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## Note

# Gas chromatographic separation of organic acids on graphitized thermal carbon black

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High association of carboxyl-containing substances on the surface of graphitized thermal carbon black (GTCB) results in very diffuse fronts of their chromatographic peaks, with the adsorption isotherms convex to the pressure axis. To reduce the adsorption of aromatic acids and their association, the GTCB surface has been modified by orthophosphoric, 1,4-benzenedicarboxylic, 2,6-naphthalenedicarboxylic and 4,4'-diphenylsulphonicdicarboxylic acids. Optimal amounts of modifying acids are in the range 1–2 mg m$^{2}$. When the GTCB surface is modified by these acids, the adsorption isotherms of aromatic acids become straightened. The adsorbents obtained have been used for the gas-chromatographic separation of isomeric monocarboxylic acids with methyl, chloro, methoxy and nitro substituents in the benzene ring. With the same adsorbents separations of dicarboxylic aliphatic acids with mono- and dimethyl esters were carried out.

Mono- and dicarboxylic acids are used in polymer production. The ability of carboxyl-containing substances to undergo association determines their properties, *i.e.* low volatility and high boiling temperature, and hinders their direct chromatographic determination. The determination of high-boiling carboxyl-containing substances by gas–liquid chromatography is more often carried out after their conversion into more volatile derivatives, otherwise it requires specially synthesized liquid stationary phases or additional processing of the carriers[1–7].

GTCB[8] is highly selective with respect to the geometry of molecules, and the possible application of this adsorbent in the gas chromatographic analysis of acids was therefore studied.

There have already been publications on the separation of some substituted aromatic monocarboxylic acids on Sterling FT carbon black modified by FFAP liquid stationary phase[9].

This paper deals with the gas-adsorption chromatographic separation of monocarboxylic aromatic acids having methyl, chloro, methoxy and nitro substituents in the ring without converting them into volatile derivatives.

## EXPERIMENTAL

GTCB with a specific surface area of 8.5 m$^{2}$/g was used as the adsorbent. A Tsvet chromatograph equipped with a flame-ionization detector was used in all experiments. Glass columns (0.5 m × 1.5–2.0 mm I.D.), filled with the adsorbent of particle size 0.20–0.31 mm were used. The carrier gas velocity varied from 15 to 40 ml/min.

## RESULTS AND DISCUSSION

The chromatography of benzoic acid revealed that the first portions are adsorbed by the GTCB surface. The irreversibly bound amount of benzoic acid comprises not more than 1 % of the monolayer[10]. On the surface of such an adsorbent, with the acid to be analysed partially modified by the residual GTCB areas, the chromatographic peaks of methylbenzoic acid are greatly asymmetric, with a diffused front and almost vertical rear line, indicating adsorbate–adsorbate interaction.

Thus, despite the high selectivity of GTCB towards isomeric aromatic acids, it cannot be used for the gas chromatographic analysis of acids.

To weaken the adsorbate–adsorbate and adsorbate–adsorbent interactions, the GTCB surface was modified with orthophosphoric, 1,4-benzenedicarboxylic, 2,6-naphthalenedicarboxylic and 4,4'-diphenylsulphonicdicarboxylic acids[11]. To prepare the adsorbents the acids were dissolved (the mineral acid in acetone and the organic acids in dimethylformamide) by heating in a water-bath. The GTCB samples modified by orthophosphoric acid were heated at 200 C for 10 h. The adsorbents obtained by modification by dicarboxylic acids were evacuated at a pressure of approximately 10 mmHg at ambient temperature.

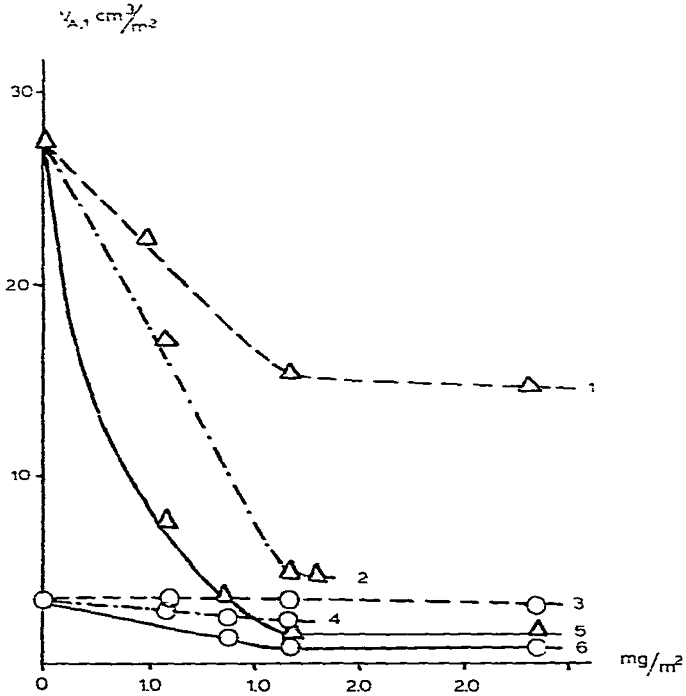

Fig. 1. Dependence of $V_{A,1}$ of benzoic acid (○) and *p*-methylbenzoic acid (△) on the amount of 4,4'-diphenylsulphonicdicarboxylic acid (curves 5 and 6), 2,6-naphthalenedicarboxylic acid (curves 2 and 4) and orthophosphoric acid modifiers (curves 1 and 3).

The adsorbents were analysed chromatographically. Use was made of the absolute retention volume, $V_A$, where $V_A = V_g/S$, *i.e.*, the specific retention volume ($V_g$) divided by the specific surface area of the adsorbent ($S$). For low coverages this value is Henry's constant $V_{A,1} = K$. Fig. 1 shows the dependences of $V_{A,1}$ for benzoic and *p*-methylbenzoic acids on the amount of modifying acids applied to the GTCB. Small amounts of modifying acids on the GTCB surface reduce the peak asymmetry, and at the same remove the irreversible adsorption of the sample acids. As can be seen from Fig. 1, $V_{A,1}$ for benzoic acid depends only slightly on the amount of modifying acids (curves 3, 4 and 6), whereas $V_{A,1}$ for *p*-methylbenzoic acid decreases sharply when the modifying agents are applied (curves 1, 2 and 5). With a further increase in the amount of modifier (more than 1.2 mg/m$^2$) the retention volume remains constant.

These adsorbents were used for obtaining adsorption isotherms for *p*-methylbenzoic acid at 210°C. As can be seen in Fig. 2, all of the modified GTCB samples

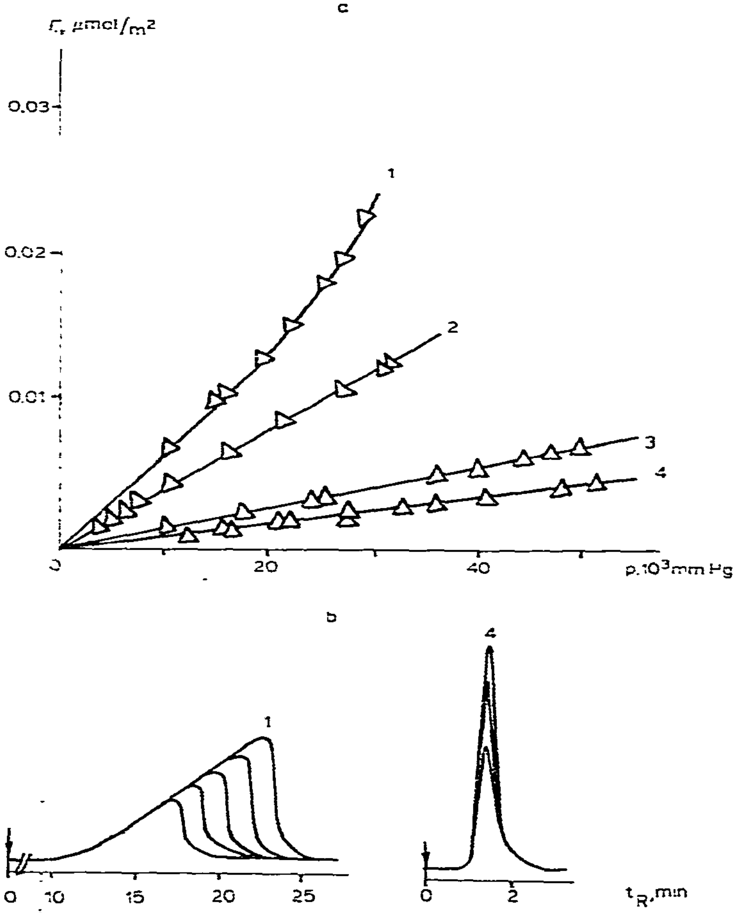

Fig. 2. (a) Isotherms of *p*-methylbenzoic acid adsorption at 210°C on GTCB unmodified (1) and modified by orthophosphoric acid (2), 2,6-naphthalenedicarboxylic acid (3) and 4,4'-diphenylsulphonicdicarboxylic acid (4). (b) Chromatographic peaks of *p*-methylbenzoic acid on GTCB unmodified (1) and modified by 4,4'-diphenylsulphonicdicarboxylic acid (4).

showed linear adsorption isotherms for *p*-methylbenzoic acid. An adsorption isotherm for *p*-methylbenzoic acid on the non-modified GTCB surface is also given for comparison. The isotherm is convex to the pressure axis, which indicates strong adsorbate–adsorbate interactions. The interactions are considerably reduced by the surface modification.

The adsorption values, $\Gamma$, of the acids studied on the unmodified GTCB are reduced on modification by orthophosphoric and 2,6-naphthalenedicarboxylic acids. at the same vapour pressure. The least adsorption of the *p*-methylbenzoic acid is observed on GTCB modified by 4,4′-diphenylsulphonicdicarboxylic acid.

Thus the deposition of mineral and dicarboxylic organic acids on to the GTCB surface in amounts of 1.0–1.5 mg/m$^2$ considerably reduces the adsorption of benzene and *p*-methylbenzoic acids.

Table I gives $V_{A,1}$ values for benzoic and *p*-methylbenzoic acids, and also peak resolution values, $K_s$. $K_s$ values for two substances were calculated using the equation $K_s = 2\,\Delta y/(y_1 + y_2)$, where $\Delta y$ is the distance between the heights of two separated peaks and $y_1$ and $y_2$ are the widths of the peaks of the separated substances at half-height.

TABLE I

CHROMATOGRAPHIC DATA FOR GTCB MODIFIED BY VARIOUS ACIDS

| *Modifier** | $V_{A,1}^{210^\circ C}$ cm$^3$/m$^2$ | | $K_S$** | | | |
|---|---|---|---|---|---|---|
| | *Benzoic acid* | *p-Methylbenzoic acid* | *Benzoic–o-methylbenzoic acid* | *m-Methylbenzoic–n-methylbenzoic acid* | *p-Chlorobenzoic–m-chlorobenzoic acid* | *m-Chlorobenzoic–p-chlorobenzoic acid* |
| $H_3PO_4$ | 3.5 | 14.7 | 1.0 | 1.0 | 0 | 0.5 |
| 1,4-BDC | 3.8 | Asymmetric | 0 | 0.4 | – | – |
| 2,6-NDC | 2.1 | 4.7 | 0.6 | 0.9 | 1.0 | 0.8 |
| 4,4′-DPHSDC | 0.9 | 1.4 | 1.4 | 0.6 | 1.0 | 0.5 |

* BDC = benzenedicarboxylic acid; NDC = naphthalenedicarboxylic acid; DPHSDC = diphenylsulphonicdicarboxylic acid.

** Separation coefficient of the isomers of substituted benzoic acids.

Compound pairs that are difficult to separate were chosen: benzoic and *o*-methylbenzoic acids, *m*- and *p*-methylbenzoic acids. *o*- and *m*-chlorobenzoic acids and *m*- and *p*-chlorobenzoic acids. Values of $K_s$ close to or greater than 1 were obtained for these acid pairs on GTCB modified by 2,6-naphthalenedicarboxylic and 4,4′-diphenylsulphonicdicarboxylic acids.

Deposition of various modifying agents affects the retention characteristics of the aromatic acids. At 180°C columns filled with GTCB modified by 2.35 mg/m$^2$ of orthophosphoric acid (Fig. 3a) separate the isomers more slowly than under the same conditions using columns filled with GTCB modified with 4,4′-diphenylsulphonicdi-

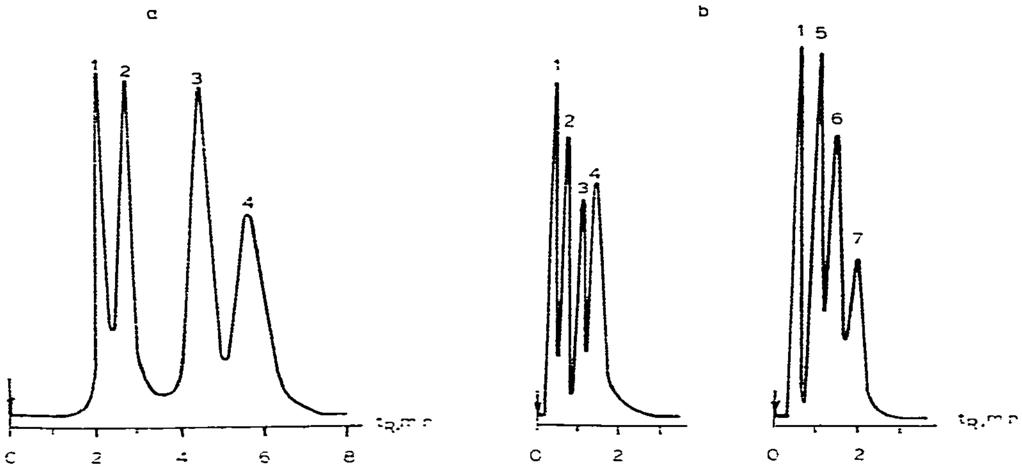

Fig. 3. Chromatograms of a mixture of benzoic acid (1) and *ortho-* (2), *meta-* (3) and *para-* (4) isomers of methylbenzoic acid and a mixture of *ortho-* (5), *meta-* (6) and *para-* (7) isomers of chlorobenzoic acid on GTCB modified by 2.35 mg m$^{-2}$ of (a) orthophosphoric acid and (b) 4,4'-diphenylsulphonicdicarboxylic acid.

carboxylic acid. The same column copes well with the separation of all isomers of chlorobenzoic acid.

The presence of methoxy and nitro groups in the ring of benzoic acid enhances its ability to associate. The chromatography of such acids therefore requires higher temperatures. Mixtures of benzoic and *o-*, *m-* and *p-*isomers of methoxybenzoic acid are separated at 205 C (Fig. 4a), whereas nitrobenzoic acid isomers are separated at 225 C (Fig. 4b). A better separation of these high-boiling acids occurs on GTCB modified by 2,6-naphthalenedicarboxylic acid. Probably the flat structure of this acid protects the residual active sites of GTCB better than any of the other modifying studied.

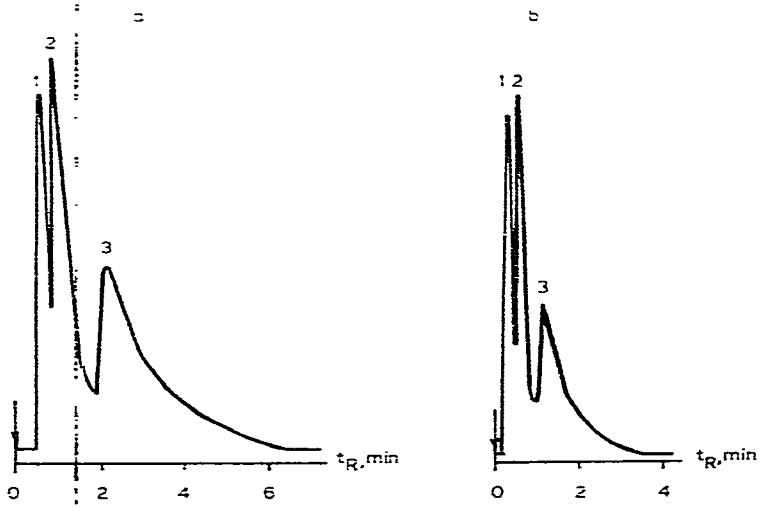

Fig. 4. Chromatograms of (a) a mixture of *ortho-* (1), *meta-* (2) and *para-* (3) isomers of methoxybenzoic acid and (b) a mixture of *ortho-* (1), *meta-* (2) and *para-* (3) isomers of nitrobenzoic acid on GTCB modified with 1.18 mg m$^{-2}$ of 2,6-naphthalenedicarboxylic acid.

Aliphatic dicarboxylic acids and their di- and monomethyl esters are separated by gas-adsorption chromatography using GTCB modified by 4,4'-diphenylsulphonicdicarboxylic acid. Fig. 5 shows chromatograms of the separation of mixtures of adipic (Fig. 5a) and sebacic (Fig. 5b) acids and their di- and monomethyl esters.

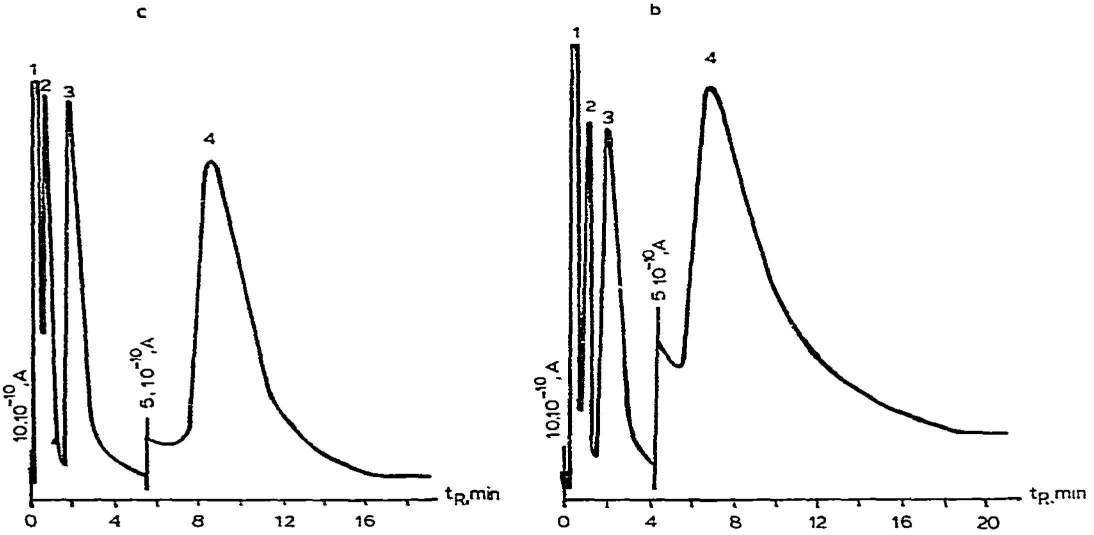

Fig. 5. Chromatograms of solutions of (a) adipic acid and (b) sebacic acid (4) with their monomethyl (3) and dimethyl (2) esters in dimethylformamide (1) on GTCB modified with 1.18 mg/m$^2$ of 4,4'-diphenylsulphonicdicarboxylic acid.

Admixtures of dimethyl adipate and adipic acid in monomethyl adipate have been quantitively evaluated using the external standard method. The minimal determinable amount of dicarboxylic acid is 0.5 % (w/w) and of the diester 0.05 % (w/w). The relative standard deviation ($p$ = 0.9, $n$ = 6) does not exceed 0.5 for dimethyl adipate and 2.0 for adipic acid.

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