = per cent transmission at position H, $d = \log_{10} \left(\frac{1}{T \cdot 10^{-2}}\right)$

d = optical density on the photographic plate

D = diameter of the drop image on the photographic plate, mm

$\Delta C = C_{sw} - C'_{sw}$

C_{sw} = concentration in the water phase corresponding to the transmission T, gm/L

C'_{sw} = concentration in the water phase which blocks out as much light as the toluene drop of concentration C_t and thickness D.

DROP 52 - 1

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.000	00.00
0.1	28.0	0.060	9.72
0.3	30.0	0.090	10.35
0.5	30.0	0.100	10.20
0.7	29.0	0.115	9.88
0.9	28.0	0.120	10.30
1.1	34.0	0.115	7.93
1.3	34.8	0.115	7.46
1.5	35.0	0.105	8.20
1.7	38.0	0.090	7.74
1.9	----	0.070	-----
2.1	----	0.000	00.00

DROP 52 - 2

H,mm	% T	D,mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.000	00.00
0.1	25.0	0.050	9.55
0.3	23.0	0.080	12.58
0.5	24.0	0.100	12.55
0.7	24.2	0.120	12.38
0.9	24.0	0.135	18.00
1.1	24.0	0.155	10.78
1.3	28.0	0.160	7.51
1.5	30.0	0.165	7.10
1.7	33.5	0.165	3.80
1.9	34.0	0.165	3.63
2.1	38.5	0.155	2.48
2.3	40.0	0.150	2.10
2.5	----	0.130	-----
2.7	----	0.090	-----
2.9	-----	0.000	00.00

DROP 52 - 3

H,mm	% T	D,mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	20.0	0.70	13.00
0.3	16.0	1.05	17.56
0.5	16.5	1.35	17.52
0.7	18.5	1.65	15.00
0.9	18.5	1.80	14.05
1.1	18.0	1.90	13.90
1.3	21.5	2.00	9.00
1.5	23.0	2.15	5.80
1.7	23.0	2.20	5.06
1.9	24.5	2.20	3.52
2.1	28.0	2.15	10.75
2.3	34.0	2.00	-----
2.5	35.5	1.80	0.54
2.7	37.0	1.65	1.81
2.9	----	1.30	-----
3.1	----	0.85	-----
3.2	----	0.00	00.00

DROP 52 - 4

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^6$ gm-mm/L
0.0	----	0.00	00.00
0.1	17.0	0.60	13.15
0.3	13.5	1.10	19.90
0.5	13.0	1.70	21.40
0.7	13.0	1.70	21.60
0.9	14.2	1.90	19.20
1.1	14.5	2.10	17.85
1.3	13.8	2.15	18.30
1.5	14.2	2.20	17.40
1.7	16.0	2.25	14.19
1.9	20.0	2.25	8.01
2.1	21.0	2.20	6.82
2.3	22.0	2.10	7.76
2.5	24.5	2.00	7.00
2.7	25.0	1.80	7.74
2.9	28.0	1.65	7.10
3.1	33.5	1.30	7.01
3.3	----	0.90	-----
3.4	----	0.00	0.00

DROP 53 - 1

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	20.0	0.60	11.94
0.3	22.0	1.10	13.75
0.5	23.0	1.35	12.55
0.7	24.0	1.55	10.80
0.9	29.0	1.65	6.44
1.1	30.0	1.70	5.61
1.3	33.0	1.70	3.57
1.5	34.0	1.65	3.46
1.7	38.0	1.50	3.15
1.9	43.0	1.40	1.82
2.1	----	1.10	-----
2.3	----	0.65	-----
2.4	----	0.00	00.00

DROP 53 - 2

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	16.0	0.60	13.60
0.3	17.4	1.15	16.70
0.5	17.5	1.50	16.65
0.7	17.0	1.70	16.30
0.9	20.0	2.05	10.17
1.1	20.0	2.20	8.48
1.3	22.5	2.25	4.95
1.5	24.0	2.30	2.64
1.7	26.0	2.22	2.10
1.9	28.0	2.15	1.07
2.1	3.10	2.00	1.80
2.3	32.0	1.85	2.03
2.5	38.0	1.60	1.92
2.7	----	1.30	-----
2.9	----	0.85	-----
3.0	----	0.00	00.00

DROP 53 - 3

H,mm	% T	D,mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	18.0	0.50	11.40
0.3	17.8	1.10	16.30
0.5	17.8	1.55	16.00
0.7	19.0	1.85	13.10
0.9	20.0	2.10	9.58
1.1	19.0	2.30	8.96
1.3	19.0	2.40	7.93
1.5	19.5	2.50	5.75
1.7	19.5	2.50	5.75
1.9	19.5	2.55	5.10
2.1	21.0	2.50	3.50
2.3	22.0	2.48	2.72
2.5	23.0	2.35	3.29
2.7	27.0	2.20	1.32
2.9	31.0	2.00	1.00
3.1	36.0	1.60	-----
3.3	38.0	1.20	-----
3.5	----	0.00	00.00

DROP 53 - 4

H,mm	% T	D,mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.00	----	0.00	00.00
0.10	16.5	0.80	15.50
0.30	16.0	1.30	18.02
0.50	16.2	1.70	17.85
0.70	16.0	2.10	15.35
0.90	16.0	2.30	13.10
1.10	16.0	2.40	12.70
1.30	17.8	2.60	7.15
1.50	18.4	2.70	4.86
1.70	18.4	2.80	3.78
1.90	19.0	2.80	2.66
2.10	19.0	2.85	1.99
2.30	19.0	2.85	1.99
2.50	19.0	2.70	3.78
2.70	20.0	2.55	1.78
2.90	27.5	2.15	1.72
3.10	29.0	2.10	0.84
3.30	----	1.70	-----
3.50	----	1.15	-----
3.65	----	0.00	00.00

DROP 53 - 5

H,mm	% T	D,mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	21.5	0.60	11.50
0.3	20.0	1.25	14.70
0.5	19.0	1.60	14.72
0.7	17.8	1.90	14.25
0.9	17.8	2.20	11.65
1.1	16.2	2.40	12.50
1.3	15.0	2.55	12.74
1.5	15.0	2.70	11.32
1.7	14.0	2.75	13.20
1.9	14.2	2.90	11.30
2.1	14.8	2.95	9.15
2.3	14.8	2.95	9.15
2.5	16.0	2.95	6.80
2.7	17.0	3.00	3.90
2.9	19.0	2.80	2.94
3.1	20.0	2.70	2.05
3.3	22.0	2.65	-----
3.5	24.0	2.40	1.32
3.7	30.0	2.10	0.42
3.9	----	1.65	-----
4.1	----	----	-----
4.3	----	0.00	00.00

DROP 35 - 1

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	18.5	1.00	15.80
0.3	18.0	1.60	16.15
0.5	18.0	2.00	13.80
0.7	18.0	2.20	12.10
0.9	19.0	2.40	8.64
1.1	17.2	2.48	9.90
1.3	18.0	2.50	8.75
1.5	20.0	2.40	7.20
1.7	22.0	2.30	5.29
1.9	23.8	2.10	6.30
2.1	27.0	1.80	6.48
2.3	----	1.30	-----
2.5	----	0.00	00.00

DROP 35 - 2

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	17.5	1.00	16.30
0.3	17.3	1.96	14.90
0.5	17.2	2.20	13.20
0.7	16.0	2.60	10.80
0.9	15.8	2.85	8.68
1.1	15.8	3.00	7.05
1.3	15.8	3.10	6.04
1.5	15.8	3.15	5.50
1.7	16.5	3.15	4.10
1.9	17.0	3.10	3.72
2.1	18.0	3.00	2.70
2.3	19.0	2.85	2.85
2.5	21.5	2.60	2.34
2.7	26.5	2.20	1.98
2.9	32.0	1.96	1.57
3.1	----	1.00	-----
3.2	----	0.00	00.00

DROP 35 - 3

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.000
0.1	15.5	0.70	15.500
0.3	15.5	1.40	19.300
0.5	15.5	1.90	18.250
0.7	16.5	2.20	14.100
0.9	16.5	2.60	10.000
1.1	13.5	2.80	15.000
1.3	14.0	3.00	11.400
1.5	13.0	3.20	12.500
1.7	13.0	3.40	10.530
1.9	13.5	3.46	9.700
2.1	15.0	3.50	4.200
2.3	14.0	3.50	7.000
2.5	14.8	3.55	3.900
2.7	15.0	3.46	4.850
2.9	15.0	3.40	5.100
3.1	17.0	3.20	2.880
3.3	18.5	3.00	1.800
3.5	19.5	2.90	1.450
3.7	22.0	2.65	0.795
3.9	----	2.25	-----
4.1	----	1.70	-----
4.2	----	0.00	00.000

DROP 35 - 4

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.000
0.1	13.0	1.10	20.700
0.3	11.0	2.00	24.800
0.5	11.0	2.60	22.900
0.7	11.5	3.00	18.300
0.9	12.0	3.30	14.850
1.1	10.0	3.50	20.300
1.3	12.5	3.60	10.420
1.5	13.0	3.70	7.590
1.7	12.2	3.80	9.500
1.9	11.2	3.85	13.100
2.1	13.0	3.90	6.160
2.3	13.0	3.80	6.850
2.5	13.5	3.70	5.740
2.7	13.0	3.60	8.640
2.9	17.0	3.50	------
3.1	20.0	3.30	------
3.3	21.0	2.80	0.280
3.5	21.5	2.40	5.510
3.7	----	1.80	------
3.9	----	0.00	00.000

DROP 37 - 1

H,mm	% T	D,mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.00	----	0.00	00.00
0.10	19.0	0.60	12.48
0.30	19.0	1.20	15.80
0.50	19.5	1.60	14.55
0.70	18.0	1.80	15.10
0.90	17.4	2.05	14.25
1.10	18.0	2.20	12.10
1.30	18.0	2.20	12.10
1.50	21.0	2.25	7.42
1.70	22.0	2.22	6.76
1.90	22.0	2.00	9.00
2.30	25.0	1.80	8.45
2.50	----	1.35	-----
2.75	----	0.00	00.00

DROP 37 - 2

H,mm	% T	D,mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	17.0	0.70	14.56
0.3	18.0	1.25	16.78
0.5	18.0	1.70	15.80
0.7	18.0	2.10	13.00
0.9	18.0	2.30	11.05
1.1	15.5	2.50	13.50
1.3	15.5	2.68	12.05
1.5	17.0	2.75	7.70
1.7	17.0	2.80	7.00
1.9	20.0	2.85	1.57
2.1	21.0	2.70	1.35
2.3	21.0	2.70	1.35
2.5	21.0	2.50	4.00
2.7	22.0	2.30	5.75
2.9	24.0	2.20	5.06
3.1	----	1.70	-----
3.3	----	1.25	-----
3.4	----	0.00	00.00

DROP 37 - 3

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.00	----	0.00	00.00
0.10	16.0	0.70	15.00
0.30	15.0	1.25	19.25
0.50	15.0	1.70	19.20
0.70	15.0	2.00	17.80
0.90	13.0	2.20	20.00
1.10	13.0	2.55	17.32
1.30	12.0	2.75	18.70
1.50	13.0	2.95	14.16
1.70	13.0	3.00	10.80
1.90	13.5	3.10	11.07
2.10	15.0	3.10	8.06
2.30	15.5	3.10	7.75
2.50	15.0	2.95	9.45
2.70	16.0	2.90	7.81
2.90	16.5	2.70	8.90
3.10	18.0	2.45	9.55
3.30	----	2.15	-----
3.50	----	1.75	-----
3.76	-----	0.00	00.00

DROP 37 - 4

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	16.0	0.60	13.70
0.3	15.0	1.40	19.50
0.5	15.0	1.80	18.70
0.7	13.0	2.10	20.60
0.9	11.0	2.40	23.50
1.1	11.0	2.70	21.60
1.3	12.5	2.95	15.65
1.5	11.0	3.05	19.55
1.7	12.5	3.15	14.18
1.9	13.0	3.20	12.50
2.1	13.0	3.20	12.50
2.3	14.0	3.15	9.75
2.5	14.0	3.15	9.75
2.7	15.0	3.10	8.05
2.9	16.0	2.95	7.08
3.1	16.0	2.80	8.67
3.3	19.0	2.55	6.12
3.5	----	2.30	-----
3.7	----	1.95	-----
3.9	----	1.50	-----
4.1	----	0.00	00.00

DROP 37 - 5

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	17.0	0.60	13.30
0.3	14.0	1.10	19.60
0.5	13.0	1.60	21.90
0.7	12.5	1.90	22.40
0.9	10.0	2.30	21.60
1.1	11.0	2.60	22.20
1.3	11.0	2.90	20.60
1.5	11.0	3.10	19.20
1.7	11.0	3.35	17.75
1.9	11.0	3.45	17.25
2.1	10.0	3.65	18.60
2.3	10.0	3.65	18.60
2.5	10.5	3.55	18.10
2.7	11.0	3.55	16.30
2.9	11.0	3.50	16.80
3.1	12.0	3.25	14.95
3.3	14.0	3.20	9.28
3.5	15.0	2.95	9.45
3.7	17.0	2.70	8.10
3.9	19.0	2.35	8.50
4.1	----	2.00	-----
4.3	----	1.35	-----
4.4	----	0.00	00.00

DROP 38 - 1

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	22.0	0.60	11.64
0.3	21.0	1.30	14.30
0.5	21.0	1.70	12.75
0.7	19.0	1.90	13.10
0.9	18.0	2.15	12.68
1.1	17.0	2.30	12.40
1.3	16.5	2.30	13.60
1.5	17.5	2.35	10.82
1.7	18.0	2.30	11.00
1.9	18.5	2.20	11.20
2.1	19.0	2.10	11.30
2.3	22.0	1.90	10.42
2.5	----	1.60	-----
2.7	----	1.20	-----
2.9	----	0.00	00.00

DROP 38 - 2

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	23.0	0.80	12.90
0.3	22.5	1.30	13.50
0.5	22.0	1.80	13.50
0.7	20.8	2.00	13.40
0.9	16.5	2.30	13.30
1.1	15.5	2.50	12.80
1.3	14.8	2.70	12.40
1.5	15.0	2.75	11.55
1.7	15.0	2.75	11.55
1.9	16.0	2.75	9.35
2.1	16.5	2.70	8.90
2.3	17.0	2.60	9.23
2.5	18.0	2.40	10.20
2.7	----	2.20	-----
2.9	----	1.90	-----
3.1	----	1.60	-----
3.3	----	0.00	00.00

DROP 38 - 3

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	22.0	1.00	15.30
0.3	19.0	1.50	15.30
0.5	16.5	1.90	16.32
0.7	15.0	2.30	15.63
0.9	13.5	2.50	15.25
1.1	13.0	2.70	16.20
1.3	13.0	2.90	14.80
1.5	13.0	3.00	13.80
1.7	13.0	3.05	13.40
1.9	12.8	3.15	13.20
2.1	13.5	3.15	9.45
2.3	13.5	3.00	8.00
2.5	13.5	3.00	10.80
2.7	15.0	2.85	10.55
2.9	16.0	2.65	10.32
3.1	17.0	2.35	12.00
3.3	----	2.00	-----
3.5	----	1.50	-----
3.7	----	0.00	00.00

DROP 38 - 4

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	16.0	0.50	18.90
0.3	15.5	1.10	19.50
0.5	15.5	1.55	19.20
0.7	14.5	1.90	17.57
0.9	14.0	2.25	14.40
1.1	14.0	2.60	18.20
1.3	12.0	2.80	19.80
1.5	11.0	3.00	18.90
1.7	11.0	3.20	21.10
1.9	10.0	3.35	20.70
2.1	10.2	3.46	16.30
2.3	11.0	3.55	19.40
2.5	10.0	3.60	19.40
2.7	10.0	3.60	16.30
2.9	11.0	3.55	15.53
3.1	11.5	3.45	11.08
3.3	13.0	3.35	9.76
3.5	14.0	3.15	10.90
3.7	15.0	2.80	10.80
3.9	16.0	2.60	-----
4.1	----	2.20	-----
4.3	----	1.75	-----
4.5	----	0.00	00.00

DROP 38 - 5

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	14.5	1.20	19.90
0.3	11.0	2.05	27.00
0.5	10.0	2.65	26.00
0.7	10.5	2.00	22.80
0.9	10.0	3.35	22.80
1.1	9.5	3.60	23.00
1.3	9.4	3.70	24.80
1.5	9.6	3.80	22.00
1.7	10.0	3.90	19.10
1.9	10.5	3.95	16.60
2.1	10.0	3.95	18.55
2.3	10.5	3.90	17.20
2.5	10.0	3.80	20.10
2.7	11.0	3.70	16.80
2.9	11.0	3.60	17.65
3.1	11.0	3.35	19.40
3.3	11.0	3.00	-----
3.5	11.5	2.65	-----
3.7	----	2.05	-----
3.9	----	1.20	-----
4.0	----	0.00	00.00

DROP 56 - 1

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	28.0	0.70	10.10
0.3	25.0	1.30	10.90
0.5	22.0	1.70	10.90
0.7	20.0	1.90	11.00
0.9	19.2	2.05	10.65
1.1	18.2	2.20	10.35
1.3	18.0	2.30	9.44
1.5	18.0	2.30	9.44
1.7	20.0	2.20	7.90
1.9	24.0	2.05	5.34
2.1	25.0	1.80	6.84
2.3	----	1.40	-----
2.5	----	0.93	-----
2.6	----	0.00	00.00

DROP 56 - 2

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	20.0	0.80	13.52
0.3	18.0	1.40	15.75
0.5	17.8	1.95	13.10
0.7	16.5	2.20	12.75
0.9	14.2	2.55	13.50
1.1	14.2	2.80	11.50
1.3	14.2	2.84	11.10
1.5	14.0	2.90	11.00
1.7	13.8	2.95	10.60
1.9	15.2	2.80	9.38
2.1	17.5	2.65	6.10
2.3	18.5	2.45	7.10
2.5	19.0	2.28	8.65
2.7	22.0	1.90	8.92
2.9	----	1.40	-----
3.0	----	0.00	00.00

DROP 56 - 3

H,mm	% T	D,mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	19.0	0.80	13.90
0.3	18.0	1.40	15.75
0.5	16.5	1.80	15.70
0.7	14.8	2.20	16.10
0.9	12.8	2.50	16.50
1.1	12.2	2.80	16.10
1.3	12.2	3.00	14.85
15.	12.2	3.14	13.35
1.7	11.8	3.20	14.10
1.9	11.8	3.25	13.30
2.1	11.8	3.25	13.30
2.3	12.5	3.24	12.00
2.5	12.8	3.20	11.85
2.7	13.0	3.05	11.90
2.9	14.5	3.10	8.10
3.1	15.0	2.70	10.52
3.3	15.0	2.50	12.50
3.5	----	2.15	-----
3.7	----	1.50	-----
3.9	----	0.00	00.00

DROP 56 - 4

H,mm	% T	D,mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	22.8	0.90	12.70
0.3	16.0	1.35	17.52
0.5	12.2	1.90	26.50
0.7	12.8	2.30	17.70
0.9	10.8	2.60	20.80
1.1	10.8	2.85	19.40
1.3	10.0	3.05	21.00
1.5	10.0	3.20	20.10
1.7	10.0	3.40	19.00
1.9	10.0	3.53	18.00
2.1	10.5	3.58	15.40
2.3	10.0	3.60	17.65
2.5	10.0	3.60	17.65
2.7	10.0	3.58	14.30
2.9	11.5	3.45	13.45
3.1	12.0	3.37	12.47
3.3	12.2	3.23	13.25
3.5	12.8	3.00	12.30
3.7	13.5	2.80	12.60
3.9	14.5	2.40	13.70
4.1	15.8	2.00	13.40
4.3	----	1.10	-----
4.4	----	0.00	00.00

DROP 56 - 5

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	13.0	1.00	18.80
0.3	12.0	1.80	22.30
0.5	12.0	2.25	20.50
0.7	12.5	2.70	15.67
0.9	10.5	3.05	19.52
1.1	10.0	3.34	19.00
1.3	9.0	3.60	22.00
1.5	9.0	3.75	21.40
1.7	9.0	3.85	20.40
1.9	8.5	3.95	20.50
2.1	9.0	3.95	19.35
2.3	9.0	3.85	20.40
2.5	9.2	3.80	20.15
2.7	9.8	3.70	17.00
2.9	10.0	3.60	17.30
3.1	11.0	3.40	15.30
3.3	11.0	3.15	17.00
3.5	10.5	2.80	21.00
3.7	12.0	2.35	20.00
3.9	14.5	1.70	18.70
4.0	----	0.00	00.00

DROP 60*

H, mm	% T	D, mm	$D \cdot \Delta C \cdot 10^3$ gm-mm/L
0.0	----	0.00	00.00
0.1	22.5	1.00	9.80
0.3	21.5	1.60	12.00
0.5	20.0	2.00	13.00
0.7	21.5	2.20	11.00
0.9	21.5	2.30	10.58
1.1	19.0	2.40	11.00
1.3	19.0	2.40	13.42
1.5	18.0	2.30	15.28
1.7	21.0	2.20	13.20
1.9	22.0	2.00	11.40
2.1	24.0	1.80	10.25
2.3	24.5	1.30	10.00
2.5	----	0.00	00.00

*Calibration data on page 94
Concentration of drop solution, 102 gm/L
Conversion factor, 1.5 cm in the extractor per cm on the plate

II. Data Obtained for Drop 60 After it was Withdrawn into the Capillary

x = distance along the image of the extracted acid in X direction (x was measured in centimeters on the recorder graph)

%T = the values of per cent transmission at point x, taken from recorder graph paper

Positions 1 through 10 refer to the location of the densitometer slit with respect to the image in Y direction.

Position 1

x,cm	% T
0.00	100
0.20	90
0.30	70
0.47	50
1.00	30
1.20	28
1.50	30
1.70	50
1.75	70
1.95	90
2.10	100

Position 2

x,cm	% T
0.00	100
0.50	90
1.00	70
1.10	50
1.40	30
1.80	26
2.20	30
2.40	50
2.60	70
3.40	90
3.80	100

Position 3

x,cm	% T
0.00	100
0.35	90
0.50	70
0.70	50
1.50	30
2.10	26
2.70	30
2.90	50
3.50	70
3.75	90
4.40	100

Position 4

x,cm	% T
0.00	100
0.20	90
0.40	70
0.50	50
1.40	30
2.20	26
2.80	30
3.60	50
3.70	70
3.80	90
4.20	100

Position 5

x,cm	% T
0.00	100
0.35	90
0.50	70
0.60	50
0.80	30
2.20	25
3.70	30
3.80	50
3.90	70
4.10	90
4.40	100

Position 6

x,cm	% T
0.00	100
0.20	90
0.40	70
0.50	50
0.75	30
2.50	24
4.10	30
5.20	50
5.65	70
6.10	90
6.30	100

Position 7

x,cm	% T
0.00	100
0.50	90
0.80	70
1.00	50
2.30	30
5.00	24
7.60	30
8.00	50
8.20	70
8.40	90
8.50	100

Position 8

x,cm	% T
0.00	100
0.30	90
0.70	70
1.10	50
1.70	30
4.00	24
6.10	30
6.70	50
7.00	70
7.70	90
8.40	100

Position 9

x,cm	% T
0.00	100
0.20	90
0.22	70
0.50	50
1.20	30
3.00	25
4.60	30
5.40	50
5.70	70
6.10	90
6.50	100

Position 10

x,cm	% T
0.00	100
0.10	90
0.70	70
1.15	50
2.70	34
4.10	50
4.90	70
5.30	90
5.70	100

III - Optical Density Data of Standard Solutions from Photographic Plates for a 1.25 inch Absorption Cell

Calibration Data for Runs 76 Through 80

Conc. of Picric Acid, gm/L*	Per Cent Transmission
0.0000w	100.0
0.0050w	90.0
0.0235w	45.0
0.0325w	28.0
0.0380w	19.0
0.0478w	11.0
0.0724w	2.2
0.0814w	0.8
0.00t	100.0
7.54t	44.0
13.10t	28.0
22.38t	18.0
33.00t	10.5
62.30t	4.0

Calibration Data for Drops 52, 53, and 56

Conc. of Picric Acid, gm/L*	Per Cent Transmission
0.0000w	100
0.0145w	60
0.0242w	34
0.0341w	14
0.0528w	3
0.00t	100.0
7.54t	35.5
13.10t	21.0
22.38t	9.5
33.00t	4.2
62.30t	1.0

Calibration Data for Drops 35, 37, and 38

Conc. of Picric Acid, gm/L*	Per Cent Transmission
0.0000w	100.0
0.0050w	85.5
0.0235w	37.0
0.0325w	16.0
0.0380w	11.0
0.0478w	5.0
0.0724w	0.8
0.00t	100.0
7.54t	39.0
13.10t	21.0
33.00t	10.5
62.30t	1.5

Calibration Data for Drop 60

Conc. of Picric Acid, gm/L*	Per Cent Transmission
0.0000w	100
0.0150w	45
0.0180w	34
0.0225w	21
0.0300w	11
0.0360w	7
0.0448w	3
0.00t	100.0
9.75t	34.0
29.40t	12.0
46.80t	3.5
76.80t	-----

*w refers to water phase
t refers to toluene phase

IV - Optical Density Data Obtained from Spectrophotometer for Picric Acid Solutions as Presented in Figures 3 and 4

Concentration of Picric Acid in Water, gm/L	Per Cent Transmission	Concentration of Picric Acid in Toluene, gm/L	Per Cent Transmission
0.000	100.0	0.00	100.0
0.0208	98.0	9.75	77.5
0.1095	77.5	29.40	52.5
0.8860	12.5	46.80	37.0
12.2500	4.0	76.8	19.0

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