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Gas Chromatography with Organic Eluents

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The characteristics of the use of organic gases and vapours as the mobile phases in the elution gas chromatography as well as additives to the usual carrier gases are considered. Methods are described for the preparation of the eluents and detection, and the role of the eluent as the factor permitting the regulation of the retention of the sorbate and the shape of the chromatographic band is discussed. The considerable advantages of organic gases and the vapours of organic compounds as eluents in preparative chromatography are demonstrated.
The bibliography includes 100 references.

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I. INTRODUCTION

In the elution version of gas chromatography, the mobile phase (carrier gas) plays as a rule merely the role of a transporting agent; the concentration of the sorbate analysed in this phase is determined by the vapour pressure of the sorbate at the working temperature and the nature of the sorbent. The first studies on gas chromatography with organic eluents and with organic additives to the usual carrier gases were published as early as 1956–1959.[1-10] It was shown that the use of organic and mixed eluents makes it possible to change significantly the pattern of the chromatographic separation of substances; thus the nature of the mobile phase becomes a factor which determines to a large extent both the retention of the chromatographic band and the shape of the recorded peak.

Together with their role as transporting agents, organic eluents and additives can perform the following "active" functions: (1) the blocking of the active centres of solid carriers (polar eluents) with formation of symmetrical bands of polar sorbates; (2) adsorption on the surface of the adsorbent and formation of a liquid layer which alters the partition coefficient of the sorbate in the mobile phase—sorbing medium system and hence the retention (the latter is usually decreased); (3) dissolution in the stationary liquid and formation of a binary stationary phase whose composition determines the retention of the sorbates; (4) the shift of the phase equilibrium of the sorbate in the mobile phase (it is manifested to the greatest extent with increase of the pressure)†; (5) the formation of volatile derivatives of involatile substances (particularly metals), which can be transported along the column; (6) the increase in some cases of the sensitivity of the detectors in relation to the substances analysed.

The above characteristics of organic eluents make it possible to extend the scope of gas chromatography as a method for the analysis of polar and high-boiling compounds.

† The above phenomena are observed also when a vapour eluent is used. The relevant studies have been reviewed[11].

Other advantages of organic eluents are noteworthy: (1) the ease of condensation (which enables them to be used in preparative chromatography without the need for low-temperature cooling of the traps); (2) the availability of hydrocarbon gases in petrochemical undertakings (this facilitates the employment of these gases as eluents in industrial control). The vapour of the stationary liquid which is volatile under the selected working conditions can be used as the eluent or its component and the analysis can be carried out both under the conditions of circulation chromatography[7,8] and with continuous saturation (before the column) of the carrier gas by the vapour[9]. Thus the range of the stationary phases employed is extended to include more volatile substances.

Table 1 presents data for the conditions in the chromatographic process with organic or mixed eluents. Methane and its mixture with hydrogen were used for the first time as carrier gases in 1956 by Taramasso[1,2]. In many instances, this proved to be convenient and economical in industrial monitoring (naturally, provided that safety precautions are taken), which was subsequently confirmed[12]. Furthermore the use of methane as the carrier gas instead of nitrogen increases the sensitivity of the katharometer because of the greater thermal conductivity of methane.

In 1959 Dumazert and Ghiglione[5] suggested that the chromatographic process be carried out in ethanol vapour, which influenced significantly the nature of the sorption of the substances analysed in the column and hence also the retention and shape of the concentration bands. Thus the eluent ceased to be merely a transporting agent; its nature became a factor influencing the phase equilibrium. A year earlier, Knight[6] showed that the introduction of small amounts of polar organic additives into the usual carrier gases ensures symmetrical peaks of polar sorbates and thus reduces the requirement for the inertness of solid carriers with respect to adsorption, since polar additives block their active centres. Subsequent studies on these lines were performed by Ackman and coworkers[14-16]. Organic additives were used in 1960 to increase the sensitivity of ionisation detectors with respect to inorganic gases[39] and in 1971 in order to form volatile adducts with metals[40].

Table 1. Conditions in the separation of substances in a stream of organic eluents or their mixtures with ordinary carrier gases.

Substance	Eluent	Sorbent	Column Temp., °C	Detector	Ref.
Natural gas (C_1-C_4)	methane, methane with an admixture of hydrogen	n-hexadecane, dinonyl phthalate on Celite	25	katharometer	1,2
Methane	acetylene	wood charcoal	25	katharometer	3
Lower alcohols, water, allylamines	helium saturated by a mixture of water and n-hexylamine	di-isodecyl phthalate, tricresyl phosphate, triethylene glycol, $\beta\beta'$-oxydipropionitrile, poly(propylene glycol), DC-550 silicone on refractory brick	25-60	katharometer	4
C_2-C_5 acids	ethanol	liquid paraffin and stearic acid on refractory brick	100-110	katharometer	5
Nitrogen, ethylene, propane	methane	silica gel, dibutyl phthalate on silica gel	75	katharometer	6
Acetone, n-heptane, toluene, n-hexane, n-octane, benzene, cyclohexane, methylcyclohexane	helium with added solvent vapour	methanol, aniline on C-22 refractory brick	20-150	katharometer	7,8
C_4-C_8 hydrocarbons, oxygen compounds	helium with added solvent vapour	n-octane, n-decane on C-22 refractory brick	30,60	katharometer	9
C_5-C_7 hydrocarbons, C_1-C_5 alcohols	methane, ethane, ethylene, n-pentane	$\beta\beta'$-oxydipropionitrile, Paraplex, UCON-LB-550-X, Apiezon L, di-iso-decyl phthalate on Chromosorb W	100	katharometer	12
Isoalkenes	hydrogen, nitrogen with added solvent vapour	methanol, ethanol, acetone, ethyl methyl ketone, dioxan on a solid carrier	28-45	katharometer	13
Volatile C_2-C_6 aliphatic acids	helium with added formic acid vapour	ethyl formate, ethyl acetate, n-hexane, cyclohexane, ethylene glycol sebacate on Chromosorb W, Porapak QS, Chromosorb-101	160-200	FID	14-16
Oxygen, argon, neon, helium	nitrogen with added iso-C_5 vapour	5 Å molecular sieves	–	FID	17
Methane, propane, n-decane, n-heptane	methane, methane-propane mixture	n-decane, n-heptane on a solid carrier	–	katharometer	18
n-Pentane, isopentane, hexane, 2-methylpentane, 2,2-dimethylbutane	methane, ethane	squalane on Celite	25,50	katharometer	19
Toluene, 1-propanol, 1,2-dichloroethane, benzene, carbon tetrachloride	nitrogen, hydrogen with added benzene and 1,2-dichloroethane vapours	toluene, 1-propanol, 1,2-dichloroethane, benzene, carbon tetrachloride on Fluon, Haloport, Teflon-6	30-65	FID	20
Barbiturates	nitrogen with added formic acid vapour	Apiezon L on Chromosorb	185	FID	21
Pentane, hexane, heptane benzene, toluene, ethanol, propanol, isobutyl alcohol, acetone, water	nitrogen with added n-octane, n-nonane, n-decane, hexanol, and dibutyl phthalate vapours	ethanol, propanol, isobutyl alcohol, heptane, octane, benzene, *p*-xylene on Chromosorb and INZ-600		katharometer	22,23
Isopropylbenzene	inorganic carrier gas with added solvent vapour	dioctyl phthalate on a solid carrier	–	–	24
C_1-C_7 hydrocarbons, oxygen compounds	methanol, ethanol, isopropyl alcohol, heptane, hexane, ethyl acetate, n-butyl chloride, chloroform, and dichloroethane vapours mixtures of ethanol with methanol, heptane, benzene, hexane, and iso-octane	dioctyl phthalate on Chromosorb W A W, Porapak S and Q, activated alumina, silica gel, diethylene sebacate, silicone oil, poly(ethylene glycol) on C-22 refractory brick	80, 140-230	katharometer, u.v.cell	25-30
C_9-C_1 hydrocarbons, C_4-C_6 aliphatic alcohols	ethanol and heptane vapours	Apiezon L on INZ-600	135, 160	katharometer	31
Free C_2-C_{18} aliphatic acids, C_3-C_{18} aliphatic amines, ethylenediamine, ethanolamine	water vapour with added formic acid or hydrazine hydrate vapour	Chromosorb GAW, Corning GLC-100 porous glass beads	125-200	FID	32
C_6-C_1 hydrocarbons, amines, isomeric geranate esters, halogenoalkenes, free aliphatic acids	Freon, formic acid, and methanol vapours	poly(ethylene glycol), SKTV polydimethylpolysiloxane on Chromosorb A and Chromaton	120-175	FID, densitometer, electron capture detector	33,34
Acetone, methanol, ethanol, diethyl ether	inorganic carrier gas with added isopentyl and hexyl alcohol vapours	isopentyl alcohol, high-vacuum grease on Celite-545	50,70	katharometer	35
Nitrogen, argon, carbon dioxide, sulphur dioxide	Freon-116 vapour	silica gel	–	FID	36
Aromatic hydrocarbons	water vapour with added organic vapour (ethanol, pentane-ethylene fraction)	poly(ethylene glycol adipate), n-butylamine on Spherochrome	130	katharometer	37
Nitrogen compounds	nitrogen with added ammonia, polyethylene-amine, tetraethylene-pentamine, tetra(hydroxyethyl)-ethylene-diamine	OV-1 silicone on Chromosorb	235	FID	38

This review considers the possibility of employing organic eluents and organic additives to carrier gases in analytical and preparative chromatography and also in physicochemical measurements. Attention has been concentrated on experiments under the usual pressures. As regards fluid chromatography[41-56], which constitutes a very powerful means of increasing the mobility of involatile sorbates, only some of its aspects are discussed below, because a number of reviews have been devoted to this method[40-42,45,47]. Since the review is restricted to the discussion of elution gas chromatography, frontal and displacement versions, where the mobile phase usually consists of organic gases and vapours, and particularly chromatography without a carrier gas[57] (with the exception of the problem of the preparation of a fixed mobile phase which has a bearing on the subject of the review) remain outside its scope.

II. PREPARATION OF THE ELUENT

The organic additives are introduced into the carrier gas in the following ways: (1) by passing the stream of carrier gas through a tube or vessel with an adsorbent or

solid carrier impregnated with the volatile organic liquid; (2) by bubbling a layer of the liquid with the carrier gas; (3) by passing the carrier gas over a layer of the liquid; (4) by injecting a portion of the volatile solvent into the metering device of the chromatograph.

Thus the carrier gas has been passed[9] through a vessel with Sil-o-cel impregnated with the corresponding volatile solvent, and, in order to ensure the complete saturation of the gas, the temperature of the vessel exceeded by several degrees the working temperature of the column; after coming into contact with the solvent, the gas was cooled to the working temperature and was introduced into the chromatographic column.

In order to evaporate a mixture of water and formic acid, Nonaka[32] used a modified evaporator in the chromatograph. The carrier gas is usually saturated with formic acid vapour by passing it over a layer of concentrated formic acid[14-16].

Virtually complete saturation of the carrier gas by the organic vapour takes place when the gas is bubbled through a layer of the liquid[37,58]. An apparatus has been described[58] for a vacancy-chromatographic study of the phase equilibrium constants in which a saturator is used to saturate the carrier gas with the organic sorbate by bubbling. A device described by Benedek and Ratkovics[59] was used as the saturator.

In order to create a mobile band of the volatile liquid phase in the column, a number of workers[23,24,35] introduced the solvent directly into the column through a metering device. Evaporators of different designs have been used to obtain individual eluent vapours. Thus the generation system in one investigation[31] incorporated two steel cylindrical containers heated to 200°C. The liquid was evaporated in the first container and the resulting vapour passed to the second container, which served as a damping device and which was provided with a manometer and a fine control valve. The vapour then passed to the column through a heated capillary.

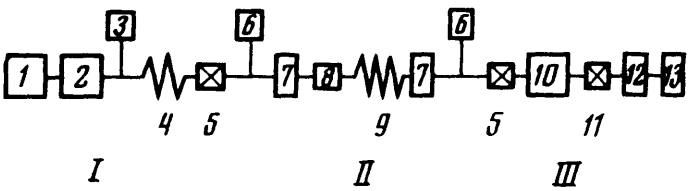


Figure 1. Schematic representation of the chromatographic apparatus with an organic vapour-phase eluent: I) gas-generating section; II) separating column; III) condenser for organic vapour-phase carrier; 1) vapour generator; 2) buffer reservoir; 3) manometer; 4) hydraulic resistance; 5) needle valve; 6) manometer; 7) detector; 8) evaporator; 9) column; 10) cooled trap; 11) cut-off valve; 12) trap with $CaCl_2$; 13) vacuum pump.

Fig. 1 illustrates schematically an apparatus where the vapour of an organic substance was used as the eluent (carbon tetrachloride, benzene, and ethanol)[26]. It consists of three parts: the gas generator, the column, and the condenser for the organic eluent. After the system had been evacuated, the reservoir *1*, containing the organic solvent, was heated to the required temperature (80° to 110°C); the vapour pressure reached 1–2 kgf cm^{-2} at this temperature and the vapour was supplied to the separating column. The flow rate of the organic eluent was controlled by the inlet and outlet pressures in the column by means of a needle valve. The pressure in the column and the gas generator temperature were limited by the level of errors in the zero line. Before connection to the rest of the apparatus, the chromatographic system was conditioned for several hours in order to ensure equilibration. Because of its prior evacuation, the system usually operated at a reduced pressure. The flow rate of the organic eluent was calculated by dividing the dead volume of the saturating column by the retention time of the non-sorbed component.

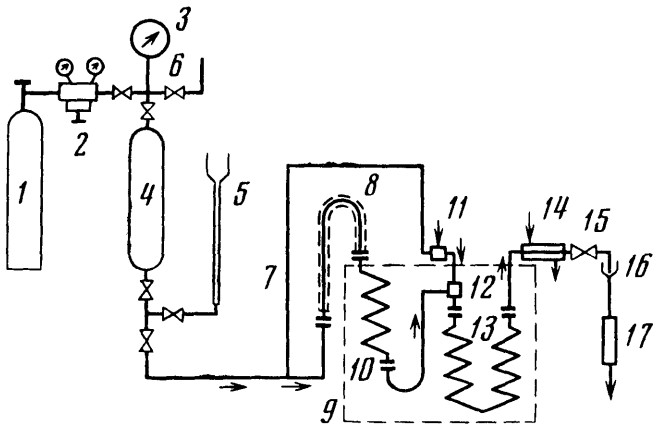


Figure 2. Schematic illustration of the apparatus for chromatography with hypercritical liquids: 1) gas cylinder; 2) reduction valve; 3) Bourdon manometer; 4) reservoir; 5) funnel; 6) valve; 7) side line; 8) heater; 9) air thermostat; 10) conditioning tube; 11) pneumatic injector; 12) three-way connector; 13) chromatographic column; 14) capillary tube; 15) needle valve; 16) degassing unit; 17) detector.

The apparatus usually employed to generate the vapours of organic eluents in fluid chromatography[45,47,48] is illustrated schematically in Fig. 2.[47] The mobile liquid phase is under nitrogen pressure in a stainless steel reservoir *4*, whence it passes to a heater *8*, where its temperature is adjusted to a value close to the critical temperature. The eluent is heated to the working temperature in the conditioning tube *10*, assembled, together with the chromatographic column *13*, in an air thermostat *9*. The pressure in the apparatus is regulated by the nitrogen pressure in the reservoir *4* and by the needle valve *15*. In later studies by the same workers[47], the pressure was generated by means of a pump.

III. DETECTION

With some exceptions[1,2,36], organic eluents greatly reduce the sensitivity of the katharometer (K) and rule out the possibility of the application of a flame-ionisation detector (FID) for analysis; the above detectors are the

most widely used in traditional gas chromatography. In chromatography with organic eluents, the FID can be used only after the introduction into the usual carrier gas of small amounts of organic additives [38], which generate a small background current, or under conditions such that the detector does not record the organic substance (for example, when pure formic acid vapour is used as the eluent [34] and also when it is added to a usual carrier gas [14-16,21]), or under special conditions, for example as the carrier gas in the analysis of inorganic gases [17,60].

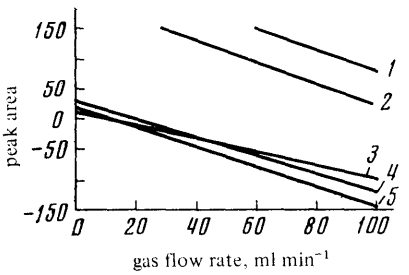


Figure 3. The influence of the flow rate of different carrier gases on the sensitivity of the katharometer to n-pentane (t_C = 100°C): 1) hydrogen; 2) helium; 3) ethane; 4) methane; 5) nitrogen.

Despite the above limitations, the katharometer is widely used in this version of chromatography, both because a sufficient difference between the thermal conductivities of the eluent and the sorbate is achieved and because of the lack of an alternative. Fig. 3 [12] illustrates the influence of the nature of the carrier gas and of its flow rate on the sensitivity of the katharometer.

In order to improve the sensitivity of the usual katharometer, it is necessary to increase the current passed through the detector, which is impossible when the thermal conductivity of the organic vapour is low. In recent years studies have been published [61-63] in which an improved version of the katharometer with a constant filament temperature is proposed. The suggested version is free from the above disadvantages and the use of eluents with a low thermal conductivity actually increases its sensitivity [61].

An ultraviolet cell, which is selectively sensitive to aromatic compounds, has been used in studies by Tsuda and coworkers [25,27-30], whose work has been most productive in chromatography employing organic eluents. The ultraviolet cell is also widely used in fluid chromatography. The possibility of its successful employment up to 290 atm without reducing the pressure before its inlet has been demonstrated [53]. However, as stated above, its application is limited owing to its selectivity.

Despite the fact that examples of the use of the densitometer [33] and the electron capture detector [34] have been described in the literature, the katharometer and the ultraviolet cell will probably remain in the immediate future the most convenient detectors for this version of gas chromatography.

A comparative analysis of the results obtained with the aid of the ultraviolet cell and the katharometer in experiments where they were incorporated in the system in succession has been published [27]. The detectors operated in the linear range; the widths of the recorded peaks at the level of half their heights for a specific flow rate of the eluent vapour (ethanol) were approximately the same. The sensitivities of the detectors to substances containing one benzene ring are likewise approximately identical; the ultraviolet cell is more sensitive (approximately by a factor ten) to polycyclic aromatic compounds. The minimum amount of substance detected by the ultraviolet cell is 10–100 ng. A two-channel scheme with two detectors, one universal and the other selective with respect to the class of compounds investigated, is available and is suitable also for eluents in the vapour phase. Fig. 4 [27] presents chromatograms for the same mixture of substances obtained with the aid of these two detectors. The ratios of the peak heights of the same substance on the u.v. and K chromatograms are 1.4, 0.1, and 15 for derivatives of benzene, olefins or ketones, and naphthalenes respectively. The *b*, *d*, and *f* peaks correspond to olefins or ketones, the *c*, *e*, *g*, *h*, *i*, and *j* peaks correspond to benzene derivatives, and the *a* peak corresponds to a saturated hydrocarbon.

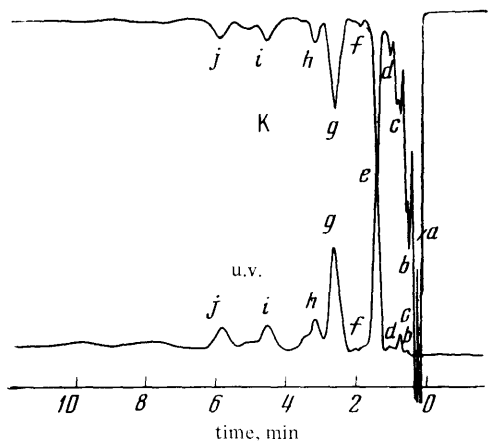


Figure 4. Combination of two detectors: sorbate—0.2 ml of petrol; column with 20 wt.% of dioctyl phthalate; t_C = 120°C.

Ionisation detectors are relatively insensitive to inorganic gases. When an organic substance is introduced into the stream of carrier gas and an inorganic gas is then injected into the detector, the ionisation current is reduced to a greater extent than after the introduction of single gas into the stream of pure carrier [39]. Methods have been developed on this basis for the chromatographic determination of inorganic gases by ionisation detectors [17,36,39,60,64-67] (with a sensitivity of 0.5×10^{-4}% to H_2, O_2, and CH_4 and of 1×10^{-4}% to nitrogen [39]).

A universal detector meeting the requirements of fluid chromatography has not yet been devised. When traditional chromatographic detectors are used, it is necessary to reduce the pressure to atmospheric before the detector, which leads to the condensation of the mobile phase or to its degassing. As already stated, the majority of workers use the ultraviolet cell. Detectors which do not require the reduction of pressure beyond the chromatographic column have been proposed [44,54].

IV. SORBENTS

In experiments with organic and mixed eluents, it is possible to use all the liquid phases and adsorbents which are employed in ordinary chromatography with inorganic carrier gases. Furthermore, in the presence of polar organic eluents and additives, requirements for the inertness of solid carriers become less stringent, and the set of possible liquid phases is extended by the inclusion of volatile solvents. Data concerning the application of liquid phases and adsorbents are presented in Table 1.

Having noted that organic eluents and additives affect the retention times of the substances analysed and the shape of the peaks, a number of workers [14-16,21,25,30,31,38,68-74] expressed different views concerning their influence on the mechanism of the interaction of the sorbate with the sorbent. The view that a thin liquid film is formed from the eluent vapour on the adsorbent surface, altering its sorption properties, is generally accepted. On the other hand, in the gas–liquid version, four factors, believed to be responsible for the change in the mechanism of the interaction of the liquid phase with the sorbate, have been isolated: (1) the formation of a liquid film on the surface of the liquid phase; (2) the formation of binary liquid phases; (3) temporary modification of the solid carrier by the molecules of the vapour phase; (4) the interaction between the sorbate and the eluent in the gas phase.

When organic eluents are used, all the above factors operate, but the role of each can be estimated only when account is taken of the specific experimental conditions: temperature, pressure, and the nature of the liquid phase or adsorbent and the eluent.

Berezkin et al. [31] analysed mixtures of alcohols and hydrocarbons in a stream of ethanol and heptane vapours and in nitrogen using Apiezon L as the liquid phase. At a high column temperature (160°C), nitrogen and ethanol vapour yielded virtually identical retention characteristics, because at an elevated temperature an eluent film is not formed on the surface of the liquid phase and a binary liquid phase is not produced, since ethanol is almost insoluble in Apiezon L. This also shows that, under the given conditions, the interaction in the gas phase does not have a significant influence on the retention. On the other hand, in the presence of heptane the retention volumes are altered, as a result of the dissolution of heptane in Apiezon L and the formation of a binary liquid phase with modified sorption properties.

An increase or decrease of the retention of propanol, octane, and toluene in ethanol and benzene vapours at a lower temperature (125°C) and using poly(ethylene glycol), dioctyl phthalate, and silicone as the stationary phases, relative to the retention of the same sorbates in a stream of nitrogen, has been explained [26] by the formation of a surface layer of condensed eluent, which prevents the mass transfer process and also by the dissolution of a small amount of the eluent in the stationary liquid. It is noteworthy that these explanations are in many respects contradictory, and the observed phenomena require a more detailed study. The retention volumes obtained in a number of studies [26,31] are listed in Table 2.

The process occurring in the column is in many respects determined by the temperature. When volatile solvents are used as the stationary phase by their partial condensation on an inert carrier in the column, a change in column temperature alters not only the partition coefficient of the sorbate in the gas–liquid system but also the thickness of the surface layer of the eluent, i.e. the amount of the stationary phase [7,8,22,23,35].

When the liquid phase and the eluent are only slightly miscible, a thick liquid film is formed on the surface of the liquid phase (according to Tsuda et al. [30], the thickness of the film corresponds to approximately 2–10 molecules when ethanol and alumina are used as the carrier vapour and adsorbent respectively at a column temperature of 100–150°C); on the other hand, when the liquid phase and the eluent are miscible, a binary phase is formed. Since the thickness of the film is determined by the sorption capacity of the support, the film is naturally thicker on an adsorbent than on a solid carrier; on the other hand, the adsorbent influences significantly the retention and the shape of the peaks.

Table 2. The ratios of the retention volumes of the sorbates for different carrier gases and liquid phases to the retention volumes for the nitrogen carrier gas [26,31].

Liquid phase	Poly(ethylene glycol)		Dioctyl phthalate		Silicone		Apiezon L	
Carrier gas	C_2H_5OH	C_6H_6	C_2H_5OH	C_6H_6	C_2H_5OH	C_6H_6	C_2H_5OH	$n\text{-}C_7H_{16}$
Ethanol	—	—	—	1.7	—	1.9	—	—
1-Propanol	0.9	1.0	0.8	1.2	0.7	1.4	—	—
1-Butanol	—	—	—	—	—	—	0.9	1.7
1-Pentanol	—	—	—	—	—	—	1.0	1.5
1-Hexanol	—	—	—	—	—	—	1.0	1.3
n-Octane	0.7	0.8	0.8	1.0	0.5	1.3	0.9	1.1
Toluene	0.7	0.9	0.7	1.0	0.6	1.1	—	—
n-Nonane	—	—	—	—	—	—	1.0	1.2
n-Decane	—	—	—	—	—	—	1.0	1.3

Pressure has a significant influence on the chromatographic process only when it is greatly increased, although there is some change in the retention characteristics when the pressure is altered, but not to an extent sufficient to affect the chromatographic separation pattern. Thus Tsuda et al. [26] showed that, when the pressure is increased by a factor of seven (from 100 to 700 mmHg), the retention of octane and toluene increases by a factor of 1.3, while that of propanol remains unchanged. A different situation is observed with increase of pressure during the condensation of the eluent vapour on the adsorbent surface. According to Rakhmankulov and Vigdergauz [75] (they used water vapour as the eluent, alumina as the adsorbent, and a column temperature of 170°C), an increase of pressure from 1.6 to 7.2 atm entails a sharp decrease of retention—by a factor of several tens for high-boiling paraffins, and significantly smaller for polar sorbates soluble in water. An analogous effect obtains also in the presence of an organic-vapour eluent [12,28,30].

In fluid chromatography, the fluid has a very strong influence on the retention, displacing the phase equilibrium in the direction of the mobile phase. In fluid–liquid chromatography, stationary liquids such as Apiezon M and UCON-50-HB-2000 are eluted from the column in several minutes [49], which necessitates the use of high-molecular-weight liquids as stationary phases. One can instead saturate the mobile phase with the vapour of the stationary liquid, or the liquid phase can be grafted onto a solid carrier [44,50,51,53].

The formation of a liquid film with a simultaneous increase of partition coefficients is also observed in fluid-adsorption chromatography under certain conditions [45].

V. THE SHAPE OF THE PEAKS AND RETENTION

The use of vapour-phase eluents permits in many instances a significant improvement of the separation as a result of the improvement in the shape of the peaks of the components to be separated and in view of the possibility of regulating the selectivity of the chromatographic column. In ordinary chromatography, the shape of the peaks is determined mainly by two factors: the influence of active adsorption centres of the carrier leading to the spreading of the rear sections of the peaks, and diffusion in the mobile phase, influencing the overall spreading. The use of vapour-phase eluents makes the peaks narrower and more symmetrical as a result of the suppression of the adsorption centres and decrease of the diffusion-induced spreading, since the extent of diffusion in vapour–vapour systems is smaller than in vapour–gas systems.

Table 3. Ratios of the retention volumes of the sorbates for different carrier gases to the retention volumes for the nitrogen or helium carrier gas [28].

Liquid phase	Carrier gas	Sorbate	Ratio of retention volumes
Dioctyl phthalate, 20 wt.% Silicone, 25 wt.%	CCl_4, He	ethylbenzene, n-decane	1.7–1.6
	CCl_4, N_2	1-propanol, n-octane, toluene	1.2–0.9
	C_2H_5OH, N_2	ditto	0.7–0.5*
	C_6H_6, N_2	"	1.4–1.1*
Porapak S	CCl_4, He	n-hexane, cyclohexane, benzene	0.18–0.15
Porapak Q	CCl_4, N_2	benzene	0.4
Alumina	C_2H_5OH, N_2	benzene	0.01

*Data of Tsuda et al. [30]

Table 4. The influence of the carrier gas (and the liquid phase) on the absolute specific retention volumes [12].

Sorbate	Liquid phase—15% UCON-LB-550-X oil on Chromosorb W (60–80 mesh)			Liquid phase—15% Apiezon on Chromosorb W (50–80 mesh)		
	He	N_2	CH_4	He	N_2	CH_4
n-Pentane	5.9	5.8	4.8	6.0	5.2	3.9
n-Hexane	10.6	10.0	9.6	11.2	10.0	9.2
n-Heptane	19.2	18.2	18.0	22.0	18.7	19.7
Hex-1-ene	7.8	9.1	10.0	9.9	9.5	8.7
Cyclohexane	20.3	17.8	17.5	20.7	20.0	19.7
Ethylcyclohexane	52.4	51.1	50.8	67.7	64.5	64.5
Cyclohexene	19.9	20.6	24.1	23.2	22.2	21.2
Benzene	22.3	21.4	20.6	19.8	18.7	17.8
Toluene	42.6	38.8	39.8	41.0	39.2	31.8
p-Xylene	75.1	74.1	72.7	81.9	78.0	78.0
o-Xylene	91.1	88.0	87.6	96.6	92.4	92.0
Isopropylbenzene	102.5	101.4	99.8	103.9	102.6	100.7
Methanol	3.5	3.6	2.6	1.7	1.2	0.8
Ethanol	5.9	5.9	5.3	3.5	2.6	1.9
1-Propanol	10.9	10.3	10.1	6.9	6.1	4.8
1-Butanol	18.8	17.8	19.7	14.2	13.1	12.0
1-Pentanol	38.7	36.5	38.5	30.6	30.9	28.4
Isopropyl alcohol	5.9	5.2	5.7	5.6	3.9	2.9
Isobutyl alcohol	15.6	15.1	13.6	12.5	9.6	9.6
Isopentyl alcohol	30.9	29.7	28.5	25.4	23.1	22.2
t-Butyl alcohol	6.6	6.7	6.1	6.0	5.2	4.8
s-Butyl alcohol	13.3	12.7	12.3	12.1	8.3	7.7

The change in the retention of substances when vapour-phase eluents are used is caused by the formation of binary stationary phases or surface films of the eluent and also by the formation of compounds more volatile than the initial sorbates (particularly in the analysis of metals) [40,76–81]. For example, the addition of aluminium chloride vapour to helium (carrier gas) made it possible to analyse metal chlorides having boiling points up to 2000°C (for t_c = 150 to 500°C), which had not been analysed previously by gas chromatography [76].

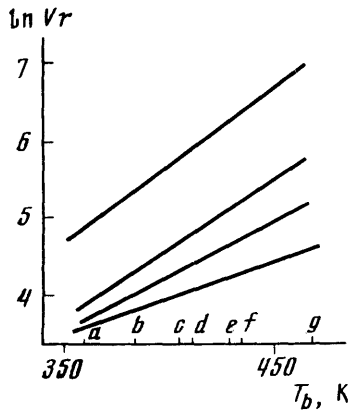


Figure 5. The influence of the nature of the carrier gas on the retention volumes in a column with activated alumina; vapour phase carrier: 1) n-hexane; 2) n-butyl chloride; 3) ethyl acetate; 4) ethanol; sorbates: *b*) toluene; *c*) chlorobenzene; *d*) ethylbenzene; *e*) bromobenzene; *f*) n-propylbenzene; *g*) iodobenzene; t_c = 150°C; vapour flow rate 200 μl min^{-1}; sensitivity of u.v. detector 0.32 or 0.16 OD. The retention volumes are quoted with allowance for the pressure drop in the column; 75 cm column with activated alumina.

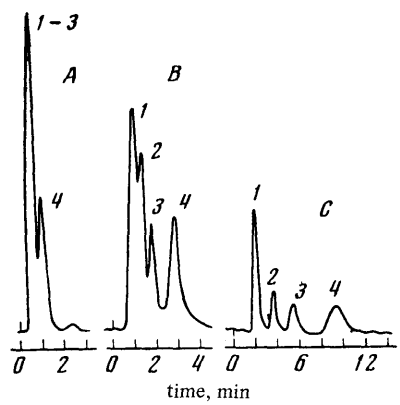


Figure 6. Chromatogram obtained using ethanol (*A*), ethyl acetate (*B*), and n-hexane (*C*) vapours as eluents. 75 cm column with activated alumina (100–300 mesh); column temperature 150°C; sample size 1–3 μl of ethanol containing 1% of different additives: 1) benzene; 2) toluene; 3) ethylbenzene; 4) n-propylbenzene.

Tables 3 and 4 and Figs. 5 and 6 [30] present data demonstrating the influence of the nature of the carrier gas on the retention volumes and chromatographic separation. When ethanol vapour and alumina are used as the carrier gas and adsorbent respectively, the retention volume of

benzene is 1/100 of the retention volume when nitrogen is used as the carrier gas in the presence of the same adsorbent.

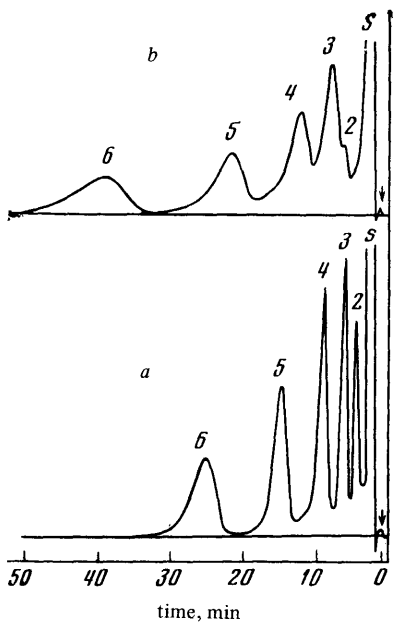


Figure 7. Chromatograms of a mixture of C_2-C_6 acids with (*a*) and without (*b*) addition of formic acid to the carrier gas; column with silicone; $t_c = 138°C$; helium flow rate 8 $cm^3\ min^{-1}$; *s*—acetone peak; the numerals against the peaks denote the number of carbon atoms.

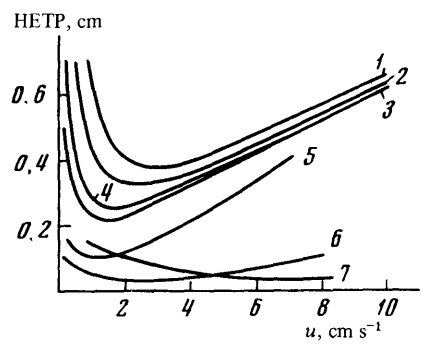


Figure 8. Variation of column efficiency (HETP) with the linear flow rate *u* and the nature of the carrier gas: 1) hydrogen; 2) helium; 3) methane; 4) nitrogen, ethane, ethylene ($t_c = 100°C$);[12] 5) carbon tetrachloride ($t_c = 90°C$);[28] 6) nitrogen; 7) helium[81].

As an illustration of the influence of the polar organic additive (formic acid) on the shape of the peaks and the degree of separation, Fig. 5 [15] presents chromatograms for the separation of volatile C_2-C_6 aliphatic acids on a column with silicone. Fig. 8 [12,28,82] illustrates the variation of HETP with the flow rate of eluents of different types. With increase of the molecular weight of the eluent, i.e. with decrease of the diffusion coefficient of the sorbate–eluent mixture (the diffusion coefficients of the hydrocarbons ethane, butane, and benzene are 0.6–0.8 $cm^2\ s^{-1}$ at 120–190°C in helium, or approximately 0.1 $cm^2\ s^{-1}$ in chloroform, carbon tetrachloride, and dichloroethane vapours at the same temperatures[28]), the HETP minimum is displaced towards lower linear flow rates of the eluent.

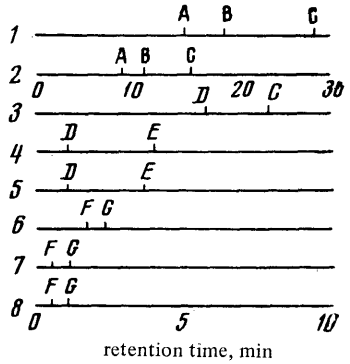


Figure 9. The influence of the nature of the carrier gas on the retention time; vapour-phase carrier: 1) benzene; 2) mixture of 10% of benzene and ethanol; 3) and 6) mixture of 1% of ethanol and iso-octane; 4) and 7) ethanol; 5) and 8) mixture of 1% of water and ethanol; flow rate 200 $\mu l\ min^{-1}$; A) phenol; B) *o*-cresol; C) *m*-cresol; D) *p*-di-isopropylbenzene; E) admixture of *p*-di-isopropylbenzene; G) cumene; F) admixture of cumene; 1) and 2) adsorbent—K-923 silica gel, column length 50 cm, internal diameter 3 mm, $t_c = 140°C$; 3)–8) adsorbent—HS-Pellumina, column length 1 m, internal diameter 2 mm, $t_c = 150°C$.

It is also possible to use multicomponent vapour-phase eluents and the components of such mixtures may be not only the vapours of organic substances but also permanent gases, water vapour, ammonia, etc. This approach makes it possible to regulate the selectivity of the chromatographic system (the stationary liquid–vapour-phase eluent system) by selecting the composition of the eluent. Thus, when the eluent was a mixture of ethanol and water vapours [30] (this method was first proposed by Mar'yakhin and Vigdergauz [37]) in the analysis of a mixture of α- and β-naphthols on a column with silica gel, the retention time of the naphthols increased by 5–8 min compared with the experiment where the carrier gas was the vapour of pure ethanol. Similar effects have also been observed when the vapours of mixtures of ethanol with methanol, iso-octane, benzene [30], and hexane [25] were used.

The influence of the nature and composition of the eluent on the retention of sorbates is illustrated by the data in Fig. 9. [30]

VI. DETERMINATION OF PHYSICOCHEMICAL PROPERTIES

Organic eluents may be used widely in the determination of the physicochemical properties of substances. The gas-chromatographic methods for the determination of physicochemical constants are based on the interaction between the sorbate, the liquid phase, and the carrier gas, so that an increase of the number of substances used as carrier gases greatly extends the range of interactions investigated.

The use of organic eluents in the corresponding systems does not affect the existing methods for the determination of diffusion coefficients [26,83-85], virial coefficients, and activity coefficients [9,18-20,22,86-93]. Thus Kobayashi and coworkers [18,89-93] investigated the gas–liquid equilibria in multicomponent systems, including gaseous and liquid hydrocarbons, and determined the diffusion coefficients [85] up to 136 atm. The employment of organic eluents makes it possible to simplify or modify some of the physicochemical methods (for example the determination of molecular weights [94-96] or of heats of desorption [30]) and to devise new ones, for example the procedure for the determination of complex-formation constants [87].

In particular, when a liquid film is formed on the surface of the adsorbent, the determination of the heat of desorption in chromatography with an organic eluent requires a modification of the method used in traditional chromatography [97]. Tsuda et al. [30] suggested that there is a relation in this case between the heats of desorption and the boiling point of the individual component analogous to Trouton's rule and obtained on this basis an approximate formula for the heat of desorption

$$\Delta H = K_2 T_b,$$

where $K_2 = K_1 T_c$, T_b is the boiling point of the individual substance (in degrees Kelvin), T_c the column temperature (in degrees Kelvin), and K_1 is determined from the slope of the linear plot based on the equation

$$\ln V_R = K_1 T_b + A_1 \quad (V_R \text{— is the retention volume}).$$

Using the equation obtained, the authors confirmed the presence of a liquid film on the adsorbent and concluded that the use of ethanol vapour is to be preferred in the analysis of high-boiling mixtures.

VII. PREPARATIVE CHROMATOGRAPHY

Only a few studies have been made on the use of organic eluents in preparative gas chromatography [33,37,98-100], although the advantages of their employment (as well as water vapour [11]) are quite evident, since, apart from the possibility of modifying the sorption properties of the stationary phase, vapour-phase eluents ensure the virtually complete recovery of the products separated.

In order to increase the degree of recovery of benzene, Tsuda and Ishii [98] added to the carrier gas (nitrogen) a stream of toluene vapour, which condensed in a cooled trap together with the benzene issuing from the column. The degree of recovery of benzene depended on the ratio of the nitrogen and toluene streams and on the rate at which they passed through the column, exceeding 90% under optimum conditions.

Vigalok and coworkers [99,100] achieved a preparative separation of *m*- and *p*-xylenes on a column with a modified synthetic zeolite at 200°C in a stream of benzene vapour. Virtually complete recovery of the high-purity products was achieved (up to 99% after the removal of benzene). Naturally, the recovery did not require low temperatures.

Vigdergauz and Mar'yakhin [37] used, together with water vapour, its mixtures with various organic vapours in preparative chromatography. After their emergence from the column (3.2 m long and with an internal diameter of 20 mm), the mixed eluents were fully condensed (together with the substances isolated in traps cooled by tap water). The version where the eluent is a mixture of water and hydrocarbon vapours is of interest [37]. By varying the composition of this eluent, it is possible to regulate the selectivity and separating capacity of the preparative column. Furthermore, aqueous and hydrocarbon layers are formed in the traps and the substances isolated may concentrate in one of them (depending on their solubility).

Freons have been used in preparative chromatography [33] on a 15 m column having an internal diameter of 10 mm with poly(ethylene glycol) on Chromosorb A, where isomers of geranate ester were separated. Another version [33] involves the use of nitrogen as the carrier gas and the injection of small amounts of Freon into the gas stream directly before entering the trap.

In connection with the considerable progress in the improvement of the productivity of preparative chromatographic apparatus and the transition from preparative chromatography to semi-industrial and industrial chromatographic processes, the use of organic vapour-phase eluents, mainly readily available pure hydrocarbons and petroleum fractions, may serve as a basis for further advances in this field.

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