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"IMPULSELESS" CIRCULATION GAS CHROMATOGRAPHY OF ISOTOPIC COMPOUNDS

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SUMMARY

The separations of isotope-containing organic compounds with $\alpha \geqslant 1.01$ were achieved by means of circulation gas–liquid chromatography. An equivalent length of a column close to 100 m was achieved. The optimal "impulseless" conditions for obtaining the maximum resolving power were established.

INTRODUCTION

The circulation technique in chromatography was proposed by Martin[1–4] nearly 20 years ago. Since then, the utilization of this method in both gas–liquid and liquid–solid chromatography has attracted many investigators. So far, about 100 papers have appeared on this subject, which has been reviewed recently[5,6].

The separation of isotope-containing molecules has also been described in the literature[7–10]. This paper describes the performance that can be obtained with the so-called "impulseless" circulation chromatography technique developed in our laboratory[11].

Two different circulation systems were compared. The results obtained show that the separation of binary mixtures of some deuterated substances can be achieved more easily by means of the circulation technique than by the use of very long packed columns.

EXPERIMENTAL

The circulation chromatographic systems used are shown in Fig. 1. The system in Fig. 1a is a modification of our earlier independent designs[12,13] and uses[10], having features similar to those described elsewhere[7,8]. The system in Fig. 1b is similar to one described in an earlier paper[14]. It has the particular feature that components to be separated do not pass through the circulation valve channels.

Two steel columns (4 m × 4 mm I.D.) were packed with Celite 545 (60–80 mesh) and impregnated with 10% of liquid phase (squalane or Carbowax 1000). No special attention was paid to the uniformity of the columns. The optimal rate of car-

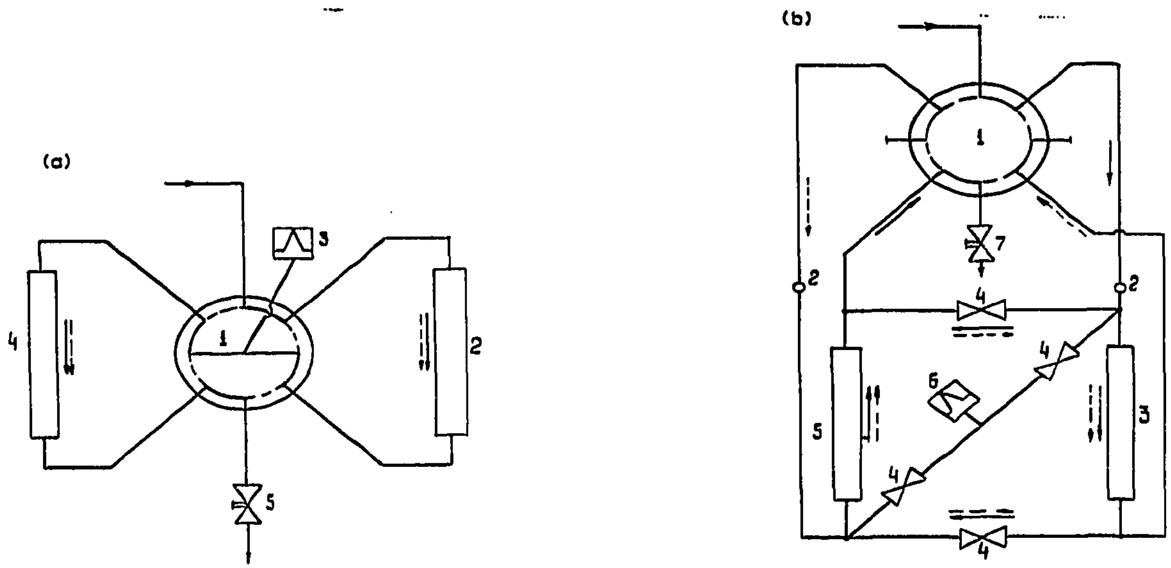

Fig. 1. (a) Schematic diagram of a circulation chromatographic system with a valve inside the column thermostat: 1 = circulation valve; 2, 4 = columns; 3 = flame ionization detector; 5 = needle valve. (b) Schematic diagram of a circulation chromatographic system with a valve outside the column thermostat: 1 = circulation valve; 2 = joints; 3,5 = columns; 4 = pneumatic resistors; 6 = flame ionization detector; 7 = needle valve.

rier gas take-off for detection, ensuring a linear increase in theoretical plate number with semicycle number, was choosen according to earlier work[15].

RESULTS

A typical chromatogram obtained is shown in Fig. 2. The chromatogram shows the almost complete separation of peaks with a resolution, R, of 1.4 after 7 h and ten semicycles ($m = 10$). There is a space on the chromatogram for two more peaks at the

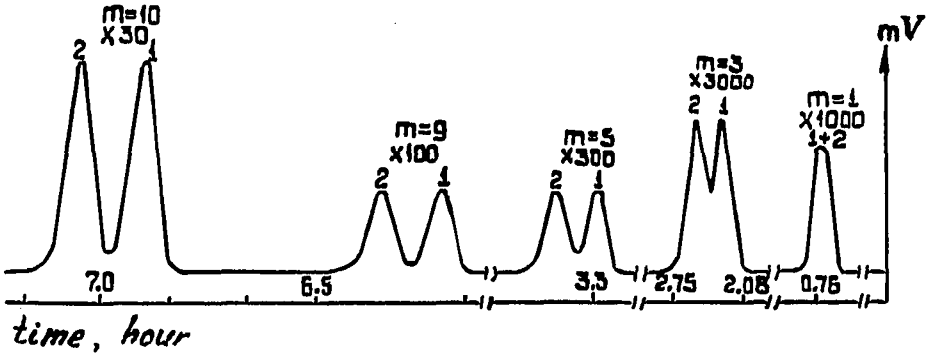

Fig. 2. Circulation chromatogram of a mixture of hexadeuterobenzene (1) and benzene (2) at 34°. Sample size = 0.05 μl; p_i = 3.87 kg/cm^2; p_o = 2.63 kg/cm^2; nitrogen flow-rate = 75 ml/min; chart speed = 240 mm/h.

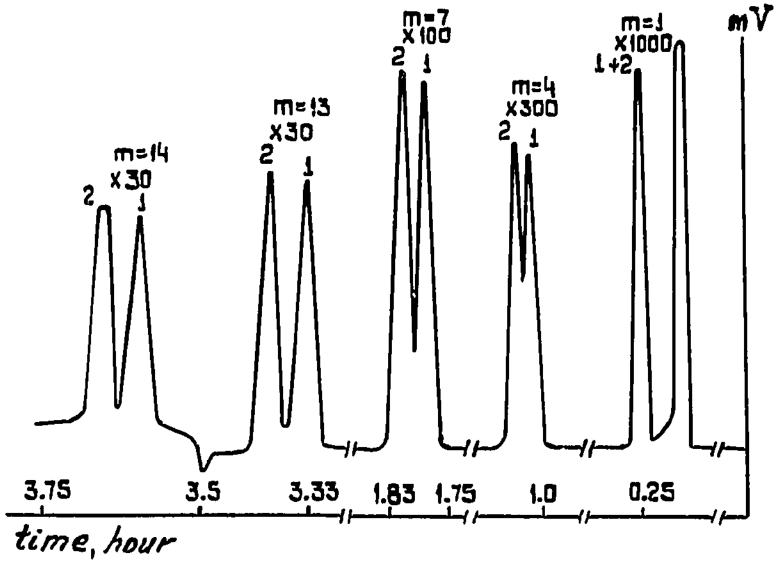

Fig. 3. Circulation chromatogram of a mixture of hexadeuterobenzene (1) and benzene (2) at 64°.

end of process. A resolution $R = 1$, sufficient for analytical purposes, was achieved at $m = 5$.

The chromatogram in Fig. 3 illustrates the substantial time reduction in the analysis of deuterobenzene at elevated temperature (64°). A column length equivalent to a sorbent layer of 60 m was achieved. The relative retention, α, was 1.025.

The separation of benzene and 1,3,5-trideuterobenzene was carried out with the same set of columns. The chromatogram recorded is illustrated in Fig. 4. The optimal rate of carrier gas take-off for detection[15] ensured a linear increase in theoretical plate number with semicycle number (Fig. 5). An equivalent column length of 100 m and a theoretical plate number of 120,000 were achieved.

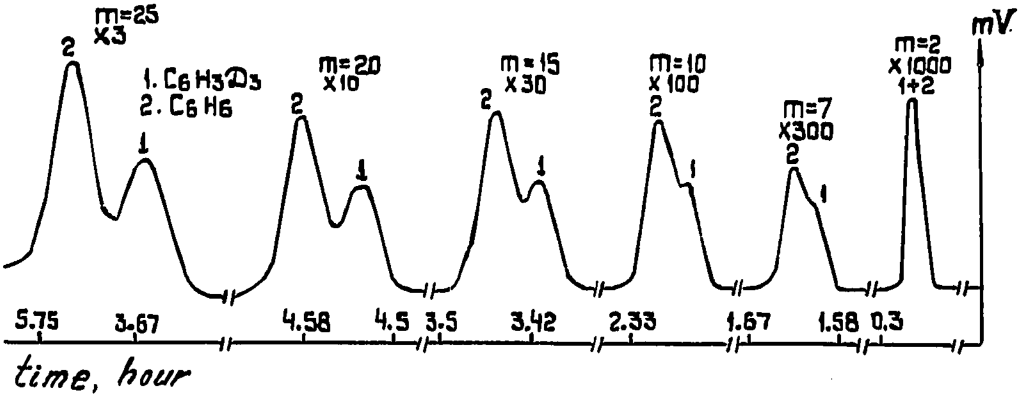

Fig. 4. Circulation chromatogram of a mixture of 1,3,5-trideuterobenzene (1) and benzene (2). Sample size = 0.05 μl; p_i = 3.66 kg/cm²; p_o = 2.04 kg/cm²; t_c = 66.5°; nitrogen flow-rate = 72.4 ml/min; chart speed = 600 mm/h.

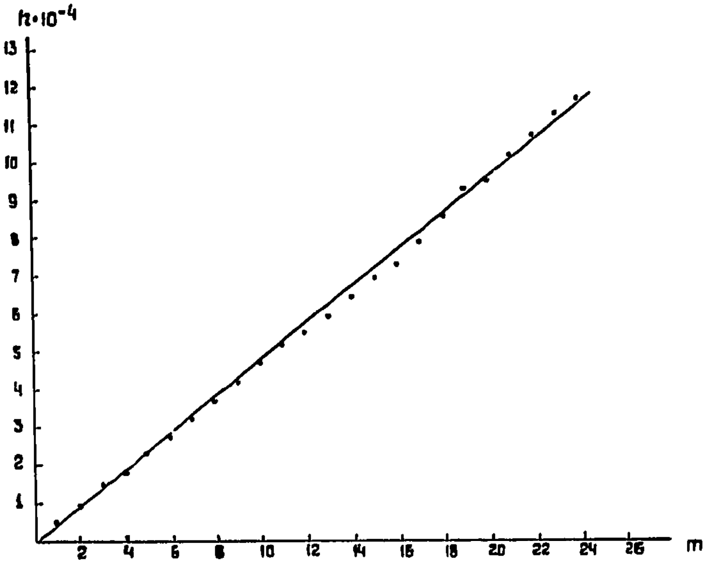

Fig. 5. Relationship between number of theoretical plates and number of semicycles for benzene.

In order to illustrate the analytical potential of the method, separations of other deuterated oxygen-containing substances were performed using polar liquid phase columns (Figs. 6–8). Adequate separations with $R = 1$ for all three mixtures were achieved in less than 1 h.

DISCUSSION

The results obtained are compared in Table I with some selected examples[16–18] of the use of very long packed columns. The efficiencies of both systems were evaluated

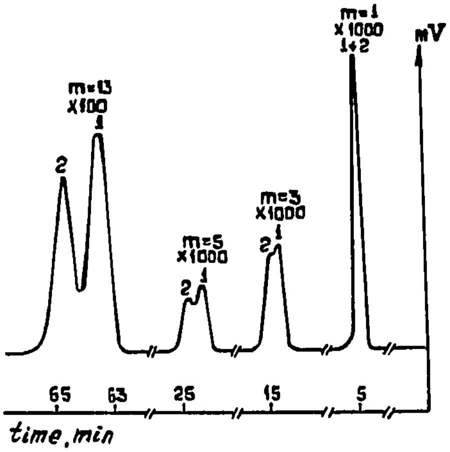

Fig. 6. Circulation chromatogram of a mixture of hexadeuteroacetone (1) and acetone (2).

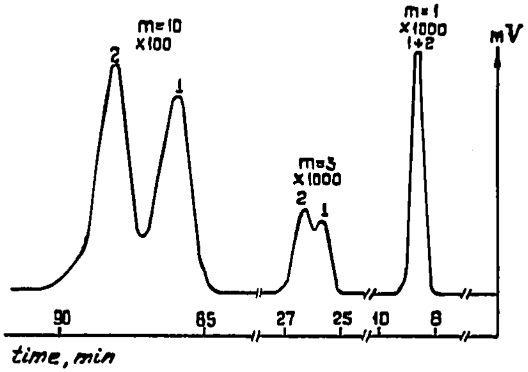

Fig. 7. Circulation chromatogram of a mixture of hexadeuteroethanol (1) and ethanol (2).

in terms of the height equivalent to a theoretical plate (HETP) and the total theoretical plate number, n. The resolution, R, characterizes the separation achieved. The relative retention, α, corrected carrier gas flow-rate, U_0, partition ratio, k', semicycle time, τ, complete analysis time, t_R, and semicycle number, m, are also included.

The results showed that the efficiency and separating power (α, R, t_R) of the circulation chromatography are not worse than those reported for long packed columns and graphitized carbon black capillary columns[20]. The substantial decrease in column length is an important advantage of the circulation method. In spite of relatively high operating temperature and considerable viscosity of the carrier gases used (helium and nitrogen) compared with hydrogen, the inlet pressure never exceeds 10 kg/cm^2.

The circulation system discussed is compatible with the usual chromatographic equipment.

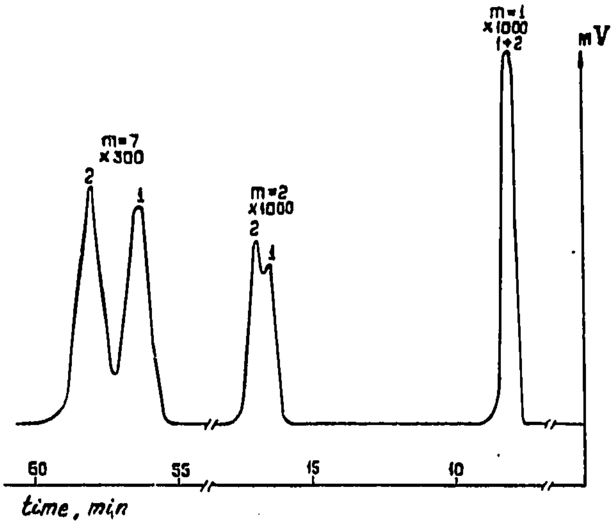

Fig. 8. Circulation chromatogram of a mixture of octadeuteroisopropanol (1) and isopropanol (2).

TABLE I

COMPARISON OF LONG PACKED COLUMNS AND CIRCULATION CHROMATOGRAPHY IN THE SEPARATION OF MIXTURES OF ISOTOPE-CONTAINING SUBSTANCES AND CLOSE ISOMERS

Mixture	*Packing*	*Column dimensions*		p_i *(kg/cm²)*	p_o *(kg/cm²)*	U_0 *(cm/sec)*
		I.D. (mm)	*Length (m)*			
$^{14}N_2$–$^{15}N_2$	Graphitized carbon black	4.00	60.0	2.70	AP*	1.60
CH_4–CH_3D	Graphitized carbon black, 40–60 mesh	4.00	120.0	16.00	AP	2.50
C_3H_8–C_3H_7D	Sterling FT, 40–60 mesh	4.00	105.0		AP	
C_3H_7D–$C_3H_6D_2$				—	AP	3.90
C_2H_6–C_2H_5D				18.00	AP	9.00
α-Glucose–α-glucose-D_7	3% SE-30 on Gas-Chrom S, 100–120 mesh	1.74	15.0	10.60	AP	4.80
β-Glucose–β-glucose-D_7		1.74	15.0	10.60	AP	4.80
Cyclothienone isomers[21]	3% SE-30 on Chromosorb W, 60–80 mesh	4.00	6.0	8.90 9.30	7.10 7.40	1.90 2.0
C_6H_6–C_6D_6	10% Squalane on Celite 545, 60–80 mesh	4.00	8.0	3.87	2.63	—
C_6H_6–$C_6H_3D_3$				3.66	2.04	—
CH_3COCH_3–CD_3COCD_3	10% PEG-1000 on Celite 545, 60–80 mesh	4.00	8.0	9.56	7.43	3.47
C_2H_5OH–C_2D_5OD						
C_3H_7OH–C_3D_7OD						
CH_3COCH_3–CD_3COCD_3	Sterling FT, porous	0.15	38.3	1.0	AP	3.62

* AP = Atmospheric pressure.

The experimental results obtained in a comparison of the circulation system shown in Figs. 1a and 1b are given in Table II, which shows almost identical inlet carrier gas (helium) pressures, p_i, for both systems. However "impulseless" conditions were achieved at different outlet pressures, p_o, which explains the difference in the mean values of the carrier gas flow-rate, U_0. The eluate take-off using a flame ionization detector was greater for the circulation system with the valve inside the column thermostat (Fig. 1a). The pressure drops in the columns and pneumatic resistors in the system in Fig. 1b were approximately equal. The parameters in Table II indicate

α	*HETP (mm)*	k'	$n \cdot 10^{-4}$	R	τ *(min)*	m	t_R *(min)*	*Column temperature (°K)*	*Carrier gas*	*Reference*
1.030	1.300	10.00	4.5	1.20	—	—	500.0	77.0	$CO + H_2$	16
1.010	1.000	4.00	12.0	0.75	—	—	300.0	195.0		17
1.022 1.008	0.810	—	13.0	1.00	—	—	565.0	273.0	H_2	18
1.012	1.430	—	7.0	1.00	—	—	570.0	195.0		
1.015	0.485	—	3.1	1.00	—	—	105.0	448.0	He	19
1.026	0.375	—	4.0	1.00	—	—	240.0	448.0		
1.023	0.560	3.12	6.4	1.04	10.00	12	120.0	508.0	N_2	This work
1.012	0.540	3.97	10.6	0.84	12.60	19	240.0	508.0		
1.025	0.800	—	7.2	1.10	16.10	14	225.0	337.0	N_2	
1.011	0.800	—	12.0	0.89	13.60	25	340.0	339.5		
1.025	1.130	1.51	4.6	1.01	4.90	13	64.0	356.0	He	
1.029	1.430	3.40	2.8	1.05	8.70	10	87.0	356.0		
1.037	1.260	3.16	2.2	1.08	8.15	7	67.0	356.0		
1.042	0.800	2.00	4.8	1.50	—	—	52.6	325.0	$N_2 + H_2O$	20

that the two systems investigated were closely similar.

The circulation system with the valve outside the column thermostat gives an unfavourable loss of carrier gas and a relatively small length of the columns.

Nevertheless, the experimental results obtained demonstrate the high separating ability of the circulation system discussed, permitting closely similar mixtures with $\alpha \geqslant 1.01$ to be resolved. The removal of the circulation valve from the column thermostat enables the circulation system to be arranged as a separate unit that can be easily combined with any suitable chromatograph.

TABLE II

COMPARISON OF TWO CIRCULATION CHROMATOGRAPHIC SYSTEMS

Mixture	*System**	*Column dimentions*		*Packing*	p_i *(kg/cm²)*	p_o *(kg/cm²)*	*Linear carrier gas velocity (cm/sec)*	*Relative retention,* α	*HETP (mm)*	*k′*	$n \cdot 10^{-4}$	*R*	*m*	t_R *(h)*	*Column temperature (°K)*
		I.D. (mm)	*Length (m)*												
C_2H_5OH	I	4	8	10% PEG-1000	10.56	8.43	3.5	1.029	1.4	3.4	2.8	1.00	10	1.45	356
CD_3OD_2	II	4	6		10.60	8.88	2.5	1.033	1.5	3.0	2.0	0.95	10	1.51	350
C_3H_7OH	I	4	8	Celite 545 (60–80 mesh)	10.56	8.43	3.5	1.037	1.3	3.2	2.2	1.10	7	1.00	356
C_3D_7OD	II	4	6		10.60	8.88	2.6	1.037	1.2	3.0	2.2	1.00	9	1.17	350

* Systems: I, with circulation valve inside column thermostat (Fig. 1a); II, with circulation valve outside column thermostat (Fig. 1b).

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