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CHROMATOGRAPHIC DETERMINATION OF SOME TRACE ORGANIC IMPURITIES IN NATURAL AND WASTE WATERS WITH PRELIMINARY ADSORPTION TRAPPING

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SUMMARY

A technique of for the determination of trace amounts of butyl acetate in industrial effluents is suggested, based on preliminary adsorption trapping on grade TSVK-11a zeolite and gas chromatographic separation on columns packed with DC-550 and Carbowax 1500. The degree of extraction and enrichment were determined. The degree of butyl acetate extraction was studied as a function of the mass of zeolite and its particle dimensions and these characteristics were compared with the data obtained under similar conditions on the polymeric sorbents Chromosorb 102 and Polysorb I.

To determine herbicides based on substituted phenylureas (monuron, diuron, etc.) in natural water, high-performance liquid chromatography was used in combination with trapping on Chromosorb 102. The sorbate was analysed on a Partisil ODS column using water–acetonitrile as the mobile phase and a 254-nm UV detector.

INTRODUCTION

In recent years the requirements for water quality have been raised considerably and it is frequently necessary to monitor water contamination at levels of 10^{-5}–10^{-7} mg/l. In such instances the direct determination of impurities is almost impossible and preliminary enrichment of impurities is needed. Liquid extraction[1,2], evaporation[3,4] and freezing-out[5–7] are commonly used for this purpose. One of the most widely used and efficient techniques is adsorption trapping[8].

The adsorption trapping of butyl acetate and substituted phenylureas on a modified aluminosilicate sorbent and on copolymers of styrene and divinylbenzene was studied in this work.

EXPERIMENTAL AND RESULTS

Equipment

Concentration was provided in a volume burette of 5 mm I.D. packed with 0.5–1.0 g of a particular adsorbent. The water to be tested was pumped through the

packed bed by a Hoppler low-lift pump. A solution of butyl acetate in acetone was analysed on a Hewlett-Packard 5700A gas chromatograph equipped with dual flame-ionization detectors and a 1.8 m × 2 mm I.D. stainless-steel column. Results were processed using a Hewlett-Packard 3373B integrator. The eluate containing substituted phenylureas was investigated on an Altex 100 liquid chromatograph equipped with a 250 × 3.6 mm I.D. column and a 254-nm UV detector. Chromatograms were evaluated by means of a Hewlett-Packard 3385A microprocessor.

Determination of butyl acetate in industrial effluents

To isolate butyl acetate from water samples, a type TSVK XI-a zeolite was employed. This adsorbent was prepared by mixing a zeolite powder with 10% (w/w) of clay (from the Glukhov deposit), calcination of the mixture at 550°C and milling until the required range of particle dimensions was obtained. Some of the zeolite characteristics are listed in Table I. As can be seen, the zeolite produced is hydrophobic, and the adsorption of heptane is about 15 g per 100 g of the adsorbent. Hence the TSVK XI-a zeolite is suitable for the selective trapping of organics from water.

The procedure for the determination of trace amounts of butyl acetate in water was as follows. A 0.5-l water sample was pumped at a flow-rate of 15–20 ml/min through a glass volume burette (200 mm × 5 mm I.D.) packed with 0.7 g of TSVK XI-a zeolite of particle dimensions 0.40–0.63 mm. The adsorbed butyl acetate was eluted from the burette with 2 ml of acetone. The solution obtained was then separated on columns packed with 10% (w/w) DC-550 or 15% (w/w) Carbowax 1500. In order to increase the accuracy of the results obtained, correction factors (K, see Abbreviations) were determined, which took account of the loss of the ingredient during sample preparation (the degree of extraction). The capabilities of the technique were as follows: limit of detection, 0.01 mg/l; relative error of determination, $\leqslant 10\%$; degree of enrichment (see Abbreviations) with the maximum permissible water volume passed, 860; and adsorption capacity of TSVK XI-a with the minimum permissible amount of the adsorbent, 3000 ml/g (for comparison, the same characteristics obtained 60–80-mesh Chromosorb 102 were 1000 and 3000 ml/g, respectively).

To study the trapping properties of the zeolite, the dependences of K on the

TABLE I

CHARACTERISTICS OF TSVK XI-a ZEOLITE POWDER

Parameter	*Dimension*	*Value*
Silica modulus (SiO_2/Al_2O_3 molar ratio)		58.0
Particle dimensions	μm	0.5–2.0
Static capacity:		
Water at $P/P_s = 0.1$ (1.9 g/m³)	g per 100 g of adsorbent	4.0
Heptane at $P/P_s = 0.4$ (87.9 g/m³)	g per 100 g of adsorbent	14.4

TABLE II

K AS A FUNCTION OF THE ADSORBENT MASS IN THE TRAPPING COLUMN

Water sample volume, 0.5 l; butyl acetate concentration, 0.1 mg/l. S_x = standard deviation; V = coefficient of variation.

Sorbent mass (g)	*Chromosorb 102 (80–100 mesh)*			*Chromosorb 102 (60–80 mesh)*			*Zeolite TSVK XI-a (0.40–0.63 mm)*		
	K	S_x	*V*	*K*	S_x	*V*	*K*	S_x	*V*
0.70	0.943	0.019	1.98	0.999	0.053	5.34	0.901	0.014	1.59
0.35	0.924	0.027	2.91	1.024	0.025	2.48	0.892	0.013	1.44
0.15	0.911	0.015	1.64	0.683	0.058	8.44	0.866	0.063	7.22
0.10	0.872	0.026	2.96	–	–	–	0.468	0.035	7.45
0.07	0.612	0.023	3.83	0.415	0.052	12.60	0.450	0.081	18.00

TABLE III

K AS A FUNCTION OF THE SORBENT PARTICLE DIMENSIONS

Water sample volume, 0.5 l; sorbent mass in the column, 0.7 g.

Sorbent	*K*	S_x	*V*
Chromosorb 102 (60–80 mesh)	0.999	0.053	5.34
Chromosorb 102 (80–100 mesh)	0.943	0.019	1.98
Polysorb I (0.50–0.80 mm)	0.463	0.019	4.15
Polysorb I (0.25–0.50 mm)	0.622	0.069	11.10
Zeolite TSVK XI-a (0.63–1.00 mm)	0.851	0.040	4.76
Zeolite TSVK XI-a (0.40–0.63 mm)	0.901	0.014	1.59

TABLE IV

K AS A FUNCTION OF THE INITIAL CONCENTRATION OF THE BUTYL ACETATE IN A SAMPLE

Water sample volume, 0.5 l; sorbent mass in the column, 0.7 g.

Sorbent type	*Initial concentration (mg/l)*	*K*	S_x	*V*
Chromosorb 102 (80–100 mesh)	0.01	0.944	0.031	3.25
	0.10	0.943	0.019	1.98
Polysorb I (0.50–0.80 mm)	0.01	0.483	0.037	7.66
	0.10	0.463	0.019	4.16
	1.00	0.464	0.036	7.83
Zeolite TSVK XI-a (0.40–0.63 mm)	0.01	0.891	0.051	5.78
	0.10	0.901	0.014	1.60
	1.00	0.911	0.048	5.29

mass of the adsorbent in the column, on its particle dimensions and on the initial concentration of butyl acetate in a water sample (Tables II–IV, Fig. 1) were determined. The data were compared with the results obtained under similar conditions on the widely used polymeric sorbents Chromosorb 102 and Polysorb I. In Tables I–IV the values of K are menas of five replicate measurements.

As can be judged from the data in Tables I–IV, TSVK XI-a and Chromosorb 102 provide approximately equal efficiencies of butyl acetate trapping together with good reproducibility of the results: the degree of extraction is 90–99% and the coefficient of variation is within 1.5–8.0%. Polysorb I proved unsuitable as an adsorbent for trapping.

Determination of herbicides based on substituted phenylureas in natural water

As the gas chromatographic analysis of substituted phenylureas suffers from certain difficulties, in particular with the necessity to convert herbicide samples, as they are thermally unstable, into more stable derivatives[9,10], and with the impossibility of separating linuron, diuron, monolinuron, buturon and monuron[11], we have developed a technique of their determination using high-performance liquid chromatography.

In order to reduce the limits of detection, the impurities under study were preliminarily trapped on porous polymeric sorbents, such as copolymers of styrene and divinylbenzene (Chromosorb 102 and Porapak Q) and the copolymer of acry-

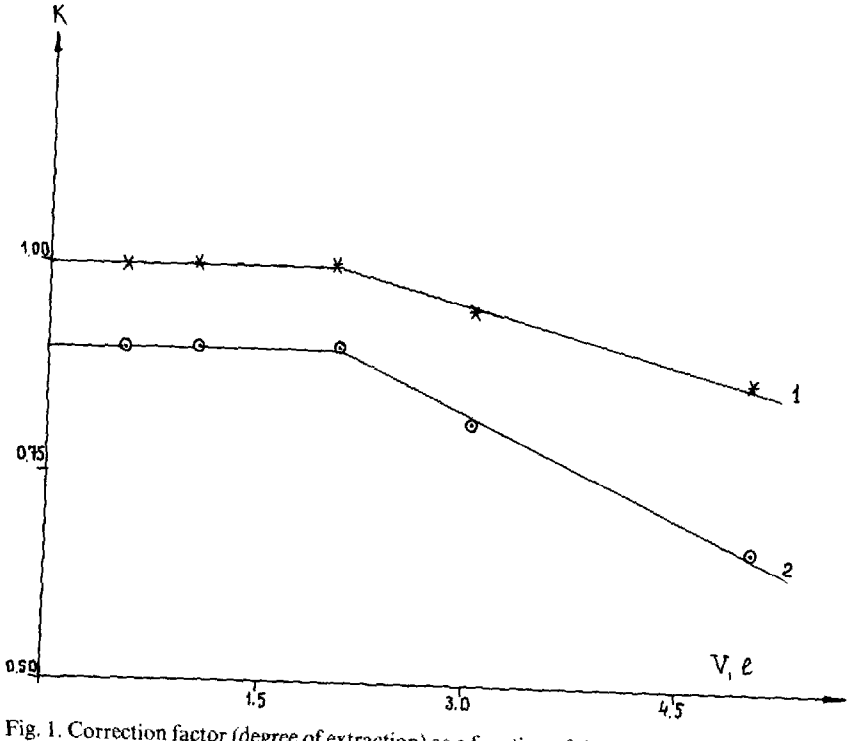

Fig. 1. Correction factor (degree of extraction) as a function of the water volume pumped through trapping column. Mass of the adsorbent: 0.7 g. 1 = Chromosorb 102; 2 = TSVK XI-a zeolite.

lonitrile and divinylbenzene (Chromosorb 104); the best results were obtained with Chromosorb 102. The trapping column was a burette packed with 1 g of a sorbent, through which a water sample of 100 ml was pumped. The adsorbed substances were eluted with 3 ml of acetone. The solution of herbicides in acetone was analysed on a column packed with Partisil ODS (5 μm). Acetonitrile–water (100:30) was used as the mobile phase. The mixture to be analysed was injected with a 200-μl loop, the flow of the mobile phase being uninterrupted. The flow-rate was 1.5 ml/min.

The technique developed makes it possible to determine fenuron, dosanex, monuron, kotoran, linuron and diuron in water with a limit of detection of 10^{-4}–10^{-5} mg/l. With allowance for the maximum permissible water volumes passed through the trapping column containing 1 g of Chromosorb 102 (840 ml for monuron and 910 ml for diuron), the degree of enrichment is 280 and 310, respectively. The degree of extraction (K) of the above two impurities is as high as 74%.

On Partisil ODS, it was possible to separate a number of phenylureas (fenuron, dosanex, monuron, kotoran, linuron and diuron), the gas chromatographic analysis of which is difficult (Fig. 2a). The incomplete separation of the dosanex–monuron pair offered no difficulties in the qualitative and quantitative evaluation of the chromatograms. The separation appears to be improved by gradient elution: the mobile phase water–acetonitrile (100:23) is passed through the column for 7 min, then the ratio is varied (100:35) for 8 min (Fig. 2b). The retention times and resolution for the substances under study are given in Table V. It also gives the limits of detection that correspond to the direct injection of a substance into the column.

As mentioned above, adsorption trapping was used to enhance the sensitivity of herbicide determination. It was found that the degree of extraction is almost independent of the initial concentration (at concentrations of 1 mg/l and below). Maximum extraction was provided by Chromosorb 102 (74% for monuron and diuron) and minimum extraction (30% for the same substances) by Chromosorb 104. It seems evident that irreversible adsorption of substituted phenylureas occurs on the polar

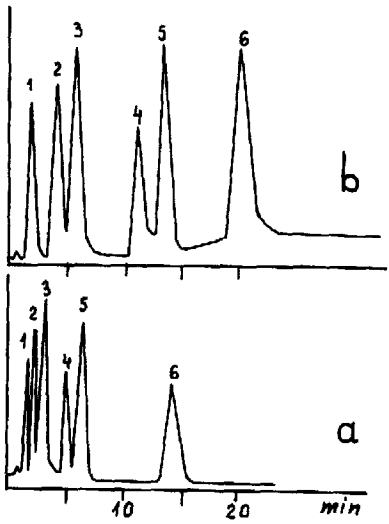

Fig. 2. Chromatograms of substituted phenylureas: (1) fenuron; (2) dosanex; (3) monuron; (4) cotoran; (5) linuron; (6) diuron. (a) Isochratic conditions; (b) gradient elution.

TABLE V

SEPARATION PARAMETERS AND LIMITS OF DETECTION OF SUBSTITUTED PHENYLUREAS WITH DIRECT SAMPLE INJECTION

Compound	*Retention time (min)*		*Resolution*		*Limit of detection (mg/l)*
	Isocratic conditions	*Gradient elution*	*Iscoratic conditions*	*Gradient elution*	
Fenuron	1.18	1.84	0.70	1.10	$1.5 \cdot 10^{-2}$
Dosanex	1.91	3.92	0.54	0.50	$0.84 \cdot 10^{-2}$
Monuron	2.51	5.34	1.06	1.87	$0.51 \cdot 10^{-2}$
Kotoran	4.52	11.22	0.59	0.67	$0.94 \cdot 10^{-2}$
Linuron	5.72	13.44	2.24	1.32	$1.50 \cdot 10^{-2}$
Diuron	13.31	19.46	—	—	$2.70 \cdot 10^{-2}$

Chromosorb 104. In our subsequent analysis of natural waters, Chromosorb 102 was used as the adsorbent in the trapping column and the degree of extraction was taken into account in the calculations.

CONCLUSION

A technique for the determination of butyl acetate in industrial effluents has been developed, which includes trapping on a new adsorbent, TSVK XI-a. As a result, it has become possible to reduce the limit of detection to 10^{-2} mg/l. The main characteristics of the zeolite employed have been presented. The degree of extraction with the TSVK XI-a zeolite was investigated as a function of its particle dimensions, of its mass in the trapping column and of the butyl acetate concentration in water samples.

A method has also been developed for the determination of substituted phenylureas (fenuron, dosanex, monuron, kotoran, linuron and diuron) in water using high-performance liquid chromatography. An increased sensitivity of determination is provided by herbicide trapping on Chromosorb 102. The limit of detection of the compounds being determined is 10^{-4} mg/l.

ABBREVIATIONS

K correction factor ($K = C_w V_w / C_e V_e$);
O degree of enrinchment ($O = C_e / C_w = V_w K / V_e$);
C_w concentration of the substance under study in water (before enrichment);
C_e concentration of the substance under study in the eluate (after enrichment);
V_w water volume, pumped through trapping column before appearing substance at column outlet;
V_e eluate volume.

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