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CONCENTRATION AND ISOLATION OF ORGANIC ACIDS ON GRAPHITIZED CARBON BLACK

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SUMMARY

The application of graphitized carbon black to the extraction of traces of organic acids has been studied. It is demonstrated that the recovery of these substances cannot be carried out without considering the nature of these compounds and their molecular structure. The amount of adsorbent and the kind of eluent required were deduced respectively from the breakthrough values and from distribution ratios.

INTRODUCTION

The importance of the determination of organic substances present at low concentration levels in natural and waste waters and in aqueous biological media has resulted in the development of numerous analytical methods using a solid matrix for the recovery of organic substances[1–12].

Any sorbent matrix must be evaluated with regard to its sorption and desorption properties, for the examined sample and substances to be recovered. As reported previously[13], the parameters to be examined during adsorption are: pH, flow-rate, salinity, breakthrough curve, particle size and column geometry; during the subsequent desorption, the flow-rate of the chosen eluent mixture must be controlled. Knowledge of the adsorption ratio (solid matrix–liquid system) helps in the choice of the solvent or solvent mixture to be used in the desorption stage.

Previously, graphitized carbon black (GCB) has been used in gas chromatography (GC)[14,15,23], in high-performance liquid chromatography[16,17], for the recovery of some organic substances from water[18–20] and for sample enrichment in traps in air pollution analysis[21]. In a recent study[19] it was shown that GCB may be a good adsorbent also for organic acids. The present work examines in more in detail the system water, GCB and some organic acids and its possible applications.

EXPERIMENTAL

Materials and reagents

The organic chemicals were purchased from E. Merck, Carlo Erba and Riedel de Haen.

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Concentrated stock solutions were prepared by weight by dissolving the pure substances in a water-soluble organic solvent, a maximum of 100 μl of organic solution per litre of water being employed for aqueous samples.

All the solvents used were either spectograde or analytical grade. The analytical grade solvents were further purified by fractional distillation whenever blank GC determinations suggested the presence of impurities detectable by a flame ionization detector.

Adsorption columns

Glass columns (0.7 cm I.D.), equipped with a PTFE stopcock, were packed with graphitized carbon black (100, 250 or 1000 mg). The adsorbent was held in place with small plugs of silanized glass wool. The graphitized carbon black (GCB) (Carbopack B; Supelco, Bellefonte, PA, U.S.A.) is characterized by a surface area of 100 m^2/g, 80–100 mesh.

Apparatus

A Dani 3900 gas chromatograph equipped with a flame ionization detector (FID) was used. All the standard mixtures and extracts were chromatographed using a porous-layer open tubular (PLOT) glass column (13 m × 0.3 mm I.D.) precoated with kaolin and coated dynamically with free fatty acid phase (FFAP)[22].

Analytical procedures

Adsorption isotherms. Solutions of various compounds ranging in concentration from 50 to 200 μg/l at pH 4 were used. Aliquots (250 ml) of these solutions were stirred at 21 ± 1°C with a weighed amount (250 mg) of GCB for 24 h, sufficient to reach the equilibrium as shown by preliminary experiments. After equilibration the liquid phase was filtered and extracted three times with 20-ml portions of methylene chloride. The combined extracts were dried with granular anhydrous sodium sulphate (5 g) and, after addition of internal standard, were concentrated by a rotary evaporator and analyzed by GC.

Breakthrough plots. The influence of the pH, flow-rate and ionic strength on the adsorption were studied. One litre of water "at different pH values" (pH range 2–11.5), containing 100 μg of each compound, was passed at a flow-rate of 240 ml/h through a glass column packed with 100 mg GCB. Equal amounts of this solution and of the percolate were extracted with three 50-ml portions of methylene chloride. The organic phase, after concentration in a rotary evaporator, was examined by GC.

For evaluating the "influence of flow", similar experiments using *p*-chloro-*m*-cresol and 2,3-dichlorophenol were carried out at pH 4 at various flow-rates in the range 80–800 ml/h with the help of a water pump. The percolate was collected and examined as above after the passage of 1000, 1250, 1500, 1750 and 2000 ml.

Finally, experiments were carried out at pH 4, with a flow-rate of 240 ml/h using water containing different quantities of NaCl and 100 μg/l each of *o*-chloro-*m*-cresol and 2,3-dichlorophenol in order to evaluate the effect of the "ionic strength".

The results of the experiments carried out with GCB packed columns (250 and 1000 mg) under optimum operating conditions (see later) were used to draw the breakthrough curves of all the compounds.

Recovery of acidic substances. The desorption of acidic substances adsorbed on

1000-mg columns of GCB was studied by passing through the column a 50-ml volume of a large number of organic solvents at a selected flow-rate of 60 ml/h and by analyzing the organic phase. Before elution, a nitrogen flow was briefly forced through the column in order to remove traces of water. The solvent mixture was selected after determination of the adsorption ratios $K = C_S/C_L$ (Table II). These values were obtained by shaking for 8 h at 25 ± 1°C the suspension obtained upon adding known amounts of a stock solution corresponding to 15 μg of the examined compounds and 500 mg GCB to 100 ml of each solvent. After equilibrium the suspension was filtered through a sintered glass filter and the organic phase, after addition of internal standard, was concentrated and analyzed chromatographically.

Samples

To check the efficiency of the method, two applications were examined: recovery of organic acid from human urine and phenols from river water.

Human urine. A 50–100-ml volume of sample (pH 4) was passed through a column (0.7 mm I.D.) packed with 250 mg GCB at a flow-rate of 240 ml/h. The adsorbed substances were recovered with 25 ml of benzene–methanol (2:1).

River water. One litre of sample (pH 4) was passed through the column packed with 1000 mg GCB at a flow-rate of 240 ml/h. The adsorbed substances were recovered with 75 ml of benzene–methanol (3:1).

RESULTS AND DISCUSSION

Fig. 1 shows the adsorption isotherms of some of the examined compounds. The isotherms of 2,3,4,6-tetrachlorophenol, myristic acid, stearic acid and benzoic acid are not reported, because in these cases the partition between the solid and the liquid phases lies completely towards the solid phase.

The isotherms show that in the examined concentration range there is a linear

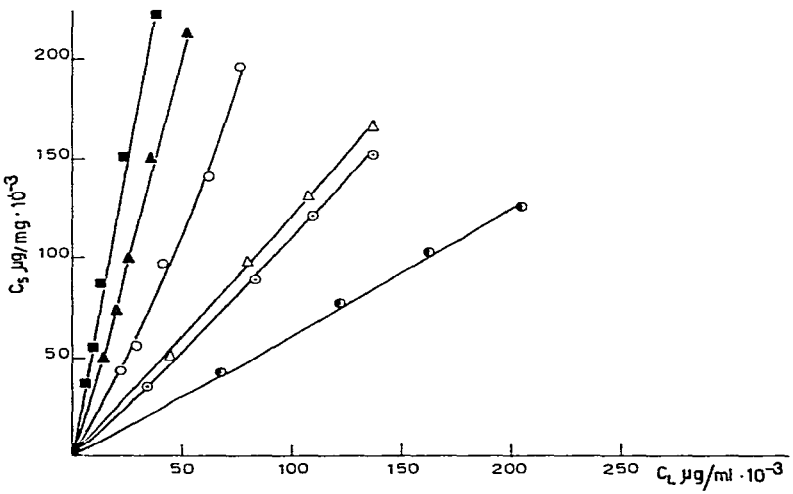

Fig. 1. Adsorption isotherms: ◐, heptanoic acid; ⊙, octanoic acid; △, *p*-chloro-*m*-cresol; ○, 2,3-dichlorophenol; ▲, 2,4,6-trichlorophenol; ■, decanoic acid.

TABLE I

ADSORPTION (%) OF MODEL ORGANIC COMPOUNDS FROM AQUEOUS SOLUTION (1000 ml) ON 100 mg OF GCB AT DIFFERENT pH VALUES

The concentration of each compound was 100 μg/l.

Compound	*pH*				
	2	*4*	*6*	*7.5*	*11.5*
Heptanoic acid	8	10	11	9	5
Octanoic acid	39	50	32	14	8
Decanoic acid	100	100	98	71	20
Myristic acid	100	100	100	74	21
Benzoic acid	98	100	98	70	18
2-Chlorophenol	34	48	30	10	6
p-Chloro-*m*-cresol	70	78	77	70	10
2,3-Dichlorophenol	89	91	92	80	7
2,4,6-Trichlorophenol	100	100	100	86	21
2,3,4,6-Tetrachlorophenol	100	100	98	88	20

relationship between the amount adsorbed on the solid and the aqueous concentration. Adsorption seems to increase with a decrease of the water solubility of the various compounds; therefore, for the fatty acids the adsorption increases with increasing chain length.

In Table I the percentages of different compounds adsorbed on GCB at different pH values is reported. The results show that in the pH range 3–6 there is no marked variation in adsorption because the studied compounds are mainly in the molecular form. At pH >7 the adsorption on GCB is very low because most of the compounds are in the salt form. A value of pH 4 was used in all further experiments.

The breakthrough plots were obtained for *p*-chloro-*m*-cresol and 2,3-dichlorophenol at three different flow-rates: 80, 240 and 800 ml/h (Fig. 2a, b). These experiments show that the collection efficiency increases with decreasing flow-rate in the range 800–240 ml/h. When the flow-rate is lower than 240 ml/h the variation in the collection efficiency is negligible. A flow-rate 240 ml/h was used in all further experiments.

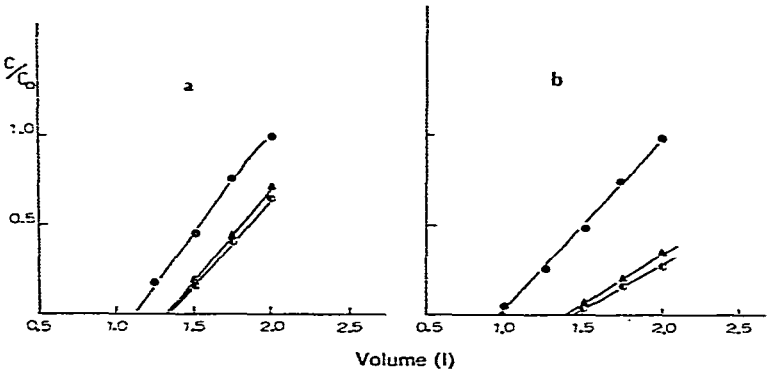

Fig. 2. Breakthrough curves at flow-rates 800 ml/h (●), 250 ml/h (▲) and 80 ml/h (◐). a, *p*-Chloro-*m*-cresol; b, 3,4-dichlorophenol.

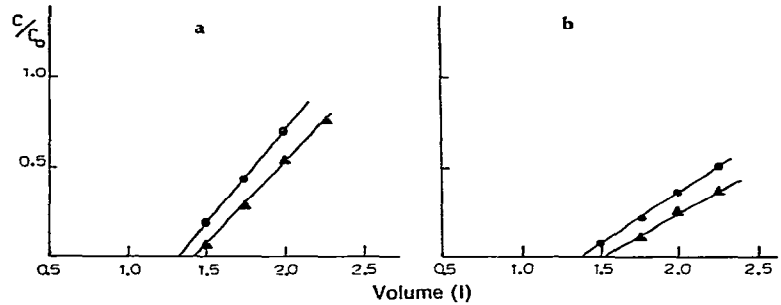

Fig. 3. Breakthrough curves at 30 g/l NaCl (●) and 0.1 g/l NaCl (▲). a, *p*-Chloro-*m*-cresol; b, 3,4-dichlorophenol.

The ionic strength effect on the collection efficiency was evaluated by using water solutions containing different quantities of NaCl. The plots for the above two compounds are reported in Fig. 3a, b. The NaCl (30 g/l) present in the water sample causes moderate variations of breakthrough volumes.

With the optimum operating conditions, the breakthrough curves of all the compounds examined were obtained (Fig. 4) using a glass column packed with 250 mg GCB. Curves for the compounds that after the passage of 2000 ml were not still present in the effluent are not shown. *m*-Cresol has the lowest retention volume.

We can optimize the size of the column using a model substance, selected in regard to the analytical problem that is to be studied. From Figs. 4 and 5 it is seen that an increase of four-fold in the length of the column and in the quantity of GCB (1000 mg instead of 250 mg) results in about a three-fold increase in the breakthrough volume.

The "GCB–solvent distribution ratios", obtained as

$$K = \frac{C_S}{C_L} = \frac{\mu g \text{ of compound per g of solid phase}}{\mu g \text{ of compound per ml of solvent}}$$

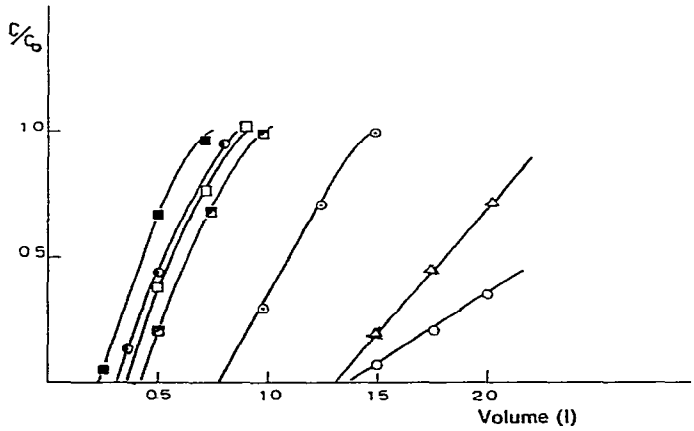

Fig. 4. Breakthrough curves of *m*-cresol (■), heptanoic acid (◐), *o*-cresol (□), 2-chlorophenol (◩), octanoic acid (⊙), *p*-chloro-*m*-cresol (△) and 2,3-dichlorophenol (○) on GCB column (250 mg).

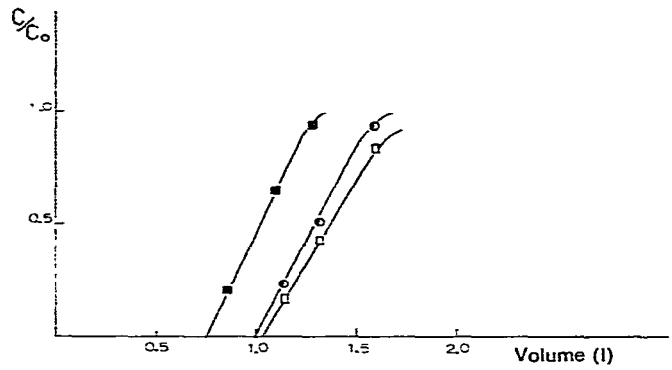

Fig. 5. Breakthrough curves of *m*-cresol (■), heptanoic acid) and *o*-cresol (□) on GCB column (1000 mg).

are reported in Table II. Benzene and methanol give the best distribution ratios for the recovery of the examined compounds from GCB; hence these substances can be recovered with benzene–methanol mixtures.

Table III shows that, while the recovery values with methanol agree with the distribution ratios, this is not the case with benzene. In fact even if the distribution ratios are favourable to benzene, the percentage recoveries are about 10–20%. However, if benzene–methanol mixtures are used, the results are in accord with the distribution ratio values. The disagreement in the case of benzene might be due to the water which coats the GCB and prevents benzene from coming into contact with the

TABLE II

ADSORPTION COEFFICIENTS IN GCB–LIQUID SYSTEMS

Amounts: GCB, 500 mg; liquid system, 100 ml; compound, 15 μg. A = Light petroleum (b.p. 40–60°C); B = diethyl ether; C = benzene; D = dichloromethane; E = methanol.

Compound	*Liquid system*				
	A	*B*	*C*	*D*	*E*
2-Chlorophenol	244	88	0	0	33
o-Cresol	82	44	0	0	47
m-Cresol	60	67	6	4	8
p-Chloro-*m*-cresol	276	265	13	10	22
2,3-Dichlorophenol	108	94	13	17	35
β-Naphthol	976	225	0	0	33
2,4,5-Trichlorophenol	467	244	22	17	38
2,4,6-Trichlorophenol	265	244	33	0	63
2,3,4,6-Tetrachlorophenol	445	225	27	22	137
m-tert.-Butylphenol	139	200	0	10	15
Heptanoic acid	27	41	30	22	0
Octanoic acid	33	53	27	27	0
Decanoic acid	33	44	17	38	0
Myristic acid	157	133	38	177	16
Stearic acid	371	139	47	326	58
Benzoic acid	340	464	67	164	100

TABLE III

RECOVERY OF MODEL ORGANIC COMPOUNDS FROM 1000 mg OF GCB USING DIFFERENT ELUENTS

A = 50 ml benzene; B = 50 ml benzene–methanol (2:1); C = 50 ml benzene–methanol (1:1); D = 50 ml benzene–methanol (1:2); E = 50 ml benzene–methanol (1:3); F = 50 ml methanol.

Compound	*Recovery (%)*					
	Eluent					
	A	*B*	*C*	*D*	*E*	*F*
2-Chlorophenol	28	88	74	92	91	71
o-Cresol	26	55	51	60	78	100
m-Cresol	19	78	84	90	96	91
p-Chloro-*m*-cresol	20	49	74	82	91	90
2,3-Dichlorophenol	25	50	81	92	90	89
β-Naphthol	0	57	98	102	100	29
2,4,5-Trichlorophenol	9	65	90	98	101	80
2,4,6-Trichlorophenol	8	48	61	79	95	101
2,3,4,6-Tetrachlorophenol	6	76	88	91	103	76
m-tert.-Butylphenol	6	22	33	55	84	101
Heptanoic acid	29	89	87	94	88	99
Octanoic acid	18	85	84	88	87	100
Decanoic acid	12	75	70	77	81	92
Myristic acid	16	85	76	79	65	63
Stearic acid	18	95	79	81	78	20
Benzoic acid	0	98	87	71	61	81

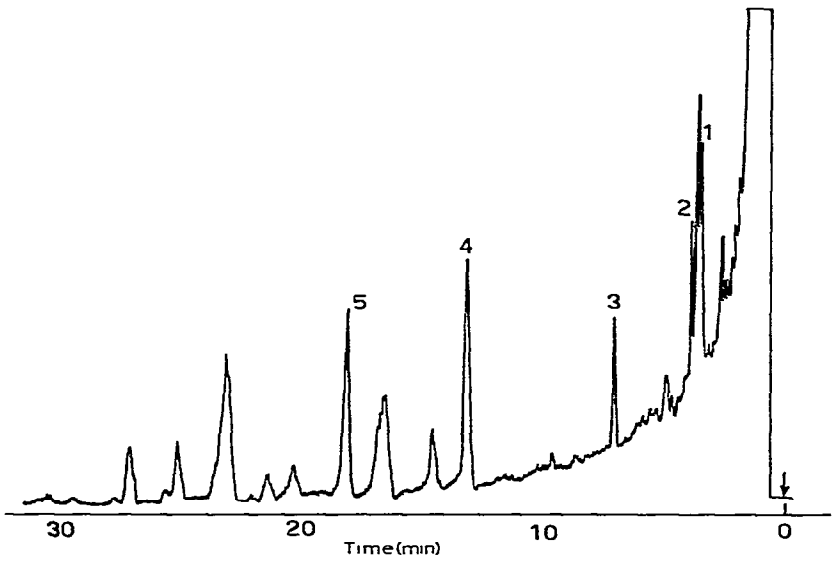

Fig. 6. Chromatogram obtained from human urine. Peaks: 1 = benzoic acid; 2 = lauric acid; 3 = myristic acid; 4 = palmitic acid; 5 = heptadecanoic acid (internal standard).

solid surface, whereas the presence of a small quantity of methanol may be sufficient to prevent the shielding of the water.

If we examine, for example, the behaviour of β-naphthol, whose distribution coefficient in methanol is 33, we find that is recovered only partially by this solvent, and in negligible quantity by benzene, even if the distribution ratio is 0. When a benzene–methanol mixture is passed through the column, the percentage recovery reaches 100%.

For the analyses of human urine and river water the amount of GCB and the volume of eluent were deduced respectively from the breakthrough values and from Table III. Fig. 6 shows a gas chromatogram obtained from human urine on a FFAP capillary column at 200°C with a carrier gas (hydrogen) flow-rate, $\bar{u}$, of 45 cm/sec. The concentrations obtained for the identified components were: benzoic acid, 10 μg/l; lauric acid, 6 μg/l; myristic acid, 14 μg/l and palmitic acid, 29 μg/l.

Fig. 7 shows the chromatogram obtained from river water by using the same column but different operating conditions: temperature, 190°C; carrier gas (hydrogen) flow-rate, $\bar{u}$ = 36 cm/sec. Four peaks were identified, two phenols and two fatty acids. The nature of the substances was confirmed by treating the samples with 0.1 *N* NaOH, followed by extraction with methylene chloride and chromatography of the extract. The identified peaks did not appear in the resulting chromatograms.

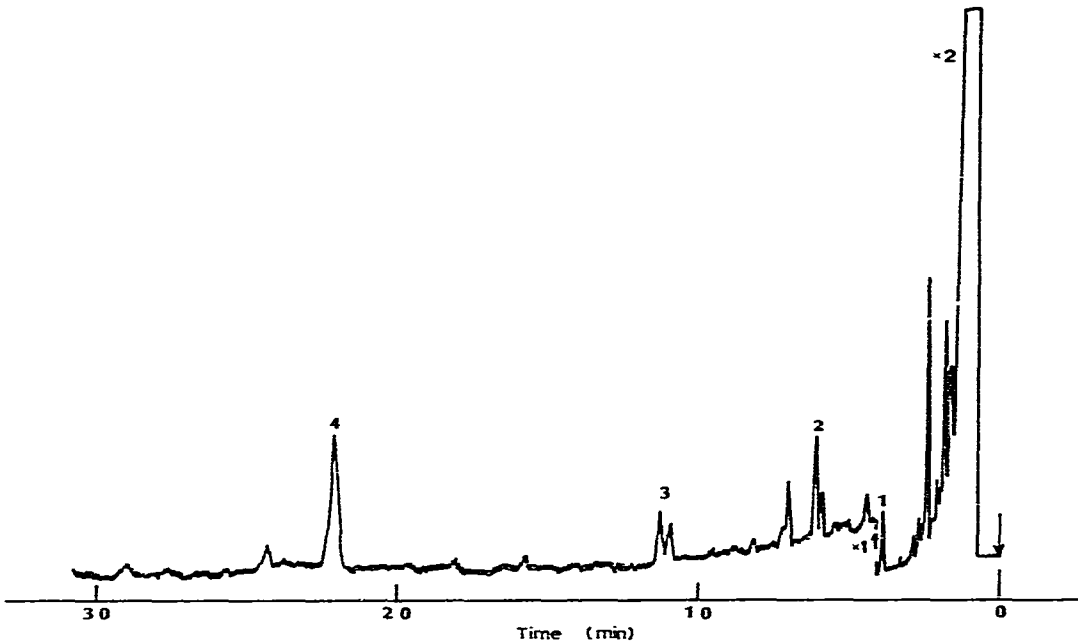

Fig. Chromatogram obtained from river water. Peaks: 1 = 2,4,6-trichlorophenol; 2 = *p*-chloro-*m*-cresol; 3 = myristic acid; 4 = palmitic acid.

CONCLUSIONS

The results show clearly that the recovery of organic acids by means of col-

umns of GCB adsorbent cannot be carried out without considering the nature of the substances to be recovered and their molecular structure.

In fact the organic acids differ considerably in solubility and in K_a values. Therefore the amount of carbon, the volume of the sample, the volume and composition of the eluent must be determined for each application.

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