

DESIGN, CONSTRUCTION, AND OPERATION OF A  
PISTON TYPE SAMPLER FOR A LIQUID-LIQUID  
EXTRACTION SPRAY COLUMN

by

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B.A.Sc., University of British Columbia, 1958

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF  
THE REQUIREMENTS FOR THE DEGREE OF MASTER  
OF APPLIED SCIENCE

in the Department of

CHEMICAL ENGINEERING

We accept this thesis as conforming  
to the required standard

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## ABSTRACT

A piston type of sampler was designed and constructed to sample the dispersed phase of a spray liquid-liquid extraction tower. The aim was to check a previous method of sampling the dispersed phase. This method depended on the use of a long probe which descended into the column from above and through which samples were removed by suction. Calculated values of the dispersed phase concentration using the piston type sampler were found to be generally lower than the corresponding concentrations using the dispersed phase probe.

The system studied was methyl isobutyl ketone (the dispersed phase)-acetic acid (the solute) - water (the continuous phase). The solute was transferred from the aqueous phase, which was saturated with methyl isobutyl ketone, to the organic phase, which was saturated with water. Mass transfer data were gathered for this system in a 1.5-in. I.D. column which was approximately 7.3-ft. in height.

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## ACKNOWLEDGEMENTS

The author would like to express sincere thanks to Dr. S.D. Cavers for the assistance, and helpful criticisms offered throughout the course of this project.

Thanks are also due to Dr. J.D.H. Strickland, Senior Scientist, of the Pacific Oceanographic Group, Nanaimo, B.C., for the use of his salinometer.

Appreciation is expressed to the National Research Council of Canada for financial assistance.

## INTRODUCTION

In continuous countercurrent solvent extraction columns, many attempts have been made to obtain mass-transfer coefficients by measuring concentration distributions within an extractor (1,2,3,4,5,6,7). This approach should be more accurate than the alternative of using a logarithmic mean driving force computed only from the concentrations of the incoming and outgoing streams.

Cavers and Ewanchyna (2), and Choudhury (1) measured concentration profiles by internal sampling of both the continuous and dispersed phases. In their work the authors obtained samples by means of long, stainless steel tubes which descended into the column to any desired height (1a). Figure 1 is a photograph of a section of the column showing Choudhury's sampling tubes in operation. Gier and Hougen (3) also measured concentration profiles for both phases.

Cavers and Ewanchyna (2) and Choudhury (1) reported concentration profiles which showed a considerable end effect at the continuous phase inlet to the column under certain operating conditions. Other workers (4,5,6,7) who sampled only the continuous phase of spray columns, also reported a

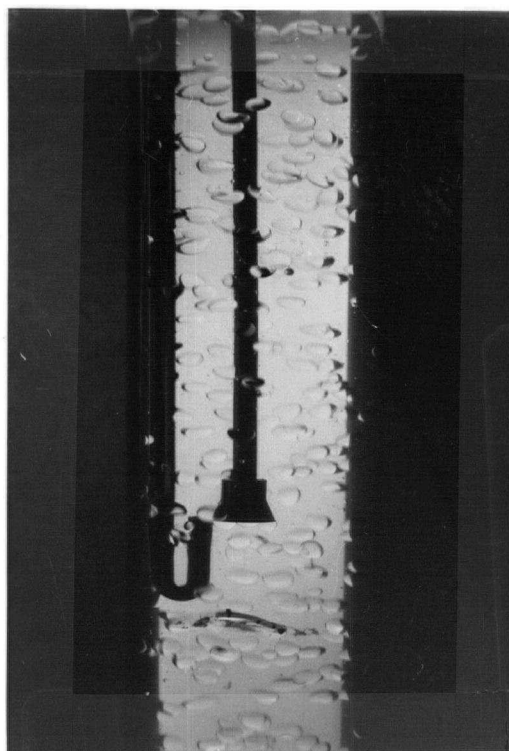


Figure 1. Sampling Tubes in Operation

considerable end effect at the continuous phase inlet to the column. This end effect is manifested by the continuous phase concentration profile showing a discontinuity at this point. From the point of view of the continuous phase an unexpectedly large portion of the total extraction appears to take place when the drops of the dispersed phase coalesce at the interface at the top of the column. Geankoplis and Hixson (4) attributed this end effect to turbulence caused by the coalescence of the drops, but suggested that changes in interfacial tension might also be important.

Newman (8) suggested that the end effect found by Geankoplis et al at the continuous phase inlet was the result of vertical mixing of the continuous phase due to the movement of the drops.

Cavers and Ewanchyna (2), upon obtaining concentration profiles for each phase, noted discontinuities in both profiles at the interface. For transfer of acetic acid from the continuous aqueous phase to the dispersed ketone phase the discontinuity in the water concentration profile could be broken into two parts: one representing the effects of drop agitation at the interface, and the other the effect of back-mixing in the aqueous phase. The discontinuity in the ketone phase concentration profile was due only to the agitation effect (2).

Choudhury, in justifying his sampling technique (1b), suggests that the rate of sampling may be an important factor to be considered in interpreting the results obtained. Low sampling rates tend to produce drop coalescence at the dispersed phase sampling probe entrance, which could influence the concentration of the drops by a similar phenomenon to that just described as taking place at the column interface. High sampling rates, on the other hand, would cause disturbances in the steady state operation of the column at the point of sampling, and, in turn, influence the concentration of both phases throughout the column.

While removing dispersed phase samples at low sampling rates, Choudhury noted that the ketone drops did not rise immediately up the dispersed phase probe. The drops lingered at the entrance for a short time (see Figure 1), coalesced, and then passed up through the probe into the sampling flasks. It was suggested that this short residence time and coalescence of the ketone drops at the probe entrance would allow an extra amount of acetic acid to be transferred into the ketone drops and therefore produce erroneously high results for dispersed phase concentrations.

Under higher sampling rates this lingering and coalescence of ketone drops at the probe entrance was not observed. Variations in sampling rates produced no appreciable changes in the measured probe concentrations of either phase (1c)\*.

The present investigation was designed to give another independent method of sampling the dispersed phase in order to check the probe method. The system studied was acetic acid-methyl isobutyl ketone-water. Much of the apparatus was the same as that used by Choudhury. However, a piston type sampling device was designed and constructed to remove quickly a sample of both phases from the extraction column which had been operating under steady state conditions. Although mass transfer between the dispersed phase and the continuous phase continued after removal of the sample from the column by means of this piston, initial ketone concentrations could be

\* As pointed out later the conditions under which these sampling rate experiments were made were far from ideal since at the location studied the phases were near equilibrium.



calculated. These have been compared with the concentrations of ketone samples which were taken with the ketone phase probe at the same location and under the same operating conditions as applied when the piston sample was taken.

Numerous cross-sectional concentration traverses of the continuous water phase were made using hypodermic syringes, the needles of which entered the column through the asbestos gaskets at glass to glass flanges.

Experimental work was limited because of construction delays. However a sufficient amount of data was collected to direct future studies.

## EXPERIMENTAL METHODS

### Apparatus

#### Flow Outline

A schematic flow diagram of the apparatus is shown in Figure 2, which is a slight modification of that given by Choudhury (1d). A key to Figure 2 is presented in Table I. The detailed description of much of the apparatus has been presented by Choudhury (1) and others and will not be repeated here.

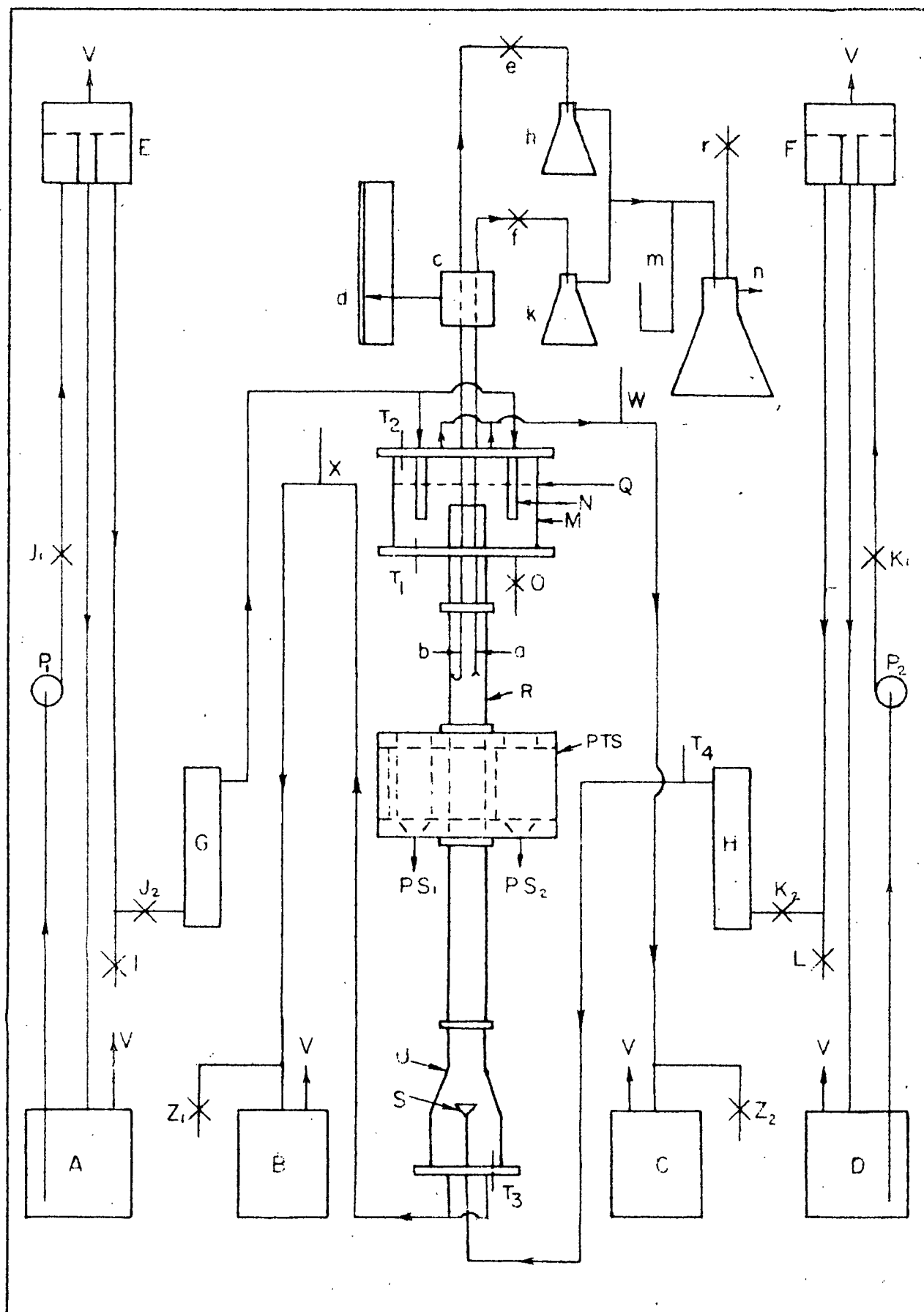


FIGURE 2. SCHEMATIC FLOW DIAGRAM

Table I

## Key to Figure 2

A - Continuous phase feed tank  
 B - Continuous phase receiver and storage tank  
 C - Dispersed phase receiver and storage tank  
 D - Dispersed phase feed tank  
 E - Continuous phase constant head tank  
 F - Dispersed phase constant head tank  
 G - Continuous phase rotameter  
 H - Dispersed phase rotameter  
 I - Continuous phase inlet sample valve  
 J<sub>1</sub>, J<sub>2</sub> - Continuous phase flow rate control valves  
 K<sub>1</sub>, K<sub>2</sub> - Dispersed phase flow rate control valves  
 L<sub>1</sub> - Dispersed phase inlet sample valve  
 M - 6 inch I.D. top end section  
 N - Continuous phase inlet pipes  
 O - Drain valve for top end section  
 P<sub>1</sub>, P<sub>2</sub> - Centrifugal feed pumps for continuous and dispersed phases respectively  
 Q - Level of Interface  
 R - Column proper 1½ inch I.D.  
 S - Dispersed phase nozzle  
 T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub>, T<sub>4</sub> - Thermometers  
 U - Bottom end section  
 V - Vent to atmosphere  
 W - Pressure equalizing vent  
 X - Control for interface level  
 PS<sub>1</sub>, PS<sub>2</sub> - Piston samples  
 PTS - Piston Type Sampler  
 m - Mercury manometer  
 h, k, - Sampling bottles  
 n - Aspirator  
 a, b, - Stainless steel sampling tubes  
 e, f, - Sample valves  
 c - Wooden block to which sampling tubes are attached  
 d - Scale

The centrifugal feed pumps  $P_1$ , and  $P_2$ , supply water and ketone to constant head tanks which in turn supply these phases to rotameters feeding the column. Methyl isobutyl ketone (ketone) is pumped from the aluminum storage tank (1f), D in Figure 2, to a constant head tank (8), F in Figure 2. Part of the organic phase overflows back to the storage tank, D, while the desired amount flows by gravity through rotameter, H, and then to the dispersed phase nozzle (1f), S in Figure 2. The nozzle disperses the ketone phase into drops which rise countercurrently to the descending water phase. The ketone drops eventually coalesce in the upper expanded section (8), M in Figure 2, and are removed from the top of the column to the storage tank, C.

The aqueous phase is pumped from storage tank, A, to the constant head tank, E, where part returns to the storage tank, A, and the desired amount flows through rotameter, G. The water phase discharges through two 1/8-inch Schedule 40 Type 304 stainless steel pipes, N, into the bottom of the expanded section, M. It then flows through the column, R, and up to the interface controller (1f), X in Figure 2. By varying the height of the interface controller the interface, Q, in the expanded section, M, can be accurately controlled. The aqueous phase passes from the interface controller arrangement to storage tank, B.

Calibration curves for the rotameters, and equilibrium relationships were obtained from Choudhury's work (1h).

The sampling tubes (1i), a and b in Figure 2, were clamped to a wooden block and could be adjusted to any desired height with respect to the nozzle tips. Sampling rates were controlled by a vacuum arrangement and by glass capillary tubes between the sample valves, e and f, and the sample collectors, h and k, respectively in Figure 2. Vacuum was created in the water aspirator, n, and controlled by an air vent leading from the atmosphere to the bottom of a mercury column the height of which could be varied. The sampling apparatus was connected above the surface of the mercury, and as long as air bubbled through the mercury from the vent the pressure in the sampling apparatus was approximately constant and equal to that exerted by the column of mercury. This arrangement is shown schematically as valve r in Figure 2. By controlling the vacuum and by use of the capillaries the sampling rates of each phase could be adjusted to any desired value. The piston type sampler, PTS in Figure 2, was flanged to the glass column by means of standard Corning Type I flanges and hard asbestos gaskets. In all cases the piston axis was 1.59-ft. above the nozzle tips. Piston samples were collected, at points  $PS_1$  and  $PS_2$  in Figure 2, into specially designed collection flasks by slamming the piston from one side to the other of its travel.



The design of the piston was such that the operation of the column was not interrupted.

### Piston

Figure 3, is a drawing showing the piston used in sampling. The piston was machined from standard brass tubing,  $3\frac{3}{4}$ -in. I.D. by  $1/8$ -in. wall thickness. One quarter inch hard brass plates were recessed to fit and soldered to the ends of the piston. Approximately  $1/32$ -in. was then machined off the O.D. of the piston.

Two holes were then bored through the piston walls perpendicular to its longitudinal axis. See Figure 4.

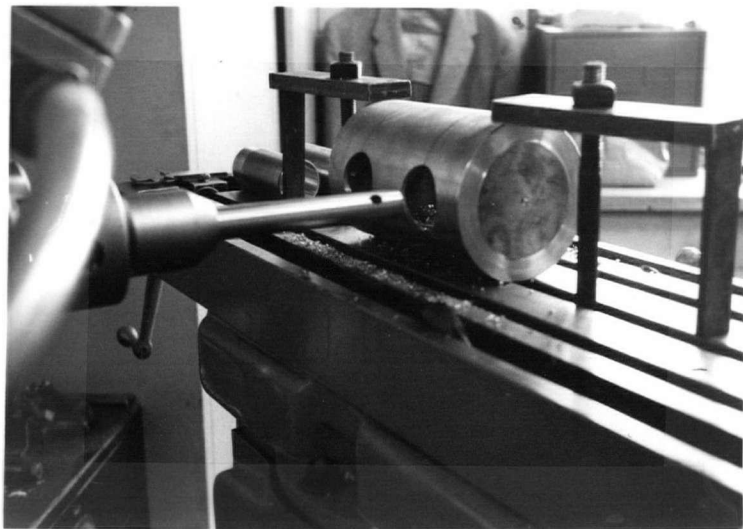


Figure 4. Boring Holes Through Piston Walls

The diameter of these holes was such that two standard brass pipes,  $1\frac{1}{4}$ -in. I.D. by  $\frac{3}{16}$ -in. wall thickness, could be force-fitted into position. These smaller brass pipes were also soldered to the piston, and, since their length exceeded the O.D. of the piston, they had to be machined down to this dimension. These two brass pipes were then bored to  $1\frac{1}{2}$ -in. I.D.

Next a coating of a 50-50 mixture of lead and tin was applied to the piston. See Figure 5.



Figure 5. Coating Piston With Solder

The coating was allowed to cool completely and then machined to fit the piston block within a tolerance of 0.001 inches. See Figure 6.



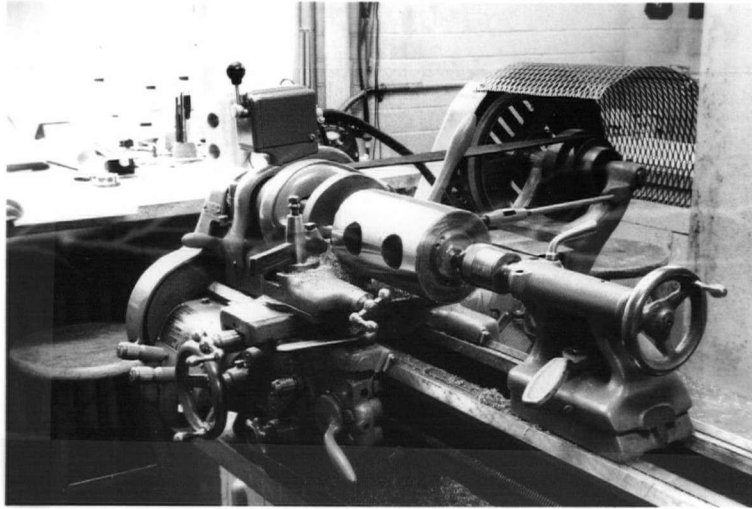


Figure 6. Machining Solder Surface of Piston

The piston is moved by means of a hand driven rod which is flanged to the piston at one end. The driving rod is fixed to the flange by means of two  $\frac{1}{4}$ -in. Allen head set screws.

The piston described above is just one piston in a series of attempts to arrive at a combination of piston and piston block dimensions that would allow easy movement and no leakage. The problems involved will be covered in detail in the next section in which the piston block is described.

## Piston Block

The piston block was pressure cast from phosphor bronze by Mainland Foundry, Vancouver, B.C. It is shown in Figure 7. The hole for the piston was drilled in the Chemical Engineering Shop at the University of British Columbia. A photograph of the block as the I.D. was being bored is shown in Figure 8. Figure 9 is a photograph after the boring had been completed.

Figure 10 is a photograph of the block having some of its dimensions reduced to decrease its weight.

After the I.D. was machined through a slight taper was found to exist from one end to the other. The piston described previously was set into the block, the block assembled into the spray extraction column, and a six foot head of water was applied by filling the column to a height of six feet above the block. The piston was found to move freely in the block but leakages as high as 25 mls./min. were encountered.

It was felt that the existing taper was the cause of the leakage and that this taper should be corrected. The cylinder was then sent out to be rebored by Canadian Car Pacific Ltd., Vancouver, B.C. Following the reboring a coating of chromium was applied electrolytically to the cylinder, but only to the inside surface, by Hudson Plating,

Material: Phosphor Bronze

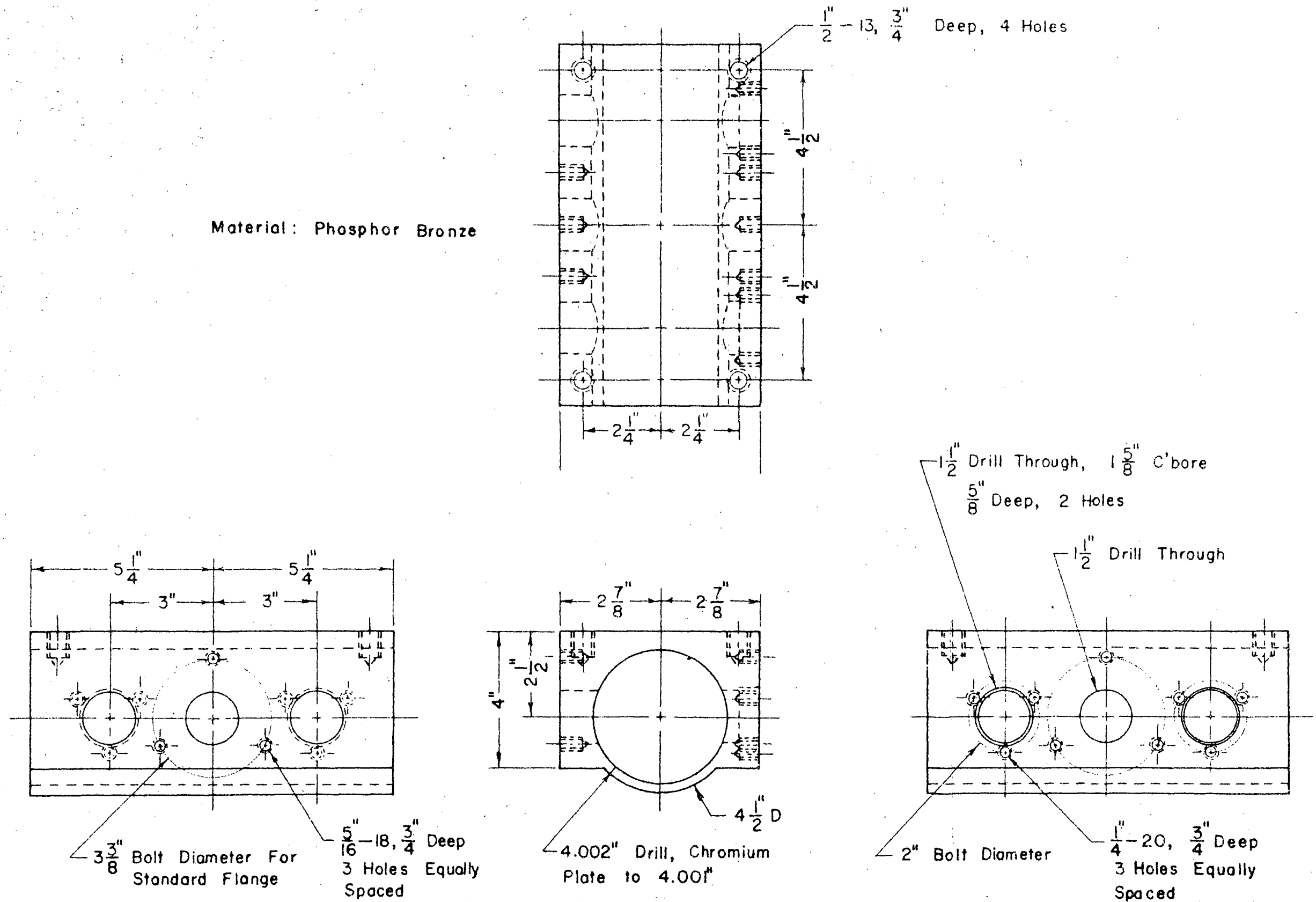


FIGURE 7. PISTON BLOCK

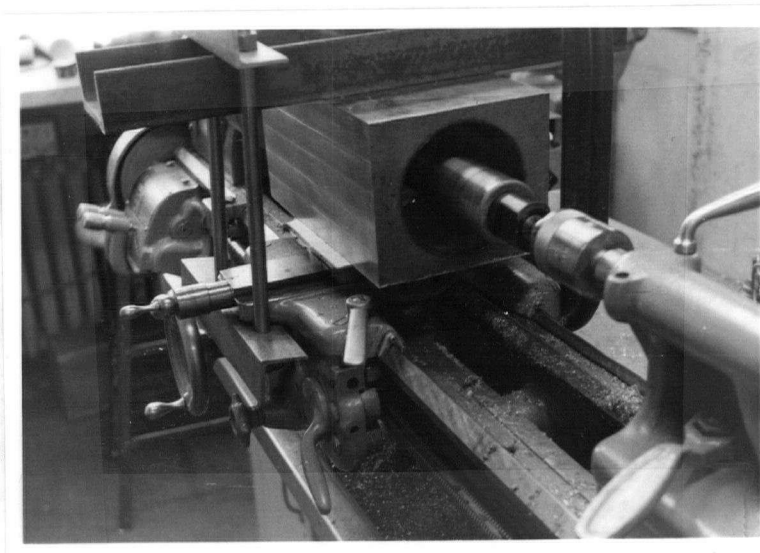


Figure 8. Boring of I.D. of Piston Block

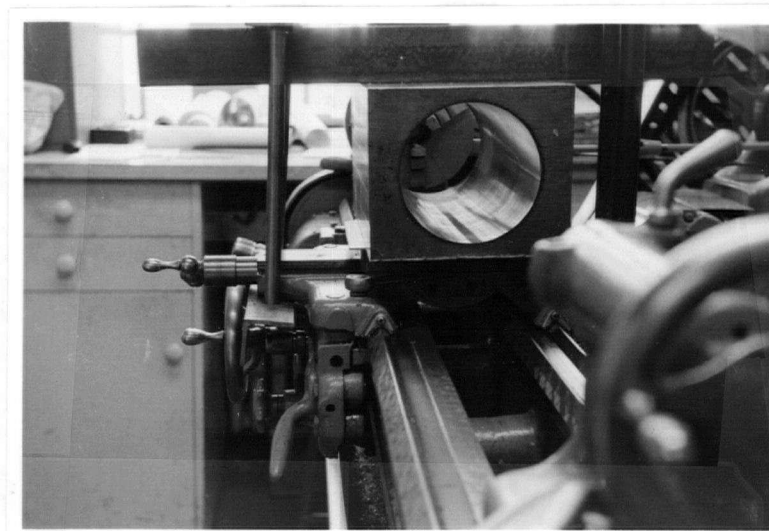


Figure 9. Completion of Boring I.D. of Piston Block



Figure 10. Reduction of Weight of Piston Block

Vancouver, B.C. The cylinder was then sent back to Canadian Car Pacific Ltd., who then attempted to hone the inside surface to the specified I.D. Some grinding was also done at the ends.

In conjunction with this work a solid aluminum piston was machined by Canadian Car Pacific Ltd. to fit the chromed cylinder. Once again this piston block was set up in the column. The aluminum piston was put into place, and a six foot head of water applied to the assembly. The aluminum piston was shoved back and forth a few times and it finally seized completely so that it was impossible to move it. However, no leakage was encountered.

The unit was taken down again and it was found that slight imperfections in the chromium plating and piston walls had caused the seizure. The piston block was sent back for rechroming by Hudson Plating and lapping by Canadian Car. The method of lapping consisted of rotating back and forth in the piston block an approximately 2½-in. long brass cylinder whose O.D. was approximately 0.005 inches less than the I.D. of the piston block. A lapping compound, which consisted of a mixture of emery dust and fine grade machine oil, was used between the two surfaces. The aluminum piston was again machined to fit the rechromed and lapped piston block.

Upon being set up a third time the aluminum piston once again seized after a few passages through the cylinder. Figure 11 is a photograph of the aluminum piston showing the damaged surface, whereas Figure 12 shows the corresponding scoring of the cylinder wall.

Once again the piston and piston block were sent back to Canadian Car. This time a Babbitt piston was made to specifications and the inside of the piston block was lapped as before except that an approximately 14-in. long C.I. pipe, machined on the surface, was used instead of the brass cylinder. Babbitt metal is a white antifriction alloy composed of copper, antimony, and varying proportions of tin. Upon being set up a fourth time the sampler was found to leak

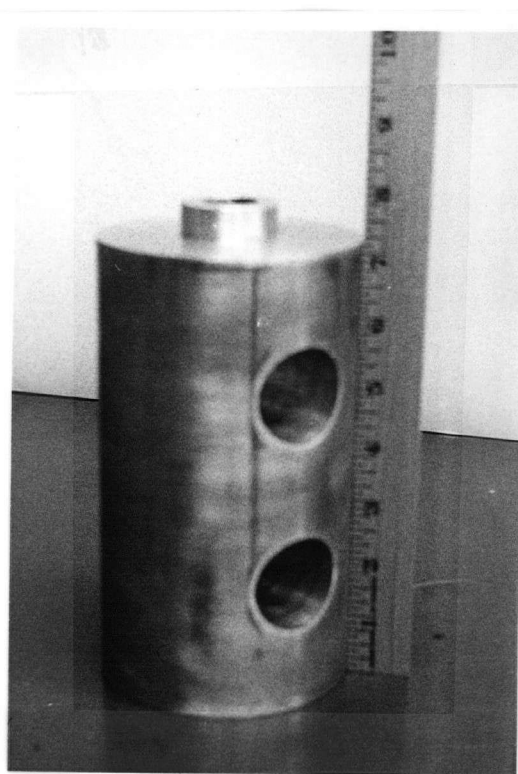


Figure 11. Damage to Aluminum Piston After Seizure

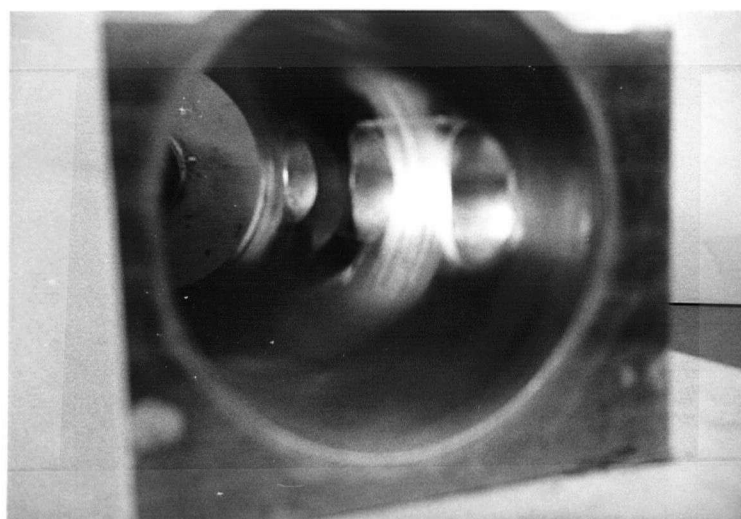


Figure 12. Scoring on Cylinder Wall

at approximately 20 mls./min. At this point the project appeared to be impossible but one more attempt was made to reduce the leakage.

The fifth attempt consisted of resoldering the original piston made in the department shop (as described earlier) and trying it in the chromed and lapped piston block. This time dimensions were such that no leakage occurred when the piston was over to the right in the block. When the piston was shoved to the left in the block a leakage rate of one to two mls./min. was encountered after a few seconds. The piston, however, moved very easily in the block, and it was possible to sample only from one side in order to keep the leakage at a minimum. Sampling was accomplished by shoving the piston from its right to left hand position in the block. Following sampling it was returned to the right hand position in which no leakage occurred. In this way steady state operation of the column could be maintained.

As much data as possible were obtained with the equipment operating in this manner.

#### Collection Funnels

Figure 14 is a drawing of a collection funnel, which fits into the outside of each of the two holes on the underside of the piston block. The funnels are fitted snugly into the countersunk portion of the holes and are



held tight by a flange arrangement to prevent leakage. See Figure 13.

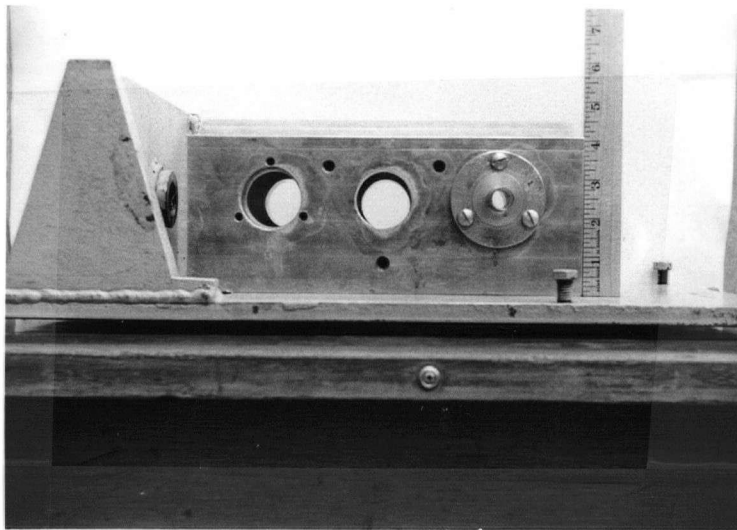


Figure 13. Collection Funnel Fitted to Underside of Piston Block

The components of the collection funnel and the assembled funnel are shown in Figure 15.

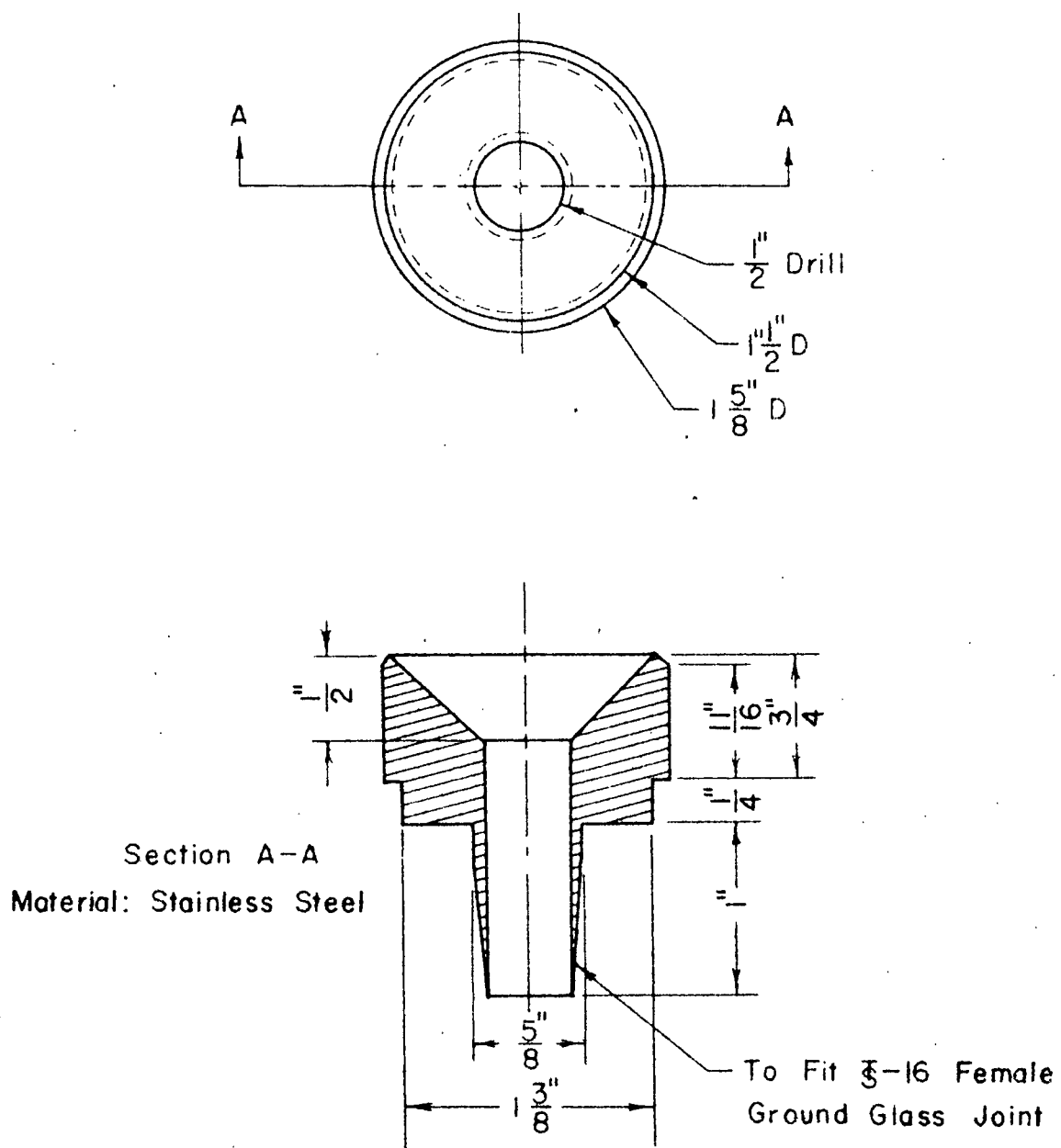


FIGURE 14. COLLECTION FUNNEL

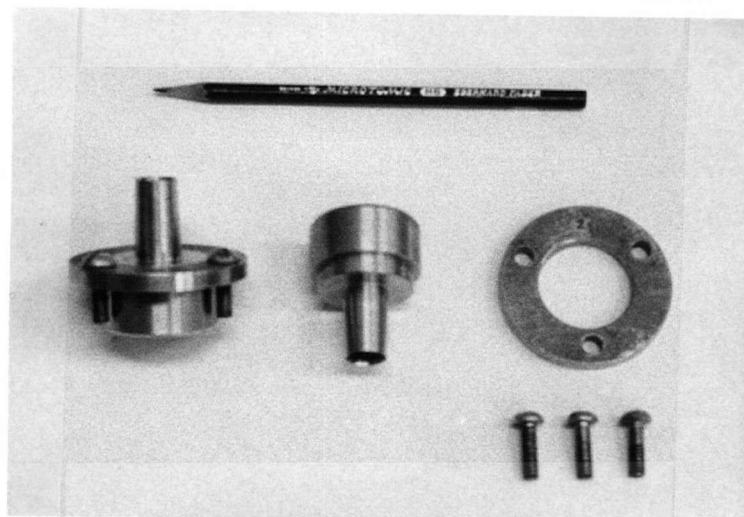


Figure 15. Assemblage of Components of Funnel

The neck of the funnel is tapered to fit the female portion of a  $\frac{3}{8}$ -16 ground glass joint.

#### Collection Flask

Figure 16 is a photograph of the collection flask shown in position on the bottom of a collection funnel. The flask was calibrated as to the total volume and the neck was calibrated by Cave and Co. Ltd. in one ml. and 0.1 ml. divisions as shown in Figure 17. The flask was designed so that the total volume of the piston sample would fall just below the top calibration mark whereas the volume of ketone expected in the sample would separate in the graduated portion

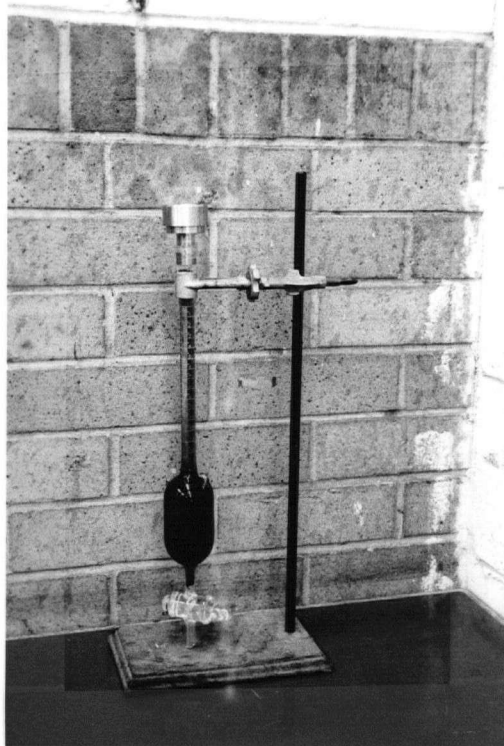


Figure 16. Collection Flask

of the neck. The top calibration mark indicated a volume of 117.0 mls. The neck was calibrated over a 15 ml. range. The neck of the funnel was fitted with a female portion of a  $\frac{1}{8}$ -16 ground glass joint, matching the taper of the neck of the collection funnels. Supporting hooks were located on the expanded section of the flask. Wire tension springs were used to hold the flask in position on the funnel as shown in Figure 18. The flask was calibrated by Cave & Co. The calibrations were checked by the writer at a total of 13 points over the 117 ml. range.

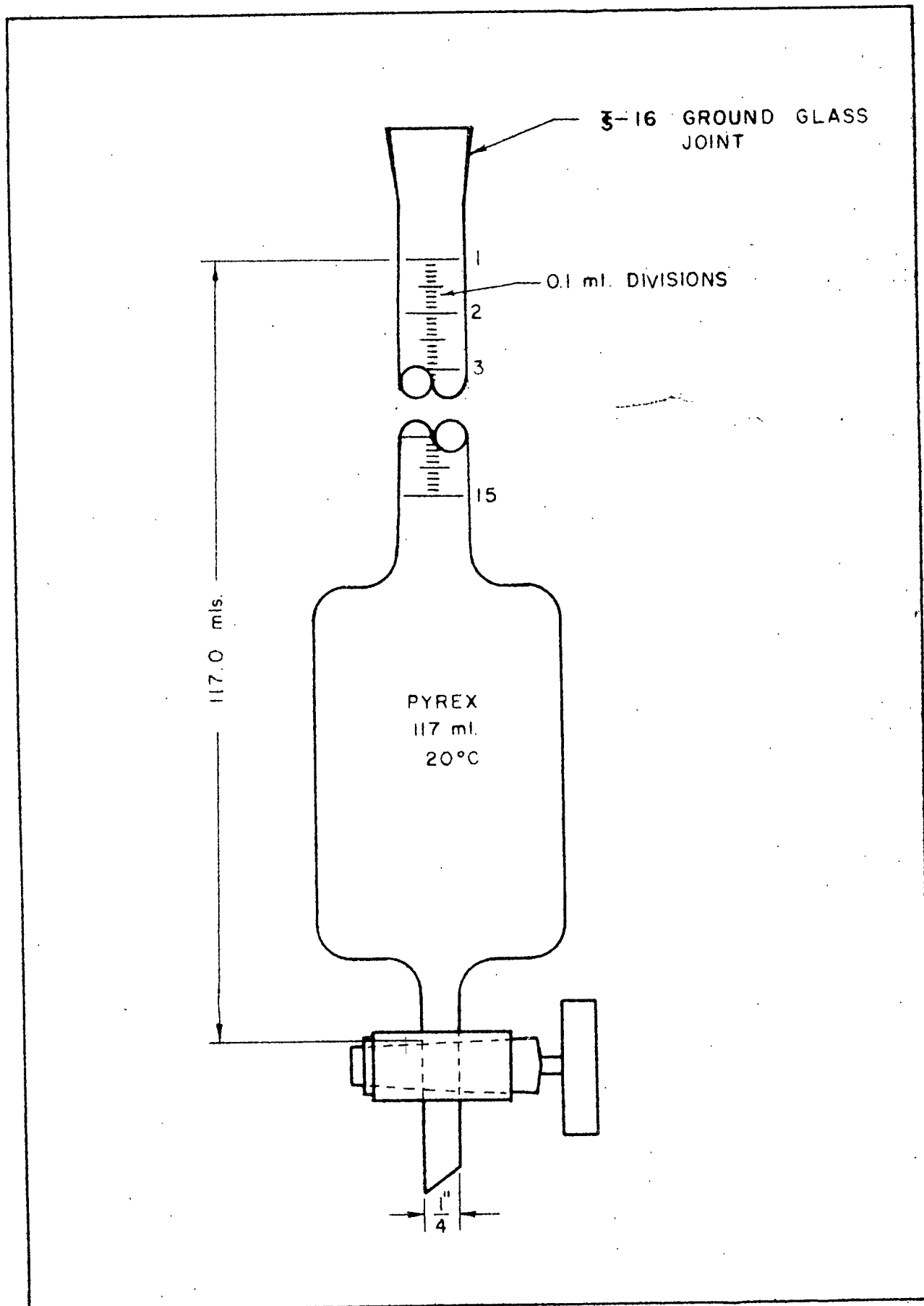


FIGURE 17. COLLECTION FLASK



Figure 18. Flask Held in Position by Tension Springs to Piston Block

### Column Support

Figure 20 is a drawing of the column support to which the various sections of the extraction column are attached. Figure 19 is a photograph of the support in an early stage of its construction.

Thirty-seven inch lengths of 1 x 1 x 1/8-in. angle iron were used to brace the three mild steel pipes together.

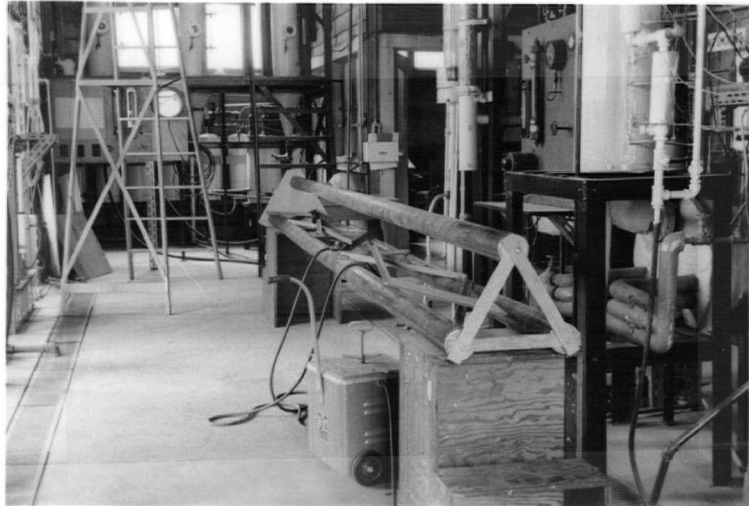


Figure 19. Column Support in Early Stages of Construction

Figure 21 is a photograph of the bracing pattern which may not be clear in Figure 20.

A 15 foot length of 2 x 2 x  $\frac{1}{4}$ -in. angle iron was welded to each of two of the pipes as shown in Figure 21. The pipes were then set upright and welded to a  $\frac{1}{2}$ -in. thick iron plate which in turn was bolted to the floor. Figure 22 is a photograph of the assembled column and also shows how the support was fixed to one of the beams in the unit operations labroatory.

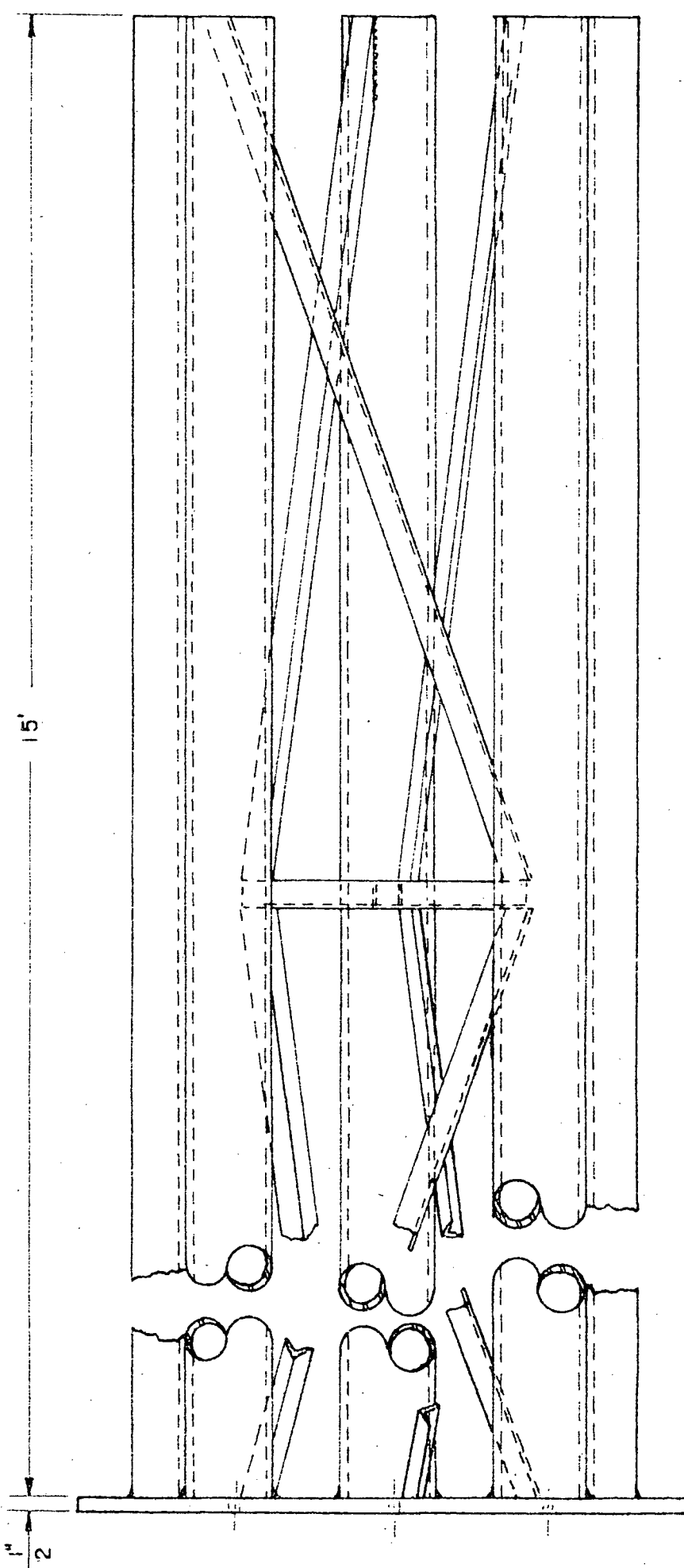
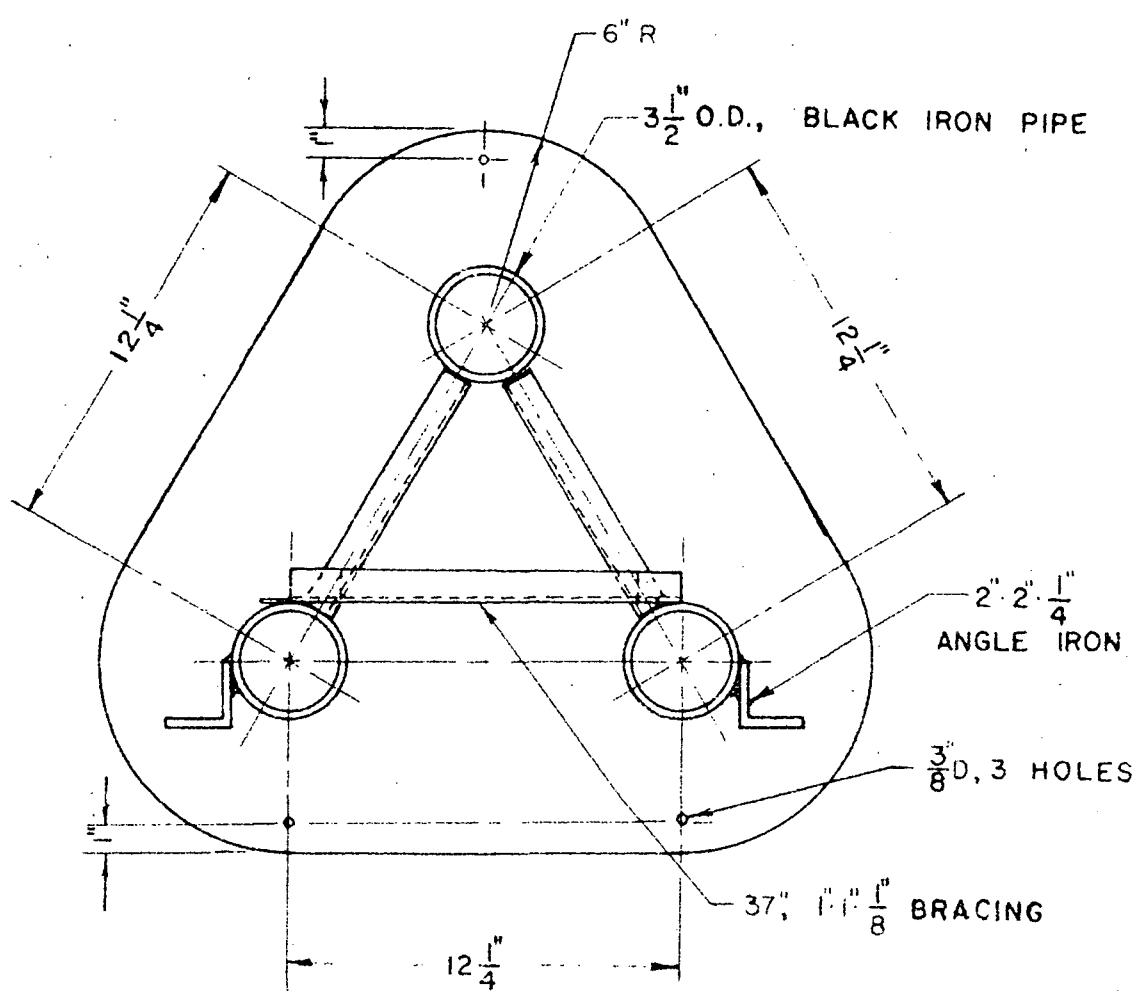


FIGURE 20. COLUMN SUPPORT



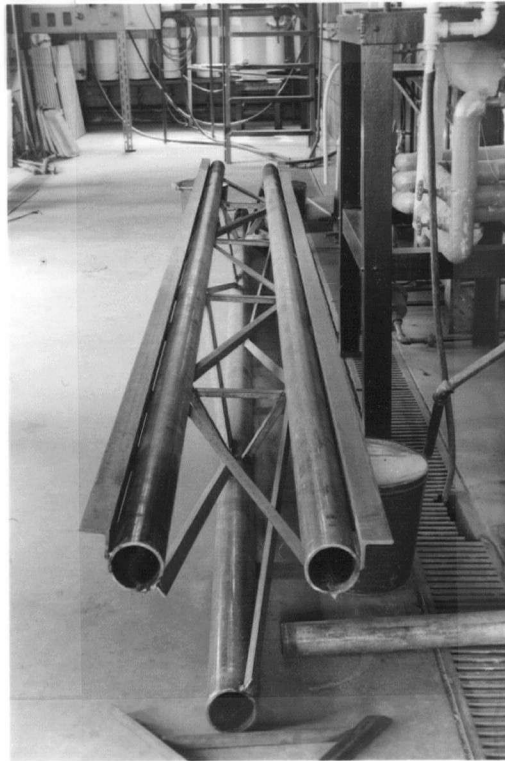


Figure 21. Bracing Pattern of Column Support

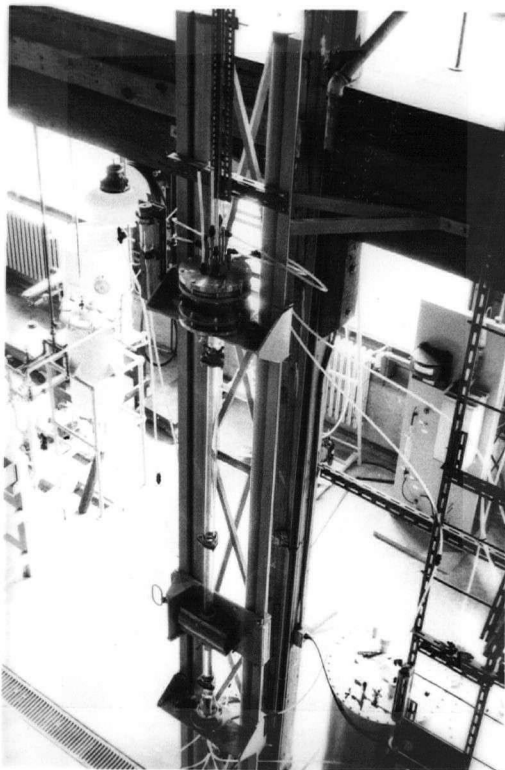


Figure 22. Assembled Column

## Elgin Head and Conical Section Supports

Figures 23 and 24 are drawings of the Elgin head support and the conical section supports, respectively. These supports can be clamped to the column support at any desired height. Figure 25 is a photograph of the Elgin head and its support, whereas Figure 26 is a photograph of the conical section and its support. Both supports are clamped to the column support by means of  $\frac{1}{2}$ -in. Allen head set screws set against  $\frac{1}{4}$ -in. thick mild steel pressure plates. This method of clamping is shown in Figure 27.

Figure 25 also shows the column interface controller which is bolted to one side of the Elgin head support.

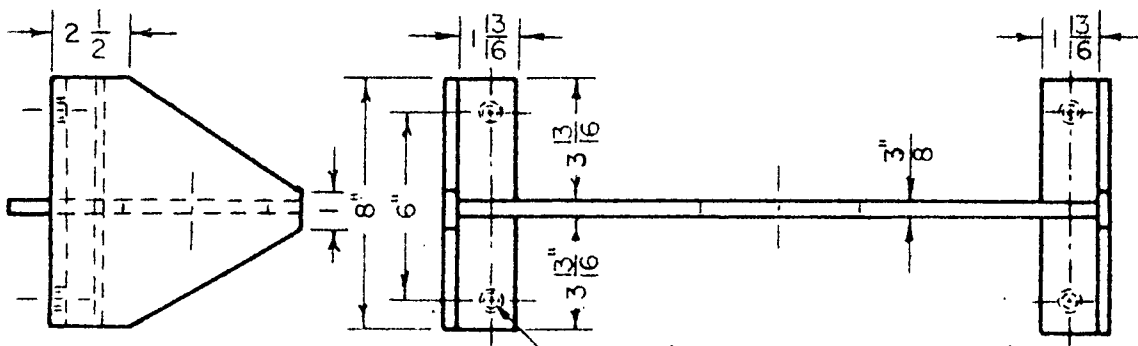
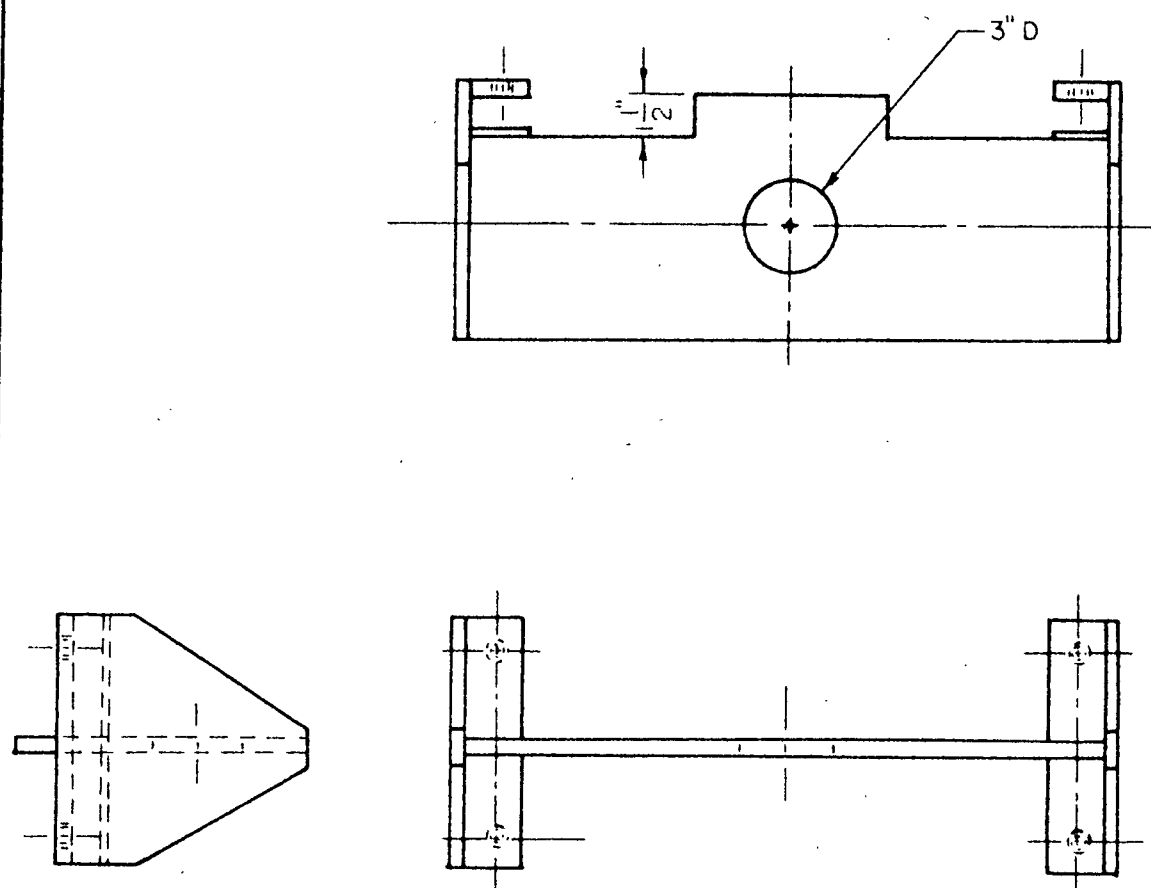


FIGURE 23. ELGIN HEAD SUPPORT



All other dimensions as in FIGURE 23.

FIGURE 24. CONICAL SECTION SUPPORT

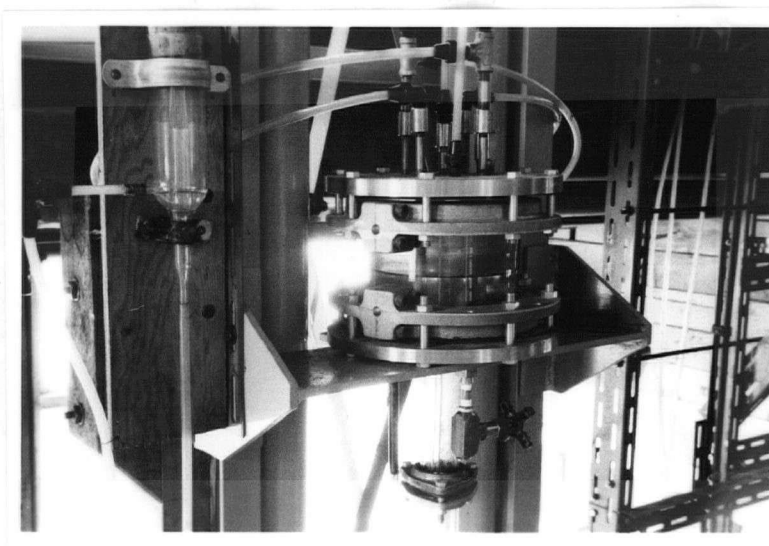


Figure 25. Elgin Head and Its Support

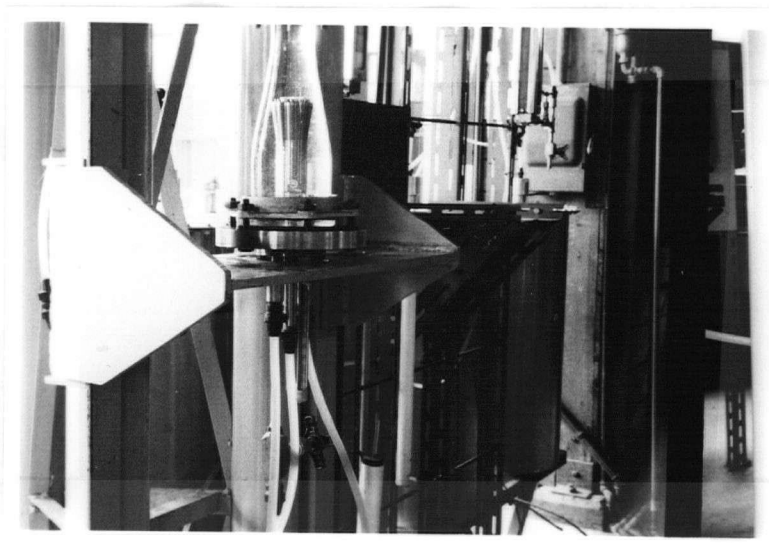


Figure 26. Conical Section and Its Support

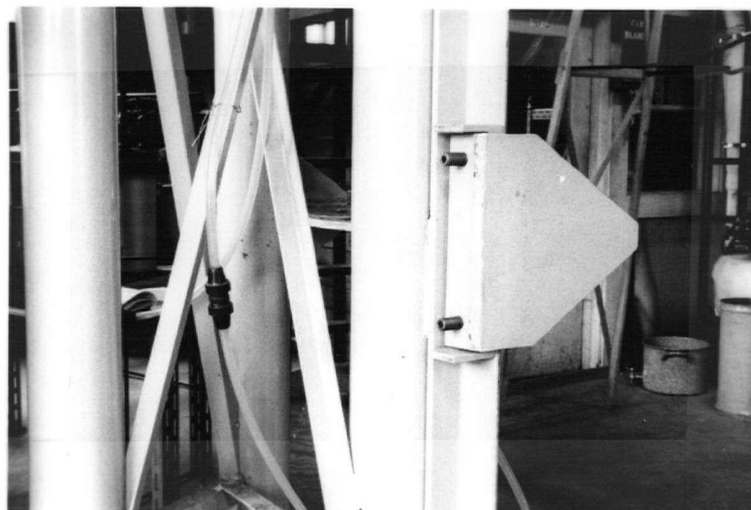


Figure 27. Clamping Arrangement

#### Piston Sampler Support

Figure 28 is a drawing of the piston sampler support. The piston block is bolted to the support by 4,  $\frac{1}{2}$ -in. machine screws. One side of the support is welded to the back of the support. A similar side, which could be bolted to the right side of the back of the support, was fabricated but no use of it was ever made. Therefore this item has been omitted on Figure 28. Figure 29 is a photograph showing how the piston sampler support was clamped to the column support.



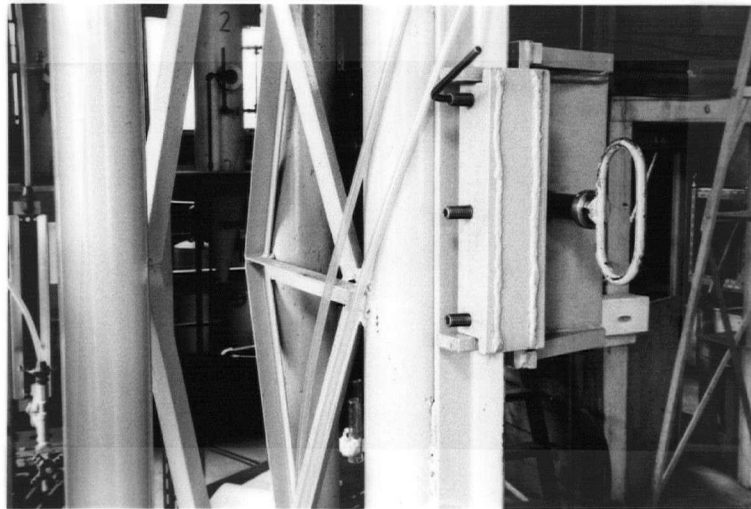


Figure 29. Clamping Arrangement for Piston Sampler Support

### Procedure

As this work is a continuation of Choudhury's work (1), in the sense of justifying his sampling technique, references should be made to his thesis for a detailed consideration of the following points:

- (a) The steady state operation of the extraction column, including interface adjustments, periodic rotameter readings, etc. (1j).
- (b) The analysis and handling of all samples taken throughout the course of the experiment (1k).
- (c) The method of sampling with the probes, including purging (1b).



- (d) The correction of the measured concentration of acetic acid in the ketone probe samples because of appreciable water entrainment (1k).
- (e) The achievement of mutual saturation (1l).\*
- (f) The description and source of all reagents (1m).

The methyl isobutyl ketone used throughout the experimental work was technical grade and was made up of various batches from different companies. The following refractive indices were obtained:

Source of MIBK	Refractive Index	Temperature
G.C. Henderson Co. Ltd.	Order No.1 1.3951	20.1°C
	Order No.2 1.3949	20.2°C
Canadian Chemical Co.	Drum No.2 1.3948	20.2°C

(No sample from Drum No. 1 was available for testing although some ketone from this drum was used in the research)

MIBK as purified and placed in aluminum tanks at time these were

commissioned (1)	1.3947	20.1°C
------------------	--------	--------

The refractive index of 99% pure MIBK is 1.3958 at 20°C(1).

\* 1-ell.

With these points covered in detail in Choudhury's work the operating procedure can be explained very briefly. The linear velocity of ketone through the nozzle tips in all cases was 0.36 ft./sec., while the direction of transfer was always from the aqueous phase to the ketone phase. Nozzle tip patterns corresponding to the various ketone flow rates may be found in Figure 30. Those for  $L_k = 36.5$  and 72.9 were also used by Choudhury.

The required flow rates were set by means of the rotameters and a sufficient amount of time was allowed for the tower to change its contents three to four times (1m).

During this time the interface controller was adjusted to hold the interface at one particular level. Throughout all the runs the interface remained three to four inches below the top of the top plate of the Elgin head. During each run the interface elevation remained steady but varied over a one inch range from run to run. Thus the height of the column (nozzle tips to interface) is reported as 7-ft.  $3\frac{1}{4}$ -in.  $\pm$  1/2-in. for all runs. Throughout the course of a run, numerous checks were made on the interface height and on the flow meter settings. It was found that little or no readjustment was necessary.

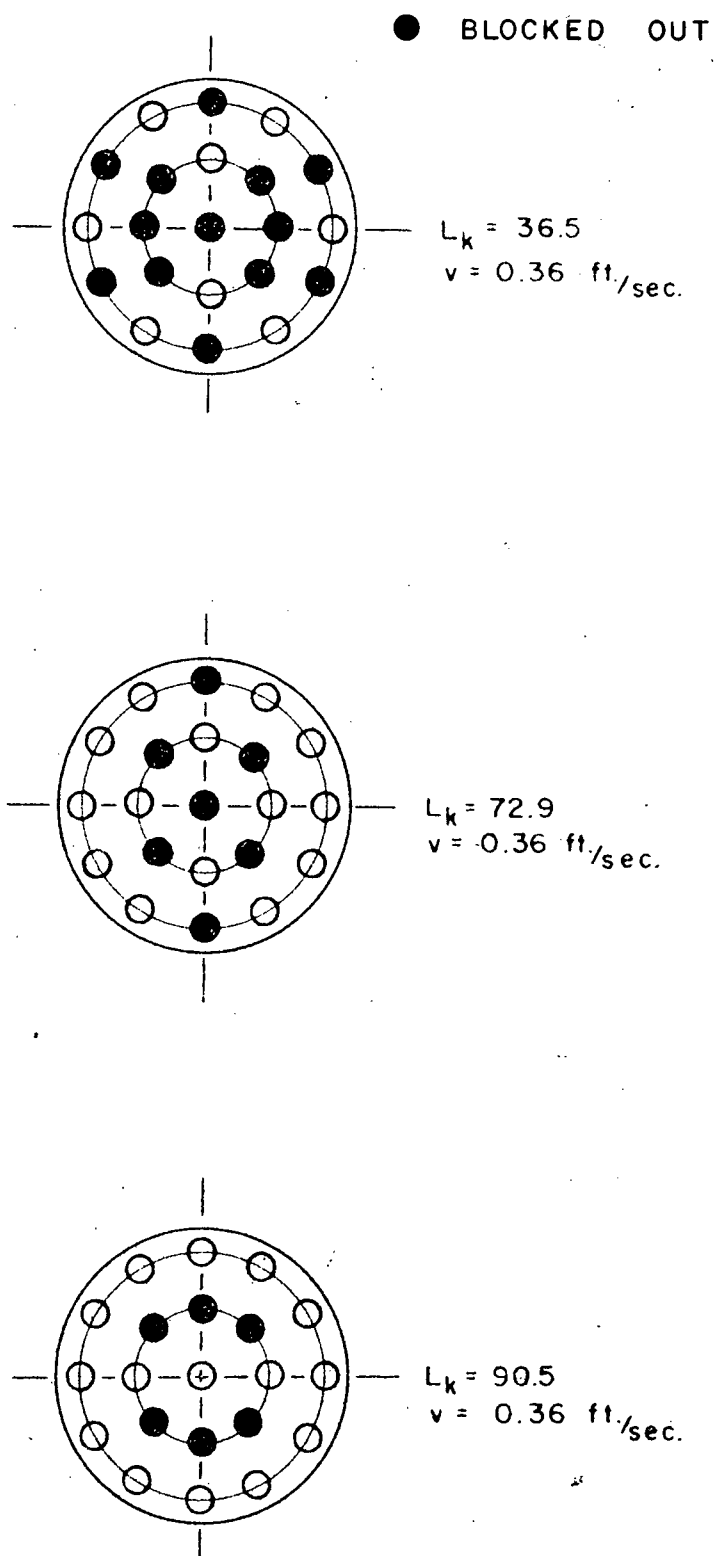


FIGURE 30. TIP PATTERNS FOR KETONE NOZZLE

Runs 71 to 73, and 76 to 78 were made to justify the syringe method of sampling the water phase and to check whether or not a concentration gradient existed in a particular cross-section in the column at right angles to the axis of the column and at a particular height above the nozzle tips. When steady state conditions were assumed to prevail in the tower hypodermic syringe samples were taken at definite positions in the cross-section. The needle<sup>✓</sup> of the syringe entered the column through the asbestos gaskets at certain flanges in the apparatus. After a syringe sample had been taken the syringe was washed with distilled water and then dried. Before another syringe sample was taken, 15 c.c. of water phase were withdrawn at the next sampling position and used to rinse the syringe. Then a 30 c.c. sample of the water phase was removed at that position and the washing, drying, and rinsing procedure repeated prior to sampling at the next position.

In Runs 74 and 75 syringe samples were taken at one position in a cross-section at various time intervals after the start-up of a run and continued well into the steady state period of operation of the column. The object was to determine whether or not the syringe samples, taken during the steady state period at this one point, would show any variation in the measured concentration of acetic acid.

\* The hypodermic needles used for sampling were Standard Yale B-D 19 with the point of the needle filed off so that the needle end lay in a plain at right angles to the needle axis.

When the piston sampler was incorporated into the apparatus the procedure was slightly different. When steady state conditions were assumed to prevail in the tower the probes were lowered to the elevation of the axis of the piston where purging and sampling of both phases took place simultaneously. Purging and sampling rates and purging times are reported later in this thesis. Inlet and outlet samples of both phases were taken when the probe samples were being taken. When sufficient volumes of both phases had been obtained, the probes were removed from the path of the piston.

Water phase samples were taken immediately above and below the piston block by means of the hypodermic syringe, the needle of which entered the column through the asbestos gaskets sealing the glass column to the piston block. The syringe was washed, dried, and rinsed in a manner described earlier after each syringe sample was taken.

The 1½-in. I.D. hole in the piston that was to slide into line with the column was filled with either water phase which had leaked from the piston or with outlet water phase from the column if there was no such leakage. In this way when a piston sample was taken the column continued to operate with no appreciable disturbance. It was interesting to observe that when a piston sample was taken a gap in the ketone phase occurred, which appeared to move up the column. This discontinuity in the ketone phase, however, disappeared after it had "risen" one to two feet.

The collection flask was connected to the funnel which was to receive the piston sample. When the piston was slammed from one position to the other, the removed section of the column would quickly empty its contents into the collection flask. The collection flask had to be removed quickly from the receiving funnel because in a few seconds water phase would start to leak into the flask.

After a piston sample had been taken sufficient time was allowed to change the contents of the column at least twice to assure steady state conditions again. The sampling procedure was then repeated with the piston being moved in the opposite direction.

In Run Nos. 82 to 85 sampling took place only from right to left, since no leakage occurred when the piston was over to the right in the piston block. After a sample had been taken the piston was immediately returned to the right-hand position and the sampling procedure repeated from right to left after sufficient time had passed for steady state to be re-established.

During Run No. 80, an appreciable volume of ketone phase was entrained in the continuous phase samples taken by the syringes in the gaskets immediately above and below the piston block. This volume was large enough so that an appreciable transfer of acetic acid took place out of the water part of the sample and into the ketone part after a

sample was taken. At this point in the work the syringe samples were discontinued because of the near impossibility of correcting for such transfer in the circumstances obtaining. It was decided that the water phase probe sample, which showed no ketone entrainment, could be used in place of the syringe samples, if it was assumed that the probe sample gave a representative sample of the water phase. This sample ordinarily was taken on the axis of the piston.

The two phases of the piston samples were allowed to separate and their volumes were measured. Part of the water phase was drawn from the flask and the remaining contents dropped into a sample bottle. Any ketone which remained in the flask was then washed into the sample bottle with the water phase portion which had been drawn from the flask earlier.

The sample bottles containing piston samples were shaken vigorously from time to time over a three to four hour period prior to analysis. After this time, and because of the small volume of ketone, it was assumed that the two phases were in equilibrium. During storage the flasks were sealed with corks covered with aluminum foil.

The samples were then analyzed for their acetic acid content by titration with sodium hydroxide solution (1k).

An attempt was made to analyze the concentrations of the water phase samples by measurement of their resistances with the salinometer of the Pacific Oceanographic Group, Fisheries Research Board of Canada, at Nanaimo, B.C. Details of construction, operation and maintenance of the salinometer may be found elsewhere (11). The bridge was specifically designed for the determination of the salinity of sea water by measurement of its electrical conductivity. Paquette (12) advises that the bridge would undoubtedly work for acetic acid solution and would yield conductance or resistance ratios if used in the proper way. The ratios are the usual Wheatstone bridge resistance ratios with respect to a reference solution.

A simplified schematic diagram of the circuit of the salinometer is shown in Figure 31. The bridge design avoids the necessity of precise temperature control in the conductivity cell by using as the adjacent resistor in the Wheatstone bridge a second, nearly identical, conductivity cell (Y in Figure 31) in the same constant temperature bath, and filled with reference solution of approximately the same concentration as the sample to be analyzed (Cell X).

In use, the unknown solution is placed in Cell X and the reference solution, in the present case a solution of concentration  $CW_1$ , is placed in Cell Y. Arm  $R_y$  is set at a value characteristic of the particular cell in use and the concentration of solution in the reference cell (700 ohms in the present case). The bridge is then brought to balance with



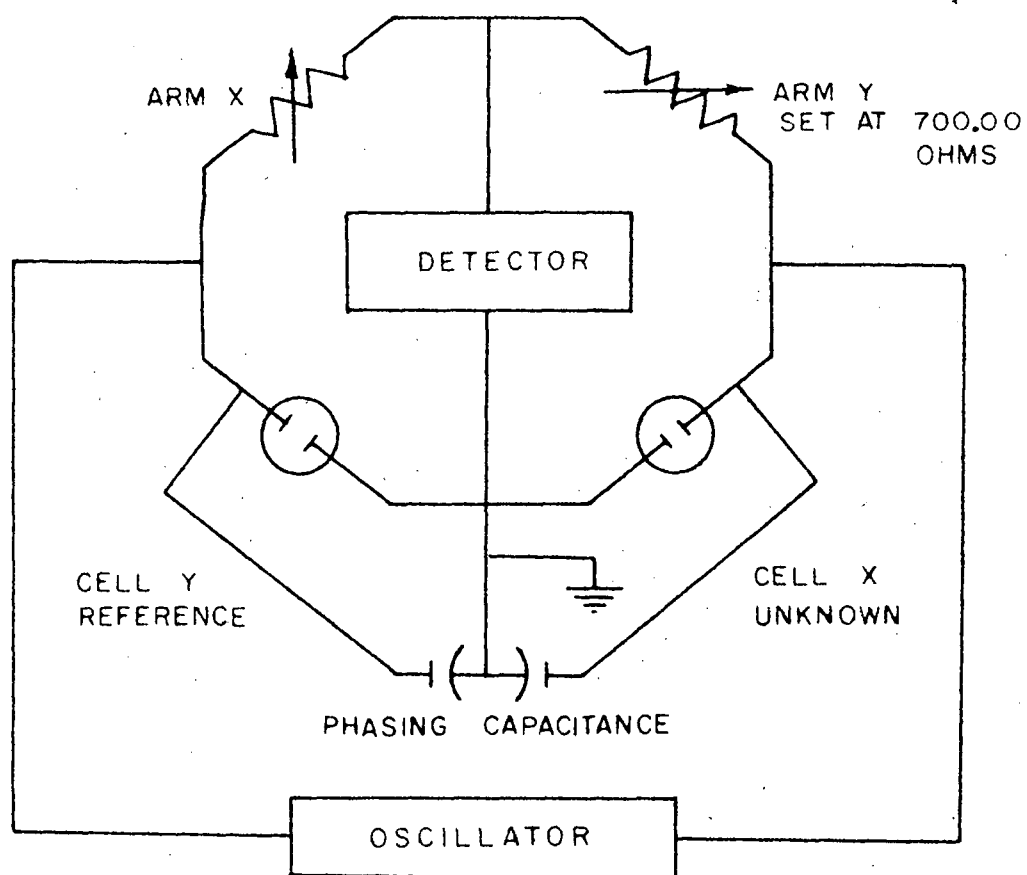


FIGURE 31. SIMPLIFIED BRIDGE CIRCUIT

Table II  
Calibration of Salinometer

Sample	Concentration of Acetic Acid in Made-up Water Phase Samples <sub>1</sub>	Resistance of Cell X <sub>2</sub>
	lb. moles/ft. <sup>3</sup> x 10 <sup>3</sup>	ohms
C <sub>w1</sub> <sup>*</sup>	50.2	694.15
C <sub>w2</sub> <sup>*</sup>	32.5	739.44
1	36.2	728.04
2	36.9	718.68
3	43.4	710.24
4	46.7	702.44

1 Samples obtained by making up various volumes of inlet and outlet water phase solution from Run 84. Concentrations of these samples were obtained by titration.

2 Inlet water phase solution from Run 84 was used as reference solution in Cell Y. Its concentration was determined by titration.

\* Samples designated by the symbol for their concentration.

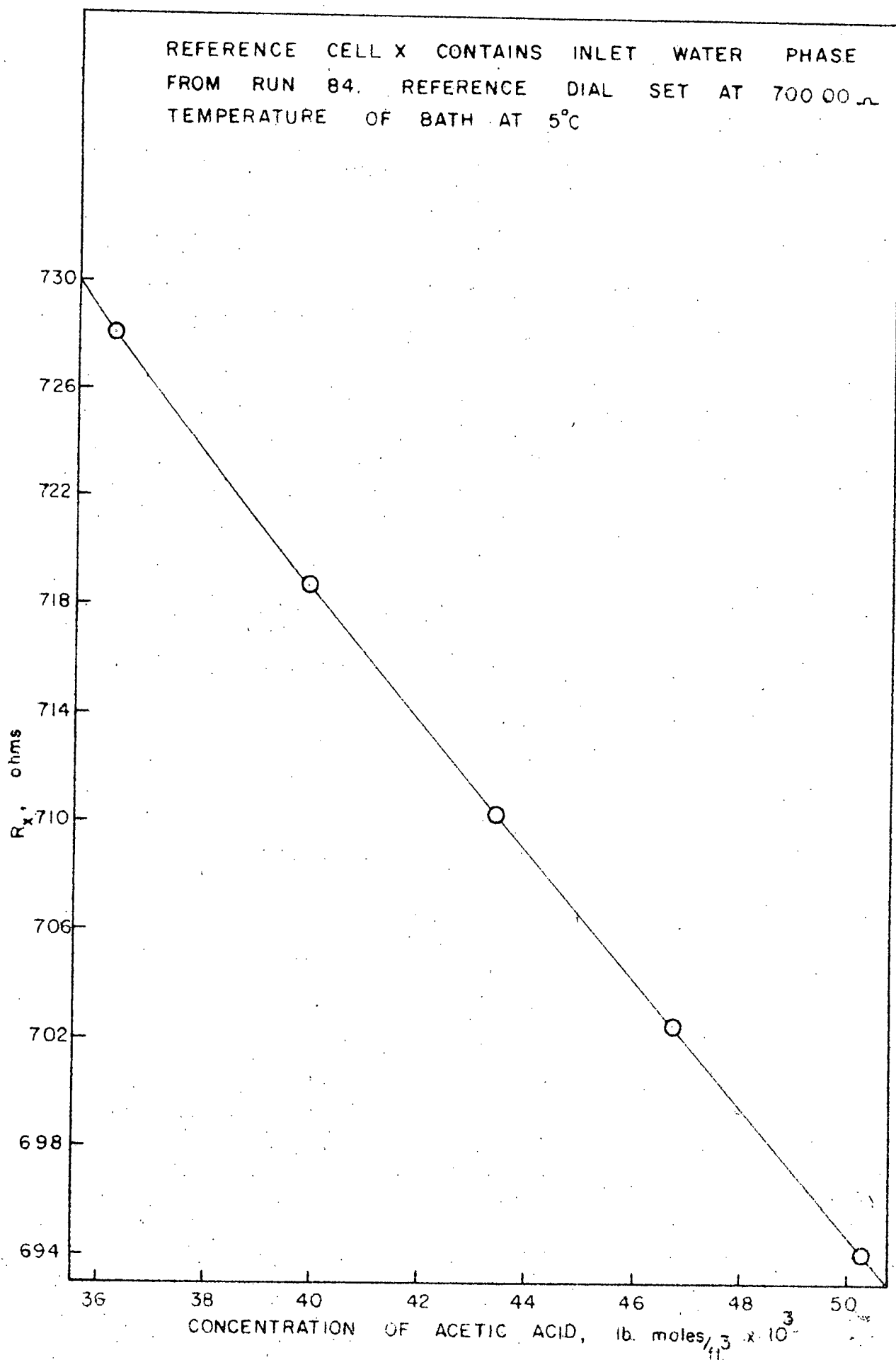


FIGURE 32. SALINOMETER CALIBRATION CURVE

Rx. Rx is now a single-valued nearly linear function of the acetic acid concentration of the water phase.

A number of water phase calibration samples were prepared by mixing various volumes of inlet and outlet water phase taken from Run 84. Piston samples from Run 84 were allowed to stand for 24 hours before the two phases were separated and analyzed by titration. The remaining water phase portions were placed in 125 ml. flasks and sealed with tin foil-covered corks. The flasks were kept at 2°C for 5 days before taking them to Nanaimo to measure their resistances. The calibration samples were sealed and stored in a similar manner for the same period and their resistances measured during the same visit to Nanaimo and with the same Ry setting as used for the piston samples. The resistances of the water phase calibration samples, whose concentration had been determined by titration, were measured,\* and the calibration curve shown in Figure 32 was prepared. Figure 32 relates the concentration of the water phase to the resistance Rx. The calibration curve, however, is specific only for Run 84 as column aqueous feed from this run (concentration  $Cw_1$ ) was used in the Reference Cell Y of the salinometer for the particular series of measurements related to that run.

Cell X was always washed three times with the water phase solution whose resistance was to be measured. The water phase solution was always pipetted from the bottom

\* See Table II.

of the sample flask to insure that any ketone, which had failed to be separated from the water phase portion, would not be taken up into the pipette. The pipette also received three thorough washings with the solution whose resistance was to be measured. Previous experience in measuring the resistance of the water phase solution with the salinometer showed that the presence of two phases in Cell X would affect the resistance readings considerably. Thus it was necessary to withdraw the water phase portion carefully with a pipette if any minor ketone layer was present.

The five piston samples from Run 84 were analyzed for acetic acid using the salinometer in conjunction with the calibration curve. The results were compared with the values obtained by titration. Unfortunately the results did not agree and the method was not used further in the present research.

#### CALCULATIONS

The rate of transfer of acetic acid across the interface in the column was calculated in lb. moles/hr. by two different equations. One was based on the total change in concentration of the water phase, and the other was based on the corresponding total change in concentration of the ketone phase. These equations were

$$N_w = L_w A (C_{w_1} - C_{w_2}) \quad 1$$

$$N_k = L_k A (C_{k_1} - C_{k_2}) \quad 2$$

Values of  $N_w$  and  $N_k$  varied slightly and an average value was determined by

$$N = \frac{N_w + N_k}{2} \quad 3$$

The percentage deviation was calculated for each run as a measure of the quality of the experimental work.

The equation used was

$$\text{Percentage Deviation} = \left( \frac{N_w - N_k}{N} \right) 100 \quad 4$$

An acetic acid balance equation was written between the initial conditions existing in the column at the time of sampling in the four inch high piston section, and the final equilibrium conditions existing in the removed piston sample. The equation was

$$C_{k_i} V_k + C_{w_i} V_w = C_{k_f} V_k + C_{w_f} V_w \quad 5$$

and when used was solved for  $C_{k_i}$ .

Figure 33 is a simplified drawing representing the sampling procedure to which Equation 5 was applied. Steady state conditions were assumed to exist in the extraction column prior to sampling and any volume changes after sampling have been neglected. Volume changes with respect to the inlet and outlet streams, have also been neglected.

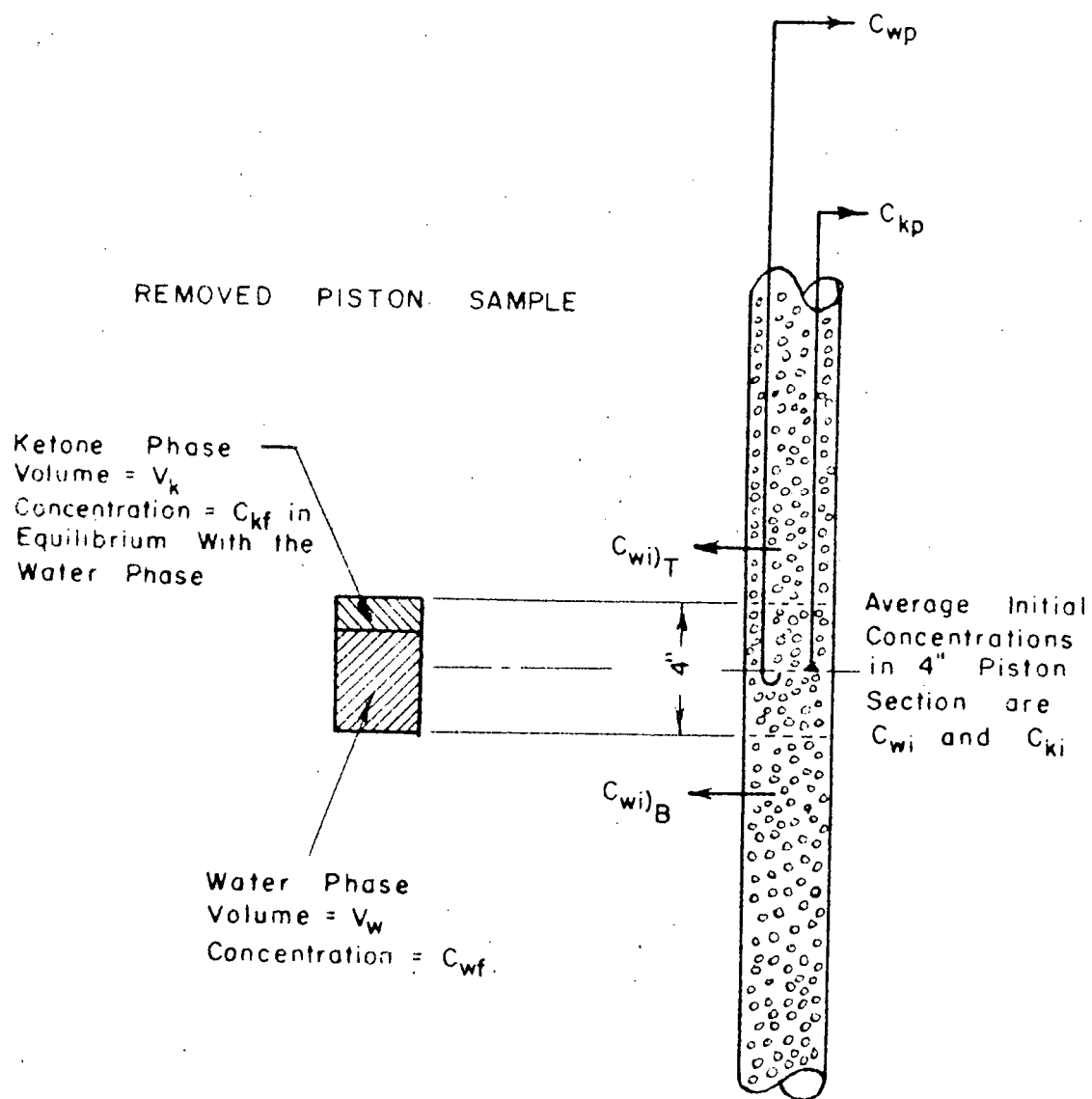


FIGURE 33. SIMPLIFIED DRAWING OF SAMPLING PROCEDURE

Volume changes might be expected as a result of acetic acid transfer and changes in the mutual solubility of ketone and water accompanying the transfer of acetic acid. A sample calculation to show why these volume changes have been neglected is included in the Appendix.

The water phase concentration profile is assumed to be linear over the six inch length of column between  $Cw_i)_T$  and  $Cw_i)_B$ . This assumption was arrived at by examination of water phase concentration profiles from Choudhury's work (1). In his work the water phase concentration profiles which showed the greatest curvature over a seven foot length of column could be assumed to be linear over a six inch length of column at any point on the profile.

In some runs, in the present work  $Cw_i$  was found before taking a piston sample by withdrawing water phase samples  $Cw_i)_T$  and  $Cw_i)_B$ , with a hypodermic syringe at the top,  $)_T$ , and at the bottom,  $)_B$ , of the piston block. Thus if a linear profile can be assumed to exist between  $Cw_i)_T$  and  $Cw_i)_B$ ,  $Cw_i$  can be approximated by

$$Cw_i = \frac{Cw_i)_T + Cw_i)_B}{2} \quad 6$$

In other runs  $Cw_i$  was obtained by taking a sample with the water phase probe at the elevation of the axis of the piston samples.  $V_k$  and  $V_w$  were obtained from the calibrations on the collection flask, whereas  $Cwf$  was obtained by analysis of the water phase portion of the piston sample after



equilibrium had been reached with the ketone phase portion.  $C_{kf}$  was obtained from the equilibrium relationship since volume  $V_k$  is insufficient for analysis at low ketone phase holdups. At higher holdups, (see Run 84, Table VIII, and Run 85, Table IX), a sufficient amount was present for one analysis. Combining Equations 5 and 6 and rearranging to solve for  $C_{k_i}$  gives

$$C_{k_i} = \frac{V_w}{V_k} \times \left\{ C_{w_f} - \left[ \frac{C_{w_i})_T}{2} + \frac{C_{w_i})_B}{2} \right] \right\} + C_{k_f} \quad 7$$

As mentioned earlier the taking of samples represented in Equation 7 by  $C_{w_i})_T$  and  $C_{w_i})_B$  had to be discontinued. When the probe sample taken on the axis of the piston sampler is used instead, on the assumption that  $C_{w_p} = C_{w_i}$ , Equation 7 becomes

$$C_{k_i} = \frac{V_w}{V_k} \times (C_{w_f} - C_{w_p}) + C_{k_f} \quad 8$$

In Run 85, the major portion of the water phase was separated from the ketone phase immediately after taking the piston samples. The ketone phase and the small remaining volume of water phase were allowed to come to equilibrium before some of the ketone phase was withdrawn for analysis. The original concentration of the ketone drops in the column could be calculated by the following material balance equation

$$C_{k_i} = C'_{w_f} \frac{V'_w}{V_k} + C''_{w_f} \frac{V''_w}{V_k} + C_{k_f} - C_{w_p} \frac{V_w}{V_k} \quad 9$$

The ketone phase holdup was calculated from the measured volumes of the ketone and water phases of the piston samples by the following equation

$$H = \left( \frac{V_k}{V_k + V_w} \right) 100\% \quad 10$$

The maximum errors that could be expected in the piston samples were calculated by the method set out by Mickley, Sherwood and Reed (10). Briefly, the method is to relate the error of the calculated quantity to the errors of the measured quantities in the form of a partial differential equation such as

$$dQ = \frac{\partial Q}{\partial q_1} dq_1 + \frac{\partial Q}{\partial q_2} dq_2 + \dots + \frac{\partial Q}{\partial q_n} dq_n \quad 11$$

in which the differentials  $dq_1, dq_2, \dots, dq_n$  of the measured quantities are replaced by small finite increments  $\Delta q_1, \Delta q_2, \dots, \Delta q_n$ , and, similarly  $dQ$  by  $\Delta Q$ . The expression takes the form

$$\Delta Q = \frac{\partial Q}{\partial q_1} \Delta q_1 + \frac{\partial Q}{\partial q_2} \Delta q_2 + \dots + \frac{\partial Q}{\partial q_n} \Delta q_n \quad 12$$

The quantities  $\Delta q_1, \Delta q_2, \dots, \Delta q_n$  may be considered as errors in  $q_1, q_2, \dots, q_n$ , and  $\Delta Q$  is, to good approximation, the error in the calculated quantity,  $Q$ . Equation 12 holds for any type of errors, providing only that they are small. On the other hand, Equation 12 does not utilize all the

information that may be available and consequently often overestimates the error in the calculated quantity. This point will be discussed later with the aid of an example.

Applying Equation 12 to Equation 5 we get the resulting expression

$$\Delta Ck_i = A' \cdot \Delta Ck_f + B \cdot \Delta Vw + C \cdot \Delta Vk + D \cdot \Delta Cw_f + E \cdot \Delta Cw_i \quad 13$$

where

$$A' = \frac{\partial Ck_i}{\partial Ck_f} = 1$$

$$B = \frac{\partial Ck_i}{\partial Vw} = \frac{1}{Vk} \cdot (Cw_f - Cw_i)$$

$$C = \frac{\partial Ck_i}{\partial Vk} = - \frac{Vw}{Vk^2} \cdot (Cw_f - Cw_i)$$

$$D = \frac{\partial Ck_i}{\partial Cw_f} = \frac{Vw}{Vk}$$

$$E = \frac{\partial Ck_i}{\partial Cw_i} = \frac{Vw}{Vk}$$

Estimated values of  $\Delta Vw$ ,  $\Delta Vk$ ,  $\Delta Cw_f$ ,  $\Delta Cw_i$ , and  $\Delta Ck_f$  have been used to calculate values of  $\Delta Ck_i$ . These values were  $\pm 0.2$  mls. for the volume variation and  $\pm 0.1 \times 10^{-3}$  lb. moles acetic acid/ft.<sup>3</sup> for all three concentration variations.

An acetic acid material balance was calculated for the overall operation of the extraction column as an additional check on the quality of the experimental work. The expression was

$$\begin{aligned}\text{Percentage Difference} &= \frac{\text{Acid In} - \text{Acid Out}}{\text{Acid In}} \times 100\% \\ &= \frac{(\text{LwACw}_1 + \text{LkACK}_2) - (\text{LwACw}_2 + \text{LkACK}_1)}{\text{LwACw}_1 + \text{LkACK}_2} \times 100\end{aligned}$$

14

A complete description of all the symbols used in Equations 1 to 14 may be found in the Nomenclature. Sample calculations using these equations may be found in the Appendix.

## RESULTS

Tables III to XI inclusive present all the data obtained in the operation of the extraction column and the various sampling devices. Table III gives the sampling rates and purging times which were used when sampling was taking place with the water phase and ketone phase probes. In some cases the purging time does not correspond to the minimum purging time to obtain uniform concentrations given by Choudhury (1n).

Table IV gives the overall transfer data for each run. Tables V and VII show the concentration data which were obtained by sampling the water phase with the hypodermic syringe at various positions in column cross-sections each of a definite elevation above the nozzle tips. The positions in the column cross-sections at which the hypodermic syringe samples were collected may be seen in Figure 34. Table VI gives the concentration of the water phase at Position 6 as a function of time after the start-up of a run.

Tables VIII and IX give the ketone phase holdups for six runs and also compares the concentrations of the ketone phase ( $Ck_i$ ), as calculated by Equations 7 and 8 with the ketone phase concentrations of the samples which were obtained with the probe ( $Ck_p$ ). Table IX gives the data for Run 85 in which the two phases were separated immediately after taking the piston sample.

Table X shows the approximate maximum error of the calculated initial ketone concentration ( $Ck_i$ ). Included in this table are the errors due to the individual variables.

Table XI shows the comparison of the concentrations of the piston samples for Run 84 as determined by the salinometer and by the titration method. The samples used in calibrating the salinometer and the piston samples were handled in an identical manner and their resistances measured with respect

to the same solution in the Reference Cell Y. Calibration samples were prepared by mixing various volumes of inlet and outlet water phases from Run 84, and titrating the mixtures.

In most cases the results have been reduced to three significant figures. However, four significant figures were used in their calculation, as can be seen from the sample calculations in Appendix 1.

Table III  
Sampling Rate and Purging Time

Run No.	Sampling rate ml./min.		Purging time min.	Minimum Purge Time as specified by Choudhury (ln), min.	
	Water phase probe	Ketone phase probe		Water phase probe	Ketone phase probe
79	6.0	6.5	10	11 + 2	12 + 2
80	5.0	6.4	15	13 + 2	12 + 2
81	7.4	3.5	15	8 + 2	20 + 2
82	5.2	4.7	24	13 + 2	16 + 2
83	5.1	5.1	30	13 + 2	15 + 2
84 *	4.8	5.4	10	13 + 2	15 + 2
	4.7	5.2	11 + x **	13 + 2	15 + 2
85	5.0	6.6	15	13 + 2	12 + 2

\* First probe sample taken before the eight piston samples, and the second after.

\*\* This figure is the total of the sampling and purge times for the preceeding probe sample. Between the two probe samples the probes were moved above the axis of the piston with the fluid in the probe tube stagnant. x is at least 10 min.

Table IV  
Over-All Transfer Data

Run No.	Inlet and Outlet Concentrations lb. moles/cu.ft. x 10 <sup>3</sup>				Flow Rates Ft. <sup>3</sup> /hr./ft. <sup>2</sup>		Overall Acetic Acid Transfer Rates lb. moles/hr. x 10 <sup>3</sup>			Percentage Deviations $\frac{N_w - N_k}{N} \times 100$	Acetic Acid Material Balance % Difference
	Water		Ketone		Water	Ketone	Water	Ketone	Average		
	In Cw <sub>1</sub>	Out Cw <sub>2</sub>	In Ck <sub>2</sub>	Out Ck <sub>1</sub>	L <sub>w</sub>	L <sub>k</sub>	N <sub>w</sub>	N <sub>k</sub>	N		
71	----	----	----	----	42.5	37.5	7.01	7.36	7.18	-----	-----
72	49.9	36.5	6.9	22.9	42.5	37.5	7.01	7.36	7.18	-4.87	-1.19
73	50.2	36.4	6.9	22.7	43.0	36.3	7.29	7.03	7.16	+3.63	+0.89
74	50.0	36.1	6.8	22.8	43.0	36.8	7.32	7.28	7.30	+0.55	+0.30
75	50.2	36.3	6.8	22.6	43.4	36.3	7.36	7.14	7.25	+3.03	+1.10
76	50.2	36.6	6.8	22.6	43.0	36.3	7.18	7.02	7.10	+2.30	+0.47
77	50.0	36.7	6.9	22.6	42.9	36.8	7.03	7.04	7.04	-0.04	-0.03
78	50.0	36.8	7.0	22.6	42.8	36.4	6.94	6.97	6.96	-0.43	-0.10
79	49.9	35.7	7.0	23.9	43.0	36.8	7.47	7.65	7.56	-2.38	-0.54
80	50.0	22.2	6.8	21.5	36.5	73.0	12.4	13.1	12.8	-5.16	-2.34
81	50.0	21.7	6.8	21.6	36.5	72.9	12.7	13.2	13.0	-3.85	-1.72
82	50.0	32.4	6.8	24.7	72.2	72.9	15.6	15.9	15.8	-1.90	-0.60
83	50.0	32.4	6.8	24.8	72.2	72.5	15.6	16.0	15.8	-2.09	-0.66
84	50.2	32.5	7.1	24.8	90.9	90.5	19.8	19.7	19.7	+0.20	+0.03
85	50.2	32.5	7.1	24.8	90.9	90.5	19.8	19.7	19.7	+0.20	+0.03



Table V

Concentration Profiles in Cross-Sections Perpendicular To The Column Axis as Determined by Sampling with the Hypodermic Needle

Position (See Fig. 34)	Concentration of Acetic Acid lb. moles/ft. <sup>3</sup> x 10 <sup>3</sup>							
	Run Number							
	71	72	73	74	75	76	77	78
1	36.2	36.7	47.5			46.8	37.1	37.4
2	36.4	36.8	47.2					
3	36.7	34.3	47.4			46.8	36.9	37.2
4	36.5	35.8	46.8					
5	36.9	36.7	46.8			46.8	36.9	37.1
6	37.7		46.5	36.4*	36.8*			
7	37.7	37.0	46.2			46.9	36.7	36.8
8								
9						46.8	36.7	36.8
10						47.1	36.9	37.0
11						46.9	36.8	37.0
12						46.9	37.0	37.0
13						46.8	36.7	37.0
14						46.8	36.8	37.0
15						46.8	36.4	36.8
16						46.8	35.8	36.9
17						47.0	35.8	36.8
18						47.1	36.4	37.1
19						47.1	36.8	37.4
Average Con- centration	36.8	36.2	46.9	36.4	36.8	46.9	36.7	37.0
Standard Deviation	±0.5	±0.9	±0.5	±0.4	±0.1	±0.1	±0.4	±0.2
Height above Nozzle Tips	4"	4"	6'4½"	4"	4¾"	6'4½"	4"	4"
Average Ketone Entrainment In Each 30 ml. Sample, mls.	0.5	0.5	0.5	1.0	0.5	0.5	0.5	0.5

\* Average of 6 samples taken at position 6 as a function of time after steady state had been reached in the column. See Table VI.

Table VI

Concentration of Water Phase at Position 6 as a Function  
of Time After Start-Up of a Run

Sample No.	Time After Start-up min.		Concentration of Acetic Acid in Sample Taken by Hypodermic Needle at Position 6 lb. moles/ft <sup>3</sup> x 10 <sup>3</sup>	
	Run 74	Run 75	Run 74	Run 75
1	3	1	33.8	
2	15	8	38.2	36.2
3	25	18	36.8*	36.7**
4	35	28	36.6*	36.7**
5	49	38	35.5*	36.9**
6	59	48	36.4*	36.8**
7	69	58	36.5*	36.7**
8	79	68	36.5*	36.7**
Average			36.4*	36.8**

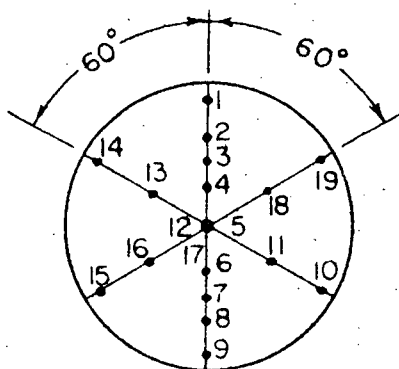
\* Samples 3 to 8 have been averaged to represent the steady state concentration of the water phase at position 6 in the cross-section. The Standard Deviation of these 6 samples is  $\pm 0.4 \times 10^{-3}$ .

\*\* Samples 3 to 8 have been averaged to represent the steady state concentration of the water phase at position 6 in the cross-section. The Standard Deviation of these samples is  $\pm 0.1 \times 10^{-3}$ .

Table VII  
Hypodermic Syringe Sampling Rates

Position (See Fig.34)	mls./min.							
	Run Number							
	71	72	73	74	75	76	77	78
1	30	7.5	8.5			10	10	10
2	30	12.6	8.6					
3	30	12.0	7.0			10	10	10
4	30	12.9	9.4					
5	30	10.3	8.6			10	10	10
6	15		8.0	10.0*	10.0*			
7	15	10.0	9.1			15	10	10
8								
9						15	10	10
10						10	10	10
11						10	10	10
12						10	10	10
13						10	10	10
14						10	10	10
15						10	10	10
16						10	10	10
17						10	10	10
18						10	10	10
19						10	10	10

\* Average ketone sampling rate in 6 samples taken at Position 6.



ACTUAL LOCATION OF  
SYRINGE SAMPLES

Full Size

FIGURE 34. POSITIONS IN COLUMN CROSS-SECTION AT WHICH  
HYPODEMIC SYRINGE SAMPLES WERE TAKEN

Table VIII

Concentrations and Comparison of Piston and Probe Samples<sup>1</sup>

Run No.	Sample Volumes mls.		Holdup %	Concentrations of Acetic Acid lb. moles/ft <sup>3</sup> x 10 <sup>3</sup>					
	Ketone V <sub>k</sub>	Water V <sub>w</sub>		H	C <sub>wf</sub>	C <sub>kf</sub>	C <sub>wi</sub>	C <sub>wp</sub>	C <sub>kp</sub> C <sub>ki</sub>
79							<sup>a</sup> 40.2	41.0	15.0
i	3.8	111.7	3.4		39.5	20.1			0.7
ii	3.7	112.0	3.3		39.6	20.2			3.8
iii	3.5	111.7	3.1		39.8	20.3			6.5
iv	4.0	111.9	3.6		39.2	19.8			-8.2
80*							<sup>a</sup> 25.3	26.8	10.3
i	9.3	106.4	8.0		25.1	12.2			9.1
81*							<sup>b</sup> 25.3	26.8	10.8
i	8.2	108.5	7.0		25.2	12.3			10.1
ii	8.4	106.2	7.3		25.6	12.5			16.2
iii	8.4	107.5	7.3						
82*							<sup>c</sup> 40.2	41.4	16.0
i	10.0	105.3	8.7		39.5	20.1			12.3
ii	9.5	105.5	8.3		39.4	20.0			10.5
83							<sup>d</sup> 40.2	40.2	15.6
i	9.6	101.8	8.6		39.4	20.0			11.5
ii	9.4	105.4	8.2		39.5	20.1			12.4
iii	9.8	105.4	8.5		39.5	20.1			12.2
iv	9.8	105.0	8.5		39.6	20.2			14.1
84							<sup>e</sup> 41.2	41.2	16.3
i	13.6	101.4	11.8		40.3	19.7			12.9
ii	13.1	101.7	11.4		40.3	19.7			12.2
iii	13.6	101.4	11.8		40.2	19.6			12.0
iv	13.1	101.6	11.4		40.2	19.6			11.1
v	14.6	100.9	12.7		40.0	19.5			11.0
vi	13.7	101.3	11.9		40.2	19.6			12.1
vii	13.7	101.3	11.9		40.3	19.7			13.0
viii	14.2	101.3	12.3		40.3	19.6			12.7
								41.2	16.4

<sup>1</sup> In all cases the axis of the piston was 1.59 ft. above the nozzle tips.

\* Probes were located one inch above piston axis, i.e. one inch too high.

a Calculated by Equation 6

c C<sub>wi</sub> taken as C<sub>wp</sub> from Run 83

e C<sub>wi</sub> taken as C<sub>wp</sub>

b C<sub>wi</sub> taken from Run 80

d C<sub>wi</sub> taken as C<sub>wp</sub>

f C<sub>kf</sub> concentrations in Run 84 obtained by titration. C<sub>kf</sub>

concentrations in Runs 79, 80, 81, 82, 83, were obtained from equilibrium curve.

Table IX

Results of Immediate Separation of the Two Phases in the Piston Samples of Run 85<sup>1</sup>

Run No.	Volumes of Piston Samples mls.				Holdup %	Concentration of Acetic Acid lb. moles/ft <sup>3</sup> x 10 <sup>3</sup>					
	V <sub>w</sub>	V <sub>w</sub> <sup>II</sup>	V <sub>w</sub>	V <sub>k</sub>		C <sub>wp</sub>	C <sub>wf</sub>	C <sub>wf</sub> <sup>II</sup>	C <sub>kf</sub> *	C <sub>ki</sub>	C <sub>kp</sub>
85											
i	100.0	1.0	101.0	13.2	11.6	41.2	40.1	38.6	19.6	11.2	17.0
ii	100.5	0.6	101.1	13.1	11.5		40.2	38.5	19.5	11.9	
iii	100.3	0.8	101.1	13.2	11.5		40.3	38.5	19.5	12.9	
iv	100.0	1.2	101.2	13.6	11.9		40.2	38.3	19.4	12.0	

<sup>1</sup> The axis of the piston was 1.59-ft. above the nozzle tips.

\* Obtained by titration.

Table X

Maximum Approximate Error of Calculated Initial Ketone Concentration,  $C_{ki}$ 

Run No.	Flow Rates ft <sup>3</sup> /hr./ft <sup>2</sup>		Piston Sample Volumes mls.		Water Phase Acetic Acid Concentrations of Piston Samples*		Error Due to Each Variable in Equation 14**					Approx. Total Max. Error
	Water	Ketone	Ketone	Water	lb. moles/ft <sup>3</sup> x 10 <sup>3</sup>	lb. moles Acetic Acid/ft <sup>3</sup> x 10 <sup>3</sup>	$A'\Delta C_{kf}$	$B\Delta V_w$	$C\Delta V_k$	$D\Delta C_{wf}$	$E\Delta C_{wi}$	$\Delta C_{ki}$
79i	43.0	36.8	3.8	111.7	39.5	40.2	0.1	0.04	1.07	2.94	2.94	7.1
ii			3.7	112.0	39.6		0.1	0.03	0.98	3.03	3.03	7.2
iii			3.5	111.7	39.8		0.1	0.02	0.73	3.19	3.19	7.2
iv			4.0	111.9	39.2		0.1	0.05	1.40	2.80	2.80	7.2
80i	36.5	73.0	9.3	106.4	25.1	25.3	0.1	0.00	0.05	1.14	1.14	2.4
81i	36.5	72.9	8.2	108.5	25.2	25.3	0.1	0.00	0.03	1.32	1.32	2.8
ii			8.4	106.2	25.6		0.1	0.01	0.09	1.26	1.26	2.7
82i	72.2	72.9	10.0	105.3	39.5	40.2	0.1	0.01	0.10	1.05	1.05	2.2
ii			9.5	105.5	39.4		0.1	0.02	0.22	1.11	1.11	2.5
83i	72.2	72.5	9.6	101.8	39.4	40.2	0.1	0.02	0.18	1.06	1.06	2.3
ii			9.4	105.4	39.5		0.1	0.01	0.17	1.12	1.12	2.5
iii			9.8	105.4	39.5		0.1	0.01	0.15	1.07	1.07	2.4
iv			9.8	105.0	39.6		0.1	0.01	0.13	1.07	1.07	2.3
84i	90.9	90.5	13.6	101.4	40.3	41.2	0.1	0.01	0.10	0.75	0.75	1.7
ii			13.1	101.7	40.3		0.1	0.01	0.11	0.78	0.78	1.8
iii			13.6	101.4	40.2		0.1	0.01	0.11	0.75	0.75	1.7
iv			13.1	101.6	40.2		0.1	0.01	0.12	0.78	0.78	1.8
v			14.6	100.9	40.0		0.1	0.02	0.11	0.69	0.69	1.6
vi			13.7	101.3	40.2		0.1	0.01	0.11	0.74	0.74	1.7
vii			13.7	101.3	40.3		0.1	0.01	0.10	0.74	0.74	1.7
viii			14.2	101.3	40.3		0.1	0.01	0.09	0.71	0.71	1.6

\* Water phase acetic acid concentrations of piston samples taken from Table VIII  
 \*\* See sample calculation in Appendix

Table XI  
Comparison of Two Methods of Analysis

Samples from Run 84	Salinometer Readings	Concentration of Acetic Acid in Water Phase Piston Samples	
	ohms	lb. moles/ft. <sup>3</sup> x 10 <sup>3</sup>	
	R <sub>x</sub>	By Salinometer Calibration (See Fig. 32)	By Titration
i *	728.99	35.9	40.3
ii	729.13	35.8	40.3
iii	728.04	36.2	40.2
iv	726.74	35.7	40.2
v	727.15	36.5	40.0
C <sub>wp</sub>	718.35	40.0	41.2

\* Lower case Roman numerals are piston samples from Run 84.



## DISCUSSION

## Operating Conditions

The over-all mass transfer results for runs of the same operating conditions were found to be fairly reproducible as shown in Table IV. The maximum error to be expected in the mass transfer rate ( $N_w$  or  $N_k$ ) was calculated from an equation similar to Equation 12 with the independent variables taken as flow rate and concentration. This maximum percentage error was  $\pm 3\%$  and occurs in runs with the smallest transfer rate. This result was based on a  $\pm 0.004$  cu.ft./hr. fluctuation in the reported flow rate, and a  $\pm 0.1 \times 10^{-3}$  lb. moles/ft.<sup>3</sup> error in the analysis for acetic acid.

At this point it should be mentioned that the author attempted to titrate all the samples to what appeared to be the same pinkish color which represented the end-point in the acid-base titration. A titration of a ketone phase blank solution showed that one drop of base turned the color of the blank considerably darker than that reached at the end-point of the samples. The blank consisted of 5 mls. of ketone, 30 to 40 mls. of ethanol, and 3 drops of phenolphthalein, which was similar to a titrated sample. As a result no blank titration correction was applied to the measured concentrations of the ketone samples. A similar blank was prepared for the water phase samples and again no blank correction was needed.

In titrating the water phase samples some difficulty was obtained in reaching the end-point because of the author's inability to distinguish the first stages of pink from the colorless solution of the initial sample. As a result, the titration of 10 samples of the same water phase solution yielded concentrations which had a standard deviation of  $\pm 0.1 \times 10^{-3}$  lb. moles/ft<sup>3</sup>. This would be equivalent to approximately  $\pm 2$  drops of the sodium hydroxide solution.

The ketone phase was much easier to titrate because of the much more distinct color changes. As the end-point of the ketone phase was approached, and, in fact, as one drop of sodium hydroxide was added the color of the solution would turn a distinct yellow. One more drop of base would cause the color to change to a distinct pink. Titration of 10 ketone phase samples of the same concentration showed no variation in the volume of base required to reach each end-point. However, a  $\pm 0.1 \times 10^{-3}$  lb. moles/ft<sup>3</sup> variation in the concentration of the ketone phase was also applied in determining the errors involved in the various measured quantities for calculation of the maximum error to be expected in the mass transfer rates ( $N_w$  or  $N_k$ ) and in the calculated initial ketone concentration ( $C_{ki}$ ).

It should also be mentioned that the same batch of sodium hydroxide solution was used to titrate all the samples from Runs 73 to 85. A check on the normality of the sodium

hydroxide solution at the end of all the experimental work showed no change in the normality of the solution from that which applied at the beginning of the experimental work.

The transfer rates and acetic acid material balances for Runs 79 to 85 have been calculated neglecting any leakage that occurred at the piston sampler. In Run 79 the average total rate of leakage was 15 mls./min. while in Runs 80 to 85 the average leakage rate was 10 mls./min. when the piston was in the left-hand position in the piston block. No leakage took place in Runs 80 to 85 while the piston was placed in the right-hand position in the piston block. As was mentioned earlier, sampling in these runs was conducted by moving the piston from right to left, the piston being returned to the right after a sample was taken.

#### Cross-Sectional Concentration Measurements

Table V shows the concentration data obtained by sampling the water phase with the hypodermic syringe at particular cross-sections at right angles to the axis of the column. No concentration gradient was observed. However, the measurements are not identical and standard deviations of  $\pm 0.9 \times 10^{-3}$  lb. moles/ft.<sup>3</sup> and less appear in Table V. These standard deviations refer to the concentration measurements of a single run as listed in the table. The concentration level corresponding to the figure of  $\pm 0.9 \times 10^{-3}$  was  $36.2 \times 10^{-3}$  lb. moles/ft.<sup>3</sup> and for the other runs approximately the same level applied.

The volume of ketone entrained along with the water phase of the syringe sample varied from 0.5 to 1.0 mls. The total volume of these samples was approximately 30 cc. A material balance calculation was made to determine approximately how much the concentration of the water phase of a typical syringe sample would change, from conditions existing in the column, because of the presence of 1 ml of ketone phase. The change was found to be from  $37.0 \times 10^{-3}$  to  $36.6 \times 10^{-3}$  or a change of  $0.4 \times 10^{-3}$  lb. moles/ft<sup>3</sup>. From the point of view of taking a number of samples at one cross-section, the concentrations should be fairly comparable since almost all the syringe samples contained approximately the same volume of ketone.

It should be noted also that in the column there were a large number of small ketone drops which did not appear to be moving very fast relative to the column walls. When these drops came near the syringe needle entrance they could be observed entering the needle. Because of the size of these drops and because of their slow ascent it is possible that they would be very close to being in equilibrium with the water phase of the elevation (above the nozzle tips) being sampled. If this hypothesis was valid, and if these drops formed the total volume of ketone entrainment in the syringe samples, little extraction would result because of the presence of this entrainment and the measured water phase concentration in the syringe samples would have been very close to the concentration of the water phase in the column at that point. However, larger

ketone drops hitting the needle entrance would also provide some entrainment presumably, so that some uncertainty in the results of the syringe samples remains.

Table VI gives the concentration of the water phase at Position 6 as a function of time after the start-up of a run. The object in Run 74 and 75 was to determine whether or not consecutive syringe samples, taken at one position in the cross-section during the steady state operation of the column would show any variation in the measured concentration of acetic acid. In Run 74 a standard deviation of  $\pm 0.4 \times 10^{-3}$  lb. moles/ft.<sup>3</sup> was calculated for six samples taken during the steady state operation of the column. A similar value of  $\pm 0.1 \times 10^{-3}$  lb. moles/ft.<sup>3</sup> was calculated for Run 75. The average concentrations for these six samples for Runs 74 and 75 were  $36.4 \times 10^{-3}$  and  $36.8 \times 10^{-3}$  lb. moles/ft.<sup>3</sup> respectively. In Run 74 one ml. of ketone was entrained in each syringe sample, whereas in Run 75 only 0.5 mls. of ketone was entrained in each syringe sample. The measured concentration of acetic acid in water phase and ketone phase samples includes a  $\pm 0.1 \times 10^{-3}$  lb. moles/ft.<sup>3</sup> variation due to the titration technique of the author. This being the case, consecutive syringe samples, taken at one position in the cross-section during the steady state operation of the column, would be expected to show some variation in the measured concentration of acetic acid.

## Piston Samples Compared To Probe Samples

Tables VIII and IX show the values of the initial ketone concentrations,  $C_{ki}$ , as calculated by Equations 7, 8, or 9, for Runs 79 to 85. Included in these tables are the values of the initial ketone concentrations,  $C_{kp}$ , as measured with the ketone phase probe and to which the values of  $C_{ki}$  are to be compared. Table III gives the sampling rates and purging times which were used to obtain all the probe samples. In some runs the values of  $C_{ki}$  and  $C_{kp}$  are not comparable for a number of reasons. In some cases the probes were sampling at a position one inch too high above the piston axis and in other cases the purge time to obtain uniform concentrations in the probe samples did not meet the minimum purge time as specified by Choudhury in his work (1n). Each run will therefore be discussed in turn to explain how values of  $C_{ki}$  were calculated despite these errors in experimental work.

### Run 79

This was the first run that was made with the piston samplers and average total leakages of 15 mls./min. were encountered. The purging time for both probes was 10 minutes which was three to four minutes less than Choudhury's recommended minimum purge time. However, it is felt that the concentration of the sample which was obtained by the probe ( $15.0 \times 10^{-3}$  lb. moles/ft.<sup>3</sup>) is fairly representative since

it agrees with Choudhury's value ( $16.0 \times 10^{-3}$  lb. moles/ft.<sup>3</sup>) obtained in Run 61 (1) for approximately the same operating conditions and at the same height above the nozzle tips. Aside from this, the values of  $C_{ki}$  as calculated by Equation 7 differ by a very wide margin from the value of  $C_{kp}$  and no real comparison between  $C_{ki}$  and  $C_{kp}$  is possible. In Run 79 the ketone holdup is very low (approximately 3.5%). This situation corresponds to a high  $V_w/V_k$  ratio. Upon examining Equation 7, it is easy to see that  $\left\{ C_{wf} - \left[ \frac{C_{wi} \tau + C_{wi} \beta}{2} \right] \right\}$  must be known very accurately in order to calculate values of  $C_{ki}$  with some degree of accuracy. If this difference is out by much, when multiplied by high  $V_w/V_k$  ratios, calculated values of  $C_{ki}$  become grossly in error, as can be seen in Table VIII. In addition it is very easy to measure  $V_w$  but much more difficult to measure  $V_k$ . At this high  $V_w/V_k$  ratio errors in  $V_k$  contribute significantly to errors in  $C_{ki}$  (see Group C  $\Delta V_k$  in Table X), as, also, do errors in  $C_{wf}$  and  $C_{wi}$  (see Groups D  $\Delta C_{wf}$  and E  $\Delta C_{wi}$ ).

It should also be pointed out that  $C_{wi}$  for Run 79 in Table VIII was obtained by taking syringe samples of the water phase immediately above and below the piston block, analyzing them, and applying the results to Equation 6. As can be seen in Table VIII this value of  $C_{wi}$  does not agree exactly with the value of  $C_{wp}$ , which was obtained by analysis of a water phase sample taken at the axis of the piston by the

water phase probe. One reason for this disagreement could be the presence of 0.5 mls. of ketone phase entrained in each syringe sample. This could produce a final calculated value of  $C_{wi}$  low by as much as  $\pm 0.2 \times 10^{-3}$  lb. moles/ft.<sup>3</sup>. A second reason could be that insufficient time was allowed for purging the probes in order to obtain a sample of the proper uniform concentration. A third reason, mentioned earlier, could be that syringe samples, taken at one point in the cross-section during the steady state operation of the column, may not always be truly representative of the water phase at that particular cross-section. This, plus the uncertainty of the titration technique could cause  $C_{wi}$  and  $C_{wp}$  to be different. Admittedly the difference between these two in Table VIII is small, but particularly for the conditions of Run 79, errors in  $C_{wi}$  are important in producing error in  $C_{ki}$  (Table X).

Upon examining the results obtained in Run 79 it was decided to readjust the flow rate valves to increase the ketone phase holdup and to create a more favourable  $V_w/V_k$  ratio. Runs 80 and 81 resulted.

#### Runs 80 and 81

In Runs 80 and 81 it was found that the probes had been located one inch too high above the piston axis when sampling was taking place with them. As a result, no matter what the purging times for the probes were, no proper comparison of  $C_{ki}$  with the resulting value of  $C_{kp}$  can be made.



However, to draw some form of comparison reference is made to Run 66 by Choudhury (1) which is a run of approximately the same operating conditions, and in which, proper purging times were used for his sampling with the probes. Choudhury's values for  $C_{wp}$  and  $C_{kp}$ , at a height above the nozzle tips at which the axis of our piston was located (1.59-ft.), were  $25.3 \times 10^{-3}$  and  $10.0 \times 10^{-3}$  lb. moles/ft.<sup>3</sup> respectively. A value of  $C_{wi}$  was obtained for each run by use of the syringe samples from Run 80 and applying them to Equation 6. The result agrees with  $C_{wp}$  from Choudhury's work in Run 66 at the same location.

Only one piston sample was taken in Run 80 because inadvertently the piston compartment, which was to slide into line with the column when a sample was taken, was not filled with water phase solution. When the piston sample was taken the operation of the column was disrupted completely and no further sampling was possible.

However, the one value of  $C_{ki}$  which was calculated,  $9.1 \times 10^{-3}$  lb. moles/ft.<sup>3</sup>, was of the correct order of magnitude but slightly lower than the value of  $10.0 \times 10^{-3}$  lb. moles/ft.<sup>3</sup> which was obtained from Choudhury's work (1).

Run 81 was a repeat of Run 80, except that the syringe samples had to be omitted because too much ketone phase (2 to 3 mls. in Run 81) was being entrained along with the water phase. However, values of  $C_{ki}$  were calculated for the two piston samples by using  $C_{wi}$  from Run 80 as already

mentioned. The first value of  $C_{ki}$  ( $10.1 \times 10^{-3}$ ) agreed very well with Choudhury's value ( $10.0 \times 10^{-3}$ ) but the second value of  $C_{ki}$  ( $16.2 \times 10^{-3}$ ) was much higher than Choudhury's value. The reason that the second piston value of  $C_{ki}$  was calculated to be so high was that  $C_{wf}$  ( $25.6 \times 10^{-3}$ ) was found to be higher than  $C_{wi}$  ( $25.3 \times 10^{-3}$ ). A third piston sample was taken to provide a check on the ketone phase holdup values of the other piston samples and analyses were not carried out.

In Runs 80 and 81 a more favourable  $V_w/V_k$  ratio was obtained, and, as can be seen in Table X, in the  $C \Delta V_k$  Group, the errors in  $V_k$  do not contribute significantly to the error in  $C_{ki}$ . However, the main difficulty in Runs 80 and 81 was that too little extraction was taking place in the column in the region of the piston sampler. In other words the phases were near equilibrium there. Thus when a piston sample was taken  $C_{wf}$  differed very little from  $C_{wi}$ . This small difference was very hard to pick up by the titration technique and it was decided to readjust the flow rates so that the greater part of the over-all extraction of the column took place in the region of the piston sampler. Runs 82 and 83 resulted.

Runs 82 and 83

In Run 82, as in Runs 80 and 81, the probes were located one inch too high above the axis of the piston when sampling with them. As a result Run 83 was made as a repeat of Run 82. The probes were relocated to sample both phases at the axis of the piston.

In Run 83 more than the minimum purge time to obtain a uniform sample with the probes was used as can be seen in Table III. For reasons mentioned earlier the syringe samples were discontinued and  $C_{wi}$  was taken as  $C_{wp}$  since no other alternative presented itself. Values of  $C_{ki}$  were calculated, both in Runs 82 and 83, with  $C_{wi}$  taken as  $C_{wp}$  from Run 83. In these two runs calculated values of  $C_{ki}$  varied from  $10.5 \times 10^{-3}$  to  $14.1 \times 10^{-3}$  lb. moles/ft.<sup>3</sup>, all of which were lower than the value of  $C_{kp}$  ( $15.6 \times 10^{-3}$ ), again from Run 83. Values of  $C_{wf}$  and of  $C_{kf}$  did not vary by more than  $0.2 \times 10^{-3}$  lb. moles/ft.<sup>3</sup> in both runs and the differences in the calculated values of  $C_{ki}$  must be attributed mostly to the differences in the  $V_w/V_k$  ratio which varied from 10.6 to 11.1, as can be calculated from Table VIII.

The flow rates in Runs 82 and 83 were such that the desired, greater percentage of the total extraction of the column took place in the region of the piston sampler. Thus after a piston sample had been taken a greater amount of extraction continued to take place from the water phase to the ketone phase of the piston sample till equilibrium was reached. As can be seen from Table VIII differences between  $C_{wf}$  and  $C_{wi}$  of  $0.6 \times 10^{-3}$  to  $0.8 \times 10^{-3}$  lb. moles/ft.<sup>3</sup> were calculated for all the piston samples of both runs.

Upon examining the results of Runs 82 and 83 it was decided to increase the ketone phase holdup still further and still maintain a great percentage of the total extraction in the region of the piston sampler. Runs 84 and 85 resulted.

## Runs 84 and 85

For the first probe sample of Run 84 the purging time used prior to sampling the water and ketone phases at the axis of the piston was lower than the minimum purge time specified by Choudhury. For the second probe samples of Run 84 and for Run 85, a repeat of the operating conditions of Run 84, sufficient purge time was allowed. However, despite the fact that sufficient purge time was not allowed in the first probe samples of Run 84, the value of  $C_{wp}$  agrees with that of the second probe sample for Run 84 and with that of Run 85.  $C_{kp}$  in Run 85 is a little higher than  $C_{kp}$  of Run 84, but the second value for Run 84 agrees with the first value for that run. In Run 84 the probes were lowered to the axis of the piston both before and after the 8 piston samples were taken. Thus there are two sets of probe samples for this run. It would seem that, in fact, purging times were really adequate for all samples in both runs.

Values of  $C_{ki}$  in Run 84 were calculated using the water phase probe value,  $C_{wp}$ , as the initial concentration of the water phase at the time of sampling,  $C_{wi}$ . The values of the calculated initial ketone concentration,  $C_{ki}$ , for the 8 piston samples varied from  $11.0 \times 10^{-3}$  to  $13.0 \times 10^{-3}$  lb. moles/ft<sup>3</sup>. Their average was  $12.1 \times 10^{-3}$  lb. moles/ft<sup>3</sup>, and their standard deviation was  $\pm 0.7 \times 10^{-3}$  lb. moles/ft<sup>3</sup>. The average volume of the ketone phase,  $V_k$ , for the 8 piston samples was 13.6 mls.

The standard deviation of this volume was  $\pm 0.5$  mls. Corresponding values for the water phase volumes,  $V_w$ , were 101.3 mls. and  $\pm 0.2$  mls. respectively. All the values of the calculated initial ketone concentration were less than the value of  $C_{kp}$  ( $16.4 \times 10^{-3}$ ).

In Run 85 the values of  $C_{ki}$  as calculated by Equation 9, were very close to the values of  $C_{ki}$  in Run 84 which were calculated by Equation 8. The average value of  $C_{ki}$  for Run 85 was  $12.0 \times 10^{-3}$  lb. moles/ft.<sup>3</sup> with a standard deviation of  $\pm 0.5 \times 10^{-3}$  lb. moles/ft.<sup>3</sup> for the four piston samples.

In all the runs the value of  $C_{ki}$ , as calculated by Equation 7 or 8, for the piston samples was smaller than the value as measured by the ketone phase probe except in one case. In most cases even the value of  $C_{ki}$  plus the corresponding expected maximum error of  $C_{ki}$  was smaller than the corresponding value of  $C_{kp}$ .

As stated earlier it was thought that values of  $C_{kp}$  possibly could be too large because of the residence time of the ketone drops at the ketone probe entrance, and because of the "interface of coalescence" sometimes created there. Both of these conditions would allow transfer of acetic acid into the ketone phase, and of course, such transfer would not have occurred if the probes had not been present.

In addition to the reliability of  $C_{kp}$  samples, a point needing consideration is whether or not  $C_{wp}$  (or,  $C_{wi}$ ) is a representative sample of the water phase concentration to be compared with  $C_{wf}$  of the piston sample.  $C_{wp}$  is assumed to be an average bulk concentration of the water phase at the sampling point. It is possible that the water phase probe does not afford adequate sampling of the region near the drops. This would suggest that the values of  $C_{wp}$  would be too high and those of  $C_{ki}$  as calculated by Equation 8, too low. In other words the water phase probe may not give true bulk concentrations of the material accompanying the drops in taking a piston sample and further investigation is required to see whether or not  $C_{wp}$  can be used for the initial water phase concentration in the material balance equation. In the case of the ketone probe samples a similar error might be much more serious because drops are collected out of proportion to the actual hold up in the column.

#### Approximation of Errors

The approximate maximum error due to each variable taken into account in Equation 13 was summarized in Table X. As can be seen the expected error due to each variable can be reduced by operating at large ketone holdups and by adjusting flow rates to encourage a large amount of the extraction to take place in the region of sampling. (See columns in Table X giving  $V_k$ ,  $V_w$ ,  $C_{wf}$  and  $C_{wi}$ ).

It can be seen that the error in a calculated quantity that is a function of several directly measured quantities depends on (a) the nature of the function, (b) the magnitudes

of the measured quantities, and (c) the magnitudes of the errors (10).

It is possible that Equation 13, as used with all signs positive, quite probably overestimates the error involved in the calculated quantity. It takes no account of the probability of compensating errors. This fact can be shown easily by simulating the taking of a piston sample. A ketone phase, called Cki, was analyzed and found to have a concentration of  $7.06 \times 10^{-3}$  lb. moles/ft<sup>3</sup>. A water phase, called Cwi, was analyzed and found to have a concentration of  $32.67 \times 10^{-3}$  lb. moles/ft<sup>3</sup>. Volumes of these phases were mixed in the collection flask in a ratio typical of a piston sample. The phases were well mixed, allowed to settle, and their volumes measured. The phases were then separated and analyzed, their concentrations being designated as Ckf and Cwf. Equation 5 was then used to calculate Cki which was compared to Cki as measured initially as  $7.06 \times 10^{-3}$ . Table XII shows the results of four such experiments. The average value of Cki, as calculated by Equation 5, was  $7.30 \times 10^{-3}$  lb. moles/ft<sup>3</sup>. Individual values differed from this average by  $\pm 0.3 \times 10^{-3}$  lb. moles/ft<sup>3</sup>.

This example illustrates how errors could tend to be compensating as the average value of the calculated Cki differs from the measured value by only  $0.24 \times 10^{-3}$  lb. moles/ft<sup>3</sup>. However, Equation 13 would lead one to believe that

Table XII  
Simulated Piston Samples

No.	Volumes mls.		Concentrations of Acetic Acid				
	Ketone	Water	lb. moles/ft. <sup>3</sup> x 10 <sup>3</sup>				
	Vk	Vw	Cwf	Ckf	Cwi	Cki	Cki
			Titrated	Titrated	Titrated	Calc'd	Titrated
1	10.0	104.9	31.89	15.15	32.67	6.97	7.06
2	10.5	104.7	31.89	15.15	32.67	7.37	7.06
3	10.3	105.2	31.89	15.15	32.67	7.19	7.06
4	10.8	104.5	31.89	15.15	32.67	7.60	7.06
Average						7.30	



maximum errors of approximately  $\pm 2.0 \times 10^{-3}$  lb. moles/ft.<sup>3</sup> would be possible for each calculated value of  $C_{ki}$ .

#### Salinometer Measurements

Table XI shows the results of the measurements of the resistances of the water phase portion of the first five piston samples taken in Run 84. It also shows the concentrations of the samples corresponding to these resistance measurements as obtained from Figure 32, the calibration curve, and compares these with concentrations determined by titration. As can be seen the two values were found to be quite different. It was found on the trip to Nanaimo that the piston samples were hazy, whereas the calibration samples were not. (Both had been kept in the refrigerator for five days). The haze was probably a fine suspension of ketone which, as mentioned earlier, would affect the resistance readings considerably. On returning from Nanaimo the concentrations of the five piston samples were analyzed again by titration and the results were found to check with the concentrations measured prior to the trip. The same could be said for the calibration samples which were also checked.

As the salinometer results did not agree with the titration results the method was not used further in the present research. Table XI suggests that the difference between the salinometer results and the titration results depends on the source of the solution. However more work would be needed to confirm this point.

## CONCLUSIONS

Concentration traverses of the continuous water phase solution were made across the cross-section of the column at definite elevations above the nozzle tips and no concentration gradients were found. However, standard deviations as high as  $\pm 0.9 \times 10^{-3}$  lb. moles/ft.<sup>3</sup> about an average concentration of  $36.2 \times 10^{-3}$  lb. moles/ft.<sup>3</sup> were reported.

The hypodermic syringe method of measuring the concentration of the water phase solution in the tower was not always operable because the presence of a small volume of ketone phase could change the concentration of the water phase as extraction would continue after a syringe sample was taken until equilibrium was reached between the two phases. The volume of ketone in the water phase samples was appreciable when the column was operated at higher ketone holdups so that the syringe method could not be used in conjunction with many of the runs in which piston samples were taken. However, when the cross-sectional traverses were made, the holdup was low and approximately the same small volume of ketone was entrained in each syringe sample. Therefore the results are not much in error and certainly comparable.

Calculated initial ketone concentrations are still uncertain until it can be determined whether or not the measured water phase probe concentrations,  $C_{wp}$ , are representative samples of the aqueous phase. In the piston method of sampling, the results are extremely sensitive to the results of the analysis of the water phase samples.

The value of the calculated initial ketone concentration for the piston samples,  $C_{ki}$ , plus the approximate maximum error of this calculated value,  $\Delta C_{ki}$ , was almost always less than the measured probe concentration,  $C_{kp}$ . Thus values of  $C_{kp}$ , are probably too large because of the residence time of the ketone drops at the ketone probe entrance and because of the interface sometimes created there. This conclusion, however, is certainly dependent on the water phase probe sample being representative.

The piston sampler proved to be a quick and easy means of literally removing a section of the operating column from the extraction tower without seriously interrupting the operation of the apparatus. It is recommended that in addition to carrying out further studies on sampling with the piston, further work be done on the effect of sampling rate on the value of the ketone concentration obtained by sampling with the probe. The work of Choudhury (1c) was done at a location in the column at which the phases were close to equilibrium so that only a small effect on the ketone concentration would result from lingering and coalescing of ketone drops at the probe entrance.

## NOMENCLATURE

## Symbols

Cw1	Concentration of acetic acid in the water phase entering the top of the column, lb. moles/ft <sup>3</sup>
Cw2	Concentration of acetic acid in water phase leaving the bottom of the column, lb. moles/ft <sup>3</sup>
Ck1	Concentration of acetic acid in the ketone phase leaving the top of the column, lb. moles/ft <sup>3</sup>
Ck2	Concentration of acetic acid in the ketone phase entering the bottom of the column, lb. moles/ft <sup>3</sup>
Cwi	Initial steady state concentration of acetic acid in the water phase in the column at the sampling point, lb. moles/ft <sup>3</sup>
Cwf	Final concentration of acetic acid in the water phase portion of the collected piston sample after equilibrium has been reached with the ketone phase portion, lb. moles/ft <sup>3</sup>
Cwp	Concentration of acetic acid in the water phase at the time of sampling with the water phase probe, lb. moles/ft <sup>3</sup>
Cki	Calculated initial steady-state concentration of acetic acid in ketone phase in the column at the axis of the piston, lb. moles/ft <sup>3</sup>
Ckf	Final concentration of acetic acid in the ketone phase portion of the collected piston sample after equilibrium has been reached with the water phase portion, lb. moles/ft <sup>3</sup>
Ckp	Concentration of acetic acid in the ketone phase at the time of sampling with the ketone phase probe, lb. moles/ft <sup>3</sup>
Cwi) <sub>T</sub>	Initial concentration of acetic acid in the water phase in the column at the top of the piston block by sampling with a hypodermic syringe, lb. moles/ft <sup>3</sup>

$C_{wi})_B$	As $C_{wi})_T$ , except at the bottom of the piston block.
" $C_{wf}$	Final concentration of acetic acid in the water phase remaining with the ketone phase after immediately drawing the major portion of the water phase from the ketone phase of the piston samples in Run 85. This value is in equilibrium with the ketone phase. lb. moles/ft <sup>3</sup>
" $C_{wf}$	Final concentration of acetic acid in the major portion of the water phase which was drawn from the ketone phase of the piston samples in Run 85, lb. moles/ft <sup>3</sup>
$\Delta C_{wi}$	Assumed error in $C_{wi}$ , lb. moles/ft <sup>3</sup>
$\Delta C_{wf}$	Assumed error in $C_{wf}$ , lb. moles/ft <sup>3</sup>
$\Delta C_{kf}$	Assumed error in $C_{kf}$ , lb. moles/ft <sup>3</sup>
$L_k$	Ketone phase flow rate, ft <sup>3</sup> /hr.ft <sup>2</sup>
$L_w$	Water phase flow rate, ft <sup>3</sup> /hr.ft <sup>2</sup>
$A$	Cross-sectional area of the column, ft <sup>2</sup>
$N_w$	Transfer rate of acetic acid based on the inlet and outlet water phase concentrations, lb. moles/hr.
$N_k$	Transfer rate of acetic acid based on the inlet and outlet concentrations of the ketone phase, lb. moles/hr.
$Q$	The calculated value of some unknown function which contains a number of measured quantities.
$q's$	The measured quantities in some unknown function.
$V_w$	Volume of water phase portion of the collected piston samples, mls.
$V_k$	Volume of ketone phase portion of the collected piston samples, mls.
" $V_w$	Small volume of water phase remaining with the ketone phase portion after immediately drawing off the major portion of the water phase in the piston samples of Run 85, mls.

$V_w$  Volume of the major portion of water phase which was immediately drawn from the piston samples in Run 85, mls.

$\Delta V_w$  Assumed error in  $V_w$ , mls.

H Percentage holdup, i.e. the percent of the total volume of the piston sample occupied by ketone.

Groups in Equation 14

A'  $\frac{\partial C_{ki}}{\partial C_{kf}} = 1$ , dimensionless

B  $\frac{\partial C_{ki}}{\partial V_w} = \frac{1}{V_k} (C_{wf} - C_{wi})$ , lb. moles/ft.<sup>3</sup>.ml.

C  $\frac{\partial C_{ki}}{\partial V_k} = - \frac{V_w}{V_k^2} (C_{wf} - C_{wi})$ , lb. moles/ft.<sup>3</sup>.ml.

D  $\frac{\partial C_{ki}}{\partial C_{wf}} = \frac{V_w}{V_k}$ , dimensionless

E  $\frac{\partial C_{ki}}{\partial C_{wi}} = \frac{V_w}{V_k}$ , dimensionless

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## A P P E N D I C E S

## APPENDIX I

## SAMPLE CALCULATIONS

The following sample calculations were made using the data from Run 84, Piston Sample i. The data usually were recorded in the data books to four significant figures whereas in the tables of this thesis the corresponding data have been rounded off to three significant figures.

1) Rate of Transfer of Acetic Acid

$$(a) \quad Nw = LwA (Cw1 - Cw2) \quad 1$$

$$\text{where } Lw = 90.9 \text{ ft}^3/\text{hr.}/\text{ft}^2$$

$$A = 0.01227 \text{ ft}^2$$

$$Cw1 = 50.23 \times 10^{-3} \text{ lb. moles}/\text{ft}^3$$

$$Cw2 = 32.52 \times 10^{-3} \text{ lb. moles}/\text{ft}^3$$

$$\therefore Nw = (90.9)(0.01227)(50.23 \times 10^{-3} - 32.52 \times 10^{-3}) \\ = 19.75 \times 10^{-3} \text{ lb. moles}/\text{hr.}$$

$$\text{reported as } = 19.8 \times 10^{-3} \text{ lb. moles}/\text{hr.}$$

$$(b) \quad Nk = LkA (Ck1 - Ck2) \quad 2$$

$$\text{where } Lk = 90.5 \text{ ft}^3/\text{hr.}/\text{ft}^2$$

$$A = 0.01227 \text{ ft}^2$$

$$Ck1 = 24.83 \times 10^{-3} \text{ lb. moles}/\text{ft}^3$$

$$Ck2 = 7.06 \times 10^{-3} \text{ lb. moles}/\text{ft}^3$$

$$\therefore Nk = (90.5)(0.01227)(24.83 \times 10^{-3} - 7.06 \times 10^{-3}) \\ = 19.72 \times 10^{-3} \text{ lb. moles}/\text{hr.}$$

$$\text{reported as } = 19.7 \times 10^{-3} \text{ lb. moles}/\text{hr.}$$

$$(c) \quad N = \frac{N_w + N_k}{2}$$

3

$$\begin{aligned} \text{from (a) and (b)} \quad N &= \frac{19.75 \times 10^{-3} + 19.72 \times 10^{-3}}{2} \\ &= 19.74 \times 10^{-3} \text{ lb. moles/hr.} \\ \text{reported as} &= 19.7 \times 10^{-3} \text{ lb. moles/hr.} \end{aligned}$$

$$(d) \quad \text{Percentage Deviation} = \left( \frac{N_w - N_k}{N} \right) 100$$

4

from (a), (b), and (c)

$$\begin{aligned} \text{Percentage Deviation} &= \frac{(19.75 \times 10^{-3} - 19.72 \times 10^{-3})}{19.74 \times 10^{-3}} \times 100 \\ &= 0.158 \% \\ \text{reported as} &= 0.2\% \end{aligned}$$

## 2. Acetic Acid Material Balance Percentage Difference

$$\text{Percentage Difference} = \frac{\text{Acid In} - \text{Acid Out}}{\text{Acid In}} \times 100$$

14

$$= \frac{(L_w A C_{w1} + L_k A C_{k2}) - (L_w A C_{w2} + L_k A C_{k1})}{L_w A C_{w1} + L_k A C_{k2}} \times 100$$

$$\begin{aligned} \text{Acid In} &= (90.9)(0.01227)(50.23 \times 10^{-3}) + (90.5)(0.01227)(7.06 \times 10^{-3}) \\ &= 63.84 \times 10^{-3} \text{ lb. moles/hr.} \end{aligned}$$

$$\begin{aligned} \text{Acid Out} &= (90.9)(0.01227)(32.52 \times 10^{-3}) + (90.5)(0.01227)(24.83 \times 10^{-3}) \\ &= 63.82 \times 10^{-3} \text{ lb. moles/hr.} \end{aligned}$$

$$\begin{aligned} \text{Percentage Difference} &= \left( \frac{63.84 - 63.82}{63.84} \right) 100 \\ &= +0.03\% \end{aligned}$$

### 3. Calculated Initial Piston Ketone Concentrations, Cki

$$C_{ki} = \frac{V_w}{V_k} (C_{wf} - C_{wi}) + C_{kf} \quad 8$$

assuming  $C_{wp} = C_{wi}$

Here,

$$V_k = 13.6 \text{ mls.}$$

$$V_w = 101.4 \text{ mls.}$$

$$C_{wf} = 40.32 \times 10^{-3} \text{ lb. moles/ft.}^3$$

$$C_{wp} = 41.23 \times 10^{-3} \text{ lb. moles/ft.}^3$$

$$C_{kf} = 19.7 \times 10^{-3} \text{ lb. moles/ft.}^3$$

$$C_{ki} = \frac{101.4}{13.6} (40.32 \times 10^{-3} - 41.23 \times 10^{-3}) + 19.7 \times 10^{-3}$$

$$= 12.9 \times 10^{-3} \text{ lb. moles/ft.}^3$$

### 4. Maximum Approximate Error

$$\Delta C_{ki} = A' \Delta C_{kf} + B \Delta V_w + C \Delta V_k + D \Delta C_{wf} + E \Delta C_{wi} \quad 13$$

$$\text{where } A' = \frac{\partial C_{ki}}{\partial C_{kf}} = 1$$

$$B = \frac{\partial C_{ki}}{\partial V_w} = \frac{1}{V_k} (C_{wf} - C_{wi})$$

$$C = \frac{\partial C_{ki}}{\partial V_k} = \frac{-V_w}{V_k^2} (C_{wf} - C_{wi})$$

$$D = \frac{\partial C_{ki}}{\partial C_{wf}} = \frac{V_w}{V_k}$$

$$E = \frac{\partial C_{ki}}{\partial C_{wi}} = \frac{V_w}{V_k}$$

$$\text{and where } C_{ki} = \frac{V_w}{V_k} (C_{wf} - C_{wi}) + C_{kf}$$

Values of  $\Delta V_w$ ,  $\Delta V_k$ ,  $\Delta V_{kf}$ ,  $\Delta C_{wf}$ ,  $\Delta C_{wi}$  have been estimated as equal to

$$\Delta V_w = \pm 0.2 \text{ mls.}$$

$$\Delta V_k = \pm 0.2 \text{ mls.}$$

$$\Delta C_{kf} = \pm 0.1 \times 10^{-3} \text{ lb. moles/ft.}^3$$

$$\Delta C_{wf} = \pm 0.1 \times 10^{-3} \text{ lb. moles/ft.}^3$$

$$\Delta C_{wi} = \pm 0.1 \times 10^{-3} \text{ lb. moles/ft.}^3$$

values have been given signs such that  $\Delta C_{ki}$  is a maximum in the following

$$\begin{aligned} \therefore \Delta C_{ki} &= (1)(0.1 \times 10^{-3}) + \frac{1}{13.6}(40.32 \times 10^{-3} - 41.23 \times 10^{-3}) \quad (0.2) \\ &+ \frac{101.4}{13.6}^2 (40.32 \times 10^{-3} - 41.23 \times 10^{-3}) \quad (0.2) + \left(\frac{101.4}{13.6}\right)(0.1 \times 10^{-3}) \\ &+ \left(\frac{101.4}{13.6}\right)(0.1 \times 10^{-3}) \\ &= (0.1 + 0.01 + 0.1 + 0.75 + 0.75)10^{-3} \\ &= 1.71 \times 10^{-3} \text{ lb. moles/ft.}^3 \end{aligned}$$

##### 5. Ketone Holdup Percentage

$$\begin{aligned} H &= \left(\frac{V_k}{V_w + V_k}\right) 100 & 10 \\ &= \left(\frac{13.6}{101.4 + 13.6}\right) 100 \\ &= 11.8\% \end{aligned}$$

The next sample calculation was made using the data from Run 85, Piston Sample i.

6. Calculation of Cki When Phases of Piston Sample Were Separated Immediately After the Piston Sample Was Taken

$$C_{ki} = C_{wf}' \left( \frac{V_w'}{V_k} \right) + C_{wf}'' \left( \frac{V_w''}{V_k} \right) - C_{wp} \left( \frac{V_w}{V_k} \right) + C_{kf} \quad 9$$

where for Run 85, piston sample i

$$C_{wf}' = 40.09 \times 10^{-3} \text{ lb. moles/ft}^3$$

$$C_{wf}'' = 38.6 \times 10^{-3} \text{ lb. moles/ft}^3 \text{ from equilibrium curve}$$

and in equilibrium with

$$C_{kf} = 19.59 \times 10^{-3} \text{ lb. moles/ft}^3$$

$$C_{wp} = 41.17 \times 10^{-3} \text{ lb. moles/ft}^3$$

$$V_w' = 100.0 \text{ mls.}$$

$$V_w'' = 1.0 \text{ mls.}$$

$$V_k = 13.2 \text{ mls.}$$

$$V_w = V_w' + V_w'' = 100.0 + 1.0 = 101.0 \text{ mls.}$$

$$\begin{aligned} \therefore C_{ki} &= \left( \frac{100.0}{13.2} \right) (40.09 \times 10^{-3}) + \left( \frac{1.0}{13.2} \right) (38.6 \times 10^{-3}) \\ &\quad + (41.17 \times 10^{-3}) \left( \frac{101.0}{13.2} \right) + 19.59 \times 10^{-3} \\ &= 11.21 \times 10^{-3} \text{ lb. moles/ft}^3 \end{aligned}$$

## APPENDIX II

## VOLUME CHANGES DUE TO CHANGES IN MUTUAL SOLUBILITY

Data for the mutual solubility for the system methyl isobutyl ketone-acetic acid-water was taken from Sherwood, T.K., Evans, J.E., and Longcor, Ind. Eng. Chem., 31, 1144, (1939). Using these data the solubility curve was drawn on triangular graph paper, as shown in Figure 35.

It was desired to know whether or not any volume changes occur, other than those due to the transfer of acetic acid because of the change in mutual solubility accompanying this transfer. As an example a single-contact mixer has been chosen. In this example acetic acid concentrations have been used for the inlet streams similar to those which applied in the experimental work. Figure 36, shows a typical single-contact extraction mixer.

The assumed composition of 100 lbs. of inlet water phase solution, saturated with MIBK, is 4.3 lbs. of acetic acid, 1.7 lbs. of MIBK, and 94.0 lbs. of water, which corresponds to the composition of 100 lbs. of inlet water phase used in the experimental work.

The assumed composition of 100 lbs. of inlet ketone phase, which is saturated with water, is 0.8 lbs. of acetic acid, 2.5 lbs. of water, and 96.7 lbs. of MIBK, which

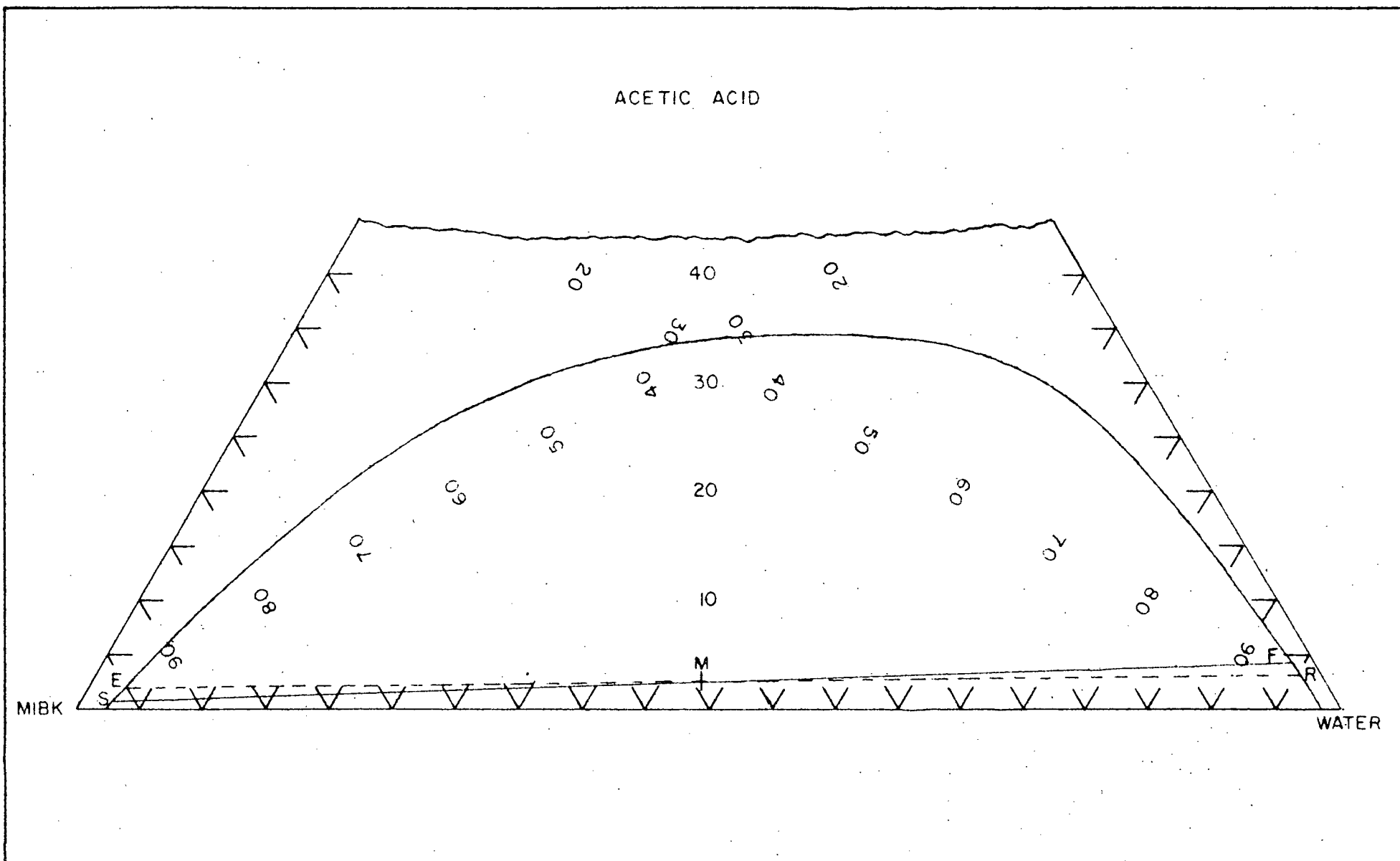


FIGURE 35. MUTUAL SOLUBILITY CURVE (WEIGHT %) FOR THE SYSTEM METHYL ISOBUTYL KETONE - ACETIC ACID-WATER AT 25°C.



corresponds to the composition of 100 lbs. of inlet ketone phase used in the experimental work.

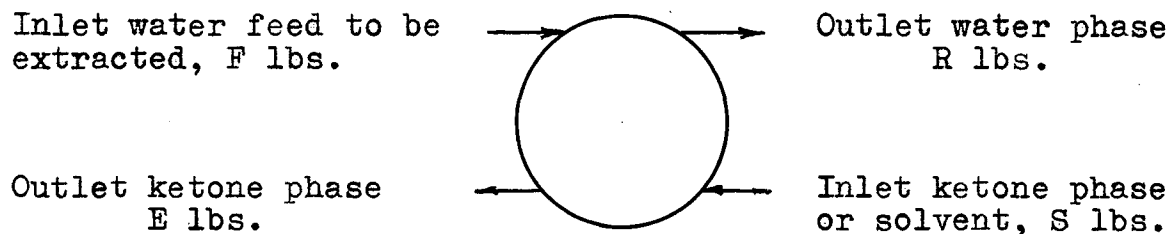


Figure 36. Single-Contact Extraction Mixer

The inlet water phase composition and the inlet ketone phase composition have been located as points F and S on Figure 35. The mixer is assumed to be an ideal stage so that equilibrium is established between the two phases. Thus the final composition of the two outlet phases will be on the opposite ends of a tie-line in the two phase region.

A material balance for the operation is

$$F + S = R + E = M = 200 \text{ lbs.} \quad 1$$

M, representing the mixture of feed and solvent, is in the two-liquid phase region as indicated on Figure 35, and is common to both inlet and outlet streams. Its location can be determined graphically on line FS through the relationship

$$\frac{F}{S} = \frac{\overline{MS}}{\overline{FM}} = 1$$

$$\therefore \text{line MS} = \text{line FM}$$

Since the mixer is an ideal stage, equilibrium is established, and the two phase mixture M produces an outlet water phase and an outlet ketone phase R and E respectively, the compositions of which are located on the ends of the tie-line through point M. The exact locations of points R and E on Figure 35 were determined graphically by trial-and-error tie-line interpolations.\*

The respective magnitudes of R and E may be computed graphically by:

$$\frac{R}{E} = \frac{\overline{EM}}{\overline{RM}} = \frac{8.3}{8.6}$$

$$\text{i.e.} \quad R = 0.965 E \quad 2$$

Substituting Equation 2 into Equation 1 to solve for E we get

$$0.965E + E = 200$$

$$E = 102 \text{ lbs.}$$

$$\therefore R = 200 - 102 = 98 \text{ lbs.}$$

The final compositions of R and E can be read from Figure 35 and were found to be as follows

\* Trybal, R.E., Liquid Extraction, McGraw-Hill Book Company, Inc., New York, First Edition, Second Impression, p-23, 1951.

Outlet water phase (98 lbs. total)

MIBK	1.7%	=	1.67 lbs.
Water	95.3%	=	93.39 lbs.
Acetic Acid	<u>3.0%</u>	=	<u>1.94 lbs.</u>
	100.0%		98 lbs.

Outlet ketone phase (102 lbs. total)

MIBK	95.0%	=	96.9 lbs.
Water	3.0%	=	3.06 lbs.
Acetic Acid	<u>2.0%</u>	=	<u>2.04 lbs.</u>
	100.0%		102 lbs.

A summary of the results appears in Table XIII. It should be noted that the final composition of both outlet streams from the spray column usually never reached the composition of the outlet streams given here. That is the positions of points R and E for the experimental work say R' and E' would be somewhere between F and R, and E and S respectively. These final compositions would be closer to the initial compositions than is true in the example.

From Table XIII it can be seen that in the water phase stream, for the ideal stage, a negligible amount of transfer occurs other than the transfer of acetic acid. The same can be said for the ketone phase stream. For the actual column operation the transfer of material, other than that of acetic acid, would be somewhat less than what has been calculated here and very much less for the piston samples.

Table XIII

Summary of Results For Sample Calculation No. 7

	Water Phase		Ketone Phase	
	lbs.		lbs.	
	Inlet	Outlet	Inlet	Outlet
	F	R	S	E
Acetic Acid	4.3	2.94	0.8	2.04
Water	94.0	93.39	2.5	3.06
MIBK	1.7	1.67	96.7	96.90
	100.0	98.0	100.0	102.0

It is therefore concluded that the volume changes corresponding to these weight changes are negligible because of the dilute concentrations of acetic acid and the small change in mutual solubility of water and ketone in the region under consideration.