CHROMSYMP. 786

VAPOUR CHROMATOGRAPHY AND CHROMADISTILLATION

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SUMMARY

Some problems are rather difficult to solve by gas chromatographic methods —for example, the introduction of large doses for analysis of admixtures, in order to prepare pure substances and to determine their physico-chemical characteristics, establishing the distribution of components according to their boiling points (especially for high boiling components), continuous separation.

In chromadistillation one makes use of the features of chromatography at vapour pressures close or nearly equal to saturation (the existence of a "restrictive regime", the efficiency of the immobile temperature gradient). The application of chromadistillation makes it possible to introduce up to 10 cm^3 of a mixture to be analysed, to achieve a sensitivity of trace determination of about $1 \cdot 10^{-6}$, to carry out the distillation of substances with boiling points near 600°C, to measure the vapour pressures for small doses (micrograms), ensuring the purity of components, and to carry out continuous separation of two-component mixtures.

Chromatography is applicable to low concentrations and doses, particulary for the selective separation of mixtures containing large numbers of components. However, for solving some problems, the opposite case, namely high concentrations and doses, is of great interest. If these concentrations correspond to the saturated vapour, chromadistillation separation of liquid mixtures is carried out[1,2]; if the concentrations are only close to a saturated vapour, chromatography of vapours close to saturated is performed[3]. Both variants are characterized by two peculiarities: the presence of a restrictive regime and improvement of the separation caused by the constant temperature gradient. In some ways the restrictive regime is the reverse of displacement in chromatography, and arises not with convex but with concave isotherms, which are always observed near the saturated vapour pressure. The regime is provided with the injection of a more volatile component before the separated mixture, which leads to the complete separation of the mixture into the adjoining bands of the separate components and moving with the same velocity in both gas–liquid and adsorption chromatography and also in chromadistillation[4].

It is well known that the stable temperature gradient in the gas chromatography of low-concentrations samples does not lead to improvements in separation.
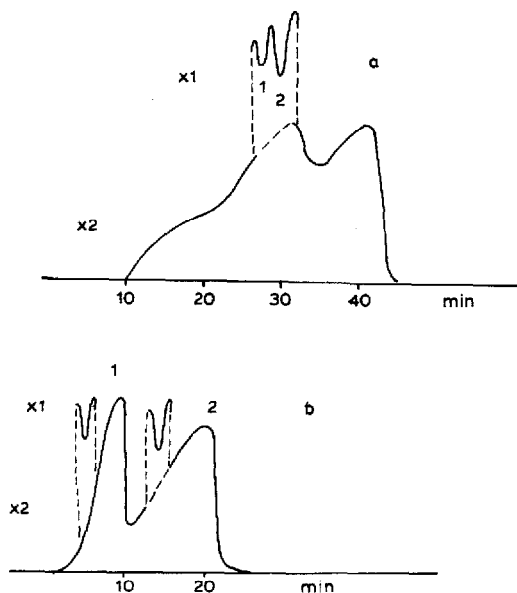
Fig. 1. Chromatography of vapours close to saturated of heptane(1)–isooctane(2) (1:1) mixture. Column, 1 m × 4 mm I.D., 40% 1-iodonaphthalene. Sample, 0.04 ml. Temperature: (a) 0°C; (b) gradient, 0–85°C.

Fig. 1 shows that a mixture of heptane and octane (dose 0.04 ml) is not separated on a column packed with Chromaton coated with 1-iodonaphthalene at a constant temperature (0°C), but is separated satisfactorily with a temperature gradient (0–85°C).

In the chromadistillation of liquids an extreme convex adsorption isotherm is observed on an inert support (when $C < C_{satur.}$, there is no sorption and when $C \geqslant C_{satur.}$ sorption increases infinitely). Hence two types of chromadistillation exist: thermal (with a temperature gradient) and restrictive (with injection of the most volatile component in front of the separated mixture). The chromadistograms, which are similar in both instances, transfer the full separation to the adjoining bands of pure components. However, the processes of distribution of components along the bed are different. In restrictive isothermal chromadistillation a carrier gas brings vapour of lighter components to the band of heavier components, where a complete separation occurs after the dissolution and distillation of more volatile components. Hence all the component bands are adjacent to the restrictor band on the column and move with the same velocity along the bed. From the balance equation it is obvious that with a constant velocity it is necessary to increase the amount of liquid per unit volume with increasing vapour pressure of the component. The largest amount occurs with the restrictor band and corresponds to the largest amount of liquid retained by the support band in the presence of a stream (0.05 cm³).

In thermal chromadistillation with transfer of component vapour by the carrier gas, and because of the temperature decrease, their condensation takes place. Liquid transfer can be caused by vaporization and subsequent condensation, and also by the liquid overloading the support as a result of displacement of the liquid by the carrier gas. Vapour condensation leads to the formation of separated bands of liquid

components, between which a small number of drops (dew) appear. Hence the restrictor gathers bands on the bed, and the temperature gradient separates them. This can be observed on a transparent column, and a new method of visual chromadistillation without detection has been developed of this basis.

The main merits of chromadistillation, determining its practical use, are connected with the large dose, which exceeds as much as 100-fold those applied in chromatography. This leads to opportunities to determine small admixtures[5] and to increase the efficiency of preparative separations, to simplify the equipment used and to use methods that do not involve detection.

The absence of stationary phases and adsorbents is also very important for the analysis of admixtures as it increases the possible temperature range applied during the experiments. The boundary broadening in chromadistillation is limited and the components of the liquid mixture approach high purity. Finally, the chromadistillation process is characterized to a great extent by the physico-chemical properties of liquid solutions, which allows these peculiarities to be defined. Hence the practical applicability of chromadistillation is connected with the analysis of admixtures, the analysis and distillation of components with high boiling points and the preparative separation and definition of physico-chemical characteristics.

Ianovskii[6] described the application of chromadistillation methods to admixture definition, so this aspect will not be discussed here.

The second peculiarity of chromadistillation is the absence of a liquid phase, which allows it to be used in the analysis of components with high boiling points. In addition, the temperature during chromadistillation experiments is lower than that during chromatographic experiments, and concentrated, not dilute, solutions are involved. The separation of components with high boiling points should be conducted in microvariants with the optimal stream velocity. Chromadistograms of a C_{18}–C_{24} alkane mixture and of squalane are shown in Fig. 2.
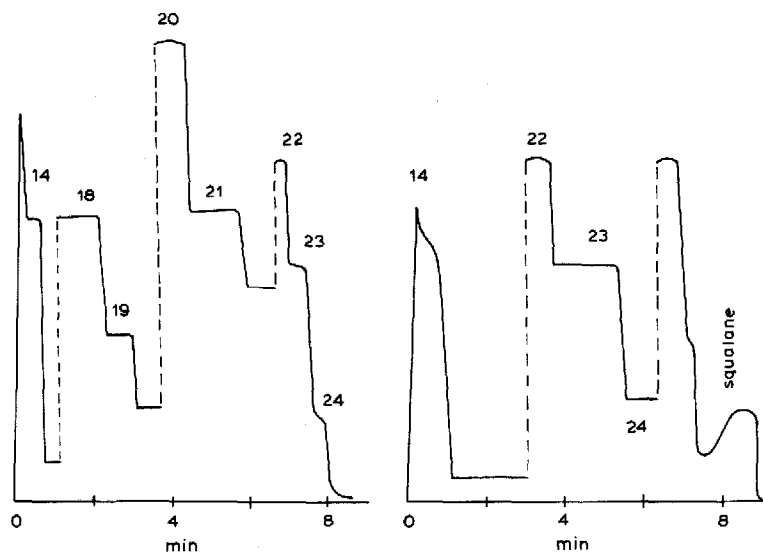

Fig. 2. Chromatogram showing the separation of C_{18}–C_{24} alkanes and squalane. Column, 78 cm × 0.2 mm I.D.; sample, 0.6 μl; flow-rate, 0.5 ml/min; temperature, gradient, 270–186°C.
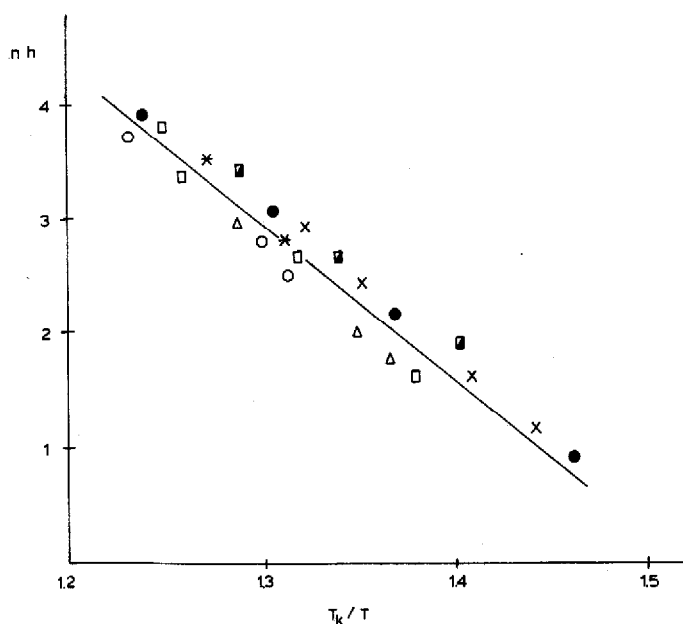
Fig. 3. Calibration graph for C_n alkanes: ●, $n = 9$; ×, $n = 10$; *, $n = 11$; ◢, $n = 14$; ○, $n = 17$; □, $n = 20$; △, $n = 24$.

The main difficulties caused by the increase in boiling temperature of the separated components are connected with the necessity for thermostating at high temperatures and the subsequent cleaning of the system, and also with the increase in viscosity, which leads to an increase in the boundary broadening of components with the high boiling points.

The advantages of chromadistillation, which allow components with high boiling points to be used, are used in chromadistillation–distillation. This method, like imitated distillation, uses a chromatogram. However, the relationship between the features of the chromatogram and the boiling points of the components is based on peaks related to the detector response and not to retention times. For calibration a linear relationship between the logarithms of the signal and ratio of the boiling temperature to the temperature of the experiment is used. Temperature programming is used in order to include all the components boiling in a broad temperature range and to decrease the time of analysis. A calibrating graph for C_9–C_{24} alkanes obtained at constant temperature is shown in Fig. 3.

Distillation curves obtained for two oils (Vangopurovskaya, curves 1 and 2, and Sementsovskaya, curves 3 and 4), obtained by chromadistillation–distillation (curves 1–3) and by imitated distillation (2–4) are shown in Fig. 4 and indicate that chromadistillation–distillation includes boiling temperatures up to 510°C and imitated distillation up to 460°C[7]. The decrease in the temperatures necessary for chromadistillation in comparison with typical distillation is explained by the fact that in the latter instance one may speak about a boiling and not an evaporation process.

The use of the temperature outages method extends the range of boiling temperatures of the components efficiently. In this method, after reaching the maximal
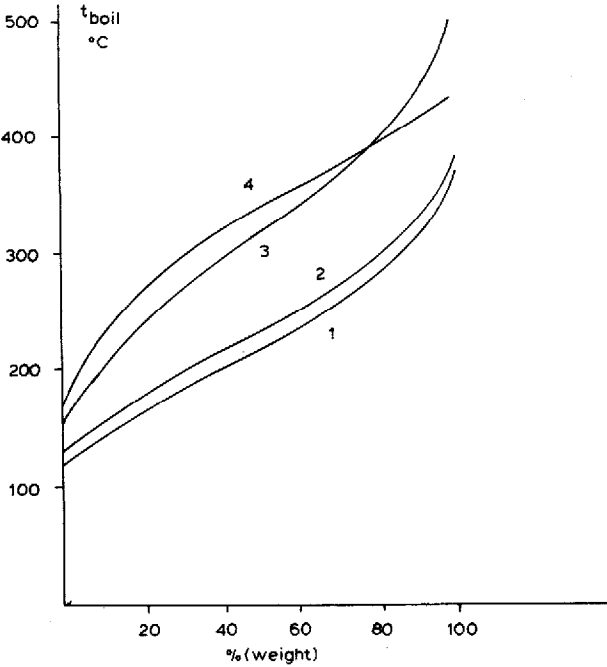
Fig. 4. Distillation curves for oils. Vangopurovskaya: 1, chromadistillation; 2, imitated distillation. Se mentsovskaya: 3, chromadistillation; 4, imitated distillation.
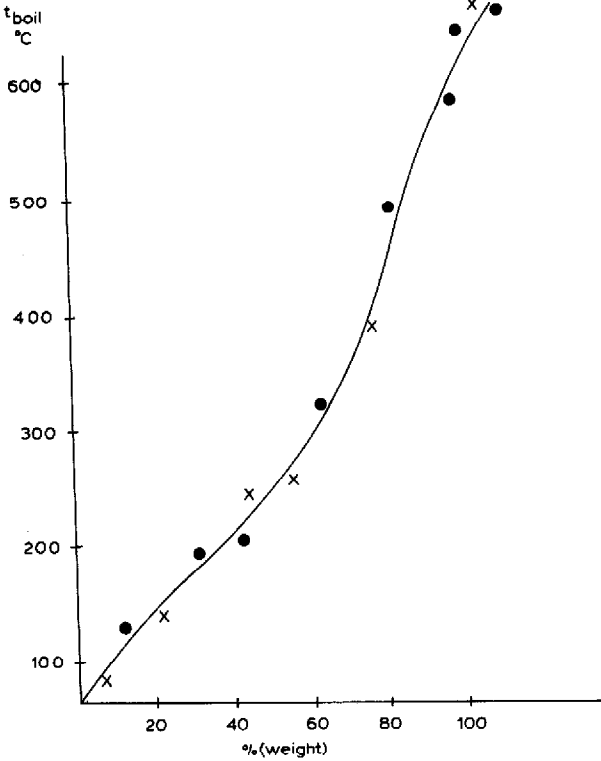

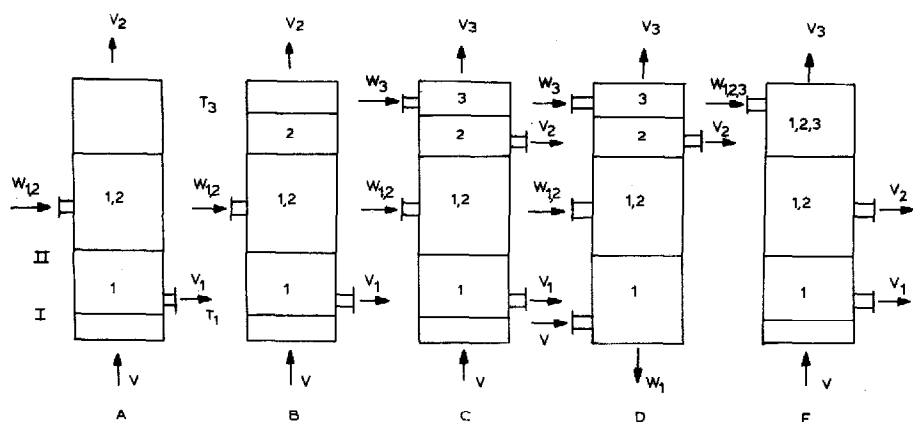Fig. 5. Distillation curve for Romashkinskaya oil.

Fig. 6. Schemes of the variants of the continuous chromadistillation separation processes.

programming temperature, the mixture is blown out at constant temperature. A distillation curve for Romashkinskaya oil is shown in Fig. 5. It is obvious that the distillation includes all the components with boiling points up to 700°C; 90% of the volume is distilled, and only 10% remain in the residue.

The application of continuous chromatography suffers from some difficulties connected with sorbent abrasion (hypersorption) and with the use of moving units. In the easiest cases chromadistillation may be carried out as a continuous process[8]. Some schemes of continuous chromadistillation are shown in Fig. 6. In variant A, a binary mixture is introduced onto a column with a support and a carrier gas is introduced from the other side to meet it. As the result, the less volatile components

TABLE I

PURIFICATION OF HEPTANE FROM ADMIXTURES

Column, 50 cm × 0.6 cm I.D.; bed, glass balls, diameter 1.1 mm; temperature, gradient, 30 to 0°C; efficiency of purification, 1.5–2.5 ml/cm² h.

	High boiling point components		Low boiling point components	
	Model mixtures (%)	Standard heptane (%)	Model mixtures (%)	Standard heptane (%)
Before purification				
Octane	1.42	$5.0 \cdot 10^{-2}$		
Sum of admixtures with high boiling point	1.45	$7.0 \cdot 10^{-2}$		
Hexane in heptane			1.4	0.145
After purification				
Octane	$4.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$		
Sum of admixtures with high boiling point	$1.5 \cdot 10^{-2}$	$3.0 \cdot 10^{-3}$		
Hexane in heptane			$1.3 \cdot 10^{-3}$	$5.0 \cdot 10^{-4}$

flow from the lower zone. The degree of separation depends on the relationship of the vapour pressure of the components and for neighbouring alkanes it is 70%. The separation of the less volatile components can be realized for any complicated mixture. The separation of a mixture of three components is shown in Fig. 6E. The scheme of continuous thermal chromadistillation for a binary mixture is demonstrated in Fig. 6B. If $T_1 > T_2$, the mixture is separated into pure components, which are removed continuously on the upper and lower parts of the column. The restrictive variant of the process is shown in Fig. 6C. The restrictor 3 is conducted (or is circulating) continuously to the upper part of the column. The less volatile components are partially removed by the carrier gas or can pour out in liquid form (Fig. 6D).

The results of the application of chromadistillation for purifying heptane from admixtures are given in Table I. Data for purification of standard heptane and a model mixture are shown. The admixture content is considerably reduced. From the data given it is obvious that the purification efficiency corresponds to that of laboratory rectifying columns.

Table II gives the results of the application of chromadistillation to measurement of the physico-chemical properties of liquids, namely, the calculation of the vapour pressure of some hydrocarbons. To exclude the influence of admixtures a dose (0.5–5 μl) was injected on to a chromadistillation column (I.D. ≈ 0.2–3 mm) and the signal was measured in the middle of the step on the chromadistogram. The temperature changed from 100°C at the beginning to the values shown in Table II at the outlet of the column. A detector based on density measurement was used. As a standard substance for substances 1 and 2, in Table II, m-xylene was used, and for the other substances decane. The vapour density was calculated using the equation:

$$P_x = \left[\frac{h_x (M_s - M_S)}{h_s (M_x - M_S)} \right]$$

where P is the pressure, h the step height and M the molecular weight of the substance (x), the standard (s) and the support (S). The exact temperature was determined from the vapour density of the standard.

TABLE II

DETERMINATION OF THE VAPOUR PRESSURE OF SOME HYDROCARBONS BY THERMAL CHROMADISTILLATION

No.	Substance	T (°C)	Ratio of steps heights (h_x/h_s)	Pressure of saturated vapour (mmHg)	
				Found	Literature
1	o-Xylene	20	0.804	4.93	4.88
2	p-Xylene	20	1.06	6.49	6.50
3	Nonane	10	3.13	1.46	1.53
4	Nonane	20	2.85	2.93	3.08
5	Undecane	20	0.320	0.257	0.259
6	Undecane	30	0.345	0.565	0.576
7	Undecane	40	0.377	1.19	1.20

In the third paragraph less exact temperature at the end of the bed was indicated. The advantages of the method lie in the simple purification of substances, in analysis times, in the small amounts of substances required and in its simplicity.

This method was developed and applied in practical situations by Revelsky and his colleagues.

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