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Chromatography in a Gas-Colloid System

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The results of the study of colloidal systems based on highly dispersed adsorbents and colloidal solutions of polymers as universal stationary phases for gas chromatography have been analysed. Particular attention has been paid to the regular features of retention on colloidal sorbents and the estimation of their selectivity and thermal stability. Possible fields of analytical application (the separation of mixtures of organic and organometallic compounds, trace analysis, and capillary chromatography) have been examined.
The bibliography contains 70 references.

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I. INTRODUCTION

In practical gas chromatography (GC), increasing use is being made of sorbents combining the properties of solvents and adsorbents. The use of sorbents operating under intermediate adsorption–absorption conditions extends gas-chromatographic analysis chiefly by making it possible to control the selective properties of the chromatographic packing by changing the relationship between the contributions of solution and adsorption in the overall retention. The use of sorbents with controllable selectivity makes it possible to reduce considerably the range of stationary phases (SP) for gas chromatography.

Sorbents of the intermediate type include: 1) macroporous carbon adsorbents, modified by liquid phases, of the Carbochrome or Carbopak type, 2) macroporous silica adsorbents, modified by liquid phases, of the Silochrome or Spherosil type, 3) porous polymers, modified by liquid phases, of the Porapak or Polysorb type, 4) adsorbents with stationary liquids chemically bound on the surface (graft sorbents of the Durapak type), 5) organic derivatives of clays (Bentones) on an inert solid carrier, 6) liquid crystals on an inert solid carrier, and 7) colloidal systems on an inert solid carrier.

Adsorption–absorption chromatography using modified Silochromes and graphitised carbon black[1-3], the use of modified polymers in gas chromatography[4], problems of chromatography on Bentone columns[5-7], analytical and physicochemical aspects of chromatography in a gas–liquid crystal system[8], and graft sorbents[9] have already been reviewed.

The modification of adsorbents by a liquid phase makes it possible to control the selectivity, eliminates the asymmetry of the peaks due to polar substances, and in the case of carbon black increases the mechanical strength of the sorbent. Usually, with increase in the quantity of stationary phase on the adsorbent carrier, the efficiency increases up to the formation of a monolayer, after which it decreases as a result of a decrease in the rate of mass exchange[2]. This restricts the range of the selectivity of modified adsorbents suitable for practical application, and naturally reduces the range of analytical problems that can be solved using a given adsorbent–modifier system.

Bentones belong to the class of intermediate sorbents because of the mixed mechanism of the interaction of the sorbates with adsorption centres on the one hand and with organic groups on the other. Since liquid crystals show simultaneously (within a short temperature range) the properties of both liquids and solids, they also act as intermediate sorbents. It should be noted that both Bentones and liquid crystals, which have a high selectivity with respect to structural isomers, have a moderate group selectivity.

Colloidal systems (colloids) in the most general sense are systems in which substances are subdivided to give very small particles (10^{-4}–10^{-7} cm). A necessary condition for the colloidal state of a system is the insolubility of one phase in the other. The existence of a physical surface between the phases, that is the heterogeneous character of colloids, represents the basic difference between them and true homogeneous solutions. From the molecular-kinetic properties typical of polymer solutions (low osmotic pressure, little diffusion of the macromolecules, and their inability to pass through a semi-permeable partition in dialysis), they must be classified as colloidal systems. This similarity is related to the fact that the dimensions of the particles, which determine the properties of the solutions of both types, are similar to one another and much greater than those of ordinary molecules.

A chromatographic study of a binary squalane–stearonitrile mixture[10] confirmed the suggestion that micelles exist in mixtures of non-polar liquids with nitriles. Thus these and similar binary liquid phases are colloidal.

Of the wide range of types of colloidal system, classified according to the state of aggregation of the dispersed phase and the dispersion medium, the systems formed by a solid and an organic liquid, that is organosols and gels of highly dispersed adsorbents and polymers, are of greatest interest from the present viewpoint. The use of these systems as sorbents is attractive because it is possible, by changing the composition, to vary smoothly the sorption characteristics of the packing in a range from the properties of the liquid to the properties of the solid, which is difficult in the classical form of gas chromatography on modified adsorbents.

If organic derivatives of clays are regarded as one-dimensional colloids in view of the "colloidal" dimensions of the particles in one of three directions[11], then Bentones were essentially the first colloidal systems to find gas-chromatographic application. Bentones mixed with liquid phases form stable colloidal systems[12]. It has been suggested[13] that on

treatment with a silicone oil, the crystal lattice of Bentone-34 is deformed, and the mixture becomes a thixotropic gel. Modified Bentones have been widely used in the analysis of aromatic isomers[5-7].

Colloidal systems can be obtained by introducing an appropriate filler into viscous organic liquids. The first examples of these stationary phases were silicone greases[14]. The influence of the silica fillers in high-vacuum silicone grease on the value of the retention has been studied[15]. Pecsok and Vary[16], working with dispersions of metallophthalocyanines in silicone oil, were among the first to demonstrate clearly the advantages of the directed use of adsorption effects in gas–liquid chromatography. It subsequently appeared appropriate to carry out detailed studies of the chromatographic properties and analytical possibilities of colloidal sorbents.

The present review examines two types of colloidal system as SP for gas chromatography—colloidal solutions of polymers and colloidal systems based on highly dispersed adsorbents. Studies carried out by the authors have shown that these stationary phases make it possible to control the selectivity of chromatographic separation over a wide range, and hence to solve a large number of analytical problems.

II. REGULAR FEATURES OF RETENTION ON COLLOIDAL SORBENTS

1. Preparation of Colloidal Sorbents

The method of preparing sorbents with colloidal polymer solutions as stationary phases is protected by a patent[17] and has been described in a number of papers[18-21]. Dispersions of macromolecular compounds corresponding to the colloidal state were obtained by the aggregation of the macromolecules in the solution by the introduction of a high-boiling liquid modifier. When the solvent was evaporated and an inert carrier added to the heated mass (80–100 °C), the solid surface was covered by aggregates of molecules of the colloidal system. Polyvinyl alcohol (PVA), polystyrene (PS), and low-pressure polyethylene (PE) were used as polymeric components. Polyethylene glycol-400 (PEG-400), dinonyl phthalate (DNP), and squalane were used as modifiers.

Ultrasonic dispersal† has been used to prepare colloidal SP based on highly dispersed adsorbents[22-26]. The Aerosil (highly dispersed silicon dioxide) or PM-15 grade carbon black was introduced into solutions of the organic liquid squalane, PEG-400, PEG-40000, polymethylsiloxane (PMS-100), or polymethylphenylsiloxane (PMPS), after which the prepared suspension was deposited on inert solid carriers. Since the particle size of the fillers used lay in the colloidal range ($\sim 10^{-5}$–10^{-6} cm), the systems based on them are colloidal. An apparatus for continuous vigorous shaking has been used to increase the thermal stability of stationary phases by adding solid highly dispersed binding agents of the Aerosil or graphitised carbon black type[27]. There is no difference between the filling of capillary columns by colloidal stationary phases[28] and that in ordinary gas–liquid chromatography.

†A similar method has been used to obtain stable coatings in capillary chromatography (see section VI).

2. Influence of the Composition of the Colloidal Stationary Phase on the Retention of Polar and Non-polar Compounds

A necessary condition for the successful gas-chromatographic analysis of a mixture is the correct choice of sorbent. The use of binary or multiple systems makes it possible to vary smoothly the selectivity of the chromatographic separation and hence to carry out a directed search for the sorbent with the optimum properties. The dependence of the elution characteristics of the components of the mixture being analysed on the composition of the combined stationary phase provides a basis for the solution of this problem. For the usual mixed liquid phases, these relationships in most cases are linear. A characteristic feature of colloidal systems is the presence of breaks and extremal points on the plots of $\lg V_g$ against composition (V_g is the specific retention volume). Anomalies in the retention process are due to specific interaction between the components of the system, and also adsorption factors.

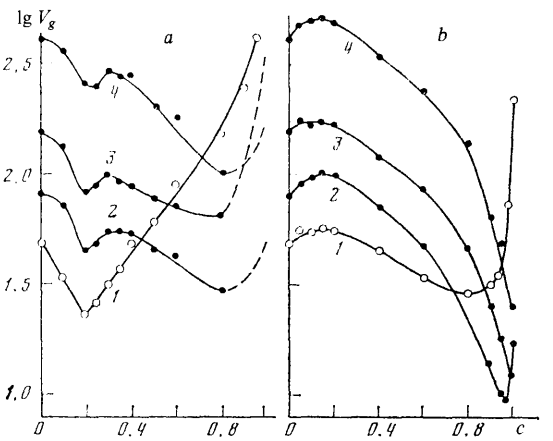


Figure 1. Dependence of the retention on the composition of colloidal SP; PEG-400–Aerosil (*a*) and PEG-400–carbon black (*b*); *1*) nonane, *2*) benzene, *3*) ethanol, *4*) nitromethane[22,25].

The dependence of the retention on the composition of colloidal SP containing highly dispersed adsorbents is given in Fig. 1 (*c* is the mass fraction of the adsorbent). The curves corresponding to the retention of alkanes on columns containing a PEG-400–Aerosil system have a minimum at $c = 0.2$.[22,26] This composition corresponds to the conversion of the colloid from the free-dispersed state (sol) into the bound-dispersed gel-like state. This agrees with data obtained by the workers who developed the Soviet Aerosil[29], and is confirmed by electron-microscope studies[26]. In addition to this minimum at $c = 0.2$ for polar compounds, there is another deeper minimum corresponding to $c = 0.8$. At this component ratio, the contribution of solution is appreciable. A higher concentration of Aerosil corresponds to a sharp increase in the retention volume, due to adsorption on the gas–Aerosil surface with the production of asymmetric peaks. The position of the extremal points on the $\lg V_g$–composition curves for the PEG-400–carbon black system[25] corresponds to the same

component ratio as in the PEG-400–Aerosil system. The colloidal conversion is accompanied by the maximum retention for this system, however.

Thus the form of the extremal point is determined by the nature of the interaction between the components of the colloidal stationary phase, since the glycol is able to form hydrogen bonds with the Aerosil, whereas its interaction with the carbon black involves chiefly non-specific forces. Fig.1 also shows that by introducing a highly dispersed carrier into the stationary phase, it is possible to change smoothly the retention of the substances being analysed, as far as a change in the order of their elution.

For the organic PS–squalane system (Fig.2), the retention characteristics pass through a maximum at equal proportions of the modifier and the polymer, indicating an interaction between the components of the colloidal stationary phase at this component ratio. The extremal points on the graph giving the dependence of the retention on composition for the PE–PEG-400 system are not so sharp as those for the sorbent based on polystyrene. Here also, however, change in the ratio of the components of the stationary phase can be used to control the selectivity of the column in the analysis of organic compounds of various classes. The sharp increase in the retention of polar sorbates on going from the pure polymer to the mixture with a small quantity of the glycol is apparently due to the influence of the adsorption factor[30].

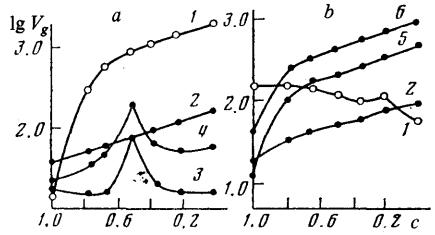


Figure 2. Dependence of the retention on the composition of colloidal SP; PS–squalane (*a*) and PE–PEG-400 (*b*); *1*) nonane, *2*) benzene, *3*) ethanol, *4*) methyl ethyl ketone, *5*) nitromethane, *6*) pyridine[18,19].

In a study of the absolute retention of benzene, allyl iodide, and chlorobenzene on the mole fraction (x_A) of strearonitrile in squalane, maxima were observed at x_A = 0.1–0.2.[10] In the opinion of the authors cited, this was due to the formation of micelles in this system.

Thus for practically all colloidal systems, the plot of the logarithm of the retention volume against the quantitative ratio of the phases is non-linear. The presence of breaks and extremal points on these curves is determined by the nature of the interaction between the components of the system, and adsorption factors. Change in the composition of the colloidal sorbent over a wide range makes it possible to control the sorption characteristics of the chromatographic packing.

3. Influence of Temperature on Retention by Colloidal Stationary Phases

The temperature of the column (T), together with the composition of the sorbent, provides an efficient means of controlling the selectivity of a chromatographic separation. This is particularly true of systems containing polymers or liquid crystals, that is materials which change their phase state in the range of temperatures used in gas-chromatographic analysis.

It is known[31] that

$$\lg V_g = A + B/T \quad . \qquad (1)$$

The coefficient A is related to the entropy of sorption, and the coefficient B is the enthalpy component. A change in the nature of the sorption in the range of the temperatures of the phase transformation of the polymer for polar and non-polar sorbates leads to a change in the absolute values of the constants A and B in Eqn.(1), leading to distortion of the plot of the logarithm of the retention volume against the reciprocal of the absolute temperature (Fig.3).[21] These distortions are observed chiefly for non-polar or weakly polar compounds (alkanes and aromatic hydrocarbons). This indicates that the modifier makes the predominant contribution to the retention of polar compounds (PS–PEG-400 system) and that there is no specific interaction between sorbates and the PE–squalane sorbent. For colloidal solutions of polystyrene and polyvinyl alcohol in squalane, the opposite picture is observed. Increase in the concentration of the polymer in the binary stationary phase leads to more clearly defined breaks on these curves for compounds whose retention is determined by the polymeric component.

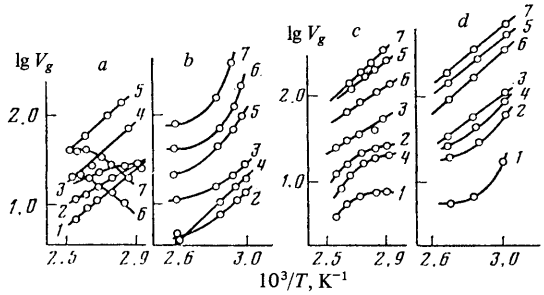


Figure 3. Plot of the retention against the reciprocal of the absolute temperature of the column; *a*) PS–PEG-400 (c = 0.67), *b*) PE-squalane (c = 0.2), *c*) PS–squalane (c = 0.4), *d*) PVA–squalane (c = 0.6); *1*) ethanol, *2*) methyl ethyl ketone (MEK), *3*) benzene, *4*) nitromethane, *5*) pyridine, *6*) n-nonane, *7*) n-decane[18,19].

A change in the selectivity of the column in the range of the temperatures of the phase transformation is particularly characteristic of the PS–PEG-400 system. When polystyrene changes from the vitreous to the highly elastic state (~100 °C), the retention of alkanes increases to such an extent that the peak of nonane is "displaced" into the middle of the chromatogram, passing in front of ethanol, methyl ethyl ketone, nitromethane, and pyridine. Thus the use of colloidal solutions of polymers as stationary phases makes it possible to control the selectivity of the chromatographic column in the temperature range of the change in the phase state of the polymer without replacing the sorbent.

A study of the temperature dependence of the retention for the colloidal stationary phases PEG-400–Aerosil and squalane–Aerosil# established[22,26] that for all sorbates they are linear,

#Here and subsequently, the squalene–Aerosil and squalane–carbon black systems are systems with the addition of 15% PEG-400 relative to the mass of Aerosil and 1.5% relative to the mass of carbon black.

since the phase state of the components does not change in the temperature range studied. The plot of the retention volume against the reciprocal of the temperature for a PEG-40000–Aerosil sorbent has been studied[24,26]. The graphs show breaks in the absence of the adsorbent, and at a relative concentration of the adsorbent $c = 0.1$ and 0.2. As with polymer solutions, the deviations from the linear relationship characterise the change from the adsorption of the substances being analysed on the surface of the solid polymer to solution, due to the diffusion of the molecules into the depth of the liquid polymer film, leading to an increase in the capacity of the sorbent. The increase in retention takes place before equilibrium absorption is reached. As the Aerosil is added to the polymer, the inflection on the retention curve gradually decreases, and it disappears completely at $c = 0.3$. An interesting feature is that the sorbent with this composition shows the strongest specific adsorption properties[24].

4. Influence of Adsorption Factors on Retention by Colloidal Stationary Phases

As already noted, the marked deviation from linearity shown by the dependence of the retention characteristics of the sorbates on the composition of the binary colloidal phase may be due to adsorption phenomena. Retention in a gas–colloid system is determined by solution in the liquid phase (the dispersion medium of the colloid), adsorption on the surface of the colloidal particles of the polymer or adsorbent (the disperse phase of the colloid), and also adsorption at the boundaries between the phases. The influence of these factors on retention has been studied[20,21,23,26].

Since the stationary phases were deposited on fairly inert silanised carriers in quantities of more than 10%, adsorption at the gas–solid carrier and liquid–solid carrier boundaries could be neglected. For the description of the adsorption effects on colloidal organic phases[20,21], an equation was proposed, relating the specific retention volume (V_g) to the distribution and adsorption constants

$$\frac{V_{g,p}}{s} = \frac{\Gamma}{s}\frac{W}{g + g_c} + \Gamma_1 \qquad (2)$$

where $V_{g,p}$ is the specific retention volume per gram of packing, $cm^3\ g^{-1}$; s the surface area of 1 g of the colloid, cm^2; Γ the coefficient of sorption by the colloid, $(g\ cm^{-3}/g\ cm^{-3})$; Γ_1 the coefficient of adsorption on the gas-colloid surface, cm; W the volume of colloidal solution in the column, cm^3; g its mass, g; and $g + g_c$ the mass of packing, g.

Since the coefficients of adsorption of polar and non-polar sorbates at the gas–colloid surface for systems containing highly dispersed adsorbents are negligible[23], the sorption by these sorbents was calculated using the equation[26]:

$$V_{g,p} = \Gamma\frac{W}{g + g_c} \qquad (3)$$

Eqns.(2) and (3) are applicable for systems containing a small quantity of a disperse phase and consisting of colloidal solutions or sols. The quantity Γ in Eqn.(2) characterises the adsorption by the colloidal particles of the polymer[20,21]:

$$\Gamma W/(g + g_c) = \Gamma_m W_m/(g + g_c) + \Gamma_m\Gamma_s s_{pl,p} \qquad (4)$$

where W_m is the volume of the modifier in the column, cm^3; $s_{pl,p}$ the surface area of the colloidal particles of the polymer, calculated for 1 g of packing, $cm^2\ g^{-1}$; Γ_s the coefficient of adsorption on the surface of the colloidal particles, cm; and Γ_m the distribution coefficient between the pure modifier and the gas phase, $(g\ cm^{-3})/(g\ cm^{-3})$.

Eqn.(4) gives

$$\frac{\Gamma}{\rho}\frac{\Pi}{\Pi + 100} = \frac{\Gamma_m}{\rho_m}\frac{1 - c}{1 + 100/\Pi} + \Gamma_m\Gamma_s s_{pl,p} \qquad (5)$$

where Π is the percentage impregnation of the solid carrier by the colloid; ρ the density of the colloid, $g\ cm^{-3}$; ρ_m the density of the modifier, $g\ cm^{-3}$; and c the mass fraction of the polymer in the mixture with the modifier.

The relationship

$$\frac{\Gamma}{\rho} = \Gamma_m\left[\frac{1 - c}{\rho_m} + \Gamma_s\left(1 + \frac{100}{\Pi}\right)s_{pl,p}\right] \qquad (6)$$

can then be brought to an equation of the form

$$\frac{\Gamma}{\rho} = \Gamma_m\left[\frac{1 - c}{\rho_m} + \Gamma_s s_{pl,pl}c\right] \qquad (7)$$

($s_{pl,pl}$ is the surface area of the particles, calculated for 1 g of polymer, $cm^2\ g^{-1}$).

If Γ_m is known from the data obtained using the pure modifier, it is possible to calculate $\Gamma_s s_{pl,pl}$, that is the adsorption by 1 g of polymer present in the colloidal state.

With increase in the proportion of the dispersed phase, the colloidal solution is converted into a gel-like state. The system loses its flow properties as a result of the agglomeration of the micro-particles to give a coagulation structure. The overall surface area of the sorbent increases. In the general case it may be assumed that the retention of the compounds being analysed for these systems is determined by the sorption by the gel. Thus

$$V_{g,p} = \Gamma_g s_g \qquad (8)$$

where Γ_g is the coefficient of sorption by the gel, cm; and s_g the surface area of the gel for 1 g of packing, $cm^2\ g^{-1}$.

The contributions of solution and adsorption to the total retention on organic colloidal sorbents can be estimated from Eqn.(4).[20] When colloidal systems containing highly dispersed adsorbents are used, part of the modifier does not take part in the sorption process, but is used up in suppressing the active centres of the solid carrier. Thus with allowance for this characteristic feature of these systems,

$$V_N = \Gamma_m(W_m - W'_m) + \Gamma_m\Gamma_a s_a \qquad (9)$$

where V_N is the effective retention volume, cm^3; Γ_a the coefficient of adsorption on the surface of the adsorbent in the colloidal state, cm; s_a its surface area, cm^2; and W'_m the volume of the modifier not taking part in the sorption process, cm^3.

The proportion of the modifier W'_m corresponds to the ratio of the components of the system at which the change to adsorption on the surface of the adsorbent takes place. This change corresponds to the retention minima on the plots of $\lg V_g$ against composition in the range of high values of c. Thus for the PEG-400–Aerosil system (Fig.1), $W'_m = 0.25g_a/\rho_m$ (g_a is the mass of highly-dispersed adsorbent in the column for the composition $c = 0.8$).

It can be shown that $g_a = W_m\rho c/(1 - c)$, so that $W'_m = 0.25W_m c/(1 - c)$. By analogy with the PEG-400–Aerosil system, for the PEG-400–carbon black system $W'_m = 0.015W_m c/(1 - c)$.

The use of these relationships for the quantitative estimation of the factors determining retention showed[20,21,26] that change in the composition of the colloidal stationary phases, and in the case of polymer solutions change in the temperature of the column, leads to a change in the ratio between the contributions of adsorption and absorption forces to the overall retention. This makes it possible to control the selectivity of separation and elution times of substances being analysed.

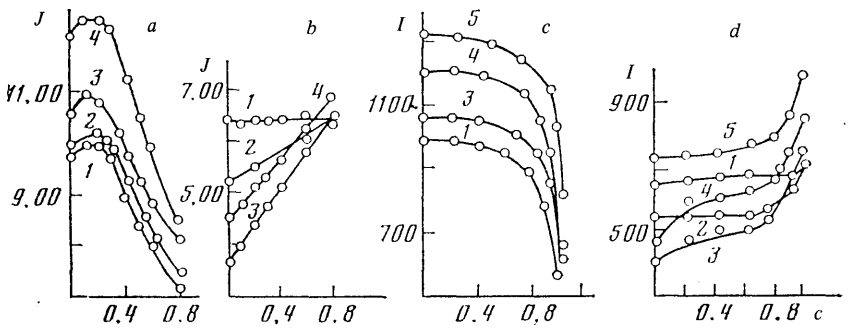


Figure 4. Dependence of the retention indices on the composition of colloidal SP: *a*) PEG-400–Aerosil, *b*) squalane–Aerosil, *c*) PEG-400–carbon black, *d*) squalane–carbon black; *1*) benzene, *2*) MEK, *3*) ethanol, *4*) nitromethane, *5*) pyridine[22,25].

III. SELECTIVITY OF COLLOIDAL STATIONARY PHASES

The range of stationary phases for GC on the world market includes more than 900 products. In spite of this, cases are frequently encountered where no known phase gives the required separation. These "selectivity gaps" are observed particularly in the selection of sorbents for the analysis of multi-component mixtures. The choice of sorbent is facilitated considerably by using different kinds of combined stationary phase, in particular colloidal systems.

1. Indices of Retention on Colloidal Sorbents

A convenient characteristic of the selectivity of a stationary phase towards a definite class of compound is provided by the logarithmic retention indices (Kovats indices) of a given substance *I* belonging to this class[32,33]. Its linear analogue *J* [33,34] is simpler in calculations. These data can be used to classify sorbents according to their polarity, and also to estimate the range of change in selectivity using combined sorbents.

Figs.4*a* and 4*b* [22,25] give the dependence of the linear retention index on the composition of colloidal stationary phases based on Aerosil. For the PEG-400–Aerosil system, the *J* curves for all the sorbates studied show maxima at the composition corresponding to the conversion of the sol to the gel. For the squalane–Aerosil system, the dependence of *J* on *c* is practically linear. The relative error in the determination of the linear retention indices did not exceed ±0.04 index unit. As a result of the change in the nature of the interaction on going from the PEG-400–Aerosil sorbent containing 20% adsorbent to the sorbent containing 80% adsorbent, the linear retention index of benzene, methyl ethyl ketone, and ethanol can be changed by 3 units, which corresponds to 300 units of the Kovats index, and that of nitromethane can be changed by 3.7 units (370 units). On pure squalane, ethanol is eluted before butane, and on a squalane–Aerosil sorbent with $c = 0.8$ it is eluted after hexane.

The dependence of the logarithmic retention index on the composition of stationary phases containing carbon black has been studied[25,26] (Figs.4*c* and 4*d*). In contrast to the PEG-400–Aerosil system, the change from the sol to the gel for the colloid containing carbon black is not accompanied by a maximum on the graph, since the interaction of polar and non-polar sorbates with the non-specific adsorbent involves dispersion forces. The greatest decrease in the retention indices begins at a carbon black concentration of 60% in its mixtures with the glycol. A different picture is observed for the squalane–carbon black system. Thus for ethanol and nitromethane, substances which tend to undergo strong specific interactions with a carbon black surface treated with a small quantity of glycol, breaks are observed on the curves at a low concentration of a highly dispersed filler. On going from the sorbent with $c = 0.2$ to the sorbent with $c = 0.985$ in the PEG-400-carbon black system, the retention indices can be changed by 280 units for benzene, by 300 units for ethanol, and by 370 units for nitromethane. On squalane, the retention index of methyl ethyl ketone is 140 units greater than that of ethanol, and on squalane containing 90% modified carbon black, the retention index of ethanol is 16 units greater than that of methyl ethyl ketone.

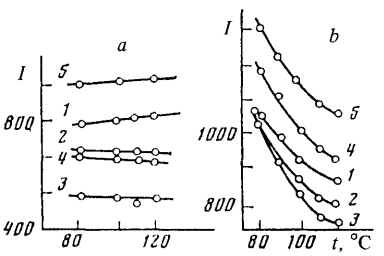


Figure 5. Dependence of the retention indices on the column temperature; *a*) PS–squalane ($c = 0.5$); PS–PEG-400 ($c = 0.5$).[21] See Fig.4 for numbering of sorbates.

Fig.5 [21] gives the temperature dependence of the Kovats indices of standard sorbates on polymeric colloidal phases. The greatest temperature "displacement of the indices" is observed for the PS–PEG-400 system. In this case the index of benzene, for example, in the range 80–100 °C decreases from 1005 units to 870 units, due to the increase in the retention of alkanes in the region of the phase transformation of polystyrene. For other colloidal solutions of polymers, the changes in *I* with change in the column temperature are slight. Thus for the PS–squalane system in the same temperature range, it changes by only 10 units (from 690 to 700).

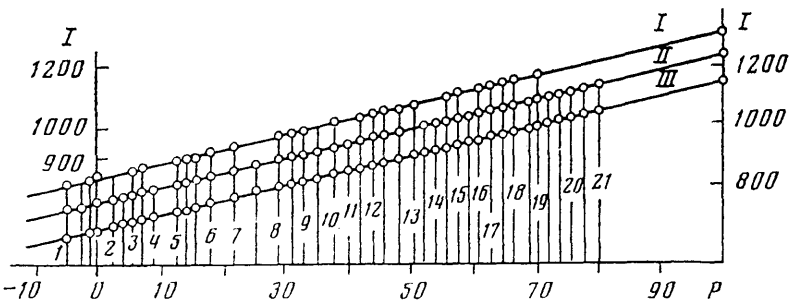


Figure 6. Dependence of the retention indices of ethylbenzene (*I*), toluene (*II*), and benzene (*III*) on the conditional chromatographic polarity[20,21]. For the numbering of the phases see Table 1.

2. Conditional Chromatographic Polarity of Colloidal Sorbents

The selection of the sorbent for the separation of a specific pair of components or a mixture of substances belonging to the same class is simplified considerably if its conditional chromatographic polarity *P*, a characteristic of the phase determined by the presence of groups other than alkyl groups, is known. According to Rohrschneider[35], who first proposed this approach to the selection of sorbents and their classification according to polarity, *P* is given by the expression

$$P = \frac{\lg r_2 - \lg r}{\lg r_2 - \lg r_1} \qquad (10)$$

where r_1 and r_2 are the ratios of the retention volumes of butadiene and butane on squalane ($P = 0$) and on β,β'-hydroxydipropionitrile ($P = 100$), and r is the corresponding ratio on the sorbent being studied.

The relative retention can be replaced by the retention indices for, for example, aromatic hydrocarbons[36]. In this case, the graphical expression of the conditional chromatographic polarity involves plotting *P* against the retention index. These plots can be used to predict the retention times of the substances being analysed and to select a sorbent with the optimum selectivity. Fig.6 gives the graph[20,21] for determining the conditional chromatographic polarity of colloidal solutions of polymers. The position of the point corresponding to the stationary phase on the abscissa was determined from the retention indices of benzene, toluene, and ethylbenzene. Table 1 gives colloidal systems in order of increasing conditional chromatographic polarity, with the column temperatures, composition, and percentage impregnation.

The change in the conditional polarity with change in the percentage impregnation of the carrier is apparently related to the sorption of the substances being analysed on the surface of the colloidal particles. The selectivity of colloidal binary phases may also be changed under the influence of the temperature factor, and if vitrification of the less polar component takes place, the decrease in its sorptive capacity leads to an increase in the overall polarity of the colloidal phases.

Fig.6 and Table 1 show that, using only six components (three polymers and three stationary liquids), it is possible, by varying their qualitative and quantitative composition, the percentage impregnation of the carrier, and the column temperature, to obtain a fairly wide range of conditional chromatographic polarity (from −5 units to 80 units). The smooth change in the properties of the colloidal systems based on polymers makes it possible to select the required phase for the solution of a specific analytical problem.

Table 1. Dependence of the conditional polarity (*P*) of colloidal polymer phases on the column temperature (*t*), the composition of the stationary phase (*c*), and the percentage impregnation (П).[20]

Phase No.	System	*t*, °C	*c*	П	*P*
1	PE	60	1.00	15	−5
2	PVA in DNP	60	0.8	15	2
3	PE in DNP	120	0.8	25	5
4	PE in DNP	60	0.4	15	9
5	PS in squalane	120	0.5	15	13
6	PES in DNP	100	0.6	25	17
7	PE in DNP	100	0.2	15	21
8	PS in DNP	100	0.5	25	29
9	PS in DNP	120	0.6	25	33
10	PE in PEG-400	150	0.3	15	38
11	PE in PEG-400	60	0.3	15	40
12	PS in PEG-400	120	0.8	25	43
13	PVA	100	1.00	15	50
14	PS in PEG-400	100	0.67	15	54
15	PS in PEG-400	100	0.67	30	57
16	PS in PEG-400	120	0.3	15	60
17	PS in PEG-400	100	0.5	30	62
18	PS	100	1.00	15	66
19	PEG-400	100	1.00	15	70
20	PS in PEG-400	80	0.5	30	76
21	PS in PEG-400	80	0.8	30	80

3. Rohrschneider's Polarity Factors for Colloidal Sorbents

Polarity factors have recently been used to characterise the selective properties of sorbents. These factors represent the differences in the retention indices ΔI of standard sorbates of different chemical character on columns with the stationary phase being studied and a non-polar liquid, for example squalane. The Rohrschneider polarity factors[37], that is the values of $\Delta I/100$ for benzene (*x*), ethanol (*y*), methyl ethyl ketone (*z*), nitromethane (*u*), and pyridine (*s*), have been calculated for the colloidal sorbents studied[20–22, 24–26] (see Table 2). These quantities make it possible to characterise in more detail the intermolecular interactions between the sorbent and the substance being analysed, and the set of values of the polarity factors provides as it were a sorbent "specification", which makes it possible to evaluate

its suitability for solving a particular separation problem. The values of the polarity factors and the overall conditional polarity of colloidal organic systems depend on the composition of the stationary phase, the percentage impregnation of the solid carrier, and the column temperature (see also Fig.7). The nature of the change in the polarity coefficients is on the whole analogous to that of the change in the overall conditional polarity (P). The change in the polarity coefficients with change in the percentage impregnation of the carrier characterises the relative contribution of adsorption and absorption factors to the retention of the corresponding standards, compared with the relative contribution of these factors to the retention of alkanes (Fig.7).

Table 2. Polarity factors of colloidal systems based on polystyrene at 100 °C and П = 25%.

System	Solutions in PEG-400					Solutions in squalane			
c	0.2	0.3	0.5	0.67	0.8	0.2	0.5	0.6	0.8
x	3.50	3.36	2.98	2.82	2.56	0.16	0.49	0.70	0.72
y	6.31	5.94	5.16	4.50	3.93	0.60	0.98	1.20	1.47
z	4.43		3.69	3.37	3.07	0.35	0.83	1.00	1.15
u	7.12	6.76	5.95	5.48	4.79	0.55	1.35	1.80	1.84
s	5.65	5.28	4.52	4.28	3.66	0.58	1.07	1.37	1.51

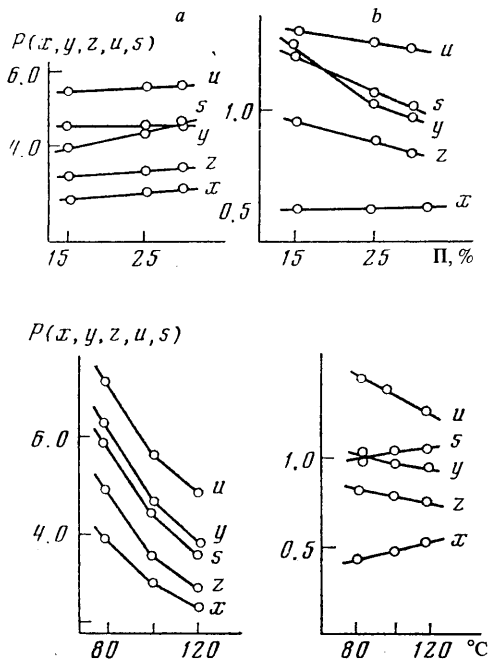


Figure 7. Dependence of the polarity factors of colloidal SP on the percentage impregnation and the column temperature: *a*) PS–PEG-400 (c = 0.67); *b*) PS–squalane (c = 0.5).[21]

The relationships given in Fig.7 can be used to select the optimum conditions for separating components of different classes. For example, to achieve the most selective separation of amines and aromatic hydrocarbons on colloidal solutions of PS in PEG-400, it is necessary to work at low column temperatures and maximum impregnation of the carrier by the liquid phase. To separate amines from nitromethane, the opposite relationship in these experiment parameters is preferred, since this case is characterised by the greatest difference in the polarity factors x and s, which play the most important role in the separation of components of these classes.

Table 3 gives the values of the polarity factors for colloidal stationary phases containing highly dispersed adsorbents. The sorbents studied are arranged in order of increasing constant x, the most universal characteristic of chromatographic polarity.

Table 3. Polarity factors of colloidal systems based on highly dispersed adsorbents[26].

System	c	x	y	z	u	s
Squalane-Aerosil	0.2	0.01	0.64	0.22	0.61	—
Squalane-carbon black	0.1	0.01	0.71	0.21	0.91	0.36
Squalane-carbon black	0.2	0.01	0.97	0.24	1.24	0.45
Squalane-carbon black	0.6	0.04	1.46	0.33	1.63	0.72
Squalane-Aerosil	0.4	0.10	1.36	0.43	1.17	—
Squalane-Aerosil	0.6	0.14	2.12	0.62	1.83	—
Squalane-Aerosil	0.8	0.20	2.83	1.08	2.38	—
Squalane-carbon black	0.9	0.24	2.45	0.82	2.76	1.36
PEG-400-Aerosil	0.8	0.61	4.23	2.07	4.00	—
PEG-400-carbon black	0.985	0.62	3.79	1.94	3.95	2.59
PEG-400-carbon black	0.9	1.59	4.91	2.77	5.29	4.44
PEG-400-Aerosil	0.6	1.84	5.20	3.01	5.46	—
PEG-400-Aerosil	0.4	2.90	6.23	4.09	6.78	—
PEG-400-carbon black	0.6	2.95	6.44	3.94	7.09	5.73
PEG-400-carbon black	0.2	3.41	6.80	4.43	7.56	6.21
PEG-400-Aerosil	0.2	3.61	6.96	4.87	7.60	—

Table 4. Standard and colloidal stationary phases based on highly dispersed adsorbents, having similar polarity factors[26].

SP	x	y	z	u	s
Squalane-Aerosil (0.2)	0.01	0.64	0.22	0.61	—
Silicone SE-30	0.16	0.20	0.50	0.85	0.48
Silicone OV-1	0.16	0.20	0.50	0.85	0.48
Silicone OV-101	0.16	0.20	0.50	0.85	0.48
Armin 2 HT	0.24	0.96	0.29	0.51	0.36
Silicone DC 560 (F 60)	0.31	0.49	0.82	1.08	0.83
Apiezon L	0.32	0.39	0.25	0.48	0.55
Squalane-carbon black (0.1)	0.01	0.71	0.21	0.91	0.36
SP-400	0.83	0.49	0.82	1.08	0.83
Armin 2SD	0.35	0.45	0.37	0.57	1.03
Squalane-carbon black (0.2)	0.01	0.97	0.24	1.24	0.45
Silicone 0-3	0.42	0.81	0.85	1.52	0.89
Armin SD	0.44	1.06	0.79	1.36	0.78
Squalane-Aerosil (0.8)	0.20	2.83	1.08	2.36	—
Fluorolube GR 362	0.51	3.16	2.48	2.51	4.00
Bis(2-ethylhexyl) sebacate	0.73	1.65	1.15	2.20	1.24
Chalkomide M-18	0.78	2.76	1.36	2.69	1.47
Di-isodecyl phthalate	0.83	1.65	1.43	2.53	1.54
Celanised ester No. 9	0.83	1.75	1.28	2.36	1.46
Algaterg T	0.89	3.18	—	2.41	2.30
Squalane-carbon black	0.24	2.45	0.82	2.76	1.36
Dinonyl phthalate	0.84	1.76	1.48	2.70	1.53
STAP	0.89	2.56	1.64	2.44	2.35
PEG-400-carbon black (0.9)	1.59	4.91	2.77	5.29	4.44
Tween 80	2.14	4.20	2.78	5.20	3.65
Bis(2-methoxyethyl) adipate	2.21	4.07	3.16	5.41	3.67
PEG-400-Aerosil (0.4)	2.90	6.23	4.02	6.78	—
Igepal CO-990	2.94	5.12	3.59	6.64	4.67
Chiproz SP-80	2.96	5.57	4.22	6.53	5.91
Ethylene glycol isophthalate	3.00	4.76	4.10	6.51	5.17
PEG-400-carbon black (0.6)	2.95	6.44	3.94	7.09	5.73
MER-21	3.16	5.28	3.78	7.04	5.07
FFAP	3.21	5.79	4.11	7.17	6.45
Carbowax-4000	3.22	5.46	3.86	7.15	5.17
PEG-400-carbon black (0.2)	3.41	6.80	4.43	7.56	6.21
Ethylene glycol adipate	3.43	5.46	4.52	7.11	6.00
Phenyldiethanolamine succinate	3.61	6.24	4.70	7.24	6.32
MER-2	3.67	5.27	4.54	7.10	5.88

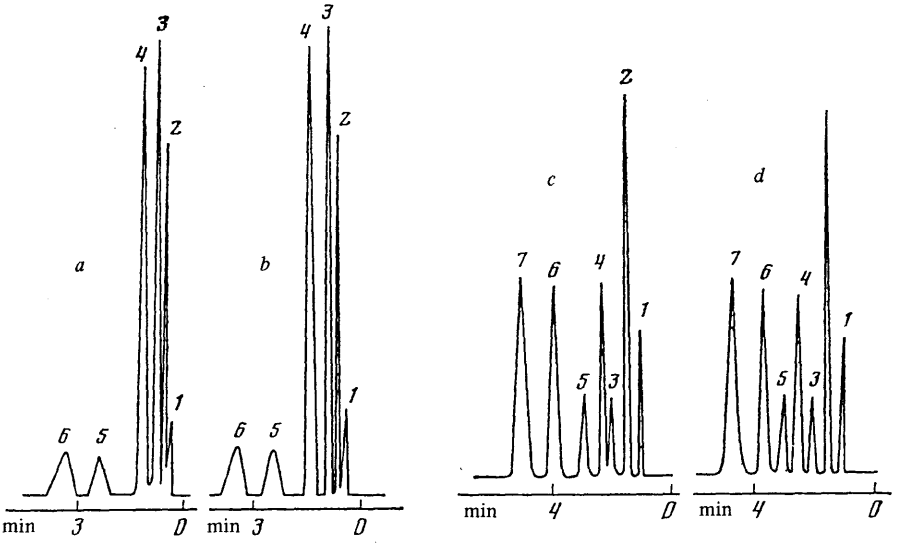


Figure 8. Chromatograms obtained for synthetic mixtures on ordinary (*a*,*c*) and colloidal (*b*,*d*) SP having similar polarity factors; 120 °C; Solid carrier Celite-545: *a*) SE-30, *b*) PS–squalane (*c* = 0.2); *1*) propionaldehyde, *2*) thiophene, *3*) n-octane, *4*) o-xylene, *5*) n-octanol, *6*) o-cresyl acetate; *c*) Reoplex-400, PS–PEG-400 (*c* = 0.5); *1*) n-pentane, *2*) acetone, *3*) chloroform, *4*) toluene, *5*) dioxan, *6*) n-butanol, *7*) isopentyl alcohol[20,21].

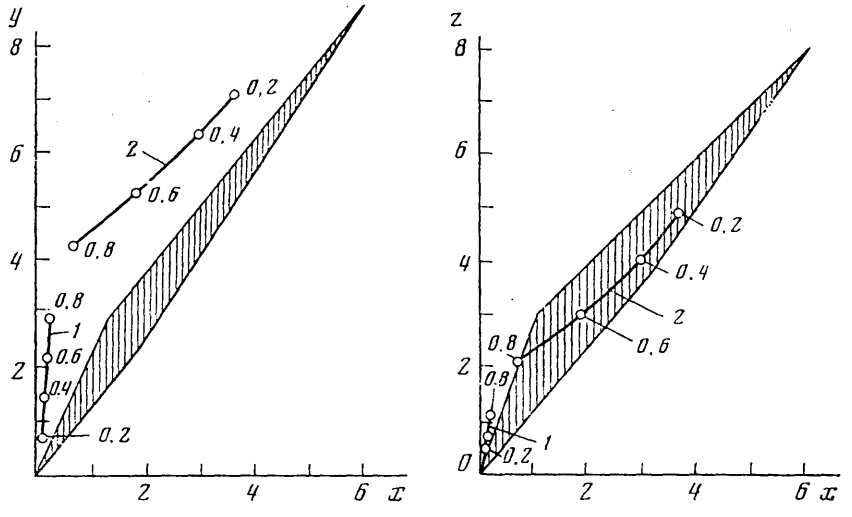


Figure 9. Dependence of the polarity factors y and *z* on the polarity factor *x*: *1*) PEG-400–Aerosil (*c* = 0.2, 0.4, 0.6, 0.8), *2*) squalane–Aerosil (*c* = 0.2, 0.4, 0.6, 0.8) (the range of stationary phases studied by Rohrschneider[37] is hatched).[39]

The data in Table 3 can be used to select a sorbent with optimum selective properties on the basis of available materials produced by Soviet industry. The data given show that the use of colloidal stationary phases based on Aerosil and carbon black and a few modifiers makes it possible to obtain a set of sorbents covering a fairly wide range of polarity. Thus the polarity factor *y*, characterising the retention of ethanol, can be changed gradually from 0 on pure squalane to 6.96 on a PEG-400–Aerosil sorbent with *c* = 0.2 [1,2,3-tris(β-cyanoethoxy)propane], which has the highest polarity factors among known stationary phases (*y* = 8.71).

Knowing the Rohrschneider polarity factors, it is possible to replace one stationary phase by another with similar values of the polarity constants. Table 4 gives the values of the polarity factors of standard and colloidal stationary phases with similar selective properties[26]. The values of the polarity factors for the colloidal sorbents were obtained at 60 °C. The data on the separation on the standard stationary phases were taken from a monograph[38]. Thus without resorting to

the use of expensive SP difficult to obtain, it is possible to achieve a similar separation on a colloidal sorbent with a definite component ratio.

A similar comparison of standard stationary phases with the colloidal organic systems PS–PEG-400 and PS–squalane has been carried out[20]. As an example illustrating the possibility of replacing the stationary phases usually employed by colloidal phases, Fig.8 gives identical chromatograms for mixtures of compounds with different structures.

Graphs giving the relationship between the composition of a binary colloidal system and the polarity factor have been published[39] (Fig.9). The colloidal systems examined have higher polarity factors y than the usual stationary liquids studied by Rohrschneider[37]. Thus colloidal sorbents not only provide an alternative, but also may ensure an original combination of polarity factors.

IV. EFFICIENCY OF COLUMNS WITH COLLOIDAL SORBENTS

To estimate the efficiency of columns with solutions of polymers as stationary phases, and also to take account of various factors influencing the spreading of the zones of the components being separated, the following characteristics have been used[20,21]: the height equivalent to a theoretical plate (H) and the height equivalent to a theoretical plate with infinite increase in the retention time (H_∞):[6]

$$H_\infty = Lb/5.545 \qquad (11)$$

where L is the column length, and b is a constant from the equation relating the half-width of the peak and the retention time ($\tau_{0.5} = a + bt_R$). The set of values of H and H_∞ can characterise the efficiency of a chromatographic column for the separation of mixtures including weakly sorbed and strongly sorbed components, that is it can indicate the limiting possibilities provided by the stationary phase being studied.

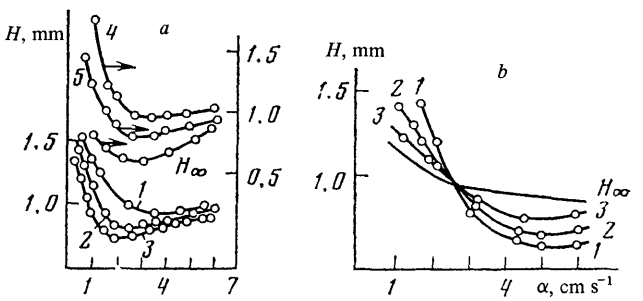


Figure 10. Relationship between the height equivalent to the theoretical plate and the linear velocity of the carrier gas at $\Pi = 15\%$ (*a*) and $\Pi = 3\%$ (*b*); PS–squalane ($c = 0.5$): *1*) hexane, *2*) heptane, *3*) nonane, *4*) benzene, *5*) toluene[20,21].

The regular features of the dependence of the efficiency of columns with colloidal stationary phases on the carrier-gas velocity, on the composition of the binary phase, and on the percentage impregnation of the carrier have been studied for a gel of polystyrene in squalane[20,21] (Fig.10). The nature of the change in the efficiency on going from one sorbent to another depends on the mechanism responsible for the broadening. The efficiency of columns with organic colloids in which the polymer is present in the liquid state is identical to that of columns with the pure modifier[20,21].

The efficiency of colloidal stationary phases based on highly dispersed adsorbents has been studied[26]. As noted above (see Fig.1), the sorptive capacities of the sorbents studied may differ considerably from one another, so that to estimate and compare their efficiencies it is appropriate to use the quantity $N = 5.545(t'_R/\tau_{0.5})^2$—the number of effective theoretical plates ($t'_R = t_R - t_0$ is the reduced retention time, and t_0 is the retention time of the non-sorbed gas). According to the data in Table 5, the efficiency of the stationary phase remains practically unchanged when a highly dispersed adsorbent is introduced into it, although in principle, a slight increase as a result of the decrease in the thickness of the liquid film should be expected[26]. Account must be taken, however, of the fact that the change to filled systems which have a higher viscosity than the pure modifiers leads to a decrease in efficiency. Thus in the final analysis, the values of N for a number of compounds are approximately the same on the individual liquid phase and on the liquid phase containing added adsorbents.

Table 5. Values of N for organic compounds on colloidal stationary phases[26].

Sorbate	PEG-400	PEG-400–Aerosil ($c = 0.2$)	PEG-400–carbon black ($c = 0.2$)
Nonane	680	670	660
Benzene	750	750	750
Methyl ethyl ketone	980	980	970
Ethanol	880	870	880
Nitromethane	690	700	690

The study of the dependence of the height equivalent to a theoretical plate on the carrier-gas velocity showed that, beginning from $V_a = 30$ cm^3 min^{-1}, the efficiency of a column with a colloidal sorbent depends little on the carrier-gas consumption for both organic and organometallic compounds[26]. Thus by using these sorbents it is possible to work in a fairly wide range of carrier-gas velocities without significant deterioration in the quality of the separation.

V. THERMAL STABILITY OF COLLOIDAL SORBENTS

One of the fundamental properties of a sorbent is its thermal stability. The limiting working temperature of sorbents can be determined in three ways: by recording the loss of liquid phase when the column is heated in a stream of carrier gas[40], by thermal analysis[41,42], and from the change in the background ion current with increase in the column temperature[43].

The most objective estimate of the thermal properties of chromatographic packing is given by thermal analysis, since in addition to the determination of the start of the mass loss from the form of the differential thermal curves, it is possible to deduce the nature of the processes responsible for the volatilisation of the stationary phase. The published thermal analysis curves[21] show that for colloidal polymeric phases, the temperatures of the start of mass losses and the start of the thermal effect generally coincide. This indicates that the changes in the mass of the colloidal stationary phases take place without significant thermal effects, and can be attributed to volatilisation.

Comparison of the upper temperature limits for colloidal stationary phases (Table 6) and the stationary phases usually employed in gas chromatography shows[19] that the thermal stability of the colloidal systems is equal to that of the individual modifiers and stationary liquids with similar polarity.

From the experimental data, it was concluded[27,43] that the stabilisation of stationary phases by Aerosil makes it possible to increase the maximum working temperature of the columns by 40–50 K, and makes it possible to increase the sensitivity of the chromatographic analysis using a flame ionisation detector by factors of 5–10, to increase the period of service of the columns, and to increase the accuracy of the treatment of the chromatograms by decreasing the distortion of the zero line.

Table 6. Maximum working temperatures of colloidal phases, determined by extrapolation (medium—nitrogen, c' is the concentration of the vapour of the stationary phase in the carrier gas, g ml^{-1}).[21]

Stationary phase	$c'=10^{-6}$	$c'=10^{-7}$	$c'=10^{-8}$
PS–squalane (c = 0.9)	230	210	192
PS–PEG-400 (c = 0.8)	205	130	70
PS + 0.01% PEG-400	240	225	210

Although the addition of a polymer has no significant influence on the thermal characteristics of stationary phases, the addition of solid highly dispersed materials leads to an appreciable decrease in volatility. In the opinion of some authors[27,43], the effect is due to the binding of molecules of the liquid in the field of the adsorption forces of the active filler. For a high degree of dispersion and a sufficient quantity of highly dispersed material, all of the liquid phase is bound by adsorption, leading to a decrease in its volatility.

Table 7. Values of K, $\bar{\Delta}$, and λ for colloidal and ordinary phases with similar polarity[20].

Mixture analysed	Stationary phase	t°, C	P	K	$\bar{\Delta}$	λ
1. Products of the catalytic dehydrogenation of butenes (acetone, acetic acid, acrylic acid, maleic anhydride)	25% PS in squalane (c = 0.4)	150	25	4.48	0.225	5.4
	25% Octoil-S	150	23	1.20	0.166	2.21
2. Products of the catalytic synthesis of isoprene (hexane, hexenes, hydropyrans, unsaturated alcohols, dimethyldioxan)	30% PS in dinonyl phthalate (c = 0.5)	100	26	1.00	0.182	3.64
	25% DNP	100	24	0.80	0.091	2.46
	15% PMPS-4	100	24	2.00	0.040	2;32
3. Aromatic hydrocarbons (benzene, toluene, cresyl acetates, naphthalene, ethylbenzene)	25% PS in squalane (c = 0.08)	150	10	2.10	0.059	3.10
	25% Apiezon L	150	9	3.48	0.040	2.32
4. C_2–C_{11} n-alcohols	25% PS in PEG-400 (c = 0.67)	180	58	1.10	0.085	0.91
	25 PEG-20000	180	64	1.43	0.032	0.71
5. C_1–C_6 aliphatic acids	25% PS in DNP (c = 0.2)	150	25	2.15	0.462	3.30
	DS-550 silicone oil	150	23	0.605	0.132	0.61
6. C_{10}–C_{24} n-alkanes	15% PS	250	62	1.00	0.704	2.08
	15% PEG-2000	250	64	1.10	1.157	1.60

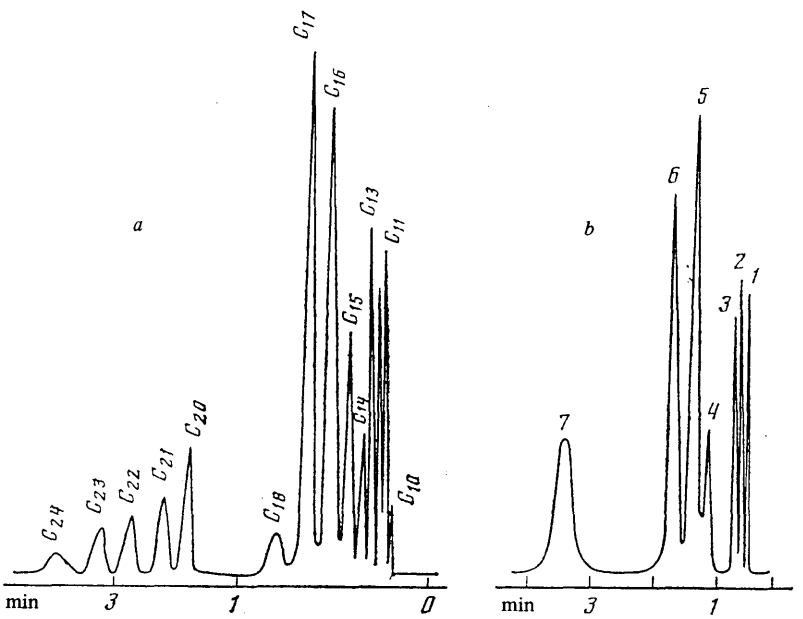


Figure 11. Chromatograms of mixtures of C_{10}–C_{24} n-alkanes (after the recording of the C_{18} peak, the diagram chart speed was decreased by a factor of 3) (*a*) and aromatic hydrocarbons and their derivatives (*b*): *1*) benzene, *2*) toluene, *3*) ethylbenzene, *4*) m-cresyl acetate, *5*) o-cresyl acetate, *6*) naphthalene, *7*) biphenyl[21].

A comparison of the thermographic curves obtained on a thermal analysis apparatus for PMS-100–Aerosil systems (c = 0.5) and for pure PMS-100, and also a study of the dependence of the mass losses by these sorbents on the time of passage of the carrier gas at 250 °C, showed that stationary phases stabilised by Aerosil have a higher thermal stability than the pure liquids[26].

VI. PRACTICAL APPLICATIONS OF CHROMATOGRAPHY IN A GAS–COLLOID SYSTEM

The universal character of colloidal stationary phases makes it possible to use them for the analysis of various organic and organometallic materials. As examples illustrating the possibilities provided by these sorbents, the conditions for the separation of various mixtures of direct practical interest are described below. In all cases, the colloidal stationary phases containing the highly dispersed adsorbents were deposited on silanised Chromaton. The solid carrier for the polymeric colloidal systems (except where otherwise indicated) was silanised Celite-545. In those cases where there is no reference to the source, the examples of the use of the sorbents developed were taken from Refs.21 and 26.

1. Analysis of Organic Compounds

Hydrocarbons. The low sorptive capacity of polymers makes it possible to use them to determine high-boiling substances at temperatures appreciably below the boiling points of the components being studied. Thus a mixture of C_{10}–C_{24} n-alkanes has been analysed on a column with polystyrene as stationary phase (Fig.11*a*) at 250 °C [b.p.(C_{24}) = 421 °C].[20] The response coefficient (Table 7) was greater by factors of ~6 and ~4 respectively than those on columns with Apiezon-L and polyphenylmethylsiloxane, usually employed in the analysis of n-alkanes. The time required for the analysis of the mixture of C_{10}–C_{24} n-alkanes was 5 min on the colloidal phase, and 30 min on Apiezon-L, for identical experimental conditions. A mixture of aromatic hydrocarbons and their derivatives was separated using a solution of polystyrene in squalane (c = 0.8) at 150 °C (Fig.11*b*).

Alcohols. The possibilities provided by the use of gas–liquid and gas–adsorption chromatography for the separation of high-boiling polar substances are limited by the low thermal stability of the polar liquid phases and the insufficient uniformity of the surface of most adsorbents, which leads to asymmetry of the peaks. The separation of C_2–C_{10} alcohols (boiling point of n-decanol 213 °C) on a column with the stationary phase PS–PEG-400 (c = 0.67) at 130 °C (Fig.12*a*) is therefore of interest.

Aliphatic acids. The analysis of free aliphatic acids (without conversion to the esters) on the usual stationary phases and diatomite carriers is extremely difficult, because of strong adsorption phenomena and the marked asymmetry of the peaks. Colloidal polymeric phases have been used for the direct separation of synthetic mixtures of C_1–C_6 aliphatic acids[20]. Fig.12*b* shows that the peaks of the acids are fairly symmetrical, and the analysis time is short (4 min). The conditions of the chromatographic separation were as follows: a 120 × 0.3 cm column was filled with a colloidal solution (15%) of polystyrene in dinonyl phthalate (c = 0.2) on silanised Chromosorb-W; 160 °C; nitrogen velocity 30 ml min^{-1}; specimen volume 0.025 μlitre.

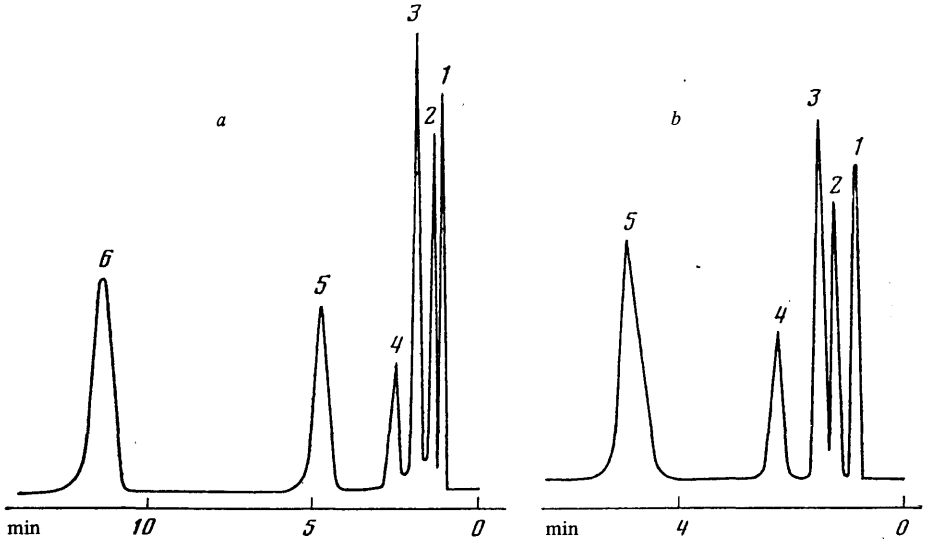


Figure 12. Chromatograms of mixtures of C_2–C_{10} n-alcohols (*a*): *1*) ethanol, *2*) propanol, *3*) butanol, *4*) pentanol, *5*) heptanol, *6*) decanol; and C_1–C_6 aliphatic acids (*b*): *1*) acetic, *2*) n-propionic, *3*) isobutyric, *4*) isovaleric, *5*) n-hexanoic.[21]

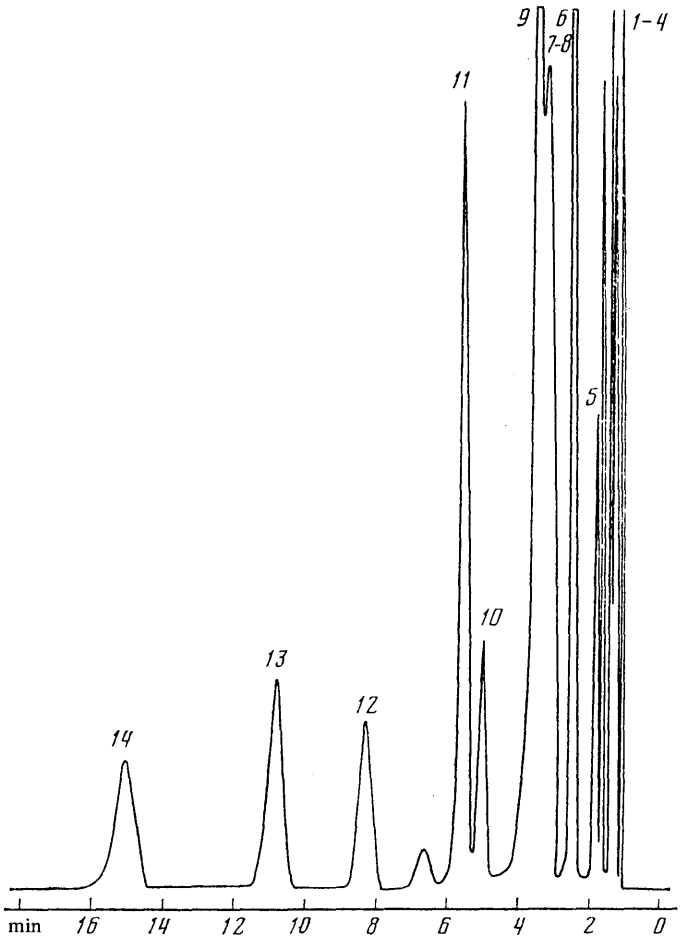


Figure 13. Chromatogram of petrol from the oxidative cracking of petroleum, boiling up to 100 °C: *1*) pentane, *2*) hexane, *3*) hexane, *4*) heptane, *5*) heptene, *6*) acetone, *7*) butyraldehyde, *8*) methyl ethyl ketone, *9*) benzene, *10*) ethanol, *11*) toluene, *12*) n-propanol, *13*) isobutyl alcohol, *14*) n-butanol[26].

Petrol from the oxidative cracking of petroleum. This petrol (fraction up to 100 °C), in addition to alkanes and aromatic hydrocarbons, contains oxygen compounds. It is difficult to separate this multicomponent mixture on an individual stationary phase. The largest number of peaks with a sufficiently regular distribution on the chromatogram was obtained using the colloidal system PEG-400–Aerosil (c = 0.5), deposited on a solid carrier in quantities of 20%. The chromatogram (Fig. 13) shows that this sorbent makes it possible to separate the hydrocarbons from one another and from oxygen-containing compounds under isothermal conditions (column temperature 80 °C) on a column of length 2 m at a carrier-gas velocity of 40 ml min^{-1}. The colloidal sorbent had the following Rohrschneider characteristics: x = 2.37, y = 5.72, z = 3.51, and u = 6.12.

Products of the catalytic synthesis of acrylonitrile. The analysis of the highly dilute aqueous solutions is possible on a two-metre column using the stationary phase PS–PEG-400 (c = 0.67) at 100 °C and a carrier-gas velocity of 40 ml min^{-1} (Fig. 14*a*).[20]

Mixture of moist air with hydrogen sulphide and ammonia. Symmetrical peaks for these substances (Fig. 14*b*) are obtained using a colloidal solution of PS in PEG-400 (c = 0.3), deposited (in quantities of 30%) on Chromosorb-W (column length 2 m). The analysis is carried out initially at 50 °C, and after the ammonia peak has passed, the temperature of the thermostat is raised to 100 °C to achieve rapid elution of water.

Solution of t-butyl hydroperoxide and its decomposition products in chlorobenzene. Colloidal systems containing PM-15 carbon black have been used to analyse peroxides with a low thermal and catalytic stability[25]. t-Butyl hydroperoxide and its decomposition products have been separated[44] on a 120 × 0.4 cm column at 50 °C and a carrier-gas velocity of 70 ml min^{-1}, using dinonyl phthalate (30%) on Celite-545 as sorbent. By using a packing consisting of 20% of the system PEG-400–carbon black (c = 0.95) on the carrier, without changing the other parameters of the experiment, it was possible to decrease the time required for the analysis of the solution to 5 min (Fig. 15*a*).

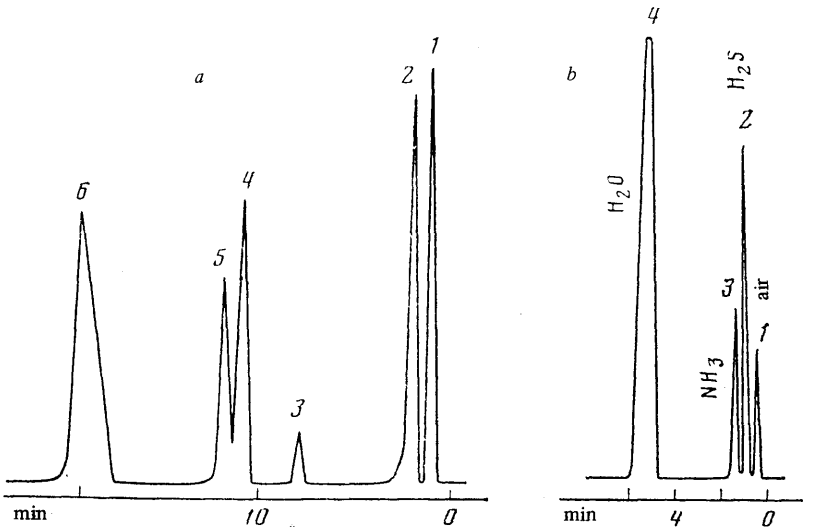


Figure 14. Chromatograms of mixtures of the products of the catalytic synthesis of acrylonitrile (AN) (*a*): *1*) air, *2*) ammonia, *3*) acrolein, *4*) AN, *5*) acetonitrile, *6*) water; and of moist air containing hydrogen sulphide and ammonia (*b*).[20,21]

Products of the catalytic dehydrogenation of butenes. The gas-chromatographic analysis of these products in the presence of large quantities of water has been carried out on a column of length 1.2 m containing a 25% colloidal solution of polystyrene in PEG-400 (c = 0.4) at 150 °C. On this sorbent, all the components were clearly separated, with completely symmetrical peaks (Fig.15*b*).

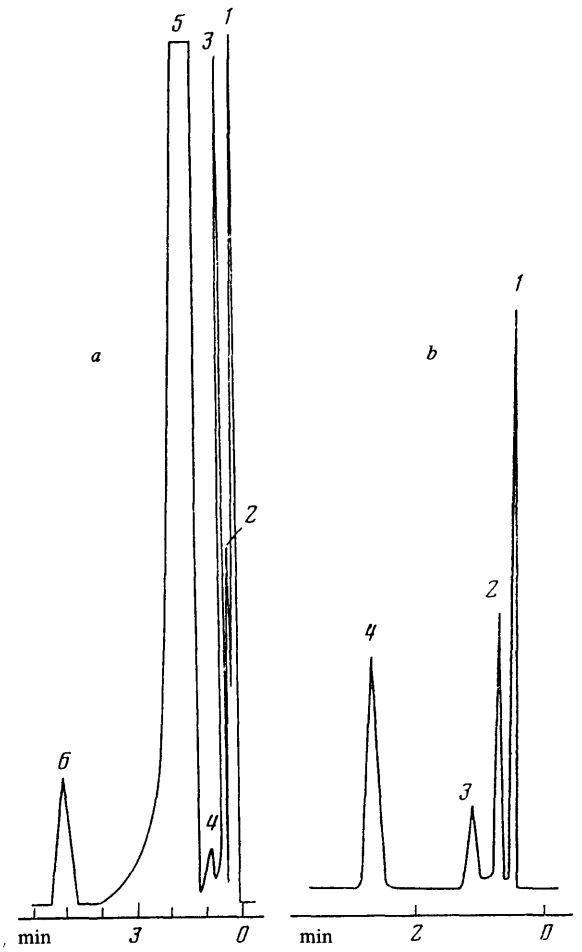


Figure 15. Chromatograms of mixtures of the products of the catalytic dehydrogenation of butenes (*a*): *1*) acetone, *2*) acetic acid, *3*) acrylic acid, *4*) maleic anhydride; and of a solution of t-butyl hydroperoxide and its decomposition products in chlorobenzene (*b*): *1*) acetone, *2*) methanol, *3*) t-butyl alcohol, *4*) di-t-butyl peroxide, *5*) chlorobenzene, *6*) t-butyl hydroperoxide[21,24].

Trace analysis. Conditions have been found for the gas-chromatographic determination of traces of biphenyl in diphenylamine, and of β-chloronaphthalene in naphthalene at 170 °C on the sorbent PEG-40000–Aerosil (c = 0.6).[26] The study of these solid solutions is of interest for the theory and practice of the production of semiconducting elements. Micro-analytical and spectral methods for the analysis of these systems are tedious and have a low sensitivity. The use of gas chromatography with colloidal sorbents has made it possible to lower the level of the quantitative determination of the impurity to 10^{-4}–10^{-5}% in the first case, and to 10^{-1} to 10^{-2}% in the second. The results of the determination of impurities in 1-ethyltricycloheptane-3-one[26] have been used to estimate the purity of the material for the precise study of its thermodynamic properties.

The results of the analysis of various synthetic mixtures and catalysates on ordinary and colloidal phases with similar polarity are given in Table 7. The following characteristics were used in the comparison of their selectivity: the degree of separation of the least effectively separated pair (K), the uniformity criterion ($\bar{\Delta}$), and the response coefficient (λ) [6]

$$\bar{\Delta} = n_c \tau K/t \qquad (12)$$

where n_c is the number of peaks, τ the width of the least broadened peak, and t the analysis time.

The response coefficient λ was calculated from the equation

$$\lambda = n_c K^2/t \ . \qquad (13)$$

Table 7 shows that the values of λ for the colloidal polymeric phases are higher than those for the ordinary phases. In the analysis of n-alcohols, PEG-20M gives a slightly better separation (K = 1.43) than the colloidal phase PS–PEG-400 (K = 1.10). If the decisive factor is the analysis time, however, it is necessary to compare the values of λ, and in this case the second phase is preferred.

Colloidal solutions of polymers have another significant advantage over the usual stationary phases: increase in temperature leads to a simultaneous increase in their selectivity and efficiency for the mixtures of substances examined, and this makes it possible to decrease the analysis time considerably without deterioration in the quality of the separation. Thus for example, the pair of substances most difficult to separate on the individual phase PEG-400 are not separated at all when the column temperature is increased from 100 °C to 120 °C, whereas under these conditions, the selectivity of columns with a colloidal stationary phase is increased by a factor of 1.1–1.4, leading to complete separation of the components being analysed[21].

2. Analysis of Organometallic Compounds

Most substances containing a metal–carbon bond are reactive and unstable to heat, and this makes it difficult to develop gas-chromatographic methods for determining organometallic compounds (OMC) and impurities in them. Thus in addition to the necessary resolving power, the chromatographic packing should have a low capacity, to ensure that the analysis can be carried out at low temperatures, and should be chemically inert with respect to the substances being analysed. These requirements are not satisfied by all liquid phases and adsorbents. Silicone stationary phases are fairly inert and hydrophobic, which is particularly important in work with readily hydrolysed compounds, and these phases have found extensive application in the gas-chromatographic analysis of OMC. Thus in a fairly complete review[45], more than 60% of all the examples of the analysis of OMC involved the use of stationary phases of the SE-30 and E-301 type. In the Soviet Union, the analogue of these SP with similar chromatographic polarity is the polymethylsiloxane liquid PMS-100.

The regular features of the chromatographic retention of alkanes and aromatic hydrocarbons by colloidal stationary phases based on PMS-100 and Aerosil have been studied[46]. It was shown that the addition of highly dispersed silica to the silicone stationary phase leads to a decrease in the specific retention volumes of heptane, benzene, biphenyl, and their derivatives. At the same time, the retention indices of aromatic compounds increase, and the selectivity of the

sorbent as a whole increases. Thus on going from the pure silicone to the sorbent with $c = 0.8$, the logarithmic retention index increases by 200 units for benzene, by 225 units for bibenzyl, and by 275 units for stilbene. Thus the possibility of achieving a smooth decrease in the sorptive capacity with an increase in the selectivity of chemically inert silicone SP by the dispersal of highly dispersed fillers in them facilitates the solution of the problem of separating and analysing OMC.

It is possible in principle to analyse a mixture of bis(arene) π-complexes of chromium (trade name Barkhos liquid) on silanised Chromaton with 6% of the colloidal system PMS-100–Aerosil ($c = 0.2$).[47] A clear-cut separation of organochromium compounds with boiling points of 315–340 °C was achieved on a 100 × 0.4 cm column at 185 °C (Fig.16). In earlier studies[48,49], Barkhos liquid was analysed at 200 °C and above. Even a slight decrease in temperature in the analysis of unstable compounds in order to decrease their decomposition in the column is theoretically and practically justified[50]. A decrease in the temperature of the experiment generally leads to an increase in the selectivity of separation. This makes it possible, by decreasing the length of the column, to reduce the analysis time, and this also leads to a decrease in the decomposition of the unstable specimen[51].

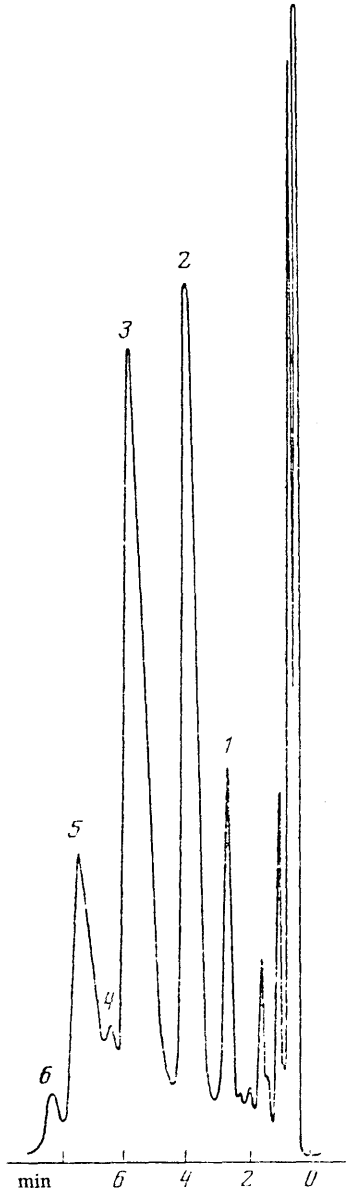


Figure 16. Chromatogram of a mixture of bis-arene π-complexes of chromium: *1*) benzene(ethylbenzene)chromium, *2*) bis(ethylbenzene)chromium, *3*) (ethylbenzene)(diethylbenzene)chromium, *4*) not identified, *5*) bis(diethylbenzene)chromium, *6*) not identified; SP—6% of the system PMS-100–Aerosil ($c = 0.2$); 100 × 0.4 cm column, 185 °C, carrier-gas velocity (hydrogen) 70 ml min^{-1}.[26]

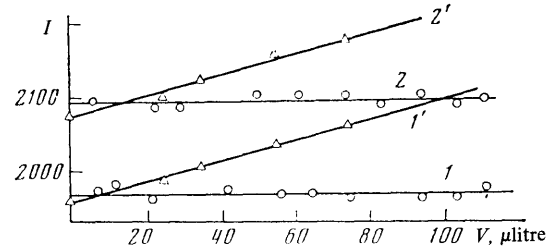


Figure 17. Dependence of the retention index on the quantity of organochromium liquid Barkhos added to the column: *1*, *2*) SP—6% of the system PMS-100–Aerosil ($c = 6$), 150 °C; *1'*, *2'*) SP—6% PMS-100, 200 °C; *1*, *1'*) bis(ethylbenzene)chromium, *2*, *2'*) (ethylbenzene)(diethylbenzene)chromium[53].

A subsequent study[52] of the dependence of the retention of the principal components of Barkhos liquid [bis(ethylbenzene)chromium and (ethylbenzene)(diethylbenzene)chromium] on the composition of the binary PMS-100–Aerosil system showed that the replacement of the silicone by the highly dispersed adsorbent, as in the case of hydrocarbons, leads to a decrease in the time required for the analysis of the organometallic compounds studied, and to an increase in the selectivity of their separation. On the basis of the observed regular features, it was suggested that the chromatographic analysis of Barkhos liquid be carried out on a column containing 6% of the colloidal system PMS-100–Aerosil ($c = 0.6$) at 150 °C, which lowered the temperature of the analysis by 35 K.[53] The usual method of lowering the temperature of the analysis by reducing saturation of the solid carrier with pure silicone does not work in this case because of the low selectivity of the lightly loaded column[53,54].

The advantage of carrying out the analysis at lower temperatures (by using a colloidal sorbent) is confirmed by the dependence of the retention indices of the OMC analysed on the number of specimens introduced into the chromatograph and expressed as the total quantity of Barkhos liquid passed through the column (volume of one specimen, 2 μlitre) (Fig.17). Fig.17 shows that on prolonged operation with a sorbent of 6% PMS-100 on Chromaton at 200 °C, there is a monotonic increase in the retention index, indicating the formation in the course of the analysis of a new stationary phase consisting of PMS-100 and the decomposition products of Barkhos liquid. This is also indicated by the almost complete change in the colour of the packing along the entire length of the column after the introduction of a total of 70 μlitre of the organochromium liquid. When 6% of the colloidal system PMS-100–Aerosil ($c = 0.6$) on the same carrier was used at 150 °C, however, the retention index and the colour of the sorbent along the entire length of the column remained practically unchanged during repeated analyses.

Colloidal SP based on Aerosil and PMS-100 have also been used to separate the organometallic compounds of the group VI elements[26,53,55]. The relative retention volumes and logarithmic retention indices have been determined[26] for arenetricarbonyl complexes of chromium (Table 8) and the hexacarbonyls of chromium, molybdenum, and tungsten at 50 °C on PMS-100–Aerosil (c = 0.4):

Compound	Chromium hexacarbonyl	Molybdenum hexacarbonyl	Tungsten hexacarbonyl
V^{rel}	1.00	2.03	4.14
I	746	826	903

Table 8. Chromatographic characteristics of the retention of chromium arenetricarbonyls (column temperature 170 °C).[53]

Compound	V^{rel}		I	
	SE-30 [56]	PMS-1000-aerosil (c = 0.4)	SE-30 [56]	PMS-100-aerosil (c = 0.4)
Benzenetricarbonylchromium	1.00	1.00	1595	1621
Toluenetricarbonylchromium	1.21	1.68	1604	1744
Mesitylenetricarbonylchromium	1.67	2.09	1722	1794
Anisoletricarbonylchromium	2.03	2.60	1805	1853
(Ethyl benzoate)tricarbonyl-chromium	2.58	3.24	1876	1906

The relative retention volumes and retention indices of all the arenetricarbonyls are greater on the column with the colloidal sorbent than on the column with SE-30. Thus in addition to dispersion interaction, the retention of the sorbates involves specific forces determined by the interaction of the carbonyl groups of the compounds studied with the Aerosil surface. The calculated retention indices can be used to identify metal carbonyls.

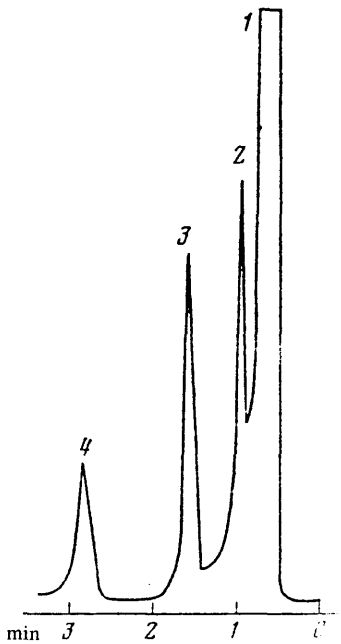


Figure 18. Chromatogram of the separation of group VI metal hexacarbonyls: *1*) chloroform, *2*) chromium hexacarbonyl, *3*) molybdenum hexacarbonyl, *4*) tungsten hexacarbonyl, SP—6% of the system PMS-100–Aerosil (c = 0.4), 200 × 0.3 cm column, 50 °C, carrier-gas velocity (hydrogen) 50 ml min^{-1}.[53]

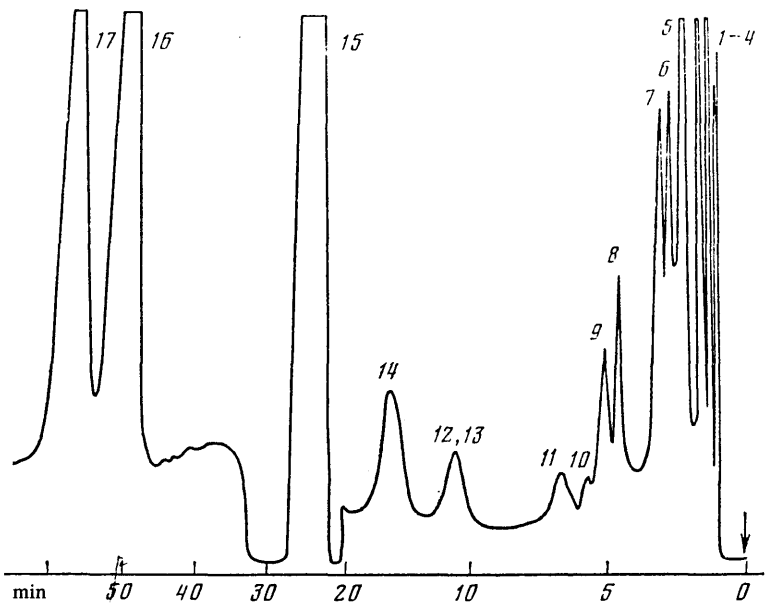


Figure 19. Chromatogram of impurities in tetraethyllead: *1*) ethane, *2*) butane, *3*) hexane, *4*) ethyl chloride, *5*) methylheptane, *6*) octane, *7*) octene, *8*) nonane, *9*) nonyne, *10*) nonadiene, *11*) benzene, *12*) ethanol, *13*) toluene, *14*) s-butyl alcohol, *15*) tetraethyllead, *16*) isobutyltriethyllead, *17*) n-butyltriethyllead, SP—20% of the system PEG-400–Aerosil (c = 0.3), 200 × 0.3 cm column, 70 °C, carrier-gas velocity (nitrogen) 20 ml min^{-1}, specimen volume 0.5 μlitre, instrument scale 10^{-11} A, recorder chart speed 600 mm h^{-1} for peaks *1–14*, 240 mm h^{-1} for peaks *15–17*.[58]

The use of the colloidal sorbent made it possible to separate the hexacarbonyls of chromium, molybdenum, and tungsten at 50 °C in 3 min (Fig.18).[53] In other studies[57], a similar mixture was separated at 90 °C in 7 min.

A stationary phase consisting of the binary system PEG-400–Aerosil (c = 0.3) has been proposed for the gas-chromatographic determination of impurities in tetraethyl-lead at the 10^{-4}–10^{-5} vol.% level[26,58,59]. It is possible to detect ~20 impurities of different chemical character (Fig.19). In the analysis, 90% of the principal component was directed past the flame ionisation detector, ensuring its stable operation.

These examples show that the gas-chromatographic analysis of organic and organometallic compounds can be carried out successfully using colloidal SP based on standard highly dispersed adsorbents or polymers. The possibility of controlling the sorptive properties, the high separating power, the symmetry of the peaks due to polar substances, the low retention times of high-boiling reactive compounds of low stability, the possibility of analysing impurities and micro-impurities, and their ready availability indicate the promising possibilities provided by the use of these colloidal sorbents in gas-chromatographic practice.

3. Colloidal Systems in Capillary Chromatography

Capillary chromatograms are being used increasingly in scientific-research and factory laboratories. They have a higher specific permeability than packed columns, and this makes it possible to carry out separations on long columns with a low pressure drop. Long column lengths combined with a high efficiency of separation ensure high separating power. Capillary chromatography is therefore being used to solve the most complex problems of separation in analytical chemistry[60–62]. Capillary columns, however, have a lower selectivity than packed columns. This can be seen from Eqn.(14), relating the selectivity of a column K_S [not to be confused with the selectivity of the stationary phase $k_S = (\Gamma_2 - \Gamma_1)(\Gamma_2 + \Gamma_1)$] with respect to two components being separated to the Henry coefficients Γ_1 and Γ_2 and the ratio of the volumes occupied by the gas and liquid phases in the column ($\varkappa$ and $\varkappa_1$ respectively):

$$K_s = 2\,\frac{(\Gamma_2\varkappa_1 + \varkappa) - (\Gamma_1\varkappa_1 + \varkappa)}{(\Gamma_2\varkappa_1 + \varkappa) + (\Gamma_1\varkappa_1 + \varkappa)} = 2\,\frac{\Gamma_2 - \Gamma_1}{\Gamma_2 + \Gamma_1 + 2\varkappa/\varkappa_1}\ . \qquad (14)$$

Packed columns usually have values of $\varkappa/\varkappa_1$ in the range 5–35, and capillary columns values in the range 50–15000. The latter are therefore less selective, and to achieve the same separation, the number of theoretical plates in them must be 10–100 times that for packed columns[60]. The change to adsorption–absorption sorbents obviously makes it possible to decrease $\varkappa/\varkappa_1$ and to bring the selectivity of capillary columns close to that of packed columns.

Since metallic capillary columns are gradually being displaced by glass columns, the interest in these sorbents is increasing to an even greater extent, since the effective use of glass columns is largely determined by their internal surface, which should ensure effective wetting of the glass capillary by the liquid phase. Special treatment makes it possible to increase both the wettability of the glass and its absorptive power. Various methods for producing intermediate coatings in capillary columns have been described[2,60–62]; analysis of these results shows that good operating characteristics can be obtained using columns with a layer of highly dispersed material, deposited on the wall of the capillary at the same time as the liquid phase. To avoid blocking of the capillary tubes when the suspension is introduced and to produce a uniform coating, the particle size of the solid filler cannot exceed 10^{-6} cm, that is it should be at the colloidal level.

Colloidal components as intermediate layers have been used and studied by Blumer[63,64] and Horning and co-workers[65–68]. Blumer[63,64] established that Aerosil treated with trimethylsilane (trade name Silanox-101) shows hydrophobic properties and forms stable suspensions in many solvents. Its dispersions in organic binding agents at a low concentration of the solid phase form thixotropic gels and adhere firmly to the surface of metal, glass, and polymers, making it possible to obtain a thin mechanically strong film of the stationary phase. Intermediate porous layers have been obtained by preparing a mixture of 0.2–0.5 g of the liquid phase (Apiezon-L, PEG-20M, FFAP, Emulphor, SE-30) in 10 ml of a solvent (methylene chloride, chloroform, or their mixtures with methanol) and 0.4–0.65 g of Silanox. Before the column was filled, the suspension was dispersed for 30 s in an ultrasonic bath. To predict qualitatively the efficiency of a column with this coating, a clean polished metal plate was wet with the prepared suspension. A smooth mechanically strong coating ensures good column operating conditions, whereas a dense granular surface with cracks and fractures after drying leads to a decrease in efficiency or to blocking of the capillary. To obtain thick porous layers, the suspension was introduced at a comparatively high rate (80 cm s^{-1}).[64] These columns have been used to separate mixtures of C_{16} to C_{18} methyl esters, normal alcohols, and homologues of benzene. For a specimen volume of 0.05 μlitre and HETT (height equivalent to a theoretical plate) = 1–1.3 mm, the separation time was several minutes.

Horning and co-workers[65,66], using intermediate layers with Silanox, obtained heat-resistant high-resolution glass columns suitable for the analysis of biological mixtures (steroids, acids, essential oils, and medicinal metabolites). Columns of length 60 m at 100–300 °C have given an efficiency of up to 100000 theoretical plates. A highly dispersed filler (6–10 μm), uniformly distributed in a surface film, prevented the formation of micro-droplets and breakdown of the stationary phase when the column was heated and cooled. The suspension was prepared by adding 2 g of Silanox to a solution of 0.5 g of SE-30 in 10 ml of CCl_4. To increase the sensitivity of the Silanox suspension, it was recommended that a solvent with a high density be used, or that a surface-active agent, for example benzyltriphenylphosphonium chloride, be added to the solution. The rate of passage of the suspension through the column was 5 cm s^{-1}. After drying for 3 h in a stream of nitrogen, the capillary column was covered with a basic layer of the stationary phase SE-30.

Glass capillary columns with heat-resistant polar phases have been described[67,68]. In the first stage, 20 m non-silanised borosilicate capillaries were wet with 1 ml of a suspension (0.1 g of the polar phase, 1 g of Silanox, and 100 ml of Silanox) (sic. Ed.of Translation), previously treated in an ultrasonic bath. The polar phase was then deposited on to the thin layer of suspension. A suspension of Silanox in a solution of the polymer of phenyl ether and phenyl sulphone (PZ-176) has been used to obtain a coating which makes it possible for a capillary column to operate at temperatures above 300 °C, and to separate the methyl esters of polyunsaturated aliphatic acids[75].

Longer columns (150 m) containing Silanox have been filled[69] by depositing intermediate coatings from a solution of 40 mg of the surface-active agent Igepol SO-880 in 10 ml of CCl_4 with the addition of 200 mg of Silanox. To increase the stability, the colloidal solution was placed for several minutes in a high-frequency furnace. The proposed method gives glass capillary columns with efficiencies of 437000–165000 theoretical plates. Their preparation is time-consuming, however (1 week).

A method for depositing colloidal intermediate layers to obtain polar capillary columns has been developed[70]. The stabilising additive was finely divided silica treated with benzyltriphenylphosphonium chloride (Cabosil), with particle size 15 nm and specific surface 190 $m^2 g^{-1}$. The suspension (0.3 g OV-225, 0.3 g silica, and 50 ml CCl_4) was treated in an ultrasonic bath and then passed through the column at a rate of 4–5 cm s^{-1}. An additional layer of OV-225 was deposited dynamically from a 10% solution in toluene. The thicknesses of the colloidal coating and the film of stationary phase, determined using the scanning electron microscope, were 0.3 μm and 0.4–1.2 μm respectively. The high stability of the film was attributed[70] to the porosity of the structure and the rheological properties of the intermediate layer. The proposed capillary columns have been used to separate mixtures of pesticides and steroid derivatives.

In the works cited, colloidal systems based on highly dispersed adsorbents were used as supports for the basic separating layer of stationary phase. The intermediate coating essentially increases the stability and capacity of the capillary column. The possible direct use of colloidal systems as stationary phases in capillary chromatography is also of interest, however.

Copper columns of length 25 m, containing as stationary phase a mixture of PEG-400 and Aerosil in the ratio 4 : 1, were recently described[28]. The suspensions were prepared in methanol solution. The separating characteristics of columns filled with pure PEG (column 1) and the colloidal stationary phase PEG-400–Aerosil (c = 0.2) (column 2) were compared. The quality of the columns was estimated from the number of theoretical plates N, the selectivity coefficient of the column K_S, and from the chromatograms of mixtures of organic compounds. Table 9 shows that, while giving almost the same efficiency, the columns containing the colloid are more selective in the separation of alcohols and hydrocarbons.

Table 9. Selectivity coefficients of the capillary columns 1 (N = 169000) and 2 (N = 162000).[28]

Substance	Column 1	Column 2
Methanol–ethanol	0.050	0.240
Ethanol–isopropyl alcohol	0.025	0.128
Ethanol–n-propanol	0.342	0.462
Decane–undecane	0.292	0.522
Benzene–decane	0.074	0.204

Thus the use of colloidal systems as intermediate stabilising layers and as stationary phases is extending considerably the possibilities provided by capillary chromatography, the most effective method of separating complex mixtures.

VII. FUTURE DEVELOPMENT OF CHROMATOGRAPHY IN A GAS–COLLOID SYSTEM

The analytical possibilities provided by chromatography in a gas–colloid system have not been exhausted. In the future, the extension of the range of application of colloidal sorbents already developed, and the production of new sorbents based on components which have not yet been studied chromatographically, can be expected. Some possible ranges of application and properties of colloidal stationary phases indicating their promising possibilities are described below.

The possibility of the extensive control of the selectivity, and the high thermal stability and availability of colloidal sorbents, can be used successfully to solve problems associated with the separation of multicomponent mixtures of substances belonging to different classes, in the analysis and trace concentrations, in analysis under programmed-temperature conditions, and in chromatographic–mass-spectrometric studies. The same properties, and the possibility of achieving a high capacity with a significant saving of stationary liquid phase, makes the use of colloidal sorbents promising in preparative chromatography. Colloidal stationary phases are used extensively in capillary chromatography, because of their high separating power and good operating characteristics. The possibility of lowering the temperature of the analysis by decreasing the capacity of the sorbent without a deterioration in the separating characteristics of the column, ensured by the use of colloidal systems, may be useful in the chromatographic analysis of compounds unstable to heat. The addition to the liquid phase of colloidal particles forming complexes with the compounds being analysed is promising in connection with the production of super-selective sorbents.

Among the important developments extending the possibilities provided by gas chromatography on colloidal sorbents is the use as fillers of higher dispersed adsorbents with chemically grafted organic groups, colloidal metals, and organometallic complexes, which make it possible to obtain heat-resistant sorbents with different selectivities. The development of analytical chromatography in a gas–colloid system will undoubtedly stimulate the use of gas chromatography as an effective method for studying colloidal systems. Reverse gas chromatography can be used to study sol–gel transitions, to determine the disjoining pressure and heats of displacement, to study adsorption at the boundary between a dispersed phase and the dispersion medium, etc. At the same time, the use of rheological methods and infrared and NMR spectroscopy will make possible a theoretically well-founded approach to the production and study of new colloidal sorbents for gas chromatography.

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