Journal of Chromatography, 115 (1975) 383–390

CHROM. 8661

THE EXTRACTION AND RECOVERY OF PHTHALATE ESTERS FROM WATER USING POROUS POLYURETHANE FOAM

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(Received March 18th, 1975)

SUMMARY

Porous polyurethane foam has been successfully used to remove some phthalate esters from water at the parts per million level. A variety of foams was tested, as well as coated foams, under flow and under static conditions. The mechanism of absorption was investigated.

INTRODUCTION

There has been much interest in recent years in the analysis for and removal of such environmental contaminants as polychlorinated biphenyls (PCBs), pesticides, and organochlorine insecticides[1]. Evidence of the ubiquity of phthalate esters, commonly used as plasticizers, has been reported by Junk *et al.*[2] who found that the phthalates are eroded from synthetic polymer tubing, to which they are added in quantities of up to 40 % (w/w), by materials passing through the tubing. Similar results have been reported by Rubin and Jaegar[3–5], and, while the phthalates have a low order of acute toxicity[6], evidence of more subtle toxicity was found in tests with rats, with the possibility of many serious effects. Because they pose a threat to the environment, a study of methods for their monitoring and removal was undertaken in this laboratory.

Of the conventional methods for the removal of dissolved organic contaminants from water, adsorption on activated carbon[7], and extraction with organic solvents[8] present many problems. Activated carbon is efficient in the removal of organics, but the recovery of adsorbed material is unreliable and usually incomplete. A further complication is the possible destruction of the adsorbed material by chemical oxidation or bacterial action. Solvent extraction is usually done on a multiple extraction basis, necessitating concentration of the resultant large volume of solvent. This can mean a loss of some of the extracted material by evaporation, and interference in the analysis from impurities already present in the solvent at low concentration[9]. Reversed liquid–liquid partitioning was employed by Ahling and Jenson[10], who passed the contaminated water through Chromosorb W coated with *n*-undecane and Carbowax

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[*] Holder of a 1967 Science Scholarship from the National Research Council of Canada.

4000. Pre-treatment with a flocculating agent, aluminum sulfate, was necessary for water with a high particle content, and recoveries were not always 100%.

The Amberlite XAD series (Rohm & Haas) has been successfully used by several groups[2,11–13] for the removal of dissolved organic compounds, but again concentration of a large amount of solvent is a necessary step[13].

Recently Ahnoff and Josefsson[14] developed and patented a method for continuous liquid–liquid extraction of water based on mixed-settling. Water is continuously drawn through a cylinder under vigorous mixing with a lighter-than-water organic solvent, which remains at the centre of the vortex created by the mixing. The water is drawn off through a side outlet at the bottom of the cylinder. As no solvent is lost, this method eliminates the need for large volumes of fresh solvent. A flow-rate of no greater than 20–35 ml/min is usually necessary to establish an equilibrium distribution between the aequeous and organic phases.

Gesser *et al.*[15] used a column filled with polyurethane foam plugs to remove PCB from water at the ppb* level, with flow-rates of 250 ml/min. The average recovery on extraction of the plugs with a small amount of organic solvent was 94%. Uthe *et al.*[16] have successfully used polyurethane foam plugs coated with various chromatographic greases to extract organochlorine insecticides from water at the ppb level, with 97–100% efficiency. Flow-rates of 250 ml/min were again satisfactory except in the case of suspensions in solution, where it was lowered to 30 ml/min.

In this paper, the removal of phthalate esters from water with coated and uncoated polyurethane foam is reported. The trends in the percent recovery of a homologous series of phthalate esters led to an investigation of the mechanism of absorption under flow and static conditions. These findings are discussed along with some of the problems previously encountered by Gesser *et al.* and by Uthe *et al.*

EXPERIMENTAL

All analyses were done on a Hewlett-Packard 402 gas chromatograph equipped with a ^{63}Ni detector operating in the pulsed mode. A glass column packed with 60–80 mesh Chromosorb W DMCS, coated with 3% OV-17 as stationary liquid phase was used in all tests.

Porous polyurethane foam was obtained commercially as plugs (38 × 15 mm), and as 50-mm thick sheets, from which plugs (50 × 38 mm and 50 × 15 mm) were cut. Foam plugs were soxhleted in acetone for 4–6 h and stored in a glass jar prior to use. The different types of foam used are listed in Table I.

TABLE I

DENSITIES OF THE FIVE TYPES OF FOAM USED

Foam	*Density (g/ml)*
A	0.030
B	0.019–0.022
C	0.047
D	0.040
E	0.011

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* Throughout this article, the American billion (10^9) is meant.

Plasticizers were taken from the "Chem Supply" plasticizer kit (Model PLZ-150; Chem Service, West Chester, Pa., U.S.A.), and used without further purification.

Hexane and acetone, distilled in glass, were obtained from Caledon Labs. (Georgetown, Canada), and used without further purification. Distilled water from the laboratory supply was re-distilled in an all-metal still, and stored in 2-gallon Pyrex bottles fitted with ground glass stoppers.

All glassware was cleaned with acetone and hexane; volumetric glass was dried under vacuum, other glassware was oven-dried at 150° overnight.

Anhydrous Na_2SO_4 was washed prior to use with acetone and hexane, about 10 ml of solvent per 2 g of solid, to remove trace contamination.

For a flow system extraction, foam plugs were pushed down an acetone-filled column (15 mm I.D.) with a 100-ml reservoir at the top, the foam plugs just touching each other, not compressed. The acetone was flushed out with about 300 ml distilled water, and the flow-rate set by adjusting a stopcock at the bottom of the column. When the water level was at the top of the foam plugs, the test solution (blank or spiked) was added. The flask which had contained the test solution was rinsed with 5 ml distilled water and this was added when the water level was again at the top of the foam column. This was followed by 100 ml of distilled water, then the column was allowed to run dry. For analysis, each foam plug was placed in a 20-ml ground glass syringe, squeezed to expel water and then extracted by taking up aliquots of solvent into the syringe and expelling the solvent and extract into a funnel of Na_2SO_4 (approx. 2 g, anhydrous) to remove water traces and thence into a 10-ml volumetric flask. Two 2-ml aliquots of acetone and three of hexane were used for each foam. A 4-μl aliquot of each solution was run on the gas chromatograph.

In the static experiments, an eccentric cam turned by a motor at 8.5 rpm depressed and released a plunger once per revolution, which squeezed and then released the foam plug placed in a beaker beneath the plunger. A glass lid with an opening in the centre to accomodate the plunger covered the beaker. In these tests, the larger foam plugs were used. The plugs were extracted as in the flow system.

Solutions of known concentration were analyzed as well as the unknown, and calibration curves based on peak height were used to determine the amount of phthalate recovered. Most experiments were done at least in duplicate.

RESULTS AND DISCUSSION

In preliminary experiments on the recovery of three of the most commonly used phthalates *viz.*, di-*n*-butyl phthalate (DnBP), di-2-ethylhexyl phthalate (DEHP), and di-*n*-octyl phthalate (DOP), one litre of water containing 0.1 μg of each of the phthalates was run through a column of three type A foam plugs at a flow-rate of 35 ml/min. One blank and two spiked solutions were run. The recovery of DnBP from spiked solutions I and II was 51 and 62%, respectively. However, neither DOP nor DEHP was recovered from either I or II. The lower recovery of DnBP, in comparison with complete recovery in later tests, was attributed to incomplete extraction of the foam plugs, in this case 3 ml of solvent per plug was used for extraction, while in later tests this was raised to 10 ml.

The inability of the foams to retain any DEHP or DOP indicated the possi-

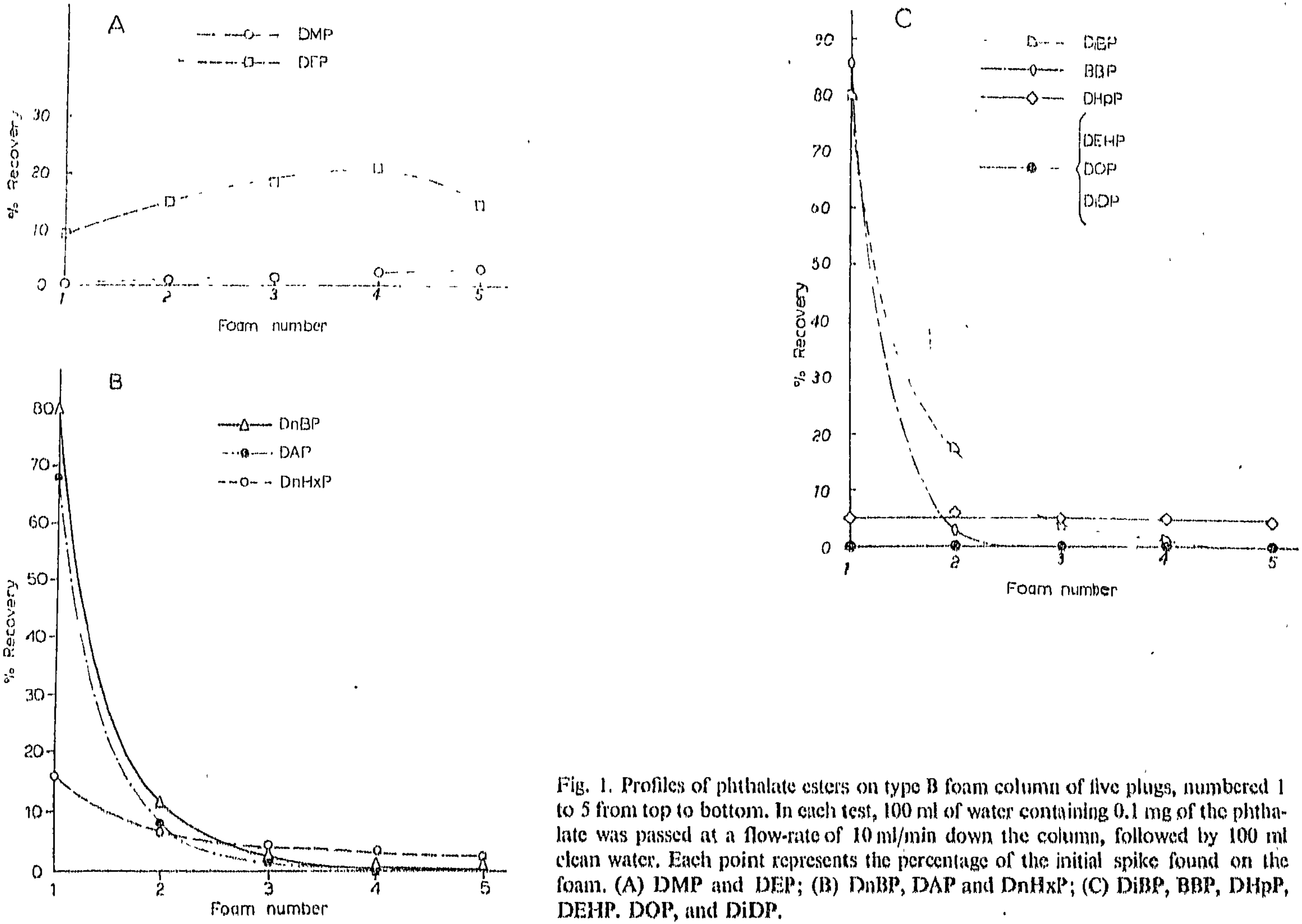

Fig. 1. Profiles of phthalate esters on type B foam column of five plugs, numbered 1 to 5 from top to bottom. In each test, 100 ml of water containing 0.1 mg of the phthalate was passed at a flow-rate of 10 ml/min down the column, followed by 100 ml clean water. Each point represents the percentage of the initial spike found on the foam. (A) DMP and DEP; (B) DnBP, DAP and DnHxP; (C) DiBP, BBP, DHpP, DEHP. DOP, and DiDP.

TABLE II

RECOVERY OF A SERIES OF PHTHALATE ESTERS UNDER FLOW CONDITIONS.

For each test, 100 ml of water spiked with 0.1 μg of each phthalate was run on a column of 5 foam plugs at 10 ml/min.

Phthalate	*Recovery (%)*	
	Type A	*Type B*
Dimethyl phthalate (DMP)	20 ± 5	8 ± 1
Diethyl phthalate (DEP)	84 ± 8	80
Di-*n*-butyl phthalate (DnBP)	102 ± 4	101 ± 1
Diisobutyl phthalate (DiBP)	93 ± 2	99 ± 2
Diamyl phthalate (DAP)*	85	80
Di-*n*-hexyl phthalate (DnHxP)	34 ± 2	33 ± 2
Di-*n*-heptyl phthalate (DnHpP)	23 ± 2	25 ± 2
Di-2-ethylhexyl phthalate (DEHP)	—	—
Dioctyl phthalate (DOP)	—	—
Diisodecyl phthalate (DiDP)	—	—
Butyl benzyl phthalate (BBP)	70 ± 3	86 ± 3

* One run only.

bility of steric limitations in the absorption process, the length of the hydrocarbon side-chains being the influential factor.

A series of tests on phthalates with side-chains varying in length from one to ten carbons was run with types A and B polyurethane foam. The results are shown in Table II.

Each of the five foams in a column was extracted into a 10-ml volumetric flask so that the distribution of the phthalates down the length of the column could be determined. The results are shown in Fig. 1.

The low recovery of DMP and DEP could be explained either by their slightly greater water solubility, and a lower affinity for the polymeric phase, by a higher rate of absorption and desorption, so that the rinse water actually washed them off the column, or by a higher rate of diffusion in the polymer, down and out of the column.

The phthalates with the longer side-chains are possibly being absorbed by the foam at a much slower rate, and therefore are not significantly absorbed by the foam on a single run at 10 ml/min.

It was shown in the following experiment that DEP (and presumably DMP) was transported in the water and not in the foam. Two foam plugs (type A) were spiked with 0.1 μg DEP in 1 ml acetone and air dried. A column of five plugs was prepared as usual and one of the spiked foam plugs placed in the column, 2 in. above the top foam. The column was washed through with 200 ml of clean water at a rate of 10 ml/min. The six plugs in the column and the second spiked plug were hen extracted with acetone and hexane into 10-ml volumetric flasks and analyzed. The results, shown in Table III, indicate that the DEP was washed off the first foam nd carried down the column in the water. Some of the DEP was lost in the drying step, when each plug was laid in a clean beaker to dry, because some phthalate-containing acetone may have seeped out.

This experiment did not differentiate between rate control and equilibrium ontrol, and so a series of static experiments to determine the equilibrium distribution

TABLE III

DISTRIBUTION OF DEP IN A COLUMN OF FOAM PLUGS

Foam plug		*Recovery (%)*
First spiked foam		20.5
Column foam no. 1		14
2		10
3		9.8
4		9.5
5		9.5
	Total	73.3
Second spiked foam		81

TABLE IV

RECOVERY OF A SERIES OF PHTHALATES UNDER STATIC CONDITIONS

In these experiments only large foam plugs were used: type B, 50 × 38 mm; types C, D and E, 50 mm cube. Each foam was extracted in a syringe as before, but with a total of 50 ml of solvent (approx. 10 ml acetone and 40 ml hexane), divided between two 25-ml volumetric flasks, for analysis.

Phthalate	*Time*	*Foam type*	*Recovery (%)*
DMP	10 min	B	46
	20 min	B	43
	1 h	B	44 ± 4
DnHxP	72 h	B	47 ± 10
	18 h	B	54
	2 h	B	65
	1 h	B	67
	1 h	C	37
	1 h	D	63
	1 h	E	25
DnHpP	72 h	B	70 ± 5
	18 h	B	87
	2 h	B	80
	1 h	B	68 ± 4
	1 h	C	56
	1 h	D	70
	1 h	E	45
DnOP	12 h	B	70 ± 1
	18 h	B	82
	2 h	B	90
	1 h	B	78 ± 2
	1 h	C	55
	1 h	D	85
	1 h	E	45
DnBP	1 h	B	100

was devised. In these tests, the duration and the type of foam plug used were varied as indicated in the results which are shown in Table IV.

Apparently both the length of the test and the type of foam are important in determining the percent recovery. Optimum conditions can be found for each phthalate ester. The densities of the five types of foam used in these tests are shown in Table I.

Phthalates are used as plasticizers because of their ability to penetrate between the polymeric chains neutralizing the secondary valence forces and decreasing the glass transition temperature of the system[14]. It has been shown by Bloch *et al.*[18] that in a dialysis using PVC as a membrane, plasticizers in the membrane formed complexes with the metal ions and carried them through the membrane by diffusion. The rate of diffusion was a controlling factor in the rate of dialysis. In the removal of phthalates from water with polyurethane foam plugs, the foam can be regarded virtually as a stationary liquid phase. The process is then one of liquid–liquid extraction and the efficiency of removal is dependent on the difference in solubility of the phthalate in the two phases, under static conditions. If the rate of diffusion of the phthalate away from the surface and deeper into the polymer network is high, the rate of desorption will be low, and recovery will still be good under flow conditions. If absorption–desorption is very fast, then in a flow system the compound will probably be washed off the column.

The absorption of intermediate-sized phthalates, notably DnBP on type B foam, are at optimum condiditions of rate and equilibrium distribution for 100% removal into the foam, in flow or static system.

Several experiments with coated foam plugs were tried (Table V) but the results differed little from those with untreated foams. The exception was DOP, of which 9% was recovered in a single run through five small foam plugs of 100 ml of 1 ppm, at a rate of 10 ml/min. As this was evenly distributed throughout the five foams, it seems that the DOP was dissolving in the oil at a slightly higher rate than in the uncoated polymer, and was not readily desorbed. It was not discovered whether the phthalate then penetrated the polymer or whether the oil was facilitating entry.

TABLE V

RECOVERY OF PHTHALATE ESTERS ON TYPE A FOAMS COATED WITH 5 mg DOW-200 SILICONE OIL PER PLUG

Coating procedure: see ref. 16.

Phtalate	*Recovery (%)*
DMP	13
DEP	70
DnBP	98
DAP	49
DOP	9.0
BBP	74

Previous work by Gesser *et al.*[15] and Uthe *et al.*[16] had shown that PCB and organochlorine insecticides can be removed from water with polyurethane foam. The CBs were removed almost entirely (94%) with untreated foams, but pesticide reoveries were only about 50%. Coating the foams improved the latter but in this case, nd with the DOP case above, the foam appears to act only as a solid support for the il. Recent work by Musty and Nickless[19] showed similar results, and after varying he flow-rates they concluded that DC-200-coated foam was more efficient than unoated foam for removing pesticides at high flow-rates as desorption was more diffiult. At low flow-rates, the uncoated foams were more efficient. The results here onfirm this as we observed a decrease in recovery on coated foams at low flow-rates.

Musty and Nickless describe the removal of pesticides by uncoated foam as a process of adsorption, which, when one considers the bulkiness of the compounds they dealt with, may be correct, and may also apply to the larger phthalates in a flow system. For smaller phthalates, or, under static conditions, all phthalates tested, the process is one of absorption.

CONCLUSION

Porous polyurethane foam has been successfully used to remove some phthalates from water at low concentrations. In the case of pesticides, the process of removal is more likely one of adsorption, so that coating the foam improves the total recovery. However, phthalates are removed by absorption, and depending on the size of the phthalate and the structure of the polymer, this may be rate controlled or equilibrium controlled.

Work on the control of selectivity of the foams by coatings and by use of different varieties of foam, as well as studies on the removal of air-borne phthalates, are presently being carried out in this laboratory.

ACKNOWLEDGEMENTS

We would like to thank Dr. C. G. Seefried, Jr., of the Union Carbide Corporation, South Charleston, W. Va., for his generous donation of two types of polyurethane foam, herein referred to as types C and D. We would also like to acknowledge support from the National Research Council of Canada.

REFERENCES

1 R. Edwards, *Chem. Ind.*, (1971) 1340.

2 G. A. Junk, J. Svec, R. D. Vick and M. J. Avery, *Environ. Sci. Technol.*, 8 (1974) 1100.

3 R. J. Jaegar and R. J. Rubin, *Science*, 170 (1970) 460

4 R. J. Rubin and R. J. Jaegar, *N. Engl. J. Med.*, 287 (1972) 1114.

5 R. J. Rubin and R. J. Jaegar, *Environ. Health Perspec.*, 3 (1973) 53.

6 C. P. Carpenter, C. S. Weil and H. F. Smythe, *Arch. Ind. Hyg. Occup. Med.*, 8 (1953) 219.

7 O. J. Sproul and D. W. Ryckman, *J. Water Pollut. Control Fed.*, 33 (1961) 1188.

8 S. Voerman, *Bull. Environ. Contam. Toxicol.*, 4 (1969) 64.

9 A. Bevenue, T. W. Kelley and J. W. Hylin, *J. Chromatogr.*, 54 (1971) 71.

10 B. Ahling and S. Jenson, *Anal. Chem.*, 42 (1970) 1483.

11 *Amberlite XAD-2, Technical Bulletin, IE-89-65,* Rohm & Haas, Ion Exchange Department, Philadelphia, Pa., 1972.

12 P. R. Musty and G. Nickless, *J. Chromatogr.*, 89 (1974) 185.

13 G. A. Junk, J. J. Richard, M. D. Grieser, D. Witiak, J. L. Witiak, M. D. Arguello, R. Vick, H. J. Svec, J. S. Fritz and G. V. Calder, *J. Chromatogr.*, 99 (1974) 745.

14 M. Ahnoff and B. Josefsson, *Anal. Chem.*, 46 (1974) 658.

15 H. D. Gesser, A. Chow, F. C. Davis, J. F. Uthe and J. Reinke, *Anal. Lett.*, 4 (1971) 883.

16 J. F. Uthe, J. Reinke and H. D. Gesser, *Environ. Lett.*, 3 (1972) 117.

17 R. Kosfield, in R. F. Gould (Editor), *Plasticization and Plasticized Processes*, American Chemical Society, Washington, D.C., 1956, p. 43.

18 R. Bloch, A. Finkelstein, O. Kedem and D. Vosfi, *Ind. Eng. Chem. Process Des. Develop.*, 6 (1967) 231.

19 P. R. Musty and G. Nickless, *J. Chromatogr.*, 100 (1974) 83.