

CHROM. 8611

CHROMADISTILLATION

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(Received May 20th, 1975)

SUMMARY

A method for the separation of mixtures based on distillation under chromatographic conditions (chromadistillation) has been developed. The mixture to be resolved is carried by the stream of carrier gas into a column packed with an inert material. The column temperature decreases from the inlet to the outlet. Four different ways were used to prove that at the column outlet adjacent zones of the pure components of the resolved mixture are recorded. The method described permits an increase in the output of pure substances in the chromadistillation process and the determination of both the qualitative and the quantitative composition of the mixture to be resolved. The fact that no stationary phase is used permits the range of boiling points of the substances investigated to be extended. A programmed temperature version of the method has also been developed. A theory of the chromadistillation process describing the retention characteristics and the broadening of zone boundaries is presented.

INTRODUCTION

In order to achieve a decisive improvement of some essential gas chromatographic characteristics, a method has been developed that lies at the boundary between chromatography and distillation. The method can be considered as fractional distillation under chromatographic conditions, or as chromatography in which the components of the mixture to be resolved and their solutions are used as the stationary phase. This method of chromadistillation offers great possibilities for improving the output of preparative chromatography, extending the range of boiling points of the components to be resolved, decreasing the broadening of zones, etc.

The basic principle of chromadistillation is the movement of the mixture to be resolved along a column packed with some inert material (*e.g.*, metallic beads) with a temperature gradient along the column providing multiple condensation. All of the factors that cause the movement of bands in chromatography (carrier gas flow, temperature variations, etc.) can also be applied in chromadistillation.

Chromadistillation, like most methods, has some predecessors. Thus, Kiva and co-workers¹⁻³ passed the carrier gas through a column packed with a liquid

coated on a support, without the use of a temperature gradient, to make a qualitative study of azeotropy. In these experiments, owing to the absence of a temperature gradient, no separation into individual components was possible, and the use of the method for separation or analysis is not feasible.

A procedure similar to chromatodistillation is the method known as thermo-chromatography⁴⁻⁷. In this method, designed for the determination of trace amounts, particularly of transuranium elements, the sample is introduced into the inlet end of the capillary through which the carrier gas is passed. The presence of a stationary temperature gradient enables each component to reach a certain zone beyond which it cannot move because of low vapour pressure. Measuring the distribution of radioactivity along the tube provides information concerning the composition of the mixture. In this method, no separation into adjacent zones of pure substances is achieved, contrary to the case in chromatodistillation. In addition, in the analysis of trace amounts by this method, adsorption plays a greater role than in distillation. In chromatodistillation, adsorption plays a negative role, resulting in "tailing".

THEORETICAL

A characteristic of chromatodistillation is a "regime of resolved components" (R.R.C.) forming adjacent zones. Let us assume that a multicomponent mixture has been introduced into the inlet end of the tube. If the volatility of the components of the mixture is high enough, the carrier gas will carry them along the column. At the rear edge of the mixture evaporation of the components takes place, while the existence of a temperature gradient provides condensation at the front edge.

Multiple steps of evaporation and condensation result in the complete resolution of the mixture into separate adjacent zones of pure components. The most volatile component reaches the detector instantaneously, if the retention time of the "air peak" is assumed to be zero. The partial pressure of a component must be equal to the vapour pressure of the component at the temperature of the outlet end of the tube.

Fig. 1 shows the distribution of the components along the column in an R.R.C. The zone of the most volatile component spreads from the first moment to the end of the tube. The amount of the component in a unit volume of the column (q) will not be constant.

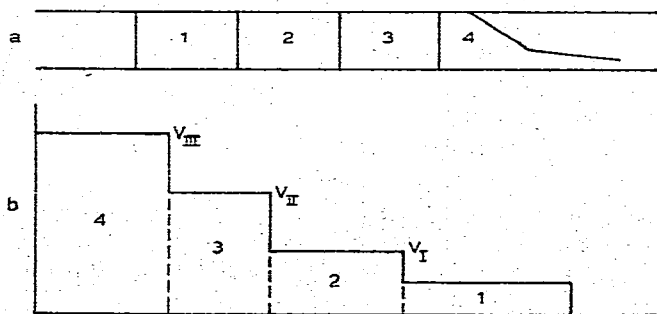


Fig. 1. Distribution of components on a column in the chromatodistillation process (a) and the corresponding chromatodistogram recorded (b).

The objects of the theory of chromadistillation, as in chromatography, are the retention volumes of the components, the velocities of movement of the boundaries of zones, and their broadening. It follows that the retention volume of the most volatile component 4 (Fig. 1) is zero. The next component 3 (Fig. 1) will appear immediately after component 4. Its concentration in the detector will be determined by the vapour pressure at the temperature of the end of the column. The retention volume of this component will be $V_{R3} = Q_4/C_4^0$, where C_4^0 is the saturated vapour pressure of component 4 at the temperature of the end of the column and Q_4 is the total amount of component 4 in the mixture being analyzed.

The general recurrent equation has the form

$$V_{R(i-1)} - V_{Ri} = \frac{Q_i}{C_i^0} \quad (1)$$

The velocity of movement of the zone boundaries in the R.R.C., as shown by the balance, is determined from the equation

$$U_i = \frac{\alpha C_i^0}{q_i} \quad (2)$$

where α is the linear velocity of the carrier gas.

It has been shown experimentally that with low temperature gradients q_i changes comparatively slightly with temperature, which results in an approximate equality of the stationary velocity of movement of the assemblage of the zones. From the equality of velocities of movement of adjacent components, the following relationship between the values of q on the two sides of the boundary can be obtained: $C_i^0/q_i = \text{constant}$.

The velocity of removal of the most volatile zone depends on the amount of the substance leaving the column; here the so-called "depletion" of the zone of the component takes place. Thus a series of steps is recorded, as shown in Fig. 1.

The characteristics of boundary broadening in the R.R.C. are obtained by solving the following equations:

$$\begin{aligned} -\alpha C_1^0 N_1 + DC_1^0 \cdot \frac{dN_1}{dx} &= -q_1 w \\ -\alpha C_2^0 N_2 + DC_2^0 \cdot \frac{dN_2}{dx} &= -q_2 w \end{aligned}$$

where N_i denotes the molar fractions (in a liquid) of the adjacent component ($i = 1, 2$), D is the effective diffusion coefficient and w is the velocity of movement of the zone boundaries. Solving these equations yields the following expression for the width of the broadened boundary:

$$\mu = H \cdot \frac{\gamma}{1 - \gamma} \left[1 + \frac{1}{\gamma} \ln \left(2 - \frac{1}{e} \right) \right] \quad (3)$$

where $\gamma = C_1^0/C_2^0$, $0 \leq \gamma \leq 1$ and H = height equivalent to a theoretical plate.

From eqn. 3, it follows that the minimum value of μ is $0.5 H$, which is significantly less than in elution chromatography. An equal width is attained in the two

methods only when γ approaches 0.95 (at a column length of 1 m). With an increase in the value of γ , μ naturally increases too, becoming ∞ at $\gamma = 1$.

A number of new possibilities are provided in chromatodistillation through the use of programmed temperature. The range of substances separated in one run is extended, the time of analysis is reduced and an additional parameter appears, namely the rate of temperature increase. The main feature of programmed temperature chromatodistillation depends on the fact that the temperature at the column outlet increases with time and hence the vapour pressure of the emerging components also increases. As a result, instead of steps, an increase in the signal is recorded, which changes to a sharp drop in the signal (after the component has been depleted) down to the level of the response corresponding to the vapour pressure of the next component. This leads to a saw-like chromatogram. If the sensitivity of the detector is the same towards all of the components, the amount of the component in the sample can be determined from the area of its zone.

EXPERIMENTAL AND RESULTS

In order to check the validity of the concepts formulated above and to illustrate the possibilities of the new method, a number of experiments were performed.

Firstly, it seemed important to demonstrate the complete separation of the individual components of a mixture in the chromatodistillation run. Such experiments were carried out with saturated hydrocarbons. The column (2 mm I.D.) was packed with steel beads (diameter 0.3–0.4 mm). The liquid sample was either injected with a syringe or was blown off from Chromaton N previously packed in an auxiliary U-tube placed before the distillation column. A thermal conductivity cell was used as the detector. The temperature gradient was achieved in two ways: either a different temperature was maintained at the two ends of the column, or the column was made up of a number of sections, each of which was maintained at a different temperature.

Fig. 2 shows a typical chromatogram for a system of saturated C_6 – C_9 hydrocarbons. The column length was 70 cm and the temperature along the column was varied from 22° to 0°. The completeness of separation was checked by several methods:

(a) A comparison was made between the heights of steps in the chromatogram of the mixture and those of the steps obtained by chromatodistillation of individual

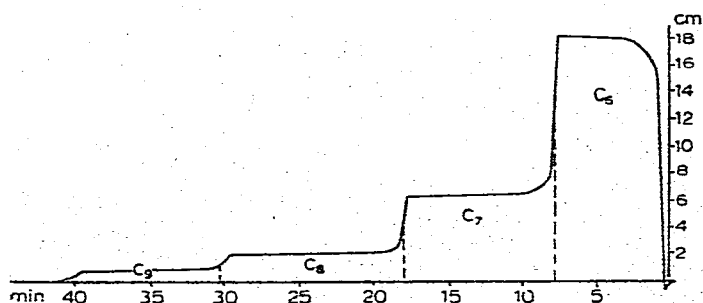


Fig. 2. Chromatogram of a C_6 – C_9 *n*-hydrocarbon mixture. Nitrogen was used as the carrier gas at a flow-rate of 8.4 ml/min.

components. Table I shows that no doubt is left as to the purity of the substances obtained as a result of the separation.

(b) A comparison was made of the ratio of areas of the steps in a chromatidistillation run with that of the areas of the corresponding peaks obtained by elution analysis of a hydrocarbon mixture. These experiments showed good agreement within the limits of the accuracy of the experiment. One of a large number of experiments made is discussed below. For the ratio of the peak areas for C_6 - C_7 hydrocarbons in both chromatidistillation and elution analysis the value of 1.5 was obtained. The ratios of areas of the steps for C_7 - C_8 and C_8 - C_9 hydrocarbons in chromatidistillation were 2.15 and 1.65, while in elution analysis the values were 2.1 and 1.6, respectively.

TABLE I

COMPARISON OF THE STEP HEIGHTS IN CHROMADISTILLATION OF A MIXTURE AND OF THOSE OF INDIVIDUAL COMPONENTS

Sample	Step height (cm)				Temperature along column ($^{\circ}$ C)
	C_6	C_7	C_8	C_9	
Mixture of C_6 - C_9 <i>n</i> -hydrocarbons	22.4	6.9	2.05	0.65	From 140 $^{\circ}$ to 22 $^{\circ}$
	22.4	6.9	2.05	0.68	
	22.2	6.8	2.05	0.60	
	21.6	6.7	2.00	0.60	
	21.8	6.7	1.95	0.55	
	22.4	6.95	2.05	0.65	
Mean	22.2	6.85	2.05	0.60	
Individual hydrocarbons	22.1	6.9	2.1	0.60	

(c) A comparison was made of the ratio of the step heights obtained with helium as the carrier gas with that of the vapour pressures of the components at the temperature of the outlet end of the column. The former ratio for C_6 - C_7 hydrocarbons was found to be 3.24, and the latter 3.42; for C_7 - C_8 hydrocarbons the values were 3.37 and 3.24, and for C_8 - C_9 hydrocarbons 3.38 and 3.40, respectively.

(d) The effluent corresponding to different steps in the chromatogram were trapped in a U-tube at the temperature of liquid air and then analyzed by elution chromatography. In such experiments significant errors may be caused by the technique of sampling used, storage of samples and adsorption on the communication lines. These measurements have nevertheless shown that in every zone the content of adjacent components did not exceed a few per cent.

A qualitative analysis by chromatidistillation should be made according to the step heights, which depend on vapour pressure and, in a more accurate analysis, also according to the temperature dependence of the step heights. The use of the properties of pure substances rather than those of binary mixtures is an advantage of chromatidistillation.

A quantitative analysis can be made from the areas of the steps and, for known substances, from their widths. In the latter case, the function of the detector can be reduced to the role of a null-point instrument.

A comparison was made between the composition of a C_6 - C_9 *n*-hydrocarbon

mixture (in molar fractions) as calculated from the step width and the composition known from the amounts of the individual substances used for preparing the mixture. In the former case, the contents (vol. %) of the component hydrocarbons were 0.675, 0.238, 0.072 and 0.016, respectively; in the latter case, the values were 0.70, 0.22, 0.070 and 0.013, respectively.

It should be noted that chromadistillation in the form described above cannot be used to separate azeotropes.

As no stationary phase is used in chromadistillation, analysis at elevated temperatures is facilitated and the use of chromadistillation with programmed temperature is justified. In Fig. 3 a chromadistogram of such a run is shown for a C_9 - C_{20} (without C_{17}) *n*-hydrocarbon mixture. Helium was used as the carrier gas. The column temperature was increased in time, the temperature gradient along the column existing during the entire programming period. The minimum column temperature did not exceed 150° . The detector temperature was 160° .

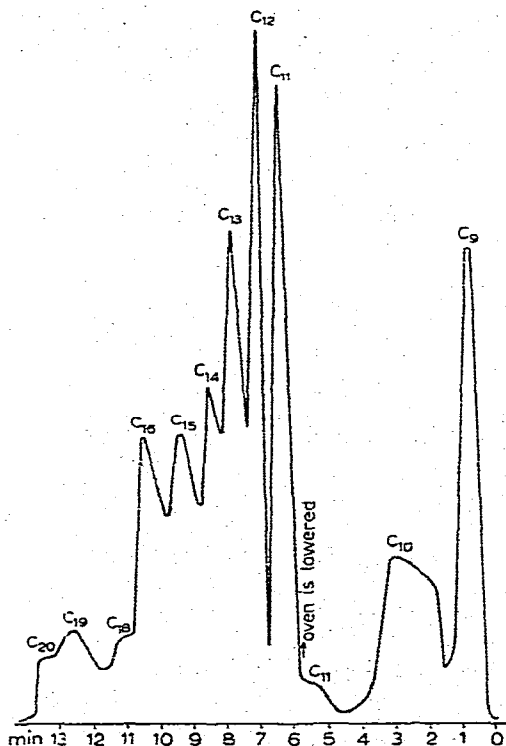


Fig. 3. Chromadistogram of a C_9 - C_{20} (without C_{17}) *n*-hydrocarbon mixture obtained in a programmed temperature run. Helium was used as the carrier gas at a flow-rate of 60 ml/min.

In Fig. 4 an analogous chromadistogram for a C_5 - C_{12} *n*-hydrocarbon mixture is shown. A quantitative determination was made from the areas of the corresponding peaks. Table II gives a comparison of the ratios of peak areas in programmed temperature distillation and in elution runs. In the elution analysis, squalane (25%, w/w) was used as the stationary phase.

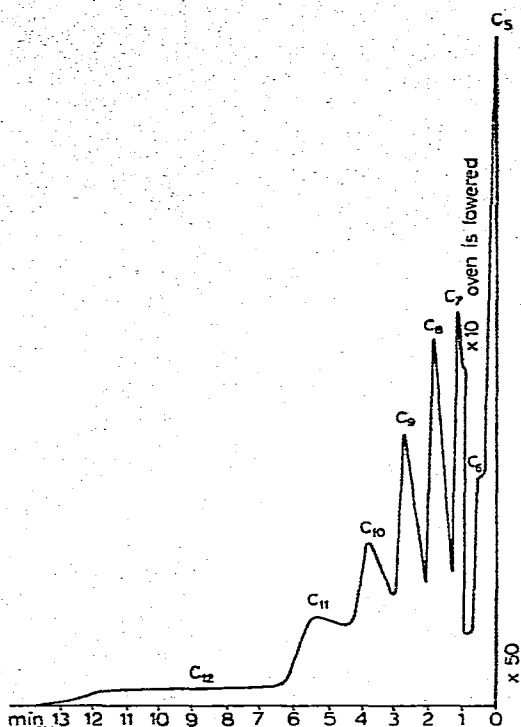


Fig. 4. Chromadistogram of a C₅-C₁₂ *n*-hydrocarbon mixture obtained in a programmed temperature run. Helium was used as the carrier gas at a flow-rate of 31.5 ml/min.

TABLE II

COMPARISON OF THE RATIOS OF PEAK AREAS IN PROGRAMMED TEMPERATURE CHROMADISTILLATION AND IN ELUTION RUNS

Method	Mixture	Ratio of peak areas			
		C ₈ /C ₁₀	C ₉ /C ₁₀	C ₁₁ /C ₁₀	C ₁₂ /C ₁₀
Chromadistillation	C ₅ -C ₁₂ hydrocarbons	1.05	1.04	0.78	0.68
		1.00	1.07	0.81	0.68
		0.95	1.03	0.91	0.73
Elution analysis		0.95	0.98	0.91	0.72

Chromadistillation also offers new possibilities for determining the thermodynamic characteristics of solutions and for the analysis of impurities.

CONCLUSIONS

A method for the resolution of mixtures has been developed involving multiple distillation under chromatographic conditions (chromadistillation). The separation of mixtures into adjacent zones of pure components has been proved experimentally.

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