

FUNDAMENTAL FACTORS AFFECTING THE EXTRACTION
EFFICIENCY IN A PULSE LIQUID-LIQUID
EXTRACTOR

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I. INTRODUCTION

Liquid-liquid extraction is that term applied to any unit operation in which one or more materials dissolved in one liquid phase are transferred to a second liquid phase. The solvent must be insoluble, or soluble to a limited extent only, in the solution to be extracted. This operation has been applied successfully in many important industrial and domestic processes. In the past the liquid-liquid extraction operation has been effected in towers employing countercurrent flow of the liquids. These conventional towers have either been equipped with bubble-cap trays, sieve plates, or any of several arrangements of baffles; made use of one or more spray heads; or been filled with various types of packing for the purpose of increasing the interfacial area. More recently mixer-settler combinations and centrifugal extractors have been employed.

The countercurrent columns suffer from the disadvantage that the only energy available for the maintenance of the large interfacial area is the density differences of the two liquid phases. Thus, the available energy, no matter how efficiently it is utilized by skillful design of packing or baffles, is too small to overcome drop coalescence and the resulting decrease in the area of contact. The many mixer-settler type of extractors,

while offering a partial solution, suffer from the disadvantage that they are inherently batch extractors in operation. Recently several new types of extractors have been developed that combine the desirable countercurrent features of the towers and the good mixing of the mixer-settler combinations. These devices usually take the form of a number of mixing sections, mounted one above another to form a column, separated by packed or baffled settling sections. An alternative design is to use an unpacked column with the fluid being forced through perforated baffles by mixers.

Another recent design for the improvement of liquid-liquid extraction equipment is a column utilizing countercurrent flow, mechanical agitation, and baffled settling zones. The column is fitted with sieve plates that may be moved up and down relative to the liquid producing the agitation, while the liquids flow countercurrently through the plates. Settling takes place during the pauses between the strokes. The operation and construction of this column can be simplified by using stationary plates and agitating by imparting a reciprocating motion to the liquids relative to the plates.

It was the purpose of this investigation to operate a pulse liquid-liquid extractor, using the system carbon

tetrachloride-acetone-water, and to study the effects of the number of plates or plate spacing, the pulse amplitude, and the plate-free-area on the extraction efficiency.

II. LITERATURE REVIEW

Treybal⁽⁸²⁾ states that phase equilibrium relations, the rate at which extraction proceeds, and the equipment used are the three major factors which must be considered in the design of an extraction process. These three factors will be considered in this review. First, however, some of the general concepts and definitions pertaining to extraction will be discussed.

Concepts and Definitions

It is the purpose of this section of the review to present some of the general concepts and definitions associated with extraction in order that the reader might become familiar with the broad principles and general theory which is the foundation of liquid-liquid extraction. In addition, this section will present the meanings which the author intends to associate with some of the controversial terms and ideas which will be used in this review.

Liquid-liquid Extraction. Periodically facing the chemical engineer is the problem of separating the components of a liquid solution. Several of the unit operations present themselves to

the engineer as possible solutions to this separation problem; however, one method is usually advantageous either because of certain properties of the system and/or because of the financial situation associated with the problem. In general, it is desired to effect this separation by physical methods rather than by chemical methods. To consider a few of the methods of separation available, distillation, evaporation, adsorption, and liquid-liquid extraction might be mentioned.

All of these separation techniques depend upon the tendency of a substance, when distributed between two phases, to occur in different concentrations in each of the phases at equilibrium⁽⁸²⁾. Liquid-liquid extraction⁽³¹⁾ is the separation process that consists of the transfer of one or more components from one liquid phase to another liquid phase.

Liquid-liquid extraction may be carried out in several different ways. The most important way is to add another liquid that is immiscible, or nearly immiscible, with one or more of the components of the original mixture⁽⁸²⁾. Alternately, the original solution may be heated or cooled to form two phases; a third component, that takes no direct part in the extraction method, may be added to cause the original mixture to form two phases; or, finally, the mixture may be treated with two

immiscible liquids each of which dissolves in a separate component of the original mixture⁽³¹⁾.

Uses of Liquid-liquid Extraction. According to Elgin⁽³¹⁾ extraction may be preferable to other separation operations when the following conditions are present: (1) the boiling points of the components of the liquid mixture are within a very few degrees of each other, (2) one or more of the liquids are sensitive to heat, (3) a comparatively small amount of solute is present in the original mixture and the solute is less volatile than the other components, and/or (4) when the solvent used has a lower heat of vaporization than the original solution. Brown⁽¹⁴⁾ adds the obvious fifth condition: that is, when the two liquids are non-volatile, or nearly so.

Treybal⁽⁸²⁾ advises that before deciding to use any extraction operation the following points must be considered. First, the addition of more components has several disadvantages; namely, a large amount of capital is tied up in inventories, the corrosion problem is increased, and the danger of contamination of the final produce is increased. Second, this extraction process must be followed by a solvent recovery process, usually distillation. This solvent recovery step quite often represents a major portion of the final cost of the extraction process.

Benedict⁽⁹⁾ states that all physical separation processes are ones in which power is expended to effect the separation. In extraction the principal use of power is in the form of heat needed to recover the solvent. Thus, if the power expended to effect a given separation is the least for extraction this is the most economical process. This factor should not be used as the sole criteria of selection⁽⁵⁵⁾ as other factors such as solvent loss, may become important.

A few of the many industrial uses of liquid-liquid extraction that should be mentioned are the refining of lubricating oils⁽⁴⁾, the extraction of acetic acid from pyrolytic acid liquors⁽³⁷⁾, the recovery of phenol⁽⁵⁶⁾, the purification and concentration of vitamins and antibiotics⁽⁸¹⁾, the refining of vegetable oils^(36,47), and the recovery of alcohols from Fischer-Tropsch synthesis gas⁽⁴⁹⁾.

Some of the more important industrial applications of liquid-liquid extraction are listed analytically on page 8.

Major Commercial Applications of Liquid-liquid

Extraction Processes ^a

- I. Petroleum Refining
 - A. Separating high purity products
 - B. Separating one or more groups of compounds from cuts of wide boiling range
 - 1. Treatment of kerosene, Edeleau
 - 2. Lubricating oils treated with solvents, Edeleau, Chlorex, Cuo-Sol, Furfural, Phenol
 - C. Dewaxing, deasphalting, and decarbonizing operations
- II. Extraction of Acetic Acid
 - A. Wood distillation
 - B. Recovery of acetic acid from dilute solutions, from cellulose acetate, etc.
- III. Phenol Recovery
 - A. Raschig process; primary phenol production
 - B. Gas works liquids, recovery, and by-product phenols
 - C. Recovery of phenol from a wide variety of solutions
- IV. Chemical Processes with Liquid-liquid Contacting
 - A. Nitration
 - B. Sulfonation
- V. Vitamins and Antibiotics
- VI. Vegetable Oil Refining
- VII. Fischer-Tropsch Synthesis of Liquid Fuels
 - A. Separation of water soluble by-products
 - B. Separation of oil-soluble oxygenated by-products

^a Morello, V. S. and N. Poffenberger: Commercial Extraction Equipment, Ind. Eng. Chem., 42, 1022 (1950).

Feed. The original liquid mixture to be separated is referred to as the feed⁽³¹⁾.

Solute. The solute⁽³¹⁾ is the component or components of the feed to be extracted. In the refining of lubricating oils, for example, impurities are extracted from the oil stocks. The impurities are extracted, and hence, were the solute, but were not the desired final product.

Solvent. The solvent⁽¹⁸⁾ is the liquid that is added to form the second phase. If no other liquid is added the solvent is the component of the extract phase that occurs in the greatest concentration, exclusive of the solute.

Carrier Solvent. The carrier solvent⁽¹⁸⁾ consists of all of the components in the original feed except the solute.

Extract Phase. The extract phase⁽⁷⁴⁾ consists of the solvent after it has been contacted and has been separated from the other phase. This layer contains, in addition to the solvent, the solute and whatever other component it has picked up. This phase is often referred to as the solvent-rich phase.

Extract. The extract phase after the solvent has been removed is referred to as the extract⁽⁷⁴⁾. The extract composition is equal to the extract-phase composition on a solvent-free basis.

Raffinate Phase. The raffinate phase⁽⁷⁴⁾ consists of the original feed after it has been contacted and separated from the solvent. This phase contains the solute that was not extracted by the solvent as well as any solvent that has not been picked up. This phase is often referred to as the carrier-solvent-rich phase.

Raffinate. The raffinate phase after the solvent has been removed is called the raffinate⁽⁷⁴⁾. The raffinate composition is equal to the raffinate-phase composition on a solvent-free basis, the two being equal when the extract phase and raffinate phase are immiscible.

Selectivity. The solvent is said to be selective⁽⁷⁴⁾ for that component of the feed which occurs in the greater ratio in the extract than in the feed. That is, the solvent is selective for the solute by definition.

The selectivity of any solvent, S, for any solute, A, is given by the following equation⁽⁸⁴⁾:

$$\beta = \frac{X_{AS}/X_{CS}}{X_{AC}/X_{CC}}$$

where:

- β = selectivity coefficient, dimensionless
- X_{AS} = concentration of solute in extract phase, weight fraction
- X_{CS} = concentration of carrier-solvent in extract phase, weight fraction
- X_{AC} = concentration of solute in raffinate phase, weight fraction
- X_{CC} = concentration of carrier-solvent in raffinate phase, weight fraction.

For extraction to take place in the desired direction, the selectivity coefficient must be greater than unity⁽¹⁴⁾.

Diffusion. Diffusion is the spontaneous transfer of a component of a fluid mixture from one point in the field to another, without respect to fluid flow⁽³⁾. According to Johnstone⁽⁴⁶⁾, molecular diffusion refers to the net transfer of materials caused by the normal Brownian movement of the molecules, while eddy diffusion refers to the mixing of fluids caused by turbulence. In both types, the net transfer of

material is proportional to the difference in concentration at the two points.

Diffusivity or Diffusion Coefficient. Diffusivity or the diffusion coefficient is a numerical coefficient representing the tendency of a component of a system to diffuse⁽⁴⁶⁾. It is analogous to heat conductivity. The coefficient represents the quantity of material which will diffuse across a unit area in unit time with unit volume concentration gradient.

Distribution. Glasstone⁽³⁵⁾ states the distribution law in the following manner: "If to a system of two liquid layers, made up of two immiscible or slightly miscible components, is added a quantity of a third substance soluble in both layers, then the substance is found to distribute, or divide, itself between the two layers in a definite manner." The definite manner being that the ratio of solute concentration in the two phases is constant. It was once thought that this ratio was independent of the absolute concentration; but it is now known that this fact is true for very few systems, and in these systems, only at low concentrations⁽⁸³⁾.

The distribution coefficient is given by the following equation⁽³⁵⁾:

$$m = \frac{X_{AS}}{X_{AC}}$$

where:

- m = distribution coefficient, dimensionless
- X_{AS} = concentration of solute in the extract phase, weight fraction
- X_{AC} = concentration of solute in the raffinate phase, weight fraction.

The distribution coefficient, m , and the selectivity coefficient, β , are often confused. The distribution coefficient expresses the equilibrium between the two phases in liquid-liquid extraction. The selectivity coefficient expresses the relative enrichment of the solute in the extract phase compared to the raffinate phase. The selectivity coefficient is equivalent to the relative volatility in distillation⁽³³⁾.

Extraction Stage. Brown⁽¹⁴⁾ states that the physical operation of extraction consists of two steps. These steps are, first, the mixing together of the two phases, with a longer or shorter time allowed for equilibrium to be reached; and, second, the separation of the two phases. Each time the

two phases are mixed and separated there has been one extraction stage.

Ideal Stage. If, after the extraction stage, the two phases leave in equilibrium, that is, if the solute is distributed as required by the distribution law, the stage is called an ideal stage⁽³¹⁾. An ideal stage represents the limiting amount of extraction for any stage.

Stagewise Contact. In any extraction process, if the two liquid phases are alternately mixed and separated the process is said to be one of stagewise contact⁽⁷¹⁾. A more rigorous definition of a stagewise extractor would be any extractor in which the interfacial area between the two phases varies with position in the equipment or with time. The classic example of stagewise contact is the bubble-cap column. If a section is taken through this column under the liquid covering the bubble caps a large interfacial area is found; however, if a section is taken through the downcomers and the disengaging section almost no interfacial area in comparison is found.

Continuous Contact. Instead of bringing the solution to be extracted and the extracting solvent into contact in separate stages with intermediate settling, it is possible to cause the liquid phases to flow continuously past each other. This type of contact is called continuous contact⁽⁷¹⁾.

Continuous contact may be further defined as any extraction process in which the interfacial area does not vary substantially with position in the column or with time during the operation of the column.

To avoid further confusion it must be thoroughly understood that the term "continuous" is used with two different meanings in extraction. One meaning is defined above. The second meaning is in the sense of a continuation of time. This point seems to cause great confusion in the literature. Wherever the word "continuous" appears care should be taken to see in which way it is used. Is the column a continuous extractor, or does the extractor merely operate without stopping? Continuous when used in this review with the latter meaning will be set off by quotation marks.

Transfer Unit. Colburn^(22,23) points out that the concept of "ideal stages" is not applicable to continuous contact. The difference in the physical mechanism of contact invalidates the ideal stage calculation. He proposed the use of the transfer unit as a basis with which to compare the efficiency of the continuous extraction process. The Colburn transfer unit is the concentration change experienced per unit of concentration difference causing this change. The transfer unit and the ideal

stage have about the same meaning; although the former applies to continuous and the latter to stagewise contact.

Classification of Extraction Operations by Solvent Systems.

A convenient method of classifying extraction operations according to Treybal⁽⁸⁵⁾ is as follows:

- I. Single solvent systems, including all of those which consist of or which may be reduced to the equivalent of, three components, the two to be separated and the solvent.
 - A. Stagewise contact
 - B. Continuous contact
- II. Mixed solvents
 - A. Stagewise contact
 - B. Continuous contact
- III. Double solvents (fractional extraction)
 - A. Stagewise contact
 - B. Continuous contact.

Classification of Extraction Operations by Flow Sheets.

Elgin⁽²⁹⁾ has proposed a more useful classification of extraction operations depending upon the arrangement of the equipment. His classification is as follows:

I. Single contact

II. Multiple contact

A. Cocurrent

1. Multistage

2. Differential

B. Countercurrent

1. Continuous

a. with reflux

b. without reflux

2. Multistage

a. with reflux

b. without reflux.

Differential cocurrent contact is the limiting case of multistage cocurrent contact in which the solvent is added in differential portions and the extract removed as fast as it is formed. Its inclusion as a separate class is due to the work of Treybal⁽⁸⁵⁾ and Varteressian and Fenske⁽⁹⁰⁾. The familiar Soxhlet extractor is an example of a differential cocurrent extractor⁽⁹²⁾.

Distillation Analogy. It is sometimes helpful to consider the close relationship between distillation and extraction⁽⁸⁵⁾. This is particularly true for the average chemical engineer because of his greater familiarity with the distillation process. In distillation a mixture of substances is separated by the creation of a second phase with heat. In extraction the second phase is formed by the addition of the solvent. In Table I, page 19, some further similarities of the two processes are presented.

TABLE I

Comparison of Nomenclature for the Diffusional
Operations of Extraction and Distillation^a

| <u>Extraction Nomenclature</u> | <u>Distillation Analogy</u> |
|---|--------------------------------|
| Addition of solvent | Addition of heat |
| Solvent mixer | Reboiler |
| Removal of solvent | Removal of heat |
| Solvent separator | Condenser |
| Solvent-rich solution saturated with solvent | Vapor at the boiling point |
| Solvent-rich solution containing more solvent than that required to saturate it | Superheated vapor |
| Solvent-lean solution containing less solvent than that required to saturate it | Liquid below the boiling point |
| Solvent-lean solution saturated with solvent | Liquid at the boiling point |
| Two-phase liquid mixture | Mixture of liquid and vapor |
| Selectivity | Relative volatility |
| Change of temperature | Change of pressure |

^a Treybal, R. E.: "Liquid Extraction," p. 129. McGraw-Hill Book Co., Inc., New York, N. Y. 1951.

Equilibrium Relations

In studies on chemical engineering equipment the equilibrium relations of the systems involved are important as a basis for comparisons and further calculations. By equilibrium relations is meant the studies on distribution and phase relations.

Distribution. The equilibrium that is of importance in liquid-liquid extraction is the distribution equilibrium⁽⁸³⁾. The ideal form of the distribution law presented on page 12, however, is inadequate in liquid-liquid extraction.

Nernst⁽¹⁹⁾ suggested that all deviations from the distribution law are caused by either association or disassociation of the solute in either or both phases. Nernst's explanation may well be correct but his equations become impossibly cumbersome when applied to most systems. This is because deviations, if caused by the mechanism postulated by Nernst, are also complicated by a change in the relative amount of disassociation or association when the absolute concentration of the solute changes.

Brancker, Hunter, and Nash⁽¹³⁾ found that the mol fraction of A in the A-rich phase when plotted against the equilibrium concentration of B in the B-rich phase gave a curved line. However, if the coordinates of the concentration of A in the

A-rich phase are adjusted to obtain a straight line these same coordinates will give a straight line for most other systems. This method is similar to the method of Cox for vapor pressure data. The authors state that solutropic systems cannot be correlated by this method. A solutropic system⁽⁷⁵⁾ is one in which the distribution ratio changes from greater than one to less than one, or vice versa, as the concentration of solute changes.

Bachman⁽⁵⁾ found that the equations of the straight lines on the Brancker, Hunter, and Nash coordinates are as follows:

$$X_{AA}X_{BB} = aX_{AA} + bX_{BB}$$

where:

X_{AA} = concentration of solvent in extract phase, weight fraction

X_{BB} = concentration of carrier solvent in raffinate phase, weight fraction

a = constant, weight fraction

b = constant, weight fraction.

Thus, if X_{BB} is plotted against X_{BB}/X_{AA} on rectangular coordinate paper straight lines should be obtained.

Othmer and Tobias⁽⁶⁰⁾ found that a plot of equilibrium values of $1 - X_{AA}/X_{AA}$ against $1 - X_{BB}/X_{BB}$ on double logarithmic coordinate paper produced straight lines.

The three previous modifications of the distribution law all suffer from the disadvantage that the concentration of the solute, C , is not in the expression. Hand⁽⁴⁰⁾ showed that a double logarithmic plot of X_{CA}/X_{AA} against X_{CB}/X_{BB} is usually rectilinear. This method is generally considered to be the most satisfactory of the many forms of the distribution law⁽⁵⁷⁾. Hand's method amounts to writing the distribution law in the form shown below:

$$\frac{X_{CB}}{X_{BB}} = k \left(\frac{X_{CA}}{X_{AA}} \right)^n$$

where:

- X_{CB} = concentration of solute in raffinate phase, weight fraction
- X_{BB} = concentration of carrier solvent in raffinate phase, weight fraction
- X_{CA} = concentration of solute in extract phase, weight fraction
- X_{AA} = concentration of solvent in extract phase, weight fraction
- k = constant, dimensionless
- n = constant, dimensionless.

Distribution for the System Carbon Tetrachloride-Acetone-Water. The distribution data⁽¹⁷⁾ for the system carbon tetrachloride-acetone-water at several temperatures are given in Table II, page 24. In Figure 1, page 25, the distribution curve is drawn on rectangular coordinates. As this system is solutropic, it was found that it could not be represented by the Hand equation.

Binodal Curves. In addition to the distribution data the composition of the saturated solutions of A and C in B and of B and C in A are needed⁽³²⁾. This type of information is usually plotted on a triangular composition diagram. The use of this type of diagram for presenting solubility and phase composition data for ternary systems has been adequately covered by Bull and Coli⁽¹⁸⁾, Brown⁽¹⁵⁾, Elgin⁽³²⁾, and Treybal⁽⁸⁵⁾. An example of this type of diagram for the system carbon tetrachloride-acetone-water is presented in Figure 2, page 26, from the data presented in Table III, page 27.

TABLE II

Equilibrium Distribution of Acetone Between
Carbon Tetrachloride and Aqueous Phases^b

| Temperature | Acetone Concentration | |
|-------------|------------------------------------|---------------------|
| | Carbon Tetrachloride Phase wt % | Water Phase wt % |
| 30 | 0.80 | 3.35 |
| 30 | 3.95 | 10.30 |
| 30 | 4.60 | 11.50 |
| 30 | 13.90 | 22.30 |
| 30 | 16.50 | 24.40 |
| 30 | 24.20 | 30.40 |
| 30 | 33.30 | 35.80 |
| 30 | 39.60 | 40.20 |
| 30 | 47.20 | 46.00 |
| 30 | 51.90 | 49.80 |
| 30 | 59.04 ^b | 59.04 ^a |
| 20.8 | 2.10 | 6.90 |
| 20.8 | 6.20 | 14.30 |
| 20.8 | 13.80 | 22.50 |
| 4 | 2.21 | 9.50 |
| 4 | 4.90 | 14.90 |
| 4 | 9.00 | 20.60 |
| 4 | 13.80 | 25.30 |

^a Plait point.

^b Bachman, R. H.: Liquid-liquid Equilibrium Data for the System Carbon Tetrachloride-Acetone-Water, Ind. Eng. Chem., 44, 2449 (1952).

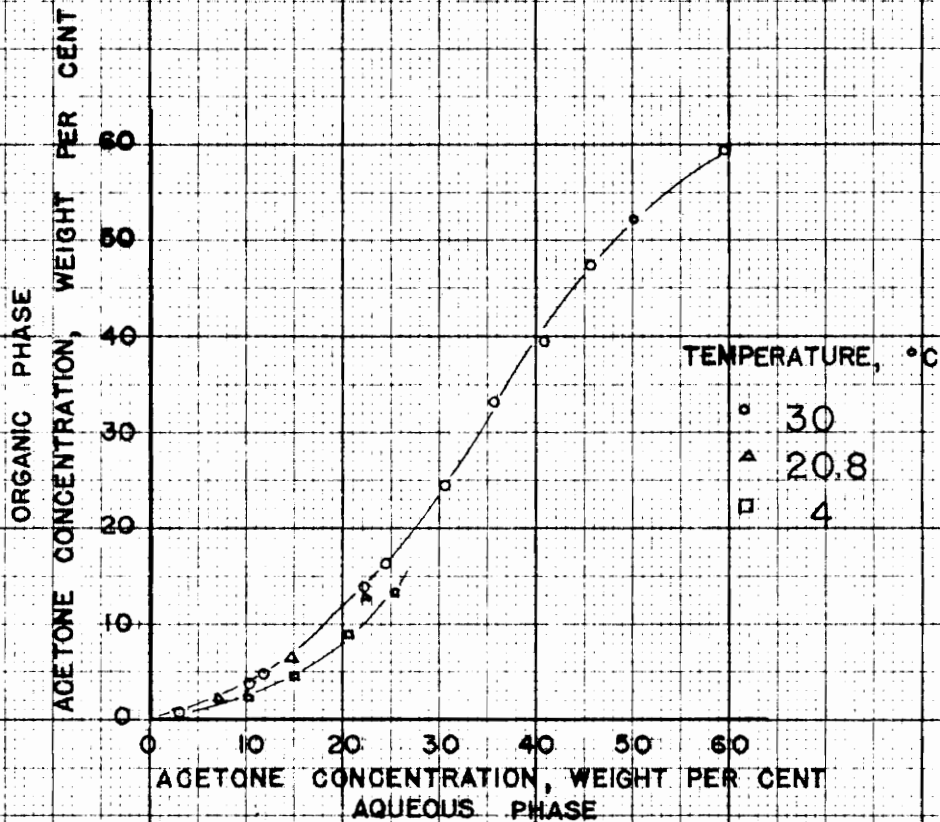


FIGURE I. DISTRIBUTION DATA FOR THE SYSTEM
CARBON TETRACHLORIDE - ACETONE - WATER

BUCHMAN, R. H.: LIQUID - LIQUID EQUILIBRIUM DATA FOR THE
SYSTEM CARBON TETRACHLORIDE - ACETONE - WATER, IND.
ENG. CHEM., 44, 2449 (1952).

Figure 2. Solubility Data for the System Carbon
Tetrachloride-Acetone-Water
at 30 °C

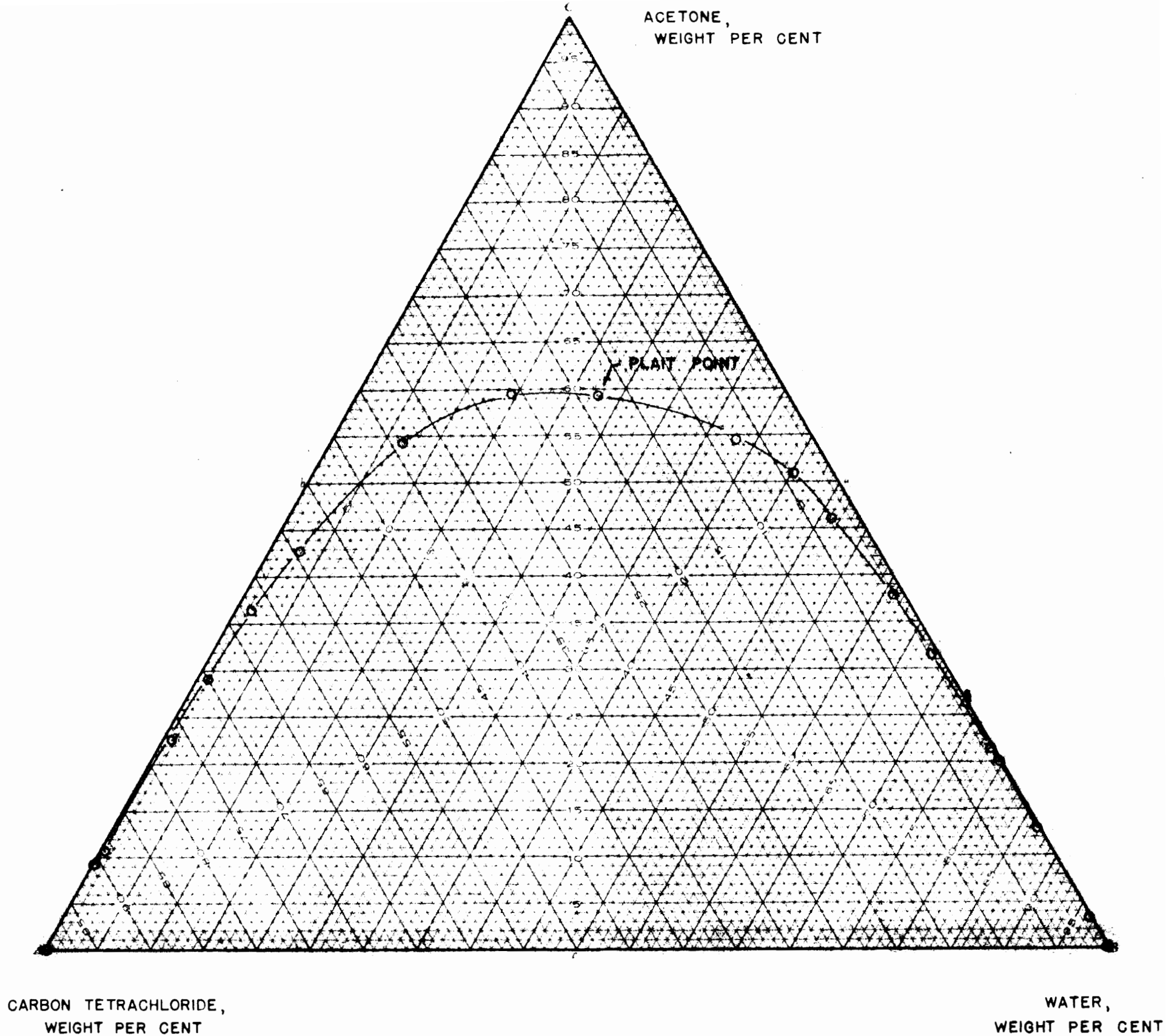


FIGURE 2. SOLUBILITY DATA FOR THE SYSTEM CARBON TETRACHLORIDE - ACETONE - WATER

BUCHMAN, R. H.: LIQUID-LIQUID EQUILIBRIUM DATA FOR THE SYSTEM CARBON TETRACHLORIDE - ACETONE - WATER, IND. ENG. CHEM., 44, 2449 (1952).

TABLE III

Solubility Data for the System CarbonTetrachloride-Acetone-Waterat 30 °C^b

| Acetone wt % | CCl ₄ wt % | Water wt % | Specific Gravity 30°/4 °C |
|-----------------|--------------------------|---------------|------------------------------|
| 00.00 | 100.00 | 0.00 | 1.5750 |
| 09.14 | 90.78 | 0.08 | 1.4410 |
| 10.58 | 89.19 | 0.23 | 1.4230 |
| 22.17 | 76.98 | 0.85 | 1.2852 |
| 29.32 | 69.61 | 1.07 | 1.2120 |
| 36.40 | 61.98 | 1.62 | 1.1470 |
| 42.63 | 54.67 | 2.70 | 1.0936 |
| 54.34 | 38.73 | 6.93 | 1.0000 |
| 59.46 | 26.15 | 14.39 | 0.9524 |
| 59.04 | 18.01 | 22.95 | 0.9330 ^a |
| 54.83 | 7.57 | 37.60 | 0.9197 |
| 50.27 | 4.69 | 45.05 | 0.9235 |
| 45.77 | 2.73 | 51.50 | 0.9292 |
| 37.32 | 1.36 | 61.32 | 0.9411 |
| 31.58 | 0.69 | 67.73 | 0.9494 |
| 21.08 | 0.40 | 78.52 | 0.9657 |
| 19.82 | 0.39 | 79.78 | 0.9680 |
| 12.83 | 0.28 | 86.90 | 0.9780 |
| 03.22 | 0.22 | 96.56 | 0.9910 |
| 00.00 | 0.00 | 100.00 | 0.9955 |

^a Plait point.^b Buchman, R. H.: Liquid-liquid Equilibrium Data for the System Carbon Tetrachloride-Acetone-Water, Ind. Eng. Chem., 44, 2449 (1952).

Equilibrium in Extraction Processes. Extraction may be carried out either in discreet steps or as a continuous counter-current process. The former process is called countercurrent stagewise extraction, and the latter process is called continuous countercurrent extraction. The equilibrium relations, representing optimum extraction, are of course different for these two processes.

Equilibrium in Stagewise Extraction. If, in any stagewise extractor, the two exit streams are in equilibrium the stage is called an ideal stage⁽⁷⁴⁾. In actual practice the stages are always less than perfect, and the two liquids leave each stage before equilibrium has been reached. This, of course, suggests that the various types of stages or contractors can be compared by means of their relative approach to equilibrium. For this purpose the stage efficiency is defined as the percentage ratio of the approach to equilibrium for any stage⁽³²⁾.

In actual practice, where several stages are mounted together to form a tower, the total number of equilibrium stages to perform the actual extraction is found. The number of real stages making up the tower divided into the number of ideal stages gives the average stage efficiency⁽³²⁾ for the column.

Equilibrium in Countercurrent Extraction. For continuous countercurrent extraction the ideal relation between the two countercurrent streams at any point is given by the following equation⁽³²⁾.

$$Y = \frac{X}{1 - X(\beta - 1)}$$

where:

Y = solute in extract phase, weight fraction

X = solute in raffinate phase, weight fraction

β = selectivity coefficient.

Thus, a measure of efficiency, similar to stage efficiency, may be calculated by comparing the ideal \underline{Y} from the above equation to the real \underline{Y} at any given point. As will be pointed out later, this method, although quite valid and general, is seldom used.

Rate Relations

Once the equilibrium rates on performance are fixed, the rate relations make it possible to calculate the time required to approach equilibrium under actual conditions. In the more general case, if the time is fixed, the actual approach to equilibrium can, itself, be calculated.

Mass Transfer Concept. The two-film theory⁽²⁴⁾, although undoubtedly inadequate to completely describe extraction behavior, has been widely accepted as the closest available approximation. In this theory the interface between the two phases is believed to be formed of two compressed, laminar films of the type encountered in heat transfer. In this theory, it is assumed that all of the resistance to transfer of the solute, from one phase to the other, takes place in the films. Experimental results show that there is a measurable resistance⁽⁷⁴⁾ to the transfer of solute from phase to phase. In effect, this means that a finite time is required for a system to approach equilibrium. The reciprocal of the equilibrium time function is called the over-all mass transfer coefficient. The over-all mass transfer coefficient is a measure of the rate at which extraction takes place.

There have been many attempts to correlate the physical properties of the extraction system and the rate constant. Among these proposed correlations may be mentioned the work of Row, Koffolt, and Withrow⁽⁶⁶⁾ and Skrzec⁽⁷⁴⁾. However, as yet, no really satisfactory method of predicting the over-all mass transfer coefficient for commercial equipment is available.

The Transfer Unit. The performance of stagewise equipment can be adequately described in terms of the stage efficiency. In order to obtain a measure of equal utility for use with continuous countercurrent extraction Colburn introduced the transfer unit. Colburn^(22,23) defined the number of transfer units as equal to the integral of the differential change in concentration divided by the difference in concentration tending to cause transfer. Stated in symbols the number of transfer units may be defined as follows:

$$N = \int_{y_2}^{y_1} \frac{dy}{(y^* - y)}$$

where:

- N = the number of Colburn mass transfer units, dimensionless
- y = concentration of solute in one phase, mol fraction
- y* = concentration of solute in the same phase that is in equilibrium with the concentration of solute in the other phase at the same point, mol fraction
- y₁ = concentration of solute in the same phase at the feed end of the column, mol fraction
- y₂ = concentration of solute in the same phase at the solvent end of the column, mol fraction.

The transfer unit is a measure of standard difficulty of extraction. Just as one equilibrium contact is a measure of extraction independent of the system, so is one transfer unit.

In multistage columns the number of theoretical stages is divided by the actual stages to give the stage efficiency. This calculation cannot be carried out for continuous extractors as there are no actual stages present. To get around this difficulty Colburn^(22,23) stated that a unit length of the column could be defined as the continuous countercurrent equivalent of a theoretical stage. Thus, the total active height of the column divided by the number of transfer units is a measure of column efficiency. As this measure has the units of length it is commonly called the height of a transfer unit or more commonly HTU. The HTU is different from efficiency in that a decrease in HTU is equivalent to an increase in efficiency. In symbols the HTU is defined as follows^(16,22,23):

$$\text{HTU} = \frac{H}{N}$$

where:

- HTU = height of a transfer unit, feet
- H = height of a column, feet
- N = number of Colburn transfer units, dimensionless.

The HTU is a direct measure of efficiency of extraction. If one column has a lower HTU than the other it is a more efficient extractor. However, the HTU can be used for comparison only for continuous countercurrent extractors; because, for stagewise extractor the integral defining HTU becomes discontinuous. The HTU is related to the mass transfer coefficient and is used to calculate the value of the latter⁽¹⁶⁾.

Height Equivalent to a Theoretical Stage. Instead of using the stage efficiency, stagewise columns may be compared by means of a height equivalent to a theoretical stage⁽³³⁾ or HETS. The HETS is the total actual height of a stagewise extractor divided by the number of theoretical stages. This number, the HETS, is a measure of extractor efficiency; but it is based on extractor height rather than on perfection of contact. The HETS is analogous to the HTU but is used for stagewise extractors where the HTU is not applicable.

Relation Between HETS and HTU. Many commercial extractors, for which performance data are available, are rated as having a certain HETS. Other commercial extractors are rated as having a certain HTU. In order to compare these extractors it is necessary that some idea be obtained of the relationship between HETS and HTU.

There is, in general, no simple, direct relation between the HTU and the HETS⁽³²⁾. If equilibrium data for the system used are available, calculations can be made and the exact equivalence found. However, without making such calculations no comparisons should be made between equipment rated by HTU's and equipment rated by HETS's.

Elgin⁽³²⁾ reports that for the special case where both the operating line and the equilibrium line are straight and parallel the HETS and HTU are equal. However, a calculation is still required to determine the operating line.

Along similar lines is the growing tendency of reporting performance of all types of extractors in HTU's. In the author's opinion this practice is to be discouraged. The calculation of HTU's for a stagewise extractor represents a mathematical fallacy. The calculation of HETS's for a continuous column is to describe the action of the column in erroneous terms. HETS and HTU when calculated as described in this paragraph have no real meaning as far as equipment performance is concerned.

The errors introduced by the indiscriminate use of HTU's and HETS's may be illustrated by an example from Hayford's⁽⁴³⁾ experience. A two-inch diameter laboratory spray tower, four feet long, used for student experimental studies gave a HTU⁽⁴²⁾

from 12 to 30 feet. Using the same conditions and the same system, but with the data calculated as if the column were stagewise a HETS⁽⁷⁸⁾ of 0.75 to 1.50 feet was obtained. The extractor was obviously the same and performing equal separation in both cases. For this particular system and extractor one transfer unit represents from 16 to 20 times as much extraction as one theoretical stage. If this fact is known, it makes little difference, from a practical standpoint, how the column is rated. However, if this fact were not known, and it seldom is, by rating the column in HETS'S it would make the column appear to be a much more efficient extracting device than it really is.

Methods of Calculating the Number of Theoretical Stages.

Algebraic methods for calculating the number of theoretical stages have been reported by Varteressian and Fenske^(90,91) and Hunter and Nash^(44,45). These methods are extremely difficult to apply except in rather special cases. Graphical simplifications of the above have been proposed by Maloney and Schubert⁽⁵³⁾, Hunter and Nash^(44,45), and Varteressian and Fenske^(90,91).

Maloney and Schubert⁽⁵³⁾ have modified the method of Ponchon and Savaritt to apply to extraction. This method makes use of the solvent content-concentration diagram for

a ternary system. It is covered in detail by Brown⁽¹⁵⁾, Perry⁽³²⁾, and Bull and Coli⁽¹⁸⁾.

The triangular phase diagram, an example of which is shown on page 25, supplies the necessary relation between the composition and quantity of the extract layer leaving any stage and those of the raffinate layer leaving the same stage. Simultaneous graphical solutions of the material balances on this chart furnish a graphical solution to a counter-current stagewise extraction operation. This method was proposed by Hunter and Nash^(44,45) and is covered in detail by Perry⁽³²⁾ and Bull and Coli⁽¹⁸⁾.

The McCabe-Thiele method may be modified to present a graphical solution to extraction problems. This method was first proposed by Varteressian and Fenske^(90,91) and covered by them and by Perry⁽³²⁾.

Equipment

In this section some of the design features of liquid-liquid extractors will be discussed. First, a general explanation will be presented of just what a liquid-liquid extractor is. This will be followed by several methods of classifying extractors, and finally a brief discussion of pulse liquid-liquid extractors will be presented.

Liquid-liquid Extractors. A liquid-liquid extractor may be defined⁽³³⁾ as any type of equipment that may be used to effect liquid-liquid extraction. Liquid-liquid extractors, like most unit operations equipment, are exemplified by a great variety of commercially-used types. This condition was caused by several factors⁽⁵⁵⁾; lack of reliable performance data on available equipment, development by different industries before the emphasis on unit operations began, attempts to modify existing distillation and absorption apparatus to extraction, the need for rather specialized extractors for several purposes, research designed to make existing equipment fit rather than design new equipment, and many others.

Continuous liquid-liquid extraction processes have been used industrially to great advantage as a means of chemical separation and purification where operations such as distillation or adsorption are impractical.

Equipment design for continuous countercurrent extraction is based largely upon various methods for obtaining a high interfacial area between the two liquids contacted. Greater efficiency of improved mass transfer is usually achieved by increasing the degree of mixing of the two phases. In spray columns, mixing is brought about by dispersing one liquid as droplets in the second liquid, while in packed columns the turbulence of flow and the film surface area are increased by utilizing packing. Mixer-settler equipment takes advantage of stagewise contact in alternate mixing and settling units, whereas perforated plate towers are essentially vertical mixer-settlers in which successive dispersion and coalescence are accomplished by perforated plates. In the latter, as well as in the spray, packed, and baffle-type columns, low stage efficiencies are encountered because of the poor mixing resulting from counterflow of the two phases past each other by virtue of their density difference alone.

Classification of Liquid Extractors. Three methods of classification of extractors are those presented by Elgin⁽³³⁾, Treybal⁽⁸⁶⁾, and Morello and Poffenberger⁽⁵⁵⁾.

Elgin⁽³³⁾ classifies extraction equipment according to either mixer-settler (batch) or "continuous" extractors. He sub-classifies further as follows:

I. Mixer-settler extractor

- A. Air agitation
- B. Mechanical mixers
- C. Flow mixers
- D. Column mixers
- E. Pumps

II. Countercurrently columns operated "continuously"

- A. Wetted wall
- B. Spray
- C. Packed
- D. Sieve of perforated plate
- E. Modified bubble plate
- F. Baffle column
- G. Columns with internal agitations.

This classification has little to recommend it, except that it is used in Perry's Chemical Engineers' Handbook.

Treybal⁽⁸⁶⁾ borrowed Elgin's classification and modified it to further subdivide the "continuous" columns. However, the distinction between "continuous" and continuous does not appear to have been used by him.

Morello and Poffenberger⁽⁵⁵⁾ used an entirely different scheme of classification. They divided the equipment into

classes depending upon the method used to separate the phases.

Their further subdivisions are as follows:

I. Two phases separated by gravity.

A. Contact made through the interfacial area as a film

1. Extended surface
2. Packed towers

B. Contact made through the interfacial area with one phase dispersed as droplets

1. No additional power required for dispersion
 - a. Spray towers
 - b. Baffle towers
 - c. Perforated plate towers
 - d. Bubble-cap towers
 - e. Packed towers
2. Additional power required to redisperse the phases
 - a. Mixer-settler combinations
 - b. Baffle tower with movable membranes

II. Two phases separated by centrifugal force.

The Use of External Power in Extraction Equipment. One of the most important questions to be solved in liquid-liquid extractor design is the utility of extractors using external power(86).

External power⁽⁵⁵⁾ may be defined as any power applied to the extractor in addition to that power necessary to cause the flow of the liquid phases.

The additional power applied, if efficiently utilized, will cause the formation of a very high interfacial area, and, consequently, achieve better extraction⁽⁶⁹⁾. However, this gain in extraction rate must be balanced against the additional mechanical complexity of the extractor and the additional cost of operation. Some of the mechanical features of power extractors that often cause trouble are leaks in stuffing boxes, undesirable flexes and strains in long shafts, and increased erosion and corrosion of moving parts⁽⁵⁵⁾.

Recently, various mechanically powered devices having higher throughputs and efficiencies than conventional extraction columns have been built. The Podbielniak⁽⁴³⁾ centrifugal contactors utilizes a high-speed rotor containing a perforated spiral ribbon for mixing and separating the two liquids, while the Scheibel⁽⁴³⁾ column consists of alternate mixing and coalescing zones in a vertical tower fitted with a central rotating shaft on which agitators are mounted in the mixing sections. The presence of the moving mechanical parts in these and other powered contactors, presents repair, leakage, and servicing problems which are

particularly objectionable if radioactive or highly corrosive solutions are to be processed.

Pulse Column. Van Dijck⁽⁸⁹⁾ recognized some of the practical difficulties in the design he proposed. The bulky mechanism for obtaining motion of the plates, bad enough in itself, was located inside of the column. Here, the mechanism would be subjected to corrosion, and would be extremely inaccessible for maintenance work. Thus, Van Dijck was led to propose an alternate design. This alternate design was to make the plates stationary and move the liquids past the plates by means of a reciprocating piston. This type of extractor has been called a pulse column⁽⁵²⁾. Columns are made of glass or stainless steel, built up by slipping plates and spacers alternately on a supporting rod located along the axis of the column.

The plate perforations in a pulse column are small enough so that countercurrent flow of the two phases will not occur from density difference alone, but an additional force must be applied to overcome the resistance to flow. A cyclic pulse, usually imparted to the light liquid stream entering the bottom of the column, produces alternate surges of liquid in both directions. Thus, countercurrent flow occurs because of

density difference in the region between successive plates and because of mechanical pulsing through the plate perforations.

Between pulsations at low pulse frequencies the two phases separate into two distinct layers in each section between adjacent plates. On the upsurge of the pulse cycle the lighter phase beneath each plate is dispersed into the heavier phase above each plate. The droplets rise through this layer and coalesce beneath the plate above. On the downsurge the heavy phase is dispersed downwards through the lighter layer in a similar fashion. Neither phase may be considered truly continuous in the column as both move countercurrently from plate to plate by alternate dispersion and re-coalescence. Since fresh surface is created with each pulse, mass-transfer rates can be greater than for a similar packed or spray column.

At higher pulse frequencies re-coalescence between pulses is incomplete, and the distinction between continuous and discontinuous phases becomes more apparent. The degree of dispersion and turbulence are both increased, resulting in higher extraction efficiencies. Greater throughputs are also obtainable with the increased pulsing capacity that accompanies the use of higher frequencies. By proper combinations of pulse displacement or amplitude and frequency, a great variation in flow behavior may be achieved. Changes in these variables may

be likened to changes in the packing characteristics for packed columns.

The main advantage of the pulse column is the small HTU as compared to packed or spray columns. Satisfactory pulse column operation has been obtained for density differences as small as 0.05.

If the plates of a pulse column fit so snugly that leakage is prevented, small scale-up factor will be involved in comparing columns of different size. Channeling will be almost negligible in a pulse column if the plates are level. In addition to varying the flow rates, it is possible to vary the pulse frequency, pulse shape, pulse displacement, hole size, free area, and plate spacing. The chief disadvantages of pulse columns are small throughputs, a greater tendency to emulsify, and the cost and operating difficulties of the pulser.

Pulse Column Operations. Feick and Anderson⁽³⁴⁾

studied the performance of packed extraction columns in which reciprocal motion was imparted to both liquids by means of an excentric-driven diaphragm at the base of the column. Similar work with a packed pulse column has been performed by Von Berg and Wiegandt⁽⁹³⁾ at Cornell University. Their results indicate that the column height required to effect a given extraction is

reduced by a factor of five, in some instances, under pulsating conditions.

Similar columns have been investigated by the Oak Ridge National Laboratories⁽⁵²⁾, and the Departments of Chemical Engineering at North Carolina State⁽⁶²⁾, Oregon State⁽⁷⁹⁾, Iowa State⁽²¹⁾, and Georgia Institute of Technology⁽⁹⁵⁾.

Iowa State University Pulse Column. The extractor at Iowa State University⁽²¹⁾ consists of a pyrex column one inch in diameter and 20 inches high. This column contains ten perforated plates. The perforations are 0.040 inch in diameter and constitute a total of nine per cent of the area of the plate. The pulsating motion is imparted to the liquids by a diaphragm pump with the check valves removed. Stroke frequencies in the range of 35 to 72 cycles per minute were found to give the best operation.

North Carolina State University Pulse Column. The column at North Carolina State University⁽⁶²⁾ consists of a precision bore glass tube 1.5 inches in diameter and eight inches long. This column contains four plates with a two-inch plate spacing. The plates are drilled with 0.0590-inch holes, and

the area of these holes totals to twenty per cent of the plate area. The agitation is furnished by a constant volume feed pump with the checks modified to permit pulsing. Twenty-four strokes per minute were used, each stroke producing 1.20 inches of liquid travel in the empty column.

Oak Ridge Pulse Column. The Oak Ridge National Laboratories⁽⁷⁷⁾ employ a pulse column to effect the separation of rare earth isotopes and radioisotopes.

Column Description. The Ellison laboratory pulse column which is used at Oak Ridge is made of three-foot sections of 1/2-inch pyrex tubing, and since tubing of the proper tolerance is not available, the column sections are made from standard tubing by inserting a 1/2-inch stainless steel mandrel into the tube, maintaining a vacuum within the tube and heating to 600 °C in an oven for eight hours. The glass shrinks to mandrel size. The cost of a three-foot section is about \$5.00.

The column is built up of the required number of sections by bolting them together with stainless steel flanges and polythene

gaskets. At the top and bottom of the column, one-inch diameter separating sections about six inches long are welded on by bell reducers. The feed lines are 1/4-inch stainless steel tubing and are carried through the expanded section of the column to prevent possible mixing with the liquids leaving the column. Feed rates are controlled qualitatively by rotameters and are measured quantitatively by timing the flow rate from a graduated sight glass. The flooding rate is about 700 gallons per hour-square foot of the column cross-section for the organic phase. Stainless steel tanks are used to hold the feed and product, and stainless steel or tygon tubing is used for the feed lines.

The central stringer is 3/32-inch stainless steel welding rod sanded smooth. The circular plates are made from nineteen- or twenty-two-gage stainless, and contain thirty-two 0.039-inch holes arranged at the corners of equilateral triangles and corresponding to a free area of twenty-one to twenty-three per cent. Spacers are made of stainless steel welding rod

slightly larger than the stringer and drilled to fit over the stringer. Normally, thirty-four plates are used for a three-foot section. The cost is about \$1.00 per plate, including the cost of stringer and spacer. The pulse pump is a stainless steel bellows type having a 3/4-inch bellows three inches long and a variable stroke. Its cost is about \$125.00.

Operational Features. In addition to the bellows pulser, positive displacement pumps with all valves removed have also been used for pulsing laboratory columns. Variable speed drives are used to control the pulse frequency. In connecting the column to the pulser, operating difficulties may occur if the line is too long or too small. Thus, when the pulser reverses to withdraw liquid down the column, the velocity of the liquid in all the lines suddenly reverses and the pressure at the pulser becomes negative with respect to the pressure at the bottom of the column. If the pressure drop through this line connecting column and pulser is too high, the absolute pressure at the pulser may be less than the vapor pressure of

the material being pulsed, and vaporization or cavitation may occur. This will prevent satisfactory operation of the pulser.

Two experimental studies of the performance of pulse columns were made at Oak Ridge by Griffith, Jasny, and Tupper, who studied the extraction of nickel and copper, using water and methyl isobutyl ketone as solvents. The aqueous phase was maintained continuous in their experiments⁽³⁹⁾. The HTU of the extraction column varied from 1.1 inches for low flow rates to a maximum of thirty-four inches at high flow rates, but in every case was below the value measured for a spray tower. The flooding velocity of the pulse column was smaller, however, namely, 955 gallons per hour-square foot of column cross-section as compared with a value of 1,820 for the spray tower. The plate spacing was one inch, and in all cases the volumetric ratios of the dispersed to the continuous flow rates were 1.57.

Belaga and Bigelow⁽⁸⁾ studied the system water-acetic acid-methyl isobutyl ketone with the organic phase continuous. All experiments were made at constant flow rates and the HTU varied from 2.63 to 6.25, depending on pulse height and frequency. These values are lower than those reported by other investigators for this system; values as low as six inches were reported for a 1.2-inch packed column and 7.5 inches for a wetted-wall extraction column.

Pulse Column Applications. Peppard⁽⁶¹⁾ of the Argonne National Laboratory devised a process whereby he could recover stable isotopes of the lanthanide rare earths using liquid-liquid extraction.

Weaver⁽⁹⁴⁾ of the Oak Ridge National Laboratory has now taken Peppard's process, devised equipment for increased throughput, and is well along in a project to recover stable isotopes for distribution to other research workers.

Briefly, the process involves countercurrent extraction of rare earth oxides dissolved in nitric acid with tri-n-butyl phosphate. Repeated extractions, evaporations, and recombinations of fractions led to the desired purification.

To effect the scale-up, Weaver and coworkers designed a two-inch diameter glass column in which the aqueous phase (nitric acid) is fed in the top, the rare earth oxides (in nitric acid) in the middle, and the organic phase (tri-n-butyl phosphate) in the bottom. Spaced at one-inch intervals in the column are 140 stainless steel plates. These plates are pierced by 1/32-inch holes which cover twenty-three per cent of the plate's area.

Flow rates used are in the order of one to three gallons per hour for each of the feeds. Since this flow rate is too low to force the liquids through the holes, a valveless, piston pump is attached to the system. This pump pulses the material in the column at a rate of about thirty pulses per minute, forcing it through the holes in the plates. In doing so, it breaks the liquids up into small drops, increasing contact area and separation efficiency. Throughput is about one pound of rare earth oxides per hour.

Rate Relations and Flow Capacities

In this section the rate relations and flow capacities important to an evaluation of the pulse column will be discussed.

Flow Capacities. The capacity of an extractor is limited by the flooding velocity. The flooding velocity is defined⁽⁸⁷⁾ as the velocity of flow of one phase at which the other phase is just kept from flowing through the extractor. The limit on capacity caused by this phenomenon is an important design consideration.

Van Dijk⁽⁸⁹⁾ states that the flooding velocity for a pulse column is equal to the flooding velocity of a spray tower of equal column diameter. The flooding velocity also appears to be independent of the free area of the plates. The Iowa State⁽²¹⁾ pulse column flooded at a flow of about 660 gallons per hour-square foot of column cross-section. This is equivalent to a flooding mass velocity of 5500 pounds per hour-square foot of column cross-section.

Elgin and Foust⁽³⁰⁾ present a chart correlating flooding data in spray towers. From this chart values in the range of 10,000 to 20,000 pounds per hour-square foot of column

cross-section or even higher are obtained for flooding, depending upon the system and the relative velocities.

Rate Relations for Pulse Columns. The pulse column, as a countercurrent stagewise extractor, should be rated in terms of either the HETS or the stage efficiency. However, the two columns, for which data are available, are calculated as if they were continuous countercurrent columns; that is, they are rated in HTU's. For the reasons discussed previously, these results should be viewed with caution, especially when comparing to pulse columns rated in terms of the HETS.

For the column at Iowa State⁽²¹⁾ values of the HTU as low as 5.7 inches were reported. As no additional data were given the equivalence of the HETS and the HTU could not be calculated.

For the column at North Carolina State⁽⁶²⁾ values of the HTU as low as 0.14 foot were reported. The complete experimental results and data for this column are presented in Table IV, page 55. The results for this column were obtained using the two component system of benzene-water. As a theoretical stage for a two component system results in the saturation of the respective phases, and as the phase did not leave saturated, it can be stated that the column did not have one complete theoretical stage. However, as the composition data of the respective phases are also available, HETS's for this column may be calculated.

TABLE IV

Plate Efficiencies for a 1/2-inch Pulse Extractor
Operating with a Pulse Frequency of 24 Cycles per
Minute and an Amplitude of 1.20 Inches^a

| Continuous Phase | Flow Rates | | Plate Efficiency ^b % |
|------------------|-------------------|-----------------|------------------------------------|
| | Benzene ml/min | Water ml/min | |
| Benzene | 107 | 353 | 17.2 |
| Benzene | 70 | 107 | 15.7 |
| Water | 73.5 | 235 | 20.2 |
| Water | 76 | 109 | 18.7 |
| Water | 77.5 | 106 | 18.7 |
| Water | 153 | 600 | 22.8 |
| Water | 43.6 | 598 | 24.2 |

^a Pike, F. P., D. S. Arnold, and C. A. Plank: The performance of Contractors for Liquid-liquid Extraction. Unpublished Progress Report, Department of Engineering Research, North Carolina State College, Raleigh, N. C., July 1, 1952.

^b Calculated by Hayford⁽⁴³⁾ from data obtained from the report.

III. EXPERIMENTAL

The experimental portion of this investigation consists of the purpose of investigation, plan of experimentation, materials, apparatus, method of procedure, data and results, and sample calculations.

Purpose of Investigation

It was the purpose of this investigation to build and operate a pulse liquid-liquid extractor, and, using the system carbon tetrachloride-acetone-water, to study the effects of the pulse amplitude, plate-free-area, and number of plates or plate spacing on the extraction efficiency of the column.

Plan of Experimentation

The plan of experimentation that was followed in this investigation consisted of a review of the literature on liquid-liquid extraction, a study of the materials of construction for the extraction equipment, reconstruction of the pulse extractor, operation of the column, determination of the effects of several operational variables on the extraction efficiency, and correlation of data.

Literature Review. The literature review was designed to acquaint the author with the principles of extraction, and, in particular, extraction as applied to the pulse column. To accomplish this purpose a study of the general principles of extraction and some important definitions was made. Next, a study of the equilibrium relations important in extraction was executed. The equilibrium data for the system carbon tetrachloride-acetone-water which is used in this investigation were covered in detail. The operational relations by which equipment can be compared was studied. Next, a brief review of equipment types and materials of construction for extraction equipment was presented. Several improved extractor designs, among them the pulse extractor, were covered in greater detail. Last, a study of the operational variables for the pulse extractor and some other recent designs of extractors was made.

Materials of Construction. An intense study of materials of construction was made in order to find those materials for the reconstruction of the pulse extraction equipment which would be noncorrosive in the presence of the system carbon tetrachloride-acetone-water.

Reconstruction of Column. Those parts of the extraction equipment which come into direct contact with the system carbon tetrachloride-acetone-water were rebuilt from new materials,

noncorrosive to the system. The redesigned flow diagram for the pulse liquid-liquid extractor installation is shown in Drawing 9, page 91.

Operation of the Column. The pulse liquid-liquid extraction column was operated under the standardized procedure of operation as established by Hayford⁽⁴³⁾. The feed composition, liquid flow rates, and pulse frequency were held constant while the pulse amplitude, plate-free-area, and number of plates or plate spacing were varied.

Operational Variables. The pulse amplitude, plate-free-area, and number of plates were varied independently over an adequate range in order to determine the effect of each variable and all combinations thereof on the extraction efficiency of the column.

Correlation of Data. The experimental data obtained were correlated and presented in such a manner as to clearly indicate the effect of each of the operational variables studied on the extraction efficiency of the column. Statistical methods were employed for this purpose. Complete analysis-of-variance tests were made to determine the effect of each individual variable and the interaction effects of all combinations thereof.

Materials

The specifications of the materials used in this investigation are presented in the following section.

Acetone. Reagent grade, Baker and Adamson lot No H297J. Obtained from the General Chemical Division, Allied Chemical and Dye Corporation, New York, New York. Used as the solute in the demonstration system.

Air. Compressed air at the extractor site furnished from lines in the Unit Operations Laboratory, Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Virginia. Pressure varied from fifty to seventy-five pounds per square inch, gage at compressor site. Used as the motive force for the heavy and light phases.

Carbon Tetrachloride. Reagent grade, Baker and Adamson lot No B 052. Obtained from the General Chemical Division, Allied Chemical and Dye Corporation, New York, New York. Used as the carrier solvent in the demonstration system.

Castor Oil. Purified, colorless, medium grade. Manufacturer unknown. Obtained from Tech Drug Store, Blacksburg, Virginia. Used as a lubricant for the push rod bearing assembly.

Flux. Meets specification U. S. N. 51F4A, Army Air Corps No 11316A, and Army Ordnance Department No AXS - 500. Manufactured by Handy and Harman, Inc., New York, New York. Used as flux for silver soldering of copper tubing-fitting connections.

Graphite Lubricant. Mixture of purified, greaseless graphite flakes and standard grade machine oil. Manufacturer unknown. Obtained from the Industrial Engineering Machine Shops, Industrial Engineering Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Used as a contact lubricant for the push rod-cam assembly.

Phenoline 300. Stage A phenolic resin. Compositions of components unknown. Ordered as one quart size experimental kit of Phenoline 300. Obtained from Carboline Co., 331 Thornton Avenue, St. Louis, Missouri. Used as a protective coating for all metal parts of the pulse liquid-liquid extractor that were exposed to direct contact with the demonstration system of carbon tetrachloride-acetone-water.

Solder. Sil-fos, fifteen per cent silver content alloy, starts to melt at 1185 °F and is completely liquid at 1300 °F. Distributed by Southern Oxygen Company, Roanoke, Virginia. Used in welding numerous connections in the construction of the pulse liquid-liquid extractor.

Water. Tap water at extractor site obtained from lines located in the Unit Operations Laboratory, Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Virginia. Used as the solvent in the demonstration system. Water analysis was as follows: Total hardness, ppm, 328; calcium, ppm, 192; magnesium, ppm, 136; phenolphthalein alkalinity, ppm, 0; methyl orange alkalinity, ppm, 228; sulfate, ppm, 112; chloride, ppm, 1.5; silica, ppm, 11.3; pH, 7.3; total iron, ppm, 0.1.

Apparatus

The apparatus used in this investigation are described in the section that follows:

Balance. Solution type beam balance, capacity twenty kilograms, sensitivity one gram. Obtained from the Fisher Scientific Company, Silver Spring, Maryland. Used to weigh the feed, solvent, extract, and raffinate samples from the pulse extractor in the flow rate determinations.

Constant-temperature Bath. Constant-temperature bath constructed by the Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Virginia. Controlled by an Aminco Thermal Switch, manufactured by the American Instrument Company, Silver Spring, Maryland. Used as a source of constant temperature water for the refractometer.

Miscellaneous Glassware. Laboratory glassware obtained from the Fisher Scientific Company, Silver Spring, Maryland. Used for standard analytical and laboratory purposes.

Mixer. "Lightnin" model L mixer, serial No 502260, 110 volts, 50-60 cycles, single phase. Manufactured by the Mixing Equipment Company. Obtained from the Fisher Scientific Company, Silver Spring, Maryland. Used to mix the feed for the pulse extractor.

Pails. Five-gallon (Esso Lubricating Oil) pails. Obtained from the Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Virginia. Used to collect the extract phase and the raffinate phase from the pulse extractor during the experimental tests.

Pulse Extractor. The pulse extractor was constructed in the Department of Chemical Engineering from purchased and manufactured parts. A detailed drawing of this column is found on page 66. The bill of materials for the column is contained in Table V, page 67. To aid in understanding Drawing 1, details of the column top plate are found in Drawing 2, page 68; details of the column bottom plate are found in Drawing 3, page 69; details of the perforated baffle plates are found in Drawing 4, page 70; and details of the top bellows flanges are found in Drawing 5, page 71. The parts shown in these last four drawings are also contained in Table V, page 67.

Pulse-Extractor and Push-Rod Frame. The pulse-extractor and the push-rod frame were constructed in the Department of Chemical Engineering for this investigation. Details of this frame may be seen in Drawing 6, page 72. The bill of materials for the frame is contained in Table V, page 67.

Pulse-extractor Cam Assembly. The cam assembly was constructed in the Department of Chemical Engineering for this investigation. Details of the cam assembly are shown in Drawing 7, page 73. The bill of materials for this assembly may be found in Table V, page 67.

Pulse-extractor Push-rod Assembly. The push-rod assembly was constructed in the Department of Chemical Engineering for this investigation. Details of this assembly are shown in Drawing 8, page 74. The bill of materials for the push-rod assembly may be found in Table V, page 67.

Pulse-extractor Tubing and Storage. The tubing and storage were constructed for this investigation in the Department of Chemical Engineering. The materials required for this part of the apparatus are shown in Table V, page 67.

Refractometer. Abbe, A. O. Spencer model 1777, range 1.3000 to 1.7100, sensitivity 0.0002, reads directly in n_D units, serial No 789326721. Obtained from the Fisher Scientific Company, Silver Spring, Maryland. Used to determine the refractive index of the feed, solvent, extract, and raffinate samples from the pulse extractor.

Thermometer. Mercury in glass, range -10 to 120 °C. Obtained from the Fisher Scientific Company, Silver Spring, Maryland. Used to measure the temperature of the stream samples in connection with the refractometer.

Timer. Standard electric clock, continuous, graduated in one-second intervals by a sweep second hand, 115 volts, 60 cycle, 5 watts. Obtained from the Fisher Scientific Company, Silver Spring, Maryland. Used to time experimental tests.

Tools. Various hand tools, welding equipment, vises, drills, and lathes were used in the construction of the pulse extractor and its auxiliary apparatus. Available in the Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Virginia.

Drawing 1. Detail Drawing of Pulse Extractor

LIGHT PHASE OUTLET, WHITEHEAD 3115-2H6T6 BULKHEAD UNION, BRAZED TO FLANGE, 1 REQUIRED

HEAVY PHASE INLET, WHITEHEAD 3115-2H6T6 BULKHEAD UNION, BRAZED TO FLANGE, 1 REQUIRED

3/8" BOLT, WELDED TO PIPE

CORNING STANDARD 2" FLANGE

TOP COLUMN FLANGE

TEFLON GASKET

1/8" BRASS ROD

CORNING STANDARD 2" PYREX BRAND PIPE

1/8" STEEL PIPE, WITH 3/8" BOLTS WELDED IN EACH END

NUT WITH SET SCREW

BAFFLE PLATE,

COLUMN FRAME

8 PLATES AT SPACING - 32"

1/8" HEX NUT

CORNING STANDARD FLANGE SET
2- CORNING 2" FLANGES
2- CORNING 2" INSERTS
WITH TEFLON GASKET

3/8 T X 3/8 M ELBOW

3/8" COPPER TUBING

CORNING STANDARD 4" FLANGE

CORNING STANDARD 4" INSERT

TEFLON GASKET

BOTTOM COLUMN FLANGE

1/4 X 2 ROUND HEAD STOVE BOLTS, 1/4-NC-20-2 SQUARE NUT, 6 REQUIRED

WHITEHEAD 3115-2H6T6 BULKHEAD UNION, 2 REQUIRED, FRONT, HEAVY PHASE OUT; BACK, LIGHT PHASE IN.

CORNING STANDARD 4" INSERT

CORNING STANDARD 4" FLANGE

1/4 X 2 ROUND HEAD STOVE BOLTS, 1 4-NC20-2 SQUARE NUT, 6 REQUIRED

CORNING JM 84-8, 4" GASKET

BASE PLATE

TEFLON GASKET

BELLOWS FLANGE, SOLDERED TO COPPER - BELLOWS FLANGE

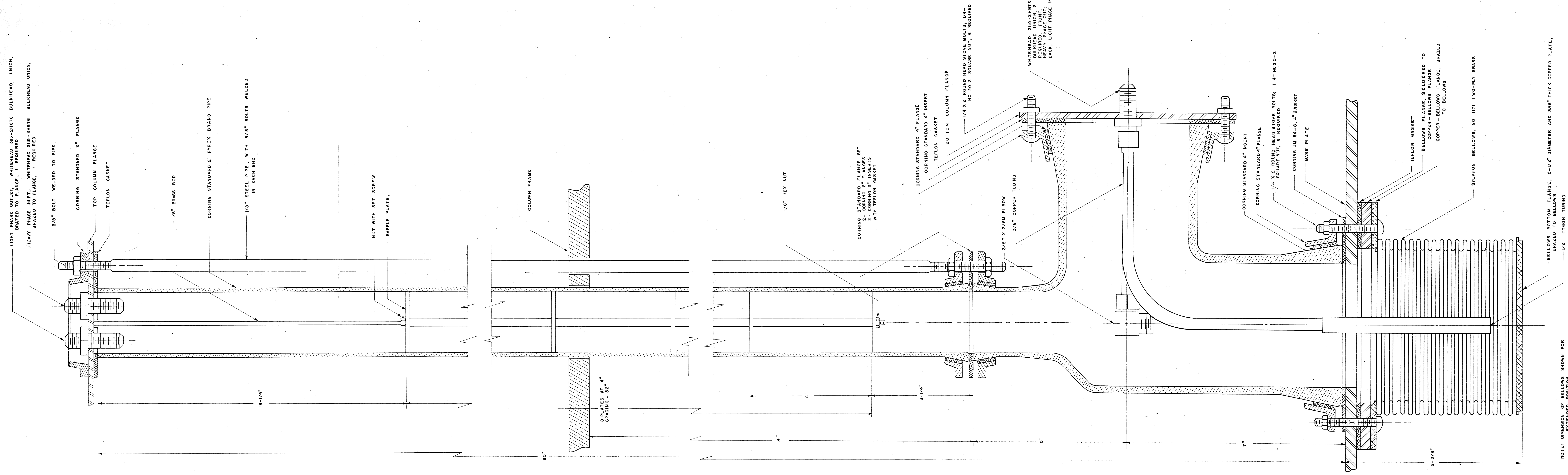
COPPER - BELLOWS FLANGE, BRAZED TO BELLOWS

SYLPHON BELLOWS, NO 1171 TWO-PLY BRASS

BELLOWS BOTTOM FLANGE, 5-1/2" DIAMETER AND 3/16" THICK COPPER PLATE, BRAZED TO BELLOWS

1/2" TYGON TUBING

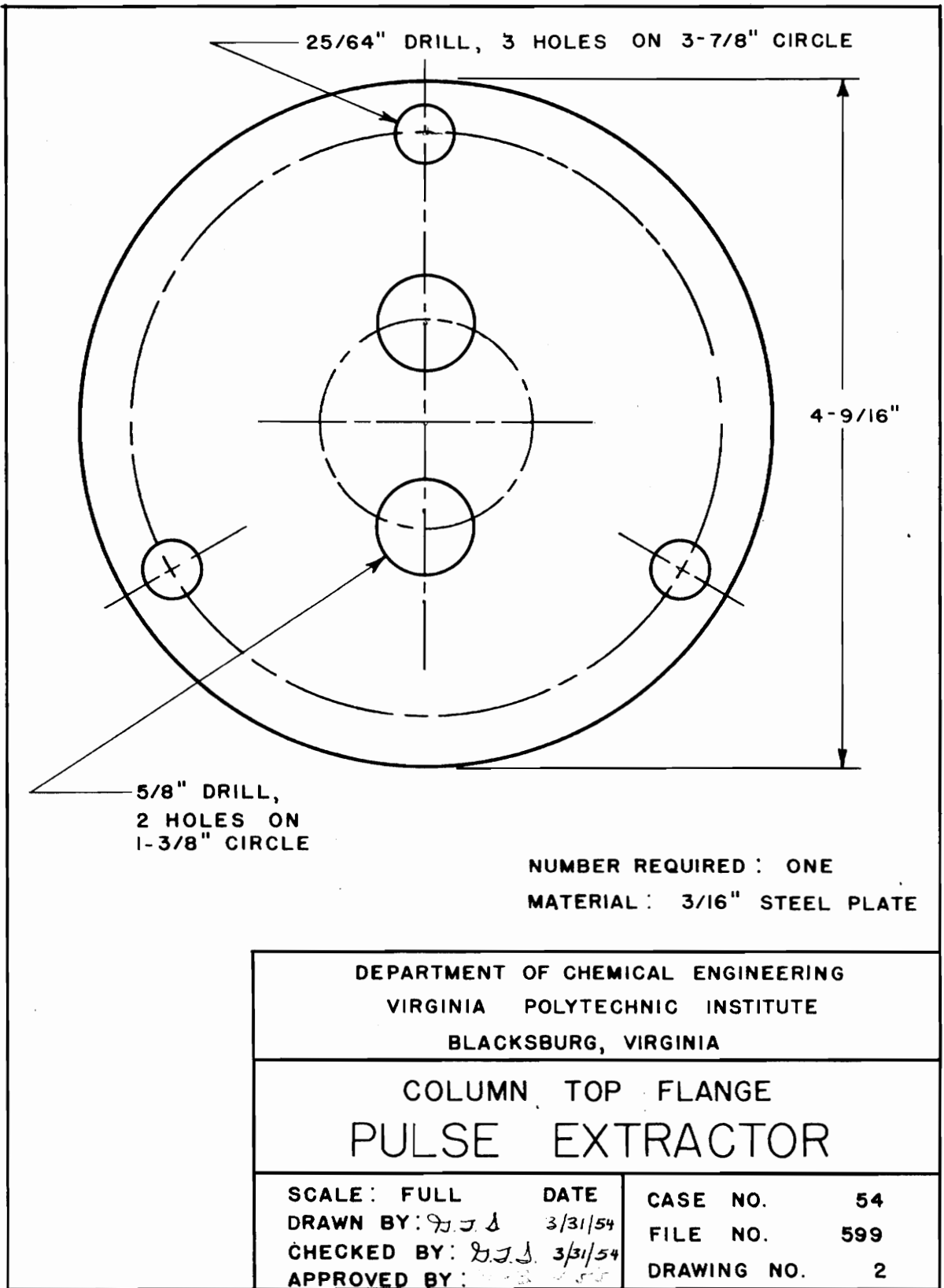
NOTE: DIMENSION OF BELLOWS SHOWN FOR EXTENDED POSITION.

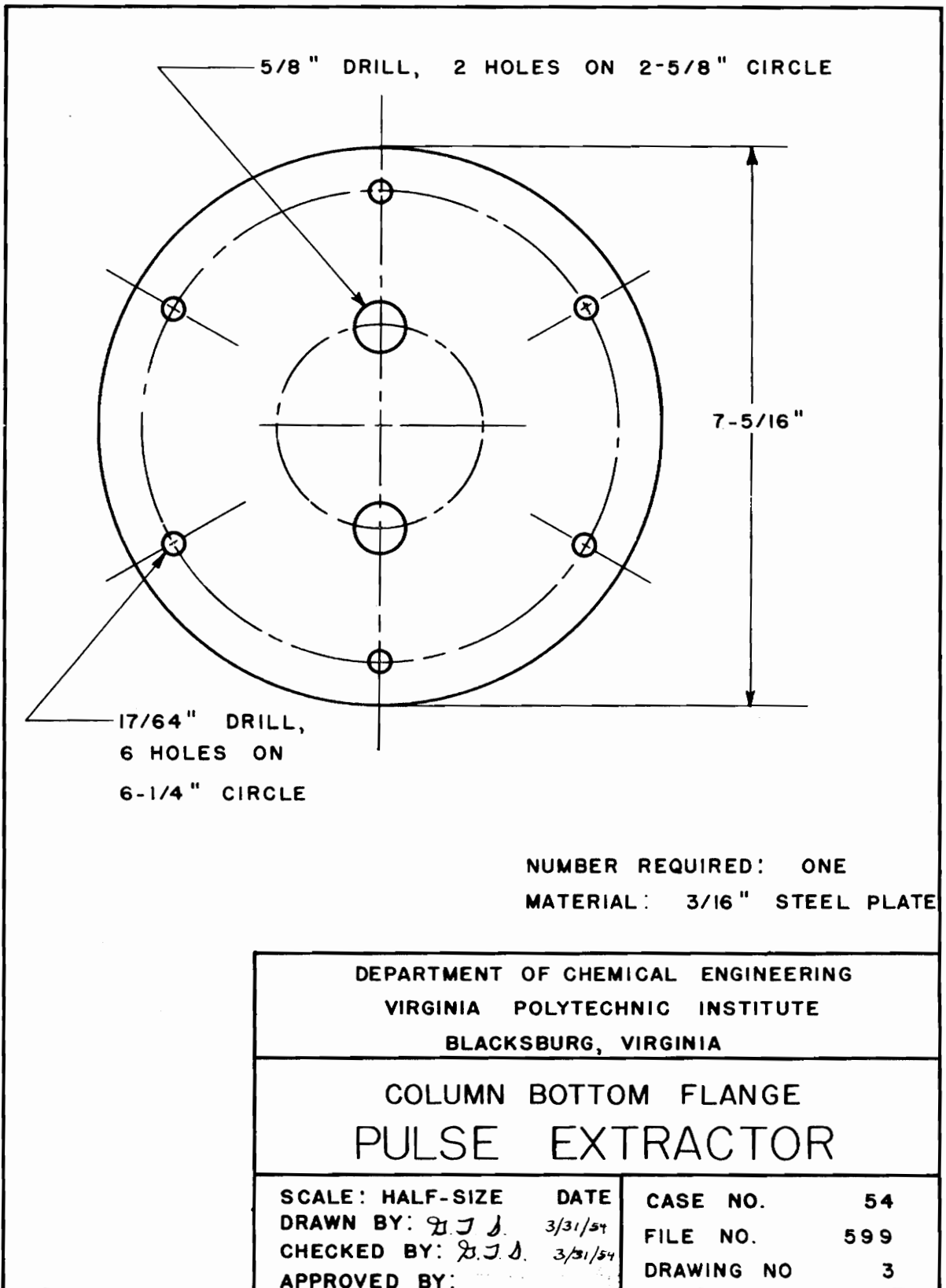


| | |
|--------------------------|--|
| REVISIONS | DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA |
| | PULSE EXTRACTOR |
| FULL SCALE | CASE 64 |
| DRAWN BY: [Signature] | FILE 699 |
| DATE: 4/14/54 | DRAWING 1 |
| APPROVED BY: [Signature] | |

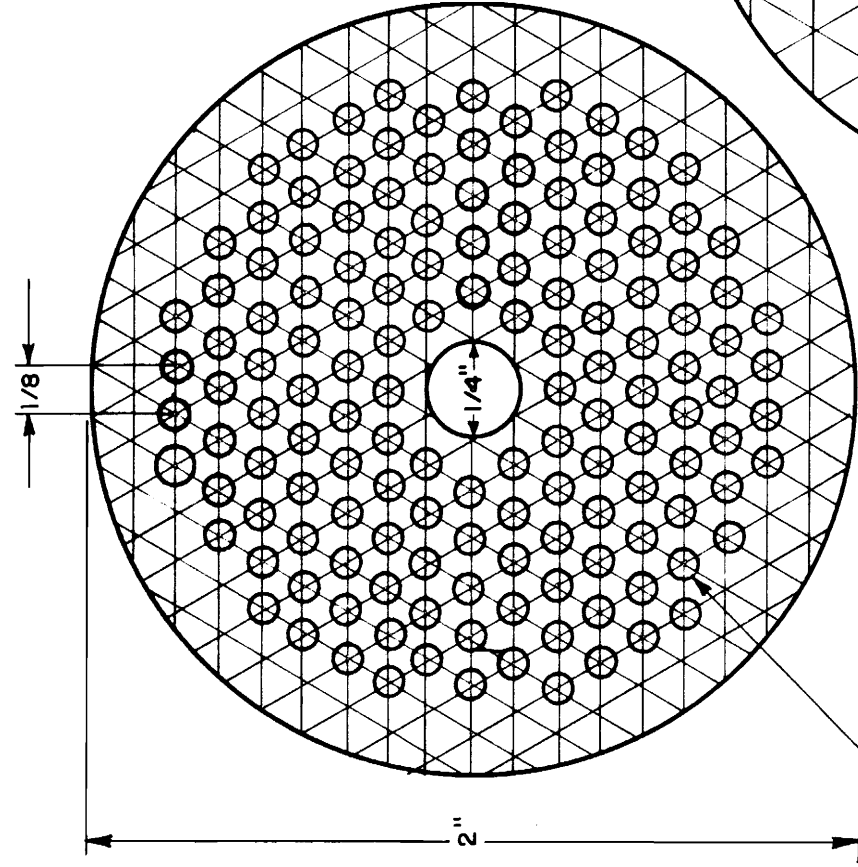
TABLE V
Bill of Materials for an Experimental Two-inch Pulse Extractor and Auxiliary Apparatus

| Item | Quantity | Description | Supplier |
|-----------------------------------|----------|---|---|
| Bellows | 1 ea | Syphon No 1171 2-ply brass | Fulton Syphon Div. Knoxville, Tenn. |
| Glass pipe | 4 ft | 2-inch flanged pyrex | Sentinel Glass Co., Hatboro, Pa. |
| Glass tee | 1 ea | 4 x 2 x 4-inch pyrex | Sentinel Glass Co., Hatboro, Pa. |
| Motor | 1 ea | 1/4 hp, 1720 rpm, 110 volts, 60 cycle induction | Montgomery Ward Baltimore, Md. |
| Pressure gages | 4 ea | Ascroft -30 in Hg to 100 lb per sq in | Noland Co., Roanoke, Va. |
| Reducer | 1 ea | Boston gear 80 to 1 ratio, input 0.15 hp at 1500 rpm | Noland Co., Roanoke, Va. |
| <u>Hardware</u> | | | |
| Bearings | 2 ea | Babbitt sleeve type, 3/4" x 1-1/2" | Ind. Eng. Shops, V. P. I., Blacksburg, Va. |
| Belt | 1 ea | Type A-31 VeeLocs link V-belt | Noland Co., Roanoke, Va. |
| Tanks | 4 ea | Ten-gallon stainless steel, 500 PSI, 12" x 24", G-1-W | A. C. Tank Co., Burlington, Wis. |
| Clamps | 5 ea | 1/2-inch tubing | Noland Co., Roanoke, Va. |
| Collars | 2 ea | 3/4-inch shaft | Noland Co., Roanoke, Va. |
| Coupling | 1 ea | 3/4 x 1-inch bell type | Noland Co., Roanoke, Va. |
| Flange sets | 2 ea | 2-inch Corning standard | Sentinel Glass Co., Hatboro, Pa. |
| | 1 ea | 4-inch Corning standard | Sentinel Glass Co., Hatboro, Pa. |
| Funnel | 1 ea | 9-inch polyethylene | Fisher Scientific Co., Silver Spring, Md. |
| Gaskets | 3 ea | 1/8-inch x 9-inch diameter Teflon | U. S. Gasket Co., Camden 1, N. J. |
| | 2 ea | 1/8-inch x 3-inch diameter Teflon | U. S. Gasket Co., Camden 1, N. J. |
| | 2 ea | 2-inch Corning JM-84-S | Sentinel Glass Co., Hatboro, Pa. |
| | 2 ea | 4-inch Corning JM-84-S | Sentinel Glass Co., Hatboro, Pa. |
| | 4 ea | 1/8-inch x 1-1/2-inch diameter, Teflon | U. S. Gasket Co., Camden 1, N. J. |
| Orifice plates | 2 ea | 1/32-inch x 1-1/2-inch diameter, copper | Mfg. in Ch. E. Dept., V. P. I., Blacksburg, Va. |
| Orifice flanges | 4 ea | 1/16-inch x 1-1/2-inch diameter, copper | Mfg. in Ch. E. Dept., V. P. I., Blacksburg, Va. |
| Pulleys | 1 ea | 1/2 x 2-inch single V-belt | Noland Co., Roanoke, Va. |
| | 1 ea | 3/4 x 4-inch single V-belt | Noland Co., Roanoke, Va. |
| <u>Structural Shapes</u> | | | |
| Angle | 9 ft | 3/4 x 3/4 x 1/16-inch steel | Noland Co., Roanoke, Va. |
| | 6 ft | 2 x 2 x 1/4-inch steel | Noland Co., Roanoke, Va. |
| Channel | 14 in | 4 x 2 x 1/4-inch steel | Noland Co., Roanoke, Va. |
| Lumber | 5 ft | 1 x 4-inch finished | New River Lumber Co., Blacksburg, Va. |
| | 5 ft | 2 x 4-inch semi-finished | New River Lumber Co., Blacksburg, Va. |
| | 6 ft | 2 x 4-inch finished | New River Lumber Co., Blacksburg, Va. |
| Plate | 2 ea | 3/16-inch x 8-inch diameter copper | Ind. Eng. Dept., V. P. I., Blacksburg, Va. |
| | 16 ea | 1/4-inch steel, 2 x 2-inch | Noland Co., Roanoke, Va. |
| | 1 ea | 1/4-inch steel, 24 x 28-inch | Noland Co., Roanoke, Va. |
| | 2 ea | 3/16-inch steel, 8-inch diameter | Noland Co., Roanoke, Va. |
| | 1 ea | 3/8-inch steel, 13-1/2 x 12-inch | Noland Co., Roanoke, Va. |
| | 3 ea | 3/8-inch steel, 13-inch diameter | Noland Co., Roanoke, Va. |
| | 1 ea | 3/8-inch steel, 8-inch diameter | Noland Co., Roanoke, Va. |
| Round stock | 4 ft | 1/4-inch brass welding rod | Southern Oxygen Co., Roanoke, Va. |
| | 11 in | 3/4-inch steel | Noland Co., Roanoke, Va. |
| | 14 in | 3/4-inch steel | Noland Co., Roanoke, Va. |
| <u>Fasteners</u> | | | |
| Anchors | 8 ea | 1/4-inch U.S.F. Korker | Noland Co., Roanoke, Va. |
| | 6 ea | 5/16-inch U.S.F. Korker | Noland Co., Roanoke, Va. |
| Bolts | 100 ea | 1/4 x 1-1/2-inch square head | Noland Co., Roanoke, Va. |
| | 50 ea | 1/4 x 2-inch square head | Noland Co., Roanoke, Va. |
| | 20 ea | 1/4 x 4-inch square head | Noland Co., Roanoke, Va. |
| | 8 ea | 3/8 x 2-inch square head | Noland Co., Roanoke, Va. |
| | 8 ea | 1/2 x 1-1/2-inch square head | Noland Co., Roanoke, Va. |
| | 3 ea | 1/2 x 2-inch square head | Noland Co., Roanoke, Va. |
| Log screws | 8 ea | 1/4 x 2-inch square head | Noland Co., Roanoke, Va. |
| | 8 ea | 3/8 x 2-inch square head | Noland Co., Roanoke, Va. |
| Nuts | 16 ea | 1/4-NC 20-2 square | Noland Co., Roanoke, Va. |
| | 2 ea | 3/4-NC 10-2 hex head | Noland Co., Roanoke, Va. |
| Screws | 6 ea | 1-inch No 9 | Noland Co., Roanoke, Va. |
| | 36 ea | 1-1/2-inch No 11 | Noland Co., Roanoke, Va. |
| Stove bolts | 12 ea | 1/4 x 2-inch round head | Noland Co., Roanoke, Va. |
| | 6 ea | 5/16 x 2-inch round head | Noland Co., Roanoke, Va. |
| Washers | 100 ea | 1/4-inch | Noland Co., Roanoke, Va. |
| | 20 ea | 3/8-inch | Noland Co., Roanoke, Va. |
| | 3 ea | 1/2-inch | Noland Co., Roanoke, Va. |
| <u>Pipe and Fittings</u> | | | |
| Bushings | 1 ea | 1/4 x 3/8-inch black iron | Noland Co., Roanoke, Va. |
| | 2 ea | 3/8 x 1/2-inch galvanized | Noland Co., Roanoke, Va. |
| Aspirator | 1 ea | 3/4-inch chrome plated | Noland Co., Roanoke, Va. |
| Couplings | 4 ea | 1/4-inch black iron | Noland Co., Roanoke, Va. |
| Elbows | 7 ea | 1/4-inch black iron | Noland Co., Roanoke, Va. |
| | 2 ea | 3/8-inch galvanized | Noland Co., Roanoke, Va. |
| Flanges | 8 ea | 1/2-inch No 7 black iron | Noland Co., Roanoke, Va. |
| | 4 ea | 1/2-inch No 9 black iron | Noland Co., Roanoke, Va. |
| | 4 ea | 1-inch A.S.M.F. 125-pound | Noland Co., Roanoke, Va. |
| Nipples | 9 ea | 1/4-inch close black iron | Noland Co., Roanoke, Va. |
| | 8 ea | 1/4 x 1-inch black iron | Noland Co., Roanoke, Va. |
| | 12 ea | 1/4 x 2-inch black iron | Noland Co., Roanoke, Va. |
| | 8 ea | 1/4 x 3-inch black iron | Noland Co., Roanoke, Va. |
| | 2 ea | 1/4 x 6-inch black iron | Noland Co., Roanoke, Va. |
| | 3 ea | 3/8-inch close galvanized | Noland Co., Roanoke, Va. |
| | 5 ea | 3/8 x 1-inch galvanized | Noland Co., Roanoke, Va. |
| | 2 ea | 3/8 x 4-inch galvanized | Noland Co., Roanoke, Va. |
| | 2 ea | 3/8 x 6-inch galvanized | Noland Co., Roanoke, Va. |
| Pipe | 1 ea | 1 x 4-inch black iron | Noland Co., Roanoke, Va. |
| | 6 ft | 1/4-inch black iron | Noland Co., Roanoke, Va. |
| | 6 ft | 3/8-inch galvanized | Noland Co., Roanoke, Va. |
| | 13 ft | 1/2-inch black iron | Noland Co., Roanoke, Va. |
| Reducers | 1 ea | 1/4 x 3/8-inch galvanized | Noland Co., Roanoke, Va. |
| | 1 ea | 3/4 x 1-inch black iron | Noland Co., Roanoke, Va. |
| Street elbows | 2 ea | 1/4-inch black iron | Noland Co., Roanoke, Va. |
| | 4 ea | 3/8-inch galvanized | Noland Co., Roanoke, Va. |
| Tees | 13 ea | 1/4-inch black iron | Noland Co., Roanoke, Va. |
| | 4 ea | 3/8-inch galvanized | Noland Co., Roanoke, Va. |
| Unions | 2 ea | 1/4-inch black iron ground joint | Noland Co., Roanoke, Va. |
| | 2 ea | 3/8-inch galvanized ground joint | Noland Co., Roanoke, Va. |
| Valves | 4 ea | 1/4-inch gate, brass | Noland Co., Roanoke, Va. |
| | 5 ea | 1/4-inch globe, brass | Noland Co., Roanoke, Va. |
| | 1 ea | 1/4-inch diaphragm air reducing | Noland Co., Roanoke, Va. |
| | 1 ea | 1/4-inch swing check | Noland Co., Roanoke, Va. |
| | 3 ea | 3/8-inch gate, brass | Noland Co., Roanoke, Va. |
| | 2 ea | 3/8-inch needle, brass | Noland Co., Roanoke, Va. |
| | 2 ea | 3/8-inch swing check, brass | Noland Co., Roanoke, Va. |
| Connectors | 7 ea | 1/4T x 1/4M-inch, brass | Noland Co., Roanoke, Va. |
| | 7 ea | 3/8T x 3/8M-inch compression brass | Noland Co., Roanoke, Va. |
| | 3 ea | 3/8T x 3/8M-inch compression elbow, brass | Noland Co., Roanoke, Va. |
| | 4 ea | 5/16T x 1/4M-inch compression elbow, brass | Noland Co., Roanoke, Va. |
| | 4 ea | 5/16T x 1/4M-inch compression straight, brass | Noland Co., Roanoke, Va. |
| <u>Tubing and Tubing Fittings</u> | | | |
| | 7 ea | 1/4T x 1/4M-inch, brass | Whitehead Metal Products Co., Baltimore, Md. |
| | 7 ea | 3/8T x 3/8M-inch compression brass | Auto Spring and Bearing Co., Roanoke, Va. |
| | 3 ea | 3/8T x 3/8M-inch compression elbow, brass | Auto Spring and Bearing Co., Roanoke, Va. |
| | 4 ea | 5/16T x 1/4M-inch compression elbow, brass | Auto Spring and Bearing Co., Roanoke, Va. |
| | 4 ea | 5/16T x 1/4M-inch compression straight, brass | Auto Spring and Bearing Co., Roanoke, Va. |

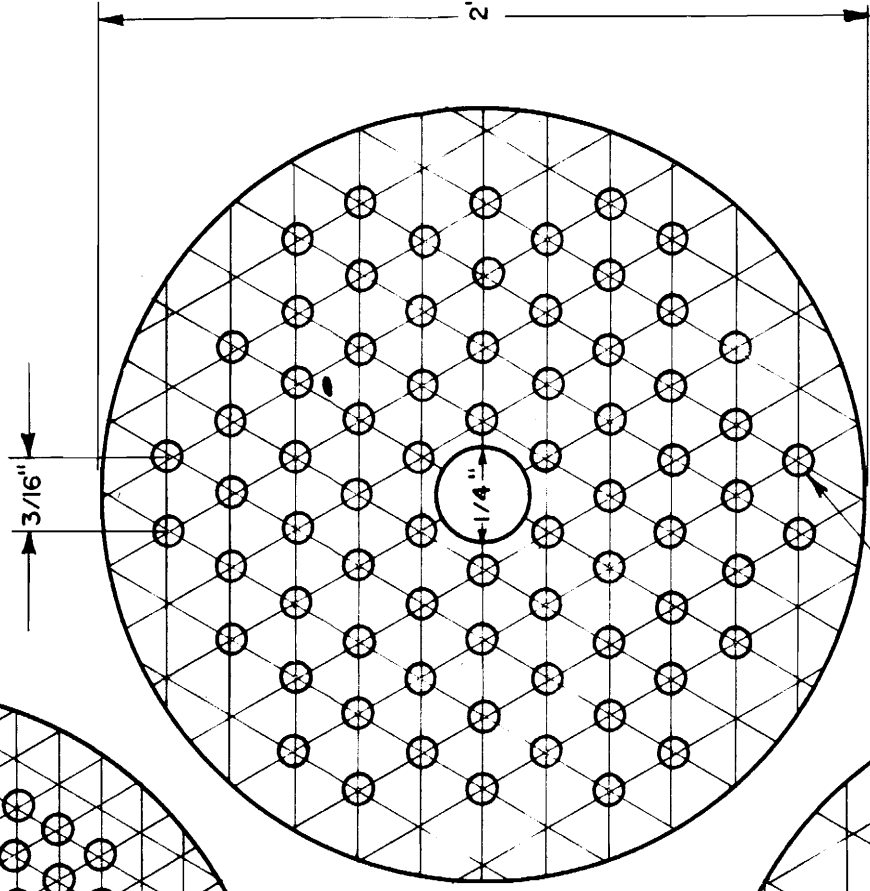




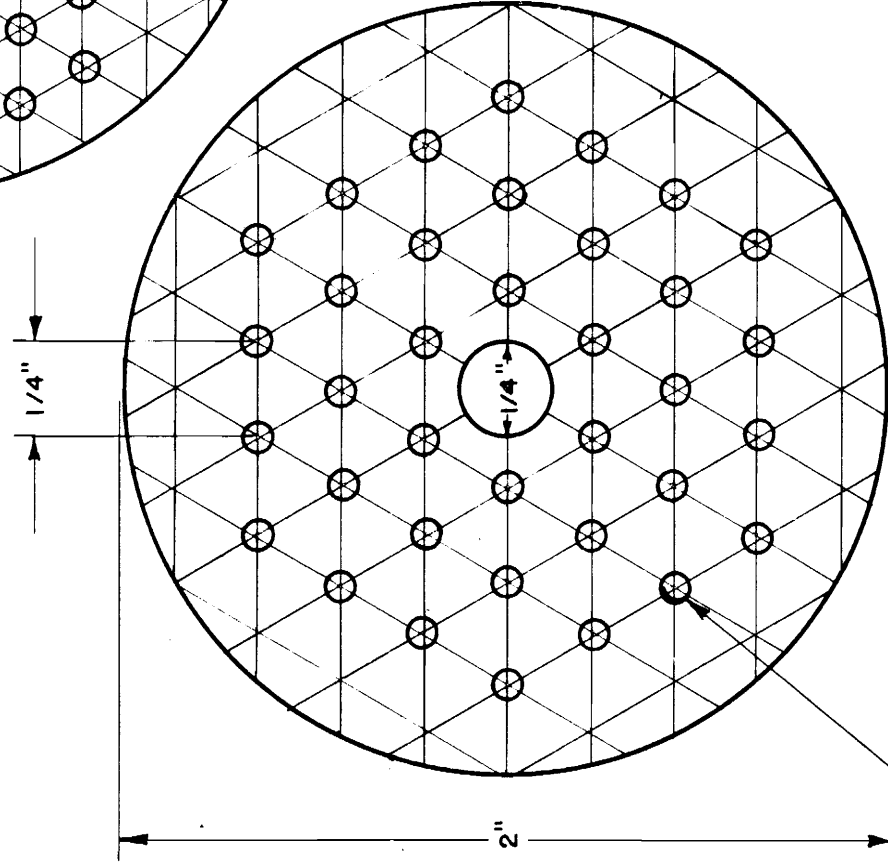
Drawing 4. Detail Drawing of Pulse Extractor
Baffle Plates



3/32" DRILL, 144 HOLES
 NUMBER REQUIRED: 12
 MATERIAL: 1/8" STEEL PLATE
 FREE AREA: 32%



3/32" DRILL, 72 HOLES
 NUMBER REQUIRED: 12
 MATERIAL: 1/8" STEEL PLATE
 FREE AREA: 16%



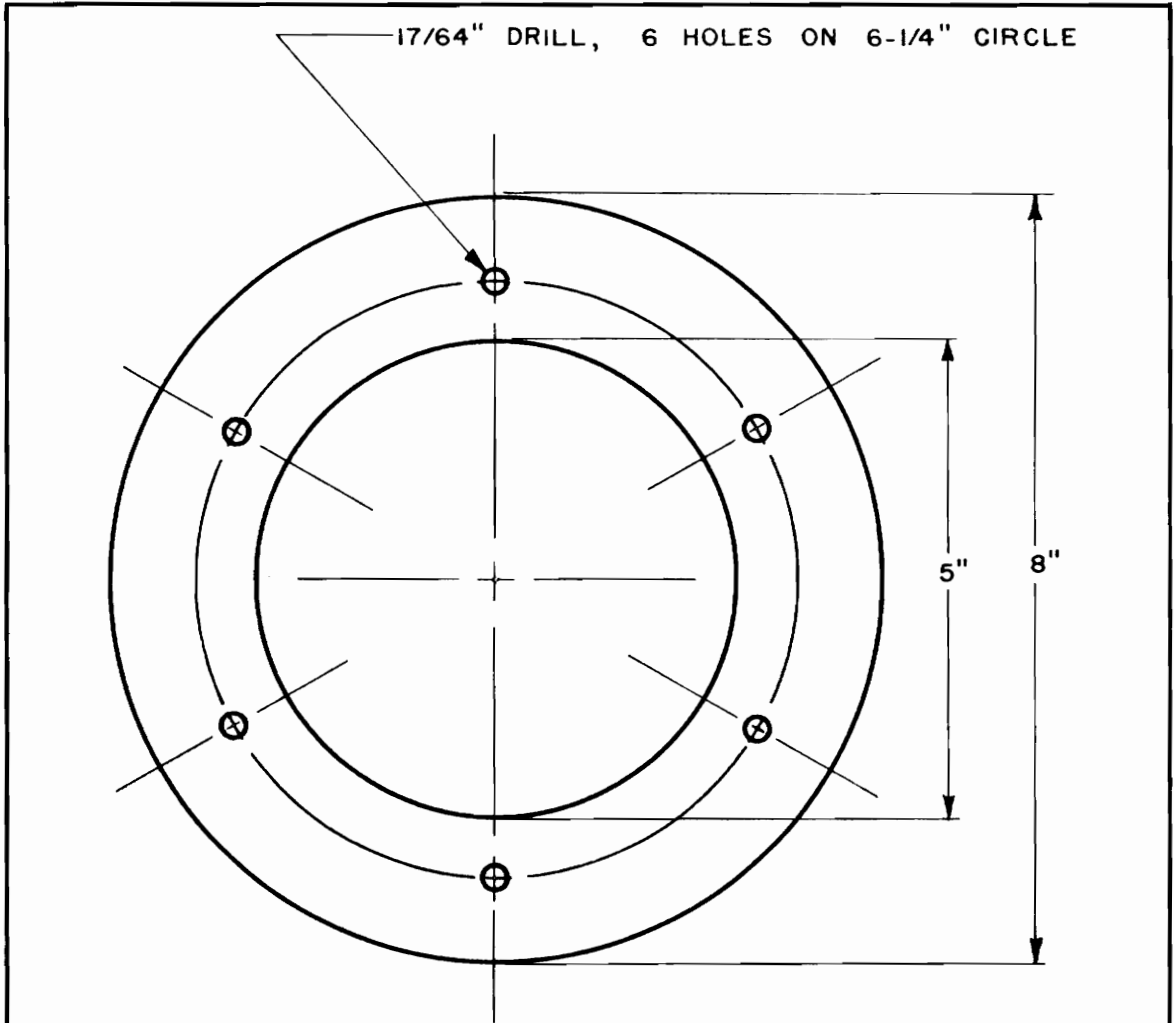
3/32" DRILL, 36 HOLES
 NUMBER REQUIRED: 12
 MATERIAL: 1/8" STEEL PLATE
 FREE AREA: 8%

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 BLACKSBURG, VIRGINIA

BAFFLE PLATE
 PULSE EXTRACTOR

SCALE: 2:1 DATE: 3/31/54
 DRAWN BY: R.J.J. FILE NO. 599
 CHECKED BY: R.J.J. 3/31/54
 APPROVED BY:

CASE NO. 54
 FILE NO. 599
 DRAWING NO. 4



NUMBER REQUIRED : TWO
MATERIAL : ONE 3/16" COPPER PLATE
ONE 3/8" STEEL PLATE

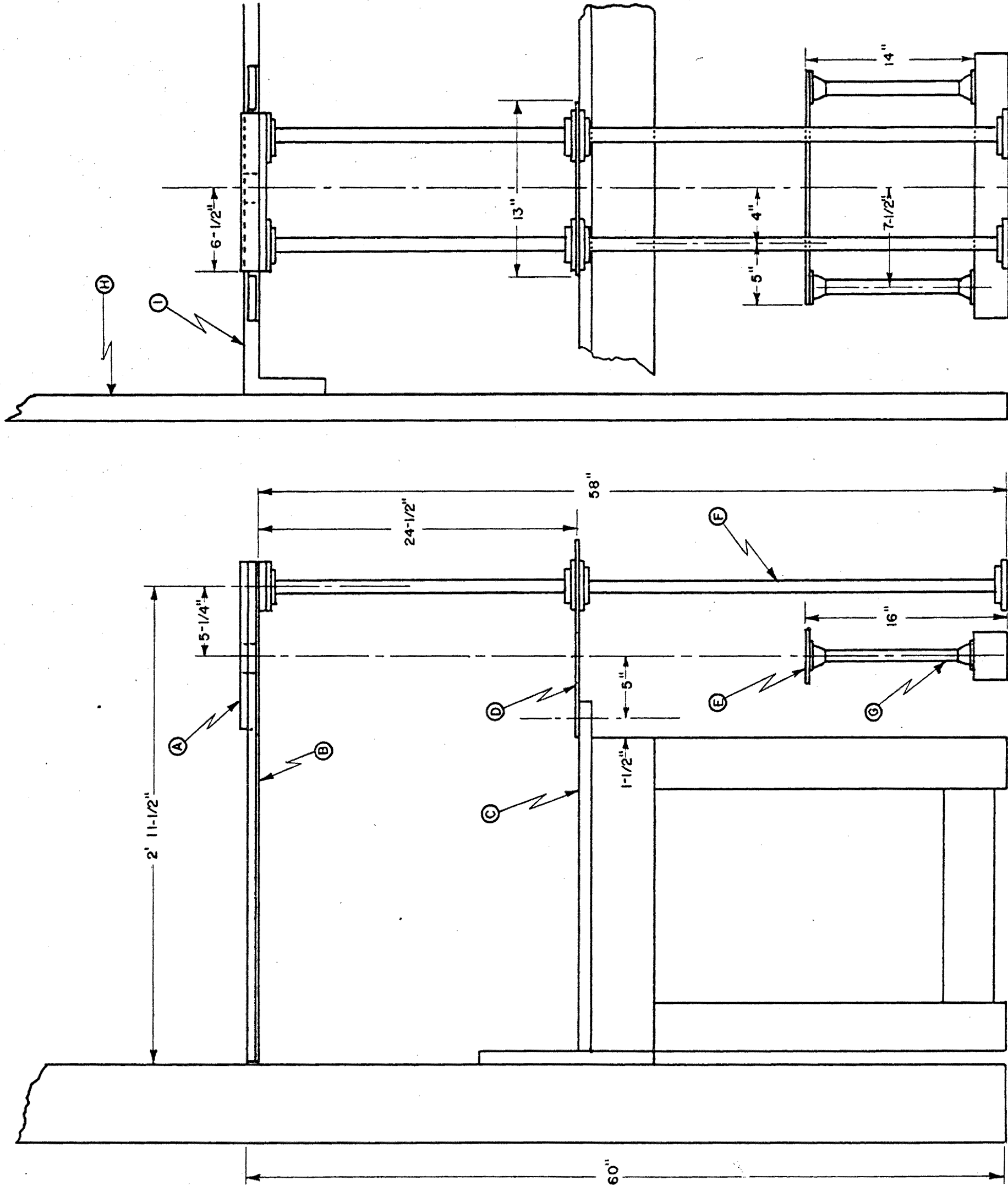
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VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VIRGINIA

BELLOWS TOP FLANGE
PULSE EXTRACTOR

SCALE : HALF SIZE DATE
DRAWN BY : *R.J.D.* 3/31/54
CHECKED BY : *R.J.D.* 3/31/54
APPROVED BY :

CASE NO. 54
FILE NO. 599
DRAWING NO. 5

Drawing 6 • Detail Drawing of Pulse Extractor
and Push Rod Frame



LEFT SIDE ELEVATION

FRONT ELEVATION

LEGEND

- (A) HORIZONTAL COLUMN SUPPORT
- (B) HORIZONTAL SUPPORT FRAME, 3/4 X 3/4 X 1/16 - IN. ANGLE IRON
- (C) TABLE
- (D) COLUMN BASE PLATE, 13 X 13 X 3/8 - IN. MILD STEEL
- (E) PUSH-ROD FRAME
- (F) COLUMN FRAME LEGS, 1/2 - IN. BLACK IRON PIPE
- (G) FRONT CAM-ASSEMBLY LEGS
- (H) GAS ABSORPTION TOWER SUPPORT
- (I) HORIZONTAL SUPPORT FRAME, 2 X 2 X 1/8 - IN. ANGLE IRON

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 BLACKSBURG, VIRGINIA

FRAME

PULSE EXTRACTOR

| | | | |
|--------------------------|--------|-------------|-----|
| SCALE: 1-1/2" = 1' | DATE | CASE NO. | 54 |
| DRAWN BY: B.J.J. | 4/1/54 | FILE NO. | 599 |
| CHECKED BY: B.J.J. | 4/1/54 | DRAWING NO. | 6 |
| APPROVED BY: [Signature] | | | |

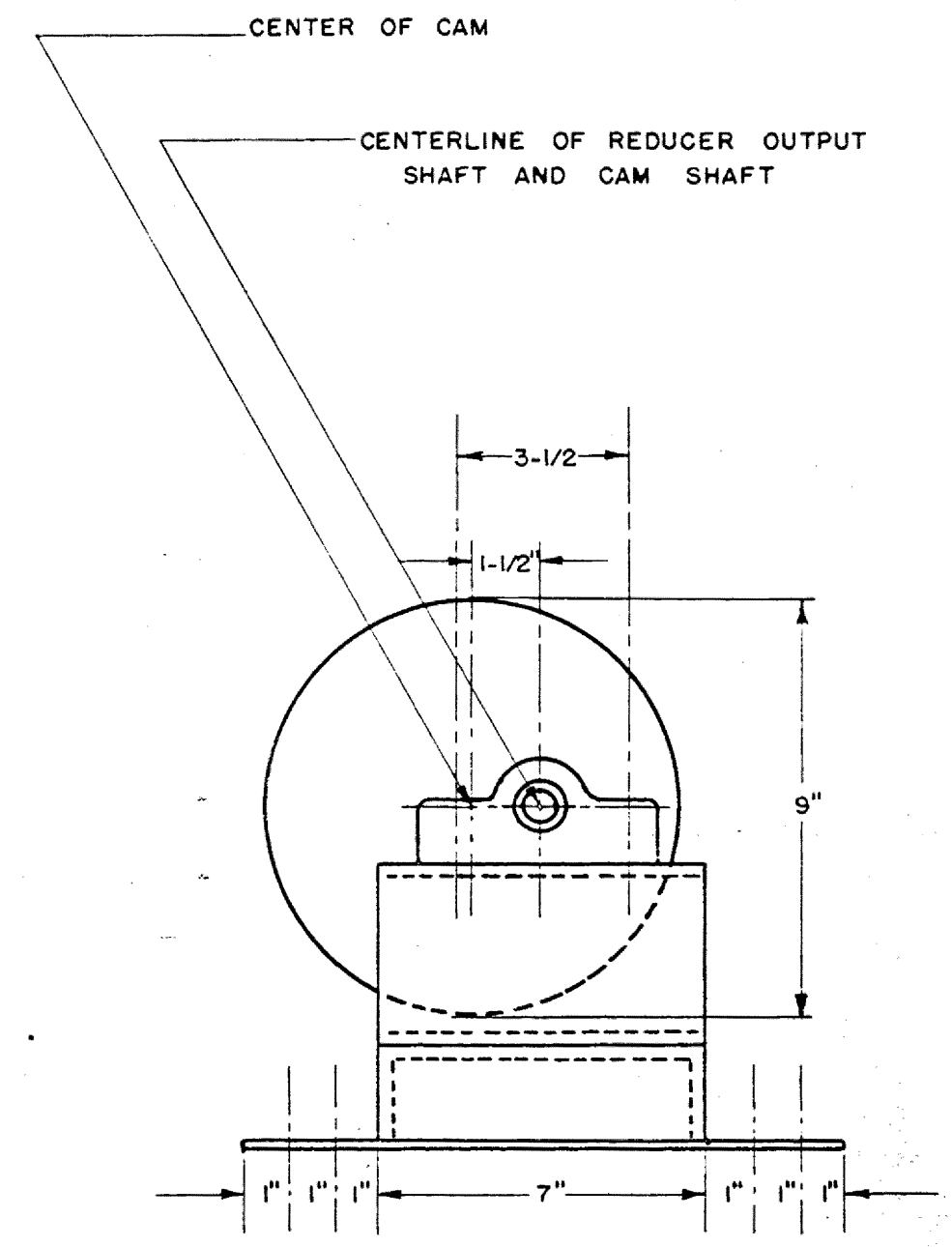
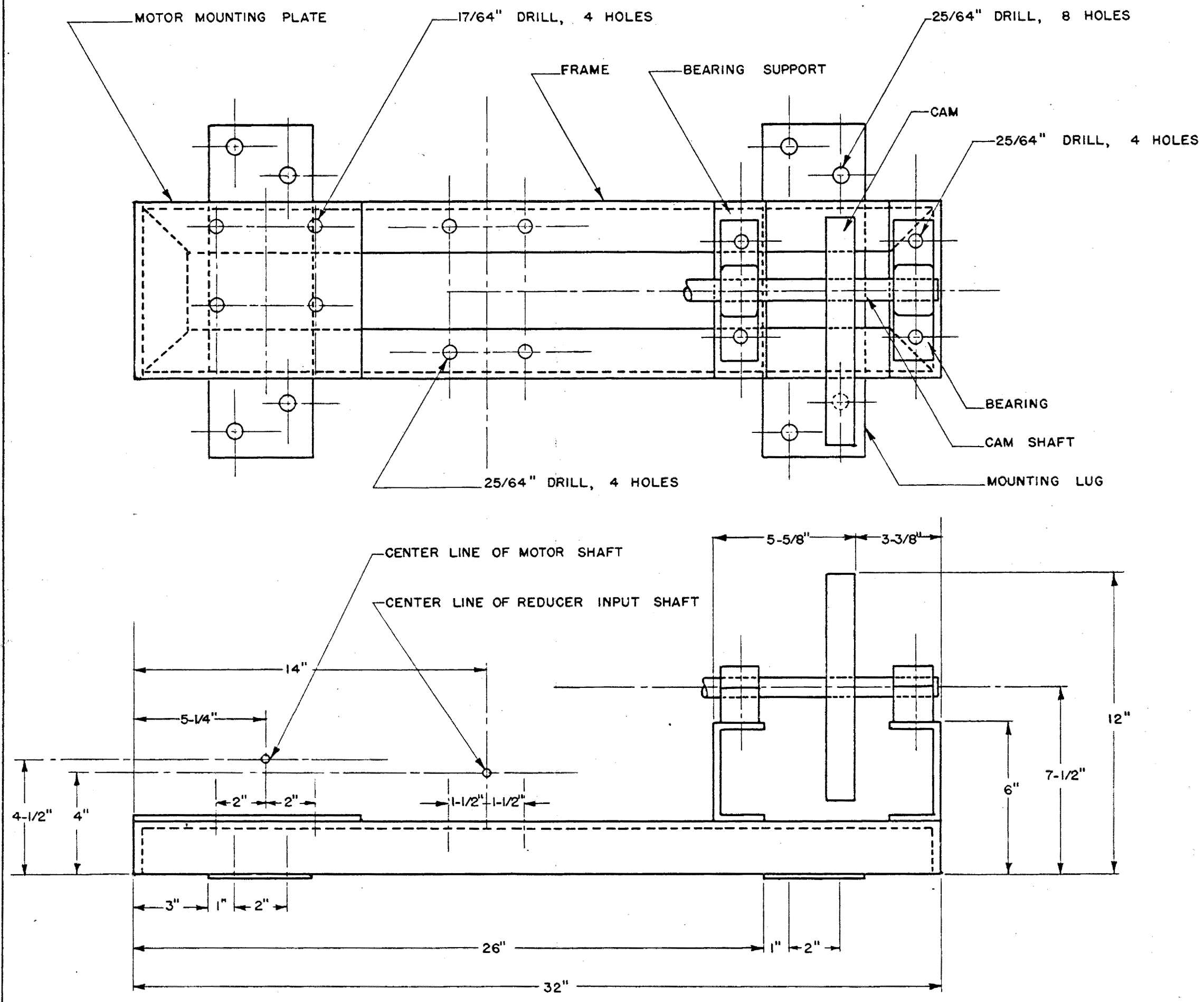
**Drawing 7. Detail Drawing of Pulse Extractor
Cam Assembly**

NOTES: FRAME OF WELDED CONSTRUCTION WITH MOTOR MOUNTING PLATE, MOUNTING LUGS, AND BEARING SUPPORT WELDED TO FRAME

PUSH ROD (SEE DRAWING 8 FOR DETAILS) MOUNTED ABOVE CAM-SHAFT CENTERLINE IN CENTER OF CAM.

CAM MADE FROM 3 PLATES. MACHINED AND DRILLED TO SPECIFICATIONS. PLATES FASTENED BY 8, 1/4" BOLTS IN A 7" CIRCLE.

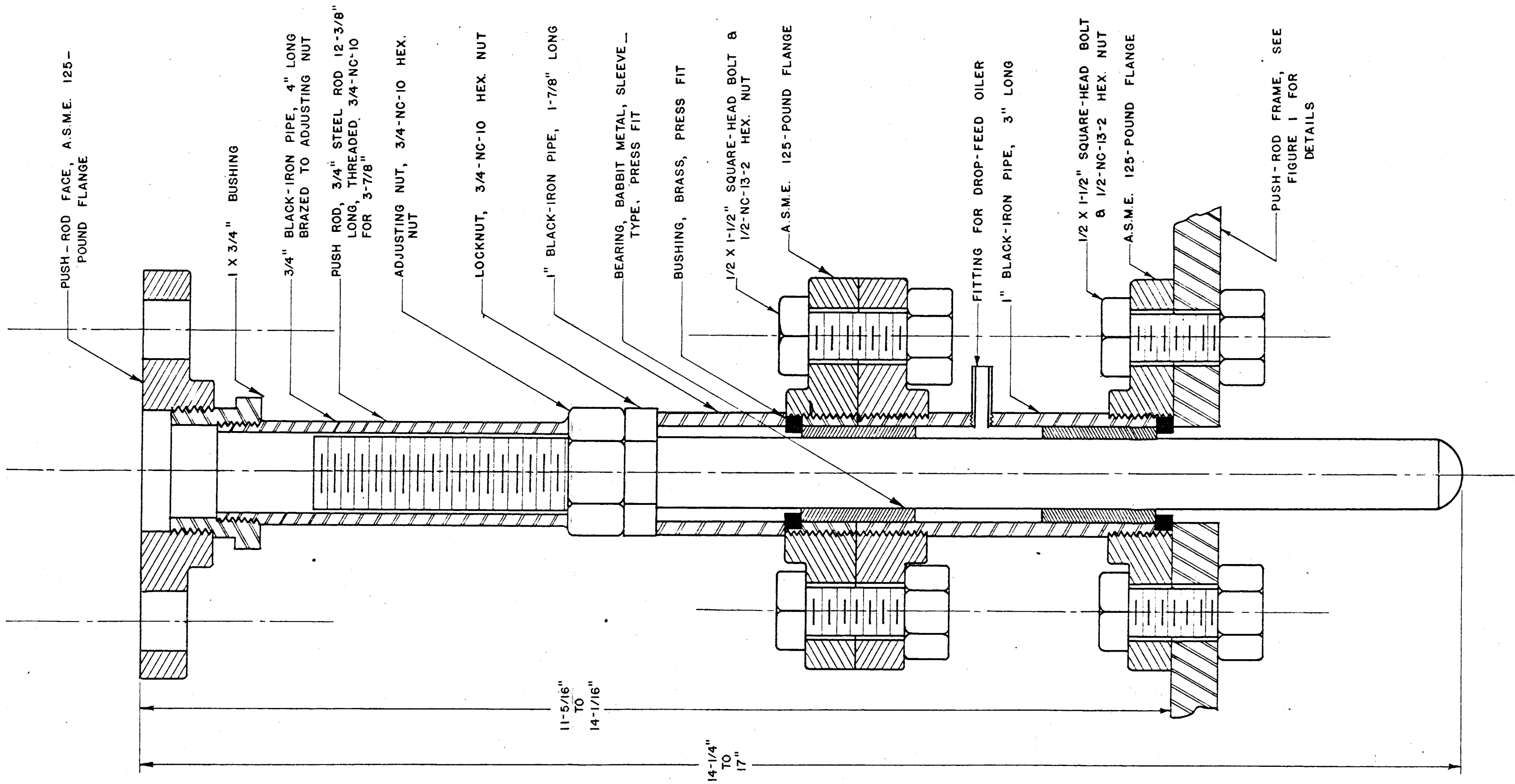
CAM BRAZED TO CAM SHAFT.



| PART | NUMBER REQUIRED | MATERIAL |
|----------------------|-----------------|----------------------------|
| CAM | 1 | 3/8" STEEL PLATE |
| CAM SHAFT | 1 | 3/4" STEEL ROD |
| BEARING | 2 | PURCHASED |
| BEARING SUPPORT | 2 | 4 X 2 X 1/4" STEEL CHANNEL |
| FRAME | 1 | 2 X 2 X 1/4" ANGLE IRON |
| MOUNTING LUG | 2 | 1/8" STEEL PLATE |
| MOTOR MOUNTING PLATE | 1 | 1/8" STEEL PLATE |

| | | | |
|--|--------|-------------|-----|
| DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA | | | |
| CAM ASSEMBLY PULSE EXTRACTOR | | | |
| SCALE: 3" = 1" | DATE | CASE NO. | 54 |
| DRAWN BY: <i>R.J.D.</i> | 4/2/54 | FILE NO. | 599 |
| CHECKED BY: <i>R.J.D.</i> | 4/2/54 | DRAWING NO. | 7 |
| APPROVED BY: <i>[Signature]</i> | 4/2/54 | | |

Drawing 8. Detail Drawing of Pulse Extractor
Push Rod Assembly



PUSH-ROD FACE, A.S.M.E. 125-
POUND FLANGE

1 X 3/4" BUSHING

3/4" BLACK-IRON PIPE, 4" LONG
BRAZED TO ADJUSTING NUT

PUSH ROD, 3/4" STEEL ROD 12-3/8"
LONG, THREADED 3/4-NC-10
FOR 3-7/8"

ADJUSTING NUT, 3/4-NC-10 HEX.
NUT

LOCKNUT, 3/4-NC-10 HEX. NUT

1" BLACK-IRON PIPE, 1-7/8" LONG

BEARING, BABBIT METAL, SLEEVE-
TYPE, PRESS FIT

BUSHING, BRASS, PRESS FIT

1/2 X 1-1/2" SQUARE-HEAD BOLT &
1/2-NC-13-2 HEX. NUT

A.S.M.E. 125-POUND FLANGE

FITTING FOR DROP-FEED OILER

1" BLACK-IRON PIPE, 3" LONG

1/2 X 1-1/2" SQUARE-HEAD BOLT
& 1/2-NC-13-2 HEX. NUT

A.S.M.E. 125-POUND FLANGE

PUSH-ROD FRAME, SEE
FIGURE 1 FOR
DETAILS

11-5/16"
TO
14-1/16"

14-1/4"
TO
17"

DEPARTMENT OF CHEMICAL ENGINEERING
VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VIRGINIA

PUSH ROD

PULSE EXTRACTOR

| | | | |
|--------------------|--------|-------------|-----|
| SCALE: FULL | DATE | CASE NO. | 54 |
| DRAWN BY: J.J.J. | 4/3/54 | FILE NO. | 599 |
| CHECKED BY: J.J.J. | 4/3/54 | DRAWING NO. | 8 |
| APPROVED BY: | | | |

Method of Procedure

The method of procedure followed in the performance of this investigation consisted of pulse column design and construction modifications, and operation of the extractor.

Design and Construction Modifications. Basically, the pulse liquid-liquid extractor used in this investigation was that designed and constructed by Hayford⁽⁴³⁾. However, for this experimentation, the author completely dismantled and thoroughly cleaned and repaired all of Hayford's equipment in preparation for the construction of a more permanent installation. In addition to rebuilding the original pulse column into a more permanent and longer-lasting installation, the author made several changes in the design features of the column in an attempt to arrive at a more effective piece of equipment from the standpoints of operation and safety. The changes made in Hayford's pulse column are briefly discussed in the paragraphs that follow.

Storage. Four ten-gallon (twelve by twenty-four inches) stainless steel tanks were substituted for the four five-gallon glass carboys in the original installation. This change was made primarily from the point of view of safety. The tanks installed were capable of

withstanding 500 pounds per square inch gage pressure, whereas the carboys originally used would burst under pressures exceeding ten pounds per square inch. In addition to preventing injuries to the operators from pieces of glass from an exploded carboy, this modification permitted the use of higher air pressures for the motivation of the feed and solvent, and thus, a smoother operation. The method in which the tanks were installed in the "set-up" can be seen in the schematic flow diagram of the apparatus shown in Drawing 9, page 91. The tanks were used in pairs; two containing the feed mixture of carbon tetrachloride and acetone, and two containing the solvent, water. The tanks, as ordered, came equipped with two one-quarter inch tapped holes, one each at the top and bottom of each tank. Flow lines were passed from the bottoms of the tanks to the pulse column. These lines conducted the feed mixture and solvent to the column. Into the tops of the tanks were affixed 5/16-inch, compression fitted, tubing tees with the tee-runs parallel to the laboratory table on which the tanks were supported. To one end of the tee-runs were connected the air lines used to pressurize the tanks during operation. To the other end of the tee-runs were connected the vacuum lines used to evacuate the tanks

during the storage-tank filling operation. The procedure used to fill the tanks will be explained in detail in the paragraph that follows.

"Vacuum-filling" System. To design an easier and more convenient method of filling the four storage tanks and to eliminate the necessity of drilling and tapping another hole in each tank, the "vacuum-filling" system shown in Drawing 9, page 91, was designed and constructed. A 3/8-inch copper tube was passed from a standard water-type aspirator through a 3/8-inch brass stopcock to each of the four storage tanks. With this arrangement any one or all of the four storage tanks could be evacuated in preparation to "drawing-up" the liquids to be stored in the tanks from the mixing containers. The step-by-step procedure by which the tanks were filled will be discussed in detail under the heading of "Preparation of Column for Operation."

Sight Glasses. Two sight glasses, one for the pair of feed storage tanks and one for the pair of solvent storage tanks, were built into the extraction system. Each sight glass was connected to its pair of tanks by a 1/2T by 1/2M brass, compression elbow, a piece of 5/16-inch copper tubing, and a 1/8-inch brass

compression valve. The sight glass was secured in the tubing end of the elbow by a rubber washer in place of the brass ferrule. When the elbow cap nut was tightened the washer was compressed in against the sight glass making a liquid-tight seal. A silver solder joint was then made between the 5/16-inch copper tubing and the male-connector end of the elbow. The 1/8-inch valve was silver soldered to the 5/16-inch copper tubing between the sight glass and the lines connecting the sight glass to its pair of storage tanks. The other ends of the two sight glasses were open to the atmosphere. For this reason the sight glasses could be used to measure the height of the liquids in the tanks only when the tanks were not pressurized or evacuated. However, since the flow rates for the feed and solvent were known and held constant, it was an easy matter to calculate just how long the column could be operated with twenty gallons of feed and solvent held in storage. Therefore, the sight glasses were used only in the storage filling operation to determine when the tanks were filled to capacity. This method of sight glass installation was employed, therefore, to eliminate the

task of building an individual sight glass on the side of each tank.

Tubing. The arrangement of copper tubing used in this investigation for liquid flow lines, air lines, and vacuum lines is shown schematically in Drawing 9, page 91. This flow arrangement is basically that used by Hayford⁽⁴³⁾. For convenience of operation and simplification of the installation several minor changes were made in the flow lay-out. The centrifugal pumps included in Hayford's original installation were omitted because they were found to be unnecessary; the air pressure in the storage tanks being sufficient as a motivating force for the feed and solvent. Before the copper tubing was used to connect the various parts of the extraction apparatus together, it was necessary to bring the water and air lines to the extractor site. Take-offs from both the air and the water lines were available near the extractor. A 3/4-inch water line was installed from the take-off point to the front left-hand edge of the table, closed by a globe valve, and connected to a standard water-type aspirator. This was to be used in connection with the "vacuum-filling" system for the storage tanks. A 1/2-inch air line was installed from the take-off point to the center of the table top. This line was connected to an air-reducing valve.

Beyond this valve the line was divided on the back of the control panel into four separate air lines, one for each of the four storage tanks. Each individual line was closed with a globe valve. On the equipment side of these globe valves, each line was equipped with a pressure gage and an air vent.

Copper tubing and brass fittings were used to connect all of the pieces of equipment in the extraction installation. The arrangement of the tubing is shown in Drawing 9, page 91. All of the connections between the copper tubing and the brass fittings were made with silver solder joints. This method of making all connections was employed to make a more permanent installation and to prevent those leaks that normally develop with use when compression fitting connections are used.

Method of Securing Top Plate of Column. Since the flared end at the top of the glass pipe used as the extraction column must be cut off in order that the baffle plates can be inserted in the column, a special method must be devised to secure the top flange to the column. Hayford⁽⁴³⁾ accomplished this by wrapping the top of the column with several turns of friction tape to improvise a flared end, and then connecting the top flange to the column with a

standard Corning triangular flange. However, this method was proved to be ineffective because of leaks around the top flange. For this investigation the method of securing the top plate of the column shown in Drawing 1, page 66, was designed. Briefly, a 1/4-inch flat-head stove bolt, three inches long, was welded to each end of three 48-inch sections of 1/8-inch black iron pipe. These rods were placed at the vertices of an equilateral triangle around the column and parallel to the vertical axis of the column. In other words, they were placed in such a manner that the stove bolts at the bottom end of the rods would fit in the holes of the standard Corning triangular flanges used to hold the bottom of the column to the pyrex tee. By using two hex-head nuts on each of the three stove bolts (one above the column flange and one below the tee flange) the two flanges used to hold the bottom of the column and tee together could be tightened together on the gasket between them thus making a liquid-tight seal. The top gasket and top plate of the column were then fitted down over the three stove bolts welded to the top of the three rods. On top of the top plate and also down over the three stove bolts was placed a standard Corning triangular flange. This flange was used to more evenly distribute the force over the top

flange or plate when the top plate was tightened down on the top of the column. By using a hex-head nut on each of the three stove bolts the triangular flange, top plate, and top gasket were tightened down on top of the column thus making a liquid-tight seal at this point. The necessary force could be applied in making this seal by this method as the majority of the stress would be in longitudinal compression of the column where the column is capable of taking the most stress.

Baffle Plates. A detail drawing of the baffle plates is shown in Drawing 4, page 70. Thirty-six baffle plates were designed for this investigation. The blanks for the baffle plates were made by cutting thirty-six 1/8-inch slices from a two-inch diameter soft iron rod. All holes drilled in the thirty-six plates were 3/16-inch in diameter with the exception of one 1/4-inch hole in the center of each plate, which was used for the supporting rod and spacers. The first twelve plates were drilled with 144 holes which constituted a plate-free-area of thirty-two per cent. The second twelve plates were drilled with seventy-two holes which constituted a plate-free-area of sixteen per cent. The last twelve plates were drilled with thirty-six holes which constituted a plate-free-area

of eight per cent. All holes were drilled at the vertices of equilateral triangles. The sides of the equilateral triangles were $1/8$ -inch, $3/16$ -inch, and $1/4$ -inch for the thirty-two per cent, sixteen per cent, and eight per cent plate-free-areas, respectively. For each of the three individual plate-free-areas a drilling die was constructed from $2\ 1/4$ -inch slice of a $2\ 1/4$ -inch diameter soft iron rod. The drilling die or guide was constructed by laying out on the die blank a two-inch diameter circle and the desired equilateral triangular arrangement. The vertices of the triangles were center-punched and drilled with $3/16$ -inch holes. The area enclosed within the two-inch diameter circle on the face of the die was then cut out to a depth of $1/8$ -inch on a lathe. A $1/4$ -inch hole was drilled in the center of each of the three drilling dies. When drilling a baffle plate the following procedure was employed. A $1/4$ -inch hole was drilled in the center of a baffle plate blank. The baffle plate blank was fitted down into the depression in the face of the die. The plate blank and the die were bolted together with a $1/4$ -inch bolt and nut. This assembly was placed under the drill press with the drilling die facing up. The desired number of holes could then be drilled in the

baffle plate with the drilling die being used as a drill guide to insure that the bit did not slip out of line.

Baffle Plate Support. The baffle plates were supported in the column by a 1/8-inch brazing rod extending up through the center of the column along its axis and plate spacers constructed from sections of 3/8-inch copper tubing. The bottom of the brass rod was threaded to a length of 1/4-inch with standard machine threads. A hex-head nut was screwed up tight on the end of the rod to act as a stop. The desired number of plates and spacers were slipped alternately down over the brass rod. Three sets of copper-tubing spacers were constructed so that regardless of whether four, eight, or twelve plates were used for a test the plates used would be equally spaced up through the column. As a result, four 0.875 foot spacers, eight 0.438 foot spacers, and twelve 0.300 foot spacers were constructed from 3/8-inch copper tubing. After the last spacer had been slipped on the brass rod a 1/4-inch hex-head nut which had one of its faces drilled and tapped, and equipped with a set screw, was slipped on the brass rod and down on top of the last spacer. By tightening the set-screw down against

the brass rod the baffle plates could be secured in position so that they could not slip up and down on the center rod.

Baffle Plate Insertion. The plates, assembled on the rod, were inserted into the column. Because of the flare near the bottom of the pyrex column, on the inside of the pipe, the plates could not pass all of the way through the column. As a result, the bottom plate could not be installed lower than three inches above the bottom of the pyrex pipe. At this point the diameter of the column was too small to allow further insertion of the plates, and therefore, it acted as a support for the string of plates.

Before the column top plate was fastened into place, the top of the brass rod that held the baffle plates in place was cut off flush with the top of the top gasket. It was necessary that this rod be the correct length to prevent any movement of the plates during the pulsation operation. If the rod were too long, a tight seal at the top of the column could not be obtained.

Column. In the original installation the pyrex pipe used as the extraction column was constructed by cutting off the flared end at the top of a standard 48-inch length of pipe. As was pointed out previously, the removal of the flared end at the top of the pipe was necessary to allow insertion of the baffle plates. However, in this investigation, a 48-inch length of pyrex pipe was ordered with only one flared end. This made it possible to have a full 48-inch extraction column. In addition, the top edge of the column was much smoother than the top edge of the column which had been cut off. The smooth top edge gave more assurance of a tight liquid seal at the top plate.

Gaskets. For this investigation teflon was used for the gasket material between the bellows, tee, and column flanges. It was found that the silicone and cork gaskets employed in the original installation would not withstand the highly corrosive action of the aqueous feed mixture of carbon tetrachloride and acetone.

Push-rod Bearings. In the original installation⁽⁴³⁾ the push-rod bearing surface consisted of two ball bearing races supported at either end of a four-inch length of one-inch pipe by an arrangement of one-inch A.S.M.E. 125-pound pipe flanges. These ball bearing races proved to be

ineffective in absorbing the thrust force of the cam, and as a result, the push-rod was badly scored. To rectify this condition, babbitt sleeves were substituted for the ball bearing races. A babbitt sleeve was press-fitted into each end of the pipe-flange arrangement originally used. Each sleeve was 1-1/2 inches in length and had a one-inch outside diameter and a 3/4-inch inside diameter.

Lubrication. It was found necessary to use special lubricants on the push-rod bearing assembly and the cam assembly. The lubricants employed are discussed in the paragraphs that follow.

Push-rod Bearing Lubrication. The grease cup that was used in connection with the lubrication of the push-rod bearing assembly in the original installation was removed, and a drop-feed oiler was installed in its place. The oiler was filled with and the push-rod bearings were lubricated with purified, colorless, medium weight castor oil.

Cam Assembly Lubrication. Ordinary chassis grease proved to be ineffective in alleviating the frictional resistance of the push-rod rubbing against the cam. To rectify this condition, a "tacky" mixture of standard weight machine oil and purified

greaseless graphite was employed as a lubricant. The graphite built up a lubricating layer on the surfaces of both the push rod and the cam.

Protective Coating. Because of the highly corrosive action of the aqueous feed mixture of carbon tetrachloride and acetone on metal, it was found necessary to provide a protective finish for all of those metal parts of the extractor which came into direct contact with the system. The protective finish used consisted of one coat of phenoline 301 orange primer and one coat of phenoline 300 finish. These materials are phenolic resins obtained in the form of paint from Carboline Corporation in St. Louis, Missouri.

Operating Procedure. The procedure followed in the performance of the experimental tests of this investigation will be discussed under the headings of analytical procedure, preparation of the column for operation, operation of the column, and experimental tests.

Analytical Procedure. For this investigation it was necessary to determine for each experimental test made the concentration of acetone present in the feed mixture entering the column and the raffinate and extract streams leaving the column. Since there were data available in the

literature⁽⁴³⁾ showing the relationship between the refractive indices and the concentration of acetone in the respective phases for the system carbon tetrachloride-acetone-water it was necessary only to make refractive-index measurements of the respective flow streams according to standard techniques⁽⁷⁾. These measurements were made at a temperature of 67 ± 1 °F using an Abbé refractometer.

Preparation of the Column for Operation. The preparation of the column for operation involved several steps. These steps consisted of the preparation of the feed, the filling of the feed and solvent storage tanks, the adjustment of the pulse amplitude, the establishment of the plate-free-area and the number of plates or plate spacing, and the starting and filling of the extractor. All references to equipment and valves in the procedure that follows will refer to Drawing 9, page 91.

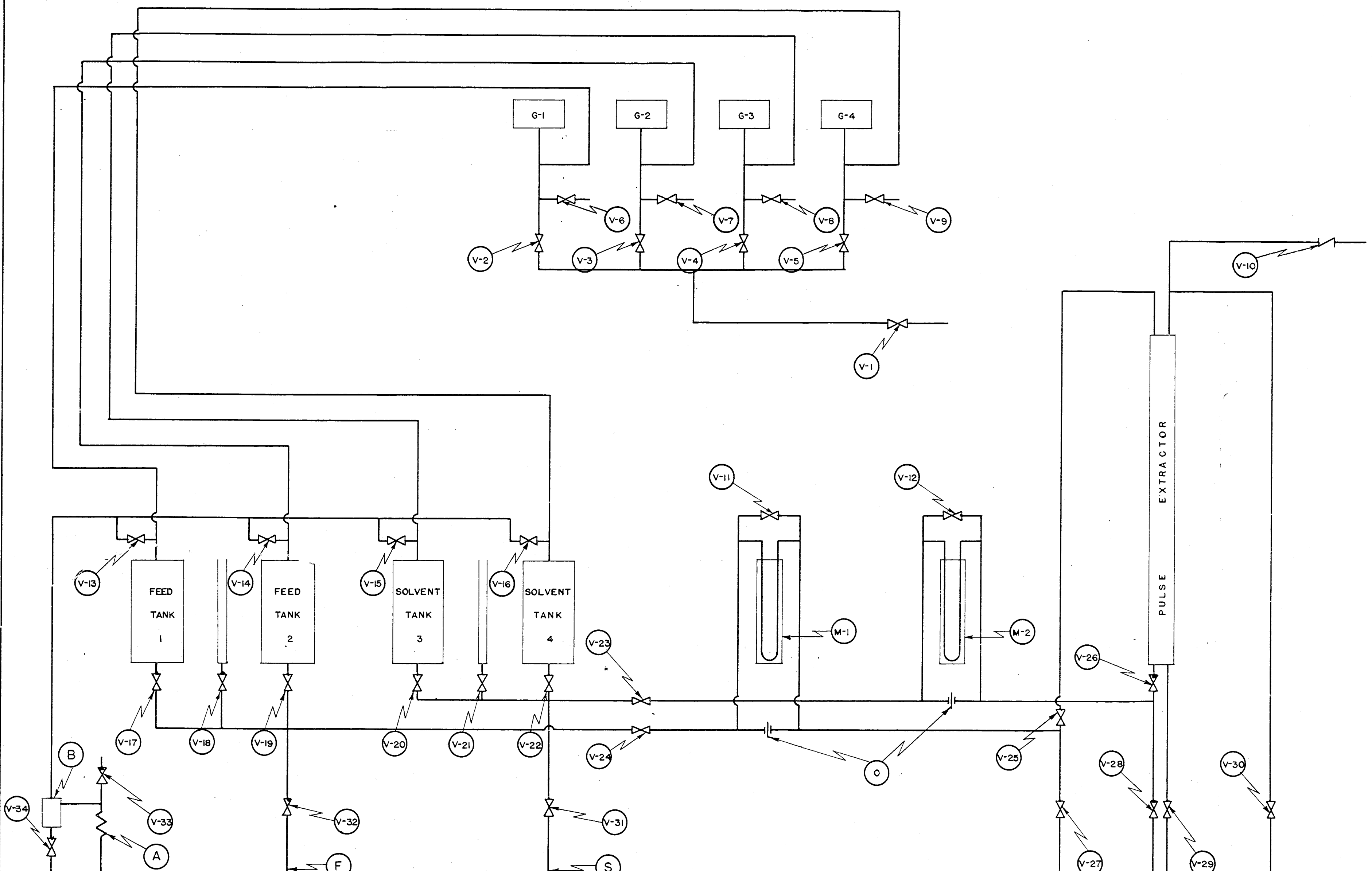
Preparation of Feed. During the experimental tests, a feed consisting of approximately ten weight per cent acetone in carbon tetrachloride was used. Initially, 250 pounds, or approximately twenty gallons, of this feed mixture were prepared. The 250 pounds of feed mixture were arrived at by mixing together, in a tub, 225 pounds of carbon tetrachloride and twenty-five

pounds of acetone. A high-speed propeller-type mixer was used to agitate the feed. A mixing period of approximately 20 minutes was employed for this operation. The feed mixture, as prepared, was stored in the pair of feed tanks for use in the experimental tests. The method by which the feed was placed in the storage tanks will be discussed in detail under the heading of filling the feed and solvent storage tanks. During the experimental tests make-up feed was prepared by adding enough acetone to the raffinate collected from the extractor to replenish its acetone concentration to ten weight per cent. Because of the absence of continuous agitation during the experimental tests, and because of the evaporation of acetone, the acetone concentration in the feed varied between eight and twelve per cent from test to test. However, the feed composition was determined for each individual experimental test made.

Filling of the Feed and Solvent Storage Tanks.

All references to equipment and valves in the discussion that follows will refer to Drawing 9, page 91. When filling the feed and solvent storage in preparation for an experimental test, the first step was to

Drawing 9. Schematic Flow Diagram for Pulse
Extractor



LEGEND

- A__ASPIRATOR
- B__VACUUM RECEIVER
- F__FEED INLET
- G-1__PRESSURE GAGE, TANK 1
- G-2__PRESSURE GAGE, TANK 2
- G-3__PRESSURE GAGE, TANK 3
- G-4__PRESSURE GAGE, TANK 4
- M-1__FEED MANOMETER
- M-2__SOLVENT MANOMETER
- O__ORIFICE
- S__SOLVENT INLET

- V-1__MAIN AIR VALVE
- V-2__AIR VALVE, TANK 1
- V-3__AIR VALVE, TANK 2
- V-4__AIR VALVE, TANK 3
- V-5__AIR VALVE, TANK 4
- V-6__VENT VALVE, TANK 1
- V-7__VENT VALVE, TANK 2
- V-8__VENT VALVE, TANK 3
- V-9__VENT VALVE, TANK 4
- V-10__COLUMN VENT VALVE
- V-11__BYPASS VALVE, M-1

- V-12__BYPASS VALVE, M-2
- V-13__VACUUM VALVE, TANK 1
- V-14__VACUUM VALVE, TANK 2
- V-15__VACUUM VALVE, TANK 3
- V-16__VACUUM VALVE, TANK 4
- V-17__FEED VALVE, TANK 1
- V-18__FEED SIGHT GLASS VALVE
- V-19__FEED VALVE, TANK 2
- V-20__SOLVENT VALVE, TANK 3
- V-21__SOLVENT SIGHT GLASS VALVE
- V-22__SOLVENT VALVE, TANK 4

- V-23__FEED CONTROL VALVE
- V-24__SOLVENT CONTROL VALVE
- V-25__COLUMN FEED VALVE
- V-26__COLUMN SOLVENT VALVE
- V-27__FEED DRAIN VALVE
- V-28__SOLVENT DRAIN VALVE
- V-29__RAFFINATE VALVE
- V-30__EXTRACT VALVE
- V-31__SOLVENT INLET VALVE
- V-32__FEED INLET VALVE
- V-33__WATER VALVE

- V-34__VACUUM RECEIVER VENT VALVE

| | | | |
|--|--------|-------------|-----|
| DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA | | | |
| SCHEMATIC FLOW DIAGRAM PULSE EXTRACTOR | | | |
| SCALE: NONE | DATE | CASE NO. | 54 |
| DRAWN BY: <i>F.J.L.</i> | 4/4/54 | FILE NO. | 599 |
| CHECKED BY: <i>F.J.L.</i> | 4/4/54 | DRAWING NO. | 9 |
| APPROVED BY: <i>HWB</i> | 4/5/54 | | |

close all valves, V-1 through V-34. To fill the feed and solvent storage tanks an absolute pressure corresponding to 1.5 inches of mercury was maintained in tanks T-1, T-2, T-3, and T-4 by the aspirator, A. To accomplish this valves V-33, V-13, V-14, V-15, and V-16 were opened. When an absolute pressure of 1.5 inches of mercury was registered on gages G-1, G-2, G-3, and G-4, valves V-17, V-19, V-20, and V-22 were opened. The feed inlet, F, was placed into the tube containing the twenty gallons of feed mixture, and the solvent inlet, S, was placed into the tub containing the twenty gallons of water. Valves V-32 and V-31 were opened allowing the feed and the solvent to be drawn up into the two feed tanks and the two solvent tanks, respectively. After the feed and solvent had been drawn up into their respective storage tanks, valves V-32, V-31, V-17, V-19, V-20, V-22, V-13, V-14, V-15, V-16, and V-33 were closed. At this point valves V-6, V-7, V-8, V-9, and V-34 were opened releasing the vacuum in tanks T-1, T-2, T-3, and T-4. All valves in the system, V-1 through V-34, were again closed, and the column was made ready for operation.

Adjustment of the Pulse Amplitude. It will be noted here that the pulse frequency employed for all of the experimental tests performed in this investigation was held constant at 10.5 cycles per minute.

The pulse amplitude was adjusted by turning the push-rod face relative to the remainder of the push rod. Before adjusting the pulse amplitude, however, it was necessary to fill the column to within eight inches of the top plate with the solvent, water, so as to be able to make a measurement of the amplitude. The pulse amplitude was defined as the distance that the liquid level moved up and down the column itself.

To fill the column with solvent, valves V-1, V-4, and V-5 were opened allowing tanks T-3 and T-4 to be pressurized with air from the air compressor. When the pressure in tanks T-3 and T-4 had attained forty pounds per square inch gage as indicated by gages G-3 and G-4, valves V-20, V-22, V-23, and V-26 were opened allowing water to pass into the column. When the correct liquid level in the column had been reached, valves V-26, V-23, V-22, V-20, V-4, and V-5 were closed, and the tanks T-3 and T-4 were vented to the atmosphere by opening valves V-8 and V-9. When the pressure in the two tanks had

been released, valves V-8 and V-9 were again closed. The cam assembly motor was started to cause a pulsation in the column. The pulse amplitude was adjusted by turning the push-rod face relative to the remainder of the push rod. When the desired pulse amplitude was obtained, the push-rod length was fixed by tightening the lock nut. At this point all of the valves in the system were closed and the extractor was ready for operation.

Establishment of the Plate-Free-Area and Plate Spacing. For each of the twenty-seven individual experimental tests the desired number of baffle plates with the desired plate-free-area were selected, secured on the column center rod, and inserted in the column. The method by which these operations were accomplished has been previously discussed.

Starting Column Operation. After the above operations had been performed, the pulse extractor was ready for operation. The first step in putting the extractor into operation was to start the cam assembly motor. It is assumed here that the column is still full of water from the pulse amplitude adjusting operation, and that all of the valves in the system are closed. Next,

valves V-1, V-2, V-3, V-4, and V-5 were opened allowing the storage tanks T-1, T-2, T-3, and T-4 to become pressurized with air from the air compressor. When the pressure in the storage tanks attained forty pounds per square inch, gage as indicated on the gages G-1, G-2, G-3, and G-4, the column was ready for operation. At this point valves V-17, V-19, V-20, and V-22 were completely opened. Valves V-25, V-26, and V-30 were also completely opened. Valve V-24 was partially opened and adjusted so that a differential of two inches of mercury could be read on manometer M-1. Valve V-23 was partially opened and adjusted so that a differential of three inches of mercury could be read on manometer M-2. After the column had been in operation for approximately ten minutes the heavy phase collected in the lower disengaging section and filled up the bellows until its top level could be seen in the pyrex tee. At this point valve V-29 was partially opened and adjusted until the top level of the heavy phase or lower interface was held constant at the top edge of the base flange of the tee. The feed and solvent flow rates were held constant by observing manometers M-1 and M-2 and by adjusting valves V-24 and V-23.

The lower interface was held constant by observing its level and by adjusting valve V-29. The extract flow rate valve, V-30, was left completely open. The extract and raffinate streams were collected in five-gallon pails during the entire operation. The feed and solvent flow rates (two inches of mercury on M-1 and three inches of mercury on M-2, respectively) were determined by preliminary operation and observation of the column. The extractor was set into operation as previously described, and the feed and solvent flow rates were varied until optimum extractor operation was obtained; namely, until there was no evidence of dumping, coning, blowing, heavy-phase flooding, light-phase flooding, entrainment, etc. The existing feed and solvent flow rates used under these conditions were observed and recorded. The flow rates were held constant and used for all of the subsequent twenty-seven individual experimental tests. The extractor was then ready for the attainment of steady state conditions and the recording of data.

Operation of Column. It was found that no special operational technique was required to operate the pulse extractor. Any adjustments in the heavy-phase flow rate were made by adjusting valve V-24. Any adjustments in the light-phase flow rate were made by adjusting valve V-23. The interface in the top disengaging section was fixed by the conditions of operation. However, the interface in the lower disengaging section had to be maintained at a constant level by adjusting valve V-29. The feed and solvent flow rates were found to be slightly sensitive to fluctuations in the air pressure. For this reason the manometers M-1 and M-2 had to be adjusted frequently. Both flow rates were, of course, affected by an appreciable rate of change of the interface. After steady state conditions were reached, the column required very little attention.

Experimental Tests. Three important aspects of the experimental testing procedure will be dealt with in this section. The three aspects are the determination of steady state conditions, the procedure followed in the efficiency tests, and the procedure followed in determining the feed, solvent, raffinate, and extract flow rates.

Steady State Conditions. For the purpose of this investigation "steady state condition" was defined as that condition obtained within the extractor, when for successive ten-minute readings, commencing not before two complete liquid changes in the extractor, there was no change in the acetone concentration in either the extract or raffinate stream. By no change the author means that for any of the last four readings there was no greater variation than three units in the fourth place after the decimal of the refractive index measurement, corresponding to 0.2 per cent acetone by weight. It was found that two liquid changes occurred in the column after approximately ten minutes of operation. Therefore, the first reading was not made until the column had been in operation for at least ten minutes. The system used in this investigation was so easy to extract that it was found that generally the first four readings after the first reading indicated steady state conditions.

Efficiency Testing Procedure. While the extractor operated at steady state conditions several readings and observations were made from which the efficiency of the

pulse column could be calculated. Samples of the feed, raffinate, and extract were collected in sample bottles through valves V-32, V-29, and V-30, respectively. All operating features of the extractor that could be observed were noted and recorded. This included all operating features, such as flooding, dumping, coning, blowing, entrainment, etc., that could be observed within the column itself and any unusual changes in the operation of the extractor that might affect its efficiency.

Flow Rate Determination. While the extractor was operating at steady state conditions the extract and raffinate flow rates were determined. Extractor operation was suspended while the feed and solvent flow rates were determined. A tared one-gallon jug was used to collect and contain the material of all four flow streams, one at a time, during the collection period of the flow rate determination procedure. A collection period of five minutes was employed for all flow rate determinations. At the end of the collection period the contents of the one-gallon jug were weighed and recorded as grams collected per five minutes. To determine the extract flow rate the jug was placed

under valve V-30. To determine the raffinate flow rate the jug was placed under valve V-29. To determine the solvent flow rate valve V-26 was completely closed, and valve V-28 was completely opened. The jug was placed under valve V-28, and the differential reading on manometer M-2 was maintained at three inches of mercury. To determine the feed flow rate valve V-25 was completely closed, and valve V-27 was completely opened. The jug was placed under valve V-27, and the differential reading on manometer M-1 was maintained at two inches of mercury.

Completion of Tests. As soon as a series of tests were completed the column and storage tanks were drained and cleaned. To stop the feed and solvent from flowing into the extractor valves V-23 and V-24 were completely closed. The cam motor was kept running until all of the heavy phase was worked down into the bottom of the column. After this, the cam was stopped. The above was followed assuming that after the feed and solvent flow rate determinations valves V-27 and V-28 were closed and valves V-25 and V-26 were opened. Next, valve V-29 was opened and the column was drained. Then valve V-29 was closed and valve V-23 was

opened, and the column was filled with water. The water was allowed to overflow through the column and valve V-30 until it became clear. Valves V-30 and V-23 were closed and valve V-29 was opened so that the column could again drain. Valves V-29, V-25, V-26, V-17, V-19, V-20, V-22, V-1, V-2, V-3, V-4, and V-5 were closed. Valves V-6, V-7, V-8, and V-9 were opened, and the pressure in tanks T-1, T-2, T-3, and T-4 was released. Valves V-6, V-7, V-8, and V-9 were closed. Valves V-17, V-19, V-20, V-22, V-32, and V-31 were then opened and the four storage tanks were drained. Finally, all of the valves in the system, V-1 through V-34, with the exception of valve V-33, were opened and the flow lines were drained. The surrounding area was cleaned, and the equipment was inspected.

Data and Results

The data and results obtained from this investigation are presented in the following section.

Refractive-index Data. The refractive-index data obtained by Hayford⁽⁴³⁾ are presented in Table VI, page 106. These data present the refractive index measurements obtained for various amounts of acetone present in both the carbon tetrachloride phase saturated with water and the water phase saturated with carbon tetrachloride. In Figure 3, page 107, the relation between the concentration of acetone in and the refractive index measurement of the two saturated phases is shown. Figure 3 was employed in this investigation to determine the amount of acetone present in the streams entering and leaving the pulse column for each test from refractive index measurements of samples of each of the streams.

Distribution Data. The distribution data obtained by Hayford⁽⁴³⁾ are presented in Table VI, page 106. These data show the concentrations of acetone present in the carbon tetrachloride phase saturated with water and the water phase saturated with carbon tetrachloride at a state of equilibrium. In Figure 4, page 108, the experimentally determined distribution data are graphically presented. These data are similar

to and should be compared with the data presented in Figure 2, page 26. Figure 4, page 108, was employed in this investigation to establish the tie lines and conjugate line on the triangular plots which were used to graphically determine the theoretical number of transfer stages.

Pulse-extractor Operating Data. In Table VII, page 109, the operational data for the pulse extractor are presented. These data include the refractive-index measurements and corresponding acetone concentrations for the streams entering and leaving the pulse column during each of the twenty-seven individual experimental tests. Included in this table, also, are the operational parameters that were studied. These parameters are the pulse amplitude, number of baffle plates, and plate-free-area. At the bottom of this table are reported the operational constants; namely, the operating temperature, the feed, solvent, raffinate, and extract flow rates, and the pulse frequency.

Transfer Stages. In Table VII, page 109, are presented the number of theoretical transfer stages required to perform the extraction in each of the twenty-seven individual tests. The number of theoretical transfer stages here reported were calculated by graphical methods employing the Elgin triangular plot method.

Stage Efficiencies. The stage efficiencies for the pulse column as operated under each of the twenty-seven individual sets of operating conditions are presented in Table VII, page 109.

Operational Parameter Trends. The effects of pulse amplitude, number of plates, and plate-free-area on the stage efficiency of the pulse column are presented graphically in Figure 5, page 110, Figure 6, page 111, and Figure 7, page 112, respectively. Each of the three figures presents nine curves indicating the effects of one of the three variables mentioned above under each of the nine individual sets of operating conditions employed in this investigation.

Analysis of Variance. The results of the analysis-of-variance test are presented in Table VIII, page 113. This particular method of presentation is that suggested by Dixon and Massey⁽⁹⁶⁾.

Comparison of Statistics. In Table IX, page 114, is presented a comparison of the calculated and tabled or standard values of the "F" statistic for the pulse amplitude, number of plates, plate-free-area, and all second order combinations thereof. According to Dixon and Massey⁽⁹⁶⁾, if the calculated value of the "F" statistic is greater than the tabled or standard value of the "F" statistic the effect

of the variable being considered is significant. The tabled values of the "F" statistic employed in this investigation were selected at the ninety-five per cent level of significance.

TABLE VI

Distribution and Refractive-index Data for the System
Carbon Tetrachloride-Acetone-Water at 22 °C

| Carbon Tetrachloride Phase | | | Water Phase | | |
|----------------------------|---------------------|---------------------|--------------------------|---------------------|---------------------|
| Acetone Concentration | Specific Gravity | Refractive Index | Acetone Concentration | Specific Gravity | Refractive Index |
| wt % | 30°/4 °C | n_D^{20} | wt % | 30°/4 °C | n_D^{20} |
| 0.00 ^a | 1.5768 | 1.4628 | 0.00 ^a | 0.9946 | 1.3320 |
| 0.00 ^b | 1.5764 | 1.4594 | 0.00 ^b | 0.9952 | 1.3330 |
| 0.49 | 1.5698 | 1.4588 | 2.87 | 0.9913 | 1.3341 |
| 1.73 | 1.5513 | 1.4568 | 5.98 | 0.9872 | 1.3365 |
| 2.38 | 1.5418 | 1.4558 | 8.14 | 0.9844 | 1.3376 |
| 5.53 | 1.4947 | 1.4503 | 14.83 | 0.9758 | 1.3419 |
| 8.68 | 1.4480 | 1.4446 | 17.79 | 0.9709 | 1.3449 |
| 12.81 | 1.3966 | 1.4377 | 21.93 | 0.9643 | 1.3479 |
| 17.39 | 1.3419 | 1.4302 | 26.88 | 0.9566 | 1.3508 |

a. Analysis of original component.

b. Analysis of original component saturated with other phase.

Figure 3. Refractive Index of Equilibrium
Solutions for the System Carbon
Tetrachloride-Acetone-Water

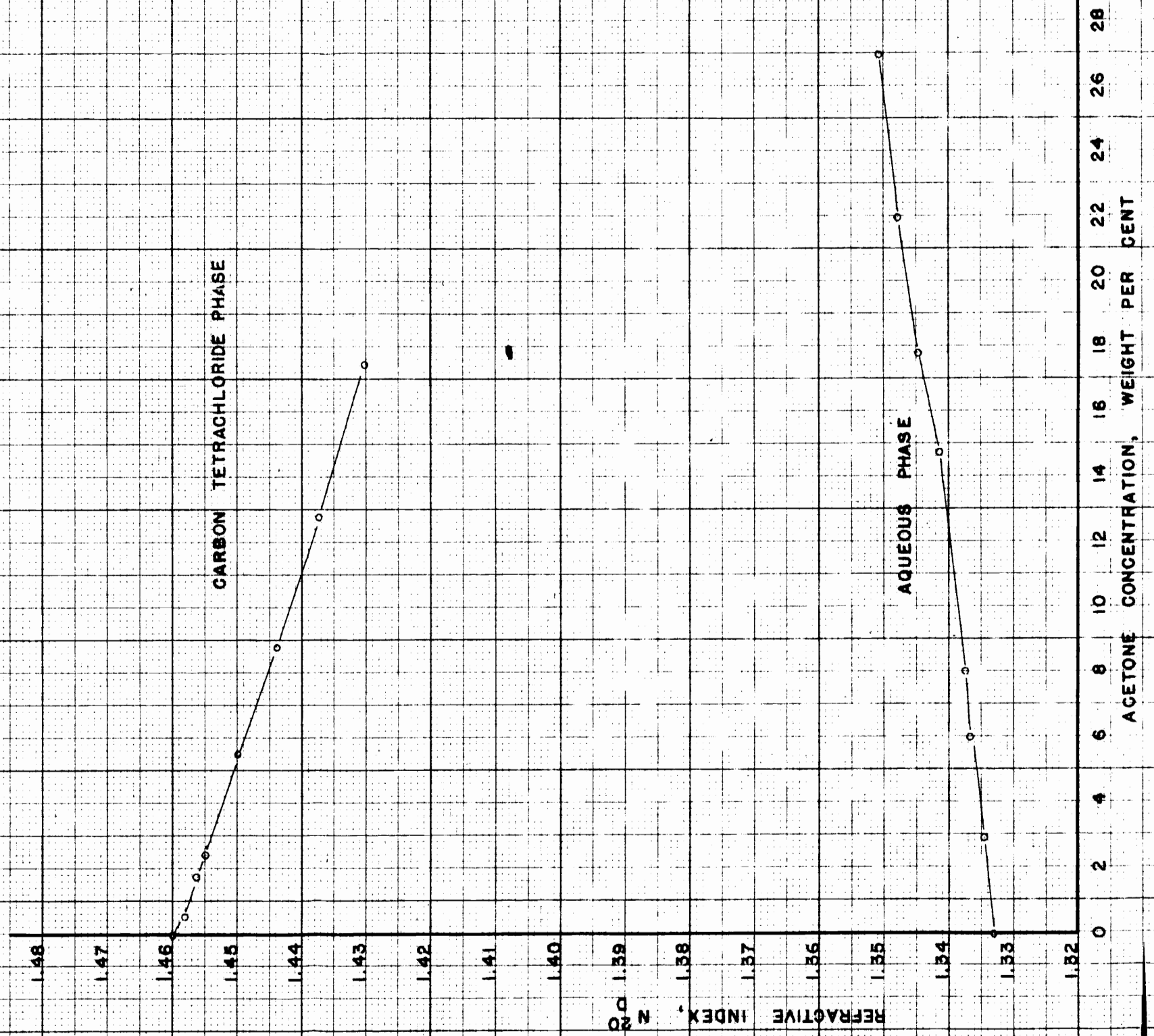


FIGURE 3. REFRACTIVE INDEX OF EQUILIBRIUM SOLUTIONS FOR THE SYSTEM CARBON TETRACHLORIDE - ACETONE - WATER

HAYFORD, D.A.: DESIGN, CONSTRUCTION, AND OPERATION OF A LIQUID-LIQUID PULSE EXTRACTOR UNPUBLISHED M. SC. THESIS, LIBRARY, VA. POLY. INST., BLACKSBURG, VA., (1953).

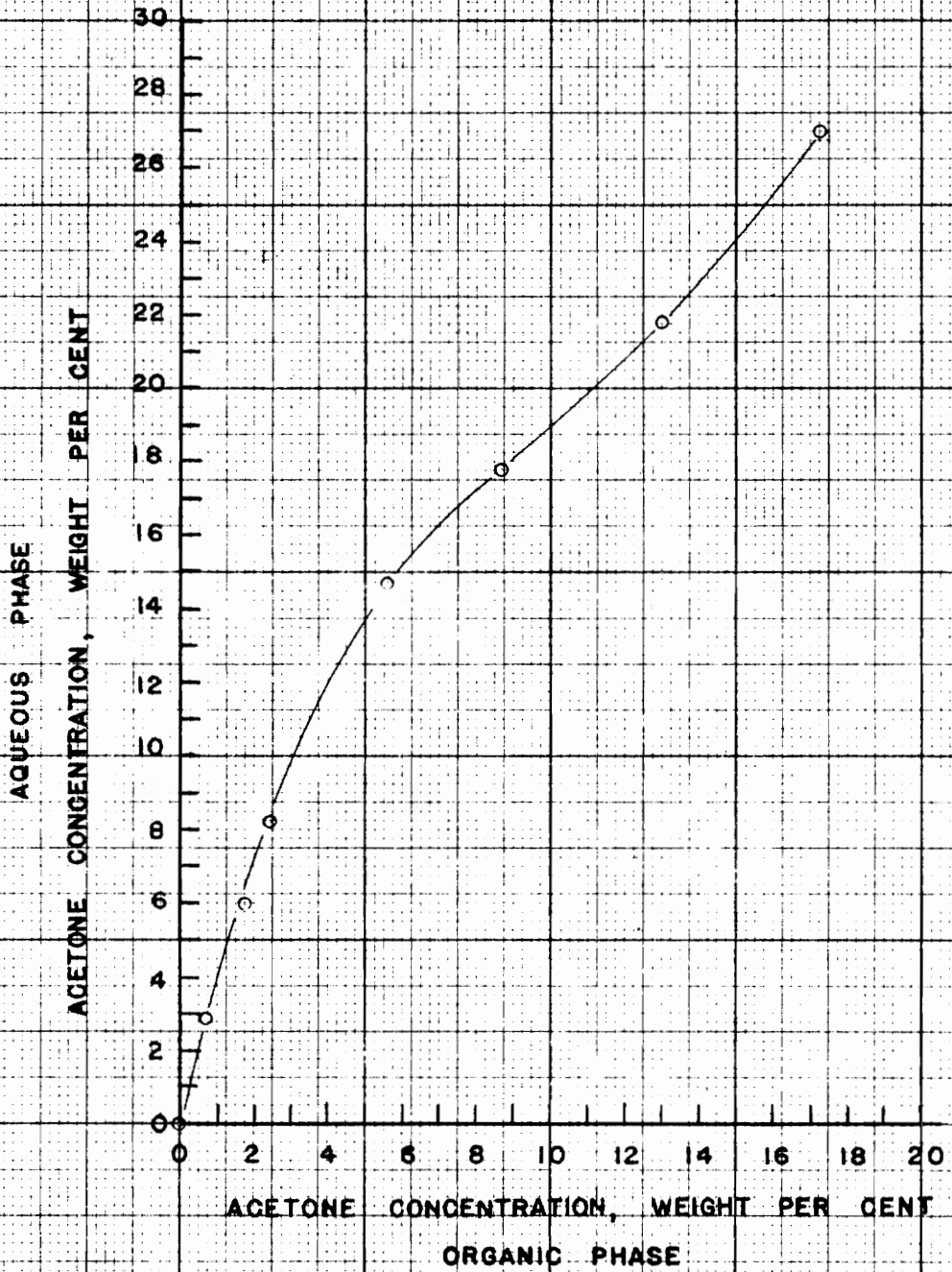


FIGURE 4. DISTRIBUTION OF ACETONE BETWEEN
CARBON TETRACHLORIDE AND WATER
AT 22° C

TABLE VII

Operational Data for a Two-inch Experimental
Pulse Extraction Column Extracting Acetone
from Carbon Tetrachloride with Water

TABLE VII

Operational Data for a Two-inch Experimental Pulse Extraction Column
Extracting Acetone from Carbon Tetrachloride with Water

| Test No | Phase | Refractive Index | Acetone Concentration | Pulse Amplitude | Plate-free area | No of Plates (Actual) | No of Plates (Theoretical) | Stage Efficiency % |
|---------|-------------------|------------------|-----------------------|-----------------|-----------------|-----------------------|----------------------------|--------------------|
| | | n_D^{20} | wt % | in. | % | | | % |
| 111 | Feed | 1.4420 | 10.00 | 1 | 8 | 4 | 1.203 | 30.10 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4575 1.3372 | 1.20 7.60 | ----- | ----- | ----- | ----- | ----- |
| 211 | Feed | 1.4420 | 10.00 | 2 | 8 | 4 | 1.965 | 49.15 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4590 1.3375 | 0.30 8.00 | ----- | ----- | ----- | ----- | ----- |
| 311 | Feed | 1.4420 | 10.00 | 3 | 8 | 4 | 2.635 | 65.85 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4595 1.3379 | 0.10 8.40 | ----- | ----- | ----- | ----- | ----- |
| 121 | Feed | 1.4422 | 9.80 | 1 | 8 | 8 | 2.260 | 28.25 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4591 1.3380 | 0.20 8.80 | ----- | ----- | ----- | ----- | ----- |
| 221 | Feed | 1.4422 | 9.80 | 2 | 8 | 8 | 3.725 | 46.50 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4595 1.3381 | 0.10 9.20 | ----- | ----- | ----- | ----- | ----- |
| 321 | Feed | 1.4422 | 9.80 | 3 | 8 | 8 | 3.465 | 43.40 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4600 1.3383 | 0.10 9.50 | ----- | ----- | ----- | ----- | ----- |
| 131 | Feed | 1.4415 | 10.30 | 1 | 8 | 12 | 2.317 | 19.30 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4600 1.3375 | 0.10 8.00 | ----- | ----- | ----- | ----- | ----- |
| 231 | Feed | 1.4415 | 10.30 | 2 | 8 | 12 | 2.437 | 20.30 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4600 1.3380 | 0.10 8.80 | ----- | ----- | ----- | ----- | ----- |
| 331 | Feed | 1.4415 | 10.30 | 3 | 8 | 12 | 3.253 | 27.10 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4595 1.3385 | 0.10 9.70 | ----- | ----- | ----- | ----- | ----- |
| 112 | Feed | 1.4425 | 9.70 | 1 | 16 | 4 | 1.033 | 25.85 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4562 1.3371 | 1.85 7.40 | ----- | ----- | ----- | ----- | ----- |
| 212 | Feed | 1.4425 | 9.70 | 2 | 16 | 4 | 1.209 | 30.20 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4570 1.3375 | 1.40 8.00 | ----- | ----- | ----- | ----- | ----- |
| 312 | Feed | 1.4425 | 9.70 | 3 | 16 | 4 | 1.298 | 32.40 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4570 1.3380 | 1.40 8.80 | ----- | ----- | ----- | ----- | ----- |
| 122 | Feed | 1.4415 | 10.30 | 1 | 16 | 8 | 1.535 | 19.20 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4585 1.3373 | 0.60 7.80 | ----- | ----- | ----- | ----- | ----- |
| 222 | Feed | 1.4415 | 10.30 | 2 | 16 | 8 | 1.476 | 18.45 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4585 1.3372 | 0.60 7.60 | ----- | ----- | ----- | ----- | ----- |
| 322 | Feed | 1.4415 | 10.30 | 3 | 16 | 8 | 2.532 | 31.60 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4591 1.3385 | 0.20 9.70 | ----- | ----- | ----- | ----- | ----- |
| 132 | Feed | 1.4425 | 9.70 | 1 | 16 | 12 | 1.955 | 16.30 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4589 1.3375 | 0.40 8.00 | ----- | ----- | ----- | ----- | ----- |
| 232 | Feed | 1.4425 | 9.70 | 2 | 16 | 12 | 2.382 | 19.85 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4591 1.3379 | 0.20 8.40 | ----- | ----- | ----- | ----- | ----- |
| 332 | Feed | 1.4425 | 9.70 | 3 | 16 | 12 | 2.207 | 18.40 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4591 1.3375 | 0.20 8.00 | ----- | ----- | ----- | ----- | ----- |
| 113 | Feed | 1.4440 | 8.80 | 1 | 32 | 4 | 1.112 | 27.80 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4570 1.3369 | 1.40 6.65 | ----- | ----- | ----- | ----- | ----- |
| 213 | Feed | 1.4440 | 8.80 | 2 | 32 | 4 | 1.600 | 25.00 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4560 1.3371 | 2.05 7.40 | ----- | ----- | ----- | ----- | ----- |
| 313 | Feed | 1.4440 | 8.80 | 3 | 32 | 4 | 1.171 | 29.30 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4570 1.3371 | 1.40 7.40 | ----- | ----- | ----- | ----- | ----- |
| 123 | Feed | 1.4440 | 8.80 | 1 | 32 | 8 | 1.141 | 14.30 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4570 1.3370 | 1.40 7.00 | ----- | ----- | ----- | ----- | ----- |
| 223 | Feed | 1.4440 | 8.80 | 2 | 32 | 8 | 1.475 | 18.45 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4580 1.3375 | 0.90 8.00 | ----- | ----- | ----- | ----- | ----- |
| 323 | Feed | 1.4440 | 8.80 | 3 | 32 | 8 | 1.141 | 14.30 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4570 1.3370 | 1.40 7.00 | ----- | ----- | ----- | ----- | ----- |
| 133 | Feed | 1.4430 | 9.35 | 1 | 32 | 12 | 1.130 | 9.41 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4570 1.3370 | 1.40 7.00 | ----- | ----- | ----- | ----- | ----- |
| 233 | Feed | 1.4430 | 9.35 | 2 | 32 | 12 | 1.311 | 10.93 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4580 1.3370 | 0.90 7.00 | ----- | ----- | ----- | ----- | ----- |
| 333 | Feed | 1.4430 | 9.35 | 3 | 32 | 12 | 1.311 | 10.93 |
| | Solvent | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | Raffinate Extract | 1.4580 1.3370 | 0.90 7.00 | ----- | ----- | ----- | ----- | ----- |

Operational Constants:

1. Pulse Frequency = 10.5 cycles per minute

2. Flow Rates

- a. Feed = 1807 ± 20 lb/hr/sq ft
 b. Solvent = 2211 ± 15 lb/hr/sq ft
 c. Raffinate = 1478 ± 25 lb/hr/sq ft
 d. Extract = 2299 ± 15 lb/hr/sq ft

3. Temperature = 82 ± 5 °F

Figure 5. Effect of Pulse Amplitude on Stage
Efficiency in a Two-inch
Pulse Extractor

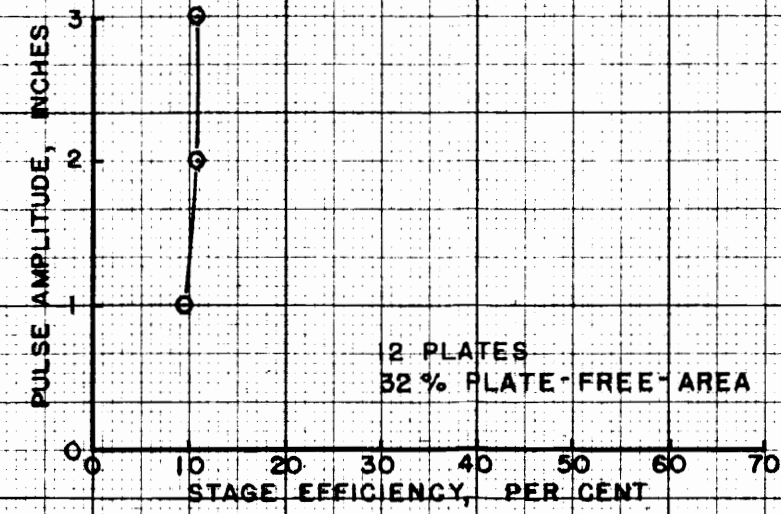
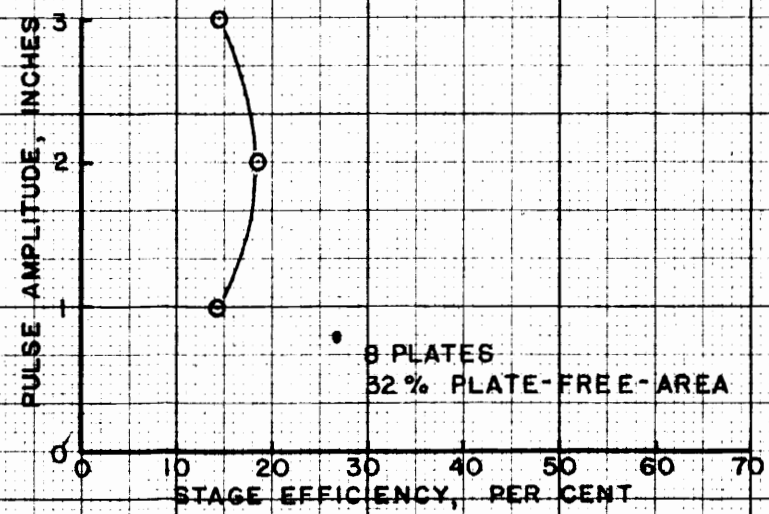
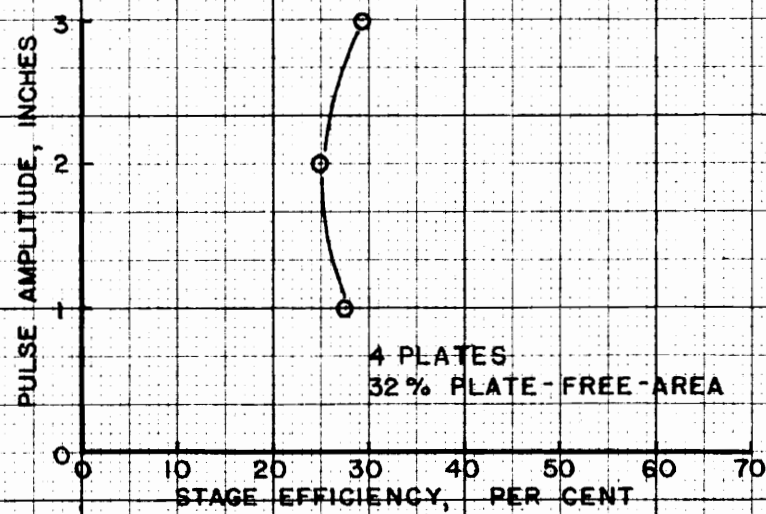
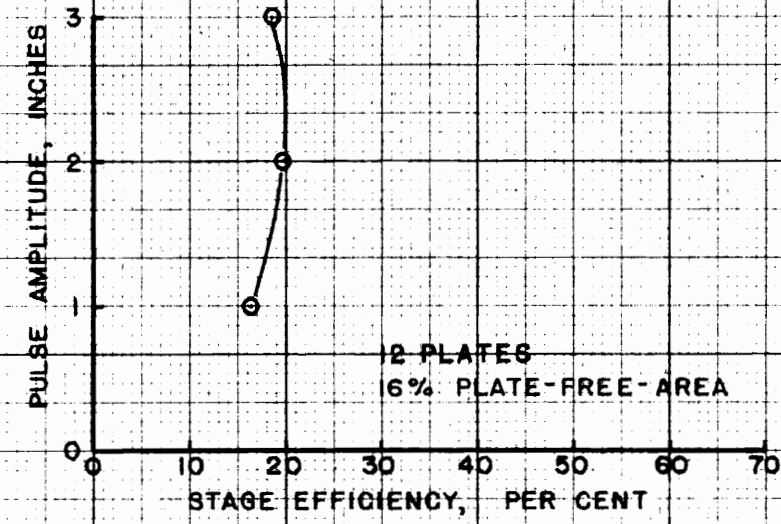
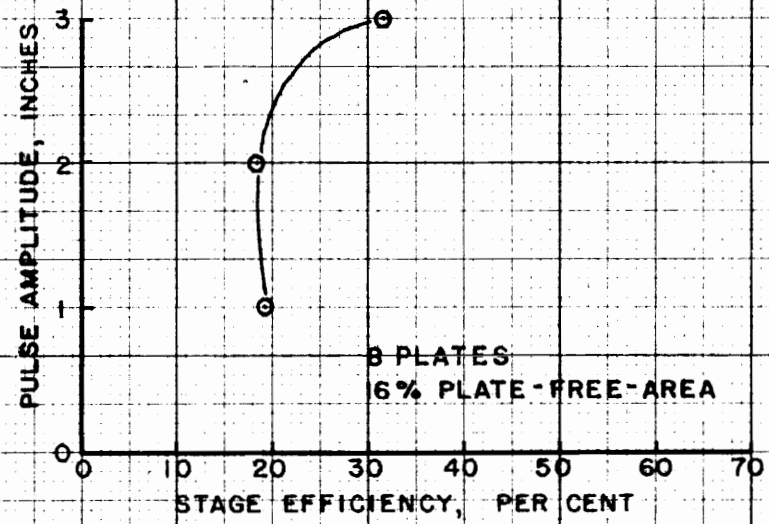
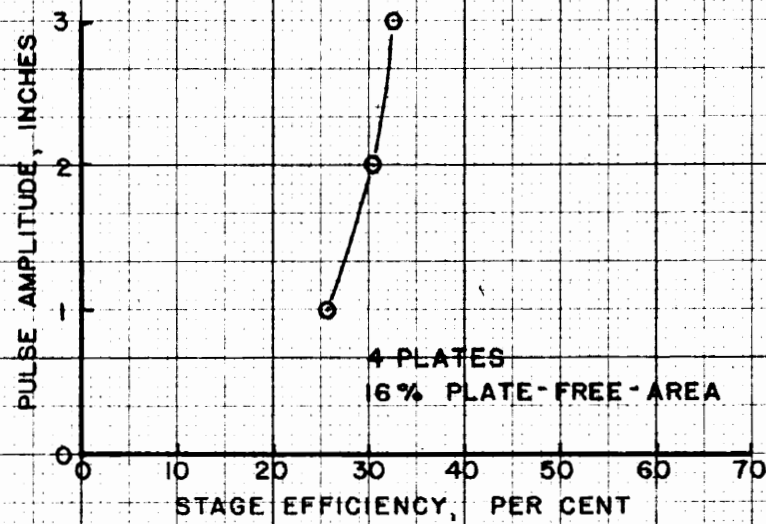
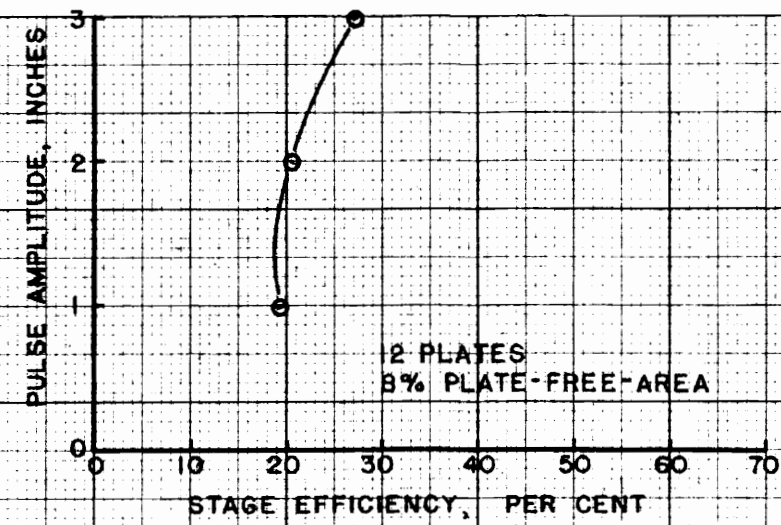
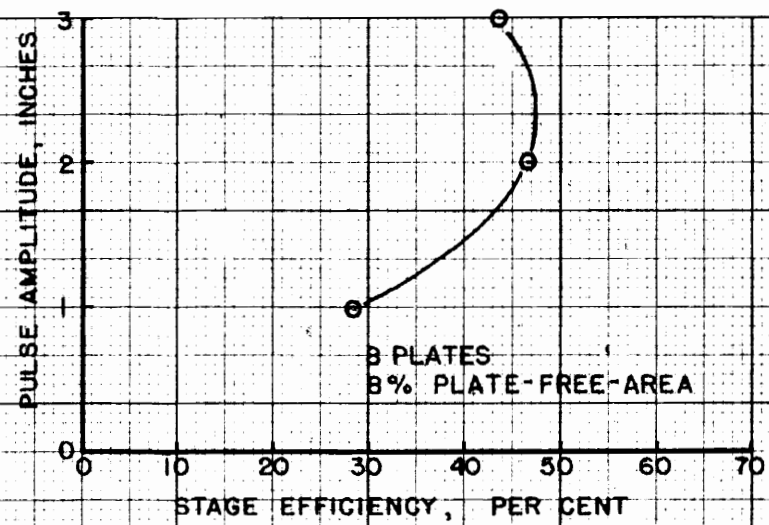
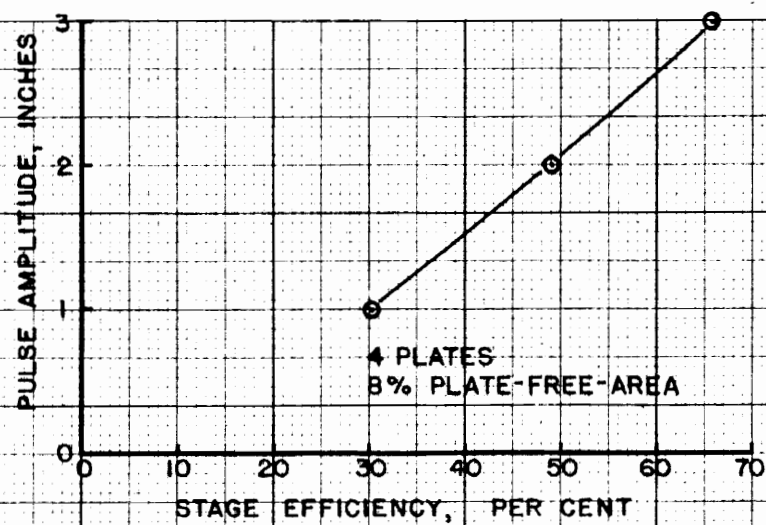
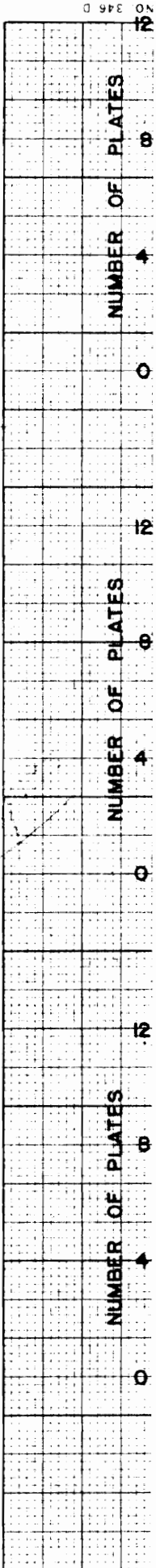


FIGURE 5. EFFECT OF PULSE AMPLITUDE ON STAGE EFFICIENCY IN A TWO-INCH PULSE EXTRACTOR

Figure 6. Effect of Number of Plates on Stage Efficiency in a Two-inch Pulse Extractor



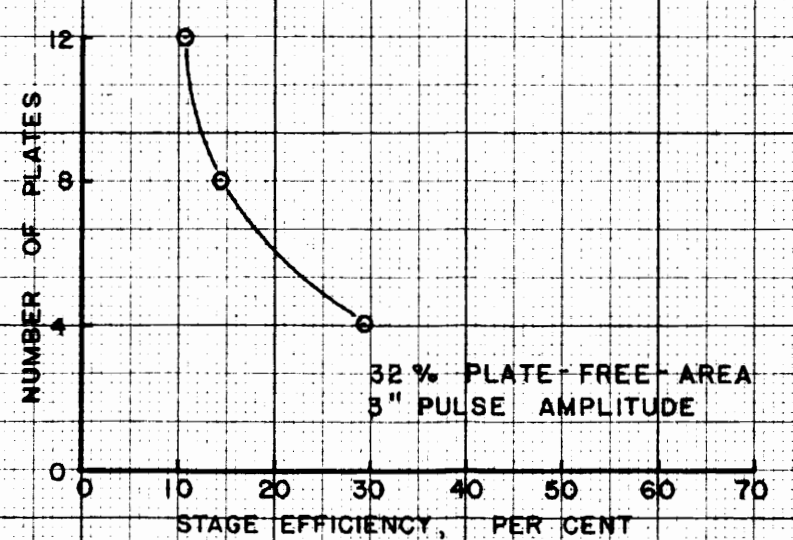
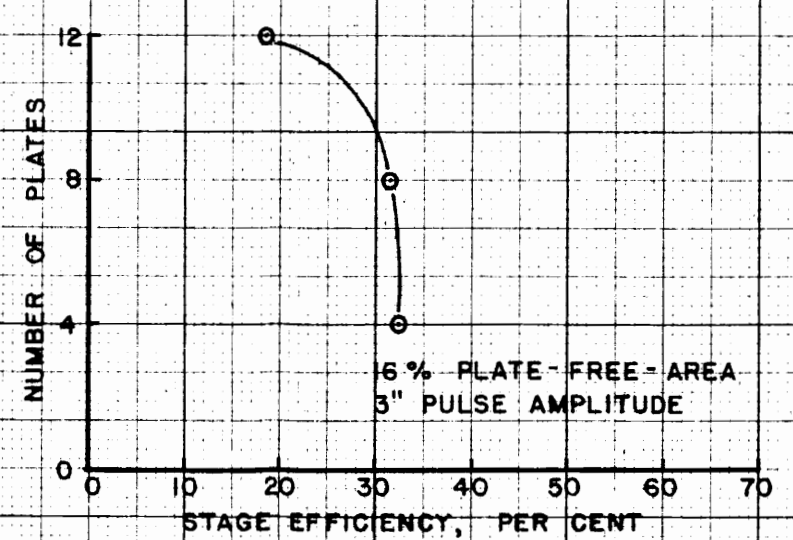
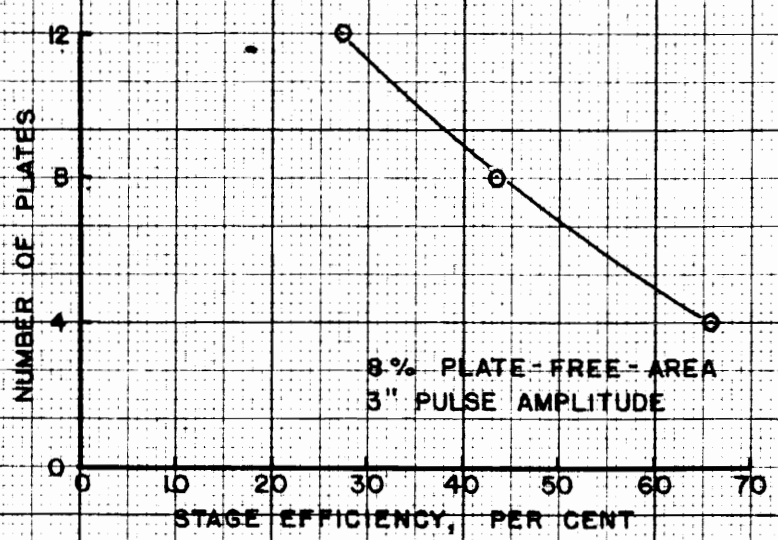
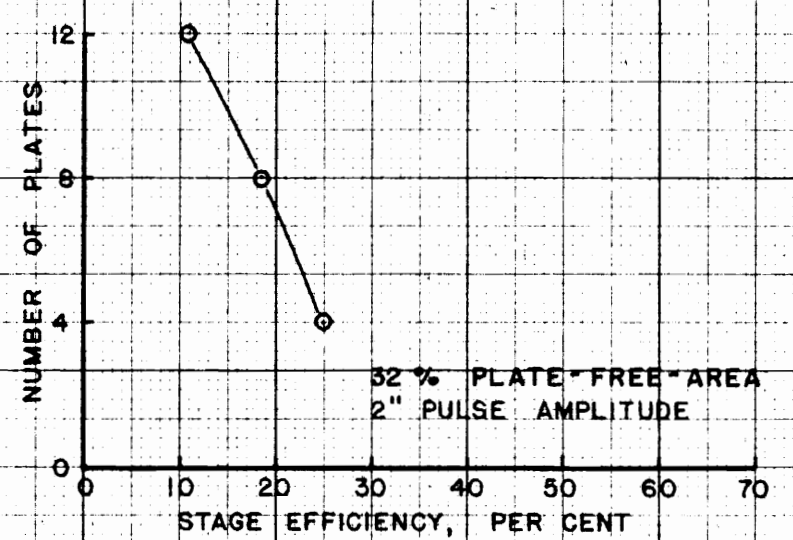
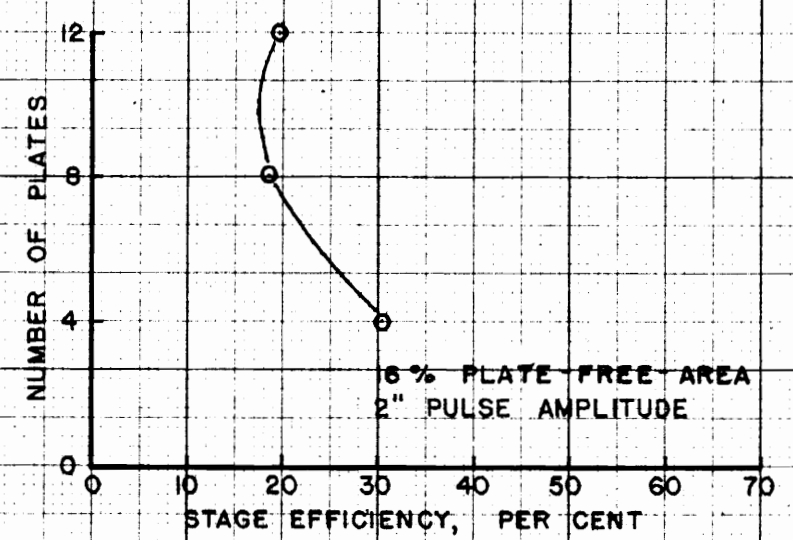
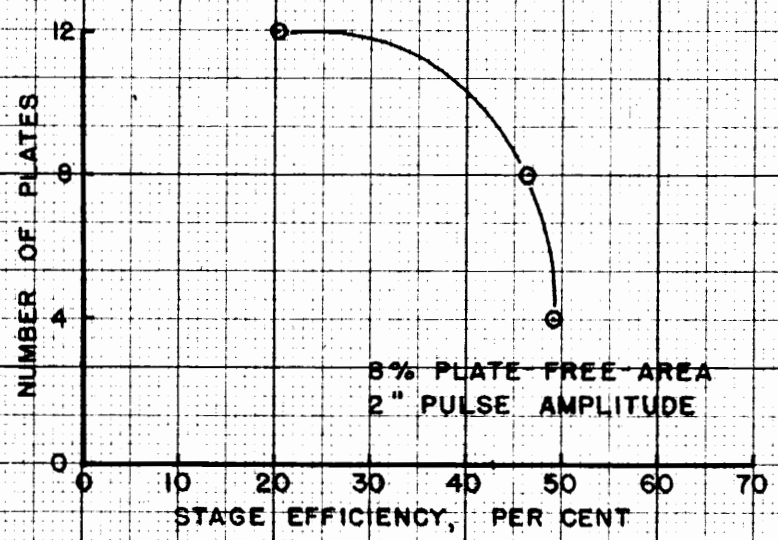
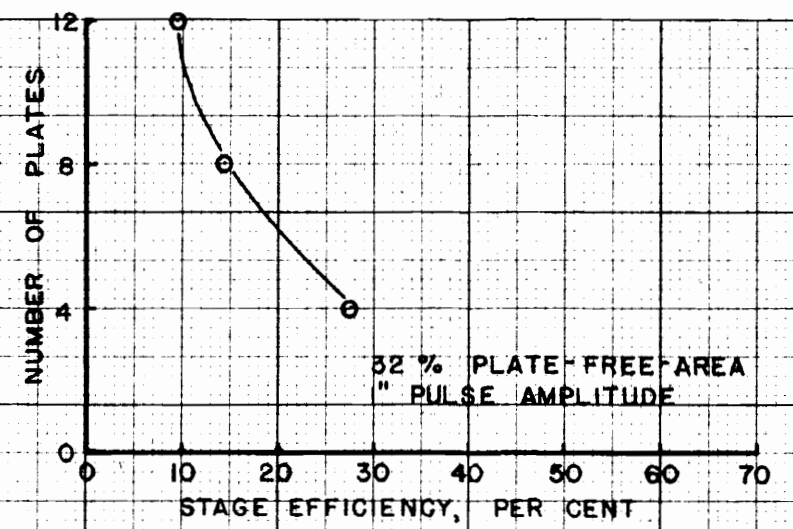
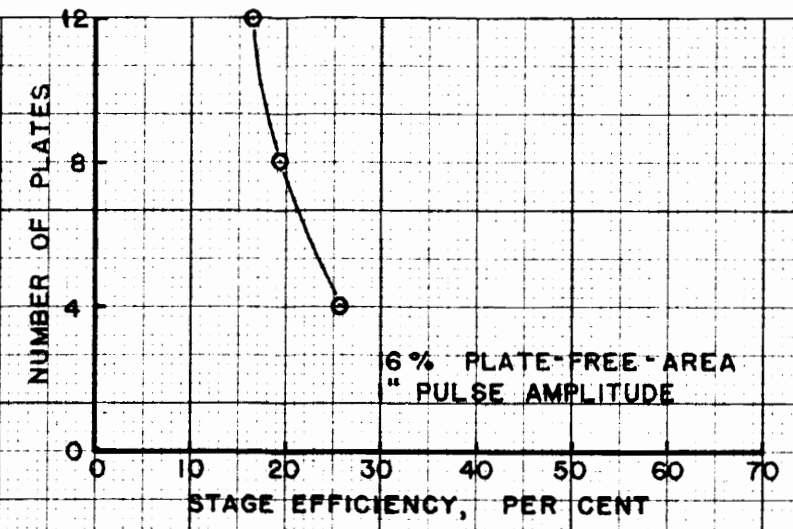
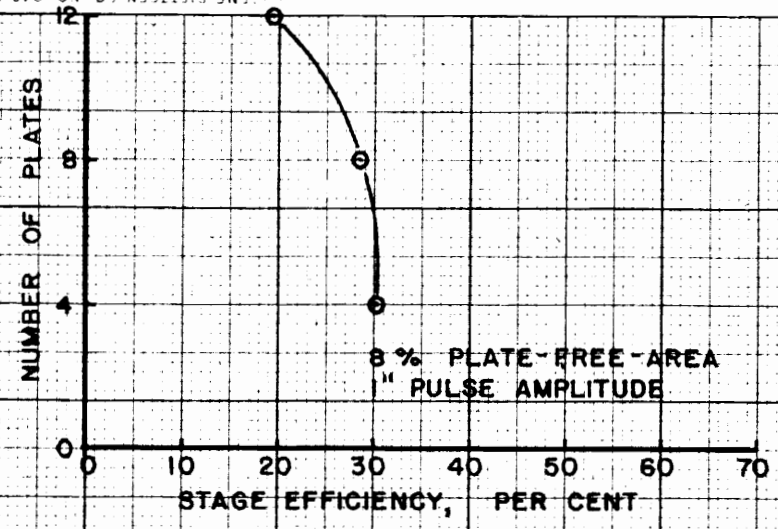


FIGURE 6. EFFECT OF NUMBER-OF-PLATES ON STAGE EFFICIENCY IN A TWO-INCH PULSE EXTRACTOR

Figure 7. Effect of Plate-free-area on Stage
Efficiency in a Two-inch
Pulse Extractor

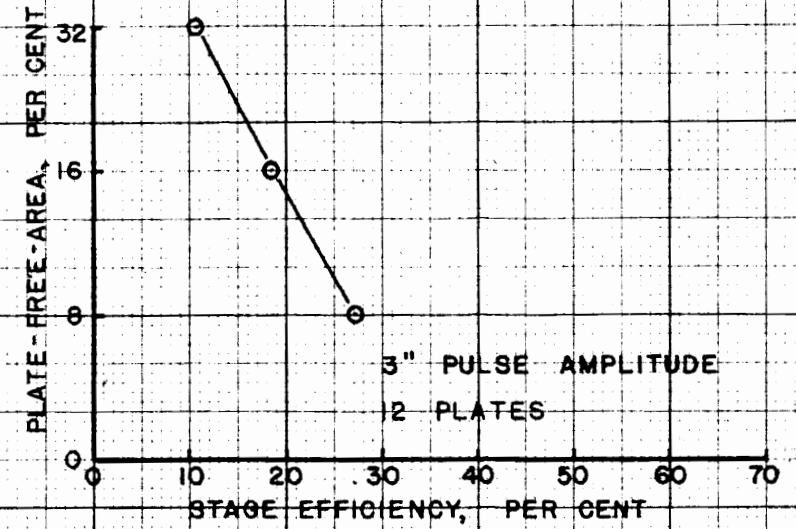
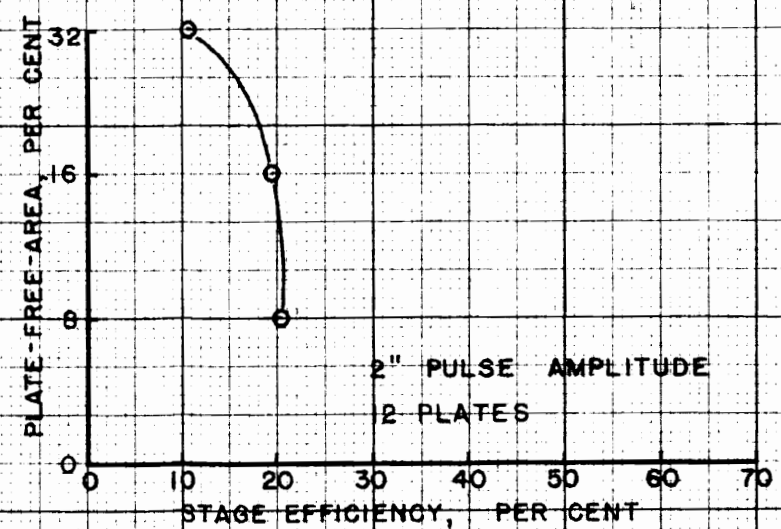
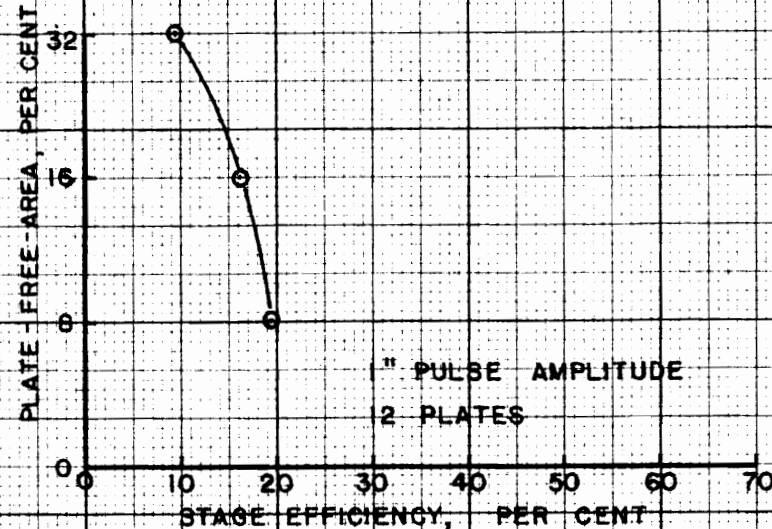
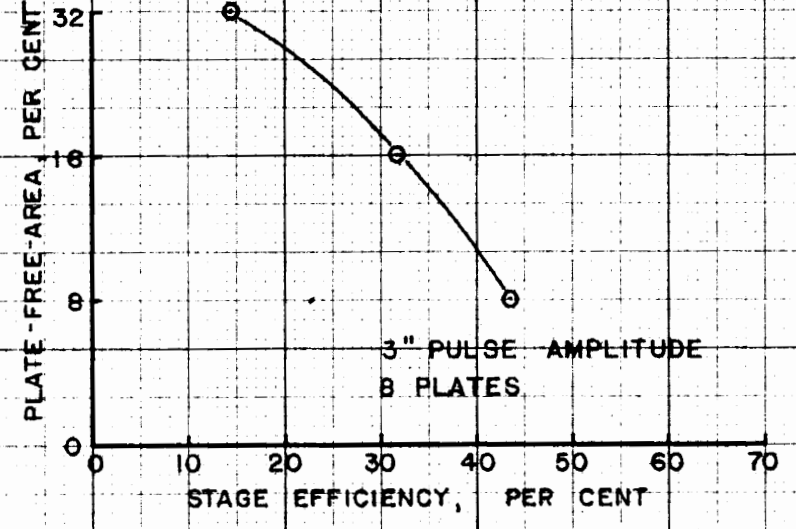
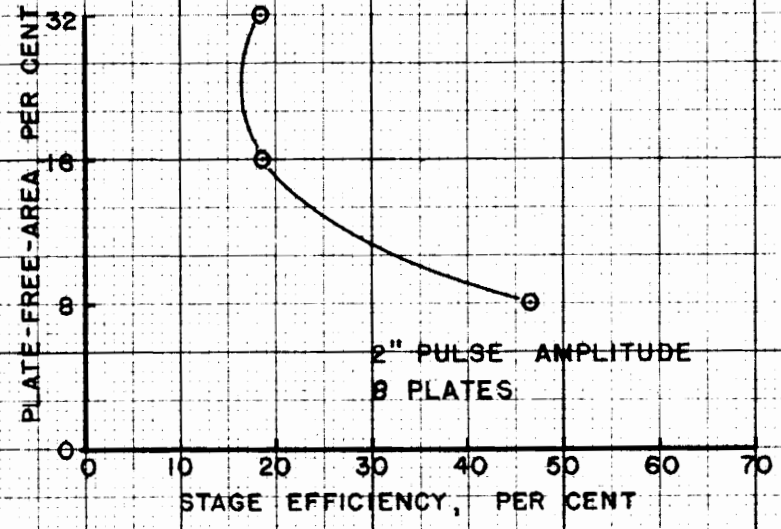
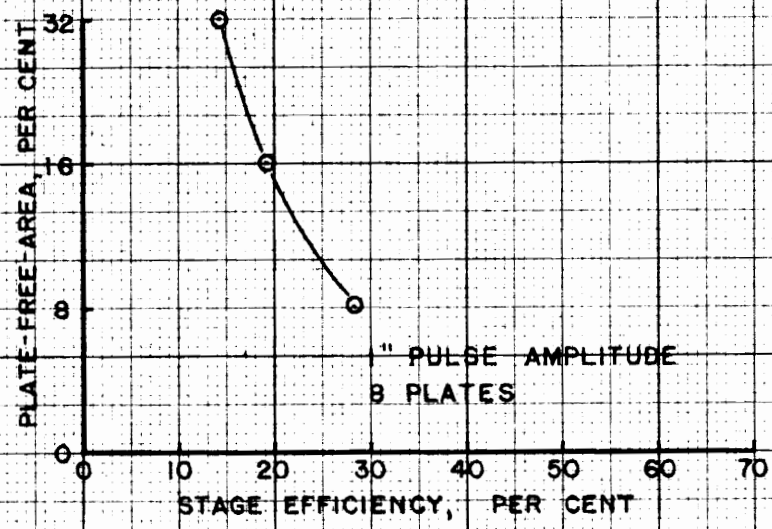
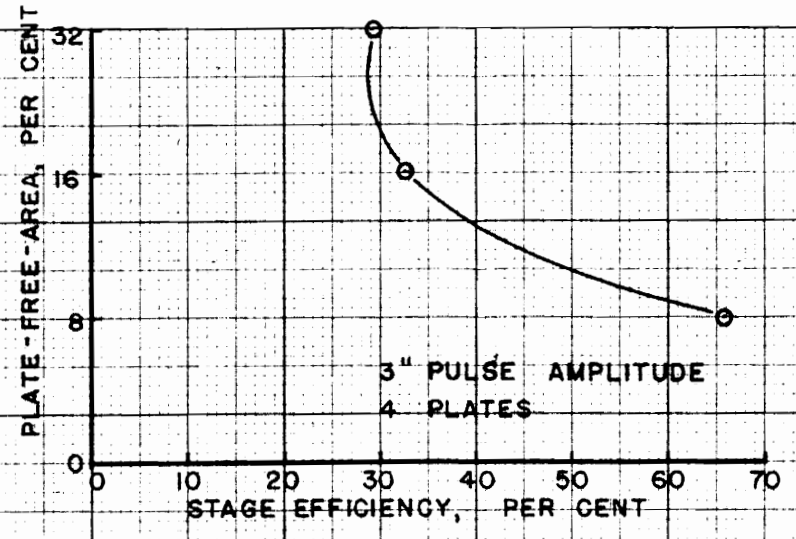
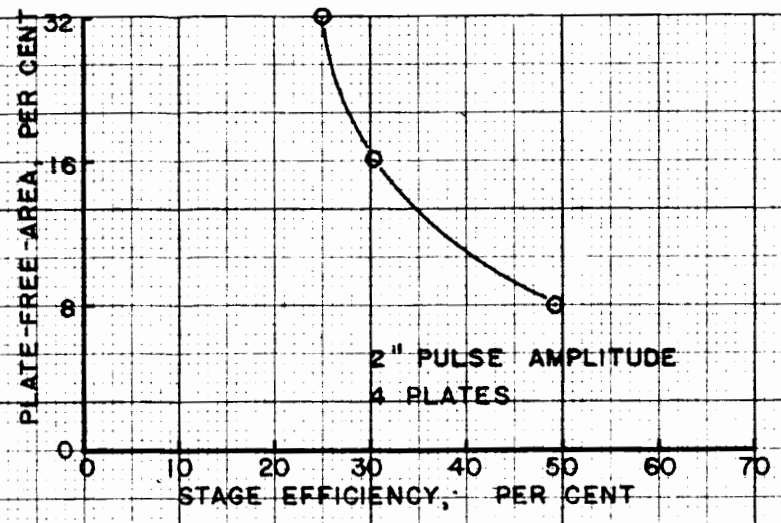
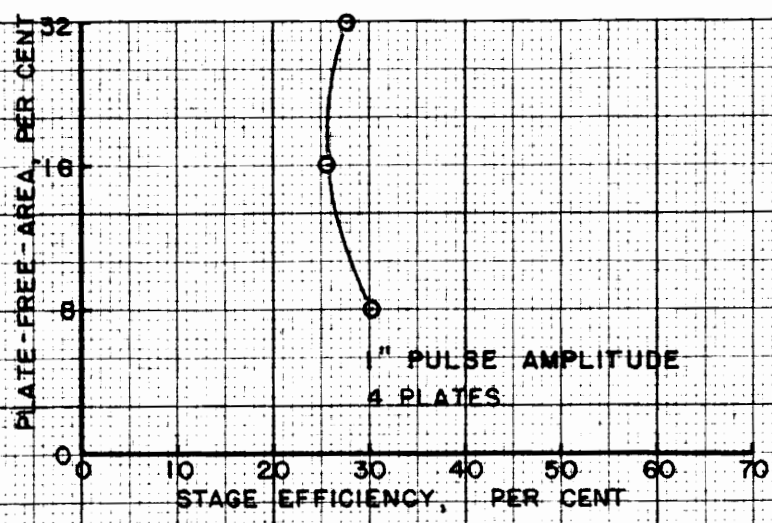


FIGURE 7. EFFECT OF PLATE-FREE-AREA ON STAGE EFFICIENCY IN A TWO-INCH PULSE EXTRACTOR

TABLE VIII

Results of Analysis-of-Variance Tests

| Variable | Sum of Squares | Degrees of Freedom | Mean Sum of Squares |
|--|----------------|--------------------|---------------------|
| Pulse Amplitude | 384.166 | 2 | 192.083 |
| Number of Plates | 1478.420 | 2 | 739.210 |
| Plate-free-area | 1677.038 | 2 | 838.519 |
| Interaction between Pulse Amplitude and Number of Plates | 97.977 | 4 | 24.499 |
| Interaction between Pulse Amplitude and Plate-free-area | 286.227 | 4 | 71.557 |
| Interaction between Number of Plates and Plate-free-area | 223.259 | 4 | 55.815 |
| Interaction between Pulse Amplitude, Number of Plates and Plate-free-area | 258.544 | 8 | 32.318 |
| TOTAL | 4405.651 | 26 | |

TABLE IX

Comparison of the "F" Statistics

| Variable | Calculated Value of the Statistic | Tabled Value of the Statistic | Effect |
|--|---|-------------------------------------|-----------------|
| | F | F _{0.95} | |
| Pulse Amplitude | 5.94 | 4.46 | Significant |
| Number of Plates | 22.87 | 4.46 | Significant |
| Plate-free-area | 25.95 | 4.46 | Significant |
| Interaction between Pulse Amplitude and Number of Plates | 0.76 | 3.84 | Not Significant |
| Interaction between Pulse Amplitude and Plate-free-area | 2.21 | 3.84 | Not Significant |
| Interaction between Number of Plates and Plate-free-area | 1.73 | 3.84 | Not Significant |

Sample Calculations

In this section examples of the calculations used in this investigation are presented.

Calculation of the Stage Efficiency. Before the stage efficiency was calculated the number of theoretical transfer stages had to be calculated. The number of theoretical transfer stages was calculated by the graphical method introduced by Hunter and Nash^(44,45). This method is more familiar in the form presented by Elgin⁽²⁹⁾ and Bull and Coli⁽¹⁸⁾. The distribution diagram determined by Hayford⁽⁴³⁾ and the conjugate line used by Elgin⁽²⁹⁾ and Bull and Coli⁽¹⁸⁾ were used in combination in this investigation for the stage-to-stage calculations in lieu of the tie lines employed by Hunter and Nash^(44,45). As both the tie lines and the conjugate line are obtained from the distribution diagram no real change in theory has been made.

The graphical solution for the number of theoretical transfer stages for test "131" presented in Table VII, page 109, is shown in Figure 8, page 116. The distribution data, also used, are shown in Figure 4, page 108.

Figure 8. Graphical Solution for the Number of
Theoretical Transfer Stages

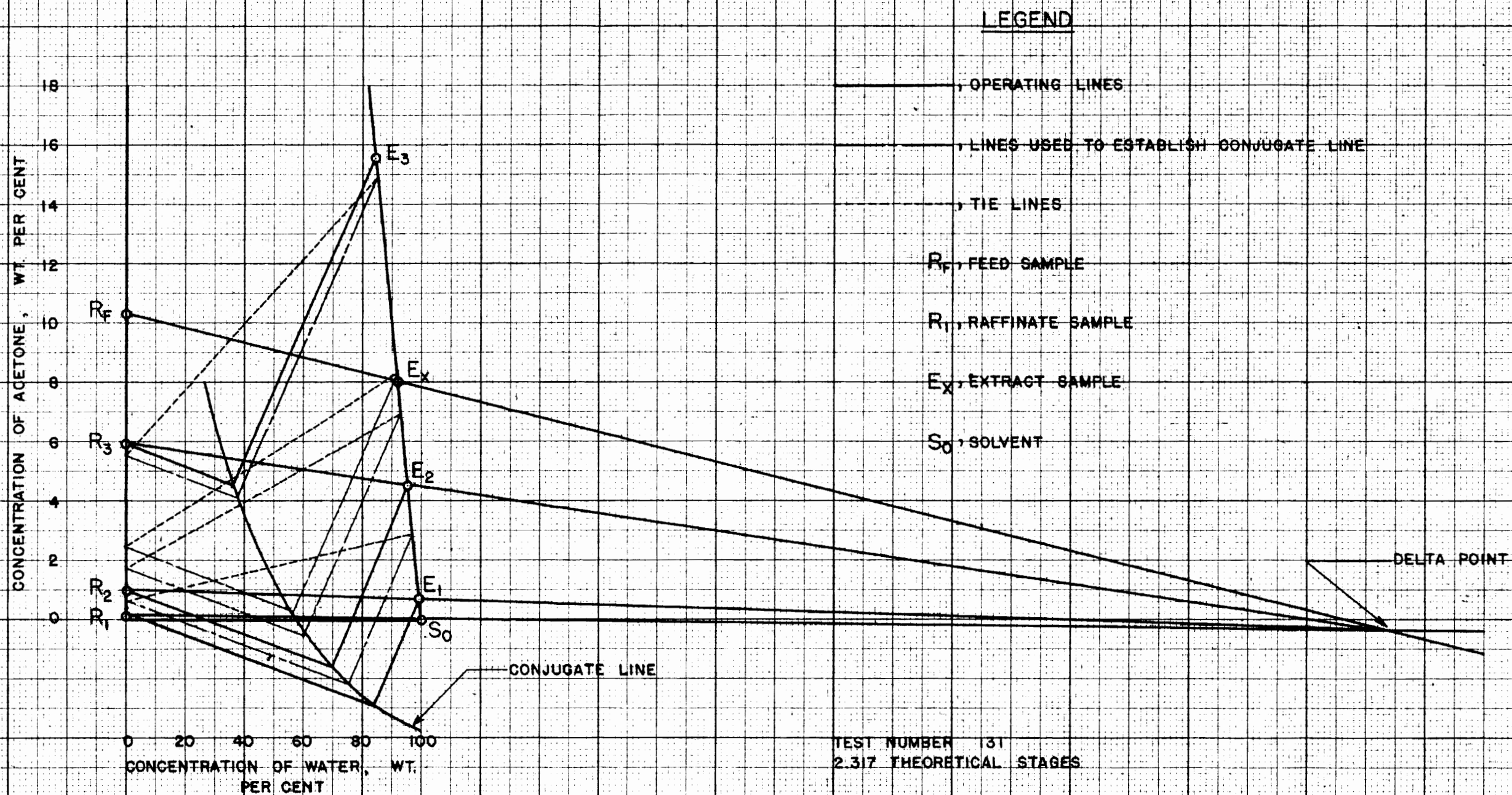


FIGURE 8. GRAPHICAL SOLUTION FOR THE NUMBER OF THEORETICAL TRANSFER STAGES

The stage efficiency was calculated as shown below:

$$y = \frac{N_s}{N_p} \times 100$$

where:

y = stage efficiency, per cent

N_s = number of theoretical stages, dimensionless

N_p = number of actual stages, dimensionless

$$y = \frac{2.317}{12} \times 100$$

$$y = 19.30 \text{ per cent.}$$

Analysis of Stage Efficiency. The results presented in Table VII, page 109, showing the variation of the stage efficiency with the operating parameters of the pulse column, are too interrelated to show any significant trends. This lack of a definite trend was caused by the masking effect of all three operating parameters varying at once. To try to eliminate the masking effect of these variations, a statistical analysis of the data was employed. The statistical methods used in this investigation were the analysis-of-variance tests suggested by Dixon and Massey⁽⁹⁶⁾. This method of statistical analysis entailed the calculation of the sums of squares, the degrees of

freedom, and the mean sums of squares for the pulse amplitude, the number of plates, the plate-free-area, and for the interactions between the pulse amplitude and number of plates, the pulse amplitude and plate-free-area, the number of plates and plate-free-area, and the pulse amplitude, number of plates, and plate-free-area. With these calculations completed it was necessary to determine the values of the "F" statistic for each variable and all second and third order combinations thereof. The methods by which all of these calculations were executed are explained in the paragraphs which follow.

Before proceeding with a detailed explanation of the methods of calculation, the author believes that some time should be expended in an attempt to clarify the coding and terminology employed hereafter. All symbols referred to in the following are those presented in Table X, page 119, and the equations that follow.

In this investigation it was necessary to perform twenty-seven individual experimental tests to be able to obtain operational data for the pulse column, the column being operated under all possible combinations of the three operating parameters studied, each parameter with a range of three operating levels. To effectively perform the experimental design and designate each of the tests a coding system was devised. Each

TABLE X

Tabulation for Analysis-of-Variance
Tests

TABLE X

Tabulation for Analysis-of-Variance Tests

| Code for Stage Efficiency Values | | Stage Efficiency Values, per cent | |
|---------------------------------------|---|-----------------------------------|--|
| T ₁₁₁ | T ₂₁₁ T ₃₁₁ | 30.10 | 49.15 65.85 |
| T ₁₁₂ (T _{11.}) | T ₂₁₂ (T _{21.}) T ₃₁₂ (T _{31.}) | T _{1.} | 25.85 (83.75) 30.20(104.35) 32.40(127.55) 315.65 |
| T ₁₁₃ | T ₂₁₃ T ₃₁₃ | 27.80 | 25.00 29.30 |
| T ₁₂₁ | T ₂₂₁ T ₃₂₁ | 28.25 | 46.50 43.40 |
| T ₁₂₂ (T _{12.}) | T ₂₂₂ (T _{22.}) T ₃₂₂ (T _{32.}) | T _{2.} | 19.20 (61.75) 18.45 (83.40) 31.60 (89.30) 234.45 |
| T ₁₂₃ | T ₂₂₃ T ₃₂₃ | 14.30 | 18.45 14.30 |
| T ₁₃₁ | T ₂₃₁ T ₃₃₁ | 19.30 | 20.30 27.10 |
| T ₁₃₂ (T _{13.}) | T ₂₃₂ (T _{23.}) T ₃₃₂ (T _{33.}) | T _{3.} | 16.30 (45.01) 19.85 (51.08) 18.40 (56.43) 152.52 |
| T ₁₃₃ | T ₂₃₃ T ₃₃₃ | 9.41 | 10.93 10.93 |
| T _{1..} | T _{2..} T _{3..} | T _{...} | 190.51 238.83 273.28 702.62 |
| T ₁₁₁ | T ₂₁₁ T ₃₁₁ | 30.10 | 49.15 65.85 |
| T ₁₂₁ (T _{1.1}) | T ₂₂₁ (T _{2.1}) T ₃₂₁ (T _{3.1}) | T _{1.1} | 28.25 (77.65) 46.50(115.95) 43.40(136.35) 329.95 |
| T ₁₃₁ | T ₂₃₁ T ₃₃₁ | 19.30 | 20.30 27.10 |
| T ₁₁₂ | T ₂₁₂ T ₃₁₂ | 25.85 | 30.20 32.40 |
| T ₁₂₂ (T _{1.2}) | T ₂₂₂ (T _{2.2}) T ₃₂₂ (T _{3.2}) | T _{1.2} | 19.20 (61.35) 18.45 (68.50) 31.60 (82.40) 212.25 |
| T ₁₃₂ | T ₂₃₂ T ₃₃₂ | 16.30 | 19.85 18.40 |
| T ₁₁₃ | T ₂₁₃ T ₃₁₃ | 27.80 | 25.00 29.30 |
| T ₁₂₃ (T _{1.3}) | T ₂₂₃ (T _{2.3}) T ₃₂₃ (T _{3.3}) | T _{1.3} | 14.30 (51.51) 18.45 (54.38) 14.30 (54.53) 160.42 |
| T ₁₃₃ | T ₂₃₃ T ₃₃₃ | 9.41 | 10.93 10.93 |
| T _{1..} | T _{2..} T _{3..} | T _{...} | 190.51 238.83 273.28 702.62 |
| T ₁₁₁ | T ₁₂₁ T ₁₃₁ | 30.10 | 28.25 19.30 |
| T ₂₁₁ (T _{1.11}) | T ₂₂₁ (T _{2.21}) T ₂₃₁ (T _{2.31}) | T _{1.1} | 49.15(145.10) 46.50(118.15) 20.30 (66.70) 329.95 |
| T ₃₁₁ | T ₃₂₁ T ₃₃₁ | 65.85 | 43.40 27.10 |
| T ₁₁₂ | T ₁₂₂ T ₁₃₂ | 25.85 | 19.20 16.30 |
| T ₂₁₂ (T _{1.12}) | T ₂₂₂ (T _{2.22}) T ₂₃₂ (T _{2.32}) | T _{1.2} | 30.20 (88.45) 18.45 (69.25) 19.85 (54.55) 212.25 |
| T ₃₁₂ | T ₃₂₂ T ₃₃₂ | 32.40 | 31.60 18.40 |
| T ₁₁₃ | T ₁₂₃ T ₁₃₃ | 27.80 | 14.30 9.41 |
| T ₂₁₃ (T _{1.13}) | T ₂₂₃ (T _{2.23}) T ₂₃₃ (T _{2.33}) | T _{1.3} | 25.00 (82.10) 18.45 (47.05) 10.93 (31.27) 160.42 |
| T ₃₁₃ | T ₃₂₃ T ₃₃₃ | 29.30 | 14.30 10.93 |
| T _{1.1} | T _{2.2} T _{3.3} | T _{...} | 315.65 234.45 152.52 702.62 |

Explanation of coding systems:

T_{abc} = stage efficiency value in general; in the subscript 1, 2, and 3 in the a, b, and c positions designate the three operating levels of the pulse amplitude, number of plates, and plate-free-area, respectively.

T₁₁₁ = stage efficiency value for a test with one inch of pulse amplitude, four plates, and eight per cent plate-free-area.

T₂₁₂ = stage efficiency value for a test with two inches of pulse amplitude, four plates, and sixteen per cent plate-free-area.

T₃₁₃ = stage efficiency value for a test with three inches of pulse amplitude, four plates, and thirty-two per cent plate-free-area.

T₁₂₁ = stage efficiency value for a test with one inch of pulse amplitude, eight plates, and eight per cent plate-free-area.

T₁₃₁ = stage efficiency value for a test with one inch of pulse amplitude, twelve plates, and eight per cent plate-free-area.

T_{11.} = T₁₁₁ + T₁₁₂ + T₁₁₃

T_{1.} = T_{11.} + T_{21.} + T_{31.}

T_{1..} = T_{11.} + T_{12.} + T_{13.}

T_{...} = sum of all twenty-seven stage efficiency values.

individual test was designated by a "T" followed by a three-digit subscript; in general - T_{abc} . Numbers (1, 2, or 3) in a, b, and c positions of the three-digit subscript indicate the various operating levels of the pulse amplitude, the number of plates, and the plate-free-area, respectively. The significance of the numbers (1, 2, or 3) can be explained as follows: the pulse-amplitude operational levels were (1) one inch, (2) two inches, and (3) three inches; the number-of-plates operational levels were (1) four plates, (2) eight plates, and (3) twelve plates; and the plate-free-area operational levels were (1) eight per cent, (2) sixteen per cent, and (3) thirty-two per cent. In other words, T_{111} would indicate a test performed with one inch of pulse amplitude, four plates, and eight per cent plate-free-area; T_{212} would indicate a test performed with two inches of pulse amplitude, four plates, and sixteen per cent plate-free-area; and T_{313} would indicate a test performed with three inches of pulse amplitude, four plates, and thirty-two per cent plate-free-area.

In computing the sums of squares for the variables it is necessary to determine various totals or sums of the stage efficiency values. An attempt has been made to remain consistent in the methods of coding these values also. Here again reference is made to the symbols presented in Table X,

page 119. The symbols for only one of each of the types of totals or sums will be defined here since the meanings of the symbols for similar values will become obvious. A symbol such as T_{111} is defined as the sum of T_{1111} , T_{1112} , and T_{1113} . Further, $T_{1.1}$ designates the sum of T_{111} , T_{211} , and T_{311} . It follows, therefore, that $T_{1..}$ signifies the sum of $T_{11.}$, $T_{12.}$, and $T_{13.}$. Finally, $T_{...}$ represents the sum of all of the twenty-seven individual test values.

With these explanations in mind it is now possible to proceed with the methods of calculation.

Calculation of the Sum of Squares. To conduct an analysis-of-variance test for this investigation it was necessary to compute the sum of squares for the pulse amplitude, the number of plates, the plate-free-area, and for the interactions between the pulse amplitude and number of plates, the pulse amplitude and plate-free-area, the number of plates and plate-free-area, and the pulse amplitude, number of plates, and plate-free-area. Since the calculation of the above mentioned sums of squares presents some possibility of confusion the computation involved in each will be presented in this section. The values of the stage efficiencies obtained experimentally were tabulated and totaled in the manner

suggested by Dixon and Massey⁽⁹⁶⁾. This tabulation supplied the totals employed in the sum-of-squares calculations and is presented in Table X, page 119.

Sum of Squares for Pulse Amplitude. The sum of squares for the pulse amplitude was calculated as shown below:

$$SSA = \frac{(T_{1..})^2}{9} + \frac{(T_{2..})^2}{9} + \frac{(T_{3..})^2}{9} - \frac{(T_{...})^2}{27}$$

where:

SSA = sum of squares for pulse amplitude

T's = previously defined

$$SSA = \frac{(190.51)^2}{9} + \frac{(238.83)^2}{9} + \frac{(273.28)^2}{9} - \frac{(702.62)^2}{27}$$

$$SSA = 384.166.$$

Sum of Squares for Number of Plates. The sum of squares for the number of plates was calculated as shown below:

$$SSB = \frac{(T_{.1.})^2}{9} + \frac{(T_{.2.})^2}{9} + \frac{(T_{.3.})^2}{9} - \frac{(T_{...})^2}{27}$$

where:

SSB = sum of squares for number of plates

T's = previously defined

$$SSB = \frac{(315.65)^2}{9} + \frac{(234.45)^2}{9} + \frac{(152.52)^2}{9} - \frac{(702.62)^2}{27}$$

$$SSB = 1478.420.$$

Sum of Squares for Plate-free-area. The sum of squares for the plate-free-area was calculated as shown below:

$$SSC = \frac{(T_{..1})^2}{9} + \frac{(T_{..2})^2}{9} + \frac{(T_{..3})^2}{9} - \frac{(T_{...})^2}{27}$$

where:

SSC = sum of squares for plate-free-area

T's = previously defined

$$SSC = \frac{(329.95)^2}{9} + \frac{(212.25)^2}{9} + \frac{(160.42)^2}{9} - \frac{(702.62)^2}{27}$$

$$SSC = 1677.038.$$

Sum of Squares for Interaction between Pulse Amplitude and Number of Plates. The sum of squares for the interaction between the pulse amplitude and number of plates was calculated as shown below:

$$SSAB = \frac{(T_{11.})^2}{3} + \frac{(T_{12.})^2}{3} + \frac{(T_{13.})^2}{3} + \frac{(T_{21.})^2}{3} + \frac{(T_{22.})^2}{3} + \frac{(T_{23.})^2}{3} + \frac{(T_{31.})^2}{3} + \frac{(T_{32.})^2}{3} + \frac{(T_{33.})^2}{3} - \frac{(T_{...})^2}{27}$$

$$SSA - SSB$$

where:

SSAB = sum of squares for interaction between pulse amplitude and number of plates

SSA = sum of squares for pulse amplitude

SSB = sum of squares for number of plates

T'S = previously defined

$$SSAB = \frac{(83.75)^2}{3} + \frac{(61.75)^2}{3} + \frac{(45.01)^2}{3} + \frac{(104.35)^2}{3} + \frac{(83.40)^2}{3} + \frac{(51.08)^2}{3} + \frac{(127.55)^2}{3} + \frac{(89.30)^2}{3} + \frac{(56.43)^2}{3} - \frac{(702.62)^2}{3} = 384.166 - 1478.420$$

$$SSAB = 97.997.$$

Sum of Squares for Interaction between Pulse Amplitude and Plate-free-area. The sum of squares for the interaction between the pulse amplitude and plate-free-area was calculated as shown below:

$$\begin{aligned} \text{SSAC} = & \frac{(T_{1.1})^2}{3} + \frac{(T_{1.2})^2}{3} + \frac{(T_{1.3})^2}{3} + \frac{(T_{2.1})^2}{3} + \frac{(T_{2.2})^2}{3} + \\ & \frac{(T_{2.3})^2}{3} + \frac{(T_{3.1})^2}{3} + \frac{(T_{3.2})^2}{3} + \frac{(T_{3.3})^2}{3} - \frac{(T_{\dots})^2}{27} - \\ & \text{SSA} - \text{SSC} \end{aligned}$$

where:

SSAC = sum of squares for interaction between pulse amplitude and plate-free-area

SSA = sum of squares for pulse amplitude

SSC = sum of squares for plate-free-area

T's = previously defined

$$\begin{aligned} \text{SSAC} = & \frac{(77.65)^2}{3} + \frac{(61.35)^2}{3} + \frac{(51.51)^2}{3} + \frac{(115.95)^2}{3} + \\ & \frac{(68.50)^2}{3} + \frac{(54.38)^2}{3} + \frac{(136.35)^2}{3} + \frac{(82.40)^2}{3} + \\ & \frac{(54.53)^2}{3} - \frac{(702.60)^2}{27} - 384.166 - 1677.038 \end{aligned}$$

$$\text{SSAC} = 286.227.$$

Sum of Squares for Interaction between Number of Plates and Plate-free-area. The sum of squares for the interaction between the number of plates and plate-free-area was calculated as shown below:

$$\begin{aligned} \text{SSBC} = & \frac{(T_{.11})^2}{3} + \frac{(T_{.12})^2}{3} + \frac{(T_{.13})^2}{3} + \frac{(T_{.21})^2}{3} + \frac{(T_{.22})^2}{3} + \\ & \frac{(T_{.23})^2}{3} + \frac{(T_{.31})^2}{3} + \frac{(T_{.32})^2}{3} + \frac{(T_{.33})^2}{3} - \frac{(T_{...})^2}{27} \end{aligned}$$

$$\text{SSB} - \text{SSC}$$

where:

SSBC = sum of squares for interaction between number of plates and plate-free-area

SSB = sum of squares for number of plates

SSC = sum of squares for plate-free-area

T's = previously defined

$$\begin{aligned} \text{SSBC} = & \frac{(145.10)^2}{3} + \frac{(88.45)^2}{3} + \frac{(82.10)^2}{3} + \frac{(118.15)^2}{3} + \\ & \frac{(69.25)^2}{3} + \frac{(47.05)^2}{3} + \frac{(66.70)^2}{3} + \frac{(54.55)^2}{3} + \\ & \frac{(31.27)^2}{3} - \frac{(702.60)^2}{27} = 1478.420 - 1677.038 \end{aligned}$$

$$\text{SSBC} = 223.259.$$

Total Sum of Squares. The total sum of squares was calculated as shown below:

$$TSS = \sum \frac{(T_{abe})^2}{1} - \frac{(T_{...})^2}{27}$$

where:

$\sum (T_{abe})^2$ = sum of squares of all twenty-seven individual stage efficiencies

$(T_{...})^2$ = square of sum of all twenty-seven individual stage efficiencies

TSS = total sum of squares

$$TSS = 22,689.905 - \frac{(702.60)^2}{27}$$

$$TSS = 4,405.651.$$

Sum of Squares for Interaction between Pulse
Amplitude, Number of Plates, and Plate-free-area.

The sum of squares for the interaction between the pulse amplitude, number of plates, and plate-free-area was calculated as shown below:

$$SSABC = TSS - (SSA + SSB + SSC + SSAB + SSAC + SSBC)$$

where:

SSABC = sum of squares for interaction between pulse amplitude, number of plates, and plate-free-area

TSS = total sum of squares

SSA = sum of squares for pulse amplitude

SSB = sum of squares for number of plates

SSC = sum of squares for plate-free-area

SSAB = sum of squares for interaction between pulse amplitude and number of plates

SSAC = sum of squares for interaction between pulse amplitude and plate-free-area

SSBC = sum of squares for interaction between number of plates and plate-free-area

$$SSABC = 4,405.651 - (384.166 + 1478.420 + 1677.038 + 97.997 + 286.227 + 223.259)$$

$$SSABC = 258.544.$$

Degrees of Freedom. Degrees of freedom as used by the statistician can be compared with degrees of freedom in the Gibbs' Phase Equation. However, there is no definite relationship or equation for which the degrees of freedom as used in statistics can be calculated. It is simply understood that a variable of one level has no degrees of freedom while a variable of two levels has one degree of freedom. Therefore, in this investigation each of the single variables (pulse amplitude, number of plates, and plate-free-area) each having three operating levels are understood to have two degrees of freedom. The degrees of freedom for an interaction is the product of the degrees of freedom of each of the variables taking part in the interaction effect. It follows then that there are four degrees of freedom for each of the second order interactions and eight degrees of freedom for the third order interaction of this investigation. All of the above mentioned variables with their respective degrees of freedom are presented in Table VIII, page 113.

Mean Sum of Squares. The mean sum of squares was calculated as shown below. This calculation is illustrated by using the data obtained for the variable, pulse amplitude:

$$MSSA = \frac{SSA}{d f}$$

where:

MSSA = mean sum of squares for pulse amplitude

SSA = sum of squares for pulse amplitude

d f = degrees of freedom for pulse amplitude

$$MSSA = \frac{384.166}{2}$$

$$MSSA = 192.038.$$

Calculation of "F" Statistic. The "F" statistic was calculated as shown below. This calculation is illustrated by using the data obtained for the variable, pulse amplitude:

$$F = \frac{MSSA}{MSSABC}$$

where:

F = "F" statistic

MSSA = mean sum of squares for pulse amplitude

MSSABC = mean sum of squares for interaction between pulse amplitude, number of plates, and plate-free-area

$$F = \frac{192.038}{32.318}$$

$$F = 5.94.$$

Determination of the " $F_{0.95}$ " Statistic. Standard values of the "F" statistic are presented in tabular form as suggested by Dixon and Massey⁽⁹⁷⁾. The two significance levels of the "F" statistic most commonly employed are the 0.95 and the 0.99. The significance level used in this investigation was the ninety-five per cent level. The standard and calculated values of the "F" statistic for each of the variables and interactions of this investigation are presented in Table IX, page 114.

IV. DISCUSSION

The results obtained during this investigation are discussed, recommendations for future work are presented, and the limitations imposed upon the investigation are stated in this section.

Discussion of Results

The discussion of results deals with the design and construction modifications of the pulse extractor, preparation of feed, establishment of flow rates, column operation, steady state conditions, sampling procedure, refractive-index measurements, flow-rate determinations, calculations, experimental errors, design features and operations of the pulse column, and analysis of stage efficiency.

Design and Construction Modifications. It was deemed wise in this investigation to redesign the original pulse column⁽⁴³⁾ so that a more practical and permanent installation could be constructed. Those modifications worthy of consideration will be discussed in this section under the headings, storage, "vacuum-filling" system, column top plate, baffle plates, gaskets, push-rod bearings, lubrication, and protective coating.

The details through which these modifications were executed have been thoroughly considered under the methods of procedure. The reasons for and the results of these modifications only will be discussed in this section.

Storage. In this investigation the four five-gallon glass carboys employed in the original installation for the storage of the feed and solvent were replaced by four ten-gallon stainless steel tanks. This change was made for two reasons - safety and efficiency of operation. First, from the safety point of view, it was necessary to pressurize the four storage tanks with air from the compressor to cause the feed and solvent to move from storage through the flow lines to the pulse column proper. It was found that pressures in the range of forty pounds per square inch, gage were necessary to effect smooth flow rates against the pulsating motion of the bellows at the base of the column. Since glass carboys have been found to explode under pressures exceeding ten to fifteen pounds per square inch, gage, the investigator would risk serious lacerations from flying pieces of glass if he were to employ glass storage tanks for the feed and solvent in this investigation. The stainless steel tanks substituted

for the glass carboys were capable of withstanding pressures up to 500 pounds per square inch, gage; thus eliminating the possibility of explosions and injuries to the investigators. Second, from the point of view of efficient and effective operation, it has already been stated that the stainless steel tanks were capable of withstanding pressures far exceeding the forty pounds per square inch, gage that was found to be necessary for the smooth and even motivation of the feed and solvent to the column. The ability to be able to secure constant flow rates for the feed and solvent is an important factor when attempting to attain steady state conditions. Not only did the ability to maintain higher pressures in the storage tanks make possible smoother motivation of the feed and solvent to the column, but it masked the effect of slight fluctuations in the pressure from the air compressor. At pressures in the range of forty pounds per square inch, gage slight increases or decreases in the air pressure from the compressor did not have a noticeable effect on the flow rates. This also made possible the maintenance of more constant control of the feed and solvent flow to the column. In addition to the above mentioned advantages for the stainless steel tanks, each tank had a

capacity of ten gallons or twice the volume of each glass carboy. This made possible longer continuous operation of the pulse extractor without stopping for storage refilling. The feed storage available (twenty gallons) proved to be adequate for all laboratory scale operations. It was found, however, that the twenty gallons of solvent available would only last for approximately three one-hour tests. It would be advantageous, therefore, to either provide for a larger storage system or devise a method by which one of the two solvent storage tanks could be filled while the other was "on stream". This would provide for even longer continuous operation without the necessity of refilling the storage tanks.

"Vacuum-filling" System. As was discussed previously, under design procedure, a "vacuum-filling" system was designed and constructed into the pulse extraction installation for this investigation. The primary objective of this modification was to eliminate the necessity of drilling and tapping additional holes in the storage tanks, and to provide a more convenient and effective method of filling the tanks. The operating procedure followed in using this system of filling the tanks has already been covered in detail in the methods of procedure, and it may be stated

here that the system was completely successful in accomplishing its purpose. In addition to satisfying the demands placed upon the "vacuum-filling" system it provided an effective method of remixing or agitating the feed mixture stored in the tanks before each experimental test. By creating a vacuum in the feed storage tanks above the liquid level and venting the bottoms of the tanks to the atmosphere through the feed inlet line it was possible to suck air into the bottoms of the tanks and up through the feed mixture. The air bubbling and rushing up through the feed mixture caused sufficient agitation to thoroughly mix the carbon tetrachloride and acetone. The ability to thoroughly agitate the feed mixture immediately before an experimental test without removing it from its storage tank made possible, for successive tests, a feed with a much more consistent composition than would have been practical by any other means available.

Column Top Plate. The flared end at the top of the pulse column (pyrex pipe) had to be removed to allow the insertion of the baffle plates. This introduced the problem of finding a satisfactory method by which the top plate of the column could be secured. The first attempt to a solution of this problem was to wrap the outside of the top of

the pyrex pipe with several turns of friction tape in order to provide an improvised flared end on which a standard glass-to-metal flange could take its grip. This method failed to do the job. As the flange and top plate were clamped together the tape slipped up the column allowing the top plate to become loose and the liquids to leak out between the top-plate gasket and the top of the column.

Next, a steel collar was fabricated to be clamped around the column at a distance of four inches from the top of the column. To construct the collar the back side of a standard glass-to-metal flange was welded to one end of a piece of a 2-1/2-inch pipe three inches long. This arrangement was then sawed into two equal halves parallel to the axis of the pipe. Two pieces of 3/4 by 3/4 by 1/8-inch angle iron, one inch long, were welded to each of the two halves of the pipe; one piece of angle iron was welded on each side of each half of the pipe with one of its faces against the pipe and the other face flush with the edge where the pipe had been sawed. The four pieces of angle iron were arranged along the axis of the pipe so that when the two halves were brought together the two angle iron faces extending perpendicular to the axis on

each side of one-half of the pipe were directly opposite the two angle iron faces extending perpendicular to the axis on each side of the other half of the pipe. Each of these four angle iron faces extending out from the two halves of the sawed pipe were then drilled with one 1/2-inch hole. The column was wrapped with rubber tape at the point where the collar was to be placed. The collar was fitted around the pyrex pipe over the tape and bolted into place by two 3/8-inch bolts two inches long; one bolt through the set of drilled angle iron faces extending out from each side of the collar. The top plate could then be bolted down to the flange which made up the top of the steel collar. This method also failed. If the collar were clamped too tightly around the pyrex pipe the pipe would break, and if it were not clamped tight enough the collar would slip up the glass column and allow the top plate to become loose. This resulted in the same type of leaks encountered in the first method. Several unsuccessful attempts were made to secure the collar to the column without slippage.

Finally, the method of securing the column top plate which is discussed in the methods of procedure was devised. With this method a 1/4-inch stove bolt three inches long

was welded to each end of each of three forty-eight-inch sections of 1/8-inch black iron pipe. The three bolts on one end of these three pieces of pipe were used to clamp together the two flanges holding the bottom of the glass column to the top of the glass tee. The three bolts on the other end of these three pipes were used to clamp the top plate down against the top of the column. This method proved to be completely successful in accomplishing its purpose. The force necessary to clamp the top plate down on the top of the column could be applied and harmlessly absorbed in longitudinal compression of the glass column.

Baffle Plates. The various combinations of the thirty-six baffle plates employed in this investigation were found to be satisfactory for determining the effects of plate spacing and plate-free-area on the stage efficiency of the pulse column. The 3/32-inch perforations in the plates used in this investigation were the same as those employed by Hayford⁽⁴³⁾. The perforations were small enough to hold the heavy phase on the plates against the force of gravity, but large enough to allow the heavy phase to be forced through the plates by the pulsations.

Even though these 3/32-inch perforations proved to be satisfactory for this investigation, it is the author's belief that a more detailed investigation should be conducted to determine the effects of perforation size and shape on the stage efficiency of the pulse column. It would be advantageous to determine the optimum perforation size and shape from both the power economy and degree of separation points of view. The perforation diameters could be varied from 1/32-inch to 3/32-inch, and the shape of the holes could be tested with straight-, conical-, and venturi-type perforations.

Gaskets. It was found⁽⁴³⁾ that cork and silicone were not suitable gasket materials to be used in direct contact with the system carbon tetrachloride-acetone-water. Therefore, in this experimentation teflon was employed as the gasket material. Because of the hardness and inflexibility of teflon considerable difficulty was encountered in clamping the flanges and joints tight enough on the gasket to provide for a liquid-tight seal. The end result, however, was that the teflon proved to be highly successful both in making possible a good liquid seal and in resisting the corrosive effects of the aqueous carbon tetrachloride system.

Push-rod Bearings. The ball bearing races which were designed to provide a bearing surface for the push rod in the original installation were not capable of absorbing the thrust action of the cam on the push rod. It was further explained in the methods of procedure that babbitt sleeve-type bearings were substituted for the ball bearing races in this investigation. It was found that the sleeve-type bearings did provide sufficient bearing surface for the push rod and eliminate the undesirable vibrations that were present in the original design. It is believed that these vibrations had been caused by scored marks on the push rod which were in turn caused by insufficient bearing surface. The author believes, however, that the bellows pulsating mechanism could be greatly improved even now if the push rod and cam assembly were replaced by a drive wheel, connecting rod, and cross-head assembly. This method of pulsating the bellows would eliminate all of the thrust action of the present design, and therefore, decrease the power requirements of the pulse column.

Lubrication. Considerable difficulty was encountered in trying to find a lubricant to eliminate or decrease the frictional effects between the push rod and the cam

surface. Approximately fifty pounds of force were present forcing the end of the push rod and cam surface together. As a result, when greases and oils were applied to the cam surface they were almost immediately scraped off. This resulted in scoring of the cam wheel and vibration of the push rod. A solution to this problem was found in using a "tacky" mixture of machine oil and pure, greaseless graphite. This mixture built up a lubricating film on both metal surfaces which lasted for almost the entire investigation.

Protective Coating. All of the metal surfaces in the pulse extraction installation which came into contact with the liquid system were coated with a phenolic resin. The surfaces were provided with one coat of Phenoline 301 orange primer and one coat of Phenoline 300 finish. Both coats were sprayed on the baffle plates and bellows, while the flanges, column base plate, and column top plate were painted with a brush. It was necessary to spray the baffle plates so that a very thin (0.015 inch) coat could be applied without clogging the perforations. Spraying methods had to also be employed in coating the inside of the bellows, because it was impossible to reach its inside surfaces with a brush. It was found that the protective coating applied in this investigation was completely

successful in eliminating the corrosion that was present in Hayford's experimentation⁽⁴³⁾. This was an important factor not only because it preserved the equipment, but because it made possible the recovery of a clean raffinate product which could be reused in subsequent experimental tests.

Preparation of Feed. In the analysis of a three-component system by physical methods, two different physical properties must be fixed in order to determine the exact composition. Thus, for example, in the system carbon tetrachloride-acetone-water if the refractive index and the density of a sample were known the exact composition of this sample could be found (assuming, of course, that data expressing the relation between the density, index of refraction, and composition were available). Such data have been experimentally determined and recorded by Hayford⁽⁴³⁾. Five of the experimentally determined points of Hayford's data were checked during this investigation and found to be in agreement. For this investigation it was necessary to know that the respective phases were saturated with the third component. A raffinate phase sample with a refractive index of, say, 1.4588 contains 0.49 per cent acetone if, and only if, the sample is also saturated with water. If each phase is not saturated with the third component the

refractive index reading, no matter how accurate, would not give the true composition. It is the author's belief that the error caused by a slight undersaturation with the third component of each sample far overshadows any inaccuracies in determining the refractive index.

In the raffinate-phase and the extract-phase samples very little trouble with saturation should have been encountered. The close and intimate contact of these phases with each other should certainly result in their being saturated with the third component. The feed sample, however, was taken before it had been contacted with solvent in the extractor. Unless some definite precautions were taken to see that the feed was, it probably would not be, saturated with water. In this investigation the feed was prepared by mechanical mixing in the presence of an excess of water.

The magnitude of the error caused by unsaturation may be illustrated by a comparison of the data in Table VI, page 106. The carbon tetrachloride used in this investigation has a refractive index of 1.4628. When the carbon tetrachloride was saturated with water, however, the refractive index was reduced to 1.4594, a difference of 0.0034. This difference is equivalent to an error of about four weight per cent acetone. For the extract phase the refractive indices for the water saturated

and unsaturated with carbon tetrachloride were 1.3330 and 1.3320, respectively. This difference is equivalent to about 2.5 per cent acetone.

Establishment of Flow Rates. Since it was decided that the feed, solvent, raffinate, and extract flow rates should be held constant in this investigation for the entire twenty-seven experimental tests, it was necessary to put the column into operation for several check tests to determine just what solvent to feed ratio would be most applicable for all of the different sets of operating conditions. Initially, a solvent to feed ratio of two to one was employed. It was found, however, that acetone is so easily extracted from a carbon tetrachloride-acetone mixture with water that almost complete extraction was taking place. Under these conditions it would be impossible to determine the effects of the operating parameters by measuring the amount of acetone left in the raffinate, because all of the samples would appear to contain almost the same concentration of acetone. It was therefore decided to purposely decrease the amount of extraction that was taking place by decreasing the solvent to feed ratio. The column was operated with a solvent to feed ratio of one-to-one, and it was found that there was an appreciable amount (0.1 to 2.5 weight per cent) of acetone left in the raffinate.

This being true, it was then possible to determine any changes in the stage efficiency of the pulse column as caused by the twenty-seven individual sets of operating conditions. With this solvent to feed ratio it was also noticed that the column seemed to be operating properly. That is to say, there were no particular evidencies of flooding, dumping, blowing, coning, etc. While the column was operating with the one-to-one solvent to feed ratio it was also noticed that the differential readings of the feed and solvent manometers were two and three inches of mercury, respectively. By maintaining these particular manometer readings throughout all experimental operations in this investigation it was possible to maintain the feed and solvent flow rates constant as was desired. The raffinate flow rate was held constant by observing the level of the interface in the lower disengaging section of the column, and maintaining it constant. Three lines were marked on the glass tee; one line was placed right at the top of the base flange, while the other two lines were placed $1/2$ inch and one inch above the top of the base flange. It was attempted to maintain the level of the interface in the lower disengaging section at the center line without letting it fluctuate above the top line or below the bottom line. By maintaining the interface level constant the raffinate flow rate was held constant. If the feed, solvent, and raffinate

flow rates were held constant the extract flow rate was automatically held constant. This was true because the extract flow consisted of the entire amount of liquid that was forced out of the top of the column. The degree of control and methods of measurement of the feed, solvent, raffinate, and extract flow rates will be covered in detail in subsequent paragraphs.

Column Operation. It was found, in general, that the pulse extractor was relatively easy to operate once it was put into operation and steady state conditions had been obtained. The only adjustments whatsoever that had to be made during operation were those necessary to maintain the feed, solvent, and raffinate flow rates constant. The raffinate flow rate was by far the more difficult to maintain constant. Attempts were made to maintain the flow rate constant to within plus or minus 1.5 per cent by maintaining the level of the interface in the lower disengaging section of the column at a constant level on a predesignated line. Because of the method (interface-level lines on the glass tee) established to determine whether or not the interface level was being held constant, there was a considerable lag from the time that the raffinate flow rate would change until it could be detected. This was bad enough in itself without the fact that the investigators had difficulty in

controlling the raffinate flow rate with the globe valve provided for that purpose. It would be possible to obtain much better actual control of the raffinate flow rate if a needle-type valve were substituted for the globe valve in the raffinate flow line. Two good needle valves should also be substituted for the globe valves which were used as control valves for the feed and solvent flow rates in this investigation. It was not discovered until the investigation was well under way that the valves available did not provide adequate control. To prevent alteration of the apparatus, and therefore the apparatus characteristics, these valves were not changed. The three control valves just mentioned are extremely important if good control over the pulse extractor flow rates is to be obtained. These valves practically determine whether or not steady state conditions can be effectively attained.

It was found that there was an undesirable fluctuation of the mercury in the feed and solvent manometers which at times made difficult an accurate reading of the mercury differential. The fluctuations were caused primarily by the pulsations of the bellows. The author believes that this effect could possibly be eliminated or at least decreased by a system of check valves or air pockets in the feed and solvent lines between the manometers and the column proper.

Steady State Conditions. The method of calculation upon which the stage efficiency is based assumes that the extractor is operating at a "steady state condition." The steady state condition is defined by Colburn and Pigford⁽²⁴⁾ as "that state in which there is no change in composition of either phase at any position with time." For this investigation the steady state condition was defined as that condition obtained within the extractor, when for four successive ten-minute readings, commencing not before two complete liquid changes in the extractor, there was no change in the acetone concentration in either the extract or raffinate stream. By no change the author means that for any of the last four readings there was no greater variation than three units in the fourth place after the decimal of the refractive index measurement, corresponding to 0.2 per cent acetone by weight.

Colburn and Pigford⁽²⁴⁾ present data on the time required to approach to within 99 plus per cent of the steady state condition. The factors they considered important in determining the time required to reach this condition were the number of theoretical stages present in the extractor and the relative flow rate. For the relative flow rate employed in this investigation, approximately two complete changes in the column liquid holdup were required before the steady state condition was reached. Colburn

and Pigford's data assume that the extractor is operating with no change in the composition or flow rate of any of the streams entering or leaving the extractor. They further assume that the extractor is filled with material of the same composition as the feed streams. In an attempt to obtain these conditions in this investigation, the column was drained and refilled before each set of three experimental tests.

The liquid holdup in the pulse extractor was 444 cubic inches. This holdup was divided between the sections as follows: 114 cubic inches contained in the bellows, 176 cubic inches contained in the bottom tee, and 154 cubic inches contained in the column, itself. Of this volume, the heavy phase occupied about 200 cubic inches, while the light phase occupied the remaining 244 cubic inches. Assuming that no acetone was present in the extractor, the heavy-phase holdup was 9.50 pounds and the light-phase holdup was 10.5 pounds. If any acetone had been present, the holdup would have been less because of the decrease in density of the phases as acetone is introduced. For the flow rates used in this investigation, holdup times of 0.083 and 0.100 hour were obtained for the heavy and light phase, respectively. Holdup time is the time required for one complete change of the liquid in the extractor. Therefore, before the first set of

stream samples was taken for any one experimental test the pulse column was left in operation for at least ten or fifteen minutes so as to allow for approximately two complete liquid changes in the extractor. In general, the first four sets of refractive index measurements obtained following this period of preliminary operation indicated that the column was operating at the steady state condition.

A question that naturally arises is whether or not the basis for the steady state condition selected for this investigation is really capable of detecting any significant changes during the operation of the extractor. Although no direct and sound answer can be given to this question, it will be mentioned that the basis for the steady state condition used for this investigation was more exacting than that mentioned in the literature⁽²⁴⁾. It was thus believed that the procedure employed for testing for the presence of the steady state condition was adequate to detect any significant trends in the extractor performance.

Sampling Procedure. The sampling procedure designed for this experimentation was simple and easy to execute and presented practically no possibility for the introduction of errors. All samples were taken directly from the flow lines that carried the streams to and from the column proper. This

assured the investigators of obtaining exact samples of the streams that were actually being employed in the process. The samples were collected in two-ounce sample bottles which had screw-type bakelite caps. The samples were capped immediately upon being secured to prevent the acetone present from partially evaporating. The bottles were thoroughly cleaned with distilled water after each time that they were used to prevent contamination. It is believed that the sampling procedure employed in this investigation was consistent and sound, and that practically no experimental error was introduced into the results by this step of the operation.

Refractive-index Measurements. Refractive-index measurements were made of the feed, raffinate, and extract streams of the pulse column with an Abbe' refractometer which has a range of 1.3000 to 1.7000 with a sensitivity of 0.0002. Even though the fourth decimal place in the refractive-index reading had to be estimated, it is believed that only a very small experimental error was introduced into the results by this operation, and that the small error that was introduced was consistent throughout the entire investigation. The error in measuring the refractive indices of the samples must definitely be considered small in comparison to those introduced by the inaccuracies of reading the refractive index versus acetone composition chart prepared

by Hayford⁽⁴³⁾, and the graphical methods employed for determining the stage efficiencies. When using Hayford's chart, because of the scales employed, it was necessary to estimate the fourth and second decimal places in the refractive-index readings and acetone composition, respectively. It is maintained, however, that the errors introduced by these operations were small and consistent throughout the entire investigation. If this is true the errors are within the limits of experimentation, and since they were consistent they would automatically compensate for themselves in the calculations and probably have no ultimate effect upon detecting the trends of the operational parameters.

There were, however, several cases where special attention had to be given to the results of the refractive-index determinations. The refractive indices for the raffinate samples for six of the experimental tests, 311, 221, 321, 131, 231, and 331, were 1.4595. This would indicate according to Hayford's data⁽⁴³⁾ that the raffinate contained zero per cent acetone by weight. This is, of course, practically impossible. It is possible, however, that there was only a trace of acetone in these raffinate samples, or that a slight error(s) was made either in determining the refractive indices of the samples or in reading the refractive index-acetone composition chart. Regardless of how the error was introduced, it was impossible

to solve for the theoretical number of plates for these particular tests (if there really was no acetone present in the raffinate samples). The upper limit of sensitivity of the refractometer was 0.0002 unit. Since 0.0002 unit corresponds to only 0.2 per cent acetone by weight, it was assumed that there was 0.1 per cent acetone by weight in each of the above mentioned raffinate samples so that the graphical calculations could be executed and the stage efficiencies determined. The author believes that the errors introduced by this assumption, fallacious as it might be, were relatively small and within the realm of experimental error.

Flow Rate Determinations. The feed, solvent, raffinate, and extract flow rates were determined at the completion of each experimental test by collecting and weighing the flow from the respective take-off lines. The materials were collected for periods of five minutes. The author thought that this period of collection was sufficient to absorb any slight fluctuations in the flow rates and provide a fairly accurate estimate of the amount of material used in the previous test. There was, however, the possibility of slight errors in the timing of the collections. This error, if any, is believed to be insignificant since it could not have possibly exceeded plus or minus two seconds. A maximum error of two seconds in the timing of the collections would

constitute only 0.67 per cent of the total period of collection.

The feed, solvent, raffinate, and extract flow rates presented in Table VII, page 109, are averages of the twenty-seven individual values for each of the flow rates. Each flow rate is presented as a range which includes the maximum and minimum value determined for each of the four streams. Since none of the maximum or minimum values constitute more than a 1.5 per cent deviation from the averages, it is believed that the four flow rates were held relatively constant.

Calculations. The calculations in an experimental investigation are often overlooked as a potential source of errors. It is believed, of course, that there are no mathematical errors present in the calculations. However, a large error could easily be introduced if the calculations or the derivation of the relationships used were based upon assumption which did not hold exactly true for the particular case at hand. Further errors could easily be introduced when the solution of the calculations entail the use of experimentally determined plots and graphs whose accuracy is limited. Thus, the following remarks are considered important enough to mention in this discussion.

During the calculation of the stage efficiencies it was assumed that the carrier solvent, carbon tetrachloride, was

immiscible with the extract phase and that the solvent, water, was immiscible with the raffinate phase. The average raffinate phase contained 0.98 per cent acetone by weight and, if saturated, 0.00 per cent water by weight. The average extract phase contained 7.25 per cent acetone by weight and, if saturated, 0.25 per cent carbon tetrachloride by weight. Any errors introduced by the assumption of immiscible phases are certainly negligible when compared to the general experimental errors normally encountered.

The methods of calculating the number of theoretical stages for an extraction process have become quite standardized. The method used in this investigation is the method suggested by Hunter and Nash^(14,45), Elgin⁽²⁹⁾, and Bull and Coli⁽¹⁸⁾. This method of calculating the number of theoretical stages has been found to be accurate within the limits of experimental error. Probably the greatest source of error encountered in this method is the fact that if care is not exercised in constructing the operating lines and in interpolating to find the last fractional stage erroneous values for the stage efficiencies will result. The calculation of the number of theoretical stages for all twenty-seven of the experimental tests was done in a similar manner; therefore, any errors introduced by this calculation are at least consistent.

Because of the relatively high acetone concentration in the extract phase, in comparison with the acetone concentration in the feed mixture, the delta points, used in connection with the graphical calculations of the number of theoretical stages, extended out a considerable distance from the actual triangular plot. Here also a great possibility exists for the introduction of errors into the results. However, a great deal of care was exercised both in locating the delta points and in employing them in connection with the stage-to-stage calculations. Regardless of this fact, the greatly extended delta points obtained in this investigation were surely the greatest possible source of error in the graphical solutions.

In this investigation, stage efficiencies, rather than HETS's were used to evaluate the pulse extractor for two reasons; namely, so that the results of this investigation could easily be compared with the results obtained by Hayford⁽⁴³⁾, and because the use of stage efficiencies does not require the investigator to make any questionable assumptions regarding the actual total active height of the pulse column as is required by the calculation of the HETS. In mentioning stage efficiency, however, it should be clearly understood that the stage efficiency is a property of the stage itself, and not a property of the entire extractor.

In calculating the stage efficiency the use of three different graphical steps were involved. These steps were the determination of the concentration of acetone from the refractive index of a sample, the determination of the equilibrium concentration from the distribution chart, and the graphical solution of the Hunter and Nash plot. In this report the steps are represented by Figures 3, 4, and 8, pages 107, 108, and 116, respectively. For inclusion in this report, however, these figures were reduced in scale. For the actual calculations enlargements of these charts were used, and it should not be assumed that the accuracy of the results of this investigation is based upon the ability to accurately read the examples of the charts presented here. The exact scale used in these enlarged charts was as follows: concentration of acetone for Figures 3 and 4 - one inch equals 0.20 per cent; concentration of acetone for Figure 8 - one inch equals 1.00 per cent; concentration of water for Figure 8 - one inch equals 10.00 per cent; and refractive index for Figure 3 - one inch equals 0.002 unit.

Summary of Experimental Errors. After considering the nature of the possible experimental errors in this investigation it is believed that the principal error was caused by the undersaturation of the feed with water for the pulse extractor. This error, if present, would result in erroneous

low values for the feed compositions. It should be noticed that a low value of the feed concentration causes errors on the safe side. That is, if greater acetone concentrations were used in the calculations, greater stage efficiencies would have been obtained.

It is believed that the other sources of error, such as the operating procedure, the sampling procedure, the flow rate determinations, the refractive-index measurements, the attainment of steady state conditions, and the calculations, introduced only errors of a small magnitude which were within the realm of experimental error expected.

Design Features and Operations of the Pulse Extractor.

Since there are several qualitative observations and notes on the design and operation of the pulse extractor that do not appear in the results of this investigation, time will be devoted to a brief discussion of the points worthy of mention in this section.

Visual Observations and Characteristics of the Pulse Extractor. An attempt will be made to describe the flow pattern for the pulse column. Following each pulse, the heavy phase and the light phase are allowed to settle. After settling, each plate is covered with a layer of the heavy phase. Similarly, underneath each

plate there is a layer of the light phase. During the upward part of the pulse, the light phase immediately underneath each plate is forced up through the plate; upon contacting the heavy phase on the top of the plate the light phase is dispersed into drops. As only a relatively thin film of the heavy phase is present on each plate, the time of passage of the light phase through the heavy phase is quite short. In the return half of the stroke the entire heavy phase on each plate is dropped through the plate. The downward motion of the phases imparts a violent swirling motion to the highly dispersed drops of the heavy phase. Settling of the heavy phase takes place during the pause before the upward half of the next stroke. Visually, it appeared as if the principal agitation took place during the downward half of the pulse.

In the pulse extractor there is no continuous or discontinuous phase in the sense that the word is usually used in extraction. That is, in the pulse extractor there are two principal interfaces, one in the top disengaging section and one in the bottom disengaging section. In between these two interfaces are located the stages,

with the interface present in each stage. In many aspects, however, the heavy phase acts as if it were a dispersed phase passing through the "continuous" light phase. Two important similarities between the heavy phase of the pulse extractor and the dispersed phase of a spray tower will be mentioned. The first similarity involves the flow patterns during flooding. Flooding, in an extractor in which one phase is dispersed, is accompanied by a carry-over of the dispersed phase with the continuous phase. This is true no matter which phase is causing the flooding. In an extractor in which there is no dispersed or continuous phase, flooding is accompanied by the carry-over of the phase not causing the flooding. In the pulse extractor, no matter which phase is causing the flooding condition, the net result of flooding is a carry-over of the heavy phase with the light. The second similarity involves the flow patterns during increased agitation. In extractors in which one phase is dispersed, the dispersed phase moves through a relatively motionless fluid. Any agitation applied to the extractor causes an increased dispersion and motion of the dispersed phase. The additional agitation has relatively little effect upon the continuous phase. In the pulse extractor an increase in agitation seems to affect only

the flow pattern of the heavy phase. In the pulse extractor an increase in agitation results in an increase in the dispersion of the heavy phase on the downward part of the stroke. In extreme cases the heavy phase was so finely dispersed that complete settling had not been obtained before the next pulse. After a few pulses at such conditions, the entire column was filled with a cloudy dispersion of the heavy phase in the light phase. Under these particular sets of operating conditions the top disengaging section was insufficient in length, and the extract phase carried out of the extractor droplets of the feed. The raffinate phase remained clear, however, and was unaffected by the increased agitation. For the operating conditions just mentioned, the extract, after removal from the extractor, settled into two layers. For the pulse extractor used in this investigation mechanical carry-over of the feed with the extract phase occurred at a pulse amplitude of three inches and a plate-free-area of eight per cent.

It should be mentioned at this point that the degree of dispersion of the heavy phase in the light phase increased as the pulse amplitude and number of baffle plates increased and as the plate-free-area decreased. When a plate-free-area of thirty-two per cent was employed the mixing was at a

minimum, and the heavy phase was dispersed in the light phase in spherical droplets about 1/8-inch in diameter. It was apparent that even though these particular baffle plates provided for good heavy-phase holdup (no dumping), there was so much free area on each plate that the plate was unable to offer very much resistance to the passage of the heavy phase; therefore, poor heavy-phase dispersion. As the plate-free-area was decreased, however, from thirty-two per cent to sixteen per cent and then to eight per cent, the degree of dispersion increased. This becomes obvious from the fact that as the plate-free-area of the baffle plates is decreased the resistance to the passage of the heavy phase through the plates is increased. The increased resistance to the passage of the heavy phase through the plates is caused by the decrease in the "plate-passage-area" which in turn caused an increase in the heavy-phase velocity (if the mass flow rates are held constant as they were in this investigation). The increase in the heavy-phase velocity is the factor which makes possible the increased degree of dispersion of the heavy phase in the light phase. It was also found to be true that as the number of baffle plates was increased from four, to eight, and then to twelve,

the degree of dispersion and mixing was increased. Particularly for the tests where twelve plates and three inches of pulse amplitude were employed, the degree of dispersion was very good. It was found that under these conditions, the heavy phase was "pulsed" through two or three plates per pulse cycle, thus providing for a more complete degree of dispersion per stroke.

Bellows. In the design of a pulse extractor considerable thought must be given to the means of pulsating the liquid phases. Two methods that might be used are, one, a constant volume pump modified to permit pulsing, and, two, a bellows equipped with a suitable driving mechanism. In at least one pulse extractor⁽⁶²⁾ in which a pump was used as the means of applying pulsation, trouble was encountered from contamination of the pump's lubricants and from leaks around the shaft seals. It can be stated that no such difficulties were encountered when using a bellows.

Pulsations. For a given frequency and amplitude the nature of the pulse can still differ depending upon the time distribution of the motion. The pulse may operate, for example, with simple harmonic motion with the desired frequency and amplitude. Alternately, the pulse may consist of simple harmonic motion interrupted at each half

stroke to allow settling. These two methods are, undoubtedly, the methods that would first occur to a designer. The construction of a mechanism to apply this type of motion to the bellows is extremely difficult. For this investigation a simple harmonic motion interrupted once during each stroke was used. The retracted, or bottom portion, of the simple harmonic pulse was cut off to allow for settling. The position of the cut-off point varied with the amplitude of the pulse. In fact, the pulse amplitude was selected by varying the cut-off. The motion of the push rod during the experimental studies was up-down-pause and repeat. If the cut-off point were eliminated the motion of the push rod would have been simple harmonic motion with a natural amplitude of about three inches and a frequency depending upon the rotational speed of the cam shaft.

The nature of the time distribution of the pulse used in this investigation had one severe disadvantage. At the start of the upward stroke the acceleration, and hence the force, applied to the push rod approached infinity (except for the deformations of the steel frame, cam, and other structures it would have been infinite). This terrific original force is extremely undesirable in

a commercial model, as it causes injurious vibrations and requires the use of heavier and stronger parts.

Column Holdup. The total liquid holdup was about three times the holdup of the active portion of the pulse extractor. This condition is undesirable in commercial extractors because of the large solvent inventories and equipment sizes required. This large holdup is also undesirable in an experimental extractor because of the greater time required for the steady state condition to be reached. This holdup could be minimized by changing the design of the bottom disengaging section and eliminating the pyrex tee.

The exact column holdup is about twenty pounds. When operating at a pulse frequency and amplitude of 10.5 strokes per minute and three inches, respectively, the holdup amounts to approximately 2.5 per cent of the hourly capacity of the pulse column.

Analysis of Stage Efficiency. Twenty-seven individual experimental tests were made to determine the effects of pulse amplitude, number of baffle plates, and plate-free-area on the stage efficiency of the pulse liquid-liquid extractor. The data from these tests are presented in Table VII, page 109.

The results deduced from these tests are presented in Table VIII, page 113, and Table IX, page 114. A discussion of these data and the statistical analysis made of these data will be presented in this section.

Reasons for the Analysis-of-Variance Test. The stage efficiency of a pulse extractor is a function of a great many variables. During this investigation an attempt was made to hold all of these variables constant with the exception of pulse amplitude, number of plates, and plate-free-area. These three variables were those that were selected to be studied in this experimentation. Under the one-factor-at-a-time method of investigating the effects of three variables one variable would be studied over a given range while the other two variables were held constant. This method is usually not too satisfactory from two points of view; namely, it normally requires the performance of a great number of experimental tests to be able to study one variable under all possible combinations of the other operating parameters, and the investigator can never be certain that he has obtained a true picture of the actual situation (i.e., his apparent results for the effects of a variable might very well be the actual results complicated and masked by the effect or combined effects of

several of the other operating parameters). The above mentioned conditions are undesirable from the points of view of economy of experimentation and reliability of results. Both of these undesirable conditions can be eliminated or at least partially eliminated by resorting to methods of statistical experimental design. By properly designing the experimentation the number of tests required for conclusive results may be decreased merely by investigating the effects of all of the necessary operating parameters simultaneously. In addition, the proper experimental design will enable the investigator to more effectively determine the exact effects of the variables being studied.

For this investigation twenty-seven individual experimental tests were performed so that all possible combinations of each of the three operating levels of each of the three operating parameters could be studied. Statistically, this particular type of experimental design is what is known as a three-level, three-variable, complete factorial design. The statistical method of analysis most applicable for this particular experimental design is the analysis-of-variance test. In this investigation the analysis-of-variance test was employed, and the significance of the effects of the pulse amplitude, the number of plates, the

plate-free-area, and all of the second-order interactions were tested.

It can easily be illustrated just why methods of statistical analysis were necessary for the analysis and correlation of the results in this investigation. The large and apparently random changes in the variables studied made it difficult to estimate from the results which variables affected the stage efficiency and to what extent. By glancing at Table VII, page 109, it is obvious that there are no readily apparent trends in the results. Because of the overlapping variations in the column conditions and the relatively small change in the stage efficiency with large changes in the column parameters, it was essential that the data be analyzed by some method not so open to subjective errors as the usual graphical interpretation of data. The statistical analysis was used as a mathematical tool to aid in the correlation of the results.

Purpose of the Analysis-of-Variance Test. Because of its very nature, the analysis-of-variance test, like other mathematical devices, cannot reveal anything that is not already implicit in the data. In simple cases the experimenter's judgment would lead him to the same conclusions as would be arrived at by the application of statistics.

The value of the latter would merely be to form an objective test for conclusions not liable to bias on the part of the observer. As the complexity of the data increases, however, it becomes more and more difficult to arrive at a reliable conclusion by unaided judgment. In such cases some form of statistical treatment is extremely helpful.

In this study it was desired to determine the effect on the stage efficiency of varying independently each of the three experimental parameters. As stated before, nothing was added to the data, the data were merely analyzed so that the effect of each variable could be studied independently of the other variables. Because of limitations in the equipment and procedure, the effect of the variables could not be separated except by a treatment such as used.

Assumptions in the Analysis. The statistical analysis employed in this report is based upon three assumptions. These three assumptions are that the experimental errors are random without bias, homogeneous, and independent. The first assumption requires that the errors inherent in the experiment vary randomly. It is generally assumed in work of this nature that the errors are random unless there is some reason to doubt this. The second assumption requires

that each experimental test be open to the same source of errors. As no change was made in the procedure of the experimental apparatus during this investigation, no reason was seen for doubting the validity of this assumption. The third assumption requires that the errors in one test be unaffected by the errors in the other tests.

Significance Level. In geometry it might be stated as a hypothesis that the sum of the angles of a triangle is 180 degrees. By accepted procedures of proof it is decided whether this hypothesis is true or false. In this case it is a mathematical proof of the hypothesis, and when the proof has been completed, the investigators are certain as to whether the hypothesis is true or false. In sciences other than mathematics there may be proposed a hypothesis or theory concerning some universe or population of individuals. This is called a statistical hypothesis, and the only way to be absolutely certain about its truth or falsity may be to examine the entire population concerned. This is frequently impractical (or impossible), and the investigators are forced to take a sample from the population and use the sample to make a decision as to whether the hypothesis is true or false. The process of using the sample to 'test' whether the hypothesis is true (or false) is called a statistical proof of the hypothesis.

Unfortunately, there is no "certainty" that a mistake will not be made.

The decision as to whether to accept or reject a hypothesis will be based on the information obtained by making observations and by what risk can be tolerated that the hypothesis may be wrong. The hypothesis must be stated (i.e., a value for a population parameter must be stated). A number of observations (the sample) are collected, and the results obtained are examined to see whether or not they are similar to the population stated in the hypothesis. If the agreement is poor, the hypothesis is rejected. To decide whether there is close agreement or not, some statistic is usually computed and the value obtained compared with the sampling distribution for this statistic under the assumption that the hypothesis is true.

In the previous paragraph it was stated that a hypothesis would be rejected if a value of a statistic occurred which, if the hypothesis were true, would be expected only rarely. Just how rare this occurrence must be for the rejection of the hypothesis, may be chosen as desired. It is called the level of significance and is universally denoted by the Greek letter alpha. Since the value of

alpha may be chosen by the experimenter and its choice will in part determine the acceptance or rejection of the hypothesis, it should be fixed before the experiment is begun. If it is a matter of serious concern when a true hypothesis is rejected, the risk, alpha, of making this error should be made small. If it is of great concern that a hypothesis be rejected if there is only little evidence against it, a larger value of alpha should be chosen.

For this investigation the level of significance, alpha, was chosen as 0.95. This means that 95 per cent of the time the investigator can be assured that he is making the correct decision.

Single-variable Effect on Stage Efficiency. The results of the analysis-of-variance test are presented in Table IX, page 114. It can be seen from this table that the independent effects of the pulse amplitude, the number of plates, and the plate-free-area on the stage efficiency of the pulse column are significant. That is to say that the three variables studied have an important, independent effect upon the stage efficiency of the column. As far as to the extent to which these variables are independently effective, it can be stated that the plate-free-area has

the greatest effect on the stage efficiency while the pulse amplitude has the least effect on the stage efficiency. This conclusion was arrived at by comparing the relative values of the 'calculated "F" statistic.' These values are 25.95, 22.87, and 5.94 for the plate-free-area, number of plates, and pulse amplitude, respectively. All three of these "F" statistics were calculated by comparing the mean sum of squares for each of the three independent variables with the mean sum of squares of the third-order interaction as the error term. This is to say that the three independent variables are significant in comparison with the third-order interaction. This being true, it is understood that each of these three variables plays an important role in determining the stage efficiency of the pulse column.

Second-order Interaction Effects on the Stage Efficiency.

The results of the analysis-of-variance test are presented in Table IX, page 114. It can be seen from this table that the second-order interaction effects between the pulse amplitude and number of plates, the pulse amplitude and plate-free-area, and the number of plates and plate-free-area on the stage efficiency of the pulse column appear to be insignificant. That is to say that the three second-order interactions studied have no important effects upon the

stage efficiency of the column. If a comparison of insignificance can be made, it can be stated that the effect of the interaction between the pulse amplitude and number of plates is the smallest while the effect of the interaction between the pulse amplitude and plate-free-area is the largest. This conclusion was arrived at by comparing the relative values of the 'calculated "F" statistic.' These values are 0.76, 2.21, and 1.73 for the interactions between the pulse amplitude and number of plates, the pulse amplitude and plate-free-area, and the number of plates and plate-free-area, respectively. All three of these "F" statistics were calculated by comparing the mean sum of squares for each of the three interactions with the mean sum of squares of the third-order interaction as the error term. This is to say that the three interactions are not significant in comparison with the third-order interaction. Generally, the effect of a third-order interaction is very small and insignificant if not negligible. If this were true for this investigation, and the second-order interactions were found to be insignificant in comparison with the third-order interaction (as they were), it would be true that the second-order interactions were insignificant as far as the overall operation was concerned. However, there is

no guarantee from the results of this investigation that the third-order interaction effect is negligibly small; therefore, it cannot be assumed that the three second-order interaction effects are insignificant as far as the overall operation is concerned. On the contrary, a study of Figures 5, 6, and 7, pages 110, 111, and 112, respectively, seems to indicate that second- and possibly third-order interaction effects are very much significant. For example, Figure 5, page 110, shows the effect of pulse amplitude on the stage efficiency of the pulse column at the nine different sets of operating conditions. It can easily be seen that practically all nine of the individual curves have a different shape and slope. This is definitely an indication that at least the second-order interaction effects were significant.

In an attempt to further analyze the results of this investigation, it would be interesting to break the results up into a "split-plot" statistical design. By doing this, the investigator would be able to determine whether or not the third-order interaction effect of this experimentation was significant, and in turn check the significance of the three second-order interaction effects.

The details of this method of statistical analysis is beyond the realm of the author's present knowledge of statistics.

Comparison of Results. The literature does not contain any records of pulse column operations as having been analyzed and evaluated by an analysis-of-variance test. It is impossible, therefore, to relate any valid comparisons of results.

Recommendations

On the basis of this investigation the following recommendations are made for future studies on pulse extraction.

Flow Rates. It is recommended that proportioning feed pumps be installed on the equipment. With the use of this type of pump, accurate control of the feed and solvent flow rates would be possible. The selected pumps should have a capacity of at least two gallons per minute. A secondary alternate for the solution of this problem would be to install needle-type control valves in the flow lines carrying the feed and solvent to the column and the raffinate from the column.

Storage. It is recommended that the available feed and solvent storage be increased from the present twenty gallons each to at least fifty gallons and preferably to 100 gallons each. In addition, the flow lines to the two pairs of storage tanks should be rearranged such that one of each of the pairs of tanks could be refilled while the other tank is "on stream." This would allow the extractor to be operated continuously at equivalent flow rates to those used in commercial equipment. For one hour of operation, approximately 400 to 500 pounds of solvent are required at flow rates approaching the flooding

velocity (20,000 pounds per hour-square foot of column cross-section).

Lower Disengaging Section. It is recommended that the lower disengaging section of the pulse column be redesigned so as to eliminate the pyrex tee. This modification would decrease the amount of liquid holdup in the column, and in turn, decrease the relatively large solvent inventory which is required at the present time.

Push-rod and Cam Assembly. It is recommended that the mechanism which imparts pulsating motion to the bellows be modified. A mechanism consisting of a drive wheel, connecting rod, and cross head should be substituted for the present push-rod and cam assembly. This modification would eliminate the cam wheel thrust on the push rod and most of the undesirable frictional forces which are now present. The change would make the pulse column more economically feasible both from the laboratory and commercial points of view because of the decrease in the external power requirements.

Plate Design. It is recommended that experimental tests be performed to determine the effect of the plate design on the stage efficiency of the pulse column. It is recommended that perforation sizes from 1/64 to 1/8 inch in steps of 1/64 of an inch be investigated while the hole shape is varied from straight

to conical and biconical. Besides the perforated plates used in this investigation other types of baffles should be studied. Two other possibilities are the bubble-cap plate and the Koch baffle.

Pulse Time Distribution. It is recommended that experimental tests be performed to determine the effect of the pulse time distribution on the stage efficiency of the pulse column. Further investigations could employ two additional, easy obtainable pulse types; namely, simple harmonic motion and simple harmonic motion interrupted in the middle of the cycle. It is possible that the pulse time distribution used in this investigation (simple harmonic motion interrupted at the end of the cycle) is not the optimum condition.

Refractive-index Measurements. It is recommended that a dipping refractometer be used instead of an Abbe refractometer for the analysis in future investigations. The dipping refractometer will provide five decimal place readings and more accurate results for the very low concentrations of acetone encountered.

Packing. It is recommended that experimental tests be performed to determine the effect on the stage efficiency of placing fine wire-mesh packing between the stages and in the disengaging section to induce coalescence. The effect of this

packing would probably become increasingly important as the plate spacing is increased. Alternately, the baffle plates could be removed and replaced entirely by packing. The column would then consist of alternately packed and unpacked layers. The extreme example of this type of packed extractor is the continually packed pulse column.

Demonstration Systems. It is recommended that as soon as the characteristics of the pulse extractor are adequately determined using the system carbon tetrachloride-acetone-water other demonstration systems be investigated. The system used is expected to affect the stage efficiency of the pulse extractor. With a different system a different plate design and arrangement for the most efficient extraction would probably be required. It is recommended that a system be used in which water is the heavy phase. An example of a system of this type that might be used is the system benzene-acetone-water.

Statistical Design. It is recommended that the results of this investigation be analyzed by a split-plot statistical design. This method of analysis would provide for the results to be investigated from a more complex point of view. Each of the sums of squares would be broken up into single degrees of freedom. A more accurate appraisal of the third-order interaction could be obtained.

Limitations

The limitations placed on the experimental work of this investigation are presented in the following section of this report.

Pulse Column. For this investigation a vertical two-inch pulse extraction column was constructed. The column was supported on a pyrex 4 by 2 by 6-inch tee. The side outlet of the tee was closed and used for the introduction of the solvent and the removal of the raffinate phase. The bottom of the tee was connected to a six-inch syphon bellows. A reciprocating motion was imparted to the bellows by means of a push rod driven by an eccentric cam. No change in the design of the extractor was made during this investigation.

System. The demonstration system used in this investigation was carbon tetrachloride-acetone-water. The direction of transfer of the solute was from the carbon tetrachloride phase into the water phase. The refractive index data for this system used as a means of analysis was determined by Hayford⁽⁴³⁾. These data were determined at 22 °C, the approximate temperature of the extraction apparatus during the experimental tests.

Variables Studied. Twenty-seven individual experimental tests were conducted. The effects of pulse amplitude, number of baffle plates, and plate-free-area on the stage efficiency

of the pulse column were investigated. The pulse amplitude was studied at one, two, and three inches of vertical liquid displacement (as measured in the column proper), while the number of baffle plates was studied with four, eight, and twelve plates. The effect of plate-free-area was investigated with free areas of eight, sixteen, and thirty-two per cent. Three sets of twelve plates were constructed; one set of twelve plates for each of the three plate-free-areas. These free areas were obtained by drilling 36, 72, and 144 holes, each hole $3/32$ of an inch in diameter spaced on $1/4$, $3/16$, and $1/8$ -inch equilateral triangular centers. For all of these tests the maximum variation of the stage efficiency was from 9.41 to 65.85 per cent.

Flow Rates. The feed, solvent, raffinate, and extract flow rates were held constant at 1807, 2211, 1478, and 2299 pounds per hour-square foot of column cross-section, respectively, with a maximum variation in any flow rate of 1.5 per cent.

Operating Temperature. The pulse column was operated at 82 ± 5 °F.

Concentration. The average values for the acetone concentration in the feed, raffinate, and extract were 10.00, 0.98, and 7.25 per cent by weight, respectively.

V. CONCLUSIONS

Extraction, using the demonstration system carbon tetrachloride-acetone-water, was performed in a two-inch experimental pulse extractor. The pulses were applied to the liquids by means of a bellows actuated by a push rod driven by an eccentric cam. Extraction was from the carbon tetrachloride phase into the water phase. The pulse amplitude was studied at one, two, and three inches of vertical liquid displacement, while the number of baffle plates was studied with four, eight, and twelve plates. The effect of plate-free-area was investigated with free areas of eight, sixteen, and thirty-two per cent. This investigation led to the following conclusions.

1. The pulse amplitude, number of plates, and plate-free-area each have a significant independent effect on the stage efficiency of the pulse column; the plate-free-area having the greatest relative effect, while the pulse amplitude has the least relative effect. This conclusion is based upon the "F" statistic values for the pulse amplitude, number of plates, and plate-free-area which are 5.94, 22.87, and 25.95, respectively, as compared to the standard value of the "F" statistic at the 95 per cent level of significance, 4.46.

2. The second-order interactions between the pulse amplitude and number of plates, the pulse amplitude and plate-free-area, and the number of plates and plate-free-area do not have a significant independent effect on the stage efficiency of the pulse column. This conclusion is based upon the "F" statistic values for the interactions between the pulse amplitude and number of plates, the pulse amplitude and plate-free-area, and the number of plates and plate-free-area which are 6.76, 2.21, and 1.73, respectively, as compared to the standard value of the "F" statistic at the 95 per cent level of significance, 3.84.

3. The feed, solvent, raffinate, and extract flow rates that should be employed for satisfactory pulse column operation are 1807, 2211, 1478, and 2299 pounds per hour-square foot of column cross-section, respectively. At these flow rates there was no evidence of flooding, dumping, blowing, coning, or entrainment.

4. The refractive index of solutions of acetone in carbon tetrachloride saturated with water may be expressed by the following equation:

$$n_D^{20} = 1.4594 - 0.0016X$$

where:

n_D^{20} = refractive index of carbon tetrachloride phase

X = acetone concentration, weight per cent.

This equation applies for acetone concentrations from zero to 17.39 per cent by weight.

5. The refractive index of solutions of acetone in water saturated with carbon tetrachloride may be expressed by the following equation:

$$n_D^{20} = 1.3330 - 0.00063Y$$

where:

n_D^{20} = refractive index of water phase

Y = acetone concentration, weight per cent.

This equation applies for acetone concentrations from zero to 26.88 per cent by weight.

VI. SUMMARY

The purpose of this investigation was to redesign, construct, and operate a two-inch experimental pulse liquid-liquid extractor, and to determine the effects of the pulse amplitude, the number of plates, and the plate-free-area on the stage efficiency of the column. The optimum liquid flow rates were also determined.

An examination of the literature was conducted for a review of the available information on pulse extractors. Although a great deal of literature was available on the topic of liquid-liquid extraction, detailed information on only two pulse extractors could be found. The results obtained during this investigation compare favorably with those reported in the literature.

A two-inch experimental pulse-type extractor was constructed. The liquids were pulsed by means of a siphon-type bellows operated by a push rod which was driven by an eccentric cam. For the satisfactory operation of the extractor various auxiliary apparatus was required; important among these were the supporting framework, the push-rod bearing, the reduction train for the cam, the storage tanks, and the tubing and fittings.

Twenty-seven individual experimental tests were conducted, extracting acetone from carbon tetrachloride with water, to determine the effects of the various operating parameters on the stage efficiency of the pulse column. During the experimental tests the following variables were studied: pulse amplitude at one, two, and three inches of vertical liquid displacement; number of plates with four, eight, and twelve plates; and plate-free-area with eight, sixteen, and thirty-two per cent free area.

It was found that the pulse amplitude, the number of plates, and the plate-free-area each have an independent significant effect on the stage efficiency of the pulse column; the plate-free-area has the largest relative effect, while the pulse amplitude has the smallest relative effect. It was further proven by this investigation that the interactions between the pulse amplitude and number of plates, the pulse amplitude and plate-free-area, and the number of plates and plate-free-area have no significant effect on the stage efficiency of the pulse column. The flow rates for satisfactory column operation are 1307, 2211, 1478, and 2299 pounds per hour-square foot of column cross-section for the feed, solvent, raffinate, and extract, respectively.

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Addenda

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IV. VITA



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