described. Only small volumes are required and relatively large samples (about 0.20 gram of alkaloid) are readily extracted.

Place sufficient solvent to cover the sintered plate in the device, introducing it through the inner funnel. Accurately weigh a sample equivalent to approximately 0.20 gram of morphine alkaloid and dissolve it in approximately 50 cc. of dilute hydrochloric or sulfuric acid. Quantitatively transfer the solution to the extractor through the side opening, using approximately 25 cc. of wash water.

Place 50 to 75 cc. of solvent and a few Carborundum chips in the boiling flask and connect flask to the extractor. Drop sufficient ammonia to render the solution faintly alkaline through the inner funnel and connect the condenser. Distill the solvent rapidly through the solution until a sample of solvent removed (through the side tube by means of a pipet) from the upper layer in the extractor is found by a suitable test (Marquis reagent) to be free of morphine. The presence of sufficient ammonia in the solution may be confirmed at the same time by holding a piece of wet litmus paper in the vapor escaping from the side tube. When extraction is complete (0.5 to 1 hour) disconnect the boiling flask, evaporate the solvent, and titrate the alkaloid in the usual way.

Under the conditions described there is a volume increase of 20 per cent in the aqueous layer due to solubility of isopropanol. The addition of ammonia in the prescribed manner renders the solution alkaline at the same time that solvent is available to extract the liberated alkaloid. This is of consequence in morphine extraction and presumably also in other cases.

The simple analytical procedure outlined is, of course, useful only where interfering substances are absent. When this is not the case, the extractor becomes even more useful. Morphine can be separated from many other alkaloids, for example, by dissolving the mixture in dilute acid, rendering the solution distinctly alkaline with sodium hydroxide, and extracting with benzene to exhaustion. The solution is acidified, then made alkaline with ammonia, and the morphine removed in fresh mixed solvent (benzene-isopropanol). A method for opium assay based on this procedure is now under consideration in this laboratory.

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Perforated Plate Columns for Analytical Batch Distillations

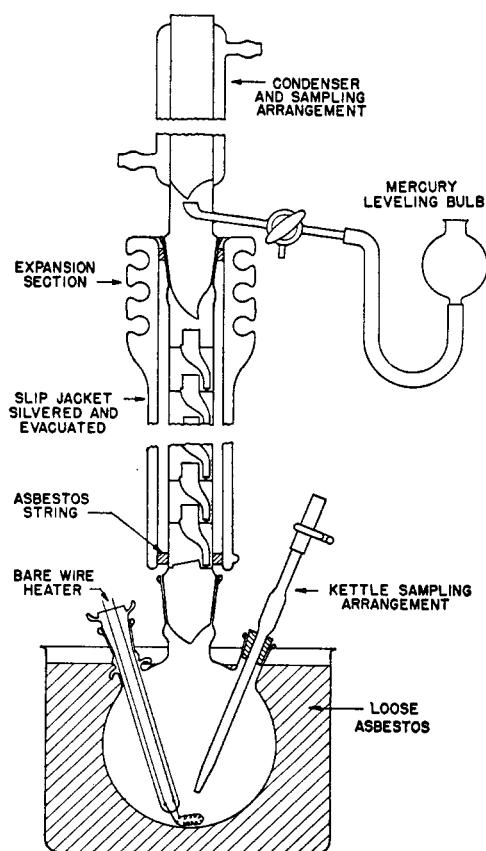C. F. OLDERSHAW, Shell Development Company, Emeryville, Calif.

FIGURE 1. PERFORATED PLATE COLUMN

ACCURATE analytical batch distillations have become increasingly important during the past few years. Of the many different columns tested in these laboratories for this purpose, the perforated plate column described in this paper has been found to be of especial value for the analysis of hydrocarbon mixtures. It combines a low operating holdup per theoretical plate and a negligible static, or nondrainable holdup, with a high capacity or reflux rate. It has a low H. E. T. P., is easy to operate, and since it is constructed entirely of glass, may be used for corrosive liquids.

Description of Column

The column (Figures 1 and 2) consists of a series of perforated glass plates sealed into a tube. Each plate is equipped with a baffle to direct the flow of liquid, a weir to maintain a liquid level on the plate, and a drain pipe. The first plate in a series serves as a small reservoir which is necessary in order to maintain a liquid seal for the drain pipe from the first regular plate.

Construction

The plates are constructed in the following manner: A tube which later will form the baffle is placed in a lathe and rapidly rotated. The protruding end of the tube is heated in an oxygen flame and flared to form the disklike portion of the plate. The perforations are then drilled with a red-hot tungsten wire. This operation, which is ordinarily somewhat time-consuming when done by hand, is now entirely performed by an automatic drilling device designed in these laboratories for the purpose. The hot tungsten wire forms a small burr on the plate which is removed with an ordinary file. After the drilling operation the plates are examined and only those having perforations of uniform diameter and spacing are selected for use. The selected plates are ground to size; if they have been correctly flared, the grinding is a minor operation.

The drain pipes are sealed in place and shaped as shown in Figure 3, and a bead 0.5 mm. high is made on the lower end of each to regulate the distance between the drain and the plate below. The baffle tube is cut off at the desired height above the plate, and two longitudinal cuts are made with small high-speed
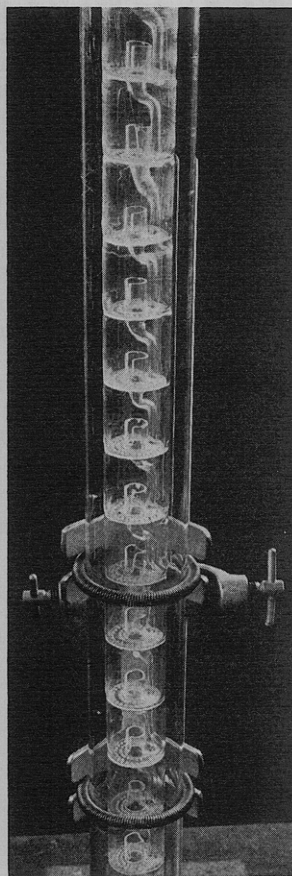
FIGURE 2. SECTION OF PERFORATED PLATE COLUMN SHOWING DETAILS OF PLATE CONSTRUCTION

emery wheels correctly spaced on a shaft. The intervening segment of the baffle is then cut off 1 mm. above the plate to form the weir. The plates are made up in large batches and carefully annealed between operations, when necessary, to remove strains. The finished plates are examined for imperfections.

The selected plates are then carefully sealed into a tube, so that each plate is level and the bead on the bottom of each drain pipe rests firmly on and in the center of the unperforated section of the plate below. The bottom of the pipe is placed sufficiently close to the plate below to ensure a liquid seal under normal operating conditions. The drain pipe is tapered from top to bottom to prevent vapor bubbles from being trapped by the overflowing liquid.

The column may be insulated in a number of ways. A slip jacket of the type shown in Figure 1 has been developed and is generally preferred in these laboratories. The jacket has a narrow window running its entire length through which the operation of the column may be observed.

Testing the Column

PLATE EFFICIENCY. Plate efficiencies were determined at several reflux rates on four columns, Nos. 1, 2, 3, and 5.

Columns 1, 2, and 3 are 25 mm. in diameter. Each plate in column 1 has 42 perforations, 0.85 mm. in diameter; those of column 2 have 44 perforations, 1.1 mm. in diameter; and those of column 3 have 44 perforations, 1.35 mm. in diameter. The plate spacing is 25 mm. in columns 1, 2, and 3. Column 5 is 32 mm. in diameter. Its plates have 81 perforations, 0.85 mm. in diameter, arranged in three concentric circles. The plates are spaced 30 mm. apart in the column to give greater flexibility of operation. A carbon tetrachloride–benzene mixture prepared from redistilled Baker's c. p. chemicals was used in these tests.

In the plate-efficiency tests, the compositions of still-head and kettle samples were determined by the method of refractive index.

Still-head samples were withdrawn by means of the special still head shown in Figure 1. The mercury leveling bulb was lowered, thereby drawing some liquid through the three-way stopcock, the stopcock was then turned, and a few drops of sample were forced out by raising the mercury level. The remainder of the liquid in the line was then forced back into the column by displacing it with mercury. Kettle samples for the tests on columns 1, 2, and 3 were withdrawn by means of the pipet shown in Figure 1. However, in testing column 5, samples were taken from the bottom plate of the column instead of the kettle by means of the reflux rate and holdup measuring device shown in Figure 5. This apparatus is similar to that described by Bragg (1).

The plate efficiencies were determined by the method of McCabe and Thiele. In order to determine when equilibrum was obtained, still-head samples were analyzed at intervals. When successive samples showed constant composition, still-head and kettle samples were taken simultaneously and analyzed. The number of theoretical plates was determined from a diagram constructed from the vapor-liquid equilibrium data of Rosanoff and Easley (5). The kettle was taken as equal to one theoretical plate; therefore, the numbers of plates in columns 1, 2, and 3 are given as one less than the total number found. The method of sampling used in testing column 5 gave directly the number of plates in the column.

REFLUX RATE. The reflux rates at which the plate-efficiency tests were made were determined on columns 1, 2, and 3 at the end of each test by simply replacing the sampling still head with the total take-off head shown in Figure 4 and measuring the liquid collected in a given time. The reflux rate and holdup measuring device shown in Figure 5 was used in all tests on column 5. Therefore, the reflux rates at which plate efficiencies were determined on column 5 were measured by simply closing the stopcock in the reflux return line. In this case the volume was determined at the boiling point of the liquid. The results of these tests are given in Table I.
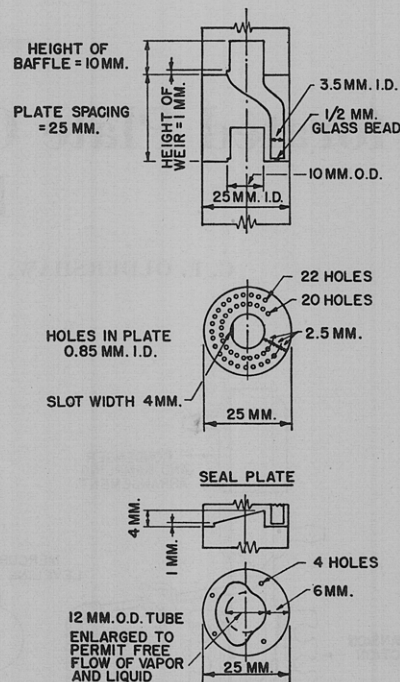

FIGURE 3. PLATE CONSTRUCTION

OPERATING HOLDUP. Operating holdup was determined at several reflux rates on columns 4 and 5. Column 4 is identical with column 1 except that it has 37 actual plates instead of 10. The reflux rate and holdup apparatus (see Figure 5) was used in these tests; Baker's c. p. benzene was used as the test liquid. The reflux rates were determined in the manner described above. The operating holdup was determined by closing the stopcock in the reflux return line and shutting off the heater simultaneously, thus allowing the liquid in the column to drain into the graduated portion of the apparatus. This method of determining the holdup was made possible by the negligible heat capacity of the bare wire immersion type heater. (This type of heater has been found very satisfactory for distilling materials that are not affected by platinum or chromel resistance wires. It is sensitive to control, constant in operation, and presents essentially no fire hazard.) The volumes were measured at a temperature very near the boiling point of the liquid. The results are given in Table II.

TABLE I. EFFICIENCY TESTS

Reflux Rate		CCl₄ Kettle	Still head	No. of Theoretical Plates in Rectifying Section (Total Plates − 1)	Plate Efficiency	H. E. T. P.
Ml./min.	Moles/min.	Mole %	Mole %		%	Inches

Column 1, 10 25-mm. plates, 42 0.85-mm. perforations per plate

6	0.065	15.4	44.0	10.0	100	0.98
13	0.141	16.7	42.5	8.9	89	1.10
18	0.195	19.0	45.2	8.8	88	1.12
24	0.260	16.7	42.0	8.6	86	1.14

Column 2, 10 25-mm. plates, 44 1.1-mm. perforations per plate

15	0.162	18.0	43.0	8.4	84	1.17
26	0.282	18.0	41.0	7.7	77	1.28
28	0.304	18.0	40.5	7.5	75	1.31

Column 3, 10 25-mm. plates, 44 1.35-mm. perforations per plate

12.5	0.136	14.8	37.5	7.8	78	1.26
23.5	0.255	14.8	34.5	6.7	67	1.47

Column 5, 32-mm. plates[a], 81 0.85-mm. perforations per plate

		Below plates	Still head	No. of Theoretical Plates in Column		
18.3	0.190	18.6	57.4	15.3	102	1.16
36.8	0.381	21.2	55.1	13.0	87	1.36
39.0	0.404	17.0	50.3	12.7	85	1.39
52.0	0.540	17.0	48.0	11.7	78	1.51
55.5	0.575	17.0	47.4	11.5	77	1.53
70.5	0.730	19.2	46.8	10.3	69	1.71

[a] Plates spaced 3.0 cm. apart in column.

TABLE II. TESTS OF HOLDUP AND REFLUX RATES

Reflux Rate		Holdup in Column
Ml./Min.	Moles/min.	Ml.

Column 4, 37 25-mm. plates, 42 0.85-mm. perforations per plate

9	0.094	20
14	0.146	26
22	0.229	53
28	0.292	58
40	0.417	67

Column 5, 15 32-mm. plates, 81 0.85-mm. perforations per plate

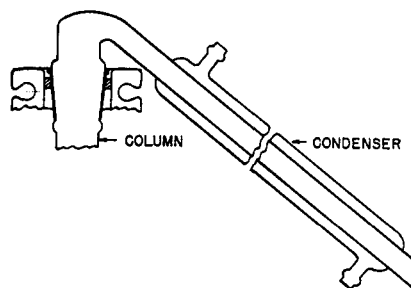|		
17	0.177	14
28	0.292	38
52	0.542	40
75	0.782	45

FIGURE 4. TOTAL TAKE-OFF STILL HEAD

instead of the holdups were determined by extrapolation.

The reflux rates in moles per minute were calculated from the molar volumes of the liquids and the reflux rates in milliliters per minute. The molar volume of benzene at 80° C., the approximate temperature at which the volumes were measured, was calculated from the molar volume at 20° C. by means of the data given by Perry (4) on the coefficient of thermal expansion. For mixtures of carbon tetrachloride and benzene and of ethylene dichloride and benzene, the molar volumes were determined from graphs of molar volume vs. molal composition. In calculating the molar volumes at the approximate boiling points of the mixtures it was assumed
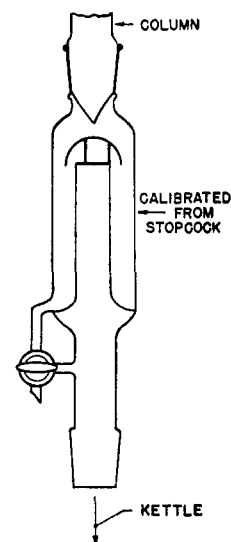

FIGURE 5. REFLUX RATE AND HOLDUP TEST APPARATUS

The performance data in Table III have been calculated from the data given in Tables I and II and Bragg's data (1) on the Stedman type packing which has been included for purposes of comparison. Similar data on columns of the helix-packed type (3, 7, 8) could not be calculated from the information given in the literature. Data on the Bruun column (2) were also omitted, since the operating holdup was not given for a specified reflux rate.

PRESSURE DROP. The pressure drop per theoretical plate was not measured; however, it is to be expected that the pressure drop per theoretical plate in a plate column will be higher than that in a packed column. The maximum pressure drop may be calculated approximately from the density of the refluxing mixture, the plate spacing, and the plate efficiency. Thus, for a mixture whose density is 0.8 at its boiling point, and which has a plate spacing of 25 mm. and a plate efficiency of 80 per cent, the maximum pressure drop per theoretical plate would be approximately 1.8 mm. of mercury.

Methods of Calculating Data

The plate efficiencies given for column 4 in Table III were determined by extrapolating and interpolating those found for column 1 to the molal reflux rates at which operating holdups were determined. The operating holdups given for column 5 in Table III were determined by interpolating those given in Table II. In the case of the highest and lowest reflux rates given for column 5 in Table III, the plate efficiencies

TABLE III. PERFORMANCE OF PERFORATED PLATE AND STEDMAN TYPE PACKED COLUMNS

Reflux Rate		No. of Theoretical Plates in Column	Plate Efficiency	H. E. T. P.	Total	Holdup Per theoretical plate	Per theoretical plate per 100 ml. of reflux per min.
Ml./min.	Mole/min.		%	Inches	Ml.	Ml.	Ml.

Column 4, 37 25-mm. plates, 42 0.85-mm. perforations per plate

9	0.094	35.1	95	1.04	20	0.57	6.4
14	0.146	32.9	89	1.10	26	0.79	5.7
22	0.229	32.2	87	1.13	53	1.65	7.5
28	0.292	31.8	86	1.14	58	1.83	6.5
40[a]	0.417	30.0	81	1.21	67	2.23	5.6
							Av. 6.3

25-mm. Stedman column, 24 inches of packing 112

3.33	0.0394	43.8	...	0.55	13	0.30	8.5
6.67	0.0790	34.8	...	0.69	22.4	0.64	9.3
8.33	0.0985	31.1	...	0.77	24.0	0.77	8.8
11.65	0.138	29.5	...	0.81	27.0	0.92	7.6
15.0	0.177	26.3	...	0.91	33.0	1.25	8.0
16.7	0.197	24.6	...	0.98	34.0	1.38	8.0
18.0[a]	0.213	24.2	...	0.99	35.8	1.48	7.9
							Av. 8.3

Column 5, 15 32-mm. plates[b], 81 0.85-mm. perforations per plate

17.0	0.177	15.5	103	1.14	14	0.90	5.3
18.3	0.190	15.3	102	1.16	17	1.11	6.2
36.8	0.381	13.0	87	1.36	39	3.00	8.1
52.0	0.542	11.7	78	1.51	40	3.42	6.6
70.5	0.730	10.3	69	1.71	44	4.37	6.2
75.0[a]	0.782	10.0	67	1.76	45	4.50	6.0
							Av. 6.4

[a] Maximum reflux rate.
[b] Plates spaced 30 mm. apart in column.

that the coefficient of thermal expansion of the mixtures was the same as that for benzene.

TABLE IV. COMPARISON OF PERFORATED PLATE WITH STEDMAN TYPE PACKED COLUMNS

	25-Mm. Perforated Plate Column	25-Mm. Stedman Column
Holdup ml. per theoretical plate per 100 ml. of reflux per minute (average)	6.3	8.3
Reflux rate, mole per min., maximum	(0.094)[a]-0.417	(0.039)[a]-0.213
H. E. T. P., inches	1.04-1.21	0.55-0.99

[a] This figure represents reflux rate at which the low H. E. T. P. was determined and not minimum reflux rate of column.

In calculating the holdup per theoretical plate per 100 ml. of reflux per minute, the reflux rate was taken as an average of that at the top and bottom of the column by assuming that the variation in rate was due to the change in molar volume with composition; changes in rates due to variation in heats of vaporization were neglected. The average reflux rates in milliliters per minute calculated in this manner for mixtures of ethylene dichloride and benzene were 4 per cent higher than those given by Bragg. It has been learned through private communication that the volumes of holdup reported by Bragg were measured near the boiling point of the liquid, and consequently no correction for expansion has been made.

Discussion of Data

SIZE OF PERFORATIONS. The data in Table I show that at comparable reflux rates the plate efficiencies decrease with an increase in the size of the perforations, and that with perforations of a given size the plate efficiencies vary inversely as the reflux rate. An examination of the data on plate efficiencies to be expected in the 25-mm. columns at a reflux rate of 0.25 mole per minute gives the following results:

0.65-mm. perforations, 90% by extrapolation
0.75-mm. perforations, 88% by extrapolation
0.85-mm. perforations, 86%
1.1-mm. perforations, 79%
1.35-mm. perforations, 68%

The 0.65-mm. perforations could be expected to increase the plate efficiency by 4 per cent over that of the recommended 0.85-mm. perforations, but on the other hand, the pressure required to force vapor through smaller perforations against the surface tension of the liquid is higher. Therefore it is necessary to increase the spacing of the plates and consequently to increase the H. E. T. P. The use of perforations larger than 0.85 mm., however, was found to decrease the flexibility in reflux rate.

The plate spacing of 25 mm. recommended for column 1 represents actually a compromise between flexibility and H. E. T. P. In the case of column 5, which was built for continuous as well as batch distillations, a plate spacing of 30 mm. was used because flexibility was considered to be of greater importance than a low H. E. T. P.

HOLDUP AND COMPARISON OF PERFORATED PLATE WITH OTHER TYPES OF COLUMNS. It may be seen from Tables II and III that the operating holdup per theoretical plate varies with the reflux rate. However, if the holdup per theoretical plate is divided by the reflux rate in milliliters of liquid per minute, a practically constant value is obtained. Now if the capacity or maximum reflux rate of the columns is expressed in moles per minute, a useful basis for the comparison of batch distilling columns of different design is established. For example, a comparison of the perforated plate column with the Stedman column by this method gives the results of Table IV.

Of the three factors given above, the holdup per theoretical plate at a fixed reflux rate is the most important in choosing a column for analytical batch distillations, since it determines the minimum volume of liquid which must occur as intermediate fractions between two essentially pure components. Thus the minimum intermediate fraction which must exist in the Stedman column would be approximately 32 per cent larger than that in the perforated plate column if both were operated at the same reflux rate. It follows that, if intermediate fractions of equal size are desired in both cases, the perforated plate column could be operated at a higher reflux rate, thus decreasing the time required to effect the separation. The actual volume of the intermediate cut could be decreased in both the perforated plate and the Stedman columns by decreasing the reflux rates. A detailed discussion of the effect of holdup and also of the effect of reflux ratio in batch distillations is given by Rose (6).

The figures obtained for reflux rate and H. E. T. P. show that the 25-mm. perforated plate column has a somewhat greater H. E. T. P. than the 25-mm. Stedman column and that the perforated plate column has a higher maximum reflux rate or capacity. Comparison with the helix-packed type of column (8) shows that the perforated plate column has a lower average holdup per theoretical plate per 100 ml. of reflux per minute. Comparison with the Bruun column (2) shows that the perforated plate column has a higher plate efficiency at high reflux rates. Since the liquid drains readily and practically completely from the perforated plate column, it is superior in this respect to the Bruun column.

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