

ОСНОВНІ ПУБЛІКАЦІЇ

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T. G. ANDRONIKASHVILI, L. G. EPRIKASHVILI,
N. V. PIRTSKHALAVA, M. A. DZAGANIA, M. G. ZAUTASHVILI

ABOUT SOME POSITIVE ASPECTS OF APPLICATION OF POLYMERS AS THE SURFACE LAYER SORBENTS IN GAS CHROMATOGRAPHY

Досліджено хроматографічні властивості полімерних матеріалів у варіанті поверхнево-шарових сорбентів. Доведено, що відсоток нанесення полімерного адсорбенту (активного агента) на твердий носій, а також його дисперсність мають значний вплив на характер хроматографічного процесу.

Модельні системи склалися із сумішей ароматичних вуглеводнів і одноатомних спиртів. Для покращення процесу хроматографічного розподілу підібрано оптимальні умови приготування поверхнево-шарових сорбентів.

Визначено переваги хроматографічних колонок, заповнених поверхнево-шаровими сорбентами порівняно з колонками, заповненими чистим активним агентом (полімером).

Исследованы хроматографические свойства полимерных материалов в варианте поверхностно-слоистых сорбентов. Показано, что процент нанесения полимерного адсорбента (активного агента) на твердый носитель, а также его дисперсность оказывают значительное влияние на характер хроматографического процесса.

Модельные системы состояли из смесей ароматических углеводородов и одноатомных спиртов. Для улучшения процесса хроматографического разделения подобраны оптимальные условия приготовления поверхностно-слоистых сорбентов.

Установлены преимущества хроматографических колонок, заполненных поверхностно-слоистыми сорбентами, по сравнению с колонками, заполненными чистым активным агентом (полимером).

Introduction

Surface layer sorbents developed and suggested first in 1959–62 [1, 2] were applied in gas chromatographic analysis by K. Bombaugh for separation of air [3]. The studies showed that application of surface layer sorbents containing

28 % finely ground zeolite 5A on the solid support "Chromosorb" increases the chromatographic columns efficiency six-fold and decreases to a great extent time of analysis compared with the columns with volumetric filling.

In the practice of gas chromatography of the last years the variant of column packing with surface-layer sorbents has been applied, that is, at this packing the active agent (adsorbent) is homogeneously distributed only on the external surface of solid support [4].

In our relatively earlier works [5, 6] on the example of synthetic zeolites used as the surface-layer sorbents, marked advantage of this method of column packing was shown compared with the columns, packed with the pure active agent (zeolite).

Polymer porous sorbents are mainly used for chromatographic separation of organic compounds (glycols, alcohols, amines, lower fatty acids etc [7, 8]). In the principle at the application of these adsorbents the volumetric packing of chromatographic columns are performed.

The results of the paper published by us earlier [9] proved that introduction of dust of polymer adsorbents into the pores of solid support exerts positive effect on the process of chromatographic separation. Although in that work the role of dispersity (particle size) of polymer material and its percentage composition in the column packing on the character of chromatographic separation was not considered.

The goal of the present study is:

- 1) to establish the necessary amount of active agent (polymer) and its dispersion to achieve more efficient process of separation;
- 2) to carry out comparative analysis for determining a number of parameters (retention time, asymmetry coefficient, separation criteria, time of analysis, chromatographic column efficiency) for columns packed according to the variants of surface-layer and volumetric (ordinary) filling.

Experimental

The porous polymers Chromosorb 103 (cross polystyrol) of Johns Manville Corp, USA and Polysorb-1 (copolymer of styrol and divinyl benzene) of former USSR were used in the present work.

The solid supports, characterized by highest retention capacity of the active agent in the macropores were used. These were: Chromosorb W (USA), Celite 545 (USA) and Chromaton NAW DMCS (Czech. Rep.) [6]. Porous polymers, prior to their packing on the solid support, were crushed in ball-mill to the powder state and definite fractions were selected. As shown in the previous work [6] the best separation was observed at the application of finest fractions (high grade of dispersion) of the active agent. In our experiments we used just two fractions of the following dispersity: 5–10 μm and 10–20 μm . Dispersion of particles of active agent was defined by means of microscope, equipped with special gauge scale.

Application of active agent (fine dispersion polymer) on the solid support was performed by mechanical shaking in the cylinder form vessel for definite time, later the surplus of polymer and solid carrier was separated from the main adsorbent. Particle size of solid support was 0,16–0,20 mm. Amount of the active sorbent over solid support was determined by the method of weighing. Surface-layer adsorbents obtained in such a way were dried to the constant weight, placed in chromatographic column and conditioned at 150 °C in the current of gas-carrier. Granulation of the sorbent-polymer was similar to that of the solid support.

The following parameters were calculated for comparative evaluation of the obtained experimental data:

t_r – Retention time of definite components, s;

K_a – Coefficient of peak asymmetry [6];

K_t – Time characteristics for the criteria of separation of binary mixture;

$K_t = K/t_r^m$, the specific characteristic – the ratio of the separation factor (K) to the mean retention time (t_r^m) for the neighboring peaks.

This formula is most convenient for estimation of separative power of surface-layer and volumetric sorbents at the similar length chromatographic columns [9, 10].

For the comparison of efficiency of the columns packed with surface-layer and volumetric sorbents, we used the formula N/t_r – efficient number of theoretical plates per of the retention time of peak of suitable components. This characteristic enabled us to compare the work of columns packed with different type sorbents [9, 10]. Number of theoretical plates was determined according to the formula:

$$N = 5,55 \frac{(l')^2}{\mu_{0,5}}$$

where l' – is a distance on chart paper (mm) corresponding to time of exit of maximum peak of the component;

$\mu_{0,5}$ – width of peak on the half of its height.

Chromatographic studies were performed in isothermal regime on the chromatograph LKhM 8MD, with a detector of thermal conductivity. Length of the column – 1 m, internal diameter – 3 mm; gas-carrier – He; consumption – 50–100 ml/min. Model systems:

1) mixture of aromatic hydrocarbons: benzene–toluene–ethylbenzene–cumene–pseudocumene;

2) mixture of monoatomic alcohols: methanol–ethanol–propanol–butanol–pentanol–hexanol–heptanol–octanol.

Results and Discussion

As is seen from the previous paper [6] among the solid supports studied by us Chromosorb-W, Celite 545 and Chromaton NAW-DMCS showed the highest retention capacity to the active agent. Therefore in the present paper we studied

the retention capacity of the polymer sorbents in relation to the above stated solid supports.

The data given in Table 1 show that quantity and extent of retained of the active agent (polymers) depends not only on the nature of a solid support, but on dispersity of the adsorbent, which enables it to penetrate into macro pores of the solid support. The data of the table show that Chromosorb-103 and Polysorb-1 with the particle sizes within the range 5–10 μm penetrate into the pores of solid support at 2 % more than the same sorbents of the fraction 10–20 μm . The greatest amount of active agent might be applied on the solid support Chromosorb-W, and therefore the present experiment was performed on this solid support. On the other hand, we showed that degree of dispersion of the active agent, zeolite taken as the example, affects the efficiency of chromatographic column [6]. Such experiment was carried out also with the polymer adsorbents. Polymer dust particles of different dispersity, in the same amounts were applied on solid support.

Table 1
Amount of polymer sorbent (in wt %) retained on the surface of solid support*

Solid support		Type of active agent	Granulation of active agent, μm	Polymer sorbent on the solid support after treatment for h, %				
Type	Specific surface area (BET), m^2/g			3	6	9	12	18
Chromosorb W (USA)	1,25	Chromosorb-103	5–10	11,20	20,14	24,30	32,10	32,40
		Chromosorb-103	10–20	9,80	18,25	23,50	30,80	31,10
		Polysorb-1	5–10	10,20	19,80	23,80	28,10	28,35
		Polysorb-1	10–20	8,45	17,90	22,30	27,20	27,50
Celite 545 (USA)	1,55	Chromosorb-103	5–10	10,80	18,25	23,10	30,20	31,00
		Chromosorb-103	10–20	8,90	17,10	22,20	28,10	28,30
		Polysorb-1	5–10	9,10	17,00	22,00	27,00	27,50
		Polysorb-1	10–20	8,25	16,10	21,65	26,10	26,80
Chromatons NAW-DMCS (Czech. Rep.)	1,00	Chromosorb-103	5–10	9,80	13,80	14,80	16,50	16,80
		Chromosorb-103	10–20	9,10	12,10	14,30	15,70	16,10
		Polysorb-1	5–10	8,50	12,80	13,15	15,50	16,00
		Polysorb-1	10–20	8,30	11,70	12,85	15,00	15,70

Note: The values correspond to the [(active agent) / support] • 100

Chromatography on such surface-layer sorbents of binary mixtures consisting of various organic compounds showed that decrease of dispersity of the active agent favors improvement of separation of the above stated mixtures (Table 2).

Table 2

Coefficients of separation of some binary mixtures (K/t_r^m) on Polysorb-1 and Chromosorb-103 of different dispersity, applied in the same amount on solid support, Chromosorb-W. Column temperature – 160 °C.

Binary mixture	Polysorb-1, content ~27 % on solid support, %		Binary mixture	Chromosorb-W, content ~30 % on solid support, %	
	Dispersity, μm			Dispersity, μm	
	10–20	5–10		10–20	5–10
Methanol–ethanol	1,32	1,43	Benzene–toluene	0,81	0,90
Ethanol–propanol	1,92	2,12	Toluene–ethyl- benzene	0,59	0,68
Propanol–butanol	1,75	1,81	Ethylbenzene– cumene	0,29	0,36
Butanol– pentanol	1,91	2,10	Cumene–pseudo- cumene	0,30	0,35

Table 3

Retention times (t_R , s) and coefficients of asymmetry* of some compounds on Chromosorb-103 at volumetric and surface-layer filling of columns, solid support – Chromosorb-W. Granulation of Chromosorb-103 – 5–10 μm ; chromatographic column temperature – 160 °C

Sorbate	Volumetric filling of the column	Surface-layer sorbent				
		Contents of active agent, %				
		11,20	20,14	24,30	32,10	32,40
Benzene	242 (1,53)	30 (1,00)	48 (1,00)	52 (1,00)	100 (1,03)	105 (1,04)
Toluene	453 (2,29)	32 (1,00)	30 (1,00)	70 (1,00)	158 (1,10)	160 (1,5)
Ethyl benzene	642 (2,81)	38 (1,00)	70 (1,00)	100 (1,00)	240 (1,12)	245 (1,2)
Cumene	902 (3,10)	50 (1,00)	100 (1,00)	130 (1,00)	323 (1,13)	330 (1,4)
Pseudocumene	1370 (3,25)	60 (1,00)	120 (1,00)	170 (1,00)	482 (1,20)	492 (1,4)
Methanol	60 (1,3)	5 (1,00)	8 (1,00)	10 (1,00)	20 (1,0)	22 (1,0)
Ethanol	91 (1,4)	8 (1,00)	10 (1,00)	21 (1,00)	41 (1,1)	43 (1,1)
Propanol	144 (1,67)	15 (1,00)	30 (1,00)	70 (1,00)	100 (1,1)	105 (1,1)
Butanol	381 (1,7)	20 (1,00)	50 (1,00)	90 (1,00)	150 (1,2)	155 (1,2)
Pentanol	560 (1,9)	30 (1,00)	70 (1,00)	120 (1,00)	180 (1,2)	187 (1,3)
Hexanol	720 (1,9)	45 (1,00)	90 (1,00)	131 (1,00)	241 (1,3)	250 (1,3)
Heptanol	980 (2,1)	55 (1,00)	111 (1,00)	140 (1,00)	321 (1,3)	330 (1,3)
Octanol	1380 (2,7)	75 (1,00)	120 (1,00)	150 (1,00)	328 (1,3)	330 (1,3)

Note: Coefficients of asymmetry of corresponding compounds are given in brackets.

Table 4

Retention times (t_R , s) and coefficients of asymmetry* of some compounds on Polysorb-1 at volumetric and surface-layer filling of columns, solid support – Chromosorb-W. Granulation of Polysorb-1 – 5–10 μm ; chromatographic column temperature – 160 $^{\circ}\text{C}$

Sorbate	Volumetric filling of the column	Surface-layer sorbent				
		Contents of active agent, %				
		10,20	19,80	23,80	28,10	28,35
Benzene	541 (1,80)	400 (1,00)	670 (1,00)	168 (1,0)	170 (1,1)	175 (1,1)
Toluene	751 (2,16)	30 (1,00)	78 (1,00)	220 (1,0)	240 (1,1)	240 (1,1)
Ethyl benzene	881 (2,51)	35 (1,00)	110 (1,00)	300 (1,0)	300 (1,0)	310 (1,1)
Cumene	1180 (2,61)	45 (1,00)	128 (1,00)	410 (1,1)	420 (1,1)	435 (1,15)
Pseudocumene	1678 (2,81)	70 (1,00)	141 (1,00)	515 (1,1)	538 (1,1)	545 (1,15)
Methanol	200 (1,5)	15 (1,00)	20 (1,00)	58 (1,0)	60 (1,0)	65 (1,0)
Ethanol	251 (1,7)	20 (1,00)	32 (1,00)	80 (1,0)	80 (1,0)	82 (1,0)
Propanol	300 (1,7)	28 (1,00)	50 (1,00)	100 (1,0)	145 (1,0)	150 (1,1)
Butanol	410 (1,8)	40 (1,00)	65 (1,00)	130 (1,0)	175 (1,0)	185 (1,1)
Pentanol	630 (2,0)	50 (1,00)	101 (1,00)	202 (1,0)	210 (1,1)	218 (1,1)
Hexanol	830 (2,1)	61 (1,00)	130 (1,00)	270 (1,1)	280 (1,1)	290 (1,1)
Heptanol	1110 (2,1)	72 (1,00)	145 (1,00)	395 (1,1)	410 (1,1)	425 (1,1)
Octanol	1500 (2,6)	83 (1,00)	161 (1,00)	471 (1,1)	480 (1,1)	495 (1,2)

Note: Coefficients of asymmetry of corresponding compounds are given in brackets.

Table 5

Coefficients of separation (K/t_r^m) of some binary mixtures on the Chromosorb-103 in the variant of volumetric and surface-layer packing of columns, solid support – Chromosorb-W. Granulation of Chromosorb-103 – 5–10 μm , column temperature – 160 $^{\circ}\text{C}$

Binary mixture	Volumetric filling of the column	Surface - layer sorbent				
		Contents of active agent, %				
		11,20	20,14	24,30	32,10	34,40
Benzene-Toluene	0,6	0,05	0,28	0,71	1,10	1,15
Toluene-Ethylbenzene	0,3	0,07	0,15	0,40	0,71	0,73
Ethylbenzene-cumene	0,2	0,04	0,20	0,31	0,40	0,41
Cumene-pseudocumene	0,2	0,02	0,14	0,28	0,40	0,42

Table 6

Coefficients of separation (K/t_r^m) of some binary mixtures on the Polysorb-1 in the variant of volumetric and surface-layer filling of columns, solid support – Chromosorb-W. Granulation of Polysorb-1 – 5–10 μm , column temperature – 160 $^{\circ}\text{C}$

Binary mixture	Volumetric filling of the column	Surface - layer sorbent				
		Contents of active agent, %				
		10,20	19,80	23,80	28,10	28,35
Methanol - ethanol	1,01	0,05	0,20	1,52	1,50	1,52
Ethanol - propanol	1,51	0,10	0,25	2,31	2,20	2,30
Propanol - butanol	1,60	0,10	0,18	1,70	1,86	1,88
Butanol - pentanol	1,60	0,10	0,17	2,00	2,20	2,30
Pentanol - hexanol	1,73	0,15	0,20	2,10	2,23	2,85
Hexanol - heptanol	1,70	0,15	0,20	2,30	2,51	2,80
Heptanol - octanol	1,68	0,20	0,95	2,22	2,42	2,50

Table 7

Specific characteristics (N/t_r) efficiency of chromatographic columns packed with volumetric and surface-layer sorbents, column temperature – 160 $^{\circ}\text{C}$

Sorbent	Volumetric sorbent	Chromosorb-103		
		Surface-layer sorbent		
		Contents of active agent, %		
		24,40	32,10	33,40
Benzene	1 020	920	1 370	1 350
Toluene	640	600	950	930
Ethyl benzene	320	280	650	625
Cumene	300	220	610	595
Pseudocumene	260	180	410	400
Methanol	284	250	648	630
Ethanol	322	307	756	740
Propanol	225	240	680	650
Butanol	248	230	710	690
Pentanol	250	210	770	750
Hexanol	238	200	800	780

Table 7 (finishing)

Sorbent	Chromosorb-103			
	Volumetric sorbent	Surface-layer sorbent		
		Contents of active agent, %		
		23,8	28,10	28,35
Benzene	1 240	1 780	1 850	1 800
Toluene	780	1 100	1 200	1 250
Ethyl benzene	420	950	980	920
Cumene	400	900	960	910
Pseudocumene	380	850	910	875
Methanol	480	1 100	1 130	990
Ethanol	421	998	1 181	1 151
Propanol	380	830	870	895
Butanol	400	981	1 021	995
Pentanol	350	810	861	840
Hexanol	368	830	890	860

Apparently it is connected more with the homogeneous distribution of polymer adsorbents on the surface of solid support.

Therefore our further experiments were carried out on the polymer adsorbents of lower dispersity 5–10 μm .

Limitations of application of gas-adsorption chromatography in volumetric packing is conditioned by the fact that most of adsorbents are characterized by nonlinear adsorption isotherm towards the adsorbed components, which in its turn leads to appearance of asymmetric peaks on the chromatogram thus greatly deteriorating the process of separation. Application of surface-layer adsorbents in gas chromatography enables us to remove this flaw [4].

To reach the optimal regime of separation in the variants of surface-layer filling of chromatographic columns great significance is attributed to the selection of amount of the active agent applied on the solid support, that is to achieve the retention of different degree of the components of the separated mixture and alongside with it, to keep symmetry of separation curves.

As is seen from the Table 3, the retention ability of surface-layer sorbents is exposed in the presence of Chromosorb-103 in the amount of 30–32 %, while retention time decreases approximately 2,5–3 times compared with the volumetric filling of columns, but simultaneously the peaks on the chromatogram are practically symmetrical for all components of the model mixture.

It should also be stated that Chromosorb-103 is characterized by higher retention ability to aromatic compounds (possessing π -link) than to alcohols.

Retention capacity of Polysorb-1 (Table 4) with respect to the compounds subjected to chromatography is rather well exposed for a large range of amount of active agents, applied on solid support in 24 to 28 % by obtaining more symmetric peaks on the chromatogram. Elution time of some compounds on the columns, filled with surface-layer sorbents and in the case of Chromosorb-103 too, is decreased two-three times compared with the volumetric filling of the column. At this moment Polysorb-1 shows higher retention ability to alcohols than Chromosorb-103. Apparently it is conditioned by the presence of more narrow pores of Polysorb-1 compared to those of Chromosorb-103, and correspondingly by the longer diffusion of straight-chain molecules of alcohols in the pores of Polysorb-1.

Although the real improvement of separation is explained not by the difference in retention time of separate components of a mixture, but by the coefficient of separation of separate binary mixtures, which are one of the major characteristics determining the expediency of application of various sorbents (in this case of surface-layer ones) in gas chromatography.

To evaluate the separative power of polymer adsorbents in the variant of surface-layer sorbents in the present experiment, we used K/t_r^m , characteristics of the value of separation criteria. (Tables 5 and 6).

As seen from the data given in Table 5, separation of vapors of aromatic hydrocarbons is better realized on the surface-layer sorbent with Chromosorb-103 32,1–32,4 %, and this index is approximately twice higher than for the same pair of hydrocarbons on the columns, filled with volumetric sorbent.

For mixtures of straight-chain alcohols on Polysorb-1, with the active agent within 24–28 %, these coefficients 1,2–1,5 times exceed the coefficients of separation of corresponding pair on sorbents of volumetric filling. At the lower content of active agent on the solid support the separation power sharply decreases (Table 6).

The obtained data correspond to the efficiency of chromatographic columns determined for some components of the separated mixtures, namely for those surface-layer sorbents, where the best separation of mixtures was achieved. The greatest efficiency of chromatographic columns was determined for columns with surface layer sorbents, which in some cases is 2–2,5 times high than the efficiency of columns with volumetric sorbents (Table 7).

All positive characteristics of surface-layer sorbents, shown on the example of application of polymer adsorbents, should be connected with the fact that sorption-separation processes in such variants of column filling proceed only in the surface layer of small depth, that equals to the thickness of the layer of active sorbent (agent), somewhat of an analogue of stationary liquid in gas-liquid chromatography.

Resistance to the mass transfer for such type of filling, compared to the volumetric filling – decreases, since the length of ways of diffusion into the depth of particles of active agent decreases. Hence time of diffusion determined by the depth penetration of fine dispersity particles of adsorbent into macro pores of solid support decreases too.

The obtained results show also that application of surface-layer sorbents in gas-chromatography enable to decrease significantly the time of analyses compared to the duration of analyses on the columns packed with volumetric sorbents.

Conclusion

Thus, application of polymer adsorbents as the active agents in the variant of surface-layer packing of chromatographic columns is characterized with a number of advantages, compared with the volumetric sorbents, and namely: decrease of time of analysis, higher separative power, more symmetric curves of separation, possibility of carrying the analyses at lower temperature of heating of chromatographic columns.

All the above stated enables us to recommend the surface-layer sorbents for their wide application in the practice of chromatographic analysis.

References

1. **Cremer E.** Prüfung für Adsorbentien und Katalysatoren mit Hilfe der Gas-Chromatographie. // *Angew.Chem.* – 1959. – 71. – № 15/16. – P. 512-514.
2. **Halasz I., Horvath Cs.** // Patent FRG 1183715m. – 1962.
3. **Bombaugh K. J.** Improved Efficiency in Gas Chromatography by Molecular Sieve Flour. // *Nature.* – 1963. – 197. – № 4872. – P. 1102-1103.
4. **Березкин В. Г., Никитина Н. С.** Поверхностно-слойные сорбенты в газовой хроматографии. // *Успехи химии.* – 1971. – Т. 40. – вып. 5. – С. 927-941.
5. **Andronikashvili T., Eprikashvili L.** Use of zeolites on standard solid supports in Gas Chromatography. // *J. Chromatogr.* – 1989. – V. 286. – P. 3-10.
6. **Andronikashvili T., Eprikashvili L., Eprikashvili Z.** Influence of the Nature of solid support and the Dispersity of the Active Agent on the Performance of Chromatographic columns Packed with Surface-Layer sorbents. // *Chromatographia.* – 1997. – V. 46, № 3/4. – P. 156-160.
7. **Сакодынский К. И., Панина Л. И.** Полимерные сорбенты для молекулярной хроматографии. М.: Наука. – 1977. – 165 с.
8. Руководство по газовой хроматографии. /Под ред. **Лейбница Э., Штруппе Х.** – М.: Мир. – 1988. – вып. 1. – 479 с.
9. **Andronikashvili T., Eprikashvili L., Berezkin V., Abulashvili E., Gogitidze N.** Effectiveness of chromatographic columns filled with polymeric surface-layer sorbents. // *Chromatography 87.* H. Kalasz and L. S. Ettre (Eds), Akademiai Kiado, Budapest. – 1988. – P. 17-22.
10. **Desty D. H., Goldup A., W. T. Swanton.** In: *Gas Chromatography. Third Intern. Symposium in America, June 13-16, 1961.* Ed. by N. Brenner, J. N. Callen, M. D. Weiss., Acad. Press, New York-London – 1962. – P.105-135.

Институт физической и органической
химии им. П. Г. Меликишвили
0186, г. Тбилиси, ул. Джикия, 5
тел.: (+99532) 320519
e-mail: physorgchem@pochta.ru

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