# A Method for Gas-Liquid Multiplicative Distribution on a Preparative Scale

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When traces of a volatile compound dissolved in other volatile materials have to be isolated for further identification, the amount of material may be too small, and the number of components too many, to be dealt with conveniently in a column for extractive distillation. On the other hand, a preparative gas chromatographic column having the large effective plate volume needed requires a gas flow rate [1] at which it may be impossible to condense eluted trace components efficiently. In the case of known substances, it is desirable to be able to calculate accurately the plate numbers needed for a separation, and the position of the elution bands. An approach to these problems has been made by constructing a simple apparatus for multiplicative gas-liquid distribution together with a device for the rapid determination of gas-liquid distribution coefficients over a wide concentration range.

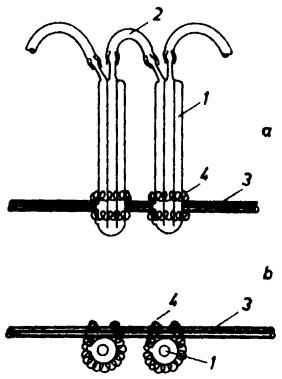


*Fig. 1.* Section of the distribution apparatus. a. Side view. b. View from above. 1. Glass tube. 2. Teflon tubing. 3. Steel rod. 4. Spring.

*Experimental.* The countercurrent distribution apparatus differs from an apparatus for extractive distillation [2] in that the liquid phase is efficiently stirred. The apparatus consists of a train of glass tubes (inner Ø = 1.2 cm, length = 11 cm) connected to each other by capillary tubes (Fig. 1). Two kinds of capillaries have been tried: (*a*) steel capillary, inner Ø = 0.4 mm; in this case the tubes must be closed with screw lids to which the capillaries are silver soldered, because of the pressure gradient; (*b*) Teflon tubing, inner Ø = 2 mm. The simple Teflon-to-glass seal (Fig. 1) is well able to withstand the pressure needed to drive the mobile phase through the train. The glass tubes are attached to a steel rod (Ø = 6.6 mm) by means of spiral springs made of 0.6 mm steel thread. The force constant of a spring is about 460 Newton/m. One end of the steel rod is connected to an electromagnetic vibrator (type "Vibromix", 40 W, frequency 100 c/sec), so that the rod oscillates in the longitudinal plane. The vibrator can take a load of 100 tubes weighing about 19 g each. The tubes are attached 5 cm below their centre of gravity. When the liquid content of each tube is between 0 and 5 cm$^3$, the tubes' own frequency is sufficiently near to that of the vibrator for resonance to occur between the tubes and the vibrating rod. Then efficient mixing of the tube contents is achieved. With prolonged vibration steel capillaries may be broken by fatigue whereas the Teflon tubing withstands the vibration. Either the gas or the liquid may be used as the mobile phase.

For the rapid determination of gas-liquid distribution coefficients, and for the evaluation of the liquid phases for use in the countercurrent distribution apparatus, an exponential dilution method modified from that described by Lovelock [3] for the calibration of gas chromatographic detectors is developed. Carrier gas is passed through a vessel with the gas volume $V_g$, containing a known volume $V_L$ of the "nonvolatile" liquid to be tested, to a vapour detector. The detector should have as large a linear range as possible; a hydrogen flame ionization detector is suitable for this purpose. If efficient mixing is provided for the gas and the liquid phases within the vessel, and a volatile substance is introduced into the vessel, the relation between the concentration $C_g$ of the substance in the gas phase and time is given by

$$\ln C_g = \ln C_{go} - \frac{U}{V_g + kV_L} \cdot t \qquad (1)$$

where $C_{go}$ is the concentration at time $t = 0$, $U$ the gas flow velocity and $k$ the distribution coefficient $C_{L\,liquid}/C_{gas}$. Thus, a plot of the

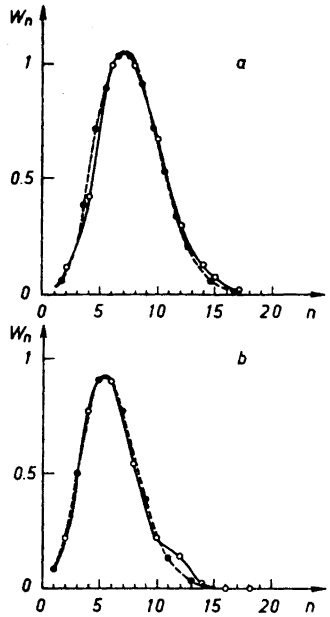


*Fig. 2.* The distribution of benzene between nitrogen and eucalyptol. 0.5 ml liquid phase/tube. Total amount of benzene: 0.25 ml. Room temperature. Capillary Ø: 0.4 mm. Ordinate: Amount of benzene/tube, arbitrary units. Abscissa: Tube number. O Experimental values. ● Calculated Poisson distribution assuming 1 plate/tube. a) Flow rate: 3 cm³ $N_2$/min. Time: 27 h. b) Flow rate: 150 cm³ $N_2$/min. Time: 1 h.

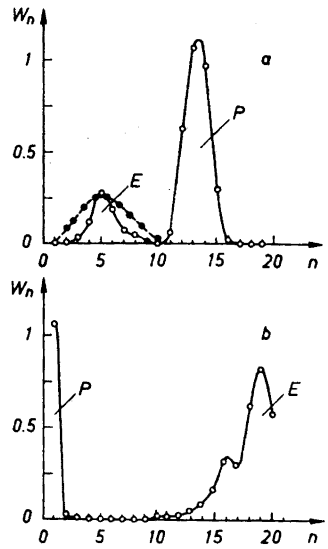


*Fig. 3.* Separation of ethyl ether (E) and *n*-pentane (P). Ordinate: Amount of substance/tube, arbitrary units. Abscissa: Tube number. Total amount of mixture: 20 mg. Room temperature. Capillary Ø: 2 mm. a) Mobile phase: nitrogen, flow rate 32.5 cm³/min. Stationary phase: water, 1 cm³/tube. Time: 5.5 min. O Experimental values. ● Calculated Poisson distribution assuming 1 plate/tube. b) Mobile phase: water, average flow rate 2 cm³/min. Time: 24 min. Average amount of water/tube: 1 ml. Stationary phase: air.

logarithm of the recorder signal against time gives a straight line in the case of linear distribution, and $k$ is obtained from the slope of this line.

Some properties of the distribution apparatus described are listed below:

One plate or slightly more per tube is obtained over at least a gas velocity range of from 3 cm³/min to 150 cm³/min at room temperature when the capillaries connecting the tubes have an inner Ø of 0.4 mm (Fig. 2). With the tubes shown in Fig.1, five plates/tube have been observed (Fig. 3a). According to preliminary experiments, the gas velocity need not be more than just sufficient to overcome the rate of diffusion in the gas phase, which is rather slow.

When gas is the mobile phase, a pressure difference of 1.6 atm between the ends of the apparatus does not seem seriously to diminish the number of plates obtained, though such an effect might be expected when the distribution isotherm is influenced by pressure.

"Reversed phase" gas liquid distribution is easily performed with this apparatus (capillary Ø = 2 mm). In this case the pressure gradient has a visible effect upon the distribution owing to the compressibility of the gas; the amount of liquid per tube gradually decreases towards the end of the apparatus (Fig. 3b).

The liquid phases used must not be too viscous.

The sample is introduced into the apparatus in liquid form.

To perform a separation, a specific liquid phase is chosen with the aid of the dynamic method for the determination of distribu-

tion coefficients. With quinoline as the stationary phase (5 cm³/tube), 10 g of benzene-cyclohexane mixture (1:1) was separated in one run, the efficiency being equivalent to slightly more than one plate per tube (tube number = 20; room temperature).

To get a separation with the least possible number of tubes, use should also be made of the fact that the separation factor $a^*$ for two compounds (1 and 2) increases with the absolute value of their distribution constants towards the limiting value given by the ratio of the distribution constants ($k_1$ and $k_2$):

$$a^* = \frac{n_1}{n_2} = \frac{V_G/V_L + k_2}{V_G/V_L + k_1} \quad (2)$$

($V_G$ and $V_L$ are the gas and the liquid volumes; $n_1$ and $n_2$ are the tubes containing the maxima of compounds 1 and 2, respectively). Eqn. (2) is easily derived from the formula $V_R = n\ (V_G + kV_L)$, where $V_R$ is the retention volume [4]. Eqn. (2) also applies if $a^*$ is considered as the ratio between the retention volumes. The effect of the absolute values of the distribution constants, and of the volume ratio between the mobile and the stationary phases, upon the separation is exemplified by the separation of ethyl ether and *n*-pentane (Fig. 3a, b). With water as the stationary phase, their separation factor was 2.7, while with air it was about 19.

From the distribution coefficients determined, the number of plates required for a given separation is obtained by use of the following expression:

$$n_2 = \left(\frac{b}{a^* - 1}\right)^2 \quad (3)$$

$$\text{and } n = \sqrt{n_1 n_2} = \left(\frac{b}{a^* + (1/a^*) - 2}\right)^2 \quad (4)$$

Here, $n_2$ is the plate containing the maximum of the slower component, and $b$ is the number of standard deviations that separates the two maxima from each other. Eqn. (3) is obtained by putting $n_1 - n_2 = b\sqrt{n_2}$ and eliminating $n_1$ with the aid of (2).

Purnell [5] has given a formula for the number of plates required in GLC to just separate a pair of compounds.

This formula gives higher values for the required plate number than (4). However, with the apparatus described here, experimental agreement with formula (4) has been obtained.

This work is being continued.

The author is greatly indebted to Professor A. I. Virtanen for his kind interest in this work. The investigation is a part of a research project under U. S. Public Law No. 480, 83rd Congress.

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Received November 13, 1961.

## A Method for Kinetic Study of "Moderately Fast" Reactions. Rate of Dissociation of Monoamminenickel(II) Ion in Aqueous Solution

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Rates of formation and dissociation of labile complex ions are often too great at room temperature to follow by conventional methods. Semi-quantitative studies [1,2] of such reactions in methanol at low temperatures (*e.g.*, −75°C) have given useful information. For certain systems and purposes it is also desirable to investigate reactions in aqueous solution. Although excellent methods exist for the study of such "moderately fast" reactions, *e.g.*, the stopped-flow and quenched-flow methods, they involve the construction and calibration of complicated apparatus.

We report here a method adaptable for many reactions and especially useful for kinetic and equilibrium studies of formation and dissociation reactions of ammine and amine metal complexes, using only commercially available instruments. The principle is to use an appropriate non-complexing salt to depress the freezing

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