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ANALYSIS OF ADMIXTURES BY CHROMADISTILLATION

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SUMMARY

Chromadistillation (CD) provides many opportunities for the on-column injection of large samples in the analysis of admixtures. The analysis of the mechanisms of the processes in the initial part of the column with dosing (including the "solvent effect" in capillary columns) showed the realization of all CD variants, such as the thermal method, isothermal elution and the restrictive method.

CD processes cause the compression of the band of the components of an admixture at the boundaries between the zones of the main components. A high degree of admixture concentration (1–2 orders of magnitude) allows the components on a chromatographic column (packed or capillary) to be discharged without decreasing the separation efficiency.

Various methods based on CD for the analysis of admixtures in water and organic solvents have been worked out. The direct on-column injection of a water sample (up to 2 ml) allowed the determination of C_6–C_8 *n*-alkanes at concentrations of about 0.005 mg/l. The extraction of admixtures from water with a volatile solvent (hexane) made it possible to determine oil products up to C_{21} *n*-alkane. At the boundary between the main components of the water–ethanol mixture the concentrations of both light (C_3–C_5) and heavy (up to C_{13}) components at 0.1 mg/l in waste water and wine materials were determined. The use of circulation in CD on two columns allows the amount of sample to be increased to 10 ml.

INTRODUCTION

Some applications of chromatography require the on-column injection of large amounts of sample substances. Only the use of chromadistillation (CD) methods, developed since 1974 in the U.S.S.R., has made it possible to solve such problems[1–3].

CD is performed in a column with a solid inert support in a carrier gas flow and processes of condensation and evaporation of sample mixtures proceed in the column. The complete separation of mixtures is achieved using a temperature field with a negative gradient (thermal CD)[4] or by the preliminary on-column injection of a sample the volatility of the component of which is higher than that of any others in the mixture (restrictive CD)[5].

Isothermal elution (IE) without the introduction of a restrictor can also be classified as CD[6–8]. An intermediate position between traditional gas chromatography

and CD is occupied by the so-called "chromatography of vapours close to saturated" (CVCS)[9,10]. As in traditional chromatography, the process of CVCS proceeds on the stationary phase (SP) or on the adsorbent. The classification of the variants of CD should be made according to the character of the sorption isotherms of the separated substances (Fig. 1).

On introduction of large amounts of a liquid on to a chromatographic column, usually concave sorption isotherms are obtained, described by the equation

$$a = \frac{mp/p^0}{1 - p/p^0} \tag{1}$$

where p/p^0 is the relative volatility of the component and m is the amount of SP in the unit column volume. The initial linear part of the isotherm corresponds to classical gas–liquid chromatography (GLC). The middle, concave part of the isotherm is appropriate to CVCS. The main variant of CD (with vertical lines of isotherms) corresponds to the absence of SP ($m = 0$).

The development of CD theories and the elucidation of the mechanisms demonstrated their suitability in solving a large number of problems[11]. Zhukhovitskii has also considered such problems[12].

As a separate, particular application of CD to the analysis of admixtures on capillary columns, we considered a many papers by Grob[13,14] and other workers on the "solvent effect". Its peculiarities are described in connection with the direct (without stream splitting) on-column injection of the sample.

From the point of view of classical chromatography, a sample of 2 μl exceeds at least 10-fold the maximal value for a packed column, and the amount of sample introduced on to a capilary column should not exeed $2 \cdot 10^{-4}$ μl. However, the amount of sample in work on the solvent effect with capillary columns is 10 μl, whereas in work using CD a few millilitres are introduced on to a packed column
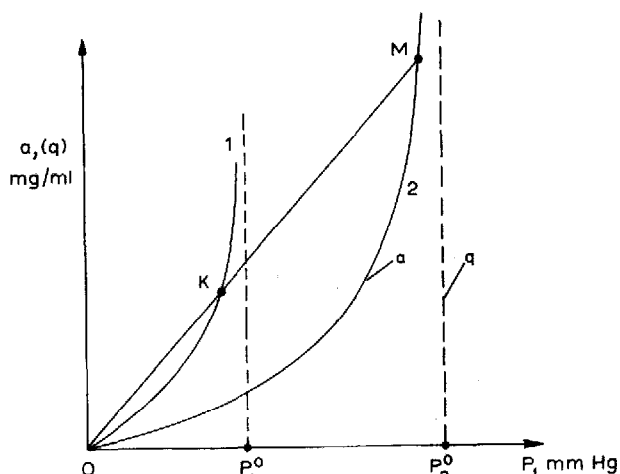

Fig. 1. Sorption isotherms at high concentration. 1 and 2, Separating components; solid lines, CVCS; dashed line, CD. a and q, Amount of the sorbate in unit column volume; p and p^0, vapour pressure of the sorbate.

without decreasing the separation efficiency. In contrast, a sharp increase in the amount of sample leads to new qualitative results. The solvent should be considered as an additional factor determining the efficiency of the analysis. If the separated substances exist in a liquid state on the column, conditions are created for the formation of narrow fronts between the zones and the concentration of admixture components at their boundaries. The presence of a solvent is necessary for the injection of samples, so no special measures should be taken to remove it from the chromatographic system.

In view of the many applications of direct methods of on-column sample injection, the number of publications on the subject has increased recently (more than 100 in 1985)[15]. However, the absence of a detailed knowledge of the theory of the solvent effect has prevented the effective development of these methods. The processes in the initial part of the column are considered to be only chromatographic, but to some extent we can regard them as distillation processes which are covered by the CD variants[16]. This paper illustrates the use of all variants of CD for the injection of large samples for chromatographic analysis.

EXPERIMENTAL

Experiments were conducted on serial Tsvet (with packed columns) and Biochrom (with capillary columns) chromatographs. Metal and glass tubes of U- and spiral shapes (40–300 cm long × 0.4 cm I.D.) were used as CD columns. The initial part of the CD column (13 cm long) was installed into the evaporator of the injector. The main part of the CD column was kept under isothermal conditions or a thermal field with a negative gradient was applied along the bed. To form the gradient a heater with a Nichrome wire wound with an alternating pitch was used, so that the temperature decreased monotonously from the evaporator to the outlet of the column.

A liquid sample was introduced on to the CD column with a gas syringe (capacity up to 2 ml) or a microsyringe (10 μl).

The maximal temperature at the bed should not be higher than the boiling point of the sample solvent. The chromatographic separation column was located on one thermostat with the CD column, or isolated with temperature programming after finishing sample injection.

Glass and metal packed columns with an SP such as SE-30, PEG-600 or Carbowax 20M and a glass capillary column with XE-60 were used. The experimental conditions are given in detail in the legends to the figures.

RESULTS AND DISCUSSION

Isothermal elution of mixtures

In IE, the sample mixture in the liquid state is placed on an inert support (without SP) and eluted from the column with a carrier gas flow at a constant temperature. IE is the first stage of any variant of CD separation. The curve recorded in such an experiment has a stepped form (Fig. 2b). Taking into consideration traditional distillation, one can assume that as in evaporation from a flask, the composition should change continuously, gradually becoming enriched with the less volatile component, so that the pure component 1 should be obtained only in the last
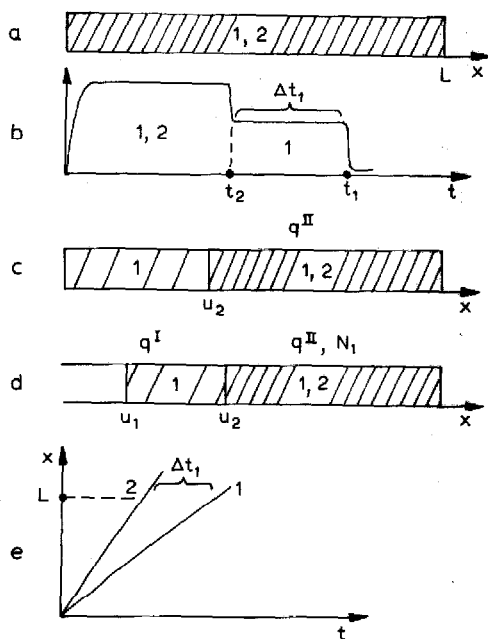
Fig. 2. Isothermal elution. (a) Initial distribution of components 1 and 2 in the bed; (b) chromadistogram; (c) distribution in the bed for non-volatile component 1; (d) as (c), but for volatile component 1; (e) graphs of the movement of the closing fronts.

drop of the solution. The observed curve (Fig. 2b) is the result of distillation processes under chromatographic conditions with the movement of the components zones along the bed (we call such a process chromadistillation). Although in this instance we do not observe the sorbent inherent in chromatography, we consider CD processes from the frontal desorption chromatography position, where the sample mixture, moving along the bed, separates "on itself". If we assume that component 1 is virtually non-volatile (Fig. 2c), it will stay on the column and the zone of component 2 will move along the bed according to the chromatographic laws with a velocity $U_2 = \alpha C_2^0/q^{II}$, determined by the flow velocity, α, the concentration of the saturated vapour of component 2, C_2^0, and the amount of liquid in unit column volume, q^{II}. If the volatility of component 1 is sufficient, its rear boundary will also move forward along the bed (Fig. 2d). The velocity of the zone boundaries (U_i) and also the composition (N_i) and the amounts of the solutions formed at the zones (q) are determined by the balance equations composed at the zones boundaries for every component.

   The velocity of the boundary movement of component 2 (U_2) does not depend on the composition of the sample mixture. The boundary of component 1 moves with a velocity $U_1 = \alpha C_1^0/q^I$, determined by the correlation of the volatility of the separated components ($\beta_{12} = C_1^0/C_2^0$) and the composition of the sample mixture as $q^I = q^{II}[\beta_{12} + (1 - \beta_{12})N_1]$.

   From the equations for the movement of the zone boundaries the discharge of admixture components at the closing front of the solvent takes place under equilibrium conditions, almost immediately after the distribution of the liquid along the bed, so far as $U_1 = U_2$ is realized (Fig. 2b and e).

Pretorius *et al.*,[17] attempted to formulate the theory of these processes. In some instances it coincides with our results, but they consider the process to be only chromatographic, their criteria for the conditions of forming admixture zone from the solvent are too approximate. They believe that an admixture film may be formed only for hydrocarbons of molecular weight > 500. We have shown[16] that under these conditions an admixture component with a molecular weight of about 150 may be discharged.

Grob[18] and Grob and Muller[19] came to the conclusion of the necessity to use the initial part of the column without an SP (the so-called "retention gap"). In the explanation of the mechanisms of the contraction of the admixture band the emphasis was placed on the fact that the frontal boundary moves more slowly than the rear boundary, which is moving along the part of the column without an SP. Such an explanation of the processes does not take into consideration the admixture concentration. From CD theory it follows that long before the rear front of the solvent reaches the main part of the column with an SP, an increased sorbate concentration has already been formed at the part of the column without an SP. The same shortcoming can be observed in the explanation of the band contraction process, which is based on the elution of the sorbate at the phase consisting of the solvent with an alternating amount of the liquid along the bed[13].

The above observations should be considered when a component of the admixture is less volatile and forms a perfect solution with the solvent. In this instance we observe at the rear front of the solvent a discharge of admixtures as a narrow peak. However, some part of the admixture component may be lost during the solvent evaporation (component 1 in Fig. 2c). The amount of this component relative to the total amount is β_{12}. In the indirect method for the determination of oil admixtures in water this mistake was taken into consideration in the calibration process[20]. After the preliminary extraction of admixtures from water with hexane, the solvent sample (0.4 ml) was introduced on to the CD column. The solvent zone was blown out into the atmosphere, and admixtures accumulated at the rear front of the solvent were directed to chromatographic analysis.

Let us consider a case where the admixture component discharges at the frontal boundary of the main component of the mixture (this applies to "light" admixtures). According to the distillation laws it is possible when the equilibrium concentration of the admixture in the gas phase above the solution, $C_2 = C_2^0 \gamma_2 N_2$, is higher than the concentration corresponding to the saturated vapour of the solvent, that $C_2 > C_1^0$ where γ_2 is the activity coefficient and N_2 is the molar fraction of component 2 in the solution. This inequality can be realized both for perfect solutions ($C_2^0 > C_1^0$) and with strong positive deviations from Raoult's law (with $\gamma_2 \gg 1$) it may be $C_2^0 < C_1^0$. As follows from the above equations for the velocity of movement of the boundary of component 2, U_2, the retention volume at this boundary is described by the equation:

$$V_2 = Q_{\text{sample}}/C_2^0 \gamma_2$$

where Q_{sample} is the total amount of sample injected on to the column. From this equation it follows that for perfect solutions the time of discharge of the admixture does not depend on the solution composition, and for imperfect solutions the time
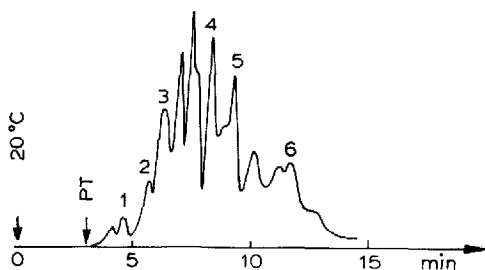
Fig. 3. Chromatogram of the quantitation of the petroleum components in water: 1 = hexane; 2 = benzene; 3 = heptane; 4 = toluene; 5 = octane; 6 = o-, m-, p-xylenes. CD spiral glass column (300 × 0.3 cm I.D.) packed with glass balls, diameter 1–2 mm; evaporator temperature, 100°C; column temperature, 20°C; dose, 0.4 ml; stainless-steel chromatographic column (100 × 0.3 cm I.D.) packed with Chromaton N with 5% silicone SE-30; temperature, programmed from 50 to 100°C at 3°C/min; scale, $2 \cdot 10^{-10}$ A.

of injection of the admixture (and accordingly the width of the band in the elution curve) can be reduced.

The last circumstance was taken into consideration in developing direct methods for the determination of alkanes in water[21,22]. (Fig. 3). CD and chromatographic columns were kept in one thermostat and were connected by a four way tap. A few minutes after sample introduction the tap was switched over and the analysis was conducted under temperature programming conditions. The process was accompanied by blowing out of water into the atmosphere.

This technique allowed the determination of n-alkanes in water at a concentration 0.005 mg/l in a sample of 2 ml with an electrometer scale of $2 \cdot 10^{-11}$ A. The solubilities of hexane and octane in water were calculated to be 10.2 and 0.72 mg/l, which coincided with the literature data.

Thermal chromadistillation

IE does not effect the final separation of the mixture into individual components (Fig. 2b). Some part of the admixture components can be discharged simultaneously with the release of the solvent zone. The loss of the admixture for neighbouring alkanes is about 30%. Depending on the character of the solution formed
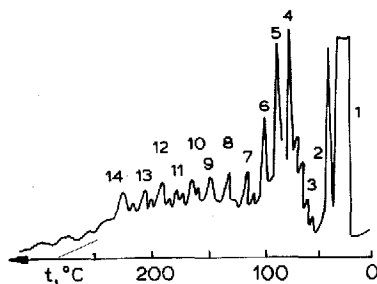

Fig. 4. Chromatogram of the effluent water from an oil refining factory. 1–14 = C_6–C_{19} n-alkanes. CD, stainless-steel spiral column (300 × 0.3 cm I.D.) packed with stainless-steel balls 0.5 mm in diameter; temperature gradient from 50 to −20°C; nitrogen flow-rate 10 ml/min; sample of hexane solution, 0.25 ml. Stainless-steel separation column and stainless-steel spiral trap (100 × 0.3 cm I.D.) packed with Celite 545 with 2 and 11% SE-30; temperature, programmed from 0°C (column) and −20°C (trap) to 250°C; flame ionization detector; scale, $2 \cdot 10^{-8}$ A.

by the admixture with the solvent, different types of distortion of the peak shapes of the sample components, with sloping parts of both the front and rear parts of the peak, may occur.

To ensure narrow and symmetrical peaks it is necessary to create conditions for the complete and rapid discharge of admixtures from the solvent. A temperature regime with a negative gradient (thermal CD) creates conditions for multiple condensation of the mixture and causes its complete separation into individual components. As a rule the amount of admixture is not sufficient to form individual zones and the admixtures discharge in the form of narrow bands at the boundaries between the zones of the main components.

In the indirect method for the determination of admixtures in water (Fig. 4), after the CD separation the admixtures were absorbed in a trap at low temperature, and then at high temperature were desorbed on to the separation column. The detection limit of the components was determined by the purity of the solvent used. After the additional distillation of hexane, the concentration of C_7-C_8 alkane admixture in it was about $5 \cdot 10^{-3}\%$ and that of less volatile components was $1 \cdot 10^{-4}-4 \cdot 10^{-4}\%$. Taking into consideration the additional enrichment obtained with the extraction, the quantitation of oil products in water was possible at the level of the allowed concentration limit (ACL) for drinking water (0.1–1 mg/l).

The solubility of hydrocarbons and alcohols in water is limited and they form solutions with large positive deviations from Raoult's law, which is why in CD processes they discharge from water as "light" admixtures at the frontal edge of the main component[23]. Fig. 5 shows the chromatogram of such an analysis. The sensitivity for alcohols is less than 0.1 mg/l. At this sensitivity the concentration of alcohols in water was found to decrease by 40–60% in 2–3 h.

Restrictive CD and chromatography

The preliminary introduction on to a column of a solvent that is more volatile than the sample components (restrictor) ensures, as in thermal CD, multiple condensation and evaporation processes. The use of a restrictor leads to a discharge of light admixtures at the rear front of the restrictor and enrichment of components.
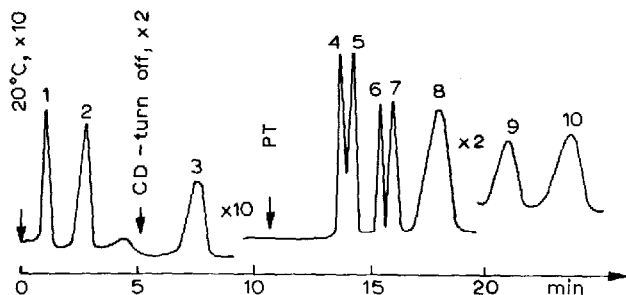

Fig. 5. Chromatogram for the determination of alkanes and alcohols in water: 1 = hexane; 2 = heptane; 3 = octane. Alcohols: 4 = C_1; 5 = iso-C_3; 6 = C_3; 7 = iso-C_4; 8 = C_4; 9 = iso-C_5; 10 = C_5. Concentration, 2–20 mg/l. CD glass column U-type (70 × 0.4 cm I.D.) packed with glass balls 1–2 mm in diameter, modified with methanol at 100°C; temperature gradient from 100 to 20°C; nitrogen flow-rate, 17 ml/min; sample, 0.5 ml. Stainless-steel separation column, U-type (100 × 0.3 cm I.D.) packed with Chromosorb P with 20% PEG-600; temperature, programmed from 20 to 90°C at 20°C/min; flame ionization detector; scale, 10^{-10} A.
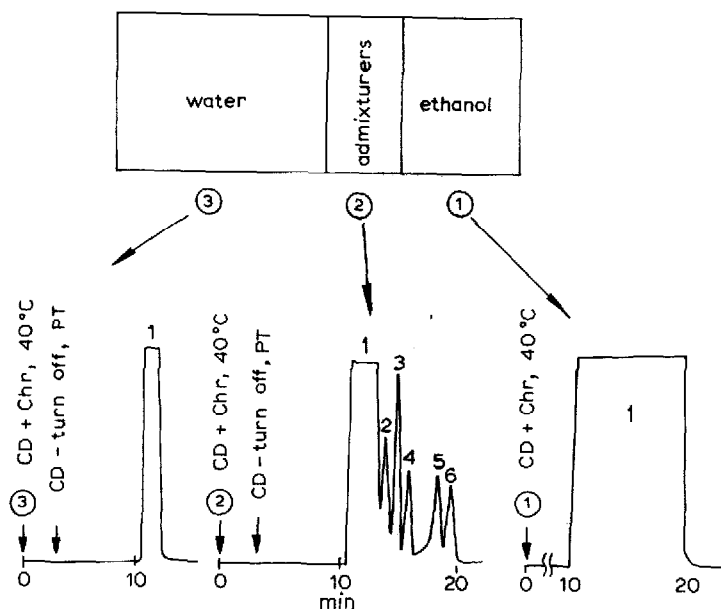
Fig. 6. Chromatograms with sampling at the outlet of the CD column in the separation of water–ethanol mixtures containing alcohol admixtures: 1 = ethanol; 2 = iso-C_3; 3 = C_3; 4 = iso-C_4; 5 = C_4; 6 = C_5. ①, ②, and ③, positions of selection of the samples; temperature, programmed from 40 to 90°C at 15 °C/min (PT).

According to the substance balance at the boundary zones, represented by the line OM in Fig. 1, the admixture components should be enriched. The maximal value of the concentration is determined by the point K in Fig. 1, where the line OM crosses the isotherm of component 2. Without an SP on the column the components are enriched up to the concentration of the saturated vapour. As the rear boundary of the mixture zone moves along the bed faster than the frontal boundary we can observe complete separation of the mixture. As a result of such a process, the admixtures are concentrated according to the solubility of the main component at each boundary. The restrictor may consist of a main component of a mixture, not containing admixture components of the sample. In the analysis of water–ethanol solutions, ethanol, discharged at CD separation, creates the restrictor zone.
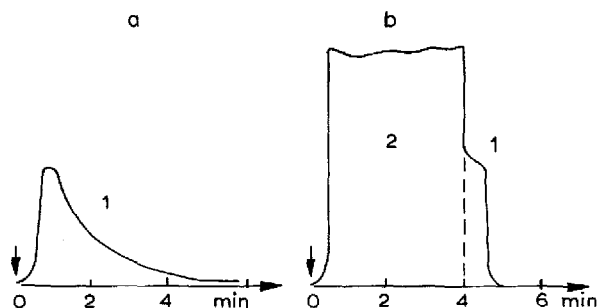

Fig. 7. Chromatograms of butanol in the analysis of (a) water and (b) water–ethanol. 1 = Butanol; 2 = ethanol. CD column as in Fig. 5.
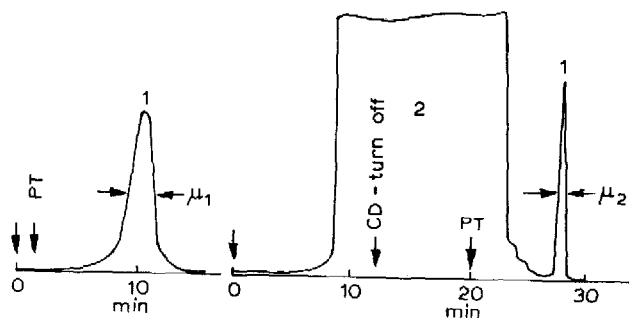
Fig. 8. Chromatograms of butanol with using CD and capillary columns in the analysis of (a) water and (b) water–ethanol. 1 = butanol; 2 = ethanol. CD column as in Fig. 5. Glass capillary column (50 m × 0.25 mm I.D.) coated with XE-60; helium flow-rate 3.1 ml/min; temperature, programmed from 20 to 170°C at 6°C/min (PT).

The results of sampling at the outlet of the CD column during the separation of water–ethanol mixtures show concentration of the admixture at the boundary between water and ethanol (Fig. 6). In the analysis of samples taken from the water zone traces of remaining ethanol are found.

With connection of CD and the chromatographic columns, the admixtures are concentrated twice, first in the CD column at the boundary between the water and ethanol zones, and then in the separation column by the CVCS restrictive processes at the rear front of ethanol[24]. Fig. 7 shows butanol discharged in the form of a stretched peak within 6 min of the water solution, and in the analysis of water–ethanol solution butanol appears as a narrow shoulder on the ethanol peak. With connection of CD and capillary columns, the width of the butanol peak for a water–ethanol solution (μ_2) was seven times less than that for a water sample (Fig. 8).

Difficulties often arise when the sample components are in an emulsion state. Thus, for the quantitation of C_3–C_{11} alcohols, ethanol was introduced into the water sample, and the homogeneous mixture obtained was used for the analysis (Fig. 9). CD separation is conducted in two stages: first, the light fraction of alcohols (up to
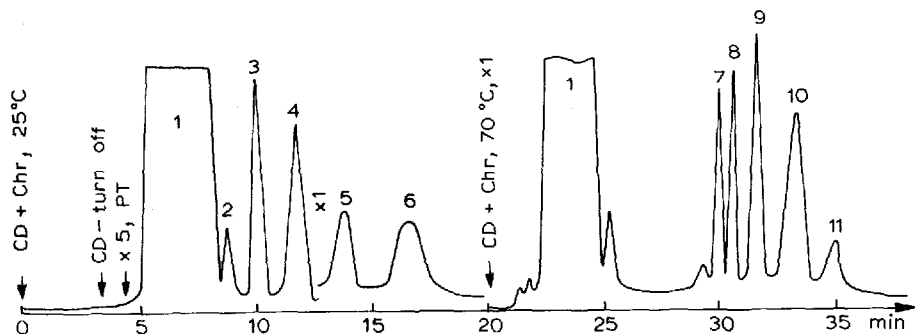

Fig. 9. Chromatogram for the determination of C_3–C_{11} alcohols in water. 1 = ethanol; 2–11 = alcohols from C_3 to C_{11}. CD column as in Fig. 5. Chromatographic column packed with Inerton with 10% Carbowax 20M; scale, 10^{-9} A. Temperature, programmed from 25 to 70°C and from 70 to 175°C at 15°C/min (PT).
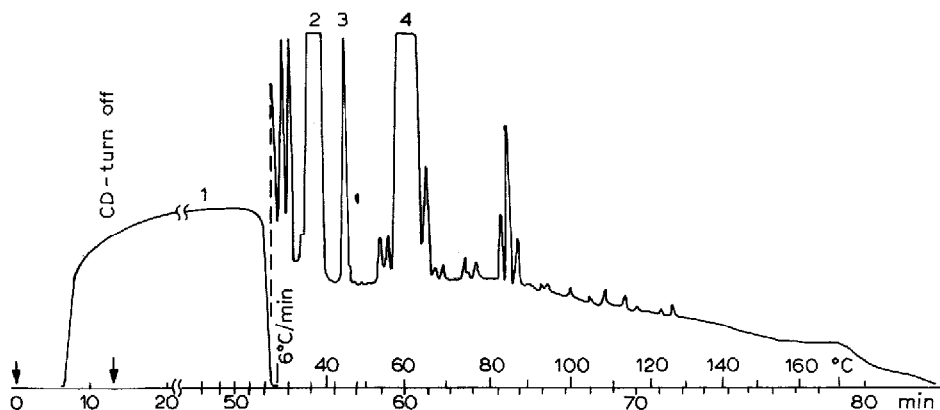
Fig. 10. Chromatogram for brandy analysis. 1 = Ethanol; 2 = isobutanol (200 mg/l); 3 = *n*-butanol (5.9 mg/l); 4 = isopentanol (380 mg/l). CD column as in Fig. 5. Dose, 40 μl. Capillary column in Fig. 8.

C_6) was discharged on to a separating column at 25°C, then heavy alcohols were discharged on to the column at 70°C.

Fig. 10 shows a chromatogram for brandy[24]. During the introduction of admixtures between the CD and capillary columns, a difference in temperatures from 70 to 20°C was created, which ensured the condensation of ethanol in the initial part of the capillary column.

A large increase in the dose injected into the chromatographic analysis is possible by applying preliminary CD concentration of the admixtures with the aid of sample circulation in two CD columns. Using an 8-way PTFE tap a gas flow scheme in the chromatograph was assembled, which made it possible to observe accumulation of admixtures after sampling of each probe. For this purpose, both katharometer chambers were connected with the outlet of the CD columns. The dose was increased up to 10 ml. In each cycle, solvent blow-out and new sampling take place (Fig. 11). Fig. 11 illustrates the linear admixture accumulation with the number of samples introduced.
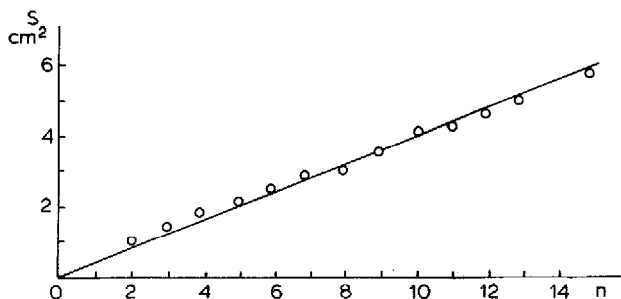

Fig. 11. Dependence of the step area (*S*) on the number (*n*) of samples introduced in circulating CD. Two CD columns were used (100 × 0.2 cm I.D.). Temperature, −200°C; sample mixture, hexane–0.1% octane; amount of sample, 0.2 ml.

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