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# THE APPLICATION OF MODERN DISTILLATION EQUIPMENT IN ANALYTICAL CHEMISTRY

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## INTRODUCTION

Distillation is one of the principal methods to be used in the isolation, purification, and identification of volatile compounds. It is normally the most simple of all separation methods since the only parameters which need be varied are temperature and pressure. It is among the cheapest, since even the most expensive stills are less costly than the preparative scale chromatographic devices that are frequently used to isolate pure compounds. Even though distillation has these obvious advantages, the modern scientific community frequently overlooks the full potential of the use of the technique. A primary reason for this is that there is little organized distillation information available, despite the fact that intensive distillation research has been conducted over the past half-century; since each researcher generally reports primarily to his own peer group. The bulk of this research has been performed in the field of chemical engineering and; though the developments of theory, principles, and refinements in equipment

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and technique could be of tremendous interest and benefit to the analytical chemist, little cross-communication occurs! As a result of this, many scientists who could utilize these multiple advantages of reduced cost and operator time, and increased product purity, are unaware of the separating potential of modern fractional distillation units. Recent development in the science have resulted in the availability of laboratory scale units which revolutionize this former alchemists' mode of separation.

## MODERN HIGH-EFFICIENCY LABORATORY STILLS

The high efficiency units described here are most ideally used to provide pure or purified materials on a small scale, where the sample size is typically 5 to 50 ml or sometimes less. Effective separation of these small portions requires that the holdup of the still be small, that material loss or decomposition be prevented, and measurement and control be accurate.[1] A good laboratory still should have low holdup to reduce cross-contamination between fractions and minimize sample requirements, low pressure drop to insure that the pot charge need not be superheated simply to achieve boilup, high throughput to allow rapid collection of purified fractions, and of course, high efficiency so that maximum purity can be attained in the shortest amount of time.

The stills often found in the analytical laboratory are usually single-plate simple stills or packed column units. The basic advantage of these is low initial cost. They both have several significant disadvantages. The simple still is just that: simple. It cannot provide pure fractions of materials with boiling point differences of less than 30 to 50°C and thus is good

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for only the most basic cleanup and purification operations. The packed column still can provide highly efficient separations, but requires large volumes of liquid to coat the inner surface before full separating capability is obtained.[2] (Recall that the separating efficiency of a distillation system depends entirely upon the amount of contact which occurs between the ascending vapor and descending refluxed liquid.) Since partitioning can only occur at the vapor-liquid interface, to gain high separating power a tightly-packed column must be used. This then in turn provides a complex torturous path to the rising vapors. This has several drawbacks, e.g., high-pot temperatures are required to provide the thermal energy necessary to overcome the high-back pressure of the partially-trapped vapor and the distillation is of necessity extremely slow. A 100-plate packed column frequently yields only several drops per hour of purified material.[3] Higher efficiencies require even tighter packings which in turn provide even higher back pressures and slower throughputs.

Several types of stills have been designed to provide high efficiency without the disadvantages of the packed column. One is the concentric tube column where the center of long narrow distillation column is filled with a tube, leaving only the doughnut-shaped annular space (usually only about 1 mm wide) for vapor to rise in. Refluxing liquid falls down both sides of the ring allowing frequent vapor-to-liquid contact.[4] Some models have spiral grooves formed in both walls to further increase liquid-holding capacity.[5] Stills of this type can have over 75 theoretical plates with almost no pressure drop and provide purified material at rates of several milliliters per hour.[6]

Probably the most commonly used modern high efficiency stills are the spinning band type (Figure 1).[7] In spinning band stills

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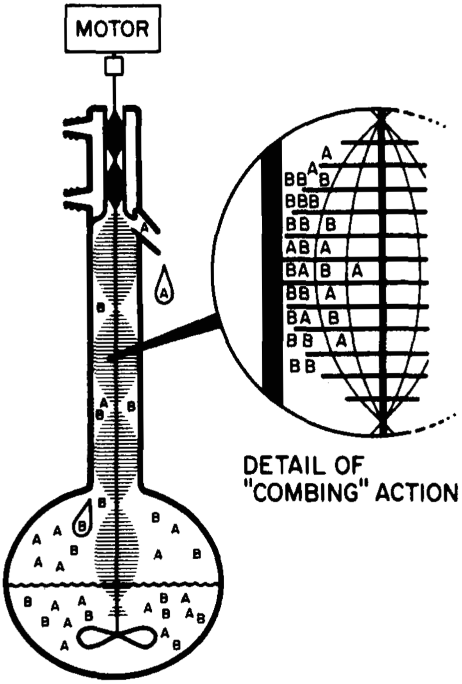

FIGURE 1

Schematic of a metal mesh spinning band still.

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a tightly-fitted band is rotated inside a long narrow column. The descending reflux on the walls of the column is constantly stirred by the edges of the band and the rising vapors are both mixed and thrown into the liquid by the vigorous spinning action. The resultant high amount of vapor-liquid contact provides separating efficiencies of up to 45 plates with throughputs of hundreds of milliliters per hour. Pressure drop is almost non-existent since the vapor has a continuous path from the pot to the head of the still. Band materials are usually of metal mesh or twisted material, and bands are usually wrapped in a spiral fashion, so that the turning action results in a downward pumping action. This helps prevent flooding, allows operation at extremely high boilup rates and contributes significantly to the high throughputs achieved with these systems.[8] Band materials are chosen for their resistance to corrosion, with stainless steel, monel, gold-plated monel and platinum, the most frequently used. Other recent models employ a material with extremely high corrosion resistance -- teflon. Another property of teflon, namely its self-lubricating capability, is utilized in these stills, where the band is normally made to provide a tight-fitting flat surface which wipes the column walls. This wiping exposes a maximum amount of liquid to the hot vapor. Efficiencies over four times those of non-polymer bands are achieved.[9] The polymer is wrapped on a solid center shaft which is normally composed of the same material, and the resulting annulus provides the same narrow vapor channel as is found in concentric tube columns.

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## APPLICATIONS OF ANNULAR DISTILLATION

An early form of the annular spinning band still was the 8 mm x 26" column seen in Figure 2. The most pertinent feature is the provision of the motor-driven helicaly-wound teflon band (2) which is responsible for the 150 - theoretical plate performance that results from the high degree of vapor-to-liquid contact as the band is rapidly rotated. An evacuated silvered outer jacket is incorporated to render the still adiabatic. That is, the column neither gains nor looses heat. In fact, a bellows must be provided to allow the isolated outer jacket to expand and contract as the inner column to which it is fused flexes thermally.

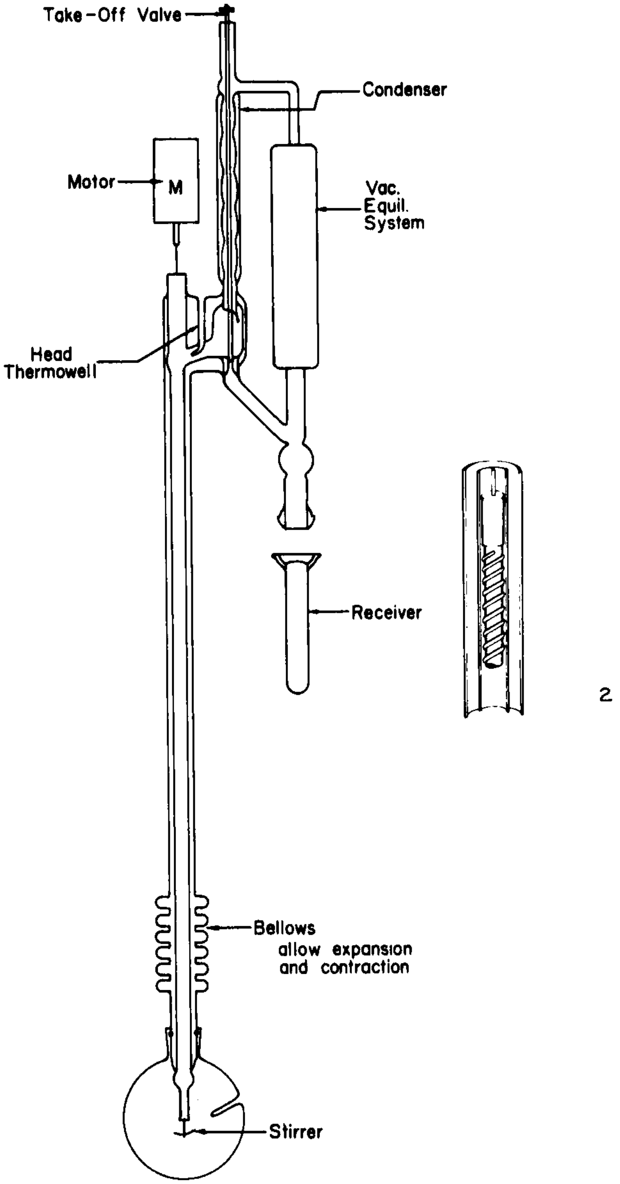

FIGURE 2

Cross section of an annular teflon spinning band still (1) and close up showing band construction (2).

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The operating principles of the Teflon spinning band still are visualized in Figure 3, where the high degree of vapor-to-liquid contact is shown.

This still was capable of separating the Nerol-Geraniol mixture seen in Figure 4, providing 7 grams of pure Nerol and 10 grams of pure Geraniol in less than 10 hours of distillation. The separation was carried out at a pressure of 3 mm of mercury. This allowed the 226 °C atmospheric pressure boiling point to be dropped

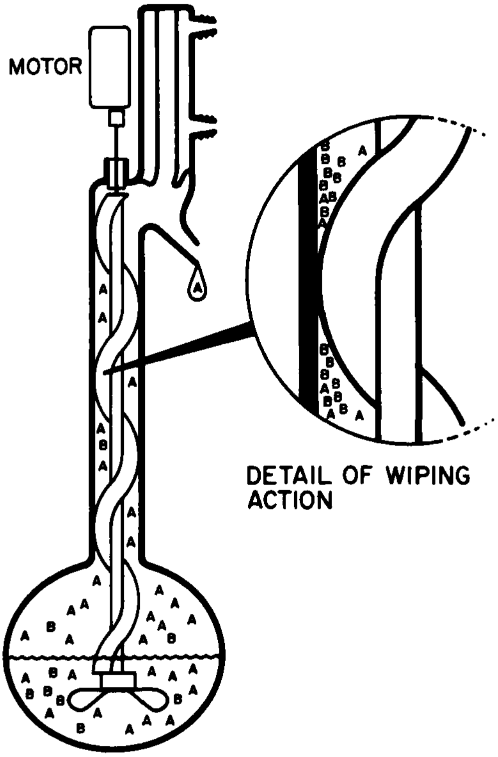

FIGURE 3

Schematic of an annular teflon spinning band still.

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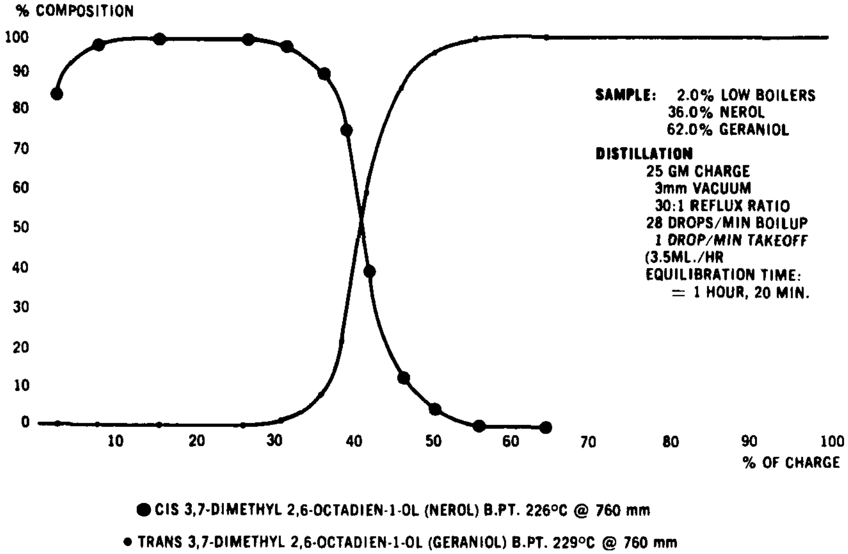

FIGURE 4

Graph of Nerol-Geraniol separation performed on a 150 theoretical plate teflon spinning band still.

to 78°C, to avoid thermal degradation of the products. Figure 5 illustrates gas chromatographic runs of (a) the combined starting material, (b) an early fraction which shows the amplified low-boiling impurities, and (c) (which is really 2 runs overlapped) showing the purity checks of the final isolated compounds. This was a 125 theoretical plate distillation separation.

Currently available annular teflon stills have a column length of 36", which results in a separating capability well in excess of 200 theoretical plates. This is illustrated in the 210 theoretical plate separation of para-xylene from a 50% para, 50% meta-xylene pot charge (Figure 6). The boiling point difference is 1°C. The boilup rate was 60 drops per minute and

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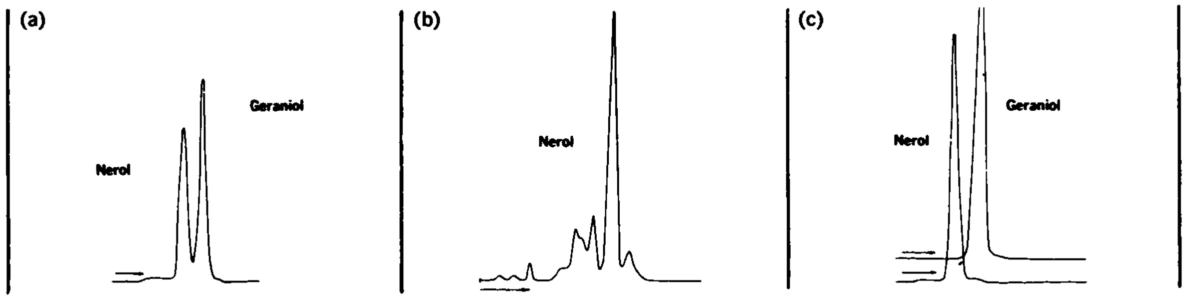

FIGURE 5

Gas chromatographic analysis of Nerol-Geraniol separation. (a) starting mixture (b) early still cut with amplified impurities (c) pure collected fractions.

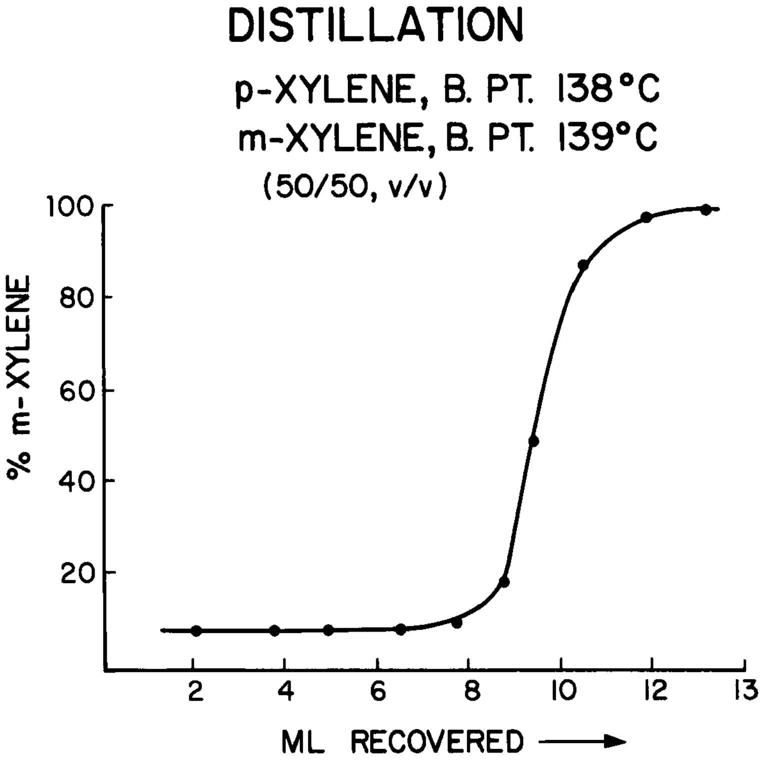

FIGURE 6

Graph of meta-para xylene distillation performed on a 210 plate still.

a 100:1 reflux ratio was used, yielding material at a rate of 1.7 ml per hour. The sharp vertical slope of the plot of recovered material is typical of these low-holdup, high efficiency stills.

Another application illustrates the use of precision distillation in the isolation and recovery of a pair of isomers; 2,4-

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dimethylhexane and 2,5-dimethylhexane, with a boiling point difference of only 0.3°C. These compounds are so difficult to separate that a 100' support coated open tubular capillary column had to be used to obtain gas chromatographic separation in monitoring the fractionation (Figure 7). Concurrent GC analysis, incidentally, is the most practical method of following distillation runs, since both quantitative and qualitative data are instantaneously available. The starting mixture shown here is composed of 19.9% 2,5 and 80.1% 2,4-dimethylhexane. Peak (c) is chlorobutane which was added at the ratio of 1 ml to 1 drop of dimethylhexane, after distillation and prior to GC analysis, to allow injection of a small enough sample of dimethylhexane to prevent column overloading on this non-splitter equipped chromatograph.

Figure 8 shows the high purity of an early still cut (Fraction 1) and the first 3 ml of material which was collected. Both were recovered at a 50 drop/min boilup rate and 100:1 reflux ratio. The combined fraction (marked 3 ml) which was collected in six hours had the composition noted on the curves. This material was then re-distilled at a boilup rate of 25 drops/min with a reflux ratio of 250:1, to obtain maximum separating efficiency.

The resultant purity is seen in Figure 9, with the first ml composed of 97% pure 2,5-dimethylhexane and the pot residue consisting of 98% 2,4-dimethylhexane. About 1 ml of cross-contaminated material was removed.

The form of the Fenske equation seen in Table I[10] was used to calculate the theoretical plate efficiency of the separation. The percentage composition figures from the second stage separation were used to establish maximum efficiency data, or, 309 theoretical plates, as seen in Table II.

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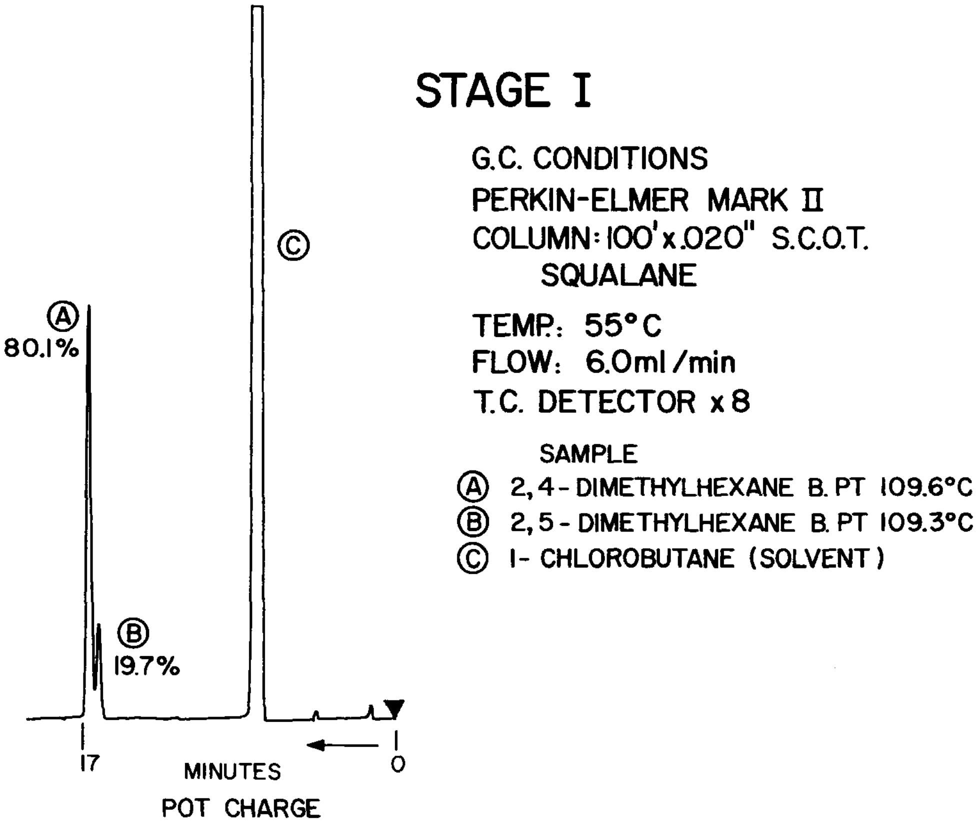

FIGURE 7. 2-stage distillation of an isomeric mixture with a boiling point difference of 0.3°C. (Pot charge).

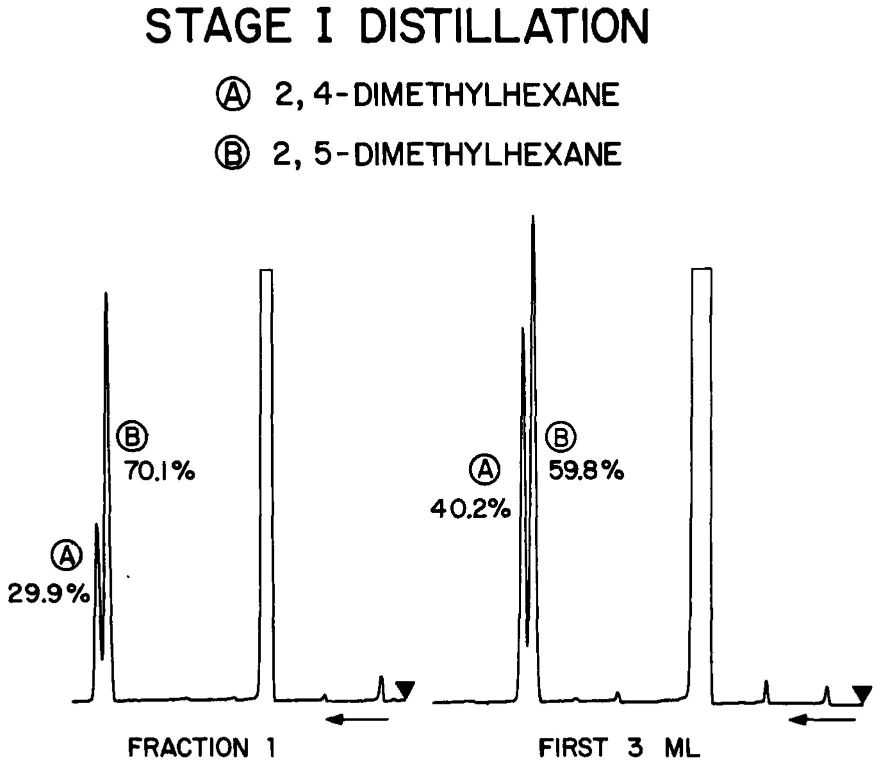

FIGURE 8

Fractions collected during first stage of isomer distillation.

The total number of distillation plates required to achieve a 98% purity separation was the combination of both runs, or over 600. 22,300 GC plates were required to achieve the equivalent gas chromatographic runs which were shown, with resolution corresponding to no better than a 95% separation.

This separation supports the general rule that to obtain maximum efficiency, the reflux ratio must closely approximate the number of plates required to perform the separation.[11]

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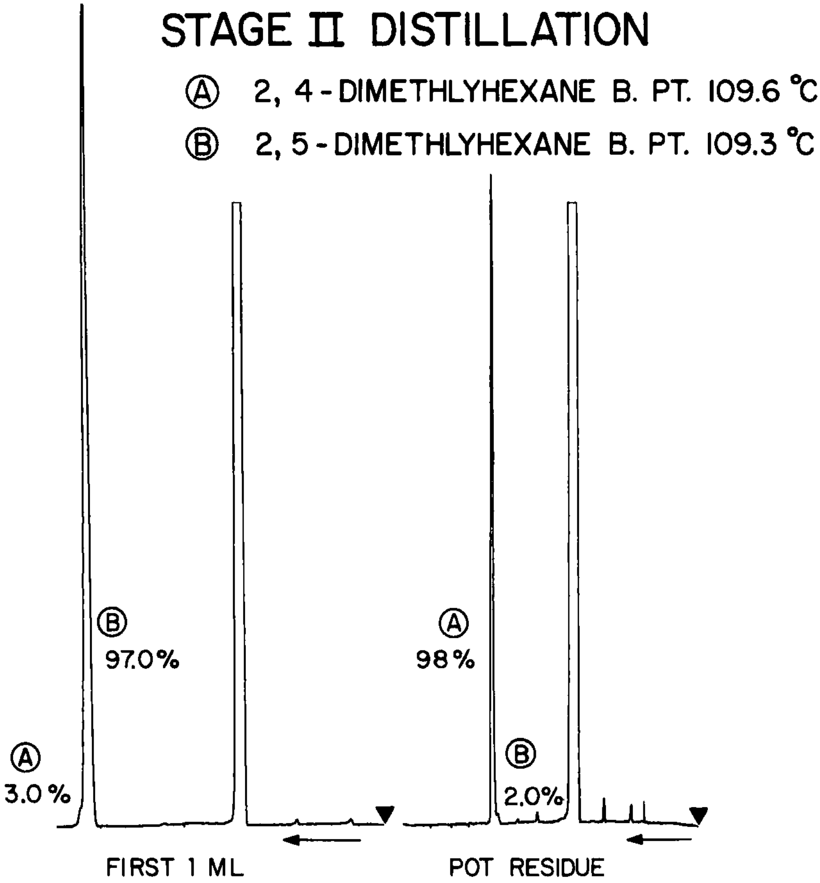

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FIGURE 9

Fractions recovered from second stage of isomer distillation.

This less complicated problem, seen in Figure 10 shows a 90:1 reflux ratio used with a boilup rate of 30 drops/min, in the 1 ml/hr recovery of 99.8% pure 1-chlorobutane from a 20:80 1-chlorobutane:cyclohexane mixture. The boiling point difference is 2.7 °C.

TABLE I

## THEORETICAL PLATE CALCULATION

$$n-1 = \frac{\text{Log}\left(\frac{xa}{xb} \times \frac{yb}{ya}\right)}{\text{Log Alpha}}$$

where Xa = % low boiler in head
Xb = % low boiler in pot
Ya = % high boiler in head
Yb = % high boiler in pot
Alpha = ratio of vapor pressures

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TABLE II

Calculation of theoretical plates.

SEPARATION OF
2,4 - DIMETHYLHEXANE B.PT 109.6°C
2,5 - DIMETHYLHEXANE B.PT 109.3°C

(Boilup Rate 25 drops/min,
Reflux Ratio 250:1)

$$n-1 = \frac{\text{Log}\left(\frac{97}{59.8} \times \frac{40.2}{3.0}\right)}{\text{Log } 1.010}$$

$$n-1 = \frac{\text{Log } 21.75}{\text{Log } 1.010} \text{ or } \frac{1.3375}{.00432}$$

$$n = 309$$

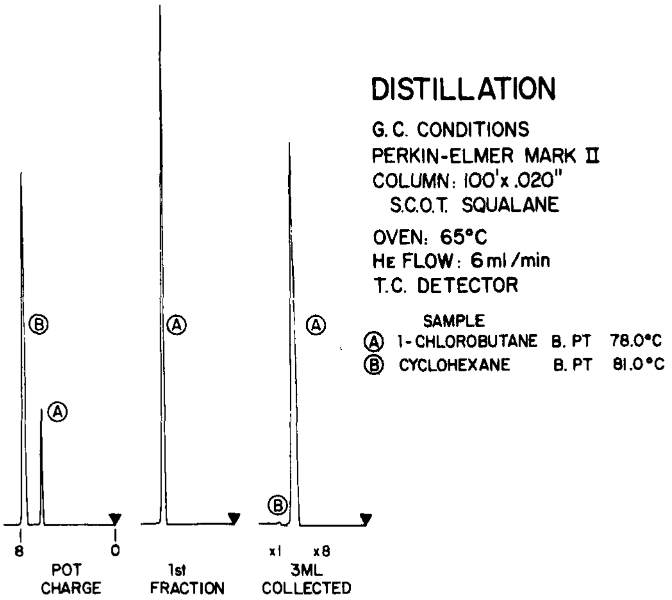

FIGURE 10

Distillation of mixture having a boiling point difference of 3.0°C.

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The relative volatility (alpha) of a mixture can be calculated, as seen in Table III to aid in calculating theoretical plate information.[12] This approximation is valid for materials with boiling points near 100°C, and is sufficient to obtain reasonably accurate plate figures.

In order to determine the size, or efficiency of, a still required to separate a given mixture, it is possible to use boiling point differences in the calculation of the number of plates required to perform the separation of a 10:90 mixture with resulting 99.5% purity of the initial 10% component (Table IV).[13]

TABLE III

### RELATIVE VOLATILITY ($\alpha$) DETERMINATION

1. $\log \alpha = \dfrac{\Delta T}{85}$

2. $\log \alpha = \dfrac{80.7-78.0}{85}$

3. $\alpha = 1.051$

TABLE IV

### B.PT vs. RECOVERY RATE (45-PLATE SPINNING BAND STILL)

| B.PT °C | RECOVERY ml/min | ml/hr |
|---|---|---|
| 1 - 5 ° | IMPRACTICAL | |
| 5 ° | 0.2 | 30 |
| 8 ° | 1 | 60 |
| 10 ° | 2 | 120 |
| 15 ° | 8 | 480 |

Note again that a reflux ratio equal to the number of plates i required to effect the desired separation. To prevent excess component loss on the internal portions of the still, it is im that the total holdup of the column be no more than 5-10% of t starting mix.

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An overall view of the separation problem can be gained from the data shown in Table V, where alpha values and the corresponding temperature differences are listed, along with the number of theoretical plates required to obtain 99.5 to 0.5% separation of a 10 to 90 starting mixture.[14] Note the sharp exponential increase in the number of plates required, as alpha approaches unity and temperature differences become extremely narrow. It is interesting to observe that it is impossible to obtain a complete separation in one pass of a mixture with a 0.5 °C boiling point difference under these starting conditions with anything less than a 600 plate still. It is also important to note that at least a 10-plate still is required to obtain effective separation of a mixture with a 20 °C boiling point difference. Of course, to obtain the listed separation, the reflux ratio should be held at the approximate plate level required. This implies that, since the product recovery rate then becomes a function of the boilup rate upon which reflux ratio is based, a large still which is capable of high boilup rates will have a higher throughput when operated within its optimum theoretical plate range than a smaller still which may have a higher number of plates.[5]

For the reasons given previously, a 45-plate, 36" x 13 mm metal mesh spinning band still is ideal for use in the recovery of solvents such as those used as eluents in liquid chromatography. Table VI illustrates some practical rates at which these increasingly difficult to obtain and even often more difficult-to-dispose-of solvents can be reclaimed, assuming a boilup rate of 50 drops/min. Many users report excellent results at boilup rates of 100-150 drops/min, thus the figures shown are minimal values which may frequently be doubled or tripled.

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TABLE V

## THEORETICAL PLATES REQUIRED FOR SEPARATION

(10/90 v/v to 99.5/0.5 v/v)

| $\alpha$ | $\Delta T^{o}C$ | PLATES REQUIRED |
|---|---|---|
| 3.00 | 30 | 8 |
| 2.00 | 20 | 11 |
| 1.50 | 10 | 20 |
| 1.20 | 5 | 45 |
| 1.10 | 2.5 | 90 |
| 1.07 | 2 | 120 |
| 1.03 | 1 | 220 |
| 1.01 | 0.5 | 600 |

(REFLUX RATIO = n PLATES)

TABLE VI

## PLATES REQUIRED FOR SEPARATION

(10/90 v/v to 99.5/0.5 v/v)

$$\text{REFLUX RATIO} = nTP = \frac{250}{T_B - T_A}$$

$T_B$ = Boiling Point, High Boiler

$T_A$ = Boiling Point, Low Boiler

Table VII lists the most common LC solvents with their boiling points. At the bottom are listed those which form azeotropes, that is; mixtures with fixed constant boiling points that cannot be

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TABLE VII

## COMMON LC SOLVENTS

| | B.PT°C |
|---|---|
| PENTANE | 36 |
| HEXANE | 69 |
| ISOOCTANE | 99 |
| CHLOROBUTANE | 79 |
| CHLOROFORM | 61 |
| METHYLENE CHLORIDE | 40 |
| TETRAHYDROFURAN | 66 |
| ISOPROPANOL | 82 |
| METHANOL | 65 |

### AZEOTROPES

| | |
|---|---|
| HEXANE-CHLOROFORM | 60°C |
| CHLOROFORM-METHANOL | 53°C |
| CHLOROBUTANE-ISOPROPANOL | 71°C |
| HEXANE-ALCOHOLS | varies |

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separated by normal distillation. If a solvent recovery program is to be carried out, azeotrope forming combinations must be avoided. Additionally, to aid in as rapid a distillation as possible, it is recommended that solvents which are to be combined be considered by their boiling point spread. Thus, good low-to-medium polarity solvents would be: pentane-chloroform, iso-octane-chloroform, or hexane-methylene chloride. Good medium-to-high polarity solvent pairs are chloroform-isopropyl alcohol and methylene chloride-methanol.

## CONCLUSIONS

In summary, distillation can be seen to be a vital technique in the modern laboratory scheme. Various types of laboratory stills are available for operations ranging from the most simple solvent removal to complex separation of mixtures with boiling point differences of as little as 0.3 °C. Typical systems in current use as high performance laboratory units include: packed columns, concentric tube columns, and spinning band columns. Spinning band columns have been shown to provide extremely high efficiencies at relatively high throughput rates, with complete recovery of all material.

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