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ADSORBENTS FOR CHROMATOGRAPHY OF OXYGEN-CONTAINING COMPOUNDS

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SUMMARY

Adsorbents for chromatography of oxygen-containing compounds were obtained by modification of thermal carbon blacks with aromatic di- and tricarboxylic acids. The acids were applied both directly to the carbon black surface and to the surface of carbon blacks prelayered with heat-resistant polymers. The adsorbents obtained were shown to be applicable for separating the homologues of aliphatic mono- and dicarboxylic acids as well as isomeric aromatic monocarboxylic and cyclic dicarboxylic acids.

INTRODUCTION

Chromatographic analysis of oxygen-containing compounds is important in the chemical, medical and food industries. Among oxygen-containing compounds, carboxyl-containing compounds present the greatest difficulty for gas chromatographic (GC) separation; therefore, prior to determination, they are most often converted into volatile derivatives. Attempts to use gas adsorption-absorption and gas adsorption chromatography to separate free acids proved most successful. Certain C₁–C₅ aliphatic acids were separated on Sterling and Graphon graphitized carbon blacks modified with PEG-1500¹, and C₁₄–C₂₀ acids were separated on a hydrogen-treated Carboxpack C modified with a mixture of polyethylene glycol (PEG) and trimesic acid (0.8% and 0.3%)². Some free aromatic monocarboxylic acids were separated on Sterling graphitized carbon black modified with a mixture of phosphoric acid and a liquid free fatty acid phase (FFAP)³. Aliphatic hydroxyacids were analysed on acid-washed Carboxpack C modified with a mixture of 5.3% PEG-20M and 0.8% trimesic acid⁴. All the methyl-, halogen, methoxy- and nitrobenzoic acid isomers were separated on graphitized thermal carbon black (GTCB) modified with dicarboxylic acids^{5–7}.

In this work we prepared adsorbents based on carbon blacks by consecutively modifying their surfaces with heat-resistant polymers, used in gas-liquid chromatography (GLC) as liquid phases, and with trimesic acid. The adsorbents were then used to separate oxygen-containing compounds⁷ and particularly free organic acids, which are the most difficult to separate.

EXPERIMENTAL

Ungraphitized thermal carbon black TG-10 (specific surface area 10 m²/g) and graphitized carbon black (GTCB) (specific surface area 8.5 m²/g) were used as supports.

The following compounds were tested as modifiers: 4,4'-diphenylsulphonic dicarboxylic acid, 1,3,5-benzenetricarboxylic acid and the liquid phases polybutanediol adipate (PBDA), polyethylene glycol (PEG-20M), the polymer of PEG-20M and nitroterephthalic acid (FFAP) or Apiezon L. Polycarboxylic acids were applied to the carbon black surfaces from their solutions in dimethylformamide; the adsorbent was then dried by pumping in vacuum at room temperature for 4 h. The samples premodified with a liquid phase were prepared as follows. First, a known amount of the liquid phase was applied from its solution in chloroform to the carbon black surface and the adsorbent was then dried. Then trimesic acid was applied to the resultant adsorbent from its solution in dimethylformamide.

The following modified carbon black samples were obtained: TG-10 with 1% 4,4'-diphenylsulphonic dicarboxylic acid; TG-10 with 1.4% trimesic acid; TG-10 with 1% PEG-20M and then with 1.4% trimesic acid; TG-10 and GTCB with 1% PBDA and then with 1.4% trimesic acid; TG-10 with 1% FFAP and then with 1.4% trimesic acid. An adsorbent based on TG-10 coated with 1% Apiezon L, and then with 1.4% trimesic acid, was also prepared. In addition, from a solution of chloroform-dimethylformamide (4:1), a mixture of PEG-20M (5.3%) and trimesic acid (0.8%) was applied to the TG-10 surface.

The adsorbents were studied on Tsvet-100 and Tsvet-1000 chromatographs equipped with flame ionization detectors. Glass columns (0.5 or 1.0 m × 2 mm) were packed with the adsorbents (particle size 0.16–20 or 0.20–0.30 mm). The adsorption isotherms were calculated from the chromatographic peaks by Glueckauf's method⁸.

RESULTS AND DISCUSSION

To examine the adsorption properties of the adsorbents obtained, the available GC data were used to calculate the adsorption isotherms of *p*-methylbenzoic acid. Fig. 1 shows the adsorption isotherms on the surface of all the adsorbents and on unmodified GTCB (1). Attempts to calculate the adsorption isotherms on the surface of unmodified TG-10 were unsuccessful since the carboxyl-containing adsorbates are adsorbed irreversibly on this surface.

The adsorption isotherms of *p*-methylbenzoic acid on carbon black surfaces modified in various ways lie lower than the adsorption isotherm (1) on the initial GTCB. The adsorption isotherms on adsorbents obtained by modifying the carbon black surfaces with polymers (PEG-20M, PBDA and FFAP) are approximately linear.

The sample modified with a mixture of the PEG-20M liquid phase and trimesic acid is characterized by the highest adsorption (isotherm 2). The adsorption isotherm (3) on TG-10 modified successively with PEG-20M and with trimesic acid lies below isotherm 2. This indicates that the use of different modification techniques affects the adsorption properties. Subsequently, we selected the procedure whereby liquid phases and then trimesic acid were applied successively to the carbon black surface.

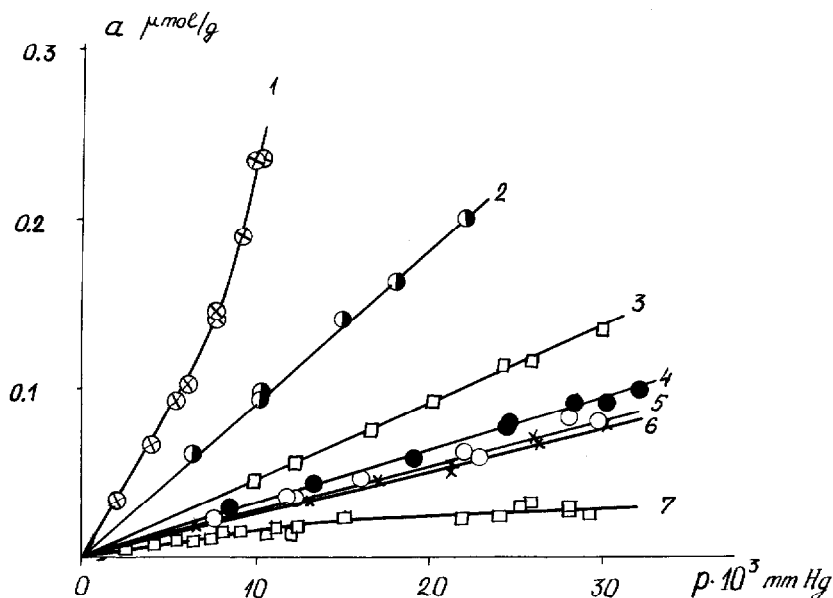


Fig. 1. Adsorption isotherms of *p*-methylbenzoic acid obtained at 170°C on the surface of GTCB (1), on TG-10 modified with a mixture of PEG-20M and trimesic acid (2), on TG-10 modified consecutively with PEG-20M and trimesic acid (3), with PBDA and trimesic acid (4), with FFAP and trimesic acid (6) and with Apiezon L and trimesic acid (7) and on GTCB modified with PBDA and trimesic acid (5).

As is apparent from Fig. 1, the adsorptions of *p*-methylbenzoic acid obtained on GTCB and TG-10 modified with PBDA and trimesic acid are approximately the same, *i.e.*, the effect of the nature of the initial carrier adsorbent on adsorption is insignificant. On the other hand, when modified solely with dicarboxylic acids, the initial adsorbent has a substantial effect on the properties of the adsorbents obtained⁷.

The isotherm (7) of *p*-methylbenzoic acid on the TG-10 surface modified with Apiezon L and then with trimesic acid lies lower than the other isotherms; it is also non-linear and concave to the pressure axis, which indicates the occurrence of adsorbate-adsorbent interactions on the surface of this adsorbent.

Table I shows the chromatographic characteristics obtained on adsorbents prepared by modifying the carbon blacks with various liquid phases, and then with aromatic polycarboxylic acids. We determined the specific retention volumes of *p*-methylbenzoic acid at 170°C, the asymmetry of its chromatographic peaks on columns packed with various adsorbents and the selectivity, k_s , of the obtained adsorbents with respect to methylbenzoic acid isomers. The most symmetric peaks of acids were obtained on graphitized and non-graphitized carbon blacks modified with polar oxygen-containing liquid phases, and then with trimesic acid. As is seen from Table I, the lowest retention volumes were obtained on TG-10 modified with Apiezon L and then with trimesic acid; however, the asymmetry of the chromatographic peaks was the highest. As shown above, even though the adsorption isotherm lies below the other isotherms, it has a convex shape, which hinders the use of the adsorbent for determinations of oxygen-containing compounds.

TABLE I
CHROMATOGRAPHIC CHARACTERISTICS OF ADSORBENTS

No.	Adsorbent	<i>p</i> -Methylbenzoic acid (170°C)		k_s for methylbenzoic acids ^o	
		V_0 (cm ³ /g)	K_{As} *** (see ref. 9)	ortho-/meta-	meta-/para-
1*	TG-10 + (5.3% PEG-20M + 0.8% trimesic acid)	418	2.6	0.8	0.1
2**	TG-10 + 1% PEG-20M + 1.4% trimesic acid	149	1.8	1.0	0
3**	TG-10 + 1% PBDA + 1.4% trimesic acid	145	2.4	1.0	0.4
4**	TG-10 + 1% FFAP + 1.4% trimesic acid	141	2.2	0.7	0
5**	GTCB + 1% PBDA + 1.4% trimesic acid	125	1.2	1.0	1.0
6**	TG-10 + 1% Apiezon L + 1.4% trimesic acid	39	5.0	0	0

* Simultaneous application.

** Consecutive application.

*** Measured at one-tenth of peak height.

Samples 3 and 5 (Table I) possess the highest selectivity for chromatographic separation of isomeric compounds which otherwise would be difficult to resolve. Hence, using a carbon black with a non-uniform surface like TG-10 as a support, one should employ polar liquid phases with oxygen-containing functional groups to screen residual oxygen-containing groups¹⁰.

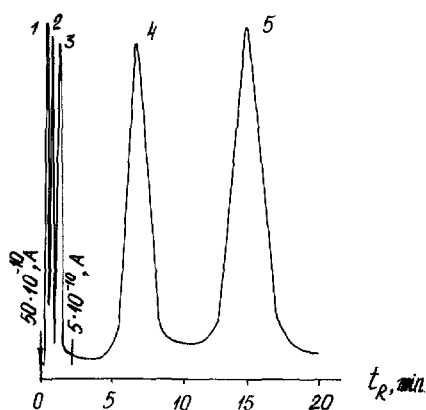


Fig. 2. Chromatogram of a mixture of dimethylformamide (1, solvent), cyclohexanecarboxylic acid (2), benzoic acid (3), 4-*cis*-cyclohexanedicarboxylic acid (4) and *trans*-cyclohexanedicarboxylic acid (5) obtained at 230°C on a 0.5-m column packed with TG-10 modified with 4,4'-diphenylsulphonic dicarboxylic acid.

Various oxygen-containing compounds, alcohols, aldehydes, diols¹⁰ and acids, were chromatographically separated on the obtained adsorbents.

By applying 4,4'-diphenylsulphonic dicarboxylic acid to the surface of TG-10, one can obtain an adsorbent highly selective to geometric isomers. Fig. 2 shows a chromatogram of a 1,4-benzenedicarboxylic acid hydrogenation products. On a 0.5-m column, the *cis*- and *trans*-isomers of cyclohexanedicarboxylic acid were separated in the presence of benzoic and cyclohexanecarboxylic acids.

Like clean carbon black surfaces, the obtained adsorbents retain a high selectivity to various geometric isomers; the symmetry of the chromatographic peaks increases by the modification.

The adsorbent obtained by modifying TG-10 with 1,3,5-benzenetricarboxylic acid was used to separate a mixture containing adipic acid and its mono- and dimethyl esters. Fig. 3 shows a chromatogram of a commercial mixture consisting of adipic acid methyl esters (total up to 90%) and adipic acid (about 1.0%). The use of 1,3,5-benzenetricarboxylic acid as a modifying agent allows not only the separation of the esters from each other, but also simultaneous detection of the adipic acid.

Adsorbents prepared by consecutive modification with liquid phases and aromatic acids were also used to separate carboxyl-containing compounds. Fig. 4 shows a chromatogram of aliphatic monocarboxylic acids on a column of TG-10 modified consecutively with PEG-20M and with trimesic acid. The peaks of myristic, palmitic and stearic acids are quite symmetrical at short retention times.

The use of the PBDA liquid phase and then of trimesic acid allowed the separation of methyl- and dimethylbenzoic acids.

Fig. 5 shows a chromatogram of a mixture of methyl-substituted aromatic acids.

The chromatographic analysis of free acids with two carboxylic groups is highly difficult. Aliphatic dicarboxylic acids were separated from glutaric (C₅) to sebacic (C₈) acids on all columns packed with TG-10 modified with the above-mentioned liquid phases and then with trimesic acid.

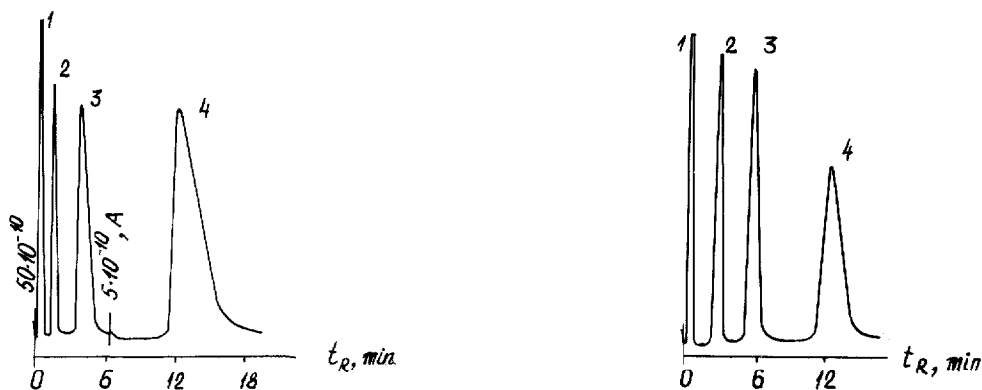


Fig. 3. Chromatogram of a mixture of adipic acid (4) and its dimethyl (2) and monomethyl (3) esters in dioxane (1) at 210°C on a column packed with TG-10 modified with trimesic acid.

Fig. 4. Chromatogram of aliphatic monocarboxylic acids: myristic (2), palmitic (3), stearic (4) in dioxane (1) at 220°C on a column packed with TG-10 modified first with PEG-20M and then with trimesic acid.

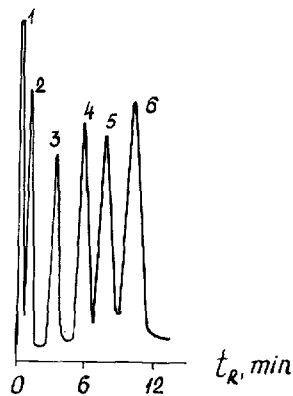
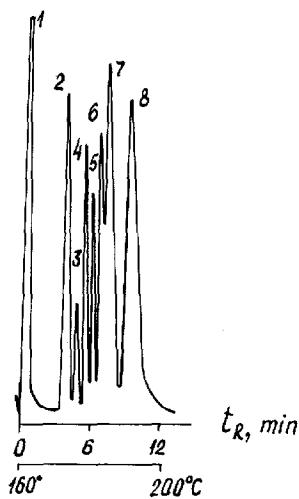


Fig. 5. Chromatogram of a mixture of benzoic acids: benzoic acid (2), *ortho* (3), *meta*- (4), and *para*-methylbenzoic (5) acid, 2,5-dimethyl- (6), 2,4-dimethyl- (7) and 3,4-dimethylbenzoic (8) acid in dioxane (1) on a column packed with GTCB modified with PBDA and then with trimesic acid. Temperature raised from 160 to 200°C at 8°/min.

Fig. 6. Chromatogram of a mixture of aliphatic dicarboxylic acids: glutaric (2), adipic (3), suberic (4), adelanic (5) and sebacic (6) acid, in dioxane (1) obtained at 200°C on a column packed with TG-10 modified with FFAP and then with 1,3,5-benzenetricarboxylic acid.

Fig. 6 shows the separation of aliphatic dicarboxylic acids at 200°C on RG-10 modified with FFAP and then trimesic acid (No. 3 of Table I).

Thus, the modification of TCB surfaces with liquid phases, and then with trimesic acid, yielded adsorbents suitable for use in the GC analysis of oxygen-containing compounds, including free monocarboxylic aromatic and aliphatic acids as well as dicarboxylic aliphatic and cyclic acids.

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