

CHREV 201

TEMPERATURE GRADIENTS IN GAS CHROMATOGRAPHY

V. G. BEREZKIN*, T. YU. CHERNYSHEVA, V. V. BUZAYEV and M. A. KOSHEVNIK

A. V. Topchiev Institute of Petrochemical Synthesis, U. S. S. R. Academy of Sciences, Leninska. Prospekt. 29., Moscow (U. S. S. R.)

(Received October 28th, 1985)

CONTENTS

| | |
|---|-----|
| 1. Introduction. | 21. |
| 2. Stationary chromathermography. | 24. |
| 3. Heat dynamic method. | 28. |
| 4. Combined chromathermographic methods. | 31. |
| 5. Elution-thermal displacement method. | 34. |
| 6. Overloaded chromathermography. | 35. |
| 7. Thermochromatography. | 36. |
| 8. Application of chromatographic methods with a temperature gradient to the determination of physico-chemical characteristics. | 39. |
| 9. Conclusion. | 41. |
| 10. Abbreviations. | 42. |
| 11. Acknowledgement. | 42. |
| 12. Summary. | 43. |
| References. | 43. |

1 INTRODUCTION

At the very beginning of chromatography¹, most attention was paid to the development of simple types of chromatography in which the parameters (conditions) were maintained constant during the experiment. However, the potential range of chromatography can be substantially extended by varying the conditions in the course of a chromatographic experiment, and it is appropriate to consider the development of new variants of chromatography. In practice, a variety of methods are used, depending on the means employed for moving the components of the sample mixture along the adsorption layer, the physical state of the mobile and stationary phases, the form of the sorption layer, etc. This review is concerned with the development of temperature gradient methods in gas chromatography.

The temperature of separation is one of the major parameters determining the duration of separations, sorbent selectivity and the spreading of the chromatographic zones, and the rational use of the thermal factor considerably extends the potential of gas chromatography. By raising or lowering the temperature of the column (sorbent), it is possible to change dramatically the properties of different substances in the gas-mobile phase system both in time and in space on the sorbent layer. The importance of this factor was demonstrated from the very first days of the development of gas-liquid chromatography by Griffiths *et al.*², who suggested a new

method consisting of temperature programming through the column. This method subsequently found wide application in chromatography. The method was discussed in detail by Harris and Habgood³ However, temperature programming is not the only method of applying the thermal factor in gas chromatography.

Another application, the use of temperature gradients, was first suggested by Zhukhovitsky and co-workers⁴⁻⁸. This variant was called chromathermography, and its discovery was a significant step in the development of the theory and practice of gas chromatographic analysis. Essentially, chromathermography is a variant of gas chromatography in which the separation occurs on the sorbent layer as a result of the effect of the carrier gas flow in the space of the temperature field in time, which is characterized by a defined gradient of temperature in the chromatographic system during the separation.

In chromathermography, the separation is effected by additional moving of the temperature field along the column, *i.e.*, the column temperature varies lengthwise with time, but not simultaneously along the column as in chromatography with temperature programming⁹. Chromathermographic separation, in contrast to separation under isothermal conditions, makes it possible to increase the concentration of substances in the maximum of the chromatographic zone and, consequently, to provide greater sensitivity of determination. The chromathermographic method is exceptionally convenient for the separation of substances that differ greatly in their properties, *e.g.*, boiling point, and it combines the advantages of thermal desorption and elution chromatography and is applicable to the analysis of the mixtures that contain components with both strong and weak sorption abilities, irrespective of their sorption isotherms. The scheme of the first chromathermograph⁴ is shown in Fig. 1. A silica gel column (1) is placed in a large electric oven (2) combined with a smaller cylindrical oven (3) moving along the length of the column, thereby heating it gradually, zone by zone. The air entering the column is purged (4, 5), then the air flows through the column filled with calcium chloride (6) where the moisture is absorbed. The air is subsequently delivered to a heat exchanger (7) housed in an electric oven (8), where it is heated to the desired temperature. The flow-rate of the air is measured by means of rotameter (9). The concentration of the substance beneath the silica gel layer is permanently controlled with the help of a gas interferometer. The procedure for analysis is as follows. A certain amount of the mixture of the substances to be separated is applied on to the silica gel. The individual components of the mixture are developed by drawing through the column whilst simultaneously heating it, zone by zone, by lowering the smaller oven along the layer at a given rate. The gas flow passes out from the column to a detecting system, where the concentrations of the components are measured.

Two versions of chromathermography were distinguished: stationary and non-stationary⁹. In non-stationary chromathermography the direction of the moving temperature field coincides with that of the carrier gas flow, and a direct temperature gradient is used (the temperature at the beginning of the oven in the direction of its travel is higher than that at the end). Non-stationary chromathermography was applied by Zhukhovitsky *et al*¹⁰ in the adsorption retention method. In the separation, weakly sorbed components move ahead over the sorbent layer within the oven and enter the higher temperature field, where their motion is accelerated. Strongly sorbed substances lag behind and enter the lower temperature zone, where their motion is

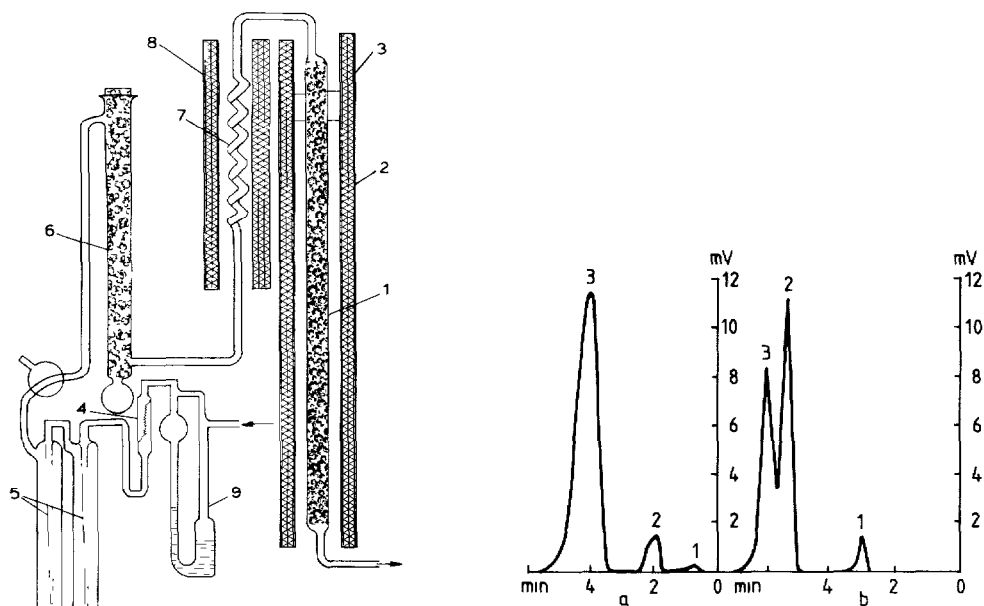


Fig. 1 Diagram of first chromathermograph 1 = Column containing silica gel; 2 = electric oven (general thermostat), 3 = smaller cylindrical heater, 4, 5 = carrier gas scavenging system, 6 = column containing calcium chloride 7 = heat exchanger, 8 = electric oven for pre-warming the carrier gas, 9 = rheometer

Fig. 2. Chromatogram of air-isobutane mixture Peaks 1 = air, 2 = isobutane, 3 = *n*-butane (a) Non-stationary chromathermography. (b) stationary chromathermography

decelerated. Thus, owing to the temperature gradient of the heater, an additional "stretching" of components takes place, giving rise to an increase in the selectivity of their separation. This is evidenced by the comparison of the chromatograms illustrated in Fig. 2. However, non-stationary chromathermography imposes very stringent requirements on the conditions of chromatography, and is therefore hardly ever used.

As in the development of any important method after its discovery, many investigators soon turned their attention to chromathermography. With regard to thin-layer liquid chromatography we may mention the method described in 1940 by Laip and Eralp¹¹. In their method, a non-fixed adsorbent layer 8 cm long was applied to a glass plate, which was placed on an inclined aluminium support. The latter was cooled from its upper edge and heated from its lower edge. The mixture to be separated was applied to the upper edge of the adsorbent and then gradually eluted down with a solvent.

In 1943, Turner¹² described a method based on creating a moving temperature gradient along a chromatographic column. The column with the sample mixture is placed in a uniform temperature field which heats the adsorption layer, zone by zone, leading to a subsequent displacement of the components. However, instead of elution chromatography with a carrier gas flow, Turner's method makes use of the displacement, the movement of the zone being effected by the displacement of the components of the sample mixture. Therefore, Turner's method can be referred to as a displacement chromathermographic method.

2 STATIONARY CHROMATHERMOGRAPHY

The second variant, stationary chromathermography, is a method in which the temperature field and the flow of the carrier gas move in the same direction, the temperature gradient being a negative value.

In the stationary chromathermographic method (the first moment of separation is shown in Fig. 3), the sample is introduced into the column and a cylindrical heater is moved on to the column, along which there is a temperature gradient; then the oven is moved by a special motor along the column at different speeds prescribed by a pre-set programme. The temperature at the beginning of the heater (in the direction of its travel) is lower than that at the end. If we introduce the sample mixture into the inlet of the column and move the travelling oven on to the beginning of the column, the sample components, depending on their nature, will move along the layer at various velocities. The substances that sorb weakly will move along the layer at a higher velocity, and when they are displaced forwards within the oven they enter a region of lower temperatures where their sorption ability increases while the rate of movement decreases. This retardation will proceed until the rate of movement is equal to that of the oven itself. Substances that sorb more strongly will move along the layer at the beginning more slowly than the oven. As the sorbing substances lag behind, they approach a region of higher temperatures, where their sorption ability decreases with increasing rate of movement. Such an increase in speed will take place until it becomes equal to the rate of movement of the travelling oven. Subsequently, all the components will travel along the layer at the same rate as the oven. In chromathermography, as distinct from traditional isothermal chromatography with temperature programming, there are special conditions that hinder the spreading of the zone and lead to their compression, *i.e.*, concentration, the compression of the zone occurring (within certain limits) automatically.

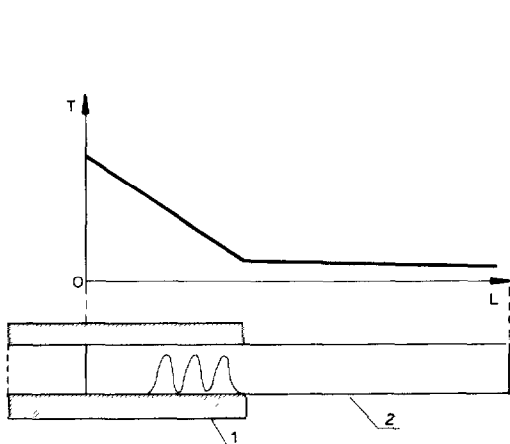


Fig. 3 Chromatographic separation of components of a sample mixture using the stationary chromathermography technique. 1 = Oven with temperature gradient, 2 = chromatographic column L = column length, T = temperature

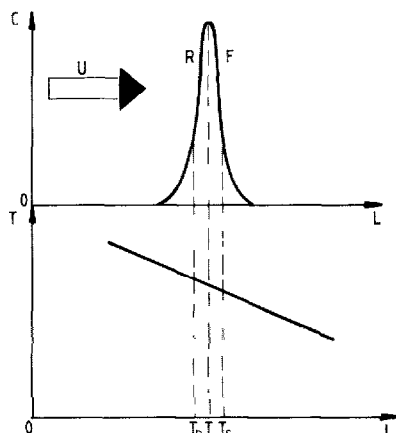


Fig. 4 Compression of chromatographic zone in chromathermography u = Linear velocity of carrier gas; C = concentration, L = column length, T = absolute temperature, T_c , T_F , T_R = temperature in the centre, front and rear of the zone, respectively, F = front of zone, R = rear of zone

Fig. 4 shows the mechanism of zone compression under conditions of stationary chromatography when the rates of movement of the zone and the heater are the same, and illustrates the connection between the zone shape and the temperature distribution. The temperature T_R corresponds to the speed of the analyzed substance i at the rear part of the zone, U_{Ri} , the temperature T_F corresponds to the speed of the substance at the front of the zone, U_{Fi} , and the temperature T_i corresponds to the speed of the substance in the central part of the zone, U_i . u is the linear velocity of the carrier gas, L is the length of the chromatographic column and C is the concentration.

Suppose a substance zone i moves at a speed U_i ; considering that the zone moves under conditions when the sorbent temperature in the front part of the zone, T_F , is lower than that in the rear part, T_R ($T_R > T_F$), the speed of movement of the molecules of the substance being chromatographed in the region of the zone front, in general, must be lower than the mean speed of the zone, U_i , whereas the speed of movement of the molecules of the sample substance in the region of the rear part of the zone must be higher than the mean speed of the zones. If we neglect the changes in the gas flow-rate and pressure in the zone, we can write

$$U_i = \frac{u}{K_i} \quad (1)$$

$$U_{Fi} = \frac{u}{K_{Fi}} \quad (2)$$

$$U_{Ri} = \frac{u}{K_{Ri}} \quad (3)$$

where U_i , U_{Fi} , U_{Ri} and u are as defined above and K_i , K_{Fi} and K_{Ri} are the coefficients of distribution of the substances to be chromatographed in the regions of the central, front and rear parts of the zone, respectively

As the distribution coefficient usually decreases with increasing temperature, *i.e.* (see Fig. 4),

$$K_{Ri} < K_i < K_{Fi} \quad (4)$$

then

$$U_{Ri} > U_i > U_{Fi} \quad (5)$$

Thus, the compression of the chromatographic bands and their movement corresponding to the speed of movement of the temperature field in chromatography are in the steady state. The characteristic value in this method is not the retention volume, but the characteristic temperature of the chromatographed compound passing through the column. Under real conditions, the chromatographic zone has limited sizes, which are determined by the effect of two opposing operating factors: zone compression (the effect of this factor was considered above) and factors whose effects lead to broadening of the band (the limiting rate of heat transfer, non-uniform

temperature gradient in the column, the limiting rate of mass exchange, etc.). The temperature gradient also causes the molecules for some reason to be drastically retarded, the motion having "outstripped" the zone, whereas the molecules that lagged behind the zone start to move faster (see Fig. 4). Thus, chromathermography provides the opportunity to achieve very narrow zones and to concentrate the substance.

Zhukhovitsky and Turkel'taub⁷ developed a theory of movement of substances in a steady-state chromathermographic regime, on the basis of which a method was suggested for determining the heat of adsorption of substances using chromatographic zone data. In addition, the problems of compression of chromatographic zones being moved by the temperature gradient have also been studied. According to this theory, the concentration maximum in the chromatographic zone will group around one characteristic temperature (T_{char}), which can be determined according to the following equation⁹:

$$T_{\text{char}} = \frac{Q}{R \ln \left(\frac{1}{K \cdot \frac{\omega}{u}} - \kappa \right)} \quad (6)$$

where u is the linear velocity of the carrier gas, ω is the linear velocity of movement of the temperature field, κ is the proportion of the gas phase in the column, Q is the heat of adsorption, R is the gas constant and K is Henry's constant.

It should be noted that the method for performing steady-state chromathermography can differ from that suggested above by Zhukhovitsky and Turkel'taub⁹.

Steady-state chromathermography is one of few chromatographic techniques by means of which absolute enrichment of components to be separated can be realized. Chromathermography can also be employed for the preliminary enrichment of a sample mixture. The process of preliminary enrichment was first described by Zhukhovitsky and Turkel'taub in 1957¹³. The process is simple, but requires a carrier gas of high purity. A quantitative comparison of the results of gas chromathermographic analyses with constant temperature and temperature gradients for an n -C₅- n -C₉ mixture was published¹⁴, and also showed that the duration and efficiency of the latter is considerably higher (Fig. 5). Kaiser^{15,16} also described the chromathermographic enrichment of a large sample in a column with a given temperature gradient with a flow of substance inside a special enrichment arrangement (Fig. 6). In Kaiser's variant, the carrier gas (sufficiently pure) is passed through the sample or over it and directed to the enrichment column together with the sample components. The packing used for the enrichment column was Dexsil 300 GC coated on a highly inert support. The main advantage of the enrichment system is the absence of a dosing operation.

Sukhorukov and Vatulya¹⁷ suggested a method for the selection of optimal enrichment parameters and proposed a calculation scheme for a preliminary determination of the enrichment of the impurities in the chromathermographic regime. In our opinion, the multi-step calculation scheme is of interest for establishing the role of the main factors that influence the enrichment process. To calculate the enrichment

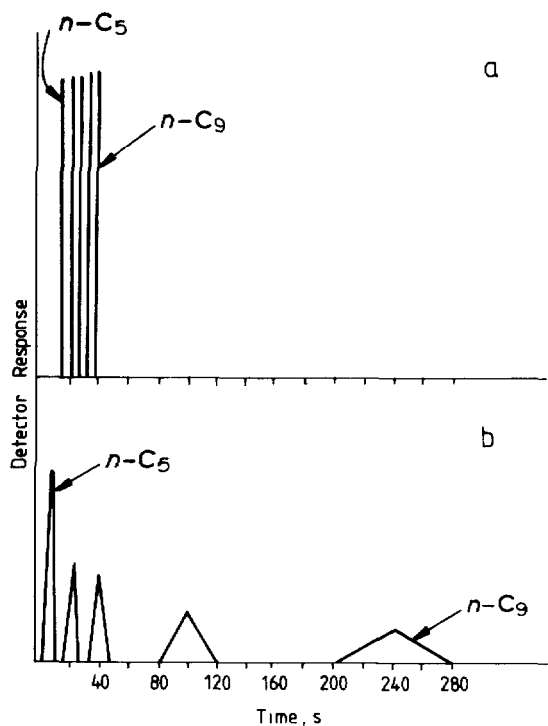


Fig 5 Chromatogram of n -C₅-C₉ alkane mixture (a) With temperature gradient, (b) isothermal conditions.

factor (O), Sukhorukov and Vatulya¹⁷ suggested the following equation:

$$O = 2 \sqrt{\frac{\text{HETP}_{\text{iso}}}{\text{HETP}_{\text{chromatherm.}}}} \cdot L\varepsilon\eta K_0 \quad (7)$$

where K_0 is Henry's constant at the temperature of introduction of the sample into the column, ε is a characteristic value that determines the compression of the band on the layer, η is the relation of the oven velocity to the linear velocity of carrier gas in the outlet of the column, HETP_{iso} is the height equivalent to a theoretical plate in isothermal experiments and $\text{HETP}_{\text{chromatherm}}$ is the height equivalent to a theoretical plate in chromathermographic experiments. The authors claimed that the suggested scheme may be varied, depending on the problem to be solved¹⁷. As indicated by Zhukhovitsky and Turkel'taub⁹, the stationary chromathermographic method has a number of advantages over conventional isothermal chromatography: rapid separation of mixtures into their components with different adsorbabilities, the possibility of obtaining symmetrical peaks even with non-linear sorption isotherms and a considerable increase in the concentration of the sample components in the central part of the chromatographic zone.

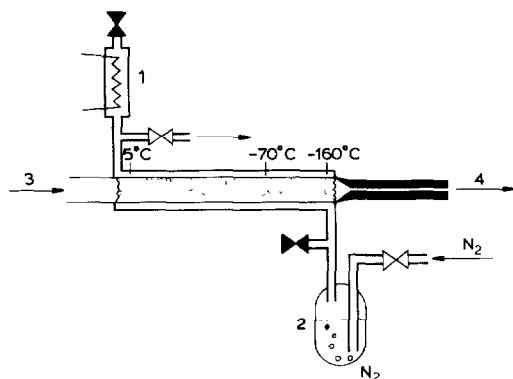


Fig. 6 Diagram of an enriched heat dynamic arrangement using a gaseous coolant 1 = Electric heater for gas flow (heat carrier), 2 = heat exchanger with liquid coolant (liquid nitrogen) for cooling the gas flow, 3 = sample gas flow, 4 = outlet for the sample gas flow

3 HEAT DYNAMIC METHOD

The next step in applying the thermal factor in gas chromatography was the heat dynamic method developed by Zhukhovitsky *et al.*¹⁸. Of all the variants of chromatography developed so far, the heat dynamic method is closest to a continuous automated separation process. Its application is of interest in both analytical and preparative problems

The heat dynamic method is a combination of frontal chromatography with moving temperature field. In this method the direction of the temperature gradient is opposite to that of the flow of the mixture to be separated. The separation is achieved in the following manner. The sample mixture is run through the column in a continuous process and travels through the adsorbent layer and, at the same time, the temperature field moves along the layer. The simultaneous effects of the adsorption layer and of the temperature field on the mixture favour its separation into individual components. According to the theory of chromatography, a given component cannot penetrate along the adsorbent layer behind the point of the temperature field where the temperature equals the characteristic temperature for a given compound. It is important to note that at the point responsible for the characteristic temperature, continuous enrichment must take place (an increase in concentration) so as to correspond to the given characteristic temperature of the component. Thus, sharp maxima (peaks) of concentrations of the individual components of the sample mixture will occur in the region of the corresponding characteristic temperatures. By making an appropriate choice of parameters, the mixture can be separated into individual components. Moreover, owing to the high temperature in the upper part of the oven, all the compounds are completely desorbed from the adsorbent, the latter thus being regenerated. After the heater has reached the lowest position, it rises automatically to the top of the column at a high speed and then moves slowly along the layer again, *i.e.*, the separation process re-starts automatically. Essentially, by this means the flow of the gas being analysed is not discontinued. As the length of the oven is smaller than that of the column, the upper part of the column becomes cooled as the oven travels along the column. The "heavy" sample components (char-

acterized by higher sorption abilities) adsorbed in the upper part of the column create a preparatively enriched sample zone for the next separation cycle.

In the analytical variant of the heat dynamic method, a detector is arranged behind the chromatographic column, which automatically records (as chromatograms) any changes in the composition of the gas flow through the column. The heat dynamic method is the most useful procedure for the separation of the least sorbable component of a mixture in the pure state or for the purpose of concentrating (and subsequent analysis) of other components of the sample mixture, and also for the preparative separation of pure substances. Fig. 7 shows schematically the creation of zones of heavy impurities in the heat dynamic method¹⁹. A circulation apparatus was constructed, supplied with two columns and two moving ovens, which provide a high degree of concentration. The heat dynamic apparatus developed by Zhukhovitsky and Turkel'taub²⁰ makes it possible to determine automatically the mean concentration of all the sample components in 5–10 min with continuous passage of the gas mixture. With two weakly adsorbable components (e.g., air–methane), their ratio is determined continuously.

The apparatus operates according to the principle of the heat dynamic method, which is intermediate between the chromathermographic method and the moving adsorbent layer method²¹. However, there are three substantial respects in which the chromathermographic method that differs from the latter method. (1) a pre-set optimal temperature gradient moves along the adsorbent layer; (2) the oven (temperature field) moves relative to the adsorbent, which eliminates numerous difficulties connected with wear of the adsorbent layer; and (3) sampling of the separated components is effected at a definite position on the adsorbent layer at the pre-set temperature, which leads to the periodic production of average concentrations during a relatively short time. Unlike the chromathermographic method, the mixture is passed

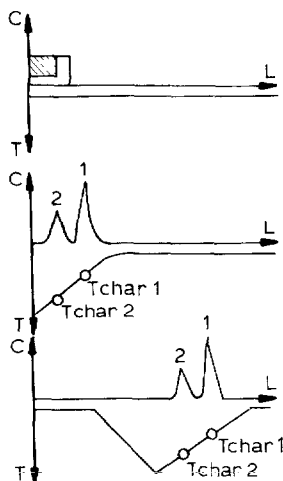


Fig. 7 Diagram of zone formation in the heat dynamic method. C = Concentration of components, T = absolute temperature, L = column length

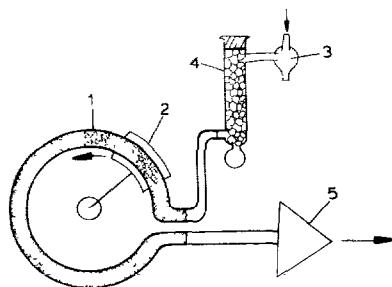


Fig. 8 Diagram of first thermodynamic installation (horizontal variant). 1 = Horizontal adsorption tube containing silica gel, having two vertical outlets, 2 = electric heater; 3 = three-way tap, 4 = desiccant (NaOH), 5 = heat-transfer detector

continuously through the layer. The adsorption column represents an open horizontal circle along which a cylindrical electric oven moves continuously, incorporating a temperature gradient.

Fig. 8 depicts a horizontal heat dynamic installation. As the oven (temperature field) travels, it concentrates all the components accumulated in the adsorbent near the characteristic temperatures and directs them alternately to the detector. The concentrations of the components are generally determined by the heights of the maxima on the basis of a calibration graph. Output curves (chromatograms) representing the separation of a propane-*n*-butane-isopentane-*n*-hexane mixture are illustrated in Fig. 9. The characteristic temperatures, measured with the help of thermocouples inserted into the end part of the layer, are given on the peaks.

Genkin and Sazonov²² developed methods for determining argon-oxygen impurities in helium, where the advantages of the heat dynamic method and the method ensuring complete component separation are combined. The experiments were carried out on a special low-temperature heat dynamic installation²³. The installation accommodates a chromatographic column fixed rigidly to a rotary shaft of a drive, so that at the same time one end of the column is inserted in a coolant bath and the other end in the heater, and as the shaft rotates along the chromatographic column the temperature field with a constant temperature gradient also travels. In this manner it is possible to determine neon, hydrogen, argon, oxygen and nitrogen with sensitivities of $5 \cdot 10^{-3}$, $3 \cdot 10^{-3}$, $2 \cdot 10^{-5}$, $2 \cdot 10^{-5}\%$ (by volume), respectively, in 9–12 min. The sensitivity increases with increasing time. The method may find application in the analysis of different mixtures that are difficult to separate.

A chromathermographic system using frontal adsorption accumulation at cryogenic temperatures (liquid nitrogen) has been described²⁴. The heat dynamic

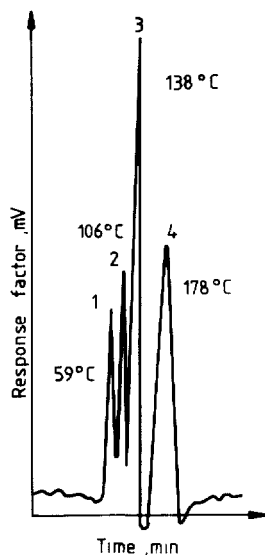


Fig. 9 Analysis of mixture separated on a chromathermographic installation 1 = Propane; 2 = *n*-butane; 3 = isopentane, 4 = *n*-hexane, $\omega = 8.7$ cm/min, $u = 78$ cm/min. The indicated temperatures correspond to the temperatures of separation of the corresponding peaks

method of enrichment employed in the installation makes it feasible to determine O_2 , N_2 , CH_4 , C_2H_6 , C_3H_8 , C_4H_{10} , NO , NO_2 , CO and CO_2 impurities in hydrogen, helium and air at concentrations of 10^{-5} – $10^{-7}\%$ (by volume).

4 COMBINED CHROMATHERMOGRAPHIC METHODS

A variety of combined methods have been suggested for the development of chromathermographic and heat dynamic methods. A variant of chromathermography in which separation is performed simultaneously along the length of the column under a negative temperature gradient was described²⁵. The method consists in the use of a constant gradient of temperatures along the column together with temperature programming. According to Zhukhovitsky and Turkel'taub⁹, the employment of a non-stationary gradient does not provide any advantages over separation under isothermal conditions. However, variation of the temperature with time with a negative gradient along the column is equivalent, to a first approximation, to the thermal field under chromathermographic conditions.

Consider the simplest case where the gradient is constant over the entire layer and unchanged with time. The relationship between temperature, length and time is expressed by the following equations.

$$T = T_0 - \gamma L + mt \quad (8)$$

$$T = T_0 - \gamma \left(L - \frac{m}{\gamma} t \right) \quad (9)$$

where T_0 is the temperature at the beginning of the column at the starting moment, m is the temperature gradient with time, γ is the temperature gradient along the length and t is time

The movement of a certain temperature field at a constant velocity is described by the following equation:

$$T = (L - \omega t) \quad (10)$$

From eqns. 9 and 10, it follows that

$$\omega = m/\gamma \quad (11)$$

In a general case, $T = f(L, t)$ for any distribution of temperature across the layer ($\gamma \neq \text{const}$) and with time, which does not comply with a certain field moving at a constant velocity.

With constant gradients the characteristic temperatures are expressed by the same equation as in chromathermography

$$T_{\text{char}} = \frac{Q}{R \ln K\omega/u} = \frac{Q}{R \ln Km/\gamma u} \quad (12)$$

where Q is the heat of adsorption, K is Henry's constant, R is the gas constant and u is the flow velocity. The width of the peak (μ) is given by an equation similar to

that in chromathermography:

$$\mu = 2\sqrt{2} u/\omega \sqrt{\frac{\text{HETP}}{\sigma}} = 2\sqrt{2} u\gamma/\omega \sqrt{\frac{\text{HETP}}{\sigma}} \quad (13)$$

where $\sigma = Q\gamma/RT_0^2$.

The selection of different gradients, including those varying with time, allows one to use the intermediate variants between chromathermography and temperature programming. Both methods have advantages, a decision should be made for each particular case as to which is preferable: a decrease in the peak width or an increase in the difference $\Delta V_g = V_1 - V_2$ (where V_1 and V_2 are retention volumes).

With a negative temperature gradient, the change in temperature with time along the column is equivalent to the moving heat field under chromathermographic conditions. In this instance, as follows from eqn. 11, the change in the rate of temperature leads to a corresponding change in the velocity of gradient field movement. In chromathermography the separation occurs only in the zone of the moving heater with a gradient, *i.e.*, on the restricted section of the chromatographic column. In the combined chromathermographic method, the separation occurs along the whole length of the column. Existence of such field is apparently an important advantage, especially when analysing complex mixtures with a wide range of boiling temperatures. In fact, when performing analyses of such mixtures, the characteristic temperatures of the first and last component may differ markedly, which necessitates the use of an oven that provides a greater difference in temperature at the cold and hot ends. If the oven is of limited length, this may necessitate the use of very sharp temperature gradients, which will have an adverse effect on the separation achieved. Apparently, the combined method allows one to achieve a large difference between the initial and final temperatures with a small gradient, as the "length" of the heater is not restricted. The analysis may be performed on a standard chromatograph with temperature programming.

The method was checked by determining, as an example, mixtures such as nonane, mesitylene and decane in toluene. A negative linear temperature gradient of 1.8°C/cm was produced with the help of a heating coil with variable winding. Spherochrom-1 solid carrier, containing 10% of apiezon L was used as the sorbent. Fig. 10 shows the chromatogram of the analysis of the mixture using a 35-cm column. The carrier gas flow-rate was 15 ml/min and the temperature programming rate was 10°C/min, which corresponds to the heat field movement of 6 cm/min. A chromatogram of the separation of the mixture with ordinary temperature programming is also presented for comparison. The combined chromathermographic variant provides a sharp compression and concentration of the samples components, giving an improved separation of nonane mesitylene, the concentration at the peak maxima being increased 10–15-fold compared with the isothermal method. The application of this method is simpler in the gas adsorption variant, where thermostable materials are used as the sorbents. By adopting the automatic heating-cooling procedure, the method may be used in the heat dynamic variant of chromathermography.

According to Nerheim²⁶, the temperature gradient along the column was produced several times in succession with a view to improving the chromatographic separation. At the beginning of the procedure the temperature gradient was less than

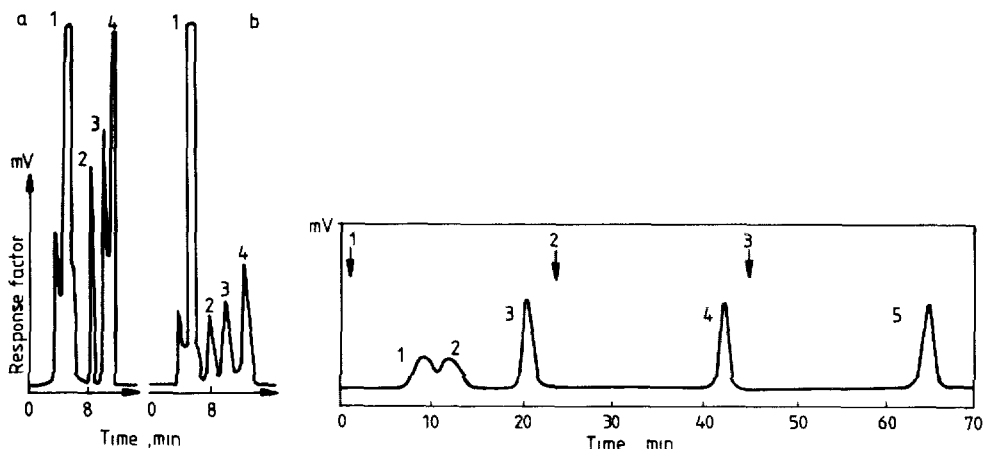


Fig 10. Chromatogram of separation of mixtures in toluene by (a) the chromathermographic method and (b) the temperature programming method. Peaks: 1 = toluene; 2 = nonane; 3 = mesitylene; 4 = decane. $\gamma = 1.8^\circ\text{C}/\text{cm}$, $m = 10^\circ\text{C}/\text{min}$, $u = 15 \text{ ml}/\text{min}$, $L = 35 \text{ cm}$

Fig 11. Chromathermography with successive passages of the heater. 1, 2, 3 = First, second and third passages of heater. Peaks: 1 = isopentane; 2 = *n*-pentane; 3 = *n*-hexane; 4 = *n*-heptane; 5 = *n*-octane

the characteristic temperature of high-boiling components, and only low-boiling components were liable to elution. Subsequently a higher gradient with higher temperatures was created that enabled the higher-boiling components to be eluted as separated peaks.

The method was exemplified by the separation of isopentane, *n*-pentane, *n*-hexane, *n*-heptane and *n*-octane. The improvement in separation resulting from multiple effects of the temperature gradient is shown in Fig. 11. The initial movement of the oven along the column has no effect on the separation of pentanes, as the rates of movement of the corresponding zones are higher, whereas the *n*-hexane zone, travelling at the speed of the oven, is compressed and becomes narrower than the zones of *n*- and isopentane. When a gradient with still high temperatures is produced for the second and third times, *n*-heptane and *n*-octane are also separated in the form of narrow zones; the *n*-octane zone, with a retention time of 65 min, is not wider than the *n*-hexane zone, with a retention time of 20 min.

Zizin and Makov²⁷ suggested a new moving gradient variant of chromathermography; they designed an installation that produces the chromathermographic effect by using a special attachment operating in an isothermal regime (Fig. 12). A chromatographic column (1) enclosed in a casing (2) (tube into tube) is accommodated in a chromatograph thermostat operating in an isothermal regime. The casing of the column is connected at the inlet and outlet with a coil (4) via a piston pump (5) in such a way that a closed contour is formed, through which the heat-carrier can circulate continuously. The coil is incorporated in a heat exchanger (6) with thermal insulation (7) and filled with a coolant. If the temperatures in the chromatograph thermostat, T_0 , and in the heater exchanger, t_0 , are constant, then if $T_0 \gg t_0$ a steady-state gradient of temperatures is fixed in the column casing, its magnitude being dependent on $T_0 - t_0$ and on the circulation velocity of the heat carrier in the closed contour

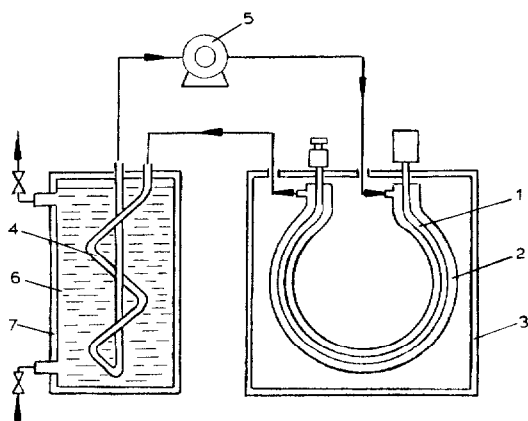


Fig 12 Diagram of chromatographic installation with liquid coolant 1 = Chromatographic column, 2 = column casing, 3 = thermostat; 4 = heat exchanger, 5 = pump, 6 = heat-exchanger casing, 7 = thermal insulation

Zizin and Makov²⁷ presented an equation expressing the temperature distribution during the movement of the gradient along the column. The process is equivalent to the movement along a heater column of infinite length with a temperature gradient varying exponentially. The suggested installation²⁷ combines the advantages of chromathermography and chromatography with temperature programming.

An original impulse-thermal method for gas analysis was developed by Dantsig²⁸. This method ensures high enrichment of admixtures during the component separation in addition to compression of the chromatographic bands in different column sections. This method involves three separation stages. (1) preliminary separation; (2) compression of the chromatographic bands on the column during movement of a narrow thermal field in the direction opposite to the flow of the carrier gas; and (3) elution of the separated components with temperature programming. This method was shown to be effective for determining ethane and ethylene in air at a $10^{-4}\%$ concentration using a device supplied with a catharometer.

5 ELUTION-THERMAL DISPLACEMENT METHOD

Berezkin and Rastyannikov²⁹ suggested an elution-thermal displacement method in which separation takes place as a result of the joint action of a moving thermal field and a low flow of carrier gas. The column filled with sorbent and purged with an inert carrier gas is supplied with an initial mixture until a part of the layer at the beginning of the column is saturated. A narrow oven then moves on to the column and a carrier gas flow is started at the same time. The moving oven causes a sharp decrease in the sorbability of the component in the heated zone, and therefore even a small gas carrier flow is sufficient to remove the component from this zone and direct it to the cold section of the sorbent. The sorbability of the component increases sharply on the cold section of the sorbent and its rate of movement slows accordingly, so that it becomes much lower than that of the heater. Thus, the heater will "overtake" the heavy component and the process of "pushing out" the com-

ponent from the heated zone by means of the carrier gas will be repeated. As the heavy component zone moves ahead it will force out the heavier component, obliging it to move at the speed of the zone. This elution-displacement method makes it possible to decrease considerably the temperature of the thermal field and reduce the contact time of the separating components with the heated zone. This allows the separation of substances that decompose or react at higher temperatures.

Further development of the thermal displacement method was carried out by Harris and co-workers^{30,31}. They showed³¹ that this method, depending on the ratio of the heater movement speed, U_H , to the carrier gas flow-rate, U_r , makes it possible to operate under different column regimes. If $U_H \gg U_r$, adsorbent condensation takes place; if $U_r \gg U_H$, the column works as under elution chromatographic conditions. Operation under thermal displacement conditions requires a particular optimal U_H/U_r ratio. Equations were suggested³¹ for the maximal dose of the initial mixture and the concentration profile in the thermal zone. The latter equation was derived from the assumption that the stationary front moving at the speed of the heater is fixed in the column. These equations were verified on binary mixtures of *n*-hexane with 2,2- and 2,3-dimethylbutane and 2- and 3-methylpentane as examples. Alumina and Porasil B were used as packings. It was shown that when the flow velocity changes and the ratio U_H/U_r is constant, the efficiency of separation can be described by a Van Deemter type equation; at low velocities the spreading of the zone is determined by the longitudinal diffusion, whereas at high velocities it is determined by the mass-transfer resistance. The shape of the bands in the thermal displacement method, as calculated from the suggested equation, is close to that derived from experiment. It has been shown³², using as an example the analysis of *o*-xylene, *n*-nonane, *n*-decane, butylbenzene and other impurities in light volatile solvents, that the chromathermographic method has several advantages over ordinary chromatography under isothermal and linear temperature programmed conditions. Under isothermal conditions, it was not possible to separate the above mixture, and the resolution obtained with linear temperature programming was significantly worse than that obtained under chromathermographic conditions.

Gel'man³³ demonstrated that methods such as chromathermographic, heat dynamic and elution-thermal preparative displacement are convenient when they are used at high concentrations. On the basis of a general chromathermography theory, he discussed the transition from chromathermography with an increase in the amount of sample to chromathermography without a carrier and, subsequently, the transition from the latter to the so-called method of concentration fixing.

6 OVERLOADED CHROMATHERMOGRAPHY

In their extensive investigations of the potential of chromathermography, Zhukhovitsky and co-workers³⁴⁻³⁶ developed a method without employing a carrier gas. This method was termed "overloaded chromathermography" (OCTG). It was found³⁵ that even in the presence of diffusion spreading under OCTG conditions, the amount of the substance in the zone is linearly dependent on the square of the band width of the component. As a rule, the band width is ascribed as time from the moment of the beginning of chromatographic zone output to the moment when the point corresponding to the characteristic temperature reaches the column output.

This method proved to be convenient for measuring both high and low concentrations of different substances. It was stated that the time corresponding to the characteristic temperature is constant, and it can be determined for each component.

The applicability of this method to the analysis of five-component mixtures, *e.g.*, C₂–C₆ *n*-alkanes, was demonstrated³⁷. The theoretical aspects of OCTG have been discussed³⁸, and in particular an equation was derived for calculating the profile of the chromathermographic curve of carbon dioxide when determining it in air on silica gel MSM. The experimental and calculated (theoretical) data were in good agreement.

The search for effective separation methods that allow a decrease in the spreading, an increase in productivity and the determination of the physico-chemical properties stimulated the elaboration of a method lying at the borderline between chromatography and distillation^{39–41}, referred to as “chromadistillation”. According to this method, the mixture to be separated is contained on a column with a solid filler (glass or metal spherules) and when the carrier gas is passed through the mixture a steady-state temperature field with a negative gradient is established. Separation of the mixture on the contacting zone of individual components takes place as a result of multiple condensation and evaporation.

The application of the chromadistillation method makes it possible to perform separations with a liquid stationary phase, which is important when analysing high-boiling compounds (including solids under ordinary conditions). The theory of chromadistillation and a variety of applications were discussed by Zhukhovitsky and co-workers^{42,43}.

Chromathermography, as has been shown above, is exceptionally efficient for the analysis of admixtures, as it makes it possible to increase the concentrations of the components at the peak maxima. Chromadistillation also allows one to enrich the components of the mixture⁴⁴. Yanovsky *et al.*⁴⁵ combined these two methods and suggested a new method which they termed “chromathermodistillation”. This method works in a similar manner to that described earlier²⁵ by combining the temperature gradient which exists in chromadistillation with temperature programming and that is equivalent to the moving of temperature field. This allows one to enhance the effects of enrichment that take place both under chromathermographic and chromadistillation conditions. As distinct from chromadistillation with a stationary temperature gradient, chromathermodistillation makes it feasible to solve a variety of problems concerning the analysis of multi-component mixtures containing components with a wide range of boiling temperatures.

7 THERMOCHROMATOGRAPHY

In connection with the development of investigations of short-lived isotopes, methods for the rapid separation and detection of elements have acquired great importance. A very promising method for the separation of elements is gas thermo-chromatography. This method is based on the entrainment of compounds by the carrier gas, which in some instances is also a reagent gas, from the high-temperature heating zone where such compounds are formed into a column having an pre-set inverse temperature gradient. As reported in a number of publications^{46–55}, the gas thermo-chromatographic method makes it possible to separate elements when their concentration in the initial sample is as low as 10^{-14} – 10^{-11} mole

Thermochromatography is usually regarded as a chromatographic method in which the separation of a sample mixture (with a sufficiently large volume) is carried out with a moving carrier gas (which in some instances also performs the function of a reagent) on a column having a constant negative temperature gradient, and the detection of the zones being separated is usually effected by scanning the column after completion of separation. As a rule, thermochromatography is employed for separating radioactive compounds, which substantially simplifies subsequent identification of the composition of the sample mixture by the scanning method.

Substances that can be separated by gas thermochromatography include a group of comparatively highly volatile oxides formed as a result of various thermochemical reactions (decomposition, combustion in an oxygen atmosphere, etc.). For example, the method was used for the rapid separation of preparations of rhenium, osmium, iridium and mercury⁴⁶. The target was metallic gold of high purity, which was placed in a special quartz ampoule and irradiated with a beam of protons for a definite period of time. After irradiation, the target was allowed to stand for about 40 h for the short-lived isotopes to decay. Volatilization of the reactive products of rhenium, osmium, iridium and mercury from the gold melt and their distribution over the length of a thermochromatographic column having a negative temperature gradient were studied under the following conditions: sublimation temperature, $1160 \pm 20^\circ\text{C}$; sublimation time, 3–60 min; carrier gas velocity, 10–40 ml/min; and carrier gas, oxygen, air and helium. Gaseous products entrained from the gold melt by the carrier gas were fed to the thermochromatographic column, which was a 480 mm \times 2 mm I.D. quartz tube. A constant negative temperature gradient was maintained with the aid of special heaters. The end of the column was connected to a special trap and detector. This method makes it possible to effect selective deposition on the walls of the column of volatile oxides of rhenium, osmium, iridium and mercury in the following sequence of decreasing temperature: Re ($500\text{--}350^\circ\text{C}$), Ir ($180\text{--}80^\circ\text{C}$), Hg ($80\text{--}25^\circ\text{C}$), Os.

Thermochromatography has also been used for the separation and identification of nuclear reaction products⁵⁶, and results for the thermochromatography of Na, K, Cs, Ba, Eu, Yb, Tm, Tl, Pb, Bi, Po, Am and Cf in a titanium column were presented. The carrier gas was helium containing small amounts of sodium or potassium. The atoms of the initial elements were entrained by evaporation from lanthanum. The column, made of titanium foil, was placed in a heater having a negative temperature gradient.

The formation and thermochromatographic behaviour of carrier-free traces of volatile oxides and hydroxide of tungsten were studied⁴⁷. The samples were metallic foils of gold and tantalum irradiated with high-energy protons in which tungsten isotopes were formed by the corresponding nuclear reactions. First, high-temperature sublimation was carried out. Oxygen saturated with water vapour was used as the reagent gas. The temperature in the reaction section of the installation was $1060\text{--}1160^\circ\text{C}$, the carrier gas flow-rate was 15–45 ml/min and the sublimation time was 5–60 min. The distribution of ^{185}W along the thermochromatographic column (550 \times 5 mm I.D.) was determined on completion of sublimation by drawing the tube in front of a scintillation detector connected to an automatic recorder. This modified gas-thermochromatographic method for the separation of radiochemically pure tungsten, under conditions without a carrier gas and without gold and tantalum targets irradiated with high-energy protons, is sufficiently effective and rapid

A study using gas thermochromatography was carried out on the rapid production of short-lived neutron-deficient isotopes of zirconium and niobium from volatile chlorides for the purpose of further nuclear-spectroscopic investigations⁴⁸. An ampoule containing silver chloride was irradiated with an ejected beam of protons on a synchrocyclotron at the Joint Institute of Nuclear Research (Dubna, Moscow Region, U.S.S R.). After the ampoule had been irradiated, it was introduced into a reaction vessel into which 3–5 min earlier a thoroughly washed thermochromatographic column had been inserted. After completing the experiment, the column was removed quickly from the vessel, cooled and cut into separate zones, then each zone was measured for radioactivity using a Ge(Li) detector to determine the total yield and distribution of the separated radioactive elements along the thermochromatographic column.

Based on the thermochemical properties of osmium and rhenium oxides, a rapid gas thermochromatographic method was elaborated for separating rhenium from a complex mixture of products that are formed as a result of irradiation of targets with high-energy protons⁴⁹. This method allows the production of radioactive preparations of rhenium for studying the nuclear spectroscopic properties of short-lived isotopes of this element, the half-life of which is several minutes.

Eichler⁵⁰ separated thermochromatographically the products of carrier-free nuclear reactions without a carrier gas. A column having a temperature gradient in the axial direction was used to separate the mixture thermochromatographically, a carrier gas being passed through the column in the direction of the temperature drop. It was shown that when the gas was passed through the column continuously, no equilibrium distribution was achieved. In an interrupted experiment, the distribution of the components along the column is "frozen" and an "internal chromatogram" is obtained in the column. An equation was derived⁵⁰ expressing the relationships between the total retention volume and the cross-section of the stationary phase, initial temperature, temperature gradient, heat of adsorption and the temperature of precipitation on the column walls. Equations that determined the precipitation temperature and described the processes of separation of the nuclear reaction products were obtained⁵¹. The method was successfully used in radiochemistry to identify elements 105^{49} and 107^{57} and to separate the products of uranium fission⁵²

Radioactive iridium and platinum compounds in a carrier-free state, which were formed at $725 \pm 25^\circ\text{C}$, were separated on a quartz thermochromatographic column. The influence of the method for producing the initial preparation and the experimental conditions was studied, particularly the effect of moisture in the carrier gas on the yield of oxygen-containing volatile compounds of iridium and platinum. Both elements formed two adsorption zones, under certain conditions the iridium zone centres were at 265 ± 20 and $175 \pm 20^\circ\text{C}$ and those of platinum at 280 ± 20 and $55 \pm 15^\circ\text{C}$ ⁵⁸.

Travnikov and co-workers^{59,60} studied the behaviour of actinides and fission products in the process of transfer of their chlorides in a column with a temperature gradient, with variable starting temperature, gradient value, carrier gas velocity and other factors. It was shown that the separation of micro-amounts of elements having similar properties could be achieved, provided that there is a difference in the characteristic temperatures of adsorption of not less than 50°C . New effective methods for the chromathermographic separation of trans-plutonium elements and chloride

were suggested. The thermochromatographic behaviour of trace amounts of rare-earth metal trichlorides was examined⁶¹. Distinct adsorption zones of the trichlorides of individual rare-earth elements were obtained in an open quartz gas thermochromatographic column of I.D. 1.25 mm. It was shown that the temperatures of the centres of gravity of the adsorption zones of the trichlorides of all the rare-earth elements were almost identical and, consequently, the gas thermochromatographic separation under these conditions was impossible.

Novgorodov⁶² studied the separation and purification of radionuclides by thermochromatography. Theoretical calculations were made of the distribution of a substance during its movement through a thermochromatographic column having a constant temperature gradient. The thermochromatographic behaviour of nuclear reaction products during the combustion of uranium and molybdenum irradiated with high-energy protons in oxygen was studied. The behaviour of trace amounts of certain rare earth elements in a tantalum column under vacuum was also investigated. A description was given⁶² of selective and rapid methods for the thermochromatographic separation of radioactive isotopes under vacuum and in a gas phase containing chlorine, hydrogen chloride, oxygen and their mixtures. Thermochromatography of ¹⁰⁶Ru and ²³³Pu was used to study the products of the reaction of fluorine containing 1% of oxygen with ruthenium and plutonium oxides and fluorides⁶³. Methods for the separation of radiochemically pure fission products developed on the basis of thermochromatography can be used in the production of radioactive isotopes valuable for applied investigations.

8 APPLICATION OF CHROMATOGRAPHIC METHODS WITH A TEMPERATURE GRADIENT TO THE DETERMINATION OF PHYSICO-CHEMICAL CHARACTERISTICS

The application of chromatography is not restricted only to the solution of problems concerning separation and analysis of complex mixtures, *i.e.*, problems of a pure analytical nature. In our opinion, the potential of chromathermography for investigating the physico-chemical properties of substances has been insufficiently studied, although its application to physico-chemical measurements was considered briefly in one of the first papers on this method⁶. The application of this method made it possible to determine the heats of adsorption of ethane, propane and butane on silica gel; the results were in good agreement with those obtained by other methods. Eichler and Zvara⁶⁴ substantiated the validity of calculations of heats of adsorption from thermochromatographic data. They also considered⁶⁵ the possibilities of determining the enthalpy (ΔH) and entropy (ΔS) of adsorption from chromatographic data obtained in a column having a constant negative temperature gradient in the direction of flow. A time retention equation was derived on the basis of the theory of linear chromatography. Equations for the entropy of adsorption were given for two models of steady-state and unsteady-state adsorption layers. Approximate methods were developed for determining ΔS and ΔH on the basis of experimental data.

Fan and Gaeggeler⁶⁶ investigated the adsorption of lead on quartz and calculated the enthalpy and entropy of adsorption from thermochromatographic results. Eichler *et al.*⁶⁷ determined the heats of adsorption of metal chlorides using thermochromatography. These methods made it possible to determine the activation

energy and the reaction order of dehydration of complexes of certain cations⁶⁸ and the kinetics of the separation of gaseous products of perchlorate decomposition⁶⁹.

A simple arrangement was suggested⁷⁰ for conducting thermochromatographic experiments on the basis of the Tsvet-100 chromatograph and testing it by comparing the data from the thermochromatographic and thermogravimetric decomposition of carbonyltriphenylphosphine complexes of rhodium, *viz.*, $\text{Rh}(\text{CO})_3(\text{PPh})_3\text{ClO}_4$ and $\text{Rh}(\text{CO})(\text{PPh})_2\text{Cl}$. Weighed amounts of ground sample were placed in a Pyrex glass reaction tube, which was incorporated in one of the chambers of the chromatograph evaporator and coupled directly to one of the heat conductivity cells. Linear heating of the evaporator in the temperature range 20–320°C at an increasing rate from 0.5 to 10°C/min was effected by means of a laboratory motor transport supplied with a small electric motor and pressure regulator.

The suggested thermochromatographic technique is more universal in application than the thermogravimetric method and can be used for studying solid-phase conversions of compounds whose heat resistance does not exceed 400°C and whose decomposition is accompanied by the evolution of volatile products.

The thermochromatographic technique was used to study the physico-chemical properties of mendelevium and a variety of other actinoids in comparison with some known metals⁷¹. The thermochromatographic method was also successfully employed for studying the chemical products of uranium fission⁷².

Another interesting physico-chemical application is associated with the study of heterogeneous catalytic reactions. In 1961, the possibility of coupling in the reactor heterogeneous catalytic reactions and the chromatographic separation of the components of the reaction mixture⁷³. In 1964, Roginsky and Yanovsky⁷⁴ indicated that in a number of instances, carrying out the reaction in a chromatographic regime under isothermal conditions is not effective. This takes place, for example, in reactions of the $\text{A} \rightleftharpoons \text{B}$ type because, irrespective of the difference in the adsorption coefficients K_A and K_B , the separation of A and B on the column does not give advantageous yields of either A or B. The same situation is observed with reactions of the $\text{A} \rightleftharpoons \text{B} + \text{C}$ type, with $K_B = K_C$. In view of this, a suggestion was made as to the prospects of employing stationary chromathermography for such reactions.

Let us introduce into the flow pulses of substance AB (which in the presence of the catalyst filling the column reacts at a limited rate in accordance with the scheme $\text{AB} \rightleftharpoons \text{A} + \text{B}$), and starting with a rate ω we displace the temperature field. The adsorption coefficient a_{AB} is high at the beginning on the cold catalyst and the rate V_{AB} of the displacement of AB along the layer of the catalytic packing is low, *i.e.*, the temperature field passes the substance AB. In view of the presence of a negative temperature gradient, the band AB moves to the region of higher temperature together with the travelling oven, and accelerates its movement. Finally, at some characteristic temperature, $T_{\text{char.}}$, AB starts to move at a velocity equal to that of the oven, *i.e.*, $V_{\text{AB}} = \omega$. The rate of movement of the oven, ω , the linear flow velocity, u , and the heat of adsorption, Q , are related as follows:

$$T_{\text{char}} = \frac{Q}{RT \ln \omega/u} \quad (13)$$

If $T_{\text{char}} < T_{\text{react.}}$, where $T_{\text{react.}}$ is the temperature at which the reaction rate becomes appreciable, AB will pass through the reactor without any change as one peak. A

gradual decrease in ω/u leads to $T_{\text{char}} = T_{\text{react}}$ and then significant formation of substances A and B begins, each of them tending to enter the zone with its own characteristic temperature, $T_{\text{char A}}$ and $T_{\text{char B}}$. These attributes make chromathermography very useful for conducting reactions under chromatographic conditions. The selection of u and ω may alter the temperature of the zone where AB is located. It should be emphasized that a reverse reaction $A + B \rightleftharpoons AB$ is suppressed not only by the process of separation, as in the isothermal pulse variant, but also by localization of at least one of the products in the low-temperature zone. By measuring the temperature $T_{\text{char AB}}$ at the outlet of the moment the maximum of AB with concentration C_{AB} appears, we are able to determine the reaction temperature ($T_{\text{char AB}} = T_{\text{react AB}}$). The application of the chromatographic method for effecting reactions under chromatographic conditions is also useful because in this instance a continuous enrichment or compression of the band takes place because the separated chromatographic band is affected by the temperature gradient and therefore the front part of the band moves slowly and the rear part faster, the concentration must be constant and determined by the external pressure. Therefore, reactions higher than first order under chromatographic conditions must proceed at elevated constant velocities in comparison with the isothermal chromatographic regime. In particular, it is advantageous under such conditions to carry out a reaction in which the sorption coefficients of the products are smaller than those of the initial substance (for instance, in high-temperature cracking), when $T_{\text{char AB}} > T_{\text{char B}} > T_{\text{char C}}$, as the reacting substance is in the zone with elevated temperatures while the products are in the zone with low temperatures, thus preventing secondary reactions.

The possibility of isomerization reactions of isohexanes, *viz.*, 3-methylpentene-2 \rightleftharpoons 3-methylpentene-1 and 4-methylpentene-1 \rightleftharpoons 4-methylpentene-2, occurring under chromathermographic conditions was studied experimentally^{7,5}. The results of a study of the catalytic reactions of double bond migration in isohexane molecules on a zinc-iron-copper catalyst under conditions of isothermal elution chromatography and under conditions of stationary chromatography were also described. Conducting the reaction under chromathermographic conditions allows one to obtain higher yields of α -olefins than are obtained under isothermal conditions. This result may be accounted for by the *coupling of the catalytic reactions and the chromatographic separation* in the reactor.

9 CONCLUSION

Methods involving temperature gradients in gas chromatography may be applied successfully in various fields of analytical and physical chemistry. Unfortunately, the advantages of these methods are not fully realized and their field of application is relatively narrow. One of the main reasons for such a situation is the absence of standard equipment and insufficient development of the technical basis of the method.

Further study and modifications of chromatographic methods with a temperature gradient should lead to new effective methods for the separation and analysis of substances and to the establishment of the areas of optimal application of existing methods. We hope that this review will arouse interest among investigators to develop further chromathermographic methods.

10 ABBREVIATIONS

| | |
|------------------------------------|--|
| u | linear velocity of carrier gas; |
| u_0 | linear velocity of carrier gas at column outlet; |
| U_i | linear velocity of substance i in the centre of the zone; |
| U_{Fi} | linear velocity of substance i in the front region of the zone; |
| U_{Ri} | linear velocity of substance i in the rear region of the zone; |
| U_{AB} | linear velocity of substance AB ; |
| ω | linear velocity of the temperature field and heater; |
| K | Henry's constant; |
| K_0 | Henry's constant at the temperature of introduction of the sample into the column; |
| K_i | Henry's constant in the centre of the zone; |
| K_{Fi} | Henry's constant in the front region of the zone; |
| K_{Ri} | Henry's constant in the rear region of the zone; |
| K_A, K_B, K_{AB} | Henry's constant for substances A , B and AB , respectively; |
| T | absolute temperature; |
| T_0 | temperature at the beginning of the column at the initial moment of time; |
| T_i, T_F, T_R | temperatures at the centre, front and rear of the zone, respectively; |
| T_B, T_C | temperature of substances B and C , respectively, |
| Q | heat of adsorption, |
| R | gas constant; |
| L | column length, |
| C | substance concentration; |
| κ | proportion of the gas phase in the column; |
| γ | dT/dL temperature gradient along the column length; |
| m | $dT/d\tau$ temperature gradient with time; |
| HETP | height equivalent to a theoretical plate; |
| HETP _{iso} | height equivalent to a theoretical plate under isothermal conditions, |
| HETP _{chromatherm} | height equivalent to a theoretical plate under chromatographic conditions; |
| ε | characteristic value for determining the compression of the band on the layer; |
| O | enrichment factor, |
| μ | peak width at half-height; |
| V | retention volume of sample substance; |
| ΔV | difference in retention volumes of two sample substances. |

11 ACKNOWLEDGEMENT

The authors thank Dr. L. S. Ettre for his help and valuable discussion.

12 SUMMARY

The main applications of temperature gradients in gas chromatography are reviewed, including stationary chromatothermography, combined chromatothermographic methods, elution-thermal displacement, overloaded chromatothermography and thermochromatography. The theoretical basis of the methods, the possibility of practical applications for analytical and physico-chemical measurements and prospects for development of the methods are considered

REFERENCES

- 1 V G Berezkin, in V G Berezkin, V S Gavrichiev, L N Kolomiets, A A Korolev, V N Lipavsky, N S Nikitina and V S Tatarinsky (Editors), *Gazovaya Khromatografiya v Neftekhimu (Gas Chromatography in Petrochemistry)*, Nauka, Moscow, 1975, p 17
- 2 J H Griffiths, D H James and O S Phillips, *Analyst (London)*, 77 (1952) 897
- 3 W E Harris and H W Habgood, *Programmed Temperature Gas Chromatography*, Wiley, New York, London, Sydney, 1966
- 4 A A Zhukhovitsky, N M Turkel'taub, O V Solotareva and V A Sokolov, *Dokl Akad Nauk SSSR*, 77 (1951) 435
- 5 A A Zhukhovitsky, V M Turkel'taub and V A Sokolov, *Dokl Akad Nauk SSSR*, 88 (1953) 859
- 6 N M Turkel'taub, V P Shvartsman and T V Georгиеvskaya, *Zh Fiz Khim*, 27 (1953) 1827
- 7 A A Zhukhovitsky and N M Turkel'taub, *Dokl Akad Nauk SSSR*, 94 (1954) 77
- 8 A A Zhukhovitsky, N M Turkel'taub and V P Shvartsman, *Zh Fiz Khim*, 28 (1954) 1901
- 9 A A Zhukhovitsky and N M Turkel'taub, *Gazovaya Khromatografiya (Gas Chromatography)*, Gosoptekhizdat, Moscow, 1962
- 10 A A Zhukhovitsky, E V Vagin and S S Petukhov, *Dokl Akad Nauk SSSR*, 102 (1955) 771
- 11 C Lapp and K. Erali, *Bull Sci Pharmacol*, 47 (1940) 49
- 12 N G Turner, *Nat Pet News*, 35 (1943) 234
- 13 A A Zhukhovitsky and N M Turkel'taub, *Dokl Akad Nauk SSSR*, 116 (1957) 986
- 14 R W. Ohline and D D De Ford, *Anal Chem*, 35 (1963) 227
- 15 R E Kaiser, in K V Chmutov and K I Sakodynski (Editors), *Uspekhi Khromatografii (Advances in Chromatography)*, Nauka, Moscow, 1972, p 193
- 16 R E Kaiser, *Fresenius Z Anal Chem*, 236 (1968) 168
- 17 O A Sukhorukov and N M Vatulya, in K I Sakodynski (Editor), *Transactions Gazovaya Khromatografiya (Gas Chromatography)*, NIFKhim im L Ya Karpov, NIITEKhim, Moscow 1970.
- 18 A A Zhukhovitsky, N M Turkel'taub and T V Georгиеvskaya, *Dokl Akad Nauk SSSR*, 92 (1953) 987
- 19 V G Berezkin and V S Tatarinsky, *Gas-Chromatographic Analysis of Impurities*, Consultants Bureau, New York, London, 1973, p 127
- 20 A A Zhukhovitsky and N M Turkel'taub, *Zavod Lab*, 10 (1956) 1252
- 21 N Berg, *Trans Am Inst. Chem*, 42 (1946) 665
- 22 Yu. M Genkin and M L Sazonov, *Gazov Delo*, 1 (1971) 19
- 23 V I Samuilov, Yu M Genkin and M D Suvorova, *Auth Cert*, No 257848, *Bvull Izobr*, No. 36 (1969)
- 24 D E Bodrina, L V Kovalev, T V Adamiya and G A Krasnova, *Zavod Lab*, 46 (1980) 216.
- 25 V G Berezkin, V S Tatarinsky and A A Zhukhovitsky, *Zavod Lab*, 11 (1970) 1299
- 26 A G Nerheim, *Anal Chem*, 32 (1960) 436
- 27 V G Zizin and N I Makov, *Zavod Lab*, 45 (1979) 1082
- 28 G A Dantsig, *Zavod Lab*, 30 (1964) 1313
- 29 V G Berezkin and E R Rastyannikov, *Izv Akad Nauk SSSR, Ser Khim*, 2 (1968) 58
- 30 C M A. Badger, J A Harris, K F Scott, M J Walker and C S G Phillips, *J Chromatogr*, 126 (1976) 11
- 31 J P Horrocks, J A Harris, C S C Phillips and K F Scott, *J Chromatogr*, 197 (1980) 109.
- 32 V G Berezkin and N G Starostina, *Chromatographia*, 8 (1957) 395
- 33 L G Gel'man, *Thesis Essay*, VNIGNI, Moscow, 1972

- 34 A A Zhukhovitsky, M L Sazonov, L G Gel'man and V P Shvarzman, *Chromatographia*, 4 (1971) 547
- 35 S. M Yanovsky, I A Silayeva, L G. Gel'man, V P Shvartsman, M L Sazonov and A A Zhukhovitsky, *Zavod Lab*, 38 (1972) 526
- 36 I A Silayeva, A A Zhukhovitsky, M L Sazonov and V P Shvartsman, *Zavod Lab*, 38 (1972) 1297
- 37 I A Silayeva and S M Yanovsky, *Zh Anal Khim*, 30 (1978) 387.
- 38 S. M Yanovsky, I A Silayeva and G. L Kogan, *Inz -Fiz Zh*, 27 (1974) 466
- 39 A A. Zhukhovitsky, *Auth Cert*, No 536429, *Byull Izob.*, No 43 (1976)
- 40 A A Zhukhovitsky, S M Yanovsky and V P Shvartsman, *Zh Fiz Khim*, 49 (1975) 2954
- 41 A A Zhukhovitskiĭ, S M Yanovskiĭ and V P Shvarzman, *J Chromatogr*, 119 (1976) 591
- 42 A A Zhukhovitsky, S M Yanovsky and V P. Shvartsman, in A. A. Zhukhovitsky (Editor), *Khromatografiya. Itogi Nauki i Tekhniki*, VINITI, Moscow, 2 (1978) 49
- 43 A A Zhukhovitsky and S M Yanovsky, *Zavod Lab*, 47 (1981) 7
- 44 A A Zhukhovitsky, B P Okhotnikov, S M Yanovsky and L G Novikov, *Zh Anal Khim.*, 34 (1979) 545
- 45 S M Yanovsky, G S Birun and A A Zhukhovitsky, *Zh Fiz Khim*, 55 (1981) 1813
- 46 B Boyar, I Votsilka, N G Zaitseva and A. F Novgorodov, *Radiokhimiya*, 16 (1974) 329
- 47 B Boyar, I Votsilka, N G Zaitseva and A F Novgorodov, *Radiokhimiya*, 16 (1974) 385
- 48 B Boyar, I Votsilka, N G Zaitseva and A F Novgorodov, *Radiokhimiya*, 16 (1974) 343
- 49 B Boyar, N G Zaitseva and A F Novgorodov, *Radiokhimiya*, 15 (1973) 553
- 50 B Eichler, *Seiffen/Erzgebirge*, (1974) 1
- 51 B Eichler and V P Domanov, *J Radioanal Chem*, 28 (1975) 143
- 52 A W Castelman and I N Tang, *Nucl Sci Eng*, 29 (1957) 2159
- 53 I Zvara and V V Belov, *Preprint Ob'edineny Institut Yadernih Issledovaniy*, Dubna, 1970, P12-5120
- 54 L Westgard, G Rudstam and O C Jonsson, *J Inorg Nucl Chem*, 31 (1969) 3747
- 55 B Boyar, N. G Zaitseva and A. F Novgorodov, *Preprint Ob'edineny Institut Yadernih Issledovaniy*, Dubna, 1971, P6-5955
- 56 S Hubener and I Zvara, *Radiochim Acta*, 27 (1980) 157
- 57 I Zvara, V P Domanov, S Hübener, M R. Shalayevsky, S N Timokhin, B L Zhuikov, B Eichler and G V Buklanov, *Radiokhimiya*, 26 (1984) 76
- 58 V P Domanov, B Eichler and I Zvara, *Radiokhimiya*, 26 (1984) 66
- 59 A V Davydov, S S Travnikov and B F Myasoyedov, *Radiokhimiya*, 17 (1975) 684
- 60 S S Travnikov, *Thesis Essay*, Institut Geokhimiĭ i Analiticheskoy Khimii AN SSSR, Moscow, 1976
- 61 Nguen Kong Chang, A F Novgorodov, M Kaskevich, A Kolachkovsky and V A. Khalkin, *Radiokhimiya*, 26 (1984) 60
- 62 A F Novgorodov, *Thesis Synopsis*, Institut Atomnoy Energii imeni I V Kurchatova, Moscow, 1982
- 63 B Joumaux, J Ledoux and J Merinis, *Radiochem Radioanal Lett*, 39 (1979) 129
- 64 B Eichler and I Zvara, *Preprint Ob'edineny Institut Yadernih Issledovaniy*, Dubna, 1975, P12-8443
- 65 B Eichler and I Zvara, *Radiochim Acta*, 30 (1982) 233
- 66 W Fan and H Gaeggeler, *Radiochim Acta*, 31 (1982) 94
- 67 B Eichler, V P Domanov and I Zvara, *Preprint Ob'edineny Institut Yadernih Issledovaniy*, Dubna, 1978, P12-9454
- 68 V. A Logvinenko, V M Gorbachov, G F Nikitchenko, L I Myachina and A. V. Nikolaev, *Izv Sib Otd Akad Nauk SSSR, Ser Khim. Nauk*, N12 (5) (1970) 11
- 69 L. Berezkina, S Borisova and N Tamm, *J Chromatogr*, 69 (1972) 31
- 70 N P Fedyann, *Zavod Lab*, 46 (1980) 1032
- 71 S Hubener and I Zvara, *Radiochim Acta*, 31 (1982) 89
- 72 A W Castelman and I N Tang, *J Inorg Nucl Chem*, 32 (1970) 1057
- 73 S Z Roginsky, M I Yanovsky and P A Gaziyev *Dokl Akad Nauk SSSR* 40 (1961) 1125
- 74 S Z Roginsky and M I Yanovsky, in *Gazovaya Khromatografiya, Proceedings, III All-Union Conference on Gas Chromatography, Moscow, May 27-30, 1964*, Dzerzhinsk, 1966, p 54
- 75 I A Degtarev and M I Yanovsky, *Kinet Katal*, 17 (1976) 973