SOME NEW CHROMATOGRAPHIC TECHNIQUES

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SUMMARY

Six new methods for chromatography without carrier gas are discussed. They allow an increase in precision, sensitivity, and speed of analysis. Examples are given of the use of these methods for the analysis of mixtures of permanent gases, enrichment of microconcentrations, and preparation of high purity gases. A discussion of the efficiency of gas chromatographic columns with a new sorbent having small and uniform channels is presented.

The special features inherent in elution analysis, in particular the necessity of precise sampling and sensitive detection, substantially restrict the possibilities of improving some of its characteristics. This is especially true with respect to the determination of trace quantities of impurities and the possibility of developing continuous analysis.

In the present article a brief description of some new techniques will be given, opening up some additional potentialities in these fields. The first group referred to is chromatography without carrier gas (CWCG). In some cases the absence of a carrier gas sharply reduces the broadening of the zones, often resulting in concentration of the components, and minimizes the requirements imposed on the detecting and sampling devices.

Four versions of CWCG will be considered. In the first (elution CWCG) the test mixture is passed continuously through the column. A change in some parameter at the inlet end of the column (injection of sample of any composition, short duration variations in temperature or flow rate, etc.) leads to the formation of a series of zones of a changed composition moving along the sorbent bed with their individual velocities. The molar fraction of the i-th component (N_i) is related to the specific retention volume (Z_j) and the Henry coefficient (Γ_i) by the equation

$$N_i = \frac{\Pi\,(Z_j - \Gamma_i)}{\Pi\,(\Gamma_k - \Gamma_i)} \qquad (\text{1})$$

Thus the composition of the mixture may be determined by measuring the retention volumes. In this case the detector plays the role of a null instrument. Using as an example the case of binary mixtures it has been shown[2] that the precision of the method is substantially higher than that of elution analysis, the error being about 0.3%.

TABLE I

RESULTS OF THE ANALYSIS OF A C_4H_{10}-C_3H_8-C_2H_6-CH_4 MIXTURE ON β,β'-IMINODIPROPIONITRILE

No. of mixture	Components	Taken (%)	Found (%)	δ^a (%)
I	Butane	35.0	35.6	+ 1.7
	Propane	30.0	31.8	— 6.0
	Ethane	16.0	15.5	— 3.1
	Methane	19.0	17.1	— 10.0
II	Butane	25.0	24.6	— 1.6
	Propane	15.0	15.2	+ 1.3
	Ethane	20.0	20.0	0
	Methane	40.0	40.2	+ 0.5
III	Butane	40.0	38.8	— 3.0
	Propane	10.0	9.5	— 5.0
	Ethane	12.9	13.4	+ 5.6
	Methane	37.1	38.3	+ 3.2
IV	Butane	20.0	21.5	+ 7.5
	Propane	28.0	26.8	— 4.3
	Ethane	20.0	20.0	0
	Methane	32.0	31.7	— 0.9
V	Butane	20.0	21.0	+ 5.0
	Propane	20.0	19.8	— 1.0
	Ethane	35.0	35.6	+ 1.7
	Methane	25.0	23.6	— 5.6

^{a} $\delta = 3.3\%$.

In Table I, the results are given for a determination of the composition of a four-component system of C_1-C_4 paraffins on β,β'-iminodipropionitrile. This stationary phase was chosen in order to use eqn. 1, which is valid only for linear isotherms. A nonpolar solvent–hydrocarbon system gives a specific deviation from linearity, causing some complications in the calculation[3]. The large magnitude of errors is due to some inaccuracy in determining the composition of the initial mixture. The elution CWCG method may be extended to more complex systems.

In differential chromatography without carrier gas (DCWCG)[4] the mixture to be analyzed is introduced into a column previously filled with a reference mixture (or vice versa). The heights of the steps produced are directly related to the values of differences in the concentrations of each component of these mixtures.

Fig. 1 represents a chromatogram of a three-component mixture (methane, nitrogen, argon), and in Table II the results are given of an analysis of a five-component mixture (CH_4, N_2, Ar, O_2, H_2) on NaX molecular sieves ($L = 70$ cm).

The differences in concentrations of the mixtures compared have been measured with an accuracy of 15 to 20%, the error in determining the concentrations themselves not exceeding 0.3–0.7%.

Thus it will be seen that the precision of DCWCG is superior to that of elution analysis. It should be noted that DCWCG permits the analysis of mixtures containing pairs of inseparable components. In the case considered here it is the argon–oxygen pair.
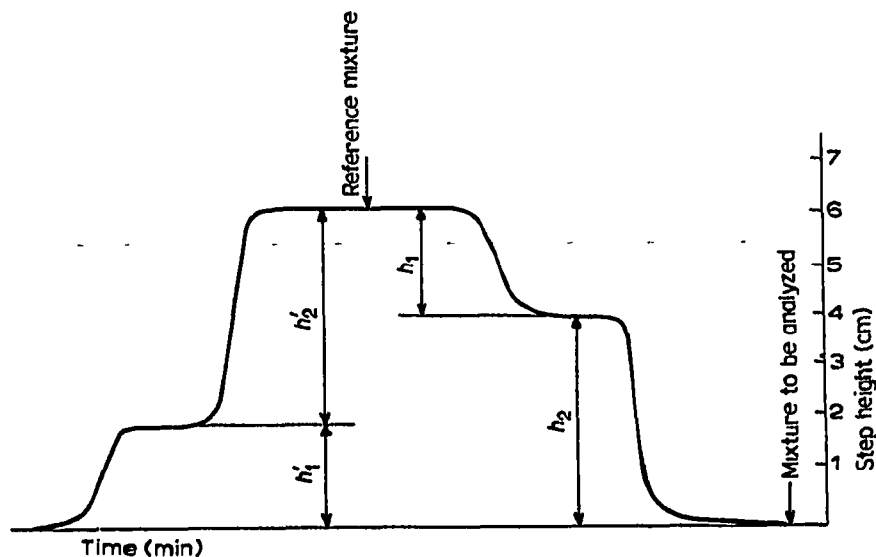
Fig. 1. Chromatogram of a three-component mixture (CH_4, N_2, Ar) obtained by the differential chromatography method.

TABLE II

RESULTS OF THE ANALYSIS OF A FIVE-COMPONENT MIXTURE BY DCWCG

($N_{CH_4} = 0.291$; $N_{N_2} = 0.20$; $N_{Ar} = 0.24$; $N_{O_2} = 0.23$; $N_1 = 0.0100$).

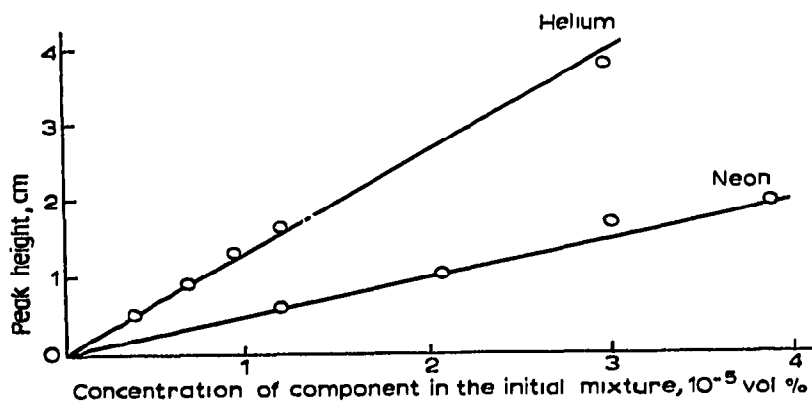| ΔN_i	ΔN_i taken	ΔN_i found	ΔN_i taken $-$ ΔN_i found	% error $\triangle N_{H_2}$	% error N_i
ΔN_{CH_4}	+1.70	+1.70	0	0	0
ΔN_{N_2}	−0.50	−0.41	−0.09	18.0	0.44
ΔN_{Ar}	−0.70	−0.54	−0.16	22 8	0 69
ΔN_{O_2}	−0.58	−0 66	+0.08	13.8	0.34
ΔN_{H_2}	−0.11	−0.09	−0.02	15.0	0.45

Fig. 2. Calibration curves for the determination of the He and Ne content in air.

In the determination of trace amounts of poorly adsorbed components it is advisable to carry out a preliminary chromatographic enrichment by filling an evacuated column with the mixture to be analyzed[5]. A small portion of the mixture enriched in the poorly adsorbed components is then transferred to the separation column where elution analysis is carried out. Either the test gas or some other gas is used as carrier. The principle of this method has been used as the basis of the Luch chromatograph designed and constructed in collaboration with the Dzerzinsk Affiliated Branch of the Experimental Construction Bureau of Automatics.

Fig. 2 shows some calibration curves for the determination of the He and Ne content in air. The sensitivity of the method is 10^{-6} to 10^{-5} vol. %. This chromatograph has been successfully applied to the determination of traces of hydrogen in argon.

In order to enrich well-adsorbed impurities it is necessary to pass a "pushing gas", which is adsorbed more strongly than any of the components of the mixture, through the bed saturated with the test mixture.

In Fig. 3 a calibration curve is shown for the determination of traces of benzene in water or in aqueous solutions. In this particular case water vapour plays the part of "pushing gas" in the chromatographic process of enrichment of trace amounts of benzene (column packed with MSM silica gel; length of column, 180 cm; temperature, 110°), and the role of carrier gas in the elution analysis (column packed with BAU charcoal, a hydrophobic sorbent; length of column, 80 cm; temperature, 110°). By increasing the volume of the sample of water (or aqueous solution) taken for analysis the sensitivity of determination may be increased to $5 \cdot 10^{-7}$ wt.%.

Finally, a combination of CWCG with the heat-dynamic method can be used successfully for preparative purposes. The mixture to be separated is continuously
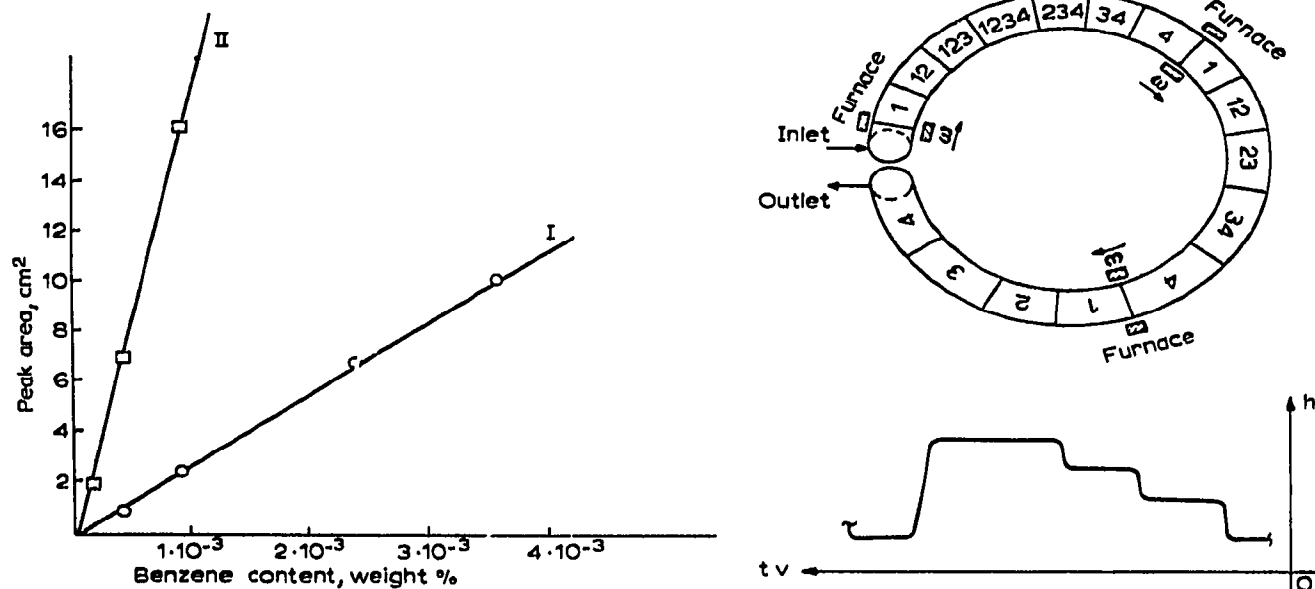

Fig. 3. Calibration curve for the determination of benzene impurities in water and in aqueous solutions.

Fig. 4. Layout of apparatus and chromatogram obtained (the initial mixture contained N_2, C_2H_6, C_3H_8, and C_4H_{10}).

passed through a column having the shape of an unclosed ring. A furnace (or several furnaces) moves continuously along the sorbent bed and pushes out the zones of pure components moving one after the other.

Fig. 4 shows a flow diagram of the device and a chromatogram of the gases emerging from the column. (The initial mixture contained nitrogen, ethane, propane, and butane.)

Belonging to the same group of techniques as the heat-dynamic method without carrier gas is a chromatographic method where fixed concentrations (FC) are used; this was recently developed by the authors in collaboration with GELMAN AND SCHWARTZMAN. If an eluent with a Henry coefficient Γ_{el} and a sufficiently large quantity of a mixture containing n components with Henry coefficients $\Gamma_1, \Gamma_2, \ldots\ldots$ Γ_n ($\Gamma_1 > \Gamma_2 > \Gamma_3 > \ldots\ldots > \Gamma_n > \Gamma_{el}$) is passed through a bed of sorbent, the pushing gas is supplied at a velocity a, and a short furnace begins to move along the solvent bed at a velocity, w, then under some definite conditions a stationary regime of movement of the binary zones can arise in the column, as shown in Fig. 5. The material
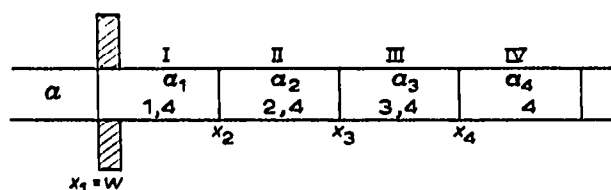

Fig. 5. Diagram of the movement of the zones. Stationary regime (FC method). a = linear velocity of the mixture within a zone, x = velocity of zone boundaries, w = velocity of the furnace.

balance equation of the components permits the derivation of a relationship between the molar fraction (N_i) of a component and the velocity of the furnace (w), flow rate (a) of the "pushing gas" and the adsorption characteristics:

$$N_i = \frac{\Gamma_i - \dfrac{a}{w}}{\Gamma_i - \Gamma_{el}} \tag{2}$$

where Γ_{el} and Γ_i are the Henry coefficients of the "pushing gas" and of the component, respectively. Eqn. 2 has been verified on a He–Ar binary system (activated carbon, length of column = 125 cm, length of furnace = 10 cm, temperature of furnace = 150°). In Fig. 6 two chromatograms are shown, obtained with samples of pure argon and of a mixture containing 20% argon and 80% helium. It will be seen that the height of
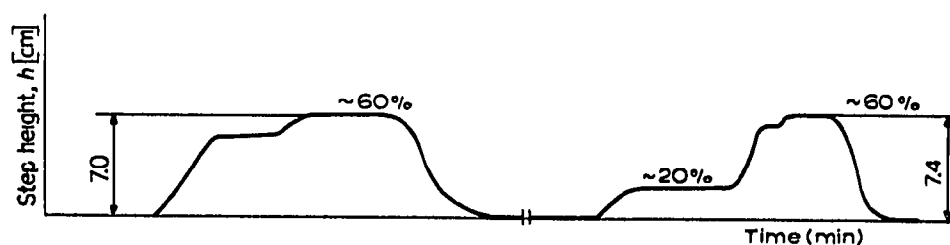

Fig. 6. Chromatogram obtained in the analysis of samples of pure argon and of a mixture of 20% argon and 80% helium.
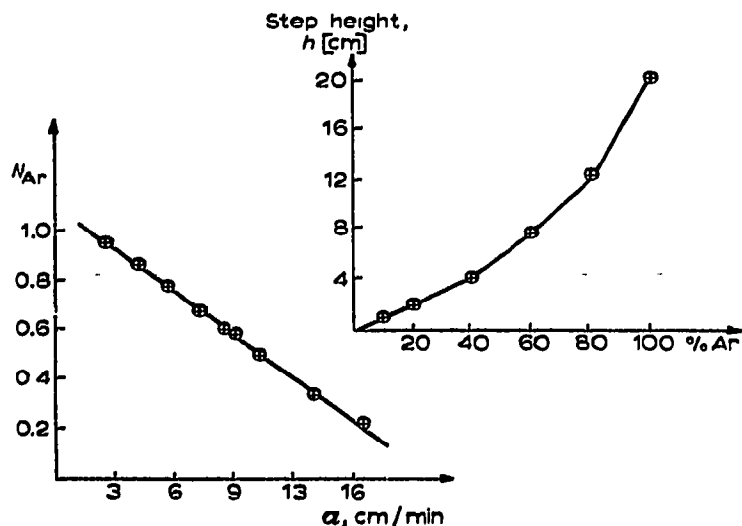
Fig. 7. Linear dependence of the argon molar fraction on the "pushing gas" flow rate and calibration curve of the detector.

the step formed does not depend on the composition of the sample. Fig. 7 shows an experimentally obtained relationship between N_{Ar} and a, which is linear in accordance with eqn. 2.

Five possible applications of the new method are suggested.

Since the value of the FC does not depend on the initial concentration in the sample, the FC method may be used to determine impurities, adsorbed better than the main gas. The advantages of the method are not restricted to the effect of a concentration increase, since the concentration in the zone produced is constant and known; the initial concentration of the impurity may be determined directly from the width of the step. The detector functions as a null instrument. As an example the determination of CO_2 in air is examined. The analyses were made on a column (length = 130 cm, diameter = 0.5 cm) packed with MSM silica gel; air was passed continuously through the column. At a flow rate of air of 20 c.c. per min, a step was produced the height of which corresponded to 0.25% CO_2; it emerged within 2.8 min. A calculation based on material balance showed the content of CO_2 in the air sample analyzed to be about 0.015 vol. %.

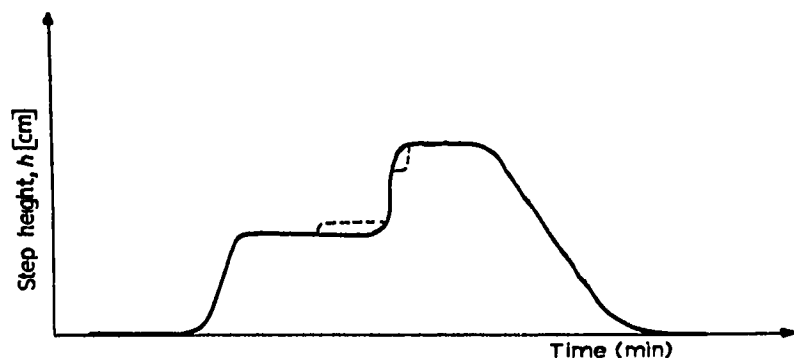In this way the possibility is opened up for the analysis of complex mixtures

Fig. 8. Chromatogram of the N_2–CH_4 mixture obtained by the FC method.

while retaining an independent calibration since the concentration of each component is determined from the width of one step only. Using the width rather than the height of the step as a parameter offers several advantages (less strict requirements imposed on the detector, decreased effect of fluctuations in the parameters, etc.).

Fig. 8 illustrates this point, where a chromatogram of a nitrogen–methane mixture is shown obtained on a column 130 cm long, 0.5 cm in diameter, packed with activated carbon. Helium was passed through the column. The steps on the chromatogram correspond to helium–nitrogen and helium–methane binary zones.

Since a complex mixture in an FC regime is separated into binary mixtures, each containing only one component of the mixture to be separated, the FC method may be applied to preparative chromatography.

As a fourth application, the determination of the thermodynamic characteristics of a sorbate–sorbent system can be considered. By varying only the "pushing gas" flow rate, characteristic equilibria may be obtained throughout the whole concentration range, using only one sample containing an unknown concentration of the component of interest.

Finally, the method may be employed to prepare a binary mixture of a definite concentration; for this purpose it is sufficient, according to eqn. 2, to fix a value of $\eta' = a/w$.

The methods described above are based on the rejection of the principle of elution chromatography. Within the limits of elution chromatography, however, there are important problems associated with the radical improvement of the characteristics of the methods. These are in the first place concerned with increasing the separation efficiency. A significant decrease in HETP requires a modification of the granular sorbents commonly used. To solve the problem it is not only the diffusion path, *i.e.* the section of the channels along which the carrier gas is moving, that should be decreased, but the uniformity of their sizes and distribution has to be secured as well. Two new approaches for solving the problem are presented*.

Decreasing the grain size of commonly used sorbents is limited by the phenomenon of agglomeration of the particles, with the result that resistance is sharply increased and the mass transfer characteristics are impaired. The agglomeration is produced by the adhesion of particles and associated with the presence of roughness of the surface. That is why in the first version of the method developed it is suggested
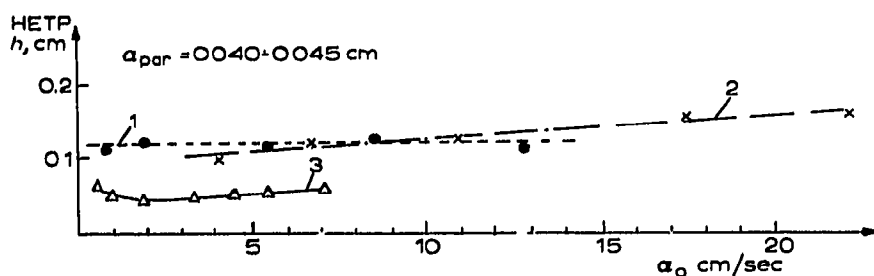

Fig. 9. HETP–a relationship for a filter (1) and for packed columns of different diameter (2, 3) with stainless-steel powder, particle diameter = 0.040–0.045 cm. 1 · filter, column length = 16 cm, diameter of column = 1.6 cm, 0.42 w/w % hexadecane. 2 · packed column, length 20 cm, diameter 0.65 cm, 0.712 w/w % hexadecane. 3 · packed column, silanized, length 7 cm, diameter 3.9 cm, 0.335 w/w % hexadecane.

* The work has been carried out in collaboration with S. M. YANOVSKI and O. N. ALKSNIS.

that very small metallic balls which can be made absolutely smooth are used as a support for a common granular bed. In the second version it is proposed that a rigid structure of the filter type which may be supported on sintered and pressed metallic balls be used. Fig. 9 shows the HETP–α relationship for a filter (Fig. 9, curve 1) and for packed columns of different diameters (curves 2, 3). An examination of curves shows that in addition to high efficiency the new proposed packings result in a very insignificant dependence of HETP on flow rate (α) and column diameter. These facts suggest that such columns may be used in high speed (express) and preparative chromatography.

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