# Experimental Determination of Residence Time Distributions on Commercial Scale Distillation Trays Using a Fiber Optic Technique

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**A fiber optic technique for obtaining multiple, simultaneous, point residence time distributions on operating, commercial scale distillation trays is described. The method has sufficient resolution to yield residence time profiles on the tray and to separate tray and downcomer effects. The results indicate severe flow nonuniformities on the tray, which are not accounted for in present models of distillation.**

In the design of any process equipment a decision must ultimately be made regarding expected flow patterns in the device. The nature of the flow is the key to predicting overall conversion rates or efficiencies for the process. Flow pattern data from commercial systems is limited and the designer must frequently rely on idealized assumptions or data from laboratory simulators. Although this information can be very reliable, there always exists some uncertainty regarding the extent to which it accurately reflects the flow behavior in specific devices. This is particularly true when scaling up from pilot plant operations.

In distillation the difficulty of measuring actual flow patterns to verify design assumptions is particularly severe. Accurate determination of flow patterns requires point measurements of residence time distribution (RTD). For numerous reasons not the least of which are safety codes, an experimental method for obtaining such measurements in commercial operations has not been available, although the need for testing the design theories has been apparent for some years.

In lieu of other information the assumption of "plug flow" with a superimposed mixing component has been recommended for purposes of tray design (*1*). In 1934 Kirschbaum (*5*) drew attention to the fact that plug flow conditions were difficult to realize and that significant flow nonuniformities could exist on trays of large diameter. However, this problem has been virtually ignored and attention has been focused on characterizing and correlating the mixing component of the flow. Numerous models have been proposed for the mixing process but with the exception of the residence time model used by Foss et al. (*3*) and Mutzenberg (*7*), Williams (*11*) has shown that they are all interrelated and for simplicity can be expressed in terms of the eddy mixing model. Gerster and co-workers (*4*) used this model to characterize the results of an extensive study of tray mixing which formed the basis for the AIChE tray efficiency prediction method (*1*). In a study of data from 5 commercial columns (*4*), the experimental efficiencies were less than those predicted in 3 cases. The disagreement was considered to be a result of nonuniform flow and consequently one of the restrictions on the AIChE method (*1*) is that the flow must be unidirectional and uniform in accordance with the assumptions used in the development of the method.

In 1959 Fractionation Research Incorporated (FRI) initiated a study in a 4-ft. diam. column, in which the response to a pulse input of dye was monitored at 3 locations by colorimetric analysis of sample streams which were continuously withdrawn from the bottoms of 3 downcomers. The details of this study have been reported by Sakata (*9*). Unsuccessful attempts were made to withdraw sample streams from the tray in order to obtain point RTD's and to separate the tray and downcomer effects. Analysis of the downcomer data, although not conclusive, showed strong evidence of severe flow nonuniformities under virtually all operating conditions.

To supply definitive information regarding the flow patterns on trays a fiber optic system under study at the University of California (*8*) was developed for application to distillation studies. The method required only optical coupling to the column and consequently could be built to meet the safety codes for flammable environments. The technique has been successfully used on both 4-ft. and 8-ft. diam. columns to obtain point measurements of the RTD simultaneously at several points on the tray.

The purpose of the study reported in this paper was to test the fiber optic technique in a large diameter column operating under commercial conditions to determine if it had sufficient resolution to obtain separable point RTD's on an operating tray. The results of this initial study and a complete description of the method are presented in this paper.

The potential applications of the fiber optic system are not limited to the distillation system described here. It may be useful in many situations requiring direct, point observation of residence time distributions in hazardous environments and in hard to reach locations.

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## DESCRIPTION OF THE METHOD

The method is based on the use of fiber optic probes to detect the presence of a fluorescent tracer which has a very rapid activation and decay time. The schema for the method is shown in Figure 1. The fiber optic probe consists of a bundle of very small randomly oriented glass fibers which have a refractive index of 1.62. Each fiber is coated with a layer of glass with a refractive index of 1.52 making the individual glass fibers totally internally reflective. At one end of the probe the fibers are divided into two separate bundles to form a bifurcation.

One limb of this bifurcation is used as a pathway to conduct light from a mercury lamp light source into the liquid. The light leaving the end of the light pipe illuminates a small volume of liquid, exciting any tracer which may be present causing it to fluoresce. A portion of this fluoresced light is then conducted up the second set of fibers, through the second limb of the bifurcation to a photomultiplier tube. The primary and secondary filters are complementary and were selected to prevent the excitation light from reaching the photomultiplier tube. There are no electrical connections to the fiber optic probe. The excitation light source and the detectors are located outside the column and can be constructed to meet explosion proof requirements.

There are several manufacturers who can provide suitable fiber optic light pipes. Those used in this work were

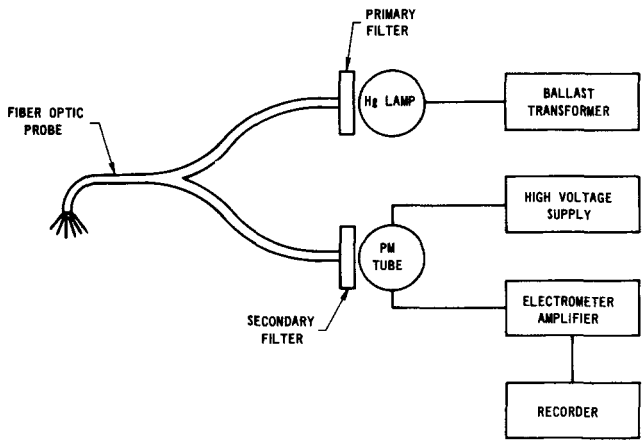



Fig. 1. Schema for the fiber optic detection system.

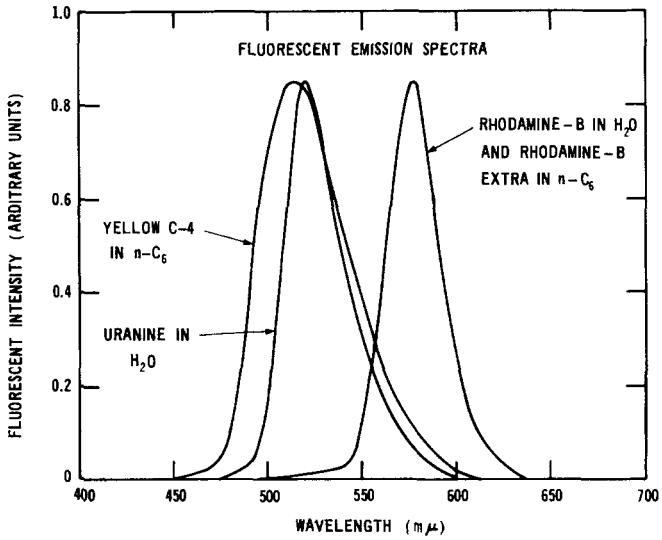



Fig. 2. Fluorescence spectra for the oil and water soluble dye tracers.

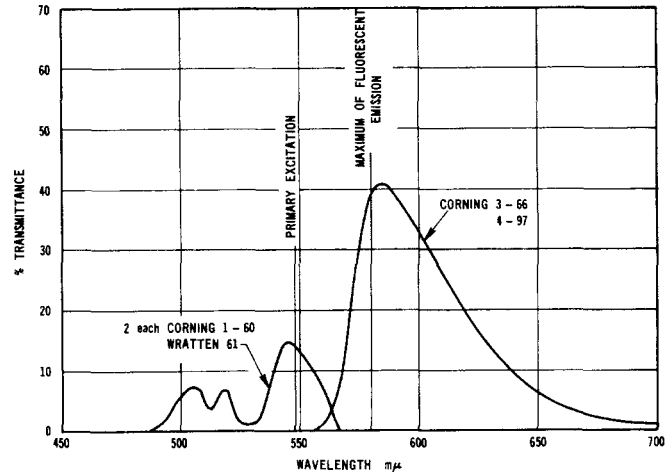



Fig. 3. Transmission spectra for the optical filter combinations to be used with Rhodamine B and Rhodamine-B extra.

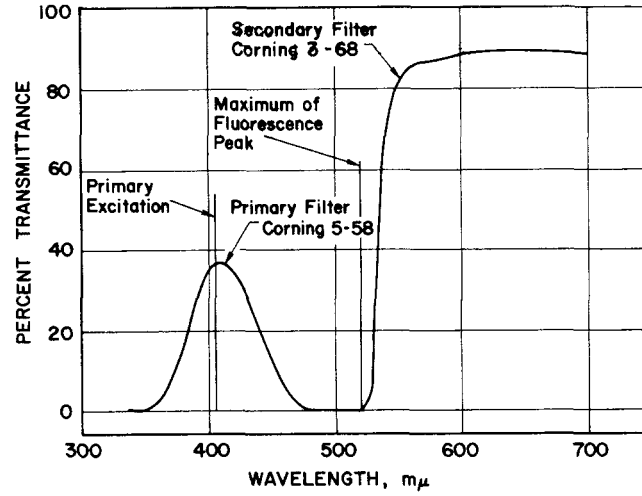



Fig. 4. Transmission spectra for the optical filter combination to be used with Uranine and Yellow C-4.

produced by Dionics Co., Inc., Wakefield, Massachusetts. They can be provided with a wide variety of sheathing materials and configurations. During the course of this study probes sheathed in PVC, flexible interlocking armor, and soft copper tubing have been used. The transmission losses in the bundles are reported by the manufacturer to be 10% per foot but probes 12 ft. long have been used with no difficulty.

## FLUORESCENT TRACERS AND OPTICAL FILTERS

The basic requirement of a fluorescent tracer for this application is that the fluorescent intensity be linearly related to concentration over some range of concentration. Two sets of tracers with different excitation, fluorescence, and solubility properties, as shown in Table 1, have been tested.

The fluorescent emission spectra for these tracers were measured with a Beckman DK-2A Spectrophotometer equipped with a fluorescence attachment and are shown in Figure 2.

The primary and secondary filter combinations for use with these tracers are given in Table 2. The spectra for these filter combinations are shown in Figures 3 and 4.

TABLE 1. FLUORESCENT TRACER PROPERTIES

| Tracer | Excitation line | Fluorescent peak | Solubility | Manufacturer |
|---|---|---|---|---|
| Rhodamine-B | 548mμ | 580mμ | water | General Aniline Corp. |
| Rhodamine-B extra | 548mμ | 580mμ | oil | General Aniline Corp. |
| Uranine | 405mμ | 520mμ | water | General Aniline Corp. |
| Yellow C-4 | 405mμ | 515mμ | oil | Patent Chemicals Corp. |

TABLE 2. OPTICAL FILTER COMBINATIONS

| Tracer | Primary | Secondary |
|---|---|---|
| Rhodamine | 2 ea Corning 1-60 | 1 ea Corning 3-66 |
| | 1 ea Wratten 61 | 1 ea Corning 4-97 |
| Uranine and Yellow C-4 | 1 ea Corning 5-58 | 1 ea Corning 3-68 |
| | | 1 ea Corning 4-97° |

° Not necessary unless there is interference from a red component.

## SIGNAL DETECTION AND EXCITATION LIGHT SOURCE

Signal conditioning amplifiers containing an electrometer and a low pass active filter, were built using operational amplifiers. Despite their relatively low construction cost (about $100) they have been entirely satisfactory. The circuit diagram is shown in Figure 5. The input impedance of the electrometer portion of the circuit is of the order of $10^{11}$ ohms and the filter portion of the circuit has pure first-order characteristics. RCA 931A photomultiplier tubes operating at −1000 VDC were used as detectors.

The excitation light source was a General Electric No. HT 100A4T10GE 100 w. mercury arc lamp powered by a General Electric No. 9T64Y01762 stabilized ballast transformer.

## DETECTION VOLUME

The excitation light leaving the end of the fiber optic probe illuminates a small volume of liquid near the tip of the probe. The size of this volume will depend on the properties of the liquid, the diameter of the light pipe, and intensity of the light source. The volume was estimated in clear liquids using 2 light pipes, one of which was ⅛ in. in diameter and 3 ft. long, and the other which was ¼ in. in diameter and 6 ft. long.

The effective distance which the probe could "see" axially from the end of the probe was determined by filling a blackened beaker with fluorescent solution and measuring the output signal as a function of distance between the end of the probe and the bottom of the beaker. The data for ⅛-in. and ¼-in. diameter fiber optic probes are shown in Figure 6. Beyond about 4 cm. the probe no longer "sees" the bottom of the beaker.

A similar experiment was conducted to find the radial dimension of the detection volume. These results are shown in Figure 7. Beyond a radius of 1 cm. there is no effect from the wall of the container.

From these data and from visual observations of the pattern of illumination it can be concluded that the detection volume in clear liquid has the shape of a frustrum of a cone whose base is 1 cm. in radius and whose height is about 4 cm. In turbid or aereated liquid the dimensions would probably be smaller.

## FLUORESCENT INTENSITY LINEARITY WITH CONCENTRATION

In general the analysis of RTD's depends only on the moments of the RTD, rather than the absolute amplitude. This analysis is discussed in detail by Levenspiel and Smith (*12*), Van der Laan (*13*), Aris (*14*), Bischoff (*15*) and in a review article by Bischoff and Levenspiel (*16*). Therefore, providing that the system is linear and the tracer concentration is in the linear intensity range it is not necessary to calibrate the system with respect to absolute concentration. The linear concentration range was estab-

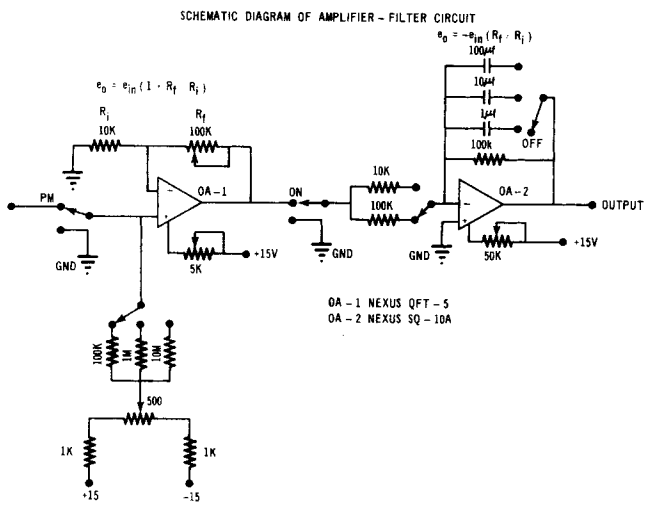



Fig. 5. Circuit diagram for the electrometer/filter amplifier.

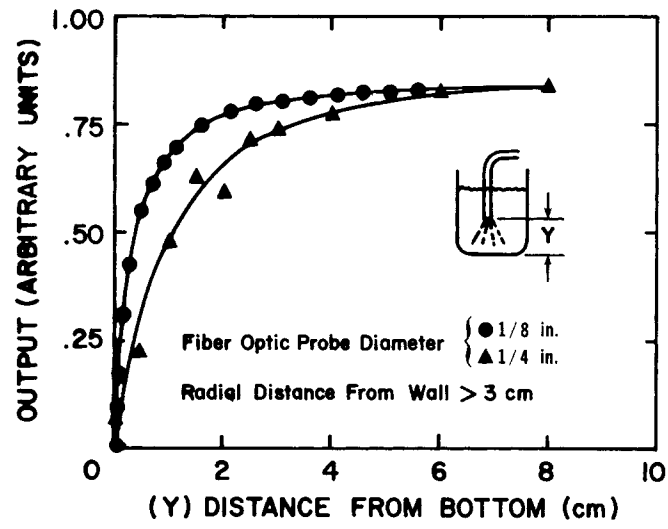



Fig. 6. Fluorescent intensity as a function of axial distance from a wall.

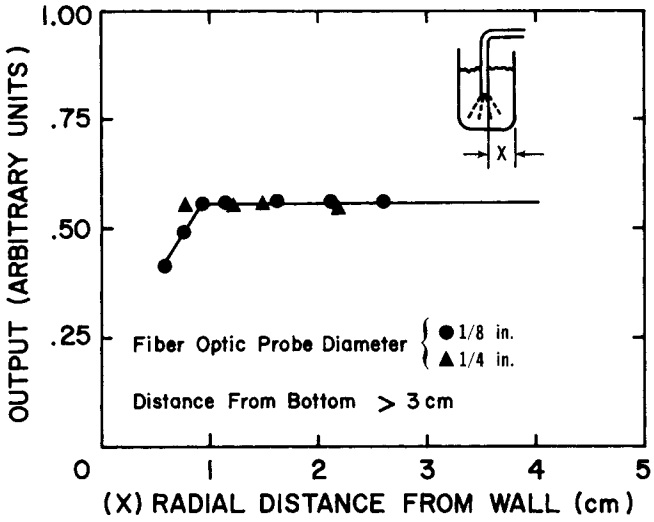



Fig. 7. Fluorescent intensity as a function of radial distance from a wall.

lished by measuring the output obtained by immersing the tip of the fiber optic probe in a tracer solution of known concentration. The volume of solution was sufficiently large that there was no wall interaction. As shown in Figure 8, at high concentration levels Rhodamine B exhibits typical self extinction behavior. At low concentration levels the output is linearly related to concentration up to about 0.4 ppm. Uranine has linear characteristics over a much wider range of concentration as also shown in Figure 8. At higher concentrations uranine exhibits self-extinction characteristics which are very similar to Rhodamine B.

## LINEARITY IN FROTHING SYSTEMS

The above linearity tests were conducted in clear liquid solutions. The ultimate application was in frothy, gas-liquid mixtures on distillation trays. Before going to the commercial scale tests it was necessary to establish that the signal-to-noise ratio was acceptable and that the response of the frothing system was linear.

Simple experiments in an aerated froth showed that for the volume "seen" by the probe, the signal to noise ratio was entirely acceptable. Linearity tests in an 11-in. diam. column simulator were performed with the air/water system. The mechanical details of the simulator are fully described by Baron (2). The probes were installed on the centerline at the inlet and outlet of two adjacent trays and at the inlet of the third tray. With the air and water flowrates to the water simulator held constant, a measured volume of tracer solution was injected into the inlet water line at the top of the column during a fixed interval of 1.0 sec. The response from each of the 5 probes in the column was recorded on a strip chart record. The peak heights as a function of tracer concentration, corrected to the superficial concentration at the tracer injection point are shown in Figure 9. The gain of the amplifiers was 10.0 and the probes are numbered starting with the probe furthest from the water inlet.

The reduction in signal strength going down the column is primarily due to dilution although there is some effect from local froth conditions. The absolute magnitude of the output signal will also depend on both liquid and gas flowrates. It is clear that there is a linear response with concentration in the froth on an operating tray. This fact received further verification during the commercial scale column tests where it was found that over a wide range of inlet dye concentration, the moments of the RTD were identical.

## EXPLORATORY EXPERIMENTS IN THE FRI 4-FT. DIAMETER SIEVE TRAY COLUMN

The commercial scale exploratory experiments were conducted in the Fractionation Research Incorporated, 4-ft. diam., high pressure column. The column contained 14% hole area sieve trays with ½-in. holes, a 2-in. outlet weir and segmental downcomers which occupied 13% of the column area. The system used was steam/water at 1 atm. pressure. In the exploratory experiments only two probes were used. The axes of the probes were oriented 1½ in. above the tray floor, on the tray centerline, parallel to the tray floor and perpendicular to the direction of flow. In one series of experiments the probes were located at the inlet of the tray and at the outlet weir. In a second series they were located at the outlet weir and at the bottom of the following downcomer. The change in the

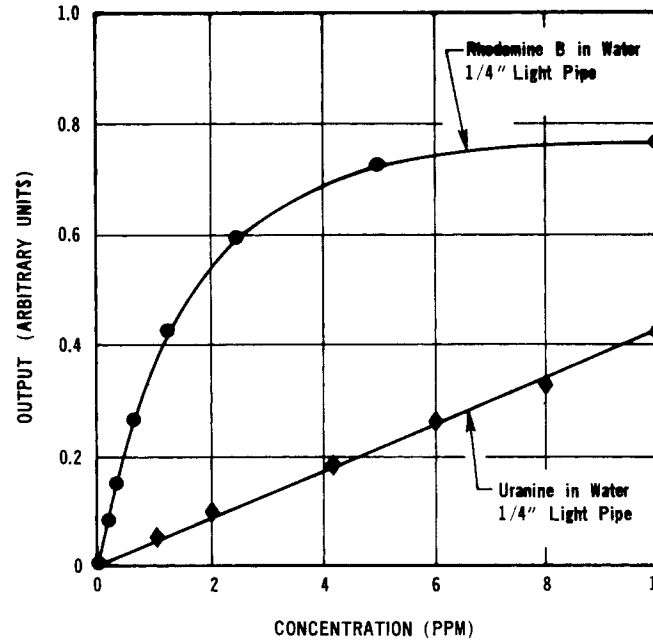



Fig. 8. Fluorescent intensity of Rhodamine B and uranine in water solution as a function of concentration.

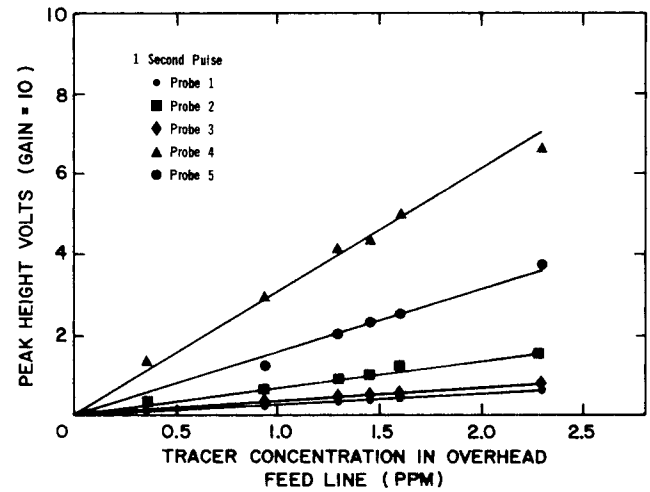



Fig. 9. Peak heights as a function of concentration (corrected to superficial tracer inlet concentration) from the 11-in. diam. air/water column simulator.

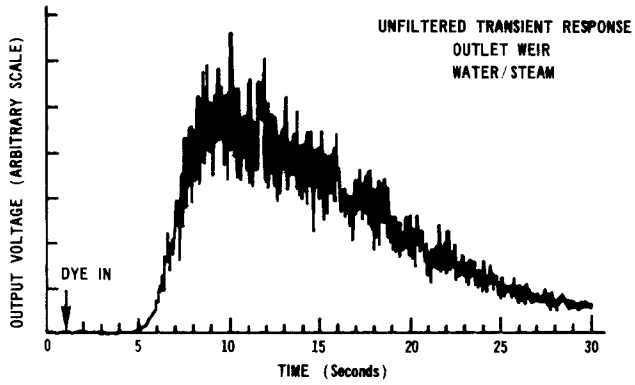



Fig. 10. A typical unfiltered RTD from the 4-ft. diam. column experiments.

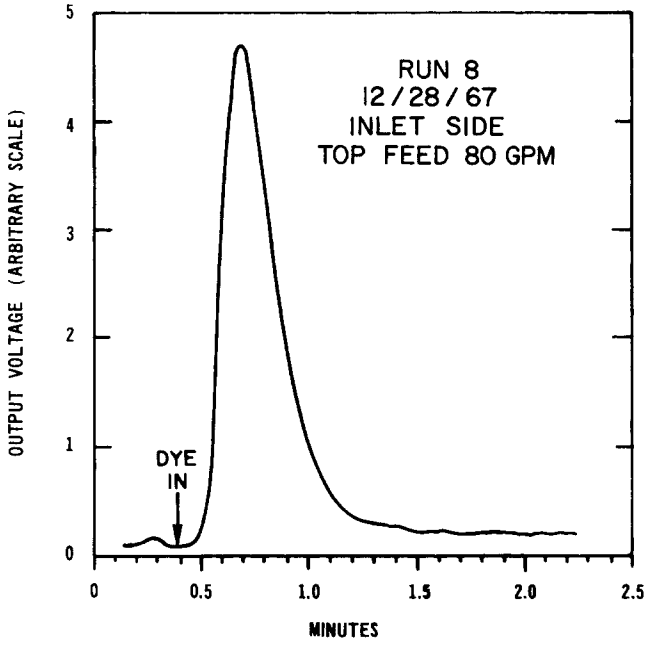



Fig. 11. A typical filtered RTD at the inlet of the 4-ft. diam. tray.

RTD was therefore independently measured both across the tray and through the downcomer. Since the detection volume was small compared to the volume of liquid on the tray the measurements can be considered "point" measurements.

A 250 cc. high pressure bottle was filled with a 10 g./L solution of Rhodamine-B and pressurized to 100 lb./sq.in. gauge with nitrogen. The dye was injected by opening an air operated motor valve between the dye bottle and the column and the entire contents of the bottle were forced into the downcomer on the top tray. The probes were mounted on the third tray from the top. The signal to noise ratio of the RTD's varied depending on where the probe was placed on the tray.

## ANALYSIS OF THE RESIDENCE TIME DISTRIBUTIONS

A typical unfiltered RTD is shown in Figure 10. To remove the high frequency noise component, a time constant of 1 or 10 sec. was used in the active filter. The time constant was chosen to be relatively small compared to the time scale of the experiments, but any effect of the time constant was removed in later analysis by virtue of system linearity.

After removal of the high frequency noise component, the response distribution at the tray inlet and the bottom of the downcomer were virtually noise free. A typical RTD obtained at the tray inlet is shown in Figure 11. These distributions could be precisely reproduced from one run to another and from day to day.

The RTD's obtained at the outlet weir contained a low frequency noise component which was not removed by filtering. A typical set of four replicates obtained at the outlet weir is shown in Figure 12. The method of treating these RTD's is similar to that used by Foss (3). If the data were sampled at discrete intervals and it is assumed that the measured RTD is the sum of the desired "true" RTD and a randomly fluctuating noise component $C_{fn}(t)$, then the $n^{th}$ replicate at time $t_i$ can be written as

$$C_n(t_i) = C_0(t_i) + C_{fn}(t_i) \tag{1}$$

The sum of $N$ replicates is then obtained as shown in Equation (2)

$$\sum_{n=1}^{N} C_n(t_i) = \sum_{n=1}^{N} C_0(t_i) + \sum_{n=1}^{N} C_{fn}(t_i) \tag{2}$$

If $C_{fn}(t_i)$ is a randomly fluctuating quantity then it follows that

$$\lim_{N\to\infty} \sum_{n=1}^{N} C_{fn}(t_i) \to 0 \tag{3}$$

In practice this term becomes sufficiently small for some finite number of replicates ($M$) which reduces Equation (1) to Equation (4).

$$\sum_{n=1}^{M} C_n(t_i) = M\, C_0(t_i) \tag{4}$$

The true RTD can then be obtained as shown in Equation (5).

$$C_0(t_i) = \frac{1}{M} \sum_{n=1}^{M} C_n(t_i) \tag{5}$$

Therefore, all that is required to recover the true RTD is to sum a sufficient number of replicates. This method of treating noisy signals is frequently called "the method of average transients."

The data shown in Figure 12 were replicated four times on each of two separate days. Each set of 4 replicates was treated as suggested by Equation (5) and are plotted together in Figure 13. It can be seen that with only 4 replicates the data were highly reproducible which suggests that the value of $M$ required in Equation (5) is a relatively small number. It should be noted that between

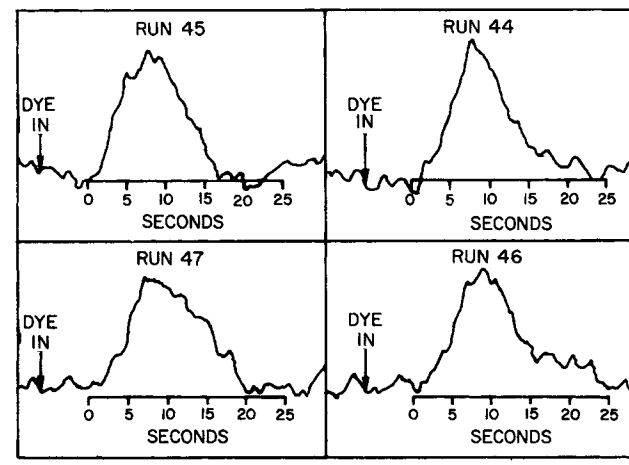



Fig. 12. Typical filtered RTD's at the outlet weir of the 4-ft. diam. tray.

the 2 sets of 4 replicates shown in Figure 13 the column was shut down and the position of the probes was changed from the inlet-outlet configuration to the outlet-downcomer configuration.

A troublesome characteristic of the RTD curves is that any noise or error in the tail of the distribution can result in significant errors in the computation of moments. Experience has shown that RTD's almost invariably exhibit an exponential decay over a wide portion of the tail of the distribution. Accordingly, the parameters of the exponential were determined by a weighted least squares technique (*6*). The moments of the RTD were then obtained by a numerical integration to the point at which exponential decay started, followed by an analytic integration to infinity using the exponential. This method has proven to be reliable and yields highly reproducible values for the moments. The exponential behavior of the average of the data in Figure 13 is shown in Figure 14.

## RESULTS OF THE EXPLORATORY STUDIES IN THE FRI 4-FT. DIAMETER COLUMN

The most important objective of the exploratory study in the 4-ft. column was to determine if the method had sufficient resolution to obtain separable point RTD's on an actual tray and to see if the mixing and residence time data for the tray and downcomer could be separated.

The parameters chosen for characterizing the data were

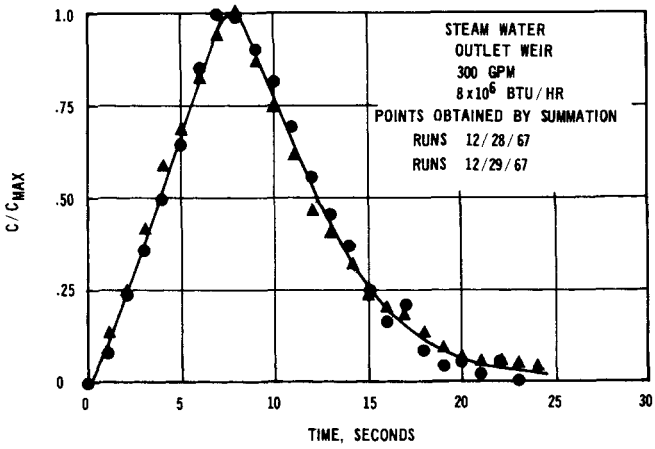



Fig. 13. Comparison of RTD's obtained by summing 4 replicates obtained on seperate days at the same conditions.

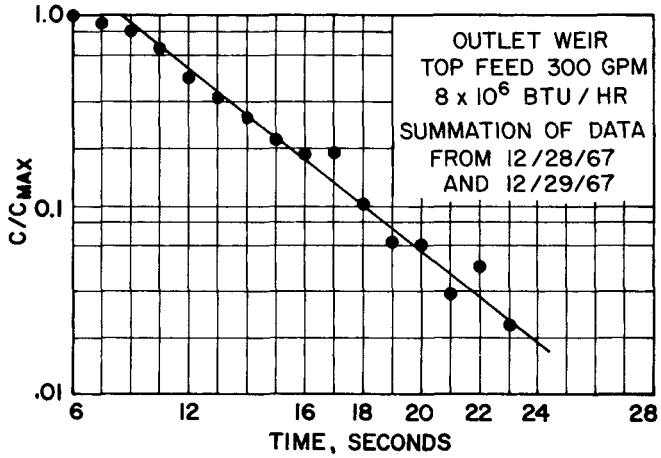



Fig. 14. The exponential behavior of the data from Figure 13.

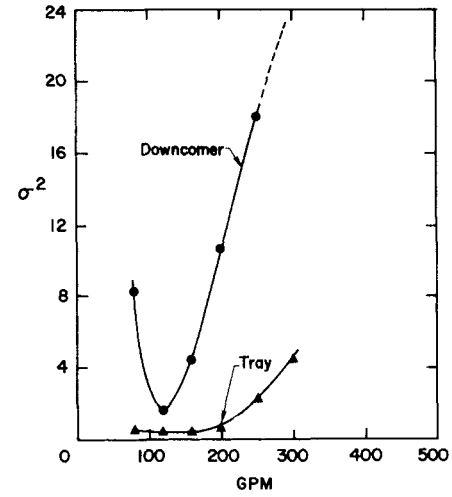



Fig. 15. Dimensionless second central moment as a function of liquid rate for constant boilup.

the mean residence time $\theta$ and the change in the dimensionless variance $\sigma^2$ between two points, as defined by Equations (6), (7), and (8).

$$\theta = \frac{\int_0^\infty t\, C_0(t)\, dt}{\int_0^\infty C_0(t)\, dt} \tag{6}$$

$$S^2 = \frac{\int_0^\infty (t-\theta)^2\, C_0(t)\, dt}{\int_0^\infty C_0(t)\, dt} \tag{7}$$

$$\sigma^2 = \frac{S^2_2 - S^2_1}{(\theta_2 - \theta_1)^2} \tag{8}$$

$S_i^2$ is the dimensional (time$^2$) second central moment of the RTD at position $i$ and $\theta_i$ is the corresponding mean residence time.

The data ($\sigma^2$) from the 4-ft. column experiments is plotted as a function of liquid flowrate at constant gas rate in Figure 15. These data demonstrate that the system does have the resolution necessary to separate tray and downcomer effects.

An interesting feature of these data is that the mixing intensity on the tray is less than that found in the downcomer. The results obtained by Thomas and Campbell (*10*) from a tray-downcomer simulator when converted to the $\sigma^2$ used in this paper show greater mixing intensity on the tray than in the downcomer. Consequently, general conclusions regarding downcomer and tray effects cannot be reached at this time. The extent of mixing in the downcomer will clearly be related to downcomer and weir design.

## EXPERIMENTS IN THE 8-FT.DIAMETER COLUMN

The steam/water data from the 4 ft. column suggested that the method had sufficient resolution to determine lines of constant residence time and second central moment on a tray. The 8 ft. diameter column operating with a hydrocarbon system was used to see if this could be done. Nine probes were installed in a 3 × 3 array on one-half of an 8 ft. sieve tray. A 10th probe was installed in the geometric center of the following downcomer. The probes were sheathed in 5/16 in. soft copper

tubing and passed through packing glands in a flange. The mercury arc lamp and the detector housings were air purged to meet safety codes. The air purge was also necessary to cool the mercury arc lamp.

The analog signals from the amplifiers were multiplexed and digitized with an IBM 1070 system. The data were then transmitted over telephone lines to an IBM 1130 computer where the data were translated from the IBM code and a deck of data cards was prepared for subsequent data analysis.

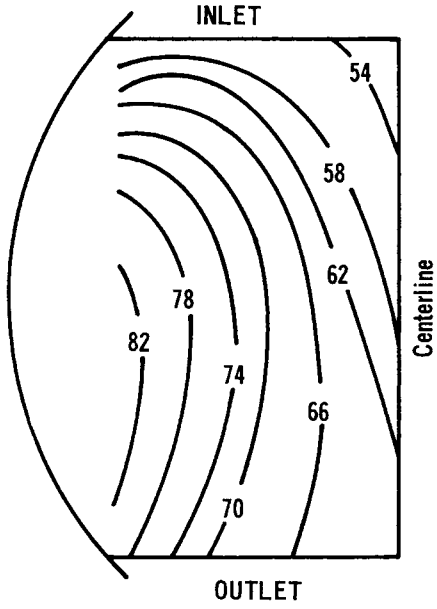
The data from these experiments were treated in a manner similar to that outlined for the 4-ft. column experiments with one exception. It was found that most RTD's were sufficiently smooth that moments could be obtained for each replicate. The results were then averaged and an estimate of absolute reproducibility was obtained. Between replicates the average percent standard deviation of the mean residence times [$\theta$, Equation (6)] was 1.84% and the percent standard deviation for the second central moments [$\sigma^2$, Equation (7)] was 11.2%. The mean values were compared to the results obtained by summing Equation (5) and the percent difference between the two methods was typically 0.5% for both mean residence times and second central moments. A typical set of lines of constant residence time, taken at total reflux conditions is shown in Figure 16 for the toluene rich end of the cyclohexane-toluene system. The results of a complete study of the 8-ft. sieve tray will be presented in a subsequent paper.

## DISCUSSION AND CONCLUSIONS

It has been demonstrated that the fiber optic system reported in this paper is an effective tool for obtaining point residence time distributions on operating distillation trays. It can be constructed to meet safety codes and can be adapted for use in high pressure columns by using a high pressure optical window. The results obtained with the system are reproducible both within a set of replicates and between sets of data obtained many days apart.

Using this method mixing on the tray can be separated from that in the downcomer. The results from the initial experiments showed that the trays under study were not meeting the assumptions of the present tray efficiency model. If the flow were uniform and unidirectional the lines of constant residence time would be evenly spaced and parallel to the tray inlet. The data also show a region of short residence time along the centerline and a region of long residence time near the wall, indicating a condition of severe channelling. It would be fortuitous if methods for predicting tray efficiency based on mixing data from narrow simulators in which flow nonuniformity did not exist would accurately predict the efficiency of these trays.

The extent to which these conditions exist on other trays and in columns of other diameters and the causes for this behavior are currently under study.




Run 9748, $F_S$ = 0.568, GPM = 120

Fig. 16. A typical residence time profile at total reflux conditions for the toluene rich end of the cyclohexane-toluene system.


## ACKNOWLEDGMENT

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## NOTATION

$C_{fn}(t)$ = the fluctuating noise component of the RTD
$C_n(t)$ = the $n^{th}$ replicate of the RTD
$C_0(t)$ = the "true" RTD
$M$ = number of replicates required for the sum of the fluctuating components to be small
$N$ = total number of replicates
$S^2$ = dimensional second central moment (time$^2$)
$\sigma^2$ = dimensionless second central moment of $C_0(t)$
$\sigma_i^2$ = dimensionless second central moment at position $i$
$t$ = time
$t_i$ = time of the $i^{th}$ discrete sample of the RTD
$\theta$ = mean residence time, first moment of $C_0(t)$
$\theta_i$ = mean residence time at position $i$

**Subscripts**

1 denotes downstream location
2 denotes upstream location

## LITERATURE CITED


1. "Bubble Tray Design Manual; Prediction of Fractionation Efficiency," Am. Inst. Chem. Engrs., New York (1958).
2. Baron, R. J., M.S. thesis, Univ. of Calif., Davis (1969).
3. Foss, A.S., J. A. Gerster, and R. L. Pigford, *AIChE J.*, **4**, 231 (1958).
4. Gerster, J. A., A. B. Hill, N. N. Hochgraf, and D. G. Robinson, *Tray Efficiencies in Distillation Columns Final Report,* Univ. of Delaware, Newark (1958).
5. Kirschbaum, *E. Forsch. Gebiete, Ingen.*, **5**, 245 (1934).
6. Mickley, H. S., T. K. Sherwood, and C. E. Reed, "Applied Mathematics in Chemical Engineering," McGraw, New York (1957).
7. Mutzenberg, I. A., *Chem. Ing. Tech.*, **34**, 8 (1962).
8. Paine, C., and R. Bailey, *Design of a Photometric Detector,* Sr. Research Report, Univ. of Calif., Davis (1967).
9. Sakata, M., *Chem. Eng. Progr.*, **62**, 98 (1966).
10. Thomas, W. J., and M. Campbell; *Trans. Inst. Chem. Engrs.*, **45**, T64 (1967).
11. Williams, B., J. W. Begley, and C. H. Wu; *Tray Efficiencies in Distillation Columns,* Final Report, Univ. of Mich., Ann Arbor (1960).
12. Levenspiel, O., and K. W. Smith, *Chem. Eng. Sci.*, **6**, 227 (1957).
13. Von der Laan, E. T., *ibid.*, **7**, 187 (1958).
14. Aris, R., *ibid.*, **9**, 266 (1959).
15. Bischoff, K. B., *ibid.*, **16**, 128 (1961).
16. ———, and O. Levenspiel, *ibid.*, **17**, 257 (1962).



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