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Surface Layer Sorbents in Gas Chromatography

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The methods of preparation, chromatographic properties, and applications of surface layer sorbents have been examined. Chromatographic columns with surface layer sorbents are characterised by a low value of HEPT (0.4-0.5 mm) and a weak dependence of HETP on the flow rate of the carrier gas and the grain diameter of the solid carrier. Compared with the usual (bulk phase) sorbents, the use of sorbents of this new type makes it possible to shorten the duration of analysis by a factor of 3-15, to decrease the experimental temperature by 30-100 deg, and to extend the range of compounds susceptible to analysis.
The bibliography includes 35 references.

CONTENTS

I.	Introduction	456
II.	Methods of preparation of surface layer sorbents	456
III.	Characteristics of gas-chromatographic separation on surface layer sorbents	458
IV.	Analytical applications of surface layer sorbents	401
V.	Applications of surface layer sorbents in physicochemical studies	403

I. INTRODUCTION

The improvement of the separation of compounds with similar properties depends in many ways on the efficiency of the columns employed and therefore an increase in column efficiency is one of the important tasks of modern gas chromatography. One of the principal causes of the spreading of chromatographic zones, particularly at high carrier gas flow rates, is the resistance to mass transfer, the magnitude of which is known to depend on the grain diameter of the sorbent employed.

The sorbents used in gas chromatography usually consist either of a solid carrier covered more or less uniformly throughout the entire bulk by a liquid phase (the absorbent) or a porous adsorbent, the adsorption properties of which are also approximately the same throughout the bulk of the grain. During recent years sorbents in which the active substance (the sorbent) are not uniformly distributed throughout the bulk of the grain but only on its "outer" surface have come to be used in gas chromatography; the active substance is not present in the bulk of the grain and consequently the compounds chromatographed are not sorbed there. The sorption processes in such sorbents occur only in a surface layer of small depth equal to the depth of the layer of the active sorbent. The resistance to mass transfer for a sorbent of this type is reduced compared with the usual bulk phase sorbents, since the length of the diffusion path into the depth of the grain is reduced. Consequently, the duration of diffusion τ, which is now determined no longer by the grain diameter of the sorbent d but by the thickness of the active layer d_r, is also shortened. We shall estimate the shortening of the diffusion time assuming that $d = 0.3$ mm and $d_r = 0.05$ mm. In this case

$$\frac{\tau_{bulk}}{\tau_{surf}} \simeq \frac{d^2}{d_r^2} \simeq \frac{0.3^2}{0.05^2} \simeq 30.$$

Thus the use of surface layer sorbents should lead to an improvement of the efficiency of the chromatographic column.

In general sorbents with a surface-active layer may be called surface sorbents, in contrast to the usual bulk phase sorbents.

We believe it is desirable to classify surface sorbents on the basis of the characteristics of the active porous layer in accordance with the scheme in Fig. 1. The surface layer sorbents discussed here are divided into two types based on the type of the solid carrier employed, which can be either uniformly porous or can have a solid impermeable nucleus (for example, porous diatomaceous carriers or glass beads). Depending on the type of carrier, the methods of preparation and certain properties of sorbents of types I and II will differ.

Surface layer sorbents of type I (with an active porous layer on the surface of a solid nucleus) were first proposed by Halasz and Horvath[1] in 1962. Sorbents of type II were first obtained by Cremer in 1959, who introduced carbon black into the pores of Sterchamol to measure its specific surface[2] by the gas-chromatographic method. Granulated surface-porous sodium-borosilicate glasses were obtained by Zhdanov et al.[3] and etched ordinary glass beads were prepared by Ohline and Yoyola[4].

The possibility of using powdered adsorbents introduced into the pores of silica gels for gas-chromatographic analysis was first stated by Vasil'eva et al.[5] Surface layer sorbents of type II were first employed in gas-chromatographic analysis by Bombaugh[6] for the separation of air on molecular sieves deposited on Chromosorb and subsequently the method was employed by Keiser[7] to separate petrol fractions on graphitised carbon black deposited on Chromosorb.

A surface layer sorbent of type II was first obtained for gas-liquid chromatography by the authors of the review[8]. The use of surface layer sorbents gives rise to new possibilities in gas-chromatographic analysis and in the application of gas chromatography to the measurement of various physicochemical characteristics. This review deals with the methods of preparation of surface layer sorbents, the characteristics of the gas-chromatographic separation on them and their principal applications.

II. METHODS OF PREPARATION OF SURFACE LAYER SORBENTS

Surface layer sorbents can be used to achieve one of the familiar types of chromatography (gas–solid, gas–liquid, gas–liquid–solid, etc.)

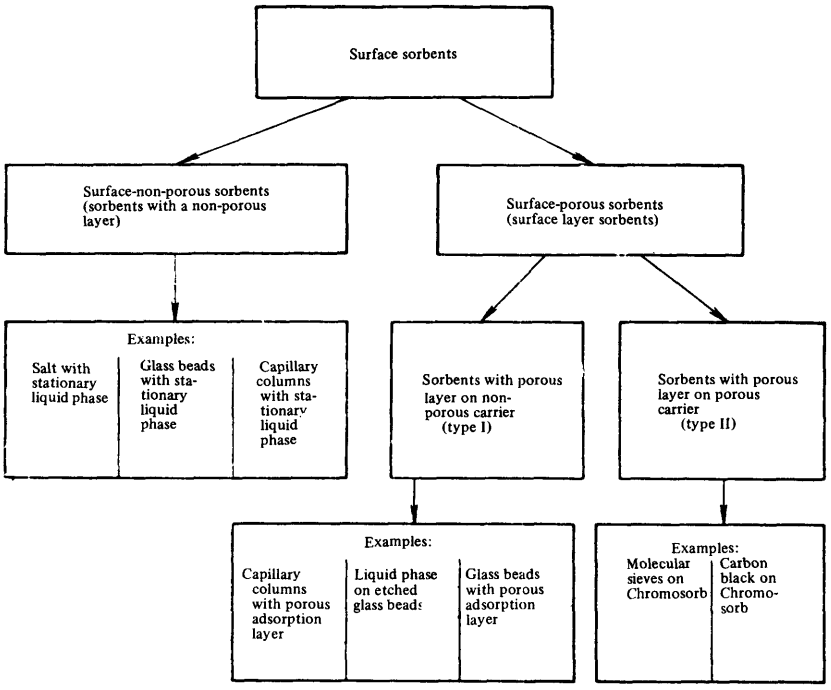


Figure 1. Scheme for the classification of surface sorbents in gas chromatography.

Halasz and Horvath[9] prepared sorbents of type I by precipitating a wide variety of adsorption materials from solutions on to the surface of non-porous glass or metallic beads, metallic spirals, and other carriers. The active sorbents employed were powdered alumina, aerosil, carbon black, or metal oxides with a stationary liquid phase [for example iron(III) oxide with polyesters]. It was found[9] that the particle size in the formation of a porous layer of metal oxides should be less than 0.1 μm. In order to obtain a more stable porous sorption layer, the glass beads were sometimes coated by a thin layer of varnish[9].

In gas–liquid chromatography a porous layer is obtained on beads using either glass microbeads (diameter 1 μm) or diatomaceous earth (diameter up to 10 μm), which are deposited together with the stationary liquid phase in a solvent. In this case the porous layer is retained on the beads by the surface tension forces of the liquid phase[10,11].

Another method for the preparation of sorbents of type I was described by Pope[12], who obtained an active porous layer on the surface of polyethylene beads on heating them to 160–170°C with graphitised carbon black. The polyethylene softens and the carbon black coats its surface.

Surface layer sorbents of type II are prepared using finely dispersed sorbents with a particle size up to 10 μm and solid coarsely porous carriers with a low specific surface: Chromosorb W, Chromosorb G, Celite-545. On mechanical shaking with solid carriers, finely dispersed adsorbents (molecular sieves, carbon black, activated charcoal, aerosil, etc.) enter into the macropores of the carriers and are retained there by adhesion forces, which determine the stability of the surface layer of the sorbent. Surface layer sorbents have been obtained in this way after prolonged mechanical shaking[6,7].

In order to determine the time required to obtain a surface layer sorbent, the variation of the amount of finely dispersed adsorbent deposited on the solid carrier with the duration of mechanical shaking was investigated[13]. This investigation was carried out on graphitised carbon black (particle size less than 1 μm) and Chromosorb W in proportions of 1 : 5. The amount of deposited carbon black was determined by elemental analysis for its carbon content. The deposition of the finely dispersed adsorbent (carbon black) in the pores of Chromosorb W terminates after 10–15 min (Fig. 2). Thus the duration of the preparation of the surface layer sorbent is as a rule short.

In the preparation of a surface layer sorbent of type II for gas-liquid chromatography, a stationary liquid phase is deposited in the usual way from a volatile solvent on a finely dispersed solid carrier with a particle size up to 10 μm, which may be obtained by sedimentation. Then the resulting finely dispersed sorbent is introduced into the macropores of an inert solid carrier by the mechanical shaking of the mixture for 10 mins.[14]

Chromosorb W or G modified by dichlorodimethylsilane or hexamethyldisilazane may be used as the inert solid carrier. Although these carriers are inert in relation to hydrocarbons and other non-polar compounds, it is recommended that for polar compounds the silylated Chromosorbs be additionally modified by a small amount (0.1%) of a polar liquid phase. Microscopic study of the distribution of the finely dispersed sorbent in the grains of a solid carrier showed that the small sorbed particles enter into the macropores of the solid carriers more or less uniformly over the entire "outer" surface, forming a surface layer to a depth of 20–50 μm with about 20% of the sorbent[13]. Another microscopic study[7] also showed that the active sorbent forms a surface layer, but its depth was

found to be 1–3 μm, the content of the active sorbent on the carrier being 5%. On surface layer sorbents of type I, the thickness of the surface layer varies between 1 and 100 μm.[9]

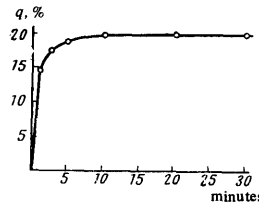


Figure 2. Variation of the amount of graphitised carbon black q deposited on Chromosorb W with time during mechanical shaking.

Thus a number of entirely satisfactory simple methods for the preparation of surface layer sorbents have now been developed.

III. CHARACTERISTICS OF GAS-CHROMATOGRAPHIC SEPARATION ON SURFACE LAYER SORBENTS

1. Retention Characteristics

In gas chromatography the retention values are some of the most important characteristics of the substance chromatographed. The retention on surface layer sorbents is in general due to the retention on the active sorbent and on the solid carrier. Therefore the reduced retention volume V_n for compounds chromatographed on surface layer sorbents can be represented by the following equation for gas-adsorption chromatography:

$$V_N = K_a S_a + K_c S_c \qquad (1)$$

or, for gas-liquid chromatography:

$$V_N = K_l V_l + K_c S_c \ , \qquad (2)$$

where K_a is the gas–active solid adsorbent partition coefficient, S_a the surface area of the absorbent in the column, K_c the gas–solid carrier partition coefficient, S_c the surface area of the solid carrier in the column, K_l the gas–stationary liquid phase partition coefficient, and V_l the amount of liquid phase in the column.

The above equations show that adsorption on a solid carrier can make a definite contribution to the retention volume (if necessary this contribution can be calculated from the equations). Therefore, in the preparation of surface layer sorbent it is desirable to employ inert solid carriers for which $K_c S_c \ll K_a S_a$ ($K_l V_l$).

Comparison of the relative retention times on sorbents of type I and bulk phase sorbents[9,15] revealed a small difference between the retention times.

With only a small contribution by adsorption on the solid carrier, the relative retention volumes of non-polar and weakly polar components on surface layer sorbents of type II correspond to the relative retention volumes on bulk phase sorbents (Table 1). This is the basis of the application of all the relations known for the identification of compounds chromatographed on bulk phase sorbents and the available tabulated relative retention values also to surface layer sorbents.

However, for polar compounds or for sorption-active carriers, such identification must involve an estimation of the contribution to the retention volume of the degree of adsorption of the substances chromatographed on the solid carrier.

Table 1. Relative retention volumes of hydrocarbons on bulk phase and surface layer sorbents of type II.

Substance analysed	Sorbent: squalane on Chromosorb W				Substance analysed	Sorbent: CaA molecular sieve	
	5% squalane		10% squalane				
	bulk phase	surface layer*	bulk phase	surface layer*		bulk phase	surface layer (CaA on Celite)
Benzene	0.18	0.19	0.18	0.18	Oxygen	0.31	0.32
Toluene	0.54	0.60	0.53	0.53	Nitrogen	1.00	1.00
n-Octane	1.00	1.00	1.00	1.00	Methane	1.81	1.75
n-Nonane	3.00	2.94	3.00	3.00	Carbon monoxide	5.30	5.60

*Surface layer sorbent: finely dispersed Chromosorb W with 5% (or 10%) of squalane deposited on Chromosorb W with a grain size of 0.4–0.25 mm.

2. Efficiency of Chromatographic Columns

The efficiency of chromatographic columns is characterised by the height equivalent to the theoretical plate (HETP), which is also determined by the type of sorbent used. Application of surface layer sorbents makes it possible to reduce HEPT, i.e. to increase the efficiency of the column compared with those containing bulk phase sorbents.

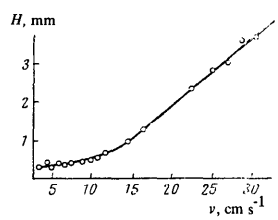


Figure 3. Variation of HETP (H) with carrier gas flow rate (v) for 3-chloropentane on a surface layer sorbent of type I. Experimental conditions: 100 × 0.2 cm column; temperature 90°C; carrier gas–nitrogen; flame ionisation detector.

In all studies dealing with surface layer sorbents of type I, a high efficiency of the columns filled with them was demonstrated. Thus Halasz and coworkers found that the minimum value of HETP on a column with glass beads and a porous adsorption layer is 0.4–0.5 mm.[16] In another study[15] the variation of HETP with the flow rate of the carrier gas for 3-chloropentane on a sorbent of this type is presented (Fig. 3). The data quoted show that HETP increases slightly as the flow rate rises to 15 cm s^{-1}, the minimum HETP being 0.38 mm. The efficiency of a column with polyethylene beads and graphitised carbon black was very high (HETP = 0.5–0.6 mm).[12]

Columns filled with glass beads on the surface of which diatomaceous earth with a stationary liquid phase had been

deposited are characterised by a minimum HETP = 0.8–1 mm.[10,11] It has been shown[4] that a column with etched glass beads (depth of pores 0.4 mm) has an efficiency higher than that of a column with unetched glass beads (Fig. 4).

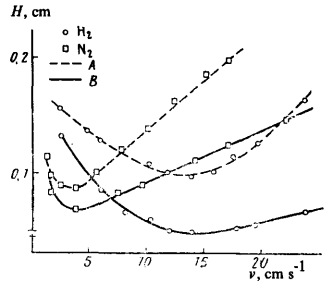


Figure 4. Variation of HETP (H) with carrier gas flow rate for n-nonane[5]: A) column with non-porous (unetched) glass beads; B) column with etched glass beads.

The efficiency of a column with a surface layer sorbent of type I has been compared with one containing a bulk phase sorbent only for porous glasses[3,17,18], and it was shown that the number of theoretical plates for the column with a surface-porous glass is higher by a factor of 2.6–7.5 compared with the column in which the glass is porous throughout the bulk phase, the duration of analysis of hydrocarbon gases being reduced by a factor of 8.

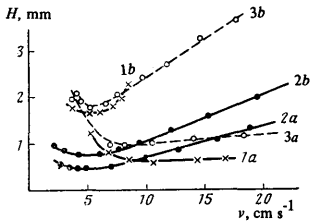


Figure 5. Variation of HETP (H) with carrier gas flow rate (v): 1) n-octane on graphitised carbon black; 2) toluene on Chromosorb W with 10% of squalane; 3) methane on CaA molecular sieves; a) surface layer sorbent; b) bulk phase sorbents.

The dependence of HETP on the mean linear flow rate of the carrier gas was investigated for columns with surface layer sorbents of type II and for the corresponding columns with bulk phase sorbents[14,19–21]. Typical relations between HETP and the carrier gas flow rate for gases on CaA molecular sieves deposited on Celite, for hydrocarbons on carbon black deposited on Chromosorb W, and for hydrocarbons on finely dispersed Chromosorb W on which squalane had been deposited are presented in Fig. 5.

The minimum HETP in these experiments on a column 4 mm in diameter was 0.45–0.50 mm (using a flame-ionisation detector) and 0.8–1.00 (using a katharometer).

A study of the dependence of HETP on flow rate established that, for columns with surface layer sorbents, (1) HETP is lower by a factor of 1.2–1.8 at the optimum carrier gas flow rate and by a factor of 1.7–3 in the range of higher flow rates compared with bulk phase sorbents, (2) the optimum carrier gas flow rate is high, particularly when surface layer sorbents are employed in gas-adsorption chromatography, and (3) the dependence of the efficiency on the rate is less pronounced than when bulk phase sorbents are employed.

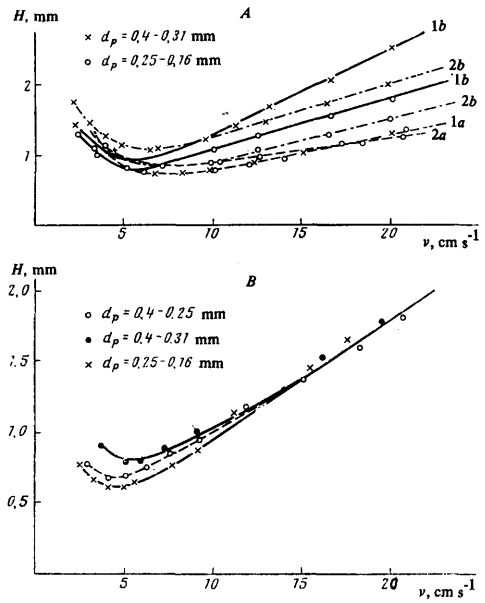


Figure 6. Variation of HETP (H) with carrier gas flow rate for n-octane (curves *1*) and toluene (curves *2*) on sorbents with different grain diameters. A): a) surface layer sorbent; b) bulk phase sorbent; detector–katharometer; carrier gas–helium; B) surface layer sorbent; n-octane; carrier gas–nitrogen; flame ionisation detector ("Khrom-2").

The effects of the grain diameter of the solid carrier on the chromatographic column efficiency has been investigated[14,19]. When surface layer sorbents of type II are used, a slight change in efficiency as a function of the carrier gas flow rate is observed for sorbents with different grain diameters only at low flow rates, while at high flow rates, where the spreading is determined by the mass-exchange kinetics, the difference in efficiency becomes smoothed out. The efficiency of columns with bulk phase sorbents measured under the same conditions decreases with the grain diameter (Fig. 6). The reason for this is that not the entire grain but only the surface layer, whose thickness is determined by the depth of the solid carrier pores and does not therefore change with the grain diameter, is involved in the mass-exchange process.

Consequently, with surface layer sorbents of type II, one can use fairly large solid carrier grains, which has

little effect on column efficiency but reduces the resistance to the carrier gas flow and makes it possible to operate at higher flow rates and with longer columns for low pressure differences.

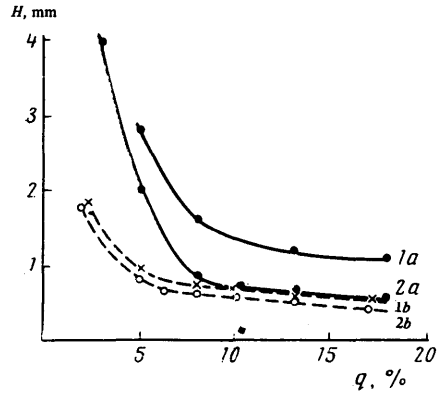


Figure 7. Variation of HETP (H) for toluene (curves *1*) and n-octane (curves *2*) on surface layer sorbents with the content of the active sorbent (g): *a*) column with graphitised carbon black on Chromosorb W; *b*) Chromosorb W with finely dispersed Chromosorb W on which 10% of squalane had been deposited.

The study of the effect on column efficiency of the amount of the active sorbent deposited on the solid carrier showed that, with increase of its content up to 8–10%, the efficiency increases rapidly and then changes only slightly (Fig. 7).

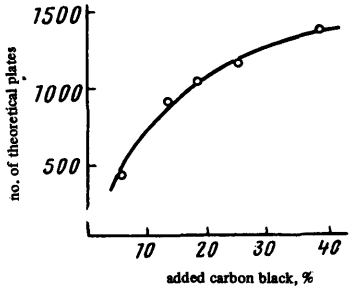


Figure 8. Variation of a number of theoretical plates for n-hexane with the content of carbon black on polyethylene beads[17].

An analogous effect of the amount of active sorbent on the efficiency of the column with a surface layer sorbent of type I was demonstrated in a study[12] where the variation of the number of theoretical plates with the amount of carbon black deposited on polyethylene beads was investigated (Fig. 8). The relation shows that, for low carbon black contents, the number of theoretical plates increases rapidly and then significantly more slowly, starting with about 20% of the black. Thus the dependence of HETP on the amount of active sorbent for surface layer sorbents is of the same type as the dependence of the coefficient of resistance to mass transfer (in the HETP equation for the usual sorbents) on the extraction coefficient[22].

In a study of the efficiency of columns with surface layer sorbents, it is interesting to estimate the contributions of various processes to the spreading of chromatographic zones. For this purpose, it is useful to employ the Giddings equation[23], which agrees well with the experimental data:

$$H = \frac{1}{1/A + 1/c_m v} + \frac{B}{v} + cv \cdot \qquad (3)$$

Here the first term describes the coupled eddy diffusion, the second the molecular longitudinal diffusion, and the third the mass exchange kinetics.

The coefficients of the Giddings equation, determined from the experimental $H = H(v)$ relations by a graphical method[24] for surface layer sorbents of type II and the corresponding bulk phase sorbents in gas-adsorption and gas liquid chromatography, are presented in Table 2, which shows that, when surface layer and bulk phase sorbents are employed, systematic relations between the coefficients of the HETP equation are observed mainly for the coefficient of resistance to mass transfer C, which is lower for surface layer sorbents by a factor of 3–4 in gas-adsorption chromatography and by a factor of 1.8 in gas-liquid chromatography.

Table 2. The coefficients in the Giddings equation for bulk phase and surface layer sorbents of type II.

Sorbent	Compound chromatographed	Expt. conditions: column length, m	Expt. conditions: temp., °C	A, cm	B_2, cm s^{-1}	C_m, s	C, s
Molecular sieve, bulk phase sorbent	methane	1	20	0.080	0.37	0.0120	0.0160
Molecular sieve on Celite, surface layer sorbent	methane	1	20	0.060	0.60	0.0020	0.0038
Aerosilogel, bulk phase sorbent	n-decane	1	120	0.070	0.78	0.0010	0.0173
Aerosilogel on Chromosorb, surface layer sorbent	n-decane	1	120	0.060	0.55	0.0020	0.0053
Carbon on Chromosorb, surface layer sorbent	n-hexane	1	80	0.014	0.12	0.0006	0.0050
Chromosorb W with 5% of squalane, bulk phase sorbent	n-octane	0,8	60	0.020	0,15	0.0020	0.0110
Chromosorb W with 5% of squalane, surface layer sorbent	n-octane	0,8	30	0.024	0.10	0.0030	0.0061

Table 2 lists the overall coefficients C in the Giddings equation reflecting the resistance to mass transfer, which includes the resistance to mass transfer in the gas (mobile) and stationary phases. In the determination of the separate contributions to mass exchange, the Perrett–Purnell method, based on the measurement of the coefficient C for two carrier gases of different types[25], was employed. The separate determination of these contributions has been made for methane on the CaA molecular sieve and for n-octane on Chromosorb W with 10% of squalane. The results are presented in Table 3, which shows that the resistance to mass transfer in the gas phase is lower by a factor of 10 for methane on the molecular sieves and by a factor of 1.7 for n-octane in gas-liquid chromatography. The explanation is that the mass exchange in the gas phase for surface layer sorbents

of type II does not depend on the grain diameter but on the thickness of the layer of the active sorbent which amounts to 20–50 μm according to microscopic measurements, i.e. is much smaller than the grain diameter. Consequently the diffusion path traversed by molecules into the bulk of the grain is shortened, since the active sorbent is located in the surface layer in the immediate vicinity of the gas stream, which accelerates the mass exchange and permits analysis at higher rates, i.e. the duration of analysis is reduced.

Table 3. Coefficients of resistance to mass transfer in gas at stationary (liquid) phases.

Type of Chromatography	Sorbent	Compound chromatographed	Resistance to mass transfer	
			gas phase	stationary phase
Gas-adsorption	CaA on Celite (surface layer sorbent)	methane	0.0002	0.0036
	CaA, bulk phase sorbent	methane	0.0020	0.0140
Gas-liquid	Chromosorb W with 10% of squalane, surface layer sorbent	n-octane	0.0013	0.0022
	Chromosorb W with 10% of squalane, bulk phase sorbent	n-octane	0.0022	0.0029

The increase of the mass transfer coefficient explains the lower minimum HETP, the less pronounced dependence of HETP on the rate, and hence the considerable decrease of HETP at high carrier gas flow rates for surface layer sorbents; hence, these sorbents are useful for rapid analysis.

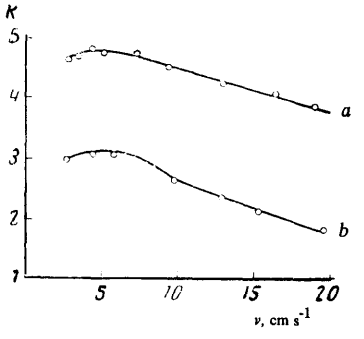


Figure 9. Variation of the separation factor K_1 (toluene–octane) with carrier gas flow rate (v) for surface layer (a) and bulk phase (b) sorbents.

3. The Separation Factor

The real improvement of separation is determined not only by the number of theoretical plates but also by the separation factor, which is one of the principal characteristics determining the usefulness of various sorbents in gas chromatography. The separation factor K_1 is defined by the following equation[26]:

$$K_1 = \frac{\sqrt{2}}{4} K_s \sqrt{N} \quad , \qquad (4)$$

where K_S is the selectivity coefficient and N the number of theoretical plates.

In studies on surface layer sorbents of type I, the separation factor was not as a rule considered as a characteristic of columns with the sorbent. Only in experiments with surface-porous glasses was it shown that the separation factor for hydrocarbon gases is higher by a factor of 1.3 compared with glasses porous throughout their bulk[3].

An experimental comparison of the separation factors for the toluene–octane pair on surface layer sorbents of type II and bulk phase sorbents has been made[14] under the conditions of a constant duration of analysis. Fig. 9 presents the relations between the separation factor and the rate under these conditions. In all cases the separation factor was higher for the surface layer sorbent by a factor of 1.2–1.5 compared with the bulk phase sorbent.

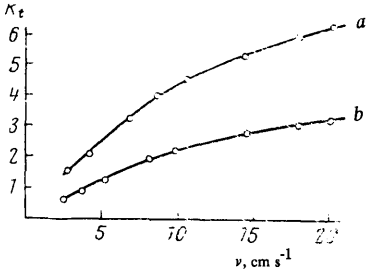


Figure 10. Variation of K_t with the carrier gas flow rate on CaA molecular sieves: a) surface layer sorbent; b) bulk phase sorbent.

Under other comparison conditions (for example, for the same volumes of the sorbent), the time characteristic of the separation factor (K_t) can be usefully employed for the estimation of the separating capacity of surface layer and bulk phase sorbents:

$$K_t = K_1 / t_R \quad , \qquad (5)$$

where K_1 is the separation factor and t_R are the mean elution times of the components for two adjacent peaks.

The separating capacity of columns with molecular sieves in the surface layer and bulk phase versions was estimated by the present authors in terms of the relation between K_t for the nitrogen–methane pair and the flow rate (Fig. 10). Fig. 10 shows that the use of the CaA molecular sieve on Celite as a surface layer sorbent shortens the duration of separation of the gases by a factor of 3 for the same separation factor compared with the bulk phase sorbent. The reduction of the duration of analysis is undoubtedly a valuable advantage of surface layer sorbents.

Thus surface layer sorbents are usually characterised by a higher separation factor and a shorter duration of analysis compared with bulk phase sorbents; they can be used at lower temperatures, which extends the range of compounds susceptible to analysis.

IV. ANALYTICAL APPLICATIONS OF SURFACE LAYER SORBENTS

Surface layer sorbents can be used in the separation of various specific systems in all known versions of gas chromatography. As already mentioned above, the

Table 4. Examples of the applications of surface layer sorbents for the separation of mixtures.

Mixture analysed	Sorbent characteristic	Duration of analysis, min	Conditions of analysis				Refs.
			column length, cm	temp., °C	carrier gas flow rate	detector*	
I. Gas mixtures							
H_2; O_2; N_2; CH_4; CO	CaA molecular sieves on Celite-545 (20 wt.%)	0.2	100×0.4	20	50 cm s^{-1}	K	19, 20
CH_4; C_2H_6; C_2H_4	Surface-porous glass	3	100×0.4	40	7 cm s^{-1}		3
C_3H_8; C_3H_6	Glass porous throughout bulk	24	100×0.4	40	7 cm s^{-1}		3
C_1–C_4 hydrocarbon gases	NaX molecular sieves on Celite-545 (20 wt.%)	18	100×0.3	30—160		FID	19, 20
II. Hydrocarbons							
C_{15}–C_{35} n-alkanes	90% glass beads, 9% iron(III) oxide, 0.9% Carbowax 4000 (monostearate), 0.1% potassium hydroxide	11	200×0.2	190	progr. pressure	FID	27
C_9–C_{16} n-alkanes	Aerosil on Chromosorb G (5 wt.%)	6.5	80×0.4	150	50 ml min^{-1}	FID	21
	Aerosil, bulk phase sorbent	52	80×0.4	150	50 ml min^{-1}	FID	21
C_9–C_{26} n-alkanes	Aerosil on Chromosorb G (5 wt.%)	15	100×0.3	120—300		FID	21
C_6–C_{13} n-alkanes	Graphitised carbon black on Chromosorb R (5 wt.%)	5.5	400×0.2	30—350		FID	7
Aromatic hydrocarbons: trimethylbenzenes, tetrahydronaphthalene, methylnaphthalenes	90% of glass beads, 9% of iron(III) oxide, 0.9% Carbowax 4000, 0.1% of potassium hydroxide		200×0.2	190		FID	15
Terphenyls	Graphitised carbon black on Chromosorb W (20 wt.%)	4	20×0.4	290	10 cm s^{-1}	FID	13
	Granulated graphitised carbon black (bulk phase sorbent)	5.5	20×0.2	360	30 ml min^{-1}	FID	28
cis- and *trans*-Decalins	Graphitised carbon black on Chromosorb W (20 wt.%)	2	100×0.3	120	10 cm s^{-1}	FID	13
	Granulated graphitised carbon black (bulk phase sorbent)	6	200×0.3	210	50 ml min^{-1}	FID	29, 30
α-, and β-isopropylnaphthalenes	Graphitised carbon black on Chromosorb W (20 wt.%)	6	100×0.3	240	12 cm s^{-1}	FID	13
Propyltoluene and xylenes	Finely dispersed Chromosorb impregnated with 15% of a mixture of DS-550 silicone oil and Bentone-245 (60:40) on Chromosorb (16 wt.%)	10	200×0.3	45	60 ml min^{-1}	FID	14
C_9–C_{12} cyclic hydrocarbons	Ditto	11	200×0.3	80—100		FID	14
III. Oxygen-containing and other compounds							
Terpenes	90% of glass beads, 9% of iron(III) oxide, 0.9% of Carbowax 4000, 0.1% of potassium hydroxide	0.5		180	16 cm s^{-1}	FID	15
ethyl esters of aliphatic acids	Finely dispersed Spherochrome-1** with 7% PEGA*** on Chromosorb G	6.5	200×0.4	175	120 ml min^{-1}	K	14
	Spherochrome-1** with 12% PEGA*** (bulk phase sorbent)	34	200×0.4	200	120	K	31
Methyl esters of C_8–C_{19} aliphatic acids	93% of glass beads, 6.3% of iron(III) oxide, 0.7% of versamide	3	200×0.2	245	progr. pressure	FID	27
C_1–C_8 n-alcohols	Graphitised carbon black on porous Teflon	8	100×0.3	60—200		FID	32
Cyclohexylchlorobenzenes	Graphitised carbon black on Chromosorb W (20 wt.%)	5	100×0.3	210	14 cm s^{-1}	FID	
Butylphenols, phenol, 2,6-dibutylphenol, *o*-butylphenol, *p*-butylphenol, 2,4-dibutylphenol	Finely dispersed Chromosorb W with 2% of neopentylglycol succinate deposited on Chromosorb G	5.5	100×0.3	100—150	12 cm s^{-1}	FID	13

Table 4 Cont'd.

Mixture analysed	Sorbent characteristics	Duration of analysis, min	Conditions of analysis				Refs.
			column length, cm	temp., °C	carrier gas flow rate	detector*	
Cresols (*ortho-*, *meta-*, *para-*)	Finely dispersed Chromosorb W with 6% of a mixture of pentaphenyl ether**** and bentone-245 (1 : 1) deposited on Chromosorb (15 wt.%)	8	200×0.3	110	7	FID	13
Nitrotoluenes (*ortho-*, *meta-*, *para-*)	Finely dispersed Sferochrome-1 with 7% PEGA on Chromosorb G (15 wt.%)	7	200×0.4	140	6	K	13

*K = katharometer; FID = flame-ionisation detector (Translator).

**Possibly a Russian name—Sferokhrom-1 (Ed. of Translation).

***Probably poly(ethylene glycol adipate) (Ed. of Translation).

****Probably pentyl phenyl ether (Ed. of Translation).

employment of surface layer sorbents has many advantages in the separation of mixtures compared with the usual sorbents. In addition they are characterised by fairly high mechanical strength. This permits the use of programmed temperatures and pressures. Table 4 presents examples of the practical applications of surface layer sorbents for the separation of various classes of compounds. In some cases the compounds were analysed for comparison on bulk phase sorbents.

V. APPLICATIONS OF SURFACE LAYER SORBENTS IN PHYSICOCHEMICAL STUDIES

Surface layer sorbents of type II can be used not only for analytical purposes but also for the measurement of physicochemical characteristics by gas chromatography.

As already stated, a surface layer sorbent of type II was first employed by Cremer[2] to determine the specific surface of carbon black introduced into the pores of Sterchamol, i.e. the first application of the surface layer sorbent in gas chromatography was its employment for physicochemical studies. Indeed, in the investigation of highly dispersed adsorbents by the chromatographic method, when they are used directly to fill the chromatographic column, it is necessary to employ very high pressures in order to achieve the required flow rate of the carrier gas. Therefore, as a rule granules and not the initial powder are employed as packing. The granules are obtained by pressing the powders or by using a binder, but the introduction of the latter into the sorbent composition in general alters its properties. Therefore we believe it simpler, more universal, and more convenient to investigate disperse adsorbents introduced into the pores of solid carriers rather than use specially prepared granules. It is noteworthy that, in the preparation of a column of the same length, a smaller amount of adsorbent is required, which is important in the study of new adsorbents.

Kiselev and coworkers employed a surface layer sorbent of type II to investigate the retention volumes and heats of adsorption of hydrocarbons on graphitised[33] and acetylene carbon blacks[34] and also to determine the specific surfaces of the blacks. A macroporous silica gel with a specific surface of 9 $m^2 g^{-1}$ was used as a solid carrier.

According to Eqn. (1), the interpretation of the chromatographic results is simplest and most accurate when the contribution of the solid carrier to the retention volume is low. Therefore one may recommend as solid carriers macroporous materials with a low specific surface (significantly lower than the specific surface of the disperse adsorbent) on which there is virtually no adsorption of the components investigated. The use of surface layer sorbents has many advantages even in those cases where the preparation of granulated material presents no difficulties. The two methods were compared in the determination of the heats of adsorption of straight-chain alkanes on a surface layer sorbent: NaX molecular sieve[35]. The heats of adsorption obtained with various types of sorbent are virtually identical. In this paper it is also noted that the use of a surface layer sorbent leads to the following possibilities compared with the bulk phase sorbents: (1) the amount of adsorbent may be reduced and very finely dispersed powder may be employed for measurement; (2) the experimental temperature may be lowered (on average by 100 deg); (3) the range of compounds investigated may be extended using higher-boiling substances; (4) measurements may be made under conditions closer to equilibrium owing to the acceleration of mass transfer. It is noteworthy that surface layer sorbents can also be used for the measurement of other characteristics, in particular in the study of kinetics under pulse conditions.

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In conclusion we may note that the advantages discovered in many fields of gas chromatography when surface layer sorbents are used and their successful applications permit their recommendation for large-scale employment in chromatographic practice.

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