THE UNIVERSITY OF MANITOBA

THE EXTRACTION AND RECOVERY OF PHTHALATES FROM WATER BY THE USE OF POLYURETHANE FOAM

BY

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Cologne*

In Kohln, a town of monks and bones,
And pavements fang'd with murderous stones,
And rags, and hags, and hideous wenches,
I counted two and seventy stenches,
All well defined, and several stinks!
Ye Nymphs that reign o'er sewers and sinks,
The river Rhine, it is well known,
Doth wash your city of Cologne;
But tell me, Nymphs, what power divine
Shall henceforth wash the river Rhine?

Samuel Taylor Coleridge

*"Selected Poetry and Prose of Coleridge", Donald A. Stauffer, ed., (The Modern Library, Random House, New York, 1951) p. 106.

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Abstract:

Open-pore polyurethane foam was successfully used to remove phthalic acid esters from water at the ppm and ppb level. The shape of the column profiles was found to vary with the length of the ester side chain, with the concentration of the phthalate, with the flow rate, and with the type of foam used. The effect of these parameters on the column profiles and on the efficiency of extraction and recovery was studied, and a two step absorption process was postulated.

Open pore polyurethane foam was also used successfully to remove phthalates from air at the ppb level, but attempts to remove polyvinylchloride monomer from air with the foam were unsuccessful.

Attempts to measure the relative surface areas of the foams by the adsorption of methylene blue dye were also unsuccessful.

The Extraction and Recovery of Phthalates from Air and from Water by the Use of Polyurethane Foam

Introduction

The history of man-made pollution of air and water goes back many centuries. The recent history of excessive and hazardous chemical pollution began with World War II, and the use of DDT. In the early nineteen fifties, organochlorine insecticides,(OCI), began to be marketed widely, but by 1956, reports of bird kills in Europe and America started to appear. These coincided with the new technique of coating cereal seeds with dieldrin, aldrin, and heptachlor— OCI used to protect the seeds from insects in the soil. A sharp decline in the raptor population was found, along with the discovery of the accumulation of OCI by fish.[1-12] In 1960, the British government established a "Toxic Chemicals and Wildlife" division, to study the effects of pesticides on wildlife.[13] In 1964, it was proven that the large fish kills in the Mississippi River each year, particularly in the late fall, were due to poisoning by endrin, another OCI.[14] The presence of endrin in the river was caused by run-off from agricultural areas, spraying of fields, and especially, improper treatment of waste discharged from endrin-producing companies situated along the river.

Public concern was aroused by a number of popular books which covered such topics as air pollution , water pollution, disappearing wildlife, garbage disposal, organic food and gardening, possible community action, government and industrial action or the lack therof, and personal survival kits in the case of disaster.[15-19]

Public concern also stimulated research into the hazards of toxic chemicals on the market, and the development of more sophisticated methods of monitoring and controlling the amount of pollutants in industrial waste effluents. The OCI and the polychlorinated biphenyls ,(PCB), presented a particularly troublesome problem because of the threat posed by the presence of very minute quantities, usually the sub-micro level, and their non-biodegradibility.

The over-all needs for pollution control can be stated generally as:

a) legislated or voluntary control of pesticide and insecticide application, with foreknowledge of their effects

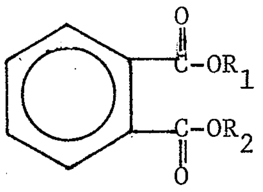
b) the means to monitor pollutant concentration in air and water and to remove them quickly and economically.

While investigating such problems, the presence of many other pollutants has been disclosed. Among those recently found are the phthalic acid esters, (PAE), largely used as plasticizers in the polyvinyl chloride industry.

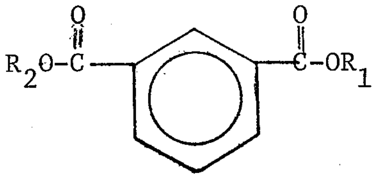
Phthalic Acid Esters

General:

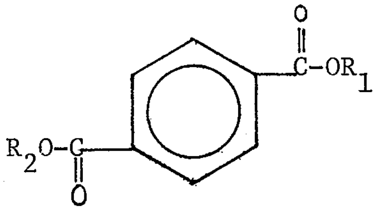
The three possible isomers of phthalic acid esters are:



phthalate



isophthalate



terephthalate

Phthalates are one of the major groups of compounds used as plasticizers by the polymer industry.[20,21] Plasticization is the process by which the plasticizing molecules penetrate between the polymeric chains, neutralizing the secondary valance forces, (Van der Waals), between the polymeric segments, thus increasing their mobility, lowering the degree of crystallinity, and lowering the glass transition temperature. Plastics which would normally be rigid at room temperature are thus made flexible. Even below the glass transition temperature, the solvent molecules (plasticizers) have been found to be mobile within the polymer cavities, as a liquid phase.[21] PAE are ideal plasticizers for polyvinyl chloride (PVC), as their structure, with long flexible aliphatic side chains, is very compatible with PVC. The lower molecular weight phthalates, (e.g.: R_1=R_2= methyl), are better able to penetrate the crystalline regions of PVC, but their higher vapour pressure and mobility results in a lesser tendency to remain within the polymer.[22] For PVC, the phthalates from di-n-butyl to di-n-octyl represent the optimum combination of size, shape, chemical composition, boiling point, diffusion rate,and compatibility.[20]

Uses:

PAE are added to PVC, which is rigid when pure, in amounts of about 60 to 70 parts per hundred parts polymer,(w/w), to impart flexibility and softness.[20] In the period between 1967 and 1973, they were produced at a rate of over one billion pounds/year. In 1972, about 90% of the seven million pints of blood used for transfusions in the United States were stored in plasticized PVC bags. Other uses include food wrap film and medical tubing. A general breakdown of the end use of phthalates and the millions of pounds for each item, in 1972, is shown in Table I, below.[23]

Non-plasticizer phthalates, such as those in insect repellent sprays, have a more direct access to the environment than those contained within a polymer matrix. However, reports within the last five years on the presence of phthalates in widespread and unexpected places[24,25,26] show that despite their low volatility and low water solubility, phthalates used as plasticizers have been gradually leached from their plastic matrices and are now distributed throughout the environment.

Table 1 : Uses of Phthalates

Uses		Millions of Pounds of PAE
construction:	wire and cable	185
	flooring	152
	swimming pool liners	20
	weather stripping	13
	window splines	10
	other	9
house furnishings :	furniture upholstery	90
	wall coverings	38
	house wares	30
	garden hose	15
	appliances	10
	other	20
food and medical :	food wrap film	18
	medical tubing	15
	closures	7
	intravenous bags	6
transportation:	upholstery and seat covers	80
	auto mats	15
	auto tops	12
	other	10

continued

Table 1 : continued

Uses		Millions of pounds of PAE
Apparel	: footwear	45
	outerwear	20
	baby pants	7
non-plasticizer uses : pesticide carriers, cosmetics, fragrances, munitions, industrial oils, insect repellent.		50
	Total:	877

Ubiquity of Phthalates

In 1970, Rubin and Jaegar[26] discovered and identified three unexpected materials which had accumulated in the plasma of the perfusion medium during experiments with isolated perfused rat liver. The first material was identified as uric acid. The other two were glycolylbutyl phthalate (GBP) and di-2-ethylhexyl phthalate (DEHP). The GBP was shown to be a metabolite of butylglycolylbutyl phthalate (BGBP), a plasticizer used in the PVC tubing of the perfusion apparatus. The DEHP, also a plasticizer used in PVC tubing, was accumulated by the the liver in unmetabolized form.

While analyzing water samples from the Mississippi River and the adjacent Gulf of Mexico for chlorinated hydrocarbon pesticides in May 1970, Corcoran[27] detected two phthalic acid esters, DEHP and BGBP. The concentrations were about 0.6ppm. The same materials had been found again in 1971. Using computerized gas chromatography-mass spectrometry for identification and high-speed, high pressure liquid chromatography for quantitation, Hites[28,29] found the di-methyl (DMP), di-ethyl (DEP), di-n-butyl(DnBP), and di-2-ethylhexyl phthalates in the Charles and Merrimak Rivers during 1972. Phthalate concentrations ranged from 0.88 to 1.9 ppb, depending on proximity to suspected sources and depth of sampling.

Thomas[30] used an ethylene glycol trap to collect phthalates from air at a municipal air sampling station. The ethylene glycol was extracted with hexane, and after cleaning the hexane extract on a Florisil column and eluting the phthalates with diethylether, GC and GC-MS analyses were performed. DnBP, DEHP, and BGBP were found in concentrations of up to 750 ng/m^3.

Wildbrett[31] reported the finding of a number of PAE in milk which was in contact with PVC tubing during processing. Several cleaning solutions were tested to study the degree of migration of the phthalates, but milk, with its high lipid content, was the most effective extracting agent.

Release of volatile constituents during the testing and flight of aerospace units,"outgassing", can be extremely detrimental to sensitive space experiments. While plasticized PVC materials are not included in any space craft, Colony and Gross[32,33] reported that phthalates are commonly found contaminants. They listed such sources as 1) contaminated wash solvents from the use of PVC containers, cap liners, or transfer tubing,2) use of vinyl gloves to handle critical experiments, 3) use of PVC tubing for purging of optics and for transfer of gases to tanks and experiments needing special atmospheres, 4) use of di-n-octyl phthalate,(DOP), or DEHP for treating filters, 5) use of PVC sheets to protect hardware during storage and shipping, 6) use of aerosol products contaminated with phthalates, 7) use of vinyl tape and adhesives containing phthalates, 8) wire insulation, 9) alkyd paints erroneously used on space craft and inside vacuum chambers, 10) dirty vacuum systems and systems using Octoil(DEHP) as pump fluid. Analysis of outgassing residues revealed the presence of many compounds, but phthalates were always among those found. A mirror which spent 31 months on the lunar surface was found to have retained phthalates and other contaminants despite the low pressure of the environment.

Mayer _et_ _al_.[34] and Stalling _et_ _al_.[35] reported the presence of traces of DnBP and DEHP in fish caught in various places in North America. Over 3,200 ng/g was found in some fish, and the accumulation of DEHP and DnBP by fish exposed to water containing 2.5 ug of PAE per litre was observed. A concentration factor of 13,400 times the water concentration, 0.1 ug/l was observed in scud after 14 days exposure. Other pathological and toxicological studies showed that after a dietary exposure of 50 or 100 ug/g of food, the mortality rate of fish fry before foraging began rose from a normal of 50% to a high of 88.5%. Altered calcium metabolism was indicated. Continuous exposue of water fleas (Daphnia magna) to 3ug DEHP/l significantly $(P<0.05)$ reduced reproductivity by 60%.

Acute Toxicity:

Krauskopf[25] recently reported on extensive studies on the acute oral toxicity and acceptable daily intake of phthalates. A few cases of accidental ingestion of phthalates by humans, at levels of about 1×10^{-3} of the single dose LD_{50} levels reported in the literature for rats, resulted in mild diarrhea, nausea, vertigo, keratitis, and toxic nephritis, but no long term after-effects. While the acute toxicity level and acceptable daily intake are in some cases as high as those of approved food additives, those levels do not reflect studies on subtle toxicological effects.

Shibko and Blumenthal[36], of the U.S. Food and Drug Administration, also reported low acute toxicity, while "no effect" levels in chronic toxicity studies in rats and dogs ranged from 65 to 1625 mg/kg body weight.They reported no unusual instances of carcinogenisis had been found. While stating that they did not expect any toxicological hazards from authorized levels of phthalates in food, they pointed out that this depended on the complete breakdown of the PAE to phthalic acid plus esters. Recent data shows that such universal metabolism cannot be assumed.[26,37,38].

Sub-Acute Toxicity:

In 1972, Rubin and Jaegar[26] reported the finding of DEHP in plasma which had been stored in PVC blood bags. At 4°C, the rate of extraction was 0.25±0.03 mg/100ml/day. The plasticizer was found in the lipid-containing and lipid-free plasma, but the red blood cells had only a minor amount. Seven out of twelve lung tissue samples, taken at autopsy from patients who had received stored blood, contained detectable amounts of plasticizer.

In 1973, Rubin and Jaegar[39] published the results of some tests on DEHP and other plasticizers, showing subtle toxicological effects. The presence of DEHP in the blood of test mice was found to prolong the anesthetic effect of hexobarbital,possibly by decreasing the rate of disappearance of the test drug from the blood stream. A similar effect has been observed in the case of OCI and PCB when administered with hexobarbital,[39,40] and was found to be related to altered enzyme metabolism in the liver. They also observed decreases in two behavioral performances, and, depending on the schedule of administration of the phthalates, either stimulation or inhibition of the clearance of foreign particles injected into the blood stream. At concentrations of 0.4ng/100ml,(equivalent to that found in human blood after one to two days storage in PVC bags), DEHP was lethal to beating chick embryo heart cells maintained in tissue culture. Finally, they reported that there was a highly significant correlation between the formation of micro-emboli,((micro aggregation of platelets), in stored blood and DEHP content in the PVC storage bags. Because micro-emboli can cause occluding of the capillary beds of the transfusion recipient, their presence indicates a deterioration in the quality of the stored blood.

Dillingham and Autian[41] administered intraperitoneal doses of six phthalates to pregnant rats at levels 1/10, 1/5, and 1/3 of the acute LD_{50}. (Acute LD_{50}- see Appendix A) Dosages of DOP and DEHP were 5 ml and 10 ml/kg. No change in fertility was observed. However, embryo-fetal toxicity ranging from 0 to 98%, fetal malformation, from

0 to 100%, resorption of embryos, and decreased fetal size were observed. There was no apparent toxicity to the female rats. Dimethoxyethyl phthalate (DMEP) was the most teratogenic PAE tested. A study on the effect of DMP and DMEP on replicating and non-replicating cell cultures showed that while the non-replicating cells were almost unaffected by a 0.004 M (1 ppt) solution, the growth of replicating cells was significantly inhibited at this level. They suggested that the low <u>in vivo</u> toxicity of phthalates was related to the low maintenance rate of cell division of somatic tissue as compared to embryonic tissue.

A study conducted in the U.S.S.R.[42] on 147 workers at a PVC artificial leather and film industry, handling large amounts of plasticizers, revealed a high incidence of polyneuritis, (47 persons), increasing with increasing length of service. Thirty-two had autonomic-sensory polyneuritis, fifteen had both autonomic-sensory and motor-sensory polyneuritis. Three workers had polyneuritis and myelopolyneuritis (spinal). Five workers had cranial nerve polyneuritis. Other abnormalities such as lowered sensitivity to vibration (34%), elevation of the pain threshold (64%), absence or lowering of excitability of the vestibulosomatic reaction (78% of 81 persons), and of the olefactory receptors, and slightly lowered blood levels of platelets, leukocytes, hemoglobin, and blood colour were seen. In general, all symptoms increased with length of service.

Methods Used For Water Clean-up

General:

A variety of methods has been developed for the removal of persistent organic contaminants which are dissolved in water at trace levels. These range from the often used method of passing the water through an activated charcoal filter, on a large scale, to sophisticated extraction techniques possible only on the laboratory scale. A more detailed review of recent developments has been published by Fishman and Erdman.[43]

Adsorption on Activated Charcoal:

This technique is widely used in chemical preparations for purification of material, and is a simple and convenient method of removing organic contaminants from water.

Rosen and Middleton[44] reported the clean-up of 2000 litres of water with activated charcoal, and subsequent elution of adsorbed material with petroleum ether or chloroform. Clean-up efficiency was 91 to 100%, but recovery, after cleaning the eluate on alumina, removing solvent under vacuum, and analyzing with IR, was only 75 to 86%, on tests with spiked water.

Briedenbach[45] reported that recovery could be improved by extracting with chloroform for 35 hours.

A further complication, the destruction of the adsorbed material by chemical oxidation or bacterial action was reported by Sproul _et al_.[46]

Liquid-Liquid Extraction:

Batch extraction with hexane was used by Schafer *et al.*[47] to analyze river water from the Mississippi and Missouri Rivers. Over five hundred grab samples of 100 ml or 3.5 l size were taken. Each was extracted by shaking with 10 ml hexane, and the hexane analyzed by G.C. Fourteen pesticides were studied. The large number of samples required to obtain a reasonable accuracy rendered such a method impractical.

Kahn and Wayman[48] constructed an apparatus for the continuous extraction of non-polar compounds from water. The apparatus consisted of three identical chambers, connected in series. A single chamber consisted of a one litre Erlenmeyer flask, with a ground glass joint, to which was attached an adapter with a side-arm. The side-arm led to a round-bottom flask, containing organic solvent, while a condenser was attached to the top of the adapter. An inlet at the bottom of the Erlenmeyer and an outlet halfway up its side led to the other two chambers. The solvent in the round-bottom flask was heated, condensed, and dripped into a tube which passed through the center of the adapter to the bottom of the Erlenmeyer. The solvent then extracted the organic contaminants as it floated up through the water, forming an upper layer in the flask. Eventually this upper layer spilled back into the round-bottom flask via the side-arm. Twenty litres of waste effluent and 135 l of polluted river water were cleaned in this way. Analysis of the extracts by GC and IR, after concentration of the extracting solvent and clean-up on alumina gel, indicated that the organics were removed with 83 to 100%

efficiency, after two chambers had been passed. Residency time for the water in each chamber had to be about 45 minutes to achieve these values. Aldrin, isodrin, dieldrin, and endrin were recovered in quantities indicating initial concentrations of 7 to 350 ppb.

Drawbacks to the liquid-liquid extraction method, even with the conservation of the extracting solvent as described above, include a slow flow rate, ((0.5 -1.0l/hr), possible loss of extracted material during the cencentration step, and incomplete recovery in tests with added pesticides.

Another method for continuous liquid-liquid extraction was developed and patented recently (1974) by Anhoff and Josefsson,[49] based on the principle of mixed settling. Water was continuously drawn through a cylinder under vigorous mixing with a lighter than water solvent usually hexane, which remained at the centre of the vortex created by the stirring. The water was drawn off through a side outlet at the bottom of the cylinder. As no solvent was lost the need for large volumes of fresh solvent was obviated. The organic solvent could be analyzed directly on the GC. In laboratory tests the recovery was 83-96% for different pesticides and different pump rates. A flow rate of 25 to 35 ml per minute was found to be necessary to establish an equilibrium distribution between aqueous and organic phases.

Reversed Liquid-Liquid Partition:

Ahling and Jenson[50] removed PCB and OCI from water with a reversed liquid-liquid partition method, in which water is passed through a filter containing Chromosorb W HMDS-AW beads, 60-80 mesh, coated with an n-undecane-Carbowax 4000 monostearate mixture. The adsorbed organics were eluted with a small amount of petroleum ether. Flow rates of between 60 and 135 ml/min. were possible on a small (3 g of coated beads) column. Addition of a flocculating agent, aluminum sulfate, was necessary in the case of water with a high particle content. Recoveries ranged from 50 to 100 % for pesticides 80% for DDT, and 93 to 100 % for PCB. Recovery of contaminants at less than the part per trillion level were possible.

Aue, Kapila. and Hastings[51] used thick films of silicones chemically bonded to diatomaceous earth particles as column packing, to extract non-polar compounds from aqueous systems. Some OCI spiked at the part per trillion range were recovered successfully, but the types of compounds which could best be recovered from this system, and optimization of the system parameters were not investigated. The flow rates used were 50 to 55 ml/min., in a column 35 cm long by 1 cm ID, containing seven grams of packing.

Adsorption on Synthetic Resins:

The Amberlite XAD series of synthetic resins was first introduced by the Rohm and Haas Co. in 1966.[52] The XAD-1 resin is a polystyrene-divinyl benzene copolymer, produced in the form of hard spherical beads.[53] Its macro-reticular physical porosity, (0.35 ml pore per ml bead), uniform pore size distribution and high surface area (100 m^2/g, dry basis), which is non-ionic, account for its good adsorbant properties.[54] XAD-2 is a similar resin, but with higher surface area (330 m^2/g), and larger pore size (0.40-0.45 ml pore per ml bead). Both are supplied in a completely hydrated state, and both selectively adsorb hydrophobic organic compounds. They are reported to be particularly useful in separating from aqueous solution an organic compound which has both hydrophobic and hydrophilic parts. By changing the hydrophobic/hydrophilic balance, the extent of adsorption can be altered, and the substance eluted. For example, a weak acid is adsorbed in the acid form, and can easily be eluted in the salt form with a basic eluant.[54] The analagous collection and separation of organic bases has also been done.[55] XAD-1 and XAD-2 also have applications in the recovery of anionic, cationic, and non-ionic surfactants from aqueous solution, sugar decolourization, and decrease in the COD content of river surface waters.[53,54] Maximum flow rate for a column of 1 cm^2 cross section by 57 cm depth was about 0.15 ml/cm^3/min.

XAD-4[56], which is similar to XAD-1 and XAD-2, has smaller pores and a larger pores to solids ratio, (0.50 to 0.55 ml pore per ml bead), and a larger surface area (750 m^2/g). Musty and Nickless[57] found that 2 g XAD-4 in a 1 cm ID column was sufficient to remove insecticides from water at the ppb level, but PCB recovery was only about 76%. The flow rate used was 8 ml/min, volume of water, 1 litre. A flow rate of 32 ml/min could be achieved with vacuum, but recoveries were poor. Amberlite XAD-2, XAD-8, and XAD-12 were also tested in these experiments, but gave very poor results. The cause for the differences was not investigated.

XAD-7,[58] a cross-linked aliphatic resin, has a slightly more hydrophilic structure and can be used to adsorb certain solutes from non-polar solvents. Its porosity is 0.50 to 0.55 ml pore/ml bead, and surface area is 750 m^2/g.

Neiderweiser and Gilberti[59] used neutral polystyrene resin, Porapak Q, to adsorb indole derivatives from aqueous solution.

Absorption in Polyurethane Foam :

In 1970, Bowen[60] suggested the use of open-pore polyurethane foam as a selective absorbant for a number of substances from dilute aqueous solution: iodine, benzene, chloroform, and phenol from water; mercury II and gold III from 0.3 M hydrochloric acid; iron III antimony V, thallium III, molybdenum VI and rhenium III from 6M HCl; and uranium VI from saturated aluminum nitrate solution.

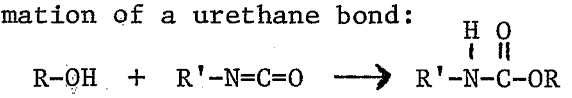
In 1971, Gesser *et al.*[61] used a column filled with open-pore polyurethane foam to remove PCB from water at the ppb level, with flow rates of 250 ml/min. The average recovery on extraction of the foam plugs with a small amount of organic solvent was 93-100%.

In this thesis, open-pore polyurethane foam plugs were used in columns as the stationary phase in separation studies. Much work has already been done in this area since Bowen's paper first appeared, both with untreated and treated foam. For this reason, polyurethane foam and the work done with it will be discussed in the next sections in more depth.

Polyurethane Foam

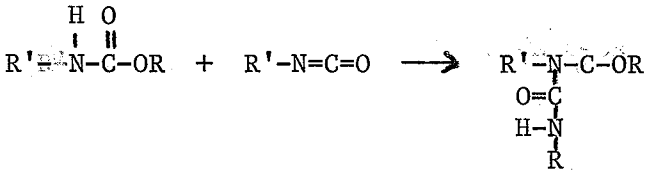
Formation, Structure, Properties[62] :

The reaction of an alcohol with an isocyanate results in the formation of a urethane bond:



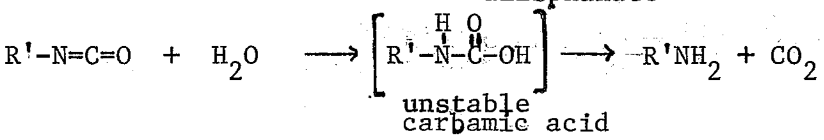
$$R{-}OH + R'{-}N{=}C{=}O \longrightarrow R'{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}OR \qquad (1)$$

The urethane is the central grouping: $[\ {-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}\ ]$. In polyurethane foam, a polyester or polyether of low molecular weight, usually 1000 to 3000, with terminal alcohol groups, is reacted with a diisocyanate, usually toluene diisocyanate (TDI), to form a polyurethane. Other reactions which are involved or can be obtained by the addition of other reagents, or by the use of a polyol with suitable side groups are:

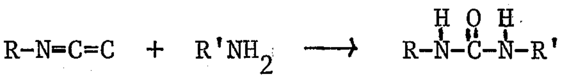


$$R'{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}OR + R'{-}N{=}C{=}O \longrightarrow R'{-}\underset{\substack{| \\ O=C \\ | \\ H-N \\ | \\ R}}{N}{-}C{-}OR \qquad (2)$$

allophanate

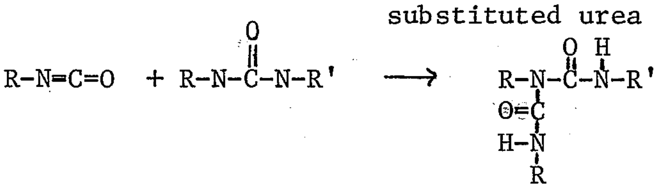


$$R'{-}N{=}C{=}O + H_2O \longrightarrow \left[R'{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}OH \right] \longrightarrow R'NH_2 + CO_2 \qquad (3)$$



$$R{-}N{=}C{=}C + R'NH_2 \longrightarrow R{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R' \qquad (4)$$

substituted urea



$$R{-}N{=}C{=}O + R{-}N{-}\overset{O}{\overset{\|}{C}}{-}N{-}R' \longrightarrow R{-}\underset{\substack{| \\ O=C \\ | \\ H-N \\ | \\ R}}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R' \qquad (5)$$

biuret structure

The product may be foamed in a number of ways[63]:

Chemical : vapourization of chemically produced water carbon dioxide from chemical reactions (e.g. equation (3)

nitrogen from reaction of diazo compounds

Physical : depressurization of dissolved gases

heat vapourization of low boiling liquids

Mechanical: air entrainment

formation of spherical interstices by use of soluble spherical fillers

formation of pores by filler removal

formation of pores by solvent evaporation and matrix shrinkage.

Lines of intersection of bubbles are called strands[64]; cell walls and windows are called membranes. Open-cell foams have at least two open windows per cell. Foams with no membranes, only strands, are called reticulated.

The foams may be flexible or rigid. The rigid foams usually have a higher cross-link density, and the polyol is generally of lower molecular weight,, with a higher degree of branching, than that used for flexible foam. Increased flexibility can be obtained by adding ethyl lactate to the incompletely formed polymer mix, to act as a chain stopper. This produces foams with long branches in the polymer chain, which seem to act as internal plasticizers.[65]

Chemically, polyurethane foams are quite stable and inert, being unaltered by water, 6 M hydrochloric acid, 4 M sulfuric acid, 2 M sodium hydroxide, 2 M nitric acid, glacial acetic acid, 2 M ammonia, benzene, carbon tetrachloride, chloroform, diethyl ether, acetone, isobutyl methyl ketone, ethyl acetate, isopentyl acetate, and alcohols.

Solvent resistance is increased at higher cross-link density, is unaffected by the type of aromatic diisocyanate used, and is decreased with the use of a large excess of diisocyanate.[66]

Applications of Polyurethane Foam

Polyurethane foam has been put to a wide variety of uses in the last few years, both as an active agent, i.e. unloaded, and as a support or matrix for the active agent(s), in experiments ranging from small scale laboratory separations to large scale oil slick cleanups.

Unloaded Foam:

In the first tests done by Bowen[60], the flexible foams were shown to be efficient absorbants for a number of compounds which can also be separated from water by liquid-liquid extraction with diethyl ether. Measurement of the surface area of the foams implied that one kilogram of foam should be capable of adsorbing 1 to 3×10^{-4} moles of adsorband. In practice, 1.5 moles of adsorband were taken up. This showed that a process of absorption, not adsorption was occurring.

Untreated polyurethane foam was used by Gesser *et al.*[61] to recover PCB from dilute aqueous solution, at the ppb level. The absorbed PCB was quickly eluted with acetone and hexane, the dried eluant concentrated, and analyzed by gas chromatography.

The Canadian Plant and Process Engineering Ltd.[67] investigated the use of flexible polyurethane foam as an oil filter to clean up oil spills in both fresh and salt water. At a flow rate of 10 gal/min/ft^2, (comparing favourably to rapid sand filtration, 3 to 4 gal/min/ft^2), and an input concentration of at least 100 ppm, flexible polyurethane foam was found to be 99 % effective in the removal of "Bunker C" oil, 70 % for marine diesel oil, 60 % for crude oil, and less than 5 % for phenol. The results for the phenol differ from those found by Bowen, but may be accounted for by physical and chemical variations in the foams. They did not attempt to regenerate the foam, but instead, recommended incineration as a method of disposal. Hydraulic performance and efficiency in separation of a number of compounds by foams with different elongation, resiliency, and density were studied. The best overall performance was found with the foam with code number 1835. Salinity had no effect on amount of removal, and a change in temperature, from 0 to 20°C did not alter hydraulic performance for flow rates of up to 26 gal/min/ft^2.

Braun and Farag[68], during experiments with loaded foams, found that gold thiourea complex is retained by unloaded foam, the amount retained decreasing with decreasing cell dimensions. The total uptake was similar to that for loaded foams, but retention was much stronger, and complete recovery of the complex was difficult. Similarly with palladium thiourea on unloaded foams, recovery of the Pd complex was not complete, even after washing with 300 ml of distilled water. The palladium complex on loaded foams was recovered entirely with 100 ml distilled water. In the loaded form, the foam acted as an inert support, whereas in the unloaded form, a different mechanism, involving the polymer itself, occurred.

Musty and Nickless[69] studied the recovery of PCB and OCI from water at the part per billion level, using six foams of different surface areas and bulk densities. They were able to achieve quantitative recoveries of OCI, and 40 to 99 % recovery of PCB by passing spiked water through the colunn at 100 ml/min. Both uncoated foams and foams coated with silicone oil (DC 200) were used. Some correlation seemed to exist between the amount of methylene blue dye adsorbed and per cent recovery of thirteen OCI. There was no correlation between per cent recovery and density.[70] Porosity and cell diameter were not given.

Lypka[71] used untreated foam to extract copper and cadmium acetylacetonates from dilute aqueous solution, about 50 ppb. Quantitative extraction and recovery was possible, as the copper II acetylacetonate was absorbed at pH 9.39, and eluted at pH 1.0.

Recovery of gallium and iron by untreated open-pore polyurethane foam has been studied extensively in this laboratory[72], with much success.

Bidleman and Olney[73] have used polyurethane foam to measure PCB, DDT, and chlordane levels in the Sargasso Sea atmosphere. Air was drawn into a sampling system consisting of a metal tube containing a glass fiber filter, and then a polyurethane foam plug, 15 cm long x 10 cm diameter. Sampling rates were 0.4 to 0.8 m^3/min. Concentrations of PCB, DDT, and chlordane measured were 0.21 to 9.4 ng/m^3, 0.01 to 0.09 ng/m^3, and 0.005 to 0.25 ng/m^3, respectively.

Bidleman and Olney[74] used a similar system with two foam plugs, 3.5 inches in diameter, in an aluminum cylinder, preceded by a glass fiber filter, to sample high volumes of air. Glass beads coated with PCB were placed in a dish in front of the collection system to serve as a known source of contaminants. Air was drawn through the system with a pump. Collection efficiency of PCB was about 90 % for concentration levels of 0.22 to 0.65 ng/m^3 at flow rates of 0.57 to 1.13 m^3/min, and a total volume of 550 to 987 m^3 of air. Air samples at High Point, Bermuda, were also taken.

Gesser et al.[75] used foam plugs to replace carbon in a standard carbon adsorption metering apparatus, to monitor water for organics. River water and treated municipal drinking water were tested at flow rates of five to ten litres per hour. Total volumes of 1.425 l of river water and 1.790 l of municipal water were tested. The foams were extracted with hexane, which was concentrated to 5 ml for for GC analysis. Estimated concentration of impurities was 0.005 to 0.010 ppb.

Loaded Foams:

A variety of physically immobilized reagents and extractants have been coated onto or soaked into the foams to improve specific extraction systems.

Uthe, Reinke, and Gesser[76] coated porous polyurethane foam with a number of different chromatographic greases and oils in an attempt to improve the recovery of pesticides. Dow Corning silicone oil, DC 200, gave better than 90% recovery in all cases, for solutions spiked at 1 ppb in 1 liter of water, with flow rate, 250 ml/min. In the case of soil suspensions, the flow was lowered to 30 ml/min. OV-25 and OV-225 gave very poor results; SE-30, QF-1, and DEGS were also poor, especially for aldrin and the DDT group.

Uthe, Reinke, and O'Brodovich[77] studied the utility of the DC-200 coated foams under field conditions by attaching the foam plugs to the bottom of a wooden float with three-inch plastic tagger tails, and placing them a) in an industrial harbour and b) in a river in an agricultural market gardening area. Apparantly only the outer part of the cylindrical foam plugs equilibrated with the surrounding water, since there was very little flow through the centre of the plugs. Water monitoring was found to be simple and reproducible.

Musty and Nickless [69] investigated the recovery of OCI and PCB with coated and uncoated foams at the ppb level. The coating used was DC-200. Recoveries were similar to those found by Uthe, but on varying the flow rate, it was found that at 10 to 30 ml/min, the uncoated foam gave better recovery, while at 250 ml/min, the coated foam was more efficient. They concluded that desorption was more difficult from the coated foam. Over a pH range of 6 to 9, no change in recovery was found.

Braun and Farag [78] used small foam cubes and cylinders as a solid support for tri-n-butyl phosphate (TBP) in reversed phase partition chromatography. Uptake of TBP, when the foams were equilibrated in it, was 2 ml/g., which compared favourably with Kel-F, at 1 ml/g. $PdCl_2$ and $NiCl_2$ could be separated by passing a feed solution of 1 ml of 1 mg/ml $PdCl_2$, 1 ml of 1 mg/ml $NiCl_2$, and 10 ml of 0.1 M perchloric acid with 3% thiourea and 1% sodium perchlorate through a column of these foams. The $PdCl_2$ formed a complex with the thiourea and was retained by the foam, while the $NiCl_2$ passed through without any measureable retention.

This system was later extended by Braun and Farag [79] to include bismuth. An additional 1 ml of 1 mg/ml of bismuth perchlorate was included with the feed solutions of $PdCl_2$ and $NiCl_2$. This was followed by 3 ml of 0.2 M perchloric acid with 6% thiourea and 2% sodium perchlorate. Elution was easily achieved with 0.1M perchloric acid containing 3% thiourea and 1% sodium perchlorate for Ni, 0.5M perchloric acid for Bi, and water for Pd. Elution at high flow rates did not affect efficiency. It was concluded that mass transfer rate was high both at the surface of and within the stationary phase, and therefore was not a limiting step.

Finely divided tetrachloro-p-benzoquinone, (chloranil), was prepared in polyurethane foams by Braun *et al.*[80] One or 3 g of chloranil was dissolved in 50 ml benzene and added to a 3 gm piece of foam, in 10 ml aliquots, with drying between additions. The column packed with these foams was then reduced with a 100 ml wash of 0.2NNaascorbic acid, and used in the redox reduction of Ce(IV), Fe(III), and V(V). The lower loaded foams presumably had chloranil in a more finely divided state, as their efficiency was much higher. In this case, the foam's only usefulness was its unique structure as a solid support.

In a system analgous to the TBP loaded foams, Braun et al.[81] prepared foams coated with tri-n-hydroxylamine hydrochloric acid for the separation of Ni and Co. Nickel was not retained by the column, while cobalt was retained and then eluted with 1.0 M HCl.

Braun and Farag[81] used the TBP treated foams for the separation of $AuCl_3$, as the gold thiourea complex, from interfering chemicals eg. Zn, Co, Ni, Fe, Cu, Sb,Bi, and Pd, and for the concentration of gold from dilute solutions. Uptake was fast and,regardless of the nature of the interfering chemicals, whether non-interacting, weakly interacting, or strongly interacting with thiourea, suitable eluting solutions for separation and concentration were found. Again, the foam acted mainly as a solid support.

Braun *et al.*[83] separated iron from copper, nickel, and cobalt in the TBP•HCl system. It was found that the distribution of the metal ions between the TBP•HCl on the foam and the water-HCl phases depended on the concentration of HCl in the system, and that the optimum concentration of HCl was close to that for ordinary liquid-liquid extractions.

In a study on the extraction of the gold-thiourea complex[68], (see "Unloaded Foams"), both TBP-loaded and unloaded foams were tested. While the unloaded foam retained about the same amount of the complexes of Au and Pd as the loaded foams, the subsequent extractions differed. The extraction of the loaded foam was similar to that of Voltalef powder coated with an equivalent amount of TBP. As Voltalef is known to be inert by itself, this substantiates the theory that in the loaded state, the foam acts only as an inert support.

Braun and Farag[84] then used polyurethane foam as a universal matrix for trace element preconcentration. A solvent, usually a plasticizer such as α-di-nonyl phthalate or di-n-octyl phthalate, was immobilized on the foam, and selective chelating agents were then dissolved in the foam. Zinc dithizonate, dissolved in α-di-nonyl phthalate, was used for the collection of silver and its separation from lead and copper.

Dithizone and diethyldithiocarbamate foams were used by Braun and Farag[85] for collection of trace amounts of mercury.

Braun and Farag[86] also prepared foams with chromogenic organic reagents dissolved in α-di-nonyl phthalate by equilibrating the clean dry foams in a solution of the reagent and phthalate. These were used for qualititative analysis of zinc, lead, copper, and cobalt at concentrations of less than 1 ppm. Only one or two ml of the metal solutions was required, under static conditions. The degree of colouring, compared to a colour scale from standard serial dilutions, was used as a quantitative measure. Rough quantitative measurements were also made by passing the dilute solutions through a column of treated foams and comparing the length of the coloured zone with that of standard solutions. These "Chromofoams" have now been patented by Braun and Farag. The mobility of the plasticizers within the polymeric network is credited with the rapid equilibration between the metal ions and the organic solution.

Chemically Altered Foams:

Braun et al.[87] prepared chemically altered foams for ion exchange. First, a heterogenous foam was prepared by adding styrene and an initiator to polyurethane foam. The foam product was then chloromethylated, and then aminated with diethylaminoethanol to yield an anion exchanger. Radiation grafting of metacrylic acid to polyurethane foam gave a weak carboxylic ion exchanger. Finely ground Varion KS resin was occluded into polyurethane during the foaming process, to produce a heterogeneous cation exchange foam. Finely divided silver sulfide[88] was precipitated in situ in polyurethane-Varion KS foam by first shaking the foam in $AgNO_3$, then washing with Na_2S. The silver sulfide foams were used for isotope exchange separations.

Mazurski, Gesser, and Chow[89] prepared sulfide treated foams by subjecting clean dry foams to an electric discharge in an H_2S

filled chamber. These foams were used for the removal of trace amounts of mercury in water, over a concentration range of 4.0 ppm to 4×10^{-4} ppm of mercury, at a flow rate of 40 ml/min. The mercury was recovered by soxhleting the foams in 2 M HCl. Saturation was observed on passing two 100 ml aliquots of 4.0 ppm through the foams.

Chromatography Supports- Rigid Foams:

Ross and Jefferson[90] prepared rigid open-pore polyurethane foam in situ for gas-solid, gas-liquid, and liquid-liquid chromatography. The rigid foam was in the form of micro-spheres, with interconnecting voids of 1 to 10 microns width. This structure was achieved by dissolving the pre-polymer mix in an inert solvent which was flushed out after gelation. A stationary liquid phase could be included in the pre-polymer mix, or added after polymerization, in a volatile solvent.

Lynn[91] studied the effect of the (-N=C=O)/(OH) ratio on gel formation and the range of excess free (-N=C=O) or (OH) groups which could be obtained. The physical properties and column performances were studied and a large number compounds separated with them.

Ross[92] has recently published a review of the uses of rigid open-pore polyurethane foam as a chromatographic medium prepared in situ for gas or liquid chromatography.

Biological Applications:

In 1965, Bauman and Goodson[93] used polyurethane foam as a support for a starch gel containing horse serum cholinesterase. These foams were placed between two platinum gray electrodes and the enzyme activity monitored electrochemically. It was suggested that they could be used as monitors of enzyme inhibitors.

In 1967 Bauman *et al.*[94] used these foams successfully to monitor enzyme inhibiting air pollutants.

Goodson extended this work[95] by adsorbing the cholinesterase on $Al(OH)_3$ before preparing it in the starch gel. He was able to detect low levels of pollutants in air and water. This method increased the lifetime of the enzyme foam.

Evans[96] coupled reticulated polyurethane foams with antibodies for the immunological binding of erythrocytes, thus separating them from myeloid and lymphoid cells, with which they occur naturally. The polyurethane foam had a polyester, not a polyether, backbone.

Plasticizer and Diffusion Studies

Bloch et al.[97] introduced a new method of metal ion separation by dialysis through high specificity membranes. Polyvinyl chloride plasticized with aliphatic or mixed aliphatic-aromatic phosphate esters: tri-butyl phosphate (TBP), cresyl di-butyl phosphate (CDBP), dicresyl butyl phosphate (DCBP), separated uranyl nitrate from an acid feed solution containing uranyl, iron, aluminum, and nitrate ions. Going from TBP to DCBP, membrane lifetime was increased, because of a slower erosion of DCBP from the membrane. Failure of a membrane was due to plasticizer elutriation, not pinhole formation. At membrane failure the PVC became a hard, totally impermeable film, but total selectivity was maintained up to that point. The latter was due to selective solubility of a metal-ligand complex in TBP in the membrane phase, followed by diffusion controlled transfer through the membrane.

Lal and Christian[98] prepared PVC with dithizone dissolved in di-pentyl phthalate as plasticizer. The membrane was mounted on a probe filled with 10^{-3}M lead nitrate solution. Lead dithizonate chelate then formed in the membrane. The probe was used as an electrode, the reference electrode being calomel dipped in 10^{-3}M lead nitrate solution. This membrane was permeable to a number of cations and anions, and enabled the authors to measure precipitation, and chelometric, redox, acid-base, and non-aqueous titrations potentiometrically.

Jagur-Grodinski et al.[99] investigated the mechanism of this selective permeation of ions through "solvent polymeric membranes" for the uranyl nitrate system. Using NMR and fluorescent probe techniques, they measured the self-diffusion rate of DCBP in the PVC membrane, and compared this to its mobility in the presence of uranyl nitrate. The results indicated that the DCBP acted both as a plasticizer and as a complexing agent. A uranyl complex, $(DCBP)_2UO_2(NO_2)_3$ formed at the membrane surface, and then diffused through the membrane as an entity. There was no evidence of a site-to-site exchange in which the uranyl nitrate would move in a series of jumps from one fixed DCBP site to another.

All this is indicative of the general fluidity and mobility of plasticizers within a polymeric membrane. Braun and Farag[86] noticed it in the rapid equilibration achieved with the reagents in plasticized foams, and in the "Chromofoams". Different mobilities were observed with different plasticizers.

PVC plasticization always involves the addition of large quantities of plasticizer[20], usually 60 to 70 parts per 100 parts polymer. At low concentrations , the effect of the plasticizer on the PVC is to make the system more rigid. Horsley[100] found that the small amount of plasticizer freed the molecular segments just enough to allow re-orientation into a more crystalline order. The higher concentrations of plasticizer redissolve these crystallites.

Polyurethane foam, the polymer dealt with in this thesis, is already above the glass transition point at room temperature. All foams used were flexible to varying extents. Plasticization _per se_ is never involved in commercial foams, though experimental loading with plasticizers has been done for specific purposes. No "antiplasticization" effects have been reported. It can probably be assumed, then, that even at low concentrations, the plasticizers would remain highly mobile in the polyurethane foam network, and that this mobility would decrease with increasing molecular size.

Basis for Research Subject

The purpose of this thesis was to investigate the possibility of removing phthalic acid esters from aqueous systems at the micro and sub-micro concentration level by absorption into open-pore polyurethane foam. A variety of foams was tested, both coated and uncoated. In the course of this research, certain trends in the per cent recovery of the phthalates led to an investigation of the mechanism of absorption, and some possible explanations will be discussed.

Removal of air-borne phthalates and of air-borne vinyl chloride monomer by polyurethane foam was also studied.

Some preliminary studies into the removal of copper and manganese from water with polyurethane foam, and subsequent analysis of the Cu and Mn on the foam by ESR, were also done.

Some attempts to measure the surface area, both by absolute measurement and by relative area determination, were done, but were unsuccessful.

Experimental

Apparatus and Chemicals:

Hewlett Packard 402 High Efficiency Gas Chromatographic

Varian E-3 Electron Paramagnetic Resonance Spectrometer

Beckman DK-2A Ratio recording spectrophotometer

Hamilton 5 μl syringes , no. 84800; 10 μl syringes, no. 84802

"Pressure-Lok" 5 μl and 10 μl syringes, Precision Sampling Corp. , Baton Rouge, LA , U.S.A.

Phthalic Acid Esters, (except for DnHxP and DnHpP), "Chem Supply" plasticizer kit, model no. PLZ-150, Chem. Service Inc.

DnHxP- prepared by Mr. M.J. Casey

DnHpP- donated by Dr. J.F.Uthe

Vinyl chloride monomer- Matheson of Canada Ltd., Whitby. Ont.

Sodium sulfate, anhydrous, reagent grade- Fisher Scientific Co.

Hexane, acetone, distilled in glass-Caledon Laboratories, Georgetown, Ontario

DOW-200 silicone fluid- Chromatographic Specialities, Brockville, Ont.

Heavy American Mineral Oil, Liquid Petrolatum U.S.P.- Rexall Drug Co. Ltd., Toronto, Canada; Los Angeles, U.S.A.

Distilled Water- laboratory supply, redistilled in an all-metal still

Polyurethane Foam- diSPo foam plugs- Canlab, Winnipeg; sizes-

    15 mm diam. x 38 mm length
    40 mm diam. x 22 mm length
    - 2" thick sheets of foam- B.F.Goodrich Co. Canada code nos. 1115, 1122, 1338. Plugs cut from these sheets sizes: 38 mm diam. x 50 mm length

15 mm diam. x 50 mm length

- Union Carbide type "A", and "B"- Dr. C.G.Seefried, Union Carbide Corp., Chemicals and Plastics, P.O.Box 8361, South Charleston, W.Virginia, U.S.A., 25303. sizes: oblong blocks, 2" x 2" x 12", and 2" thick sheets from which plugs were cut, as for the previous sheets

Pyrex columns, 15 mm diam.ID x 50 cm length, with a 100 ml reservoir at the top, and a Teflon stopcock attached at the bottom with a ground glass joint

Pyrex funnels, with a 30 mm diam. flange, stem 10 mm ID x 100 mm length

Pyrex columns, 3.8 cm ID x 25 cm length, with a Teflon stopcock at the bottom

All glassware was cleaned with acetone and hexane; volumetric apparatus was dried under vacuum, all other glassware was dried at 110°C for 24 hours. Sodium sulfate and glass wool were found to contain contaminants, and were washed with hexane prior to use. Similar contamination was found by Mayer, Stalling, and Johnson.[24] Syringes were cleaned by flushing with acetone and hexane.

Foam Preparation:

Foam plugs were soxhleted in acetone for several hours,and air-dried, then stored in clean glass bottles, in the dark.

Coated foams were prepared by dipping the clean dry foams in a solution of the desired oil in acetone or hexane, and squeezing several times. The foams were then placed on clean paper towels to dry in air. The amount of coating taken up was determined by weighing the dry foams before and after the coating procedure. A uniform distribution of the oil on the surface was assumed.

The impurities on the foams were checked by dissloving the amount of coating to be found on one foam in 10 ml hexane, and analyzing 4 μl of this on the GC. Both the DOW-200 silicone oil and the Rexall Mineral Oil were found to be satisfactory, i.e., there were no peaks evident.

General Procedure

Extraction of Phthalates from Water at the ppm Level-Flow System:

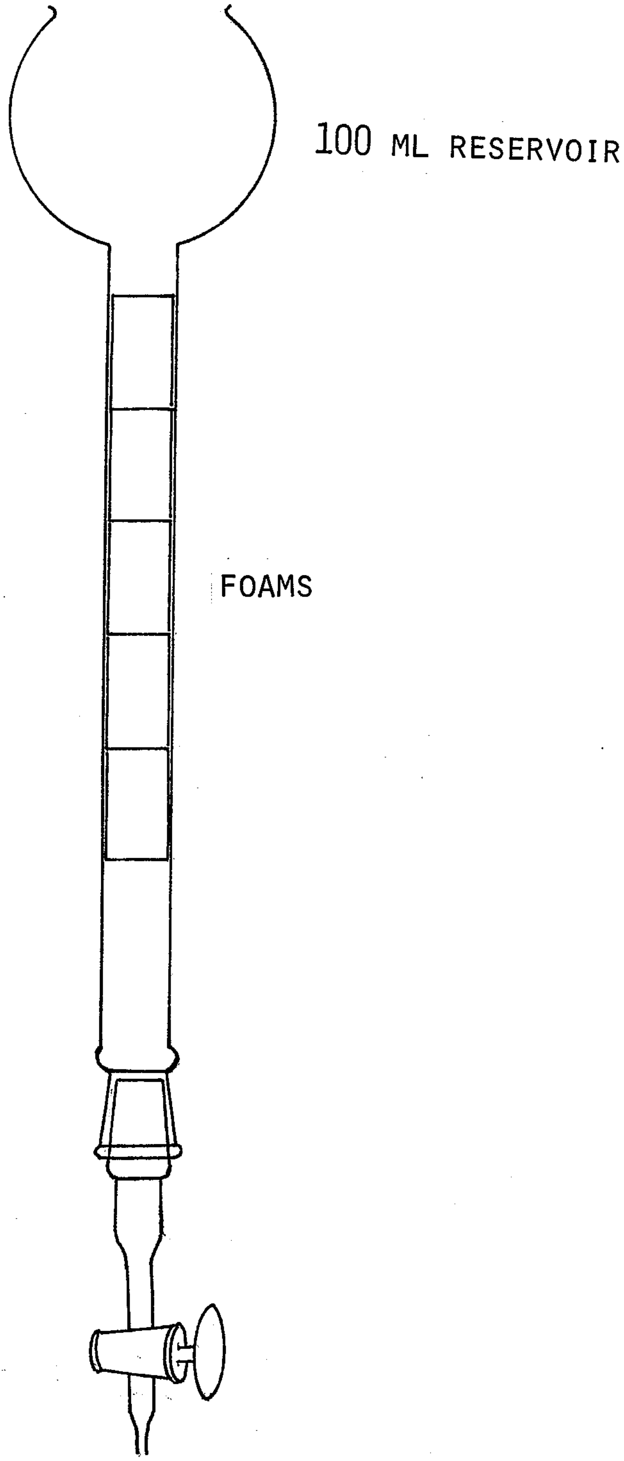
A stock solution of 100 ppm by volume was prepared by dissolving 2.5 μl of the pure phthalate in 25 ml acetone. Solutions containing from one to four phthalates, each 100 ppm, were prepared. From this stock solution, standards were prepared by the appropriate dilution in hexane. The standards ranged in concentration from 1 to 10 ppm. Aqueous solutions were prepared with 1 ml stock solution plus 99 ml water to give 1.0 ppm phthalate concentration.

Columns were prepared by pushing clean foam plugs down an acetone-filled column so that the plugs were just touching each other and were not compressed. The acetone was flushed out with about 300 ml clean water and the flow rate set by adjusting the stopcock at the bottom of the column. The exact flow rate was determined by timing the rate of fill of a 25 ml graduated cylinder with a stopwatch. When the flow rate was correct and the water level was at the top of the foam column, the 100 ml spiked solution was added. The flask which had contained the 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, in some cases, by 100 ml of distilled water, then the column was allowed to run dry. (see Figure 1)

To extract the absorbed phthalates, each foam plug was placed in a 20 cc ground glass syringe and squeezed to expel excess water. Aliquots of solvent were then taken up and expelled into a funnel containing Na_2SO_4, and thence into a 10 ml volumetric flask with a ground

Figure 1

Column for the Removal of Phthalates from Water under Flow Conditions Using Small Polyurethane Foam Plugs


100 ML RESERVOIR
FOAMS

glass stopper. Two 2 ml aliquots of acetone and three of hexane, approximately, were used for each foam, in most cases. In the first experiments, using three foams per column, less solvent was used, and all three foams were extracted into the same ten ml volumetric. Low recoveries showed that this was insufficient.

A 4 μl aliquot of each 10 ml sample was analyzed by gas chromatography, along with suitable standards, and the per cent recovery of the phthalates determined, as well as their distribution down the column.

The procedure for the extraction of phthalates from water with the larger foam plugs was identical to the above, except that a larger diameter column was used, and only one or two plugs were necessary. The foams were extracted with organic solvent as before, but a 50 ml ground glass syringe was used. The foam plug was extracted with a total of 50 ml of acetone and hexane.

Extraction of Phthalates From Water at the ppb Level - Flow System

Pyrex bottles with a capacity of ten litres, fitted with ground glass stoppers, size 45/40, were used. Four glass siphon tubes were made, with 4mm ID tubing, in the shape of a U, with arms 54 cm long, and base 20 cm. A Teflon stopcock was attached at the end of one arm. The bottles and siphon were filled with clean water, and the siphons inserted into the bottles. The stopcocks were opened and the bottles emptied until the desired volume of water remained, then the stopcocks were closed again. One ml of 100 ppm of the phthalates in acetone was added and the water was stirred well. The siphons were left in and the bottles were plugged with polyurethane foam and allowed to stand overnight to ensure complete mixing. Columns of foam were then prepared as usual and the flow rates set. The columns were placed under the stopcocks of the siphons, the stopcocks opened, and the solutions in the bottles were passed through the foam columns in the usual manner. In order to conveniently dispose of the water which had passed through the columns, a rubber tube was attached at the bottom of each column and was connected to one of the five open necks on a 100 ml round bottom flask. A larger tube led from the fifth opening to a drain in the floor. No rinse solution was passed through the column after the spiked solution had passed through. When the columns had run dry, the foams were removed, squeezed dry, and extracted separately with 2 to 3 ml acetone and 7 to 8 ml hexane each, which was dried by passing through a funnel containing Na_2SO_4 (anhydrous), and collected in a 10 ml volumetric. These extracts were analyzed by G C, so that the total recovery and the column profiles could be determined.

In the ppm tests, the volume of organic solvent required to extract the foams was about half the volume of the original aqueous solution. This was for the purpose of studying the behaviour of the phthalates. The ppb studies resulted in both the recovery and the concentration by a factor of 100 of the phthalates.

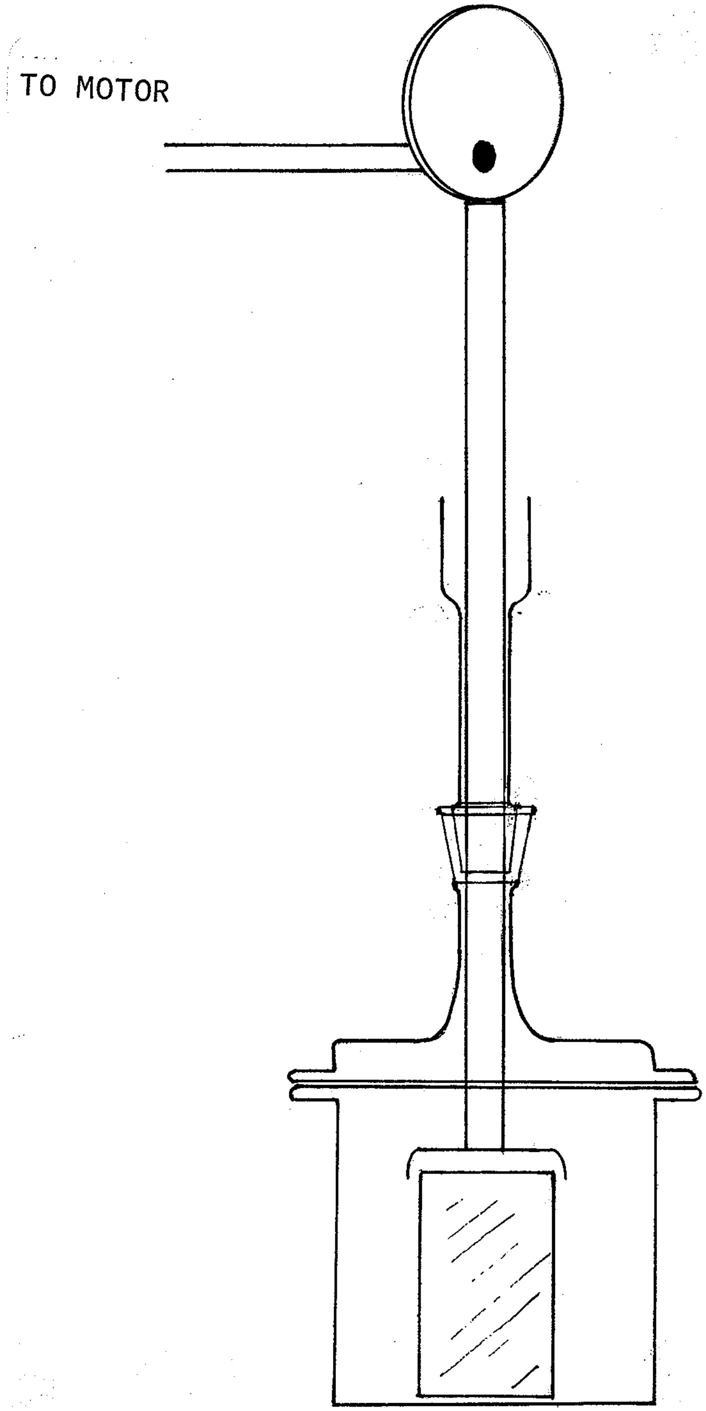
Extraction of Phthalates from Water at the ppm Level - Static System :

For the extraction of phthalates from water under static conditions, a new system was devised (see Figure 2). 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 cover, with a hole in the centre to accomodate the plunger stem, covered the beaker. A solution of the desired phthalates, 1.0 ppm each in 1000 ml water, was prepared and poured into the beaker. One large foam was placed in the beaker and squeezed to expel air bubbles. The beaker was then placed under the glass plunger of the static extraction system and the motor started. At the end of the experiment, the motor was stopped and the plugs removed, extracted with solvent, and the extracts analyzed by gas chromatography.

To carry out several experiments simultaneously, the above system was altered so that the eccentric cam depressed and released a horizontal wooden bar, 8mm x 100 mm x 500 mm, which in turn depressed and released the plungers of three static systems placed beneath it.

Figure 2

Extraction System for the Removal of Phthalates from Water under Static Conditions with a Large Polyurethane Foam Plug


TO MOTOR

Removal of Air-borne Phthalates with Polyurethane Foam:

A flow system for the removal of air-borne phthalates with polyurethane foam was designed. (see Figure 3a) In this system a cylinder of compressed air was connected via a pressure regulator and a needle valve to a copper tube, 4 mm OD, which was joined by a Swagelok connection to a glass tube. This lead to an air flow meter, which was connected to a glass column, 1.5 cm ID, containing 6 foams, to trap any contamination in the air. This was followed by a reservoir of neat phthalate, so that the phthalate vapour in the air above the reservoir was picked up and swept into a second glass column, 15 mm ID, containing another 6 foams. The column was vented into a soft vacuum by resting the end of the column inside a funnel which was connected to the laboratory vacuum outlet. This system could be left running for several days without adjustment. At the end of the run, the foams were extracted with hexane, 10 ml per foam, and analyzed by GC.

Removal of Air-borne Vinyl Chloride Monomer with Polyurethane Foam:

The system for monitoring air-borne phthalates was altered, to study the removal of vinyl chloride monomer from air with polyurethane foam. The phthalate reservoir was replaced by a round two litre flask which was connected to the system by two ground glass joints, one at the top and one at the side. (see Figure 3b) Vinyl chloride monomer was introduced by injecting the flask with 50 cc of a known concentration of the monomer, via septum (A) on the side of the flask. There were three other septa, one, (B), between the flask and the pre-cleanup column, one, (C), between the flask and the trap

Figure 3a

Apparatus for the Removal of Air-Borne Phthalates with Small Polyurethane Foam Plugs

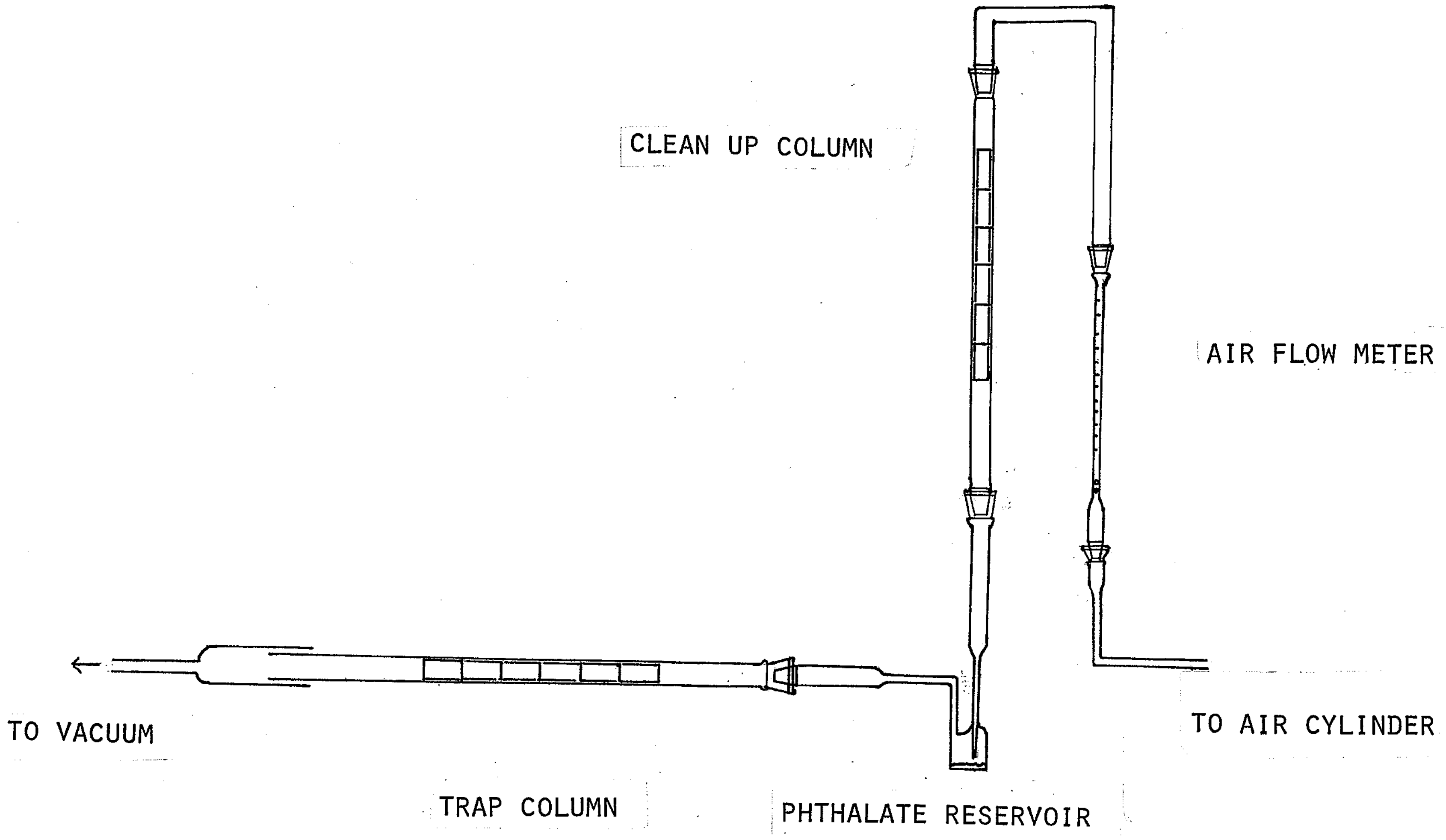
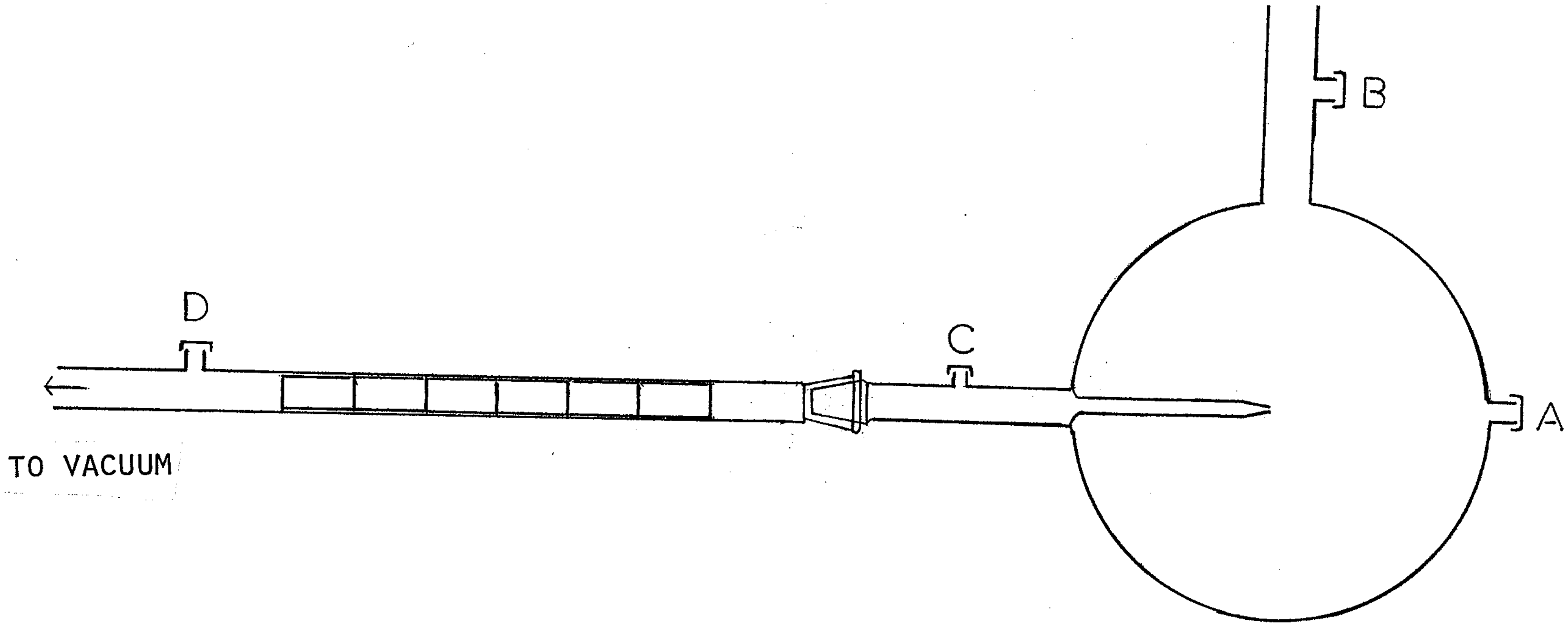

CLEAN UP COLUMN
AIR FLOW METER
TO VACUUM
TO AIR CYLINDER
TRAP COLUMN
PHTHALATE RESERVOIR

Figure 3b

Two Litre Reservoir for PVCM, Attached to Trap Column, for the Study of the Removal of PVCM from Air with Small Polyurethane Foam Plugs



PVCM RESERVOIR

column, and one, (D), beyond the six foams in the trap column. After spiking, the system was left overnight, to ensure complete mixing. Several samples from the reservoir were then analyzed to test homogeneity. The air flow was started by opening the compressed air cylinder, and the amount of vinyl chloride monomer in the air, before and after passing through the foam column, was measured by analyzing air samples taken at points C and D. Syringes for sampling from C and D were kept separate to avoid possible contamination.

Analysis by Gas Chromatography;

All samples were analyzed on a Hewlett Packard 402 high efficiency gas chromatograph equipped with a ^{63}Ni detector operating in the pulsed mode. The GC was also equipped with two flame ionization detectors and, with an effluent splitter at the column exit, one FID and the EC detector could be used simultaneously. This was done in some cases, but as the sensitivity of the EC detector was much superior to that of the FID, the EC was used alone in most cases.

A variety of coatings and solid supports was tested for suitability as a column to separate the phthalates being studied. (Table 2) The column itself was glass tubing, 4 mm ID, which was silanized before packing.

Temperature was constant during any single run. Temperature programming was experimented with, but as the EC detector is very sensitive to any slight change of temperature, this was abandoned.

Table 2 : Solid Supports and Stationary Phases Tested

Solid Support	Stationary Phase	Column Length (m)
Chromosorb W, HMDS	3% OV-225	1.3
Chromosorb W, HMDS	3% OV-17	1.3
Glass beads, 60-80 mesh	0.3% OV-17	1.3
GAW-DMCS	2% OV-17	1.0
Glass beads, 60-80 mesh	0.5% OV-17	2.0
*Chromosorb W, AW,HMDS	3% OV-17	1.3

* This column gave the best results, and was finally adopted.

The actual oven temperature depended on the phthalates being analyzed. Optimum temperatures increased with the length of the side chain on the phthalate, therefore, experiments were run with groups of phthalates which could be analyzed at the same temperature. For the series of phthalates studied, these were usually: DMP, DEP, DnBP, 180 °C; DiBP, DAP, DnHxP, 205 °C; BBP, DPP, 200 °C; DnHpP, DEHP, DOP, 225 °C; DiDP, DEHiP, 230 °C.

The flash heater at the injection port was usually 20 °C above the column temperature; the EC detector was usually about 40°C to 50° C above the column temperature.

Initially, a gas mixture of 5% methane in argon was used as carrier gas, but this was soon changed to He as carrier gas, 40 ml/min, with 10% methane in argon as purge gas, 80 ml/min, added to the gas stream just before it entered the EC detector. This lowered the retention time for the phthalates, and increased detector sensitivity.

Calibration curves for quantitative analyses were obtained from the chromatographs of a series of standard solutions. These were prepared at the same time as the solutions to be run through the foams, from the same stock solution. At first, peak areas were used, but comparison showed that peak height alone would suffice. Only in the case of DPP, peak area had to be used, because the DPP's large electron-capturing capacity resulted in very large, broad peaks.

The injection technique used was to draw about 1 μl hexane into the syringe, 1 μl of air, and then the sample, 4 μl, and then more air. This eliminated the problem of initial boil-off of sample as the septum was penetrated, and ensured delivery of the entire sample, with none remaining in the syringe after injection. This also eliminated loss of sample by blow-back up the syringe as the septum was penetrated.

Syringes used for handling the pure phthalates to prepare stock solutions were kept separate from those used for injecting GC samples.

Sample calibration curves for DMP, DEP, DiBP, DnBP, DAP, DnHxP, DnHpP, DnOP, DEHP, BBP, and DPP are shown in Figures 4 to 7.

Figure 4

Calibration Curves for DMP and DEP; Gas Chromatograph Settings: Oven : 170°C; Flash Heater : 200°C; Electron Capture Detector : 250°C; Carrier Gas : Helium, 40 ml/min; Purge Gas : 10% Methane in Argon, 80 ml/min.

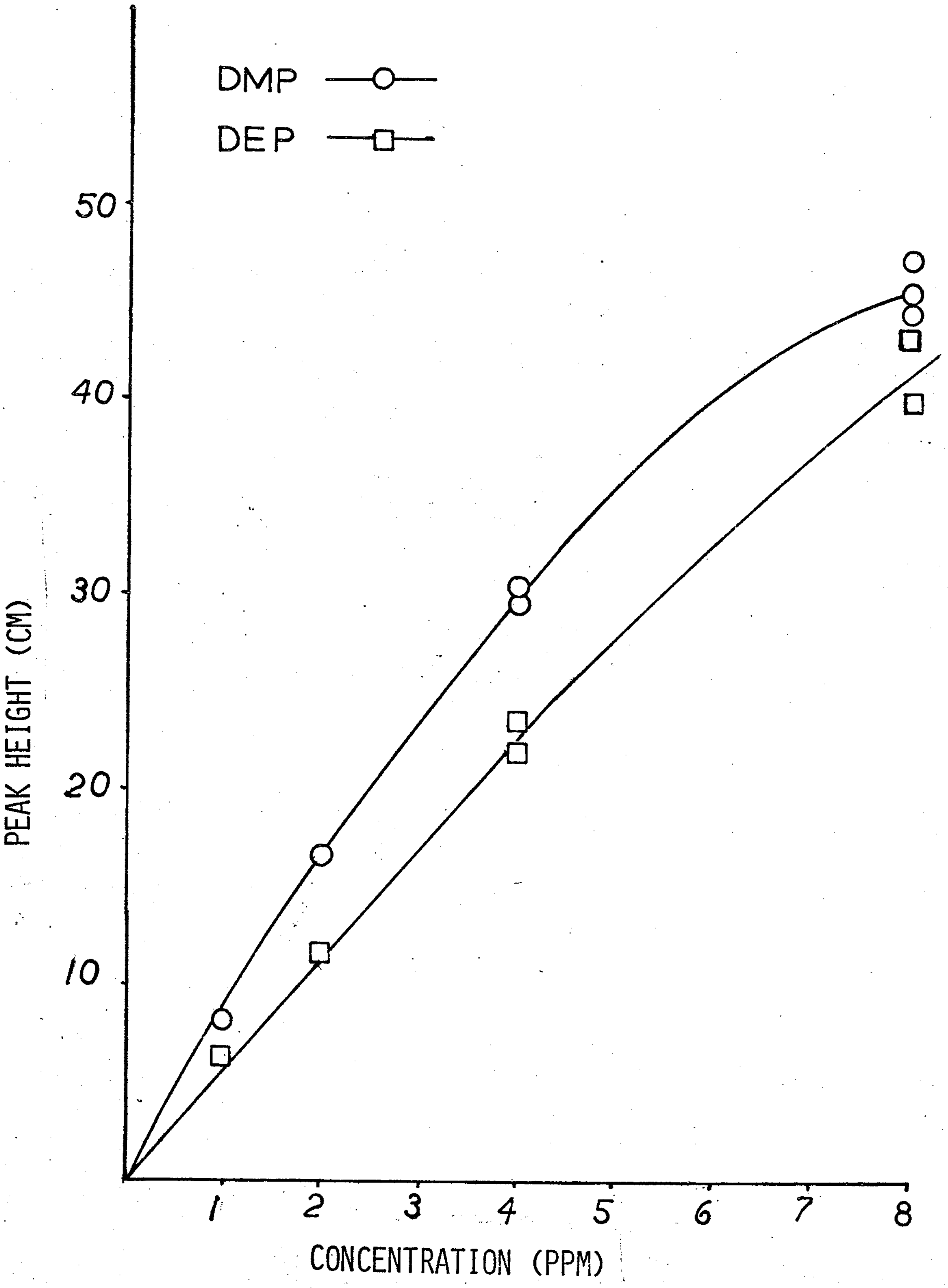

DMP ○
DEP □
50
40
30
20
10
PEAK HEIGHT (CM)
1
2
3
4
5
6
7
8
CONCENTRATION (PPM)

Figure 5

Calibration Curves for DiBP, DnBP, and DAP; GC Settings : Oven:: 200°C; Flash Heater : 230°C; EC Detector : 250°C; Carrier Gas : Helium, 40 ml/min; Purge Gas : 10% methane in Argon, 80 ml/min.

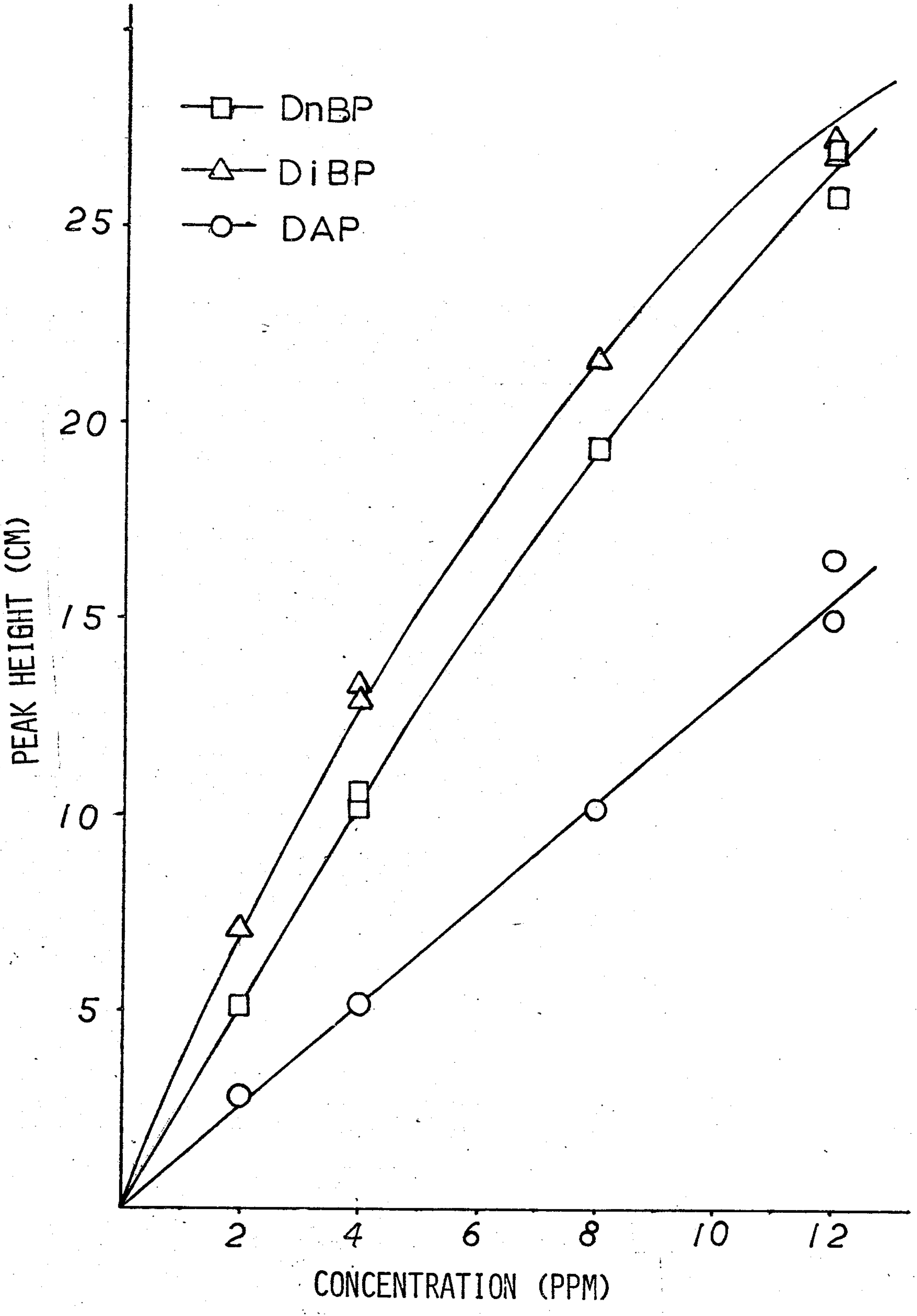
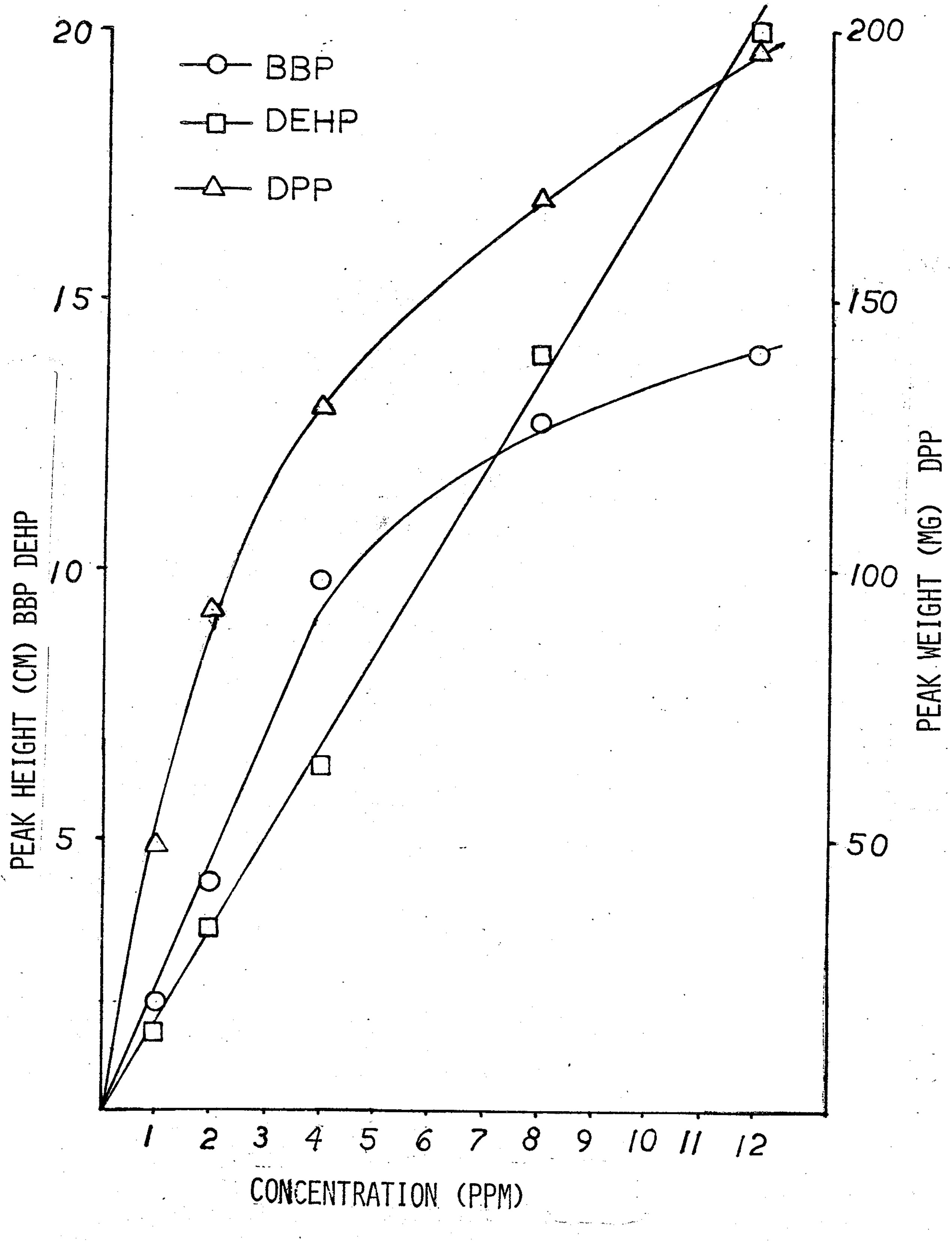

DnBP
DiBP
DAP
25
20
15
10
5
PEAK HEIGHT (CM)
2
4
6
8
10
12
CONCENTRATION (PPM)

Figure 6

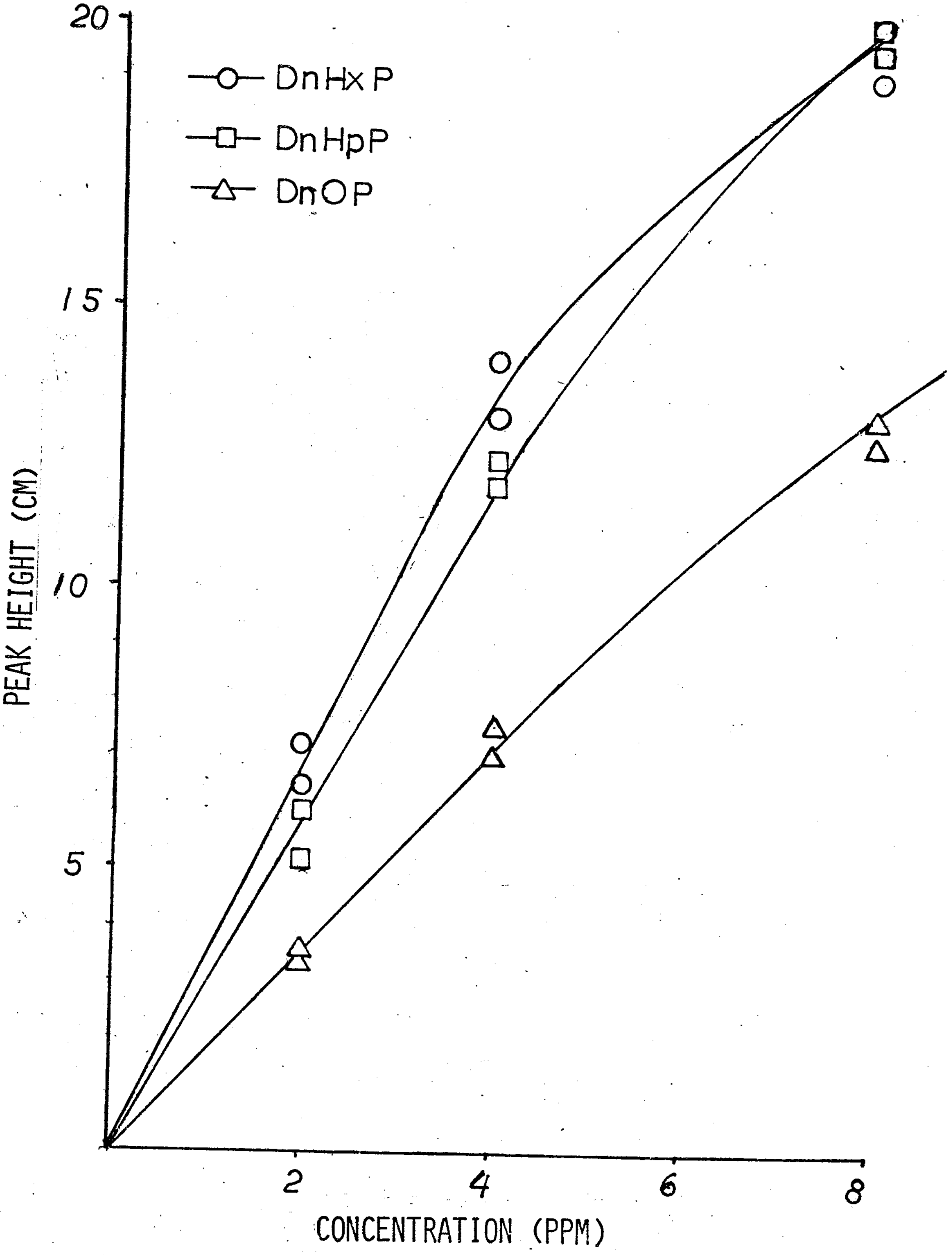
Calibration Curves for BBP, DEHP, and DBP; GGC Settings : Oven : 230°C; Flash Heater : 255°C; EC Detector : 265°C; Carrier Gas : Helium, 40 ml/min; Purge Gas : 10% Methane in Argon, 80 ml/min..



BBP
DEHP
DPP
PEAK HEIGHT (CM) BBP DEHP
PEAK WEIGHT (MG) DPP
CONCENTRATION (PPM)
20
15
10
5
200
150
100
50
1
2
3
4
5
6
7
8
9
10
11
12

Figure 7

Calibration Curves for DnHxP, DnHpP, and DnOP; GC Settings : Oven : 220°C; Flash Heater : 250°C; EC Detector : 275°C; Carrier Gas : Helium, 40 ml/min; Purge Gas : 10% Methane in Argon, 80 ml/min.


20
15
10
5
PEAK HEIGHT (CM)
2
4
6
8
CONCENTRATION (PPM)
DnHxP
DnHpP
DnOP

Part 1 : Recovery of Phthalates from Water

Section 1 : Recovery of DnBP, DnOP, DEHP from Water - Flow System

Experiment I : Two spiked solutions of 50 ppb each DnBP, DnOP, and DEHP in 4 l of water were prepared, and each solution was passed through a column consisting of three small diSPo foam plugs. The flow rate of each solution was 100 ml/min. A blank, 4 l of clean water, was also run. After the columns were run dry, the foams were extracted with acetone, using a 20 ml syringe. The acetone extracts from all the foams in one column were combined in a 250 ml round bottom flask and concentrated on a rotary evaporator to about 1 ml. Ten ml of hexane was added, and the whole concentrated down to about 5 ml. This solution was made up to volume in a 5 ml volumetric flask. Four µl of each sample were analyzed on the GC, along with suitable standards.

Experiment II : Four spiked solutions of the same three phthalates were prepared, two at a concentration of 0.10 ppm, and two at a concentration of 0.50 ppm. The total volume of each solution was 1 litre. A blank solution was also prepared. Each column consisted of three small foam plugs, and the flow rate was 35 ml/min. The foams were extracted separately in a ground glass syringe, but only about three ml of solvent was used for each foam (1 ml acetone, 2 ml hexane). The organic extracts from all three foams in one column were combined in a single 10 ml volumetric flask, after passing through the Na_2SO_4. The foams from the first of the two 100 ppb spikes were extracted with even less solvent, and collected in a single 5 ml volumetric. Four µl of each sample were analyzed by GC.

The results of experiments I and II are shown in Table 3.

Table 3 : Recoveries of DnBP, DnOP, and DEHP ≡ Flow System

Column : 3 small diSPo plugs

Experiment	Concentration (ppb)	Volume (1)	Flow Rate (ml/min)	% Recovery DnBP	% Recovery DnOP	% Recovery DEHP
I *	50	4	100	61	0	0
	50	4	100	52	0	0
II **	100	1	35	36	0	0
	100	1	35	62	0	0
	500	1	35	68	0	0
	500	1	35	40	0	0

* foams extracted with acetone only, hexane added after concentration of the acetone

** foams extracted with acetone and hexane

Discussion

The results of the experiments I and II showed the following:

1- No DnOP or DEHP were removed from water by the foams, therefore, there could be steric limitations on the absorption process which caused the exclusion of the larger molecules.

2- The recovery of DnBP was less than 100 %, so material balance had to be established before the possibility of steric limitations was investigated.

3- The DnBP peak in the GC analysis was obscured by a second peak, also found in the blank. This meant that the "clean" water was contaminated with DnBP or some other compound , which had to be removed for more accurate analysis.

In the next experiments, a material balance of DnBP was sought.

Section 2 : Recovery of DnBP from Water - Flow System - Determination of Material Balance

Experiment III : Six solutions were prepared. The first two were blanks, 1 litre each, which were passed through columns of three small diSPo plugs (columns 1 and 2) at 30 ml/min. The next two were each 1 litre of 0.1 ppm DnBP, each of which was also passed through a column of three small diSPo plugs (columns 3 and 4) at 30 ml/min. The last two were each 100 ml of 1.0 ppm DnBP, one of which was passed through a column of three small diSPo plugs (column 5) at 3 ml/min, while the other was passed through a column of 6 small diSPo plugs (column 6) at 3 ml/min. When the columns had run dry, the foams were removed and extracted with acetone and hexane as in experiment II, and the three foam extracts from column were again collected in a single 10 ml volumetric flask. The foam plugs from column 4 were extracted with hexane only, to determine the importance of acetone. For column 6, the first three plugs were extracted into one 10 ml volumetric and the lower three plugs were extracted into a second 10 ml volumetric. Four μl of each column extract were analyzed by GC.

The results from this experiment are shown in Table 4.

Table 4 : Recovery of DnBP from Water - Flow System

Columns : small diSPo foam plugs

Column	Conc'n (ppm)	Volume (l)	Flow Rate (ml/min)	Number of Foams	% Recovery DnBP
1	0	1	30	3	11
2	0	1	30	3	15
3	0.1	1	30	3	55
4*	0.1	1	30	3	9
5	1.0	0.1	3	3	82
6	1.0	0.1	3	6 (top 3)	70
6	1.0	0.1	3	6 (bottom 3)	0

* foams extracted with hexane only

Discussion

The first two columns, both of which were blanks, resulted in the recovery of an unknown, which interfered in the GC analysis of DnBP. If the unknown was in fact DnBP, it represented a concentration in clean water of about 0.01 ppm.

It was seen from the extract of the foams from column #4, which were extracted with hexane only, that acetone was necessary for the extraction of phthalate from foam. Apparently the water-miscible acetone is necessary for the removal of water from the foams; the water acted as a barrier between the hexane and the phthalates in the foam. The high electron-capturing capacity of acetone rendered it an unfavourable solvent for the GC analysis, therefore, while only a minimum amount was used in future extractions, it was not omitted.

From column # 6, it was seen that the removal of DnBP from water was complete: none was found in the bottom three foams. Therefore, either DnBP was lost during the extraction of the plugs with acetone and hexane, or it was lost by adherence to the glass walls of the flasks and columns.

Increasing the concentration by a factor of ten, and lowering the flow rate by the same factor gave a marked improvement in recovery. As increasing the concentration by a factor of five, (Section 1, experiment II), did not result in improved recovery, this increase was attributed to the lower flow rate. This was investigated further in the next experiment. The distribution of the phthalate on the column was also studied.

Experiment IV : Six solutions were prepared. The first two were blanks, each 100 ml of clean water, which were passed through columns 1 and 2 containing six small diSPo plugs, at 30 ml/min. The remaining four solutions were each 100 ml of 1.0 ppm DnBP in water. Two, (columns 3 and 4), were run at 30ml/min, and two, (columns 5 and 6), were run at 3 ml/min. Each column contained six small diSPo plugs, and each solution was followed by 100 ml of rinse water at the same flow rate as the test solution. Foams from the first four columns were extracted as in the three previous experiments, three foams per ten ml volumetric. Foams from the last two columns were extracted with about 2 ml acetone and 3 ml hexane each, two foam plug extractions per ten ml volumetric.

Results are shown in Table 5.

Table 5 : Recovery of DnBP from Water - Flow System

Columns : 6 small diSPo foams

Solutions : 1 ppm DnBP in 100 ml water

Experiment IV

Column	Conc'n (ppm)	Flow Rate (ml/min)	Foams	% Recovery DnBP
1	0	30	Top 3	5
	0	30	Bottom 3	2
2	0	30	Top 3	3
	0	30	Bottom 3	2
3	1.0	30	Top 3	60
	1.0	30	Bottom 3	2
4	1.0	30	Top 3	56
	1.0	30	Bottom 3	3
5	1.0	3	Top 2	52
	1.0	3	Middle 2	9
	1.0	3	Bottom 2	2
6	1.0	3	Top 2	47
	1.0	3	Middle 2	7
	1.0	3	Bottom 2	2

Discussion

1- These results showed only a slight increase in per cent recovery with decreased flow rate, but the loss of 40% of the DnBP had to be accounted for before any explanations could be sought.

2- The removal of DnBP from water is apparently complete, as seen by the low concentration of DnBP in the bottom foams. Therefore, as before, it was concluded that the DnBP was incompletely extracted from the foam or the DnBP was lost on the glass surfaces by adsorption. Both these possibilities were tested in the next experiment.

Experiment V : One spiked solution, 100 ml of 1.0 ppm DnBP was prepared and passed through a column of four small diSPo foam plugs at 3 ml/min. Each plug was extracted into a 10 ml volumetric, with about 2 ml acetone and 3 ml hexane. The 100 ml volumetrics which had contained the spiked solutions were rinsed with acetone and hexane, and the rinse made up to 25 ml. The column was also rinsed immediately after the plugs were removed, and the rinse made up to 25 ml. In both these rinses, about 5 ml acetone and 20 ml hexane were used. Anhydrous $MgSO_4$ was used as the drying agent instead of Na_2SO_4. The 20 ml ground glass syringe used in the extraction of the foams was rinsed with 1 ml acetone and 9 ml hexane after the extraction of each foam. The foam extracts were labelled 1, 2, 3, and 4, from the top of the column to the bottom. The syringe rinses were labelled 1A, 2A, 3A, and 4A, respectively. The samples were analyzed by GC as usual .

Experiment VI : All conditions were similar to those of experiment V, except that the first foam in the column was extracted with about 4 ml acetone and 6 ml hexane. The 20 ml syringe was not rinsed. The volumetric flask which had contained the spike solution was rinsed with 100 ml water and this was added to the column after the spike solution had passed through.

Experiment VII : All conditions were similar to those of experiment V, except that the first foam was re-extracted with 2 ml acetone and 8 ml hexane into a second ten ml volumetric, labelled 1A.

Experiment VIII : A solution containing 20 ppm DnBP in 1 ml acetone and 4 ml hexane, plus 1 drop water, was prepared and passed through an

$MgSO_4$ drying column. The eluate was collected in a 10 ml volumetric, and the column was washed with hexane which was also collected to make the solution up to volume. The $MgSO_4$ was then removed and extracted with acetone and hexane, 4:1, in a clean beaker. The extract was made up to 25 ml in a volumetric flask. The extracts were analyzed by GC and the amount of phthalate retained by the $MgSO_4$ was determined.

The results of experiments V to VIII are shown in Table 6.

Table 6 : Recovery of DnBP from Water - Flow System

Column : four small diSPo foam plugs
Solution : 100 ml of 1.0 ppm DnBP
Flow Rate : 3 ml/min

Experiment	Foam No., or Sample	% Recovery DnBP
V	1	43
	2	6
	3	2
	4	1
	column rinse	0
	volumetric rinse	5
	syringe rinse 1A	0.1
	2A	0.1
	3A	0.1
	4A	0.1
	Total	57
VI VI	1	65
	2	10
	3	1
	4	0
	column rinse	0
	volumetric rinse	1
	Total	77

continued

Table 6 : continued

Experiment	Foam No., or Sample		% Recovery DnBP
VII	1		62
	1A*		15
	2		7
	3		1
	4		1
	volumetric rinse		1
		Total	87
VIII	Eluate		80
	$MgSO_4$ rinse		17
		Total	97

* re-extraction of the first foam in the column

Discussion

The results of experiment V showed that the DnBP was lost to a small extent on the glass walls of the volumetric, but not on the glass walls of the column of on the glass syringe. The latter was not checked in the remaining experiments.

The results of Experiment VI showed that an increase in the amount of acetone used to extract the foams would be necessary despite its unfavourable qualities as a solvent in the GC analysis.

The results of experiment VII showed that the extraction of three foams into a single 10 ml volumetric was quite insufficient for complete recovery, and each foam should be extracted with at least 10 ml of solvent. It also seemed reasonable to wait for about 30 seconds to one minute between the time of taking the acetone up in the syringe and expelling it into the drying funnel, particularly in the extraction of the first foam in a column.

The results of Experiment VIII showed that the $MgSO_4$, which had been used because of its better performance as a drying agent, was retaining the DnBP to some extent. While it is possible that the DnBP retained by the $MgSO_4$ would be washed off by the solvent used to extract subsequent foams so that total recovery did not change, the distribution of the DnBP on the column would be affected. Anhydrous Na_2SO_4 was used as the drying agent in future experiments.

In the next experiments, a series of phthalates was tested on the diSPo foams, in an attempt to discover why DEHP and DnOP had not been recovered in experiments I and II.

Section 3 : Recovery of a Homologous Series of Phthalates from Water With Small DiSPo Foam Plugs - Flow System

A series of phthalate solutions, at a concentration of 1.0 ppm each in 100 ml of water, (two to four phthalates per solution), were prepared and each was passed through a column of 5 small diSPo foams at a flow rate of 10 ml/min. This was followed by 100 ml of water which had been used to rinse the 100 ml volumetric. Each foam was extracted separately with about 2 ml acetone and 8 ml hexane, and analyzed by GC as usual. Where possible, the group of phthalates included one which had been run before, as an internal reference. All were finally referred back to DnBP; 100 % recovery of DnBP being taken to indicate no experimental error. Duplicate solutions (A and B) were run in almost every case, as well as a blank : 100 ml of clean water.

Experiment IX : DMP, DEP, and DnBP were tested.
Experiment X : DMiP, DiBP, and DnBP were tested.
Experiment XI : DEHP, BBP, and DPP were tested.
Experiment XII: DEHiP, DnOP, and DiDP were tested.
Experiment XIII: DnBP, DAP, and DnHpP were tested.
Experiment XIV : DnBP, and DnHxP were tested.

The results of experiments IX to XIV are shown in Table 7, where the total recovery of each phthalate is shown. Column profiles, the distribution of each phthalate down the length of the column, are shown in Figures 8 to 12.

Table 7 : Recoveries of a Homologous Series of Phthalates from Water with Small DiSPo Foams - Flow System

Column : 5 small diSPo foams

Solution : 1 ppm of each phthalate in 100 ml water

Flow rate : 10 ml/min

Experiment	Sample	% Recovery													
		DMP	DMiP	DEP	DiBP	DnBP	DAP	DnHxP	DnHpP	DnOP	DEHP	DEHiP	DiDP	BBP	DPP
IX	Spike A	18		77		137									
	Spike B	19		91		130									
X	Spike A		2		91	99	40								
	Spike B		2		93	110	37								
	Blank		0		0	7	0								
XI	Spike A										0			76	85
	Spike B										0			82	97
	Blank										0			0	0
XII	Spike A									0		0	0		
	Spike B									0		0	0		
XIII	Spike					99	84		22						
	Blank					0	0		0						
XIV	Spike A					79		32							
	Spike B					89		36							
	Blank					0		0							

Figure 8

Column Profiles of DMP, DEP, and DnBP; Experiment IX.

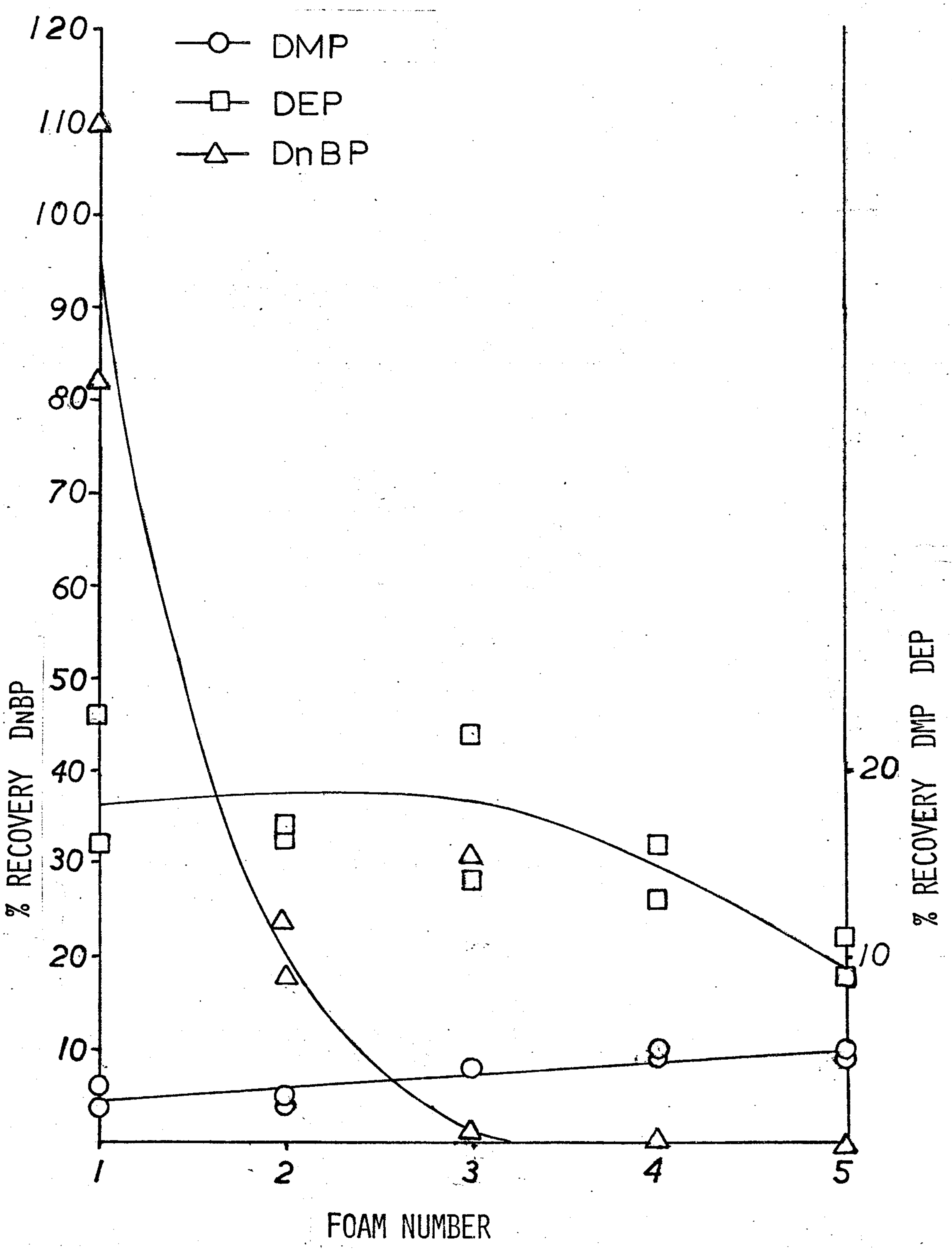

DMP
DEP
DnBP
120
110
100
90
80
70
60
50
40
30
20
10
% RECOVERY DnBP
20
10
% RECOVERY DMP DEP
1
2
3
4
5
FOAM NUMBER

Figure 9

Column Profiles for DiBP, DnBP, and DAP; Experiment X.

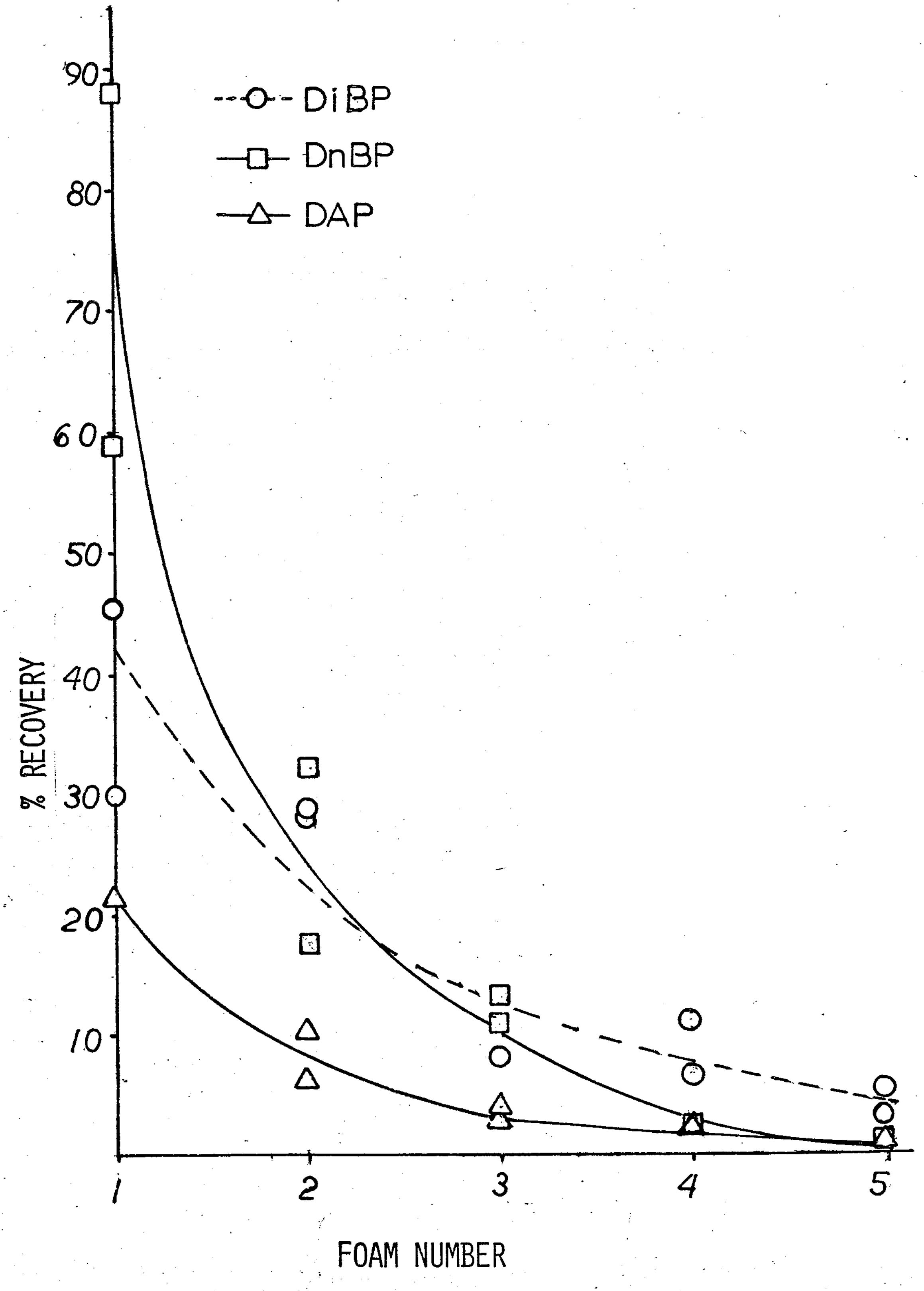

DiBP
DnBP
DAP
% RECOVERY
90
80
70
60
50
40
30
20
10
1
2
3
4
5
FOAM NUMBER

Figure 10

Column Profiles for BBP, and DPP, and DnOP; Experiment XI.

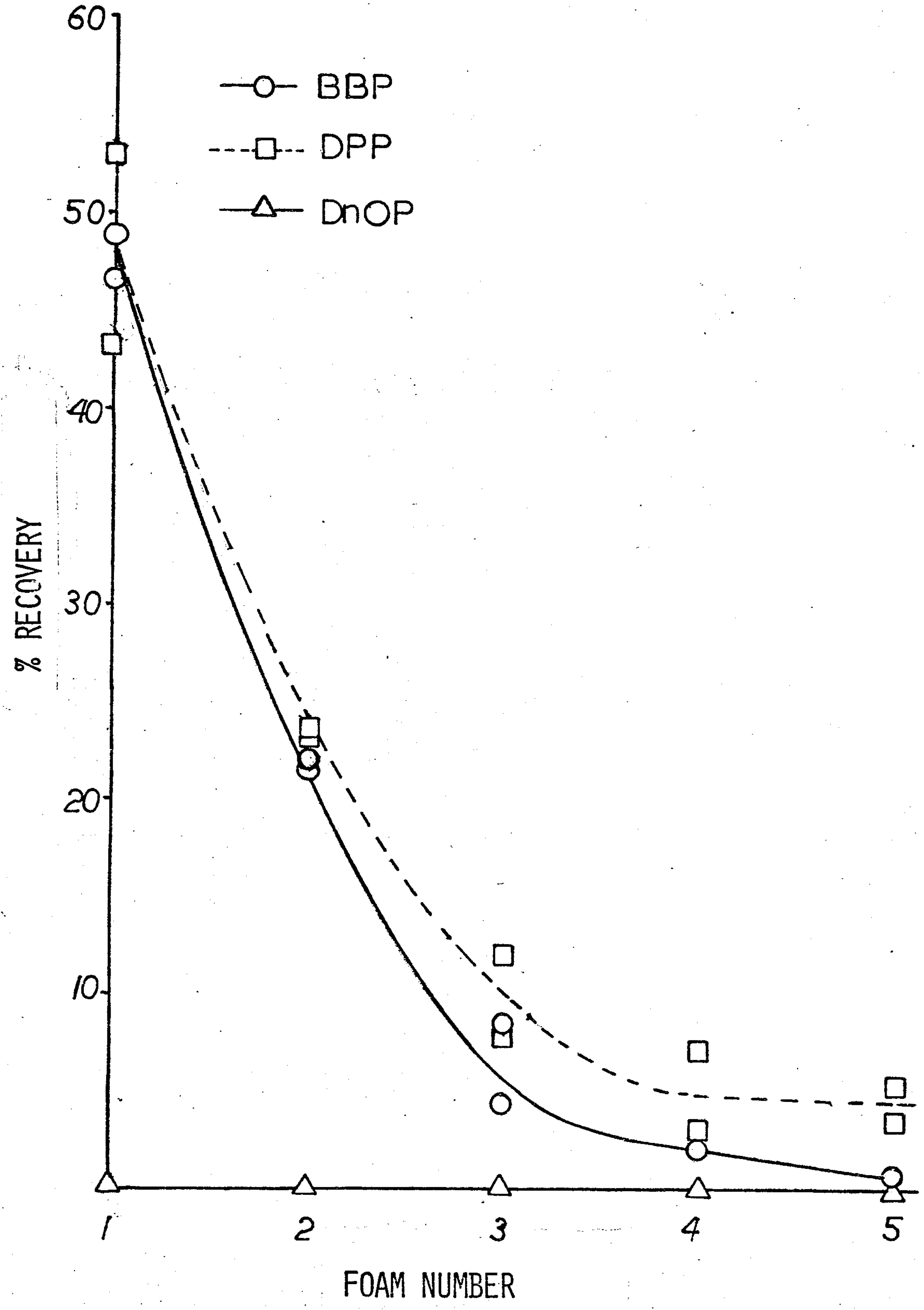

60
50
40
30
20
10
% RECOVERY
BBP
DPP
DnOP
1
2
3
4
5
FOAM NUMBER

Figure 11

Column Profiles for DnBP, DAP, and DnHpP; Experiment XIII.

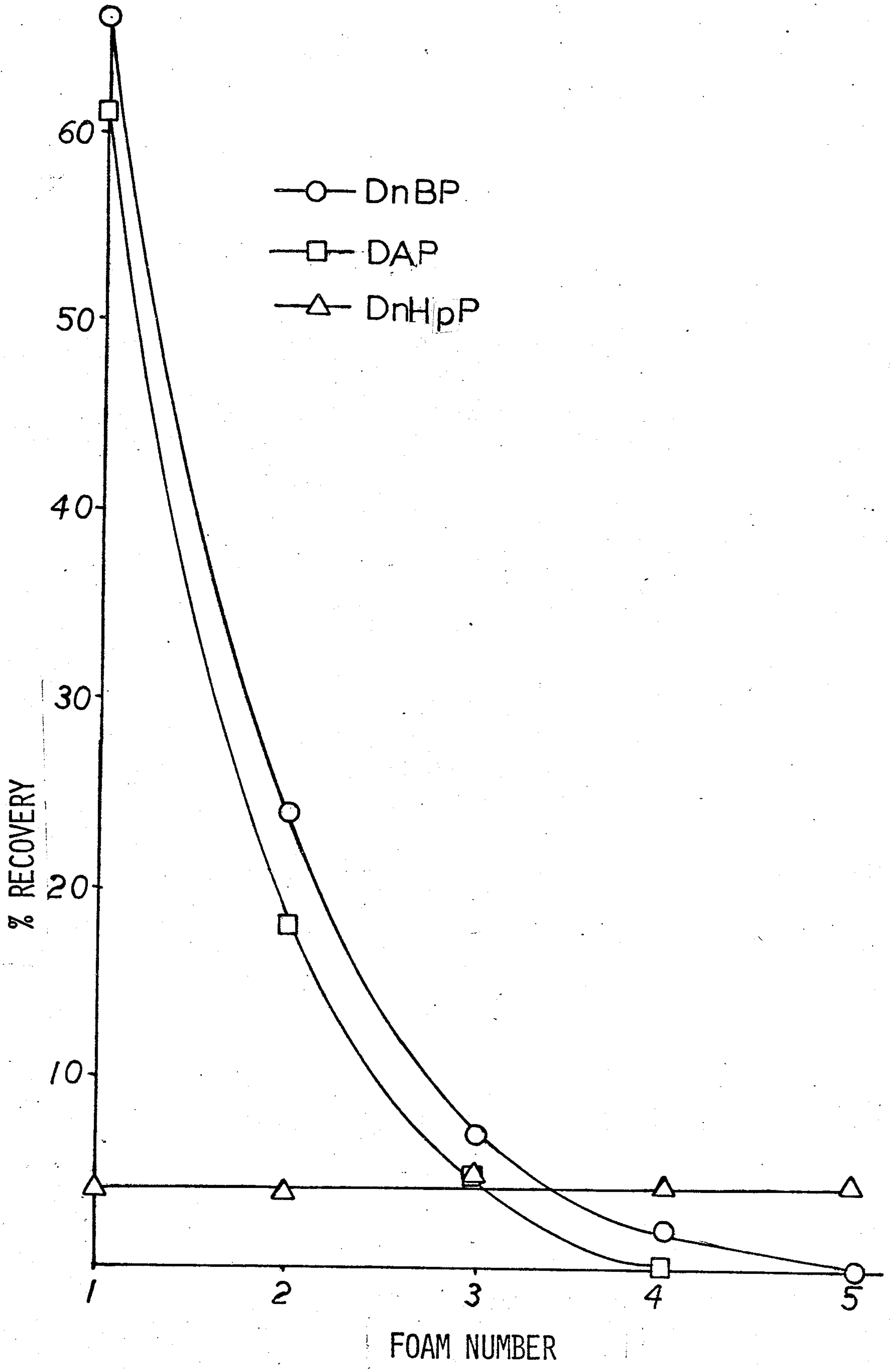
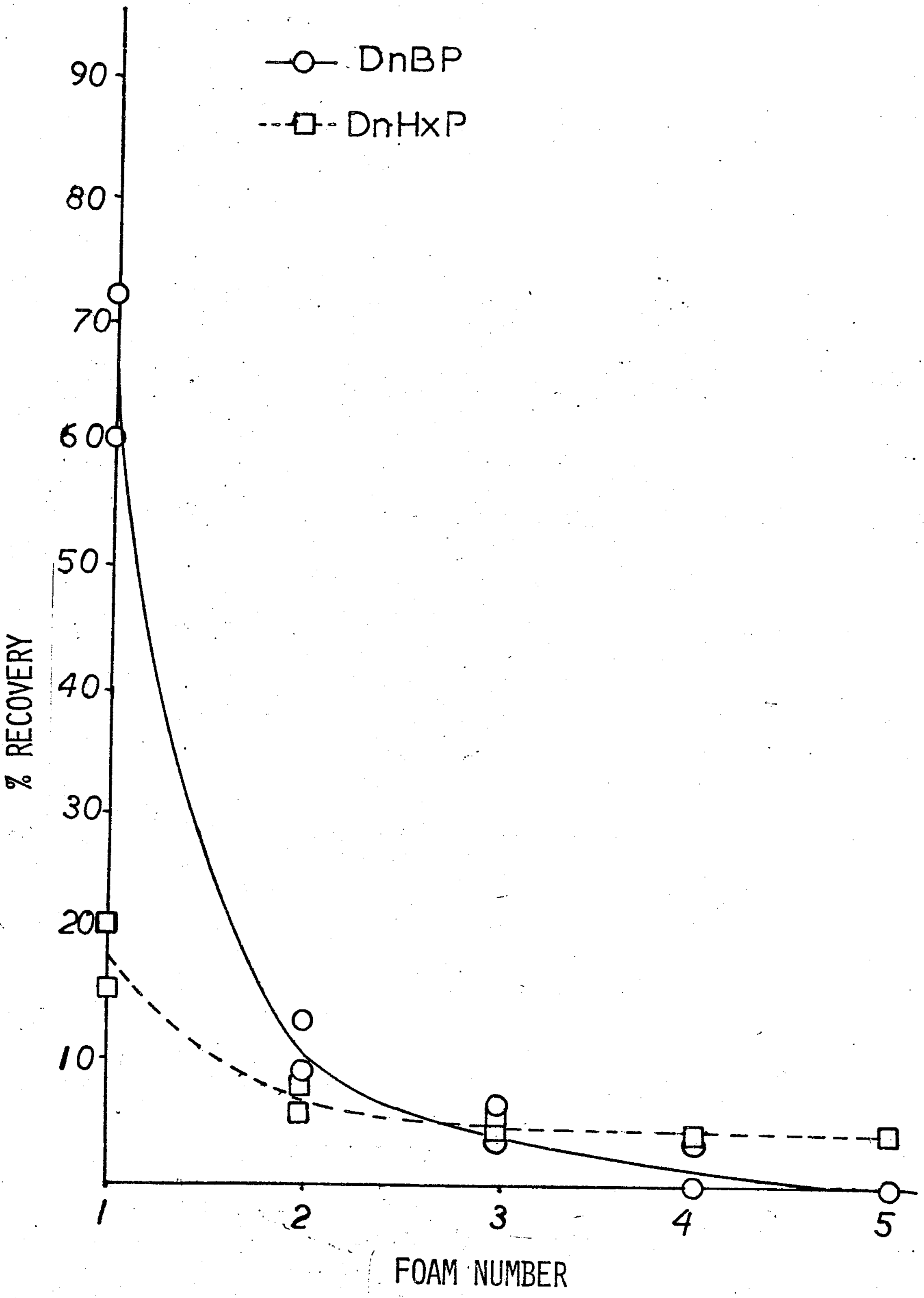

DnBP
DAP
DnHpP
% RECOVERY
60
50
40
30
20
10
1
2
3
4
5
FOAM NUMBER

Figure 12

Column Profiles for DnBP, and DnHxP; Experiment XIV.


DnBP
DnHxP
% RECOVERY
90
80
70
60
50
40
30
20
10
FOAM NUMBER
1
2
3
4
5

Discussion

In experiment IX, DMP passed through the column with almost no retention. The largest amount (see Figure 8) was in the last foam, as if the DMP recovered were the tail of a very broad peak which could have been displayed entirely on a column of about fifty foams. The DEP profile is a condensed version of this: a broad assymmetrical peak, with a maximum at about the middle of the column. This could be due to one of several reasons. First, the mobility of these two plasticizers in the polymer network may be so high that they actually travel through the column during the experiment. This would imply that the DMP is moving down the column faster than the water, which does not seem likely. The smaller phthalates are more soluble in water than the larger phthalates, (see Appendix C),so that the rinse water added to the column after the spike solution had passed through could have been responsible for the loss. This would imply that there was rapid desorption of the phthalates, that is, that $K_D = \frac{[\text{foam}]}{[\text{water}]}$ is small. This problem was investigated further in Section 5.

In experiments X and XIII, DnBP, DiBP, and DAP were recovered almost entirely, and the major fraction of each was in the first foam of the column. The addition of two or three methylene groups to the alkyl side chains in these three phthalates increases their hydrophobic characteristics and they are recovered from water more readily. Presumeably K_D has increased.

The DnHxP was recovered to some extent in experiment XIV, and the first foam still retained the largest fraction. The fact that the DnHxP was found in all foams and the last foam contained a relatively large percentage of the phthalate indicated that the remaining 65% actually passed through the column. The column profile from experiment XIII showed that DnHpP was evenly distributed on the column, approximately 5% per foam, while none of the larger phthalates in this homologous series was recovered. The decreasing rate of absorption coupled to the increasing molecular dimensions showed that though K_D would be expected to increase as the alkyl side chain increases, the rate at which equilibrium is achieved decreases. That is, the rate of diffusion of the phthalate into the foam is slower as the size of the phthalate increases.

In contrast to this, the recoveries of DPP and BBP in experiment XI were high. A large K_D and a slow approach to equilibrium were also expected for these two phthalates, not a high recovery. It was noted in the introduction that decreased mobility of plasticizers in PVC was observed by Bloch et al.[97], when dicresylbutyl phosphate was substituted for tributyl phosphate. Presumeably, DPP and BBP would exhibit lower mobilities in the polyurethane foam than the other phthalates tested. Such low mobility would not be compatible with rapid absorption, particularly when one considers the drastic reduction in recovery observed on going from DnBP to DnOP, an increase of only four carbons on the side chain. The recovery of DPP and BBP could in fact be a manifestation of multiple-layer adsorption, and not absorption at all.

In summary, it has been shown already[21,22,97,99] that the mobility of a plasticizer within a polymeric network varies with the size and shape of the plasticizer molecule. It appears from the per cent recovery and the distribution down the length of the column of the series of phthalates studied, that the efficiency of removal of a phthalate from water by polyurethane foam depends on the length of the side-chains, R_1 and R_2. The rate of absorption of the phthalates by the foam is determined by the ability of the phthalate to penetrate the foam matrix, and by its mobility within the foam matrix, away from the foam-water interface. The equilibrium distribution constant, $K_D = \frac{[\text{foam}]}{[\text{water}]}$, increases with increasing side chain length, whereas the rate at which equilibrium is established decreases as the phthalate side chain increases.

The flexibility of the chains of the polymer network should also affect the rate of absorption of the phthalates, and the degree of retention. Therefore, a number of foams of different flexibility, density, and composition were studied and are discussed in later sections. It was hoped to determine the role of the rate of diffusion of phthalate into the foam bulk away from the foam-water interface.

Increasing or decreasing the flow rate should also affect the recovery of those phthalates which have a low absorption rate, because of the longer time required for equilibrium between the foam and water phases to be established. Those which are absorbed rapidly should not be affected significantly.

Recovery of DnBP was, in several cases, greater than 100%. This was found to be due to contamination of the Na_2SO_4 used as a drying agent. While the identity of the contaminant , which coincided with DnBP in the GC analysis, was not investigated in this work, Musty and Nickless[69] reported similar contamination of Na_2SO_4, and identified it as DnBP. Washing of the Na_2SO_4 with acetone and hexane, and drying at 110°C, before use as a drying agent, removed this contamination.

Section 4 : Recovery of Phthalates from Water with # 1338 Polyurethane Foam - Flow System

Sheets of polyurethane foam, designated type # 1338, were obtained from B. F. Goodrich Co. Cylindrical foam plugs, 1.5 cm diameter x 5.0 cm length, were cut from these sheets, and cleaned with acetone by soxhleting for 4 to 6 hours. The clean plugs were then stored in glass bottles and kept in the dark. The first two digits in the foam code number indicate the average density, 1.2 to 1.35 lb/ft^3, and the last two digits indicate the compression range. Other foams in this series, # 1115, and # 1122, were studied in later sections.

The experiments with the # 1338 foams were carried out in the same manner as those with the diSPo foams, and the same series of phthalates was studied. Columns consisted of 5 foam plugs each; the flow rates of the solutions was 10 ml/min, and the foams were extracted separately with about 3 ml of acetone and 7 ml hexane. In each case, the spike solution was passed through a column and was followed by 100 ml of water which had been used to rinse the 100 ml flask which had contained the spike solution. The Na_2SO_4 was always pre-cleaned. The acetone-hexane extracts were analyzed by GC along with suitable standards. Duplicate spiked solutions (A and B) and a blank solution were run in almost every case.

Experiment XV : DMP, and DEP were tested.

Experiment XVI : DiBP, DnBP, and DAP were tested.

Experiment XVII : DEHP, BBP, and DnOP were tested.

Experiment XVIII : One solution of DnBP, DAP, and DnHpP, and a blank were tested.

Experiment XIX : DnHxP, and DnHpP were tested.

The results of experiments XV to XIX are shown in Table 8, and the column profiles are shown in Figures 13 to 16.

Table 8 : Recovery of a Homologous Series of Phthalates from Water with #1338 Foams - Flow System

Columns : 5 foam plugs, type #1338

Solutions : 1.0 ppm of the phthalates in 100 ml water

Flow rate : 10 ml/min

Exp't	Sample	% Recovery									
		DMP	DEP	DiBP	DnBP	DAP	DnHxP	DnHpP	DnOP	DEHP	BBP
XV	Spike A	8	80								
	Spike B	8	80								
	Blank	0	0								
XVI	Spike A			98	100	77					
	Spike B			103	102	82					
	Blank			0	0	0					
XVII	Spike A								0	0	90
	Spike B								0	0	75
	Blank								0	0	0
XVIII	Spike				80	71		25			
	Blank				0	0		0			
XIX	Spike A						17	?			
	Spike B						11	?			
	Blank						0	?			

Figure 13

Column Profiles of DMP, and DEP; Experiment XV.

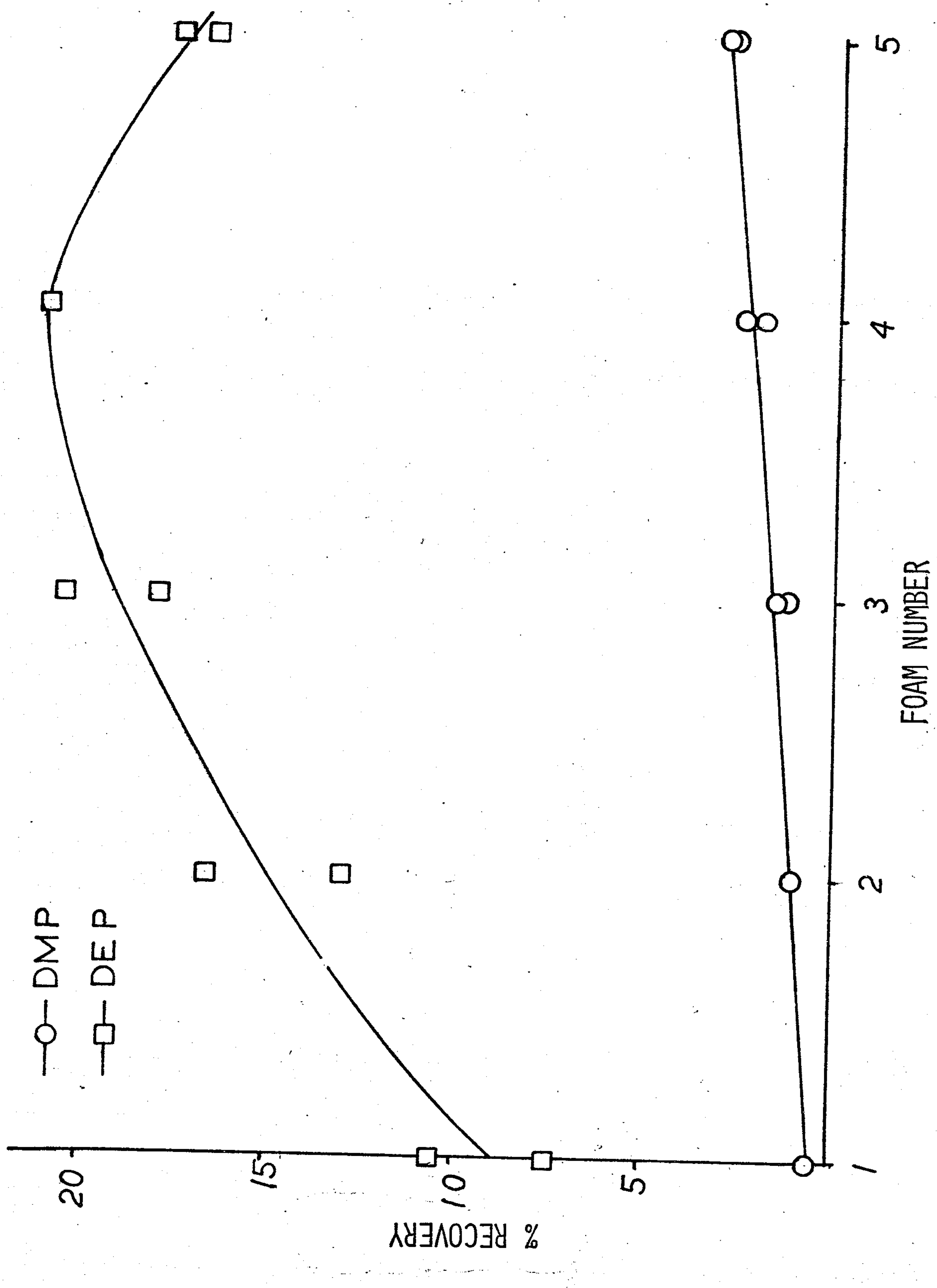
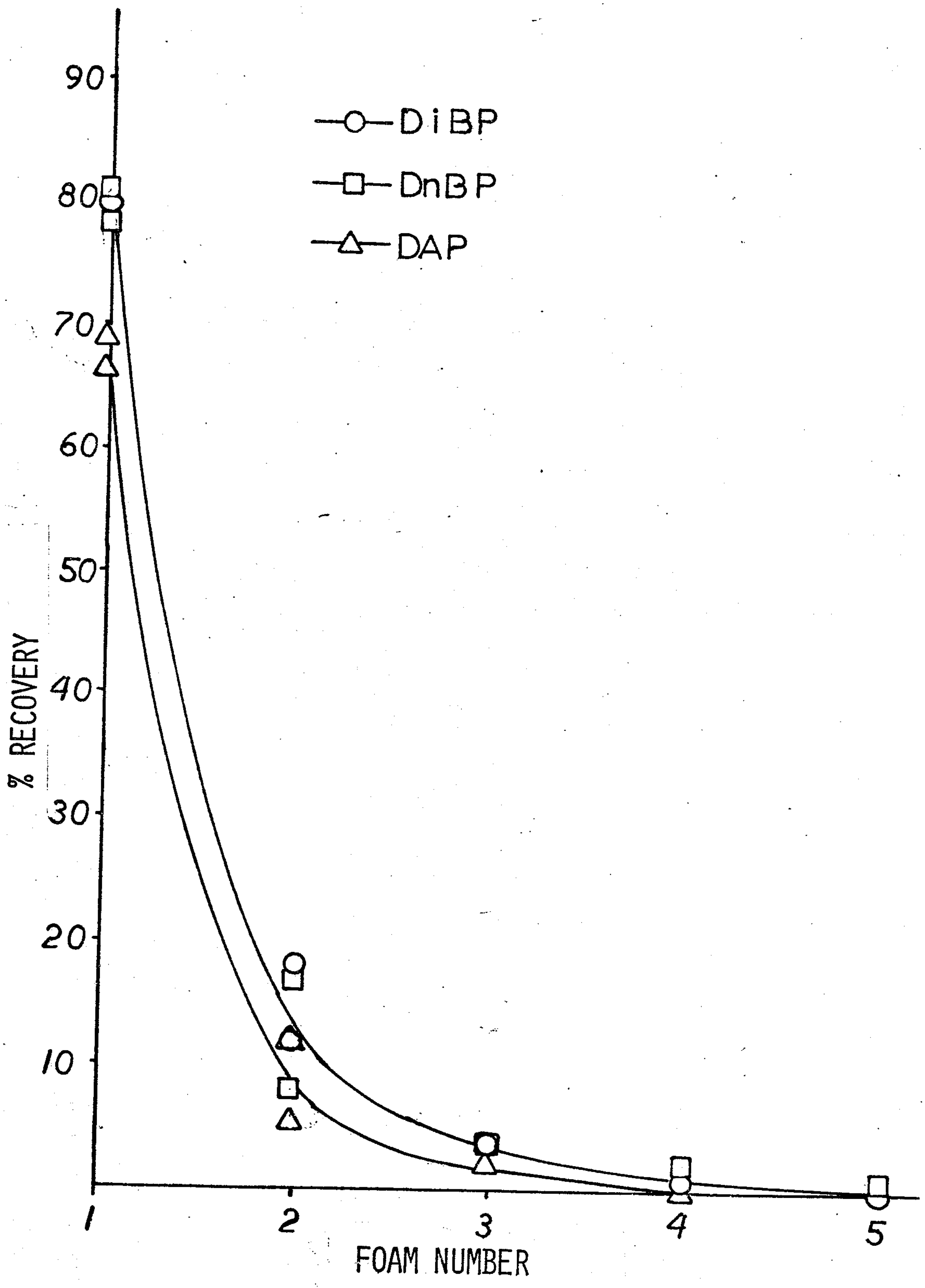

○ DMP
□ DEP
% RECOVERY
20
15
10
5
FOAM NUMBER
1
2
3
4
5

Figure 14

Column Profiles for DnBP, DiBP, and DAP; Experiment XVI



DiBP
DnBP
DAP
% RECOVERY
90
80
70
60
50
40
30
20
10
1
2
3
4
5
FOAM NUMBER

Figure 15

Column Profiles of BBP and DnHxP; Experiments XVII and XIX.

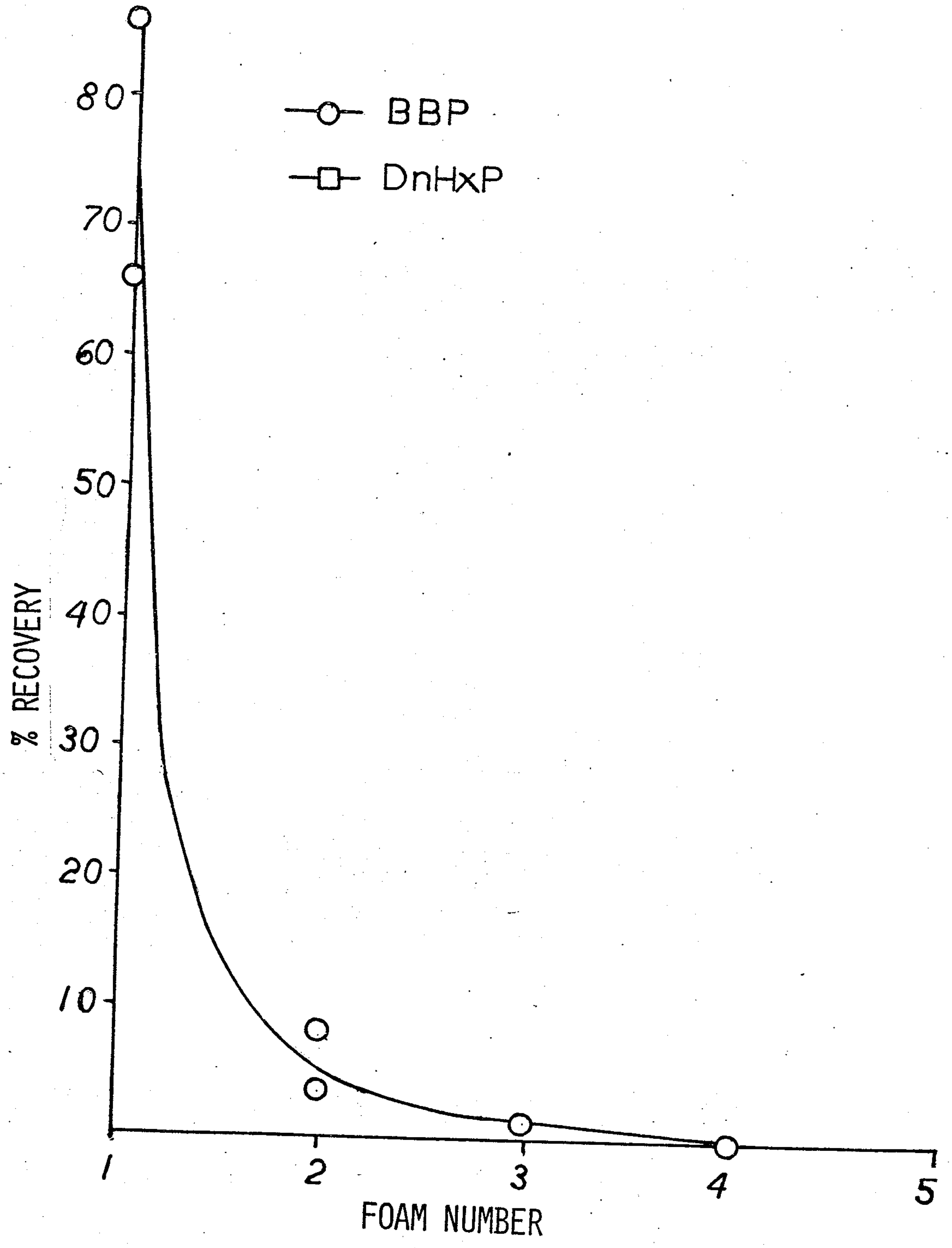
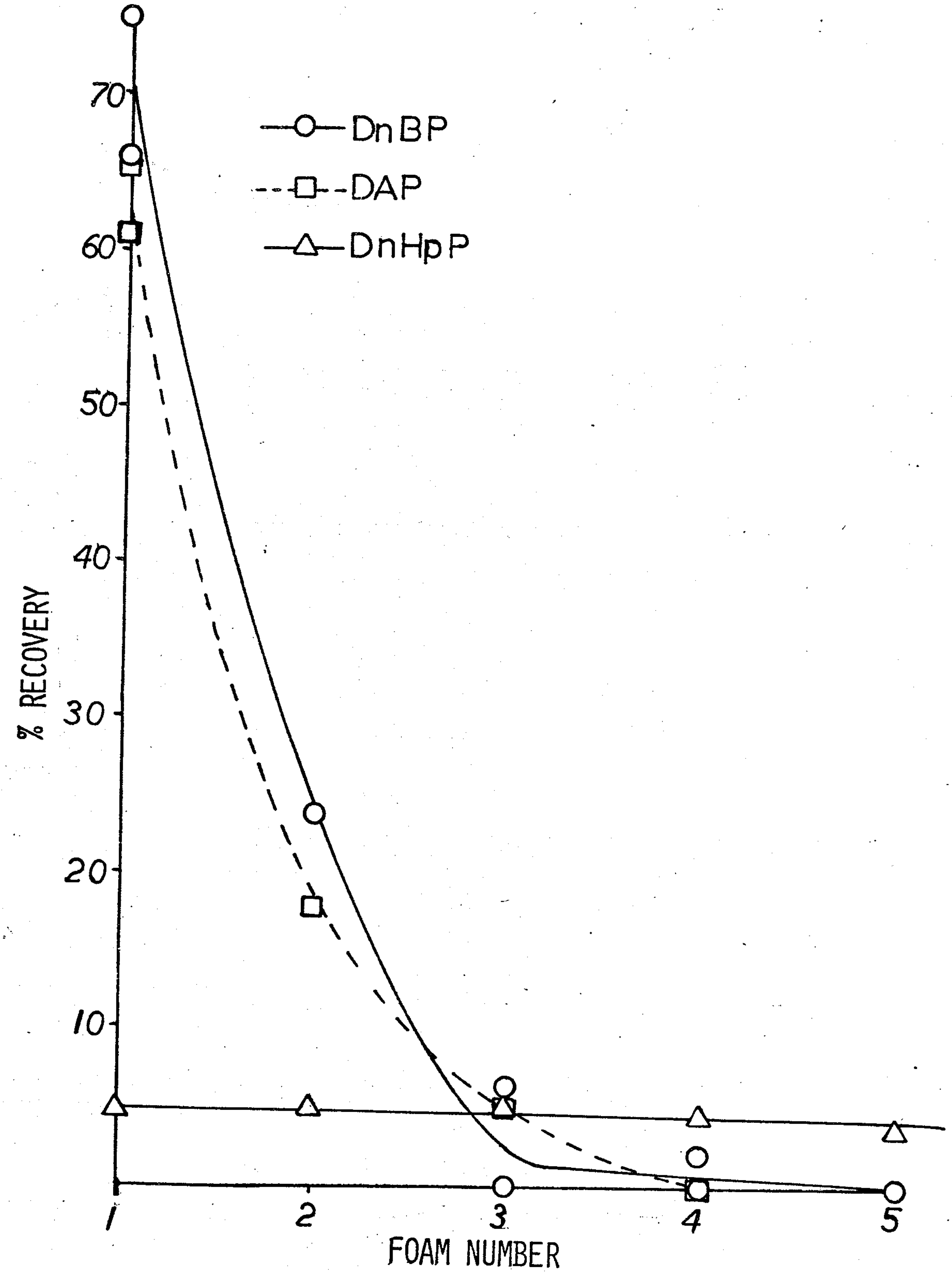

BBP
DnHxP
80
70
60
50
40
30
20
10
% RECOVERY
1
2
3
4
5
FOAM NUMBER

Figure 16

Column Profiles of DnBP, DAP, and DnHpP; Experiment XVIII


—○— DnBP
- -□- - DAP
—△— DnHpP
% RECOVERY
70
60
50
40
30
20
10
1
2
3
4
5
FOAM NUMBER

Discussion

Recoveries of DMP and DEP with the #1338 foams in experiment XV were lower than those with the diSPo foams, but only slightly, and the column profiles were similar. It was presumed that the same explanation of behaviour applied to both foamstypes.

The recoveries of DnBP and DiBP were about the same as for the diSPo foams, while the recovery of DAP was improved with respect to the results of experiment X, and about the same as those of experiment XIII. No explanation could be found for the low recovery of DAP in experiment X as compared to experiment XIII, as conditions were identical, but the similarities in the per cent recoveries of the other phthalates on the two types of foam indicate the higher value, i.e. experiment XIII, to be the more accurate of the two, when compared to the recovery with the #1338 foams. All three recoveries,of DAP, in experiment XIII, and XVIII, are in the region of 79 %.

In experiment XVII, the larger phthalates were not recovered while BBP was almost completely removed from the water. This had also occurred with the diSPo foams, and the explanations put forward in that discussion are presumed to hold here also.

In experiment XIX, the recovery of DnHxP was seen to be much lower than that with the diSPo foams, but the reference phthalate, DnHpP, was obscured by an unknown contaminant (which had not appeared before, and never reappeared), so the extent of experimental error could not be determined.

In summary, the column profiles were all very similar to those of the diSPo columns. The physical data on the flexibility of the diSPo foams was not available, so that they could not be compared to the #1338 foams, but on simple examination, the #1338 foams seemed to be more flexible. This implied a greater flexibility of the molecular segments of the polymer, which should result in a higher mobility of plasticizer molecules within the foam matrix. One would therefore expect that the rate at which equilibrium between the aqueous and polymeric phases is established would be faster than that for the diSPo foams. If the low recovery of the DMP and DEP is related to their high mobility within the polymeric phase, increased flexibility of the molecular segments of the #1338 foam with respect to that of the diSPo foam would explain the relatively lower recoveries in experiment XV compared to experiment IX. Unfortunately, even if this were the case, the increased flexibility of the foam did not extend the range of recoverable phthalates beyond DnHpP.

In the next section, the behaviour of DMP and DEP was investigated more thoroughly.

Section 5 : Investigation of the Recovery Process for DMP and DEP from Water - Flow System

Experiment XX : Two solutions of DMP and DEP, each 1.0 ppm in 100 ml water, were prepared and each was passed through a column of 5 foams. Column A was composed of diSPo foams, column B, #1338 foams. A blank solution was also run, on a column of #1338 foams. The flow rate of the solutions was 1 ml/min. The columns were allowed to run dry after the spike solutions had passed through; no rinse was added. The foams were extracted and analyzed as usual.

The column profiles are shown in Figures 17 and 18. Total recovery of DMP on column A was 28%, and on column B, 20%. Total recovery of DEP was 98% on column A, and 100% on Column B.

Discussion

The recovery of DMP improved markedly, though the profile still showed a gradual increase in absorption toward the lower end of the column. The diSPo foams were again more efficient than the #1338 foams. The improvement in recovery on lowering the flow rate, also observed for DEP on both columns, was interpreted as evidence of a two-step absorption process. The first step is adsorption onto the foam surface, which is presumed to be faster than the second step, absorption into the bulk of the foam, and diffusion away from the foam-water interface. The lower flow rate allowed more time for the surface of the foam to be cleared of adsorbed phthalate, by diffusion into the foam matrix, before more phthalate solution entered the foam region. This does not explain the shape of the DMP profile. It had been thought that the

Figure 17

Column Profiles of DMP, and DEP on Column (A), Small DiSPo Foams; Experiment XX.

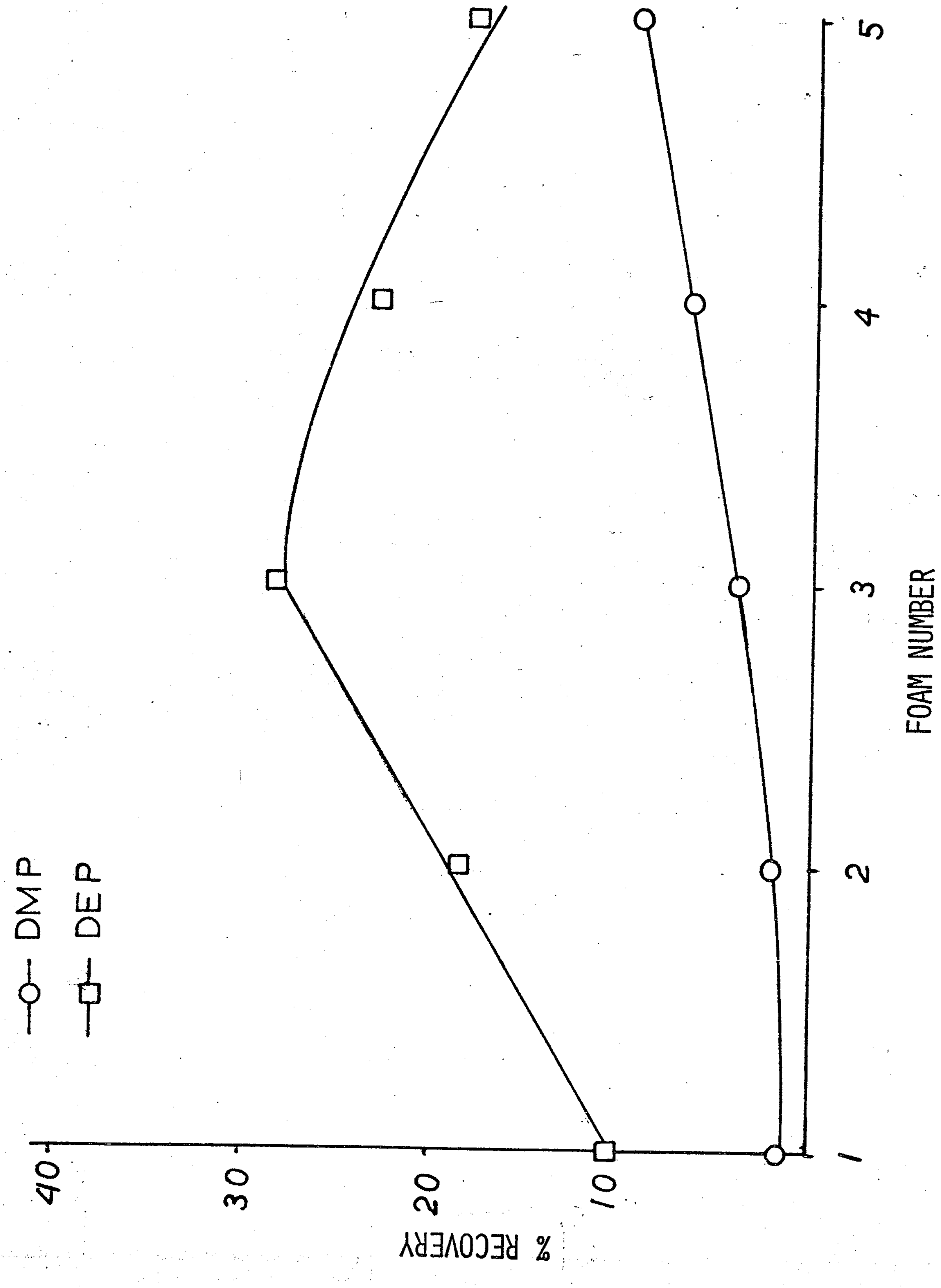
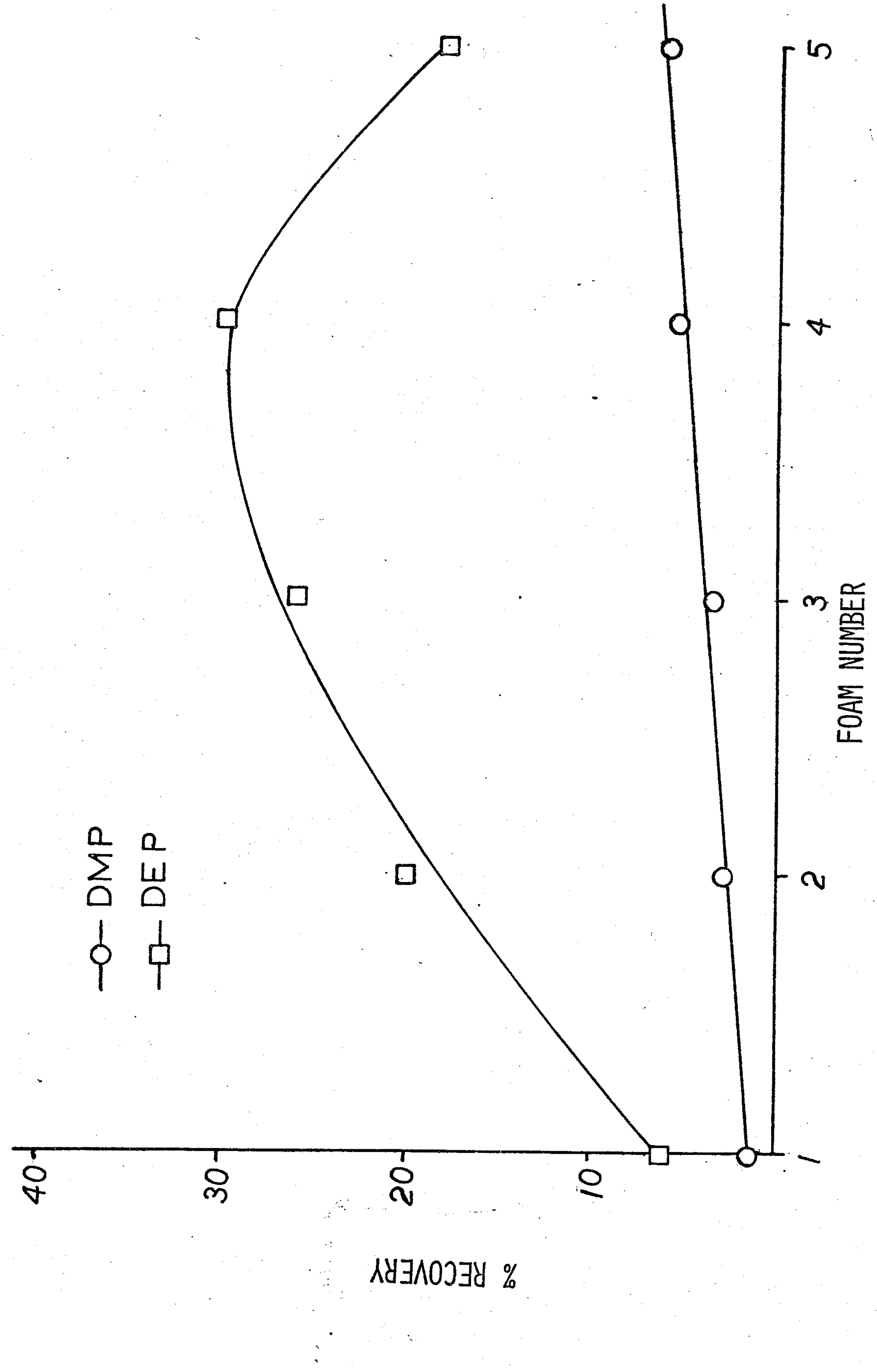

DMP
DEP
40
30
20
10
% RECOVERY
1
2
3
4
5
FOAM NUMBER

Figure 18

Column Profiles of DMP, and DEP on Column (B), Small #1338 Foams; Experiment XX.


-o- DMP
-□- DEP
% RECOVERY
40
30
20
10
FOAM NUMBER
1
2
3
4
5

omission of the rinse water would result in the recovery of about the same amount of DMP in each foam. The rate of absorption of DMP should be the fastest, as it is the smallest phthalate studied. Therefore,the rate at which an equilibrium distribution between the foam and water phases is established should also be the fastest. The equilibrium may, under the conditions used here, be such that only 5 or 6% of the DMP is recovered by any one foam, as was seen to occur with DnHpP, in experiments XIII and XVIII. The concentration of DMP in the incoming solution was always 1.0 ppm, therefore, one would not expect desorption to occur at any point in the experiment. The fact that only 1% was found in the first foam, while up to 8% was found in the last foam, shows that some other factor is at work which cannot be explained in terms of simple absorption-desorption processes. It appears that the DMP is actually running ahead of the water in the column, and even the assumption of an extremely high mobility of DMP within the polymeric network does not seem to be sufficient reason for the increase in concentration of the phthalate at the end of the column.

The DEP column profile was also shifted slightly in this experiment. Recovery was complete, and the maximum was found nearer the centre of the column. Again, desorption back into the aqueous phase cannot be used to explain the maximum concentration of the phthalate halfway down the column, while diffusion through the polymer network does not seem likely to be the major cause. The next experiment was designed to study the importance of desorption back into the aqueous phase when rinse water was passed through.

Experiment XXI : Two clean, dry diSPo foams were placed in clean glass beakers. One ml of 100 ppm DEP in acetone was pipetted onto each foam, which was then allowed to dry in air for 2 hours. The first foam, (1), was immediately extracted with 20 ml hexane, divided between two 10 ml volumetric flasks, and then with hexane and acetone into two more 10 ml volumetric flasks. A column of 5 diSPo foams was prepared as usual, but with the top foam about 10 cm from the top of the glass column. The acetone in the column was flushed out with water, and the column left filled with water. The second DEP-treated foam, (2), was placed in the column, at the top, well above the other foams, and was squeezed to expel air bubbles. Two hundred ml of clean water was passed through the column at a flow rate of 10 ml/min, to simulate the amount of water used in experiment IX. When the column had run dry, each foam was extracted as usual into a 10 ml volumetric flask. To ensure complete extraction, the tpp foam, (2), was re-extracted into a second 10 ml volumetric with 2 ml acetone and 8 ml hexane. All samples were analyzed by GC.

The results are shown in Table 9.

Table 9 : Recovery of DEP Washed Off Spiked Foam - Flow System

Experiment XXI

Flow rate : 10 ml/min

Sample			% Recovery DEP
Foam (1)	1st extract*		37
	2nd extract*		25
	3rd extract		18
	4th extract		1
		Total	81
Foam (2)	1st extract		16.5
	2nd extract		4
		Total	20.5
Column foams	1		14
	2		10
	3		10
	4		9.5
	5		9.5
		Total	53

* hexane only used as extracting solvent

Discussion

The incomplete recovery of DEP from the first foam was due to the loss of some of the 1 ml of acetone spike, which ran out of the foam and dried on the walls of the beaker.

The second spiked foam, (2), can be presumed to have lost approximately 20% of the DEP in the same way as foam (1). Of the remaining 60% not found in foam (2), 53% was found in the five column foams, and, judging from the shape of the column profile, 10 % was completely washed out. This shows the importance of omitting the rinse water, as was done in experiment XX. However, it still does not explain the shape of the DEP profile in experiment XX. The fairly even distribution of DEP on the column in experiment XXI was what had been expected for the earlier tests, where it would have been interpreted as a case of rapid establishment of the equilibrium distribution of phthalate between water and polymer phases, and a relatively low K_D with respect to those of larger phthalates. It may be that K_D varies with the concentration of DEP in the foam and in the water. In that case, the method of introducing the DEP into the water in experiment XXI could have been responsible for the change in the column profile, as the amount of DEP being desorbed into the water would initially be high, and gradually decrease. The amount of DEP entering the rest of the column would thus be gradually decreasing and the equilibrium distribution would even out over the column.

This experiment thus showed that desorption does play an important part in the recovery of the smaller phthalates when rinse water is passed through the column, but failed to explain the column profiles of DMP and DEP in experiment XX.

Section 6 : Recovery of Phthalates from Water - Static System

The recovery of phthalates from water under static conditions was studied in order to determine the equilibrium distribution of the phthalates between the aqueous and polymeric phases, and the rate at which equilibrium is established. The procedure was as described in the experimental section, except that in the first two experiments, the beaker was covered with aluminum foil, not a glass lid. After the extraction was complete, the foams were placed separately in glass columns and flushed with 100 ml clean water, unless otherwise noted.

Experiment XXII : A solution of 1.0 ppm each DnHxP, DnHpP, and DnOP in 100 ml water was extracted with a large #1338 foam for 72 hours.

The conditions for this experiment were duplicated in the next six experiments, XXIII to XXVIII, except that the duration of the experiments was varied, and after experiment XXIII the aluminum foil was replaced with a glass lid as described in the experimental section.

In the last five experiments, a slightly higher proportion of acetone to hexane was used in the first 25 ml of organic solvent, and this was allowed to remain in contact with the foam for about 1.5 minutes before being expelled into the funnel and volumetric, in an attempt to extract the foams more efficiently. The foams were sometimes re-extracted a third time, into a third 25 ml volumetric, to check that the extraction was complete.

The results of these experiments are tabulated in Table 10.

Table 10 : Recovery of Phthalates from Water - Static System

Solution : 100 ml of 1.0 ppm of each phthalate
Foam: 1 large #1338 per beaker

Experiment	Duration (hours)	% Recovery		
		DnHxP	DnHpP	DnOP
XXII*	72	29	30	50
XXIII*	3844	89	41	48
XXIV	72	37	76	69
XXV	72	56	65	71
XXVI 18	18	54	88	82
XXVII	2	66	81	91
XXVIII	1	63	71	77

*In these two experiments, the beaker was covered with aluminum foil only, not the glass lid shown in Figure 2

Discussion

The recoveries of DnHxP, DnHpP, and DnOP in experiment XXII were much lower than those in the later experiments. It was thought that an insufficient amount of acetone had been used to remove the water from the foams for the foam extraction. This was seen from the fact that the amount of phthalates in the third 25 ml extract was about the same as that of the first. For this reason the extraction method was changed slightly, as indicated in the experimental section immediately preceding Table 10.

In the remaining experiments, XXIII to XXVIII, it was seen that the recovery of the phthalates was high, though not complete, and roughly constant after 1 to 2 hours. It is not known why the amount recovered after 72 hours was less than that recovered after 2 hours. Loss of the phthalates by evaporation is a possible, but not a very likely, explanation. The volatility of the phthalates is extremely low. (see Appendix C) There is also the possibility of adsorption on the glass walls of the beaker and on the glass plunger, but these were not rinsed with acetone and hexane for GC analysis at the time to verify this idea. If such adsorption occurred, at a low rate, and if it were relatively irreversible, while the desorption and reabsorption of phthalate took place continually from the foam matrix, then, over long periods of time, adsorption on the glass walls of the beaker would effect a gradual decrease in the amount of phthalate remaining in the foam.

The question of whether absorption into the foam, or adsorption onto the foam was occurring was not resolved. Bowen[60] measured the surface areas of a number of commercial foams with radioactive stearic acid and found them capable of adsorbing from 1 to 3 x 10^{-4} moles stearic acid per kilogram of foam. This means the surface areas range from 7 to 30 m^2 per kilogram. It was assumed that the foams used in the present work fell within this range. Stearic acid molecules are regarded as rods which line up vertically on the foam surface, the hydrophilic acid end in the aqueous phase, and the hydrophobic alkyl end at the foam surface. If one of the larger phthalic acid esters were to be adsorbed on the foam surface, assuming the orientation occupying the smallest area, i.e., vertical, it would be a rod of at least twice the diameter of the stearic acid molecule. The largest number of moles that one kilogram could adsorb would then be from 0.5 to 1.5 x 10^{-4} moles of phthalate. The large #1338 foam plugs weigh about 1.6 g. The amount of phthalate which could be adsorbed by one of these plugs would then be:

$$\frac{1.6\ \text{g}}{1000\ \text{g}} \times (0.5 \text{ to } 1.5 \times 10^{-4}) \text{ moles}$$

or $\quad 0.9$ to 2.4 x 10^{-7} moles

One hundred ml of solution, containing 1.0 ppm each of DnHxP, DnHpP, and DnOP, contains a total of 3 x 10^{-7} moles of phthalate. The size of these three phthalates would be approximately the same for these purposes. So far, the occupation of the smallest possible area per molecule and the adsorption of the largest possible number of phthalate molecules has been assumed. Nevertheless, as less than 100% of each of the phthalates was taken up by any one foam in experiments XXII to XXVIII, the possibility that these larger phthalates are being recovered now because of adsorption not absorption cannot be ignored.

A further point which might be taken as an indication of adsorption and not absorption is the fact that the recovery of DnHxP was usually lower than that of DnHpP, and DnOP. If the process is absorption, one would expect that the smallest of the three phthalates would be recovered to the greatest extent, based on a higher rate of absorption. This has already been observed with the smaller phthalates under flow conditions. (experiments IX to XIX) If the process is one of adsorption, the larger phthalates might be expected to be adsorbed first, at a faster rate, because of their lower solubility in water.

The smaller foams, being only 1/10 the size of the larger foams, have been seen to take up as much as 3 x 10^{-7} moles of the smaller phthalates under flow conditions , though capable of adsorbing only 0.9 to 2.4 x 10^{-8} moles, so that absorption, and not adsorption is indicated here.

In the next experiments, the recovery of other phthalates under static conditions was studied.

Experiment XXIX : In this experiment, the multiple static extraction system, involving three plungers and beakers, as described in the experimental section, was first used. Three solutions of 100 ppm DnBP in 100 ml water were prepared, and poured into the three beakers. One large #1338 foam was placed in each beaker and squeezed to expel water. The system was assembled, and operated for one hour. The foams were then removed, and extracted into three 25 ml volumetric flasks. Four µl from each solution was analyzed by GC.

Results and Discussion

The amounts recovered from the three foams were 110%, 107%, and 101%. The excess DnBP was about what might be expected from the contamination normally found in the water. (Compare the blanks from experiment IV) It was presumed that the system was operating satisfactorily and that the procedure used for extracting the foams with acetone and hexane was adequate.

Experiment XXX : Three solutions of 1.0 ppm DMP in 100 ml water were extracted in the three beakers of the multiple extraction system with one large #1338 foam per beaker. The first solution was extracted for 1 hour, the second for two hours, and the third for three hours. At the end of the prescribed times, the foams were removed, not rinsed with water, and extracted with a total of 75 ml of acetone and hexane, into three 25 ml volumetric flasks. The organic extracts were all analyzed by GC as usual, and the total amount of DMP removed by each foam was determined.

The results are show in Table 11.

Table 11 : Recovery of DMP from Water - Static System

Experiment XXX
Solution : 100 ml of 1.0 ppm DMP
Foam : one large #1338

Beaker	Extract		% Recovery DMP
A	first		13
	second		23
	third		- 3
		Total	39
B	first		44
	second		20
	third		12
		Total	36
C	first		11
	second		1
	third		0
		Total	12

Discussion

In experiment XXX, the amount of DMP recovered by the large #1338 foams, after 1, 2, and 3 hours, was well below 50%. This had been expected from the previous tests with DMP under flow conditions, experiments IX, XV, and XXI, where the recovery was very low. The recovery under static conditions was about 0.039 μg DMP/ 1.6 g foam, or 0.025 μg DMP/g foam. Under flow conditions, the maximum recovery of DMP from one small #1338 foam plug was about 0.005 μg DMP/ 0.18 g foam, or about 0.020 μg DMP/ g foam. This latter figure is below the equilibrium distribution established under static conditions, but only slightly, and is expected from the nature of the experiment, dynamic as opposed to static. The amount recovered by one small #1338 foam situated at the top of a flow column was only 0.001 μg. If the equilibrium distribution found in the static experiments is established, then a foam, having absorbed the equilibrium amount of DMP, should not begin to desorb until the concentration of DMP in the adjacent aqueous phase has decreased. In experiment XX, this did not occur. The concentration of DMP in the incoming solution was always 1.0 ppm. It was pointed out, in the discussion following experiment XXI and it has beem confirmed here, that desorption back into the aqueous phase cannot account for the loss of DMP under flow conditions, or the higher concentration of DEP at the centre of the column. The major cause for this phenomenon could not be ascertained from these experiments.

The amount of DMP recovered after three hours was only one third as much as had been recovered after one and two hours. It was thought that evaporation of DMP might be cause of this decrease, and the next experiment was designed to test this possibility.

Experiment XXXI : A solution of 1.0 ppm DMP in 100 ml of water was extracted under static conditions for one hour. The foam plug was then removed and extracted with 5 ml acetone, and 45 ml hexane, divided between two 25 ml flasks, while the static system was left to operate for one hour without a foam in the beaker. A second foam was placed in the beaker at the end of this time, and the static extration system operated for a third hour. This second foam was then removed, and extracted with acetone and hexane as before. To ensure that the equilibrium distribution did not alter when the initial concentration was lowered slightly, a second solution of 0.6 ppm DMP in 100 ml of water was prepared and extracted for one hour with a single large #1338 foam. At the end of this period, the foam was removed and extracted as usual.

Experiment XXXII : The conditions of experiment XXX were duplicated, except that the durations of the three extractions were 10, 20, and 30 minutes. At the end of the prescribed times, the foams were removed, and extracted with acetone and hexane as usual. Four μl of each solution were analyzed by GC.

The results of these two experiments are shown in Table 12.

Table 12 : Recovery of DMP from Water - Static System

Solution : 100 ml of 1.0 ppm DMP

Foam : one large #1338 per beaker

Experiment	Initial conc'n (ppm)	Duration (hours)	% Recovery DMP
XXXI	1.0	1	47
	0.53*	1	32
	0.60	1	38
XXXII	1.0	1/6	47
	1.0	1/3	43
	1.0	1/2	37

* initial concentration was 0.53, if no evaporation or other loss occurred, since 47% had been removed by the first foam.

Discussion

In experiment XXXI, a clean foam was allowed to extract DMP for one hour under static conditions. The operation of the system without a foam for one hour allowed any possible loss by evaporation to occur as before. A second foam was placed in the beaker to extract DMP for the third hour. If no evaporation occurred, and if the distribution of DMP between the aqueous and organic phases was the same, the second foam would remove about 40% of the remaining DMP. A total of 47% was in fact removed by the first foam, and 32% by the second. It was possible that the distribution changed when the amount of DMP in the initial solution was lowered. A second solution of 0.6 ppm of DMP in 100 ml water was extracted with a large #1338 foam for one hour to test this. From the results, 38% of the original concentration was removed, the distribution was assumed to be about the same as had been found in experiment XXX.

It was concluded that the loss of DMP by evaporation was not important, and that the result from the three hour extraction of DMP in experiment XXX was due to some experimental error, such as incomplete extraction with the organic solvent.

The results of Experiment XXXII, showing the recovery of DMP under static conditions as a function of time, indicate that the equilibrium distribution is established very quickly, as had been expected for the small phthalates. Reproducibility of results was not too good, but the equilibrium distribution coefficient for DMP between water and foam under these conditions was found to be about

$$\frac{\text{443} \pm \text{60 parts phthalate/ g foam}}{\text{1 part phthalate / g water}}.$$

Section 7 : Recovery of Phthalates from Water with Coated Polyurethane Foam - Flow System

Experiment XXXIII : Small diSPo foam plugs were coated with DOW-200 silicone oil, as described in the experimental section. The average amount of oil taken up by one foam, weighing 0.20 g, was 0.0044 ± 0.0004 grams. A solution of 1.0 ppm each of DMP, DEP, and DnBP in 100 ml water was prepared and passed through a column of five coated foams at 3 ml/min. This was followed by 100 ml of water which had been used to rinse the volumetric flask which had contained the spike solution. A 100 ml blank was also run. The foams were removed from the columns, each foam was extracted with about 3 ml acetone and 7 ml hexane, as usual, and the extracts were analyzed by GC. The column through which the spiked solution had passed was washed down with 25 ml acetone and hexane (1:3), and this was also analyzed by GC.

Experiment XXXIV : A solution of 1.0 ppm DAP, BBP, and DnOP in 100 ml water was prepared and run as in experiment XXXIII.

When the columns were prepared for these experiments, they were not filled with acetone first, as had been done in the case of the uncoated foams, as this would have washed off the coating. The column was therefore filled with clean water before the foams were put in, and the foams were squeezed thoroughly with tweezers to expel air bubbles, before the spiked solutions were passed through.

The results of experiments XXXIII and XXXIV are shown in Table 13.

Table 13 : Recovery of Phthalates from Water with DC-200-Coated DiSPo Foam Plugs - Flow System

Solution : 100 ml water with 1.0 ppm of each phthalate
Flow rate : 3 ml/min
Columns : 5 small diSPo foams, each coated with 0.0044 ± 0.0004 mg oil

Experiment	Sample	Foam No.	% Recovery					
			DMP	DEP	DnBP	DAP	BBP	DnOP
XXXIII	Spike	1	1.5	8.5	78			
		2	2.5	16.5	22			
		3	3.0	18	5			
		4	2.7	14.5	0			
		5	3.0	12.5	0			
	Column rinse		1.0	4.0	0			
		Total	13.7	74	105			
	Blank	1	0	0	7			
		2	0	0	0			
		3	0	0	0			
		4	0	0	0			
		5	0	0	0			
		Total	0	0	7			
XXXIV	Spike	1				49	64	3.5
		2				1	8	1.5
		3				1	2	1.5
		4				0	1	2.5
		5				0	1	1.5
	Column rinse					0	2	3.5
					Total	51	78	14

Discussion

The overall recovery of the phthalates was similar to that found with the uncoated diSPo foam,,but slightly lower. (see Table 7) That DMP and DEP recoveries are lower is probably due to a lower solubility of the phthalates in the oil than in the foam. The recovery of DnBP is unchanged, and DAP and BBP are about the same. DnOP was recovered for the first time in a flow system in experiment XXXIV. It is doubtful that the foam actually absorbed any of the 12% recovered by the foams; it was more likely dissolved in the oil, because of its long hydrophobic sidechains. This problem was also discussed by Musty and Nickless[69], who reported that the uncoated foams recovered more PCB than DC-200-coated foams at low flow rates. When the flow rate was increased, the coated foams recovered more than the uncoated, but the maximum amount recovered by the coated foams at higher flow rates was lower than the maximum amount recovered by the uncoated foams at the lower flow rates. They concluded that the uncoated foam removed the PCB from water more quickly than the coated foams, but that the coated foams retained the PCB more strongly. In terms of equilibria, this means that the equilibrium distribution is established more rapidly between foam and water than between coated foam and water, and K_D is larger for the uncoated foams. The same may also be true for the phthalates tested here, except that, for the larger phthalates, e.g., DnOP, the situation is the reverse. Hence, there was a decrease in the recovery of the smaller phthalates, whereas DnOP was recovered to a slight extent.

Section 8 : Removal of Phthalates from Water with Other Types of Foam - Flow and Static Systems

Polyurethane foams were obtained from Union Carbide Corp., labelled type "A" and type "B". Type "A" was composed of 60 parts Niax 11-34 polyol, an oxypropylene/oxyethylene copolymer, of 5000 number average molecular weight, 40 parts of Niax 34-28 polymer-polyol, a graft dispersion styrene (20% by weight) in acrylonitrile, of 5000 number average molecular weight, and an 80:20 mixture of toluene diisocyanate and polymethylene polyphenyl isocyanate, 105 Index[*]. Type "B" was composed of 80 parts Niax 11-34 polyol, 20 parts Niax 34-28 polymer-polyol, and toluene diisocyanate, 105 Index. Type "A" was about 15 % denser than type "B", which had larger pores, of more non-uniform size , and was less flexible than type "A". Actual data on porosity, surface area, and compression range were not provided by Union Carbide Corp.

Another type of foam was obtained from B.F. Goodrich and Co., listed as #1115, a "super-soft" foam, with density 1.00 to 1.15 lbs/ft^3, and compression range of 13 to 18. This was much softer than #1338, with its density of 1.2 to 1.35, and compression range of 35 to 42. As noted in the introduction, extra super-soft foams are prepared by adding a chain-stopper (e.g. ethyl lactate) to the pre-foamed mix, so that the end product contains many long branches which can act as internal plasticizers. It was hoped that this polymer, with its more flexible structure, would more readily absorb the larger phthalates.

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[*] 105 Index means that there is a 5% excess of isocyanate groups over alcohol groups in the mixture.

Experiment XXXV : Rectangular blocks, 2.5 cm x 2.5 cm x 5.0 cm, were cut from the large blocks of type "A" foam, and cleaned as described in the experimental section. Average weight of the blocks was about 1.6 g, that is, about the same as that of a large #1338 cylindrical plug. Two solutions of 1.0 ppm each DnHxP, DnHpP, and DnOP were prepared and poured into the beakers of the static system. A blank was also prepared. One block of type "A" foam was placed in each beaker, and squeezed to expel air bubbles. Then the beakers were placed under the plungers of the multiple static extraction system, and it was operated for one hour. The foams were then rinsed with 100 ml of clean water, and extracted with acetone and hexane as usual, using a total of 50 ml for each foam, divided between two 25 ml volumetric flasks. Four μl from each sample were analyzed by GC.

Experiment XXXVI : The above experiment was duplicated, except that the foams used were (A) a cube of type "B" foam, 5 cm edge, about 5.3 g weight, (B) a cube of #1115 foam, 5 cm edge, weight about 2.3 g, and a large plug of #1338 foam. One foam was placed in each beaker, and the system was operated for 30 minutes. The foams were then removed, and extracted with a total of 75 ml of organic solvent divided between three 25 ml volumetrics. About 10 ml of acetone and 65 ml of hexane were used. Four μl of each sample were analyzed by GC and the total amount of phthalate removed by each foam was determined.

The results of experiments XXXV and XXXVI are shown in Table 14.

Table 14 : Recovery of DnHxP, DnHpP, and DnOP by Various Foams - Static System

Solution : 1.0 ppm of each phthalate in 100 ml of water

Experiment	Sample	Duration (hours)	Foam	DnHxP	% Recovery DnHpP	DnOP
XXXVI	spike	1	"A"	35	56	55
	spike	1	"A"	63	70	85
	blank	1	"A"	00	0	0
XXXVII	spike	0.5	"B"	21	68	98
	spike	0.5	#1115	25	45	45
	spike	0.5	#1338	31	64	81

Discussion

From experiment XXXV, and comparing the results with those of experiment XXVIII, it is seen that the efficiency of the Union Carbide type "A" foam was about the same as that of an equivalent amount of #1338, over the same time period of one hour. The low recovery of phthalate in the first of the two static systems containing Union Carbide type "A" foam was due to faulty operation of the static system. The plunger was not operating properly in the beaker, so that there was poor circulation of the test solution through the foam and consequently, low recovery.

From experiment XXXVI, it was seen that the Union Carbide type "B" foam gave an unexpectedly high recovery of DnOP, and an unexpectedly low recovery of DnHxP. It had been thought that the apparent rigidity of the foam was indicative of lower flexibility of the polymeric chains, and that the recovery of the larger phthalates would be low. The reverse occurred, as had happened before in the static tests with #1338 foam plugs. (experiments XXII to XXVIII) This is a further indication that the process of removal of the larger phthalates from water is one of adsorption, not absorption. The same argument which was discussed in Section 6 regarding the high recovery of DnOP compared to the low recovery of DnHxP would be expected to apply here. If the process is one of absorption not adsorption, then the type "B" foams would be expected to perform better than the #1338 foams under flow conditions, as the recovery of the larger phthalates under static conditions for the same period of time was greater for the Union Carbide type "B" foam than the #1338 foam. This was studied in experiment XXXVIII.

The super-soft foam, #1115, also gave results opposite to those expected, showing a low efficiency in the removal of phthalates. If this was due to lower solubility of the phthalates in the foam, it seemed likely that the smaller phthalates, DMP, DEP, DnBP, having higher diffusion rates to counterbalance their lower solubilities in the foam, would be recovered. The other possibility was that the low recoveries were the result of extremely high diffusion rates of the phthalates in this very flexible foam. In this case, the small phthalates would not be retained at all, and a foam of flexibility intermediate to those of #1115 and #1338, with the same solubility properties, should efficiently remove the larger phthalates. Further, a foam of greater rigidity than #1338, with still the same solubility properties, would retain DMP and DEP, the smallest phthalates. The behaviour of the #1115 foam with respect to DMP, DEP, and DnBP, under flow conditions was tested in the next experiment.

Experiment XXXVII : Six cubes of #1115 foam with a 5 cm edge were cut and cleaned as usual. These foams were then placed in three large water-filled columns, two foams per column, and squeezed to remove air bubbles. The shape of the foams resulted in crowding at the corners of the cubes, but did not distort them seriously. Two solutions of 1.0 ppm each DMP, DEP, and DnBP in 100 ml water, and one blank solution : 100 ml of clean water, were prepared and passed through a column of #1115 foams at 10 ml/min. No rinse solution was used. The foams were removed when the columns had run dry, and each foam was extracted with 50 ml of solvent, about 5 ml acetone, and 45 ml hexane. The organic extracts were analyzed by GC.

The results are shown in Table 15.

Discussion

The two smaller phthalates tested in experiment XXXVII, DMP and DEP, were not retained at all by the #1115 foam under flow conditions. While DnBP was recovered, the per cent recovery was comparatively low. It seems then, from this experiment, that the low recoveries of DnHxP, DnHpP, and DnOP, in experiment XXXVI, occurred because the equilibrium distribution in this case, lies in favour of the aqueous phase, that is, K_D is very low for all the phthalates with this foam.

Table 15 : Recovery of DMP, DEP, DnBP by #1115 Foam - Flow System

Experiment XXXVII

Solutions : 1.0 ppm of each phthalate in 100 ml water

Columns : 2 large #1115 foam plugs, (@ 2.3 g each)

Flow rate : 10 ml/min

Concentration (ppm)	Foam		% Recovery		
			DMP	DEP	DnBP
1.0	Top		0	0	15
	Bottom		0	0	10
		Total	0	0	25
1.0	Top		0	0	30
	Bottom		0	0	20
		Total	0	0	50
Blank	Top		0	0	0
	Bottom		0	0	0
		Total	0	0	0

Experiment XXXVIII : Four solutions of 1.0 ppm each DEHP and DnOP in 100 ml of water were prepared. Two cubes of Union Carbide type "A" foam, and two cubes of Union Carbide type "B" foam, all with a 5 cm edge, were cut and cleaned as usual. Four large columns were prepared, the first two, (Columns 1 and 2), containing two type "A" foams each, and the second two, (Columns 3 and 4), containing two type "B" foams each. One 100 ml solution was poured through each column at a flow rate of 10 ml/min. This was followed by 100 ml of clean water, which had been used to rinse the 100 ml volumetrics that had contained the spiked solutions. The foams were extracted in a 50 ml ground glass syringe, instead of the 20 ml syringes which had been used previously. Each foam was extracted with about 5 ml acetone and about 45 ml of hexane, divided between two 25 ml volumetrics. These solutions were analyzed by GC, and the amount of phthalate recovered by each foam was determined.

The results of this experiment are shown in Table 16.

Table 16 : Recovery of DEHP, and DnOP by Various Foams - Flow System

Solution : 1.0 ppm of each phthalate in 100 ml of water

Foams : two type "A" or type "B" foams per column, cubes, 5 cm edge

Flow rate : 10 ml/min

Experiment XXXVIII

Column	Sample	Foam type		% Recovery	
				DEHP	DnOP
1	Top foam	"A"		4	1
	Bottom foam	"A"		2	1
			Total	6	2
2	Top foam	"A"		5	1
	Bottom foam	"A"		3	1
			Total	8	2
3	Top foam	"B"		1	1
	Bottom foam	"B"		<1	<1
			Total	~1	~1
4	Top foam	"B"		1	1
	Bottom foam	"B"		<1	<1
			Total	~1	~1

Discussion

The recovery of DEHP and DnOP by the Union Carbide type "A" and type "B" foams in experiment XXXVIII was very poor, despite the excellent recoveries found under static conditions. The same results had been found for the #1338 foams where, under static conditions for one hour, 77% of the DnOP in solution was extracted by the foam, while under flow conditions of 10 ml/min, # 1338 foams of the same size recovered only 20% of the DnOP in solution, (experiment XX). It is obvious that a flow rate of 10 ml/min is too fast for an equilibrium distribution of the phthalate between water and foam to be established. The rate controlling step could be (1)adsorption onto the foam surface, or (2) diffusion from the surface into the bulk of the foam matrix, if such a diffusion does occur. Lowering the flow rate would improve the recovery, by approaching static conditions.

Section 9 : Recovery and Concentration of Phthalates from Water at the ppb Level - Flow System

Experiment XXXIX : Four solutions of 16 ppb each of DMP, and DEP in 6.2 l of water were prepared in the 10 l bottles, and allowed to stand overnight. Two columns, each containing five small diSPo foam plugs, and two columns, each containing five small #1338 foam plugs, were prepared as usual. Each spiked solution was passed through a column of foam plugs at 150 ml/min. There was no rinse solution. When the columns had run dry, the foams were removed and extracted separately with about 2 ml of acetone, and 8 ml of hexane. Four μl of each 10 ml sample was analyzed by GC.

Experiment XL : Three solutions of 16 ppb each of DnBP, DAP, and DnHxP in 6.2 l of water were prepared and allowed to stand overnight. A blank, 6.2 l of clean water, was also prepared. Four columns were prepared, using the same foam types as in experiment XXXIX. Each solution was passed through a column of foams at 10 ml/min. The foams were then removed and extracted with acetone and hexane, as usual.

Experiment XLI : The blank solution in experiment XL was found to contain more than half as much DnBP as the spiked solution, therefore the water to be used was pre-cleaned by passing it through a column of eight large diSPo foam plugs, at 10 to 20 ml/min, and collecting it in the large clean glass bottles. A solution of 20 ppb of DnBP, DAP, and DnHxP in 5 l of pre-cleaned water was then prepared and passed through a column of five small diSPo foams at 10 ml/min. A blank solution was also run, with the pre-cleaned water, through a column of 5 small diSPo foam plugs. The foams were then removed, extracted, and analyzed in the same way as in experiment XXXIX. The bottle containing the spike solution was rinsed with 25 ml acetone and hexane (1:3), and the rinse was also analyzed by GC.

Experiment XLII : Two solutions of 20 ppb each of DnHpP, DnOP, and DEHP in 5 l of water were prepared and allowed to stand overnight. Two columns of 5 foams, one of diSPo and one of #1338, were prepared as usual. The solutions were each passed through a column of foams at 10 ml/min. The foams were then removed, extracted, and analyzed as usual.

The results of experiments XXXIX to XLII are shown in Table 17. Column profiles of each phthalate on both columns, and their respective profiles from the ppm studies are shown in Figures 19 to 22.

Table 17 : Recovery and Concentration of Phthalates from Water at the ppb Level - Flow System

Columns : 5 small foams, either diSPo or #1338, per column

Expt.	Foam type	Vol. (l)	Conc'n (ppb)	Flow $\left(\frac{ml}{min}\right)$	% Recovery DMP	DEP	DnBP	DAP	DnHxP	DnHpP	DEHP	DnOP
XXXIX	diSPo	6.2	16	150	0	0						
	diSPo	6.2	16	150	0	0						
	#1338	6.2	16	150	0	0						
	#1338	6.2	16	150	0	0						
XL	diSPo	6.2	16	10			101	81	67			
	diSPo	6.2	16	10			158	88	66			
	#1338	6.2	16	10			134	72	51			
	#1338*	6.2	0	10			66	0	0			
XLI	diSPo	5.0	20	10			127	94	62			
	spike bottle rinse						12	7	13			
	diSPo*	5.0	0	10			39	0	0			
XLII	diSPo	5.0	20	10						22	tr.	tr.
	#1338	5.0	20	10						27	tr.	tr.

*blank solution

Figure 19

Column Profiles of DnBP, DAP, DnHxP, and DnHpP on Small DiSPo Foams, ppb Level, Experiments XLI and XLII.

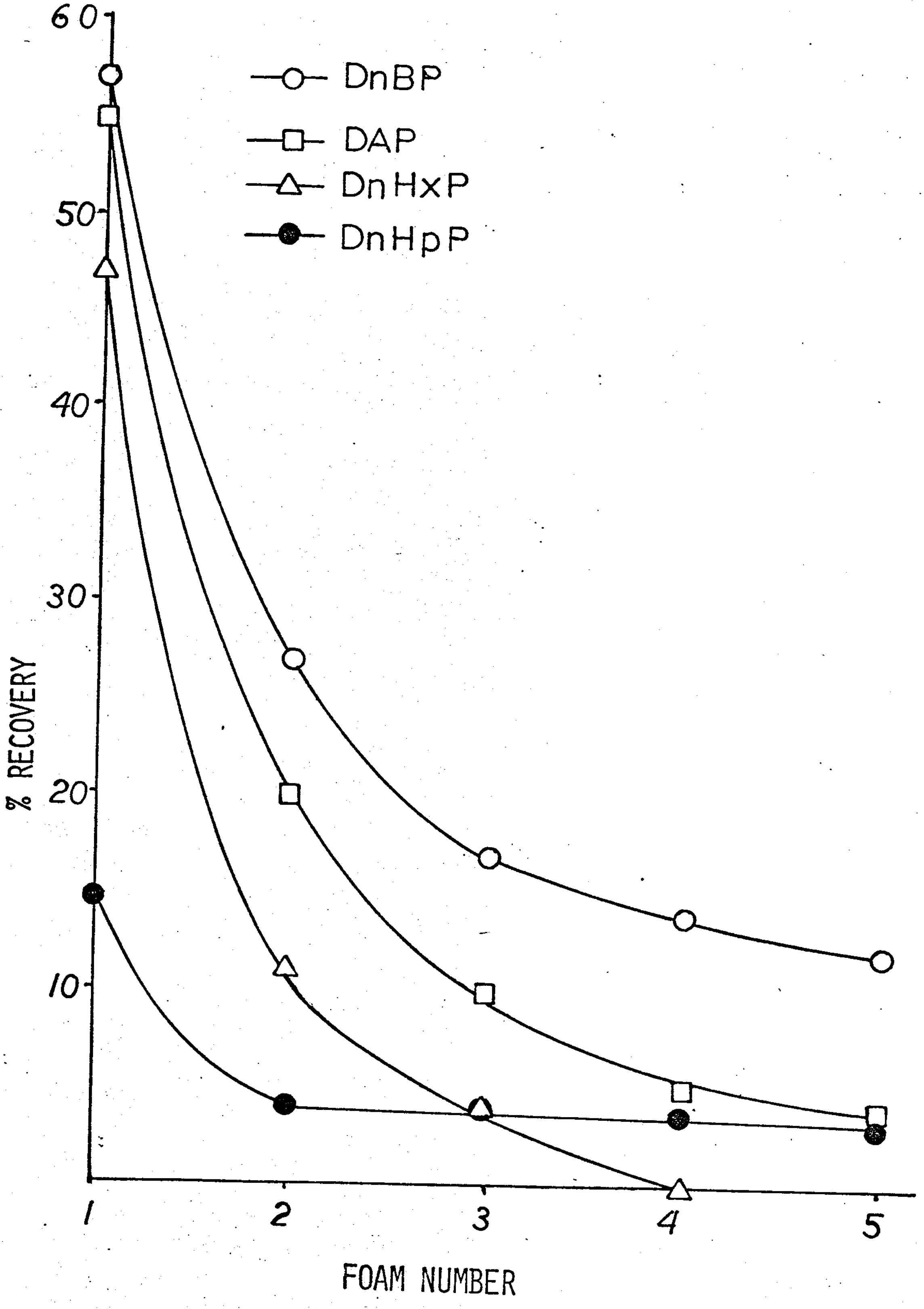

—○— DnBP
—□— DAP
—△— DnHxP
—●— DnHpP
60
50
40
30
20
10
% RECOVERY
1
2
3
4
5
FOAM NUMBER

Figure 20

Column Profiles of DnBP, DAP, DnHxP, and DnHpP on Small DiSPo Foams, at the ppm level, Experiments XIII and XIV.

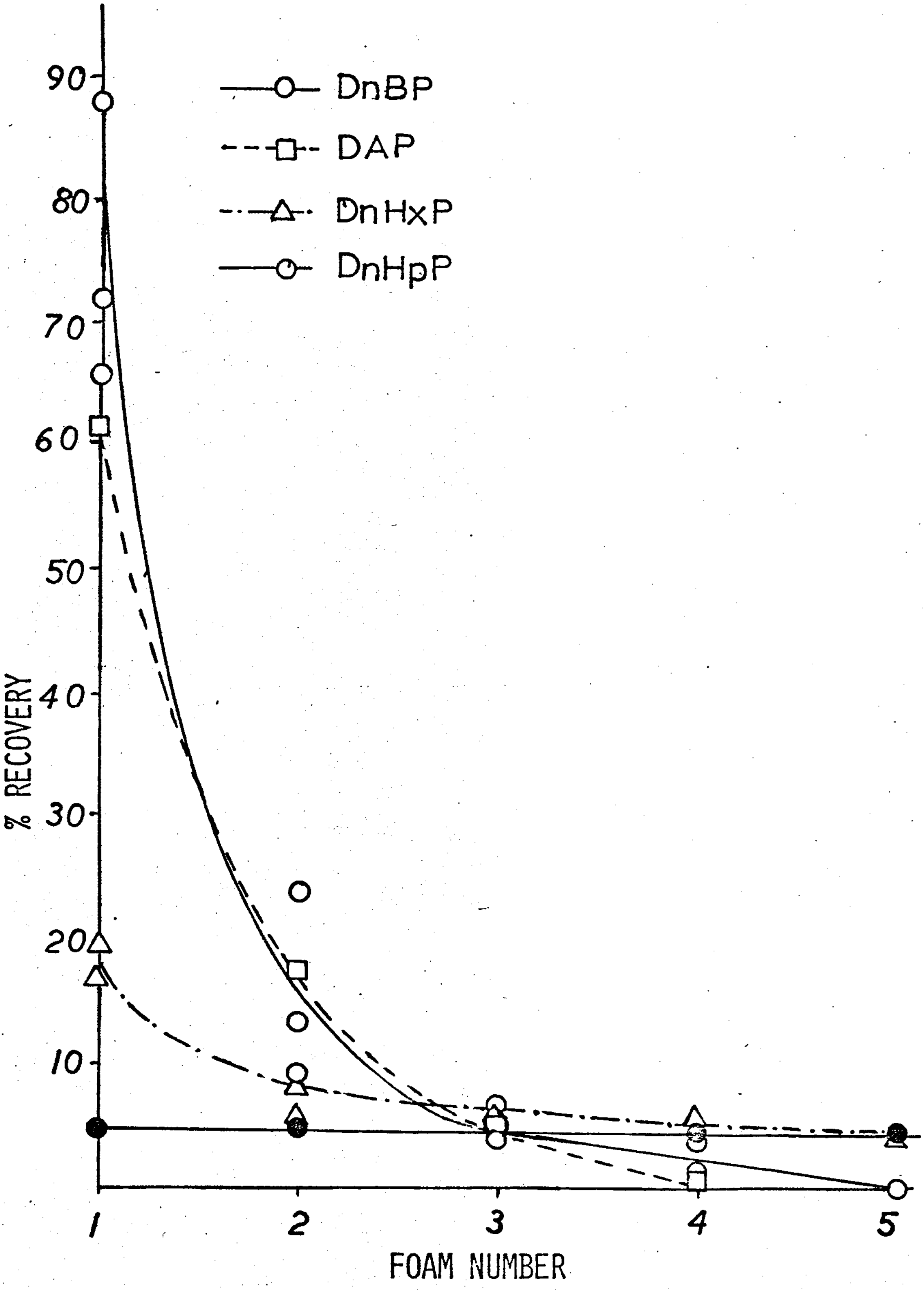

DnBP
DAP
DnHxP
DnHpP
% RECOVERY
90
80
70
60
50
40
30
20
10
1
2
3
4
5
FOAM NUMBER

Figure 21

Column Profiles of DnBP, DAP, DnHxP, and DnHpP on Small #1338 Foams, at the ppb Level, Experiments XL, and XLII.

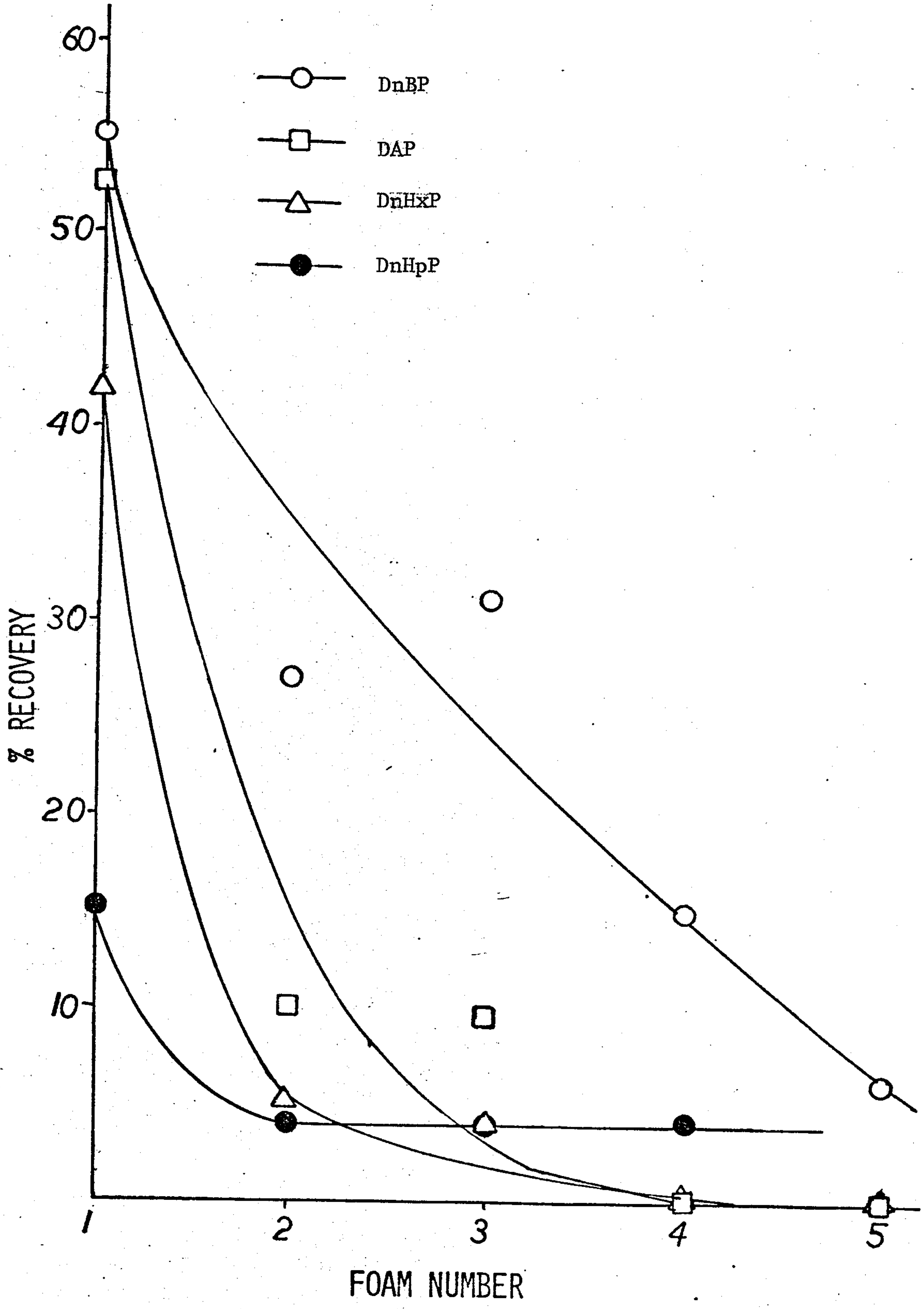
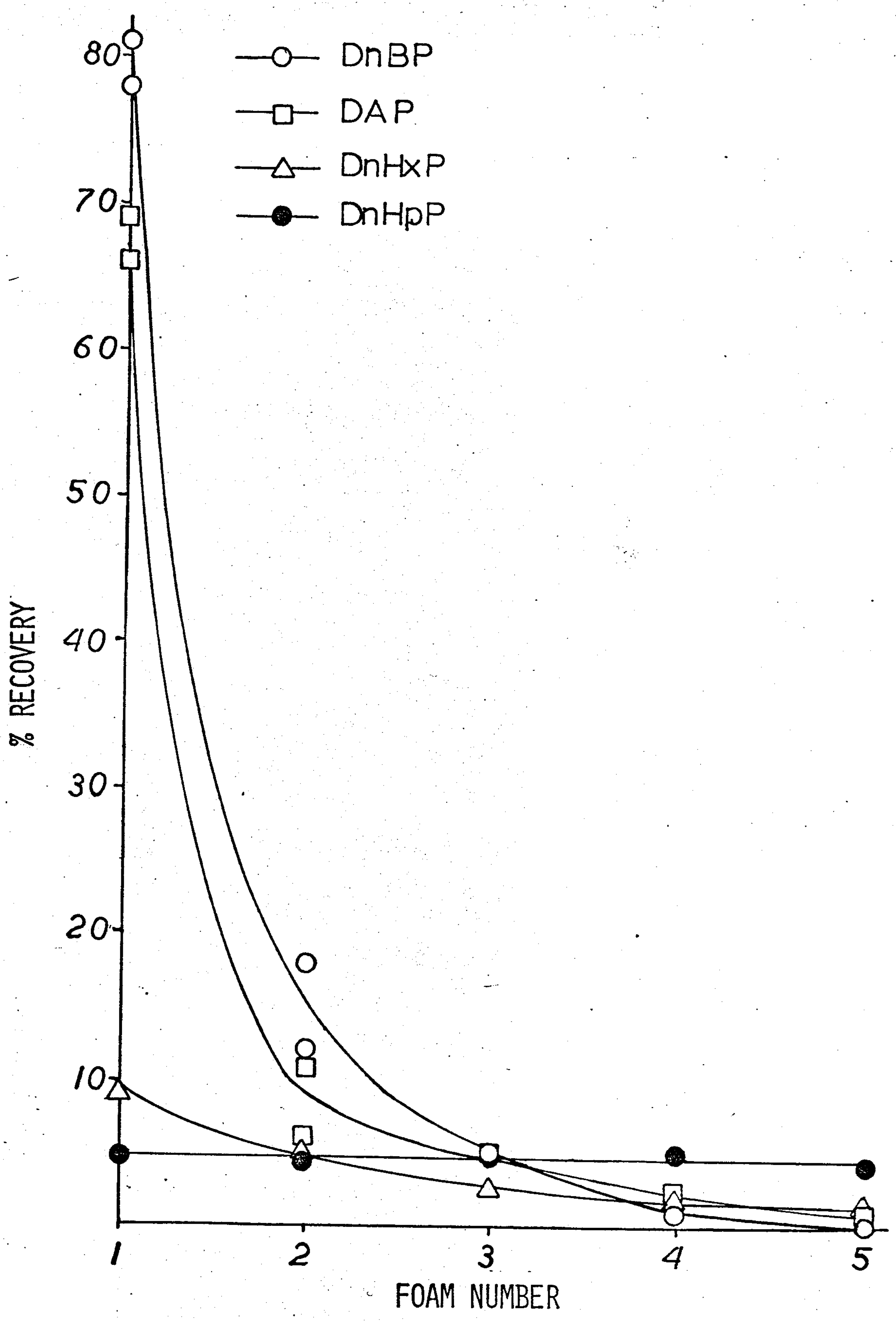

60
50
40
30
20
10
% RECOVERY
1
2
3
4
5
FOAM NUMBER
DnBP
DAP
DnHxP
DnHpP

Figure 22

Column Profiles of DnBP, DAP, DnHxP, and DnHpP on Small #1338 Foams, at the ppm Level, Experiments XVI, XVIII, and XIX.



DnBP
DAP
DnHxP
DnHpP
% RECOVERY
80
70
60
50
40
30
20
10
1
2
3
4
5
FOAM NUMBER

Discussion

It was seen, from experiment XXXIX, that DMP, and DEP were not removed from water at the ppb level. It appeared that the flow rate was much too high to allow any absorption to take place. Lowering the flow rate might improve the recovery. Alternatively, on comparison with the results from experiments IX, XV, and XX, where the DMP appeared to run ahead of the water in the column, it is doubtful whether this would alter the situation. At 20°C, 1.0 ppb of DMP and DEP should be completely dissolved in the 6.2 l of water. (see Appendix C) Thus, decreasing the concentration by a factor of 100, as was done in experiment XXXIX, might not alter the distribution of DMP and DEP between the aqueous and polymeric phases in a manner favourable to the foam.

In experiment XL, a number of factors became evident. First, DnBP was recovered as usual, despite the lower concentration used. The recovery of DAP and DnHxP was greatly improved. More importantly, the column profiles for these three phthalates differed greatly from those of earlier experiments, at higher concentration. DnBP was found not only in the first two or three foams of the column, but was spread throughout the entire length of the column, with the bottom foam containing 12% of the total amount of material. The maximum amount, while still in the first foam, was lower than that of earlier experiments. The whole profile was lowered and spread out. In contrast, the maxima of DAP and DnHxP were raised, and sharpened. Recovery of DAP was 100% for the first time, and the profiles of DAP and DnHxP resembled those of DnBP in the earlier experiments, at higher concentration.

This trend was continued in experiment XLII, where DnHpP was seen to be recovered to a greater extent, and the profile of DnHpP was seen to approximate that of DnHxP in experiment XIV. There was a maximum in the first foam, instead of the equal distribution through the length of the column which had been the case in experiment XIII.

DnOP and DEHP were still not recovered. Traces were seen in the GC analysis, but these were less than 1% of the total amount in the spike solution, and were not considered significant.

The possible explanation for the changes in the column profiles and per cent recovery is consistent with the two step absorption process proposed earlier. In the first step, the phthalate molecule is adsorbed onto the surface of the foam. If the phthalate is extremely large, for example DnOP, and if the polymer network is dense and rigid, the phthalate will, in all likelihood, remain at the surface of the foam, or be desorbed when the concentration of the phthalate in the moving aqueous phase is decreased. If the phthalate is smaller, e.g., DnHxP, and/or the foam less rigid, the phthalate may diffuse into the polymer network, The rate of absorption may or may not be sufficiently rapid for the foam surface to be cleared before the next phthalate molecule approaches that area of the foam. In this case, the probability that the DnHxP will diffuse into the foam is lower than it would be for the smaller phthalates. The surface may become entirely covered with adsorbed phthalate, while absorption continues slowly, and the incoming phthalate passes through to the next foam without any hindrance. Thus, the DnHxP is spread throughout the column, and not much is recovered, under flow conditions, and with an initial concentration of 1.0 ppm. Lowering the concentration, while keeping the flow rate constant, allows more time for the phthalate molecules to be absorbed before the incoming solution presents more phthalate molecules to the foam surface. Thus, DnHxP is recovered almost entirely in the first foam of the column under flow conditions , at a concentration of 20 ppb.

It has already been shown that the amount of phthalate present in 100 ml of 1.0 ppm or 5 l of 20 ppb is at least ten times the amount required to cover the surface of one small foam plug. An analysis of the results of experiments XL, and XLI was attempted in terms of the above reasoning. A lag time was assumed for the period while the top foam in the column became covered with phthalate. A continuous slow absorption of phthalate, which reached a maximum when the entire surface area was covered was also allowed for, and was assumed to exist from the start and to be dependent on the concentration of phthalate on the surface. Because of the extremely low concentration, (ppb), even with the assumption that every molecule was adsorbed on entering the region of the first foam until its surface area was completely covered, the lag time would be almost one half hour. Values for the adsorption and absorption rates of DAP and DnHxP into the first foam in the column were obtained. However when these values were applied to the second foam in the column, they did not fit the experimental data. They indicated, in fact, that the second foam should remove all the remaining phthalate from the water, while the experimental result was the recovery of DnHxP from the second, third, and fourth foams, and the recovery of DAP from all five foams in the column. There were several obvious reasons for this: (1) no desorption had been taken into account, a factor which could become important as the concentration of the phthalate in the foam increased; (2) there were three different phthalates present in solution, each characterized by a different rate of adsorption and absorption; all of which would be competing for adsorption on the same surface area;

and (3) it had been assumed that every molecule entering the first, and later the second, foam would be adsorbed. It would be possible to enter terms into the equations used which would account for these factors, but this would be simply mathematical machinations, and would be meaningless. It was not possible, therefore, to analyze the column profiles in this way, but the reasoning was not disproved.

Returning to the phthalate series, if the phthalate were smaller, e.g., DnBP, the rate of absorption from the surface would be larger, and the first foam would contain most of the DnBP in the column, with vanishingly smaller amounts found in the remaining foams. This was found to be true of DnBP in experiments IX, XIII, XIV, and XVI, where the initial concentration was 1.0 ppm. At the lower concentrations tested, (0.016 and 0.020 ppb) with larger volumes of water, the DnBP was spread down the column. It may be that the factors governing the loss of DMP and DEP at the 1.0 ppm level under flow conditions, are also responsible for the spreading out of the DnBP profile. From the static experiments, it was seen that the equilibrium distribution of DnBP is 100% in the foam, and 0% in the water. However, this was for the ppm level, and changes at the ppb level would not be evident here.

In the case of the smallest phthalates, DMP and DEP, it is not possible to say whether much surface adsorption would occur, or whether it would be an important factor, at either concentration studied. Apparently the DMP moves freely within the polymer network without a significant degree of retention. Being the most water-soluble of the phthalates, it has the greatest tendency to remain in the aqueous phase. DEP has a similarly high mobility, but is retained to some extent, in the experiments where the initial concentration was 1.0 ppm, and the volume of water only 100 ml. Here, most of the DEP was recovered, though it was spread down the column with a maximum near the middle of the column. When the concentration of the phthalates was decreased by a factor of 100, the DEP either tended to remain in the aqueous phase, or had sufficient time to move down the column within the polymeric network, so that none was recovered.

This reasoning has been described with reference to the diSPo and #1338 foams, which appear to be quite similar in respect to the absorption of phthalates. The effect of the rigidity of the foam on the per cent recovery was seen in the experiments with other varieties of foam - Union Carbide types "A", and "B", and B.F. Goodrich Co. foam #1115. With the latter foam particularly, it was seen that with soft enough foam, even the larger phthalates, DEHP, DnOP, and DnHpP, could exhibit behaviour similar to that of the smaller phthalates in the diSPo and #1338 foams. It can be stated fairly certainly then, that by matching the flexibility of the foam with the size and concentration of the phthalate in the water, all the phthalates discussed here, and many others, can be removed from water over a large range of concentrations with high efficiency. It should be remembered that the flow rates should be sufficiently low or the column sufficiently long, depending on the size and nature of the phthalate, to ensure complete recovery.

In the next part, the removal of phthalates from a different medium, air, was studied. Because of their extremely low volatility, a factor which would be much less important in these tests than the solubility of the phthalates in water was in the previous tests, it seemed that losses due to desorption would be negligible, and that the polyurethane foam be an ideal extractant or absorbent.

The use of polyurethane foam to remove polyvinyl chloride monomer from air was also studied. This compound was recently found to be a pollutant of the air in PVC producing factories, and was suspected of being the cause of a rare form of cancer.[102-107] It was hoped that the foams could be used to remove it from air, or at least reduce the concentration to a level below that set by the safety standards.

Part 2: Removal of Air-Borne Pollutants with Polyurethane Foam

Section 1 : Removal of Phthalates from Air with Polyurethane Foam

The flow meter for measuring the air flow through the system (figure 3a, experimental section), consisted of a graduated glass tube with constrictions at both ends, containing two small balls of different weight. The height of the balls above the zero mark was correlated to the air flow, as measured with a soap bubble flow meter attached to the exit, and a stopwatch. The calibration curve used is shown in Figure 23. This was re-checked from time to time, but did not vary. The flow meter was connected to the apparatus. Five small diSPo foams were placed in the pre-cleanup column, and five more in the trap column. A few drops of the phthalate to be tested were put in the reservoir, and the entire system was assembled. The air cylinder was opened, the air flow adjusted to the desired rate, and the system allowed to operate for a period of time. At the end of this period, the air flow was shut off; the foams were removed, and extracted with hexane, 10 ml per foam, and the hexane extracts were analyzed by GC.

Experiment XLIII : DMP was collected for two hours, at a flow rate of 10 ml/min.

Experiment XLIV : DMP was collected for 3 hours, at a flow rate of 30 ml/min.

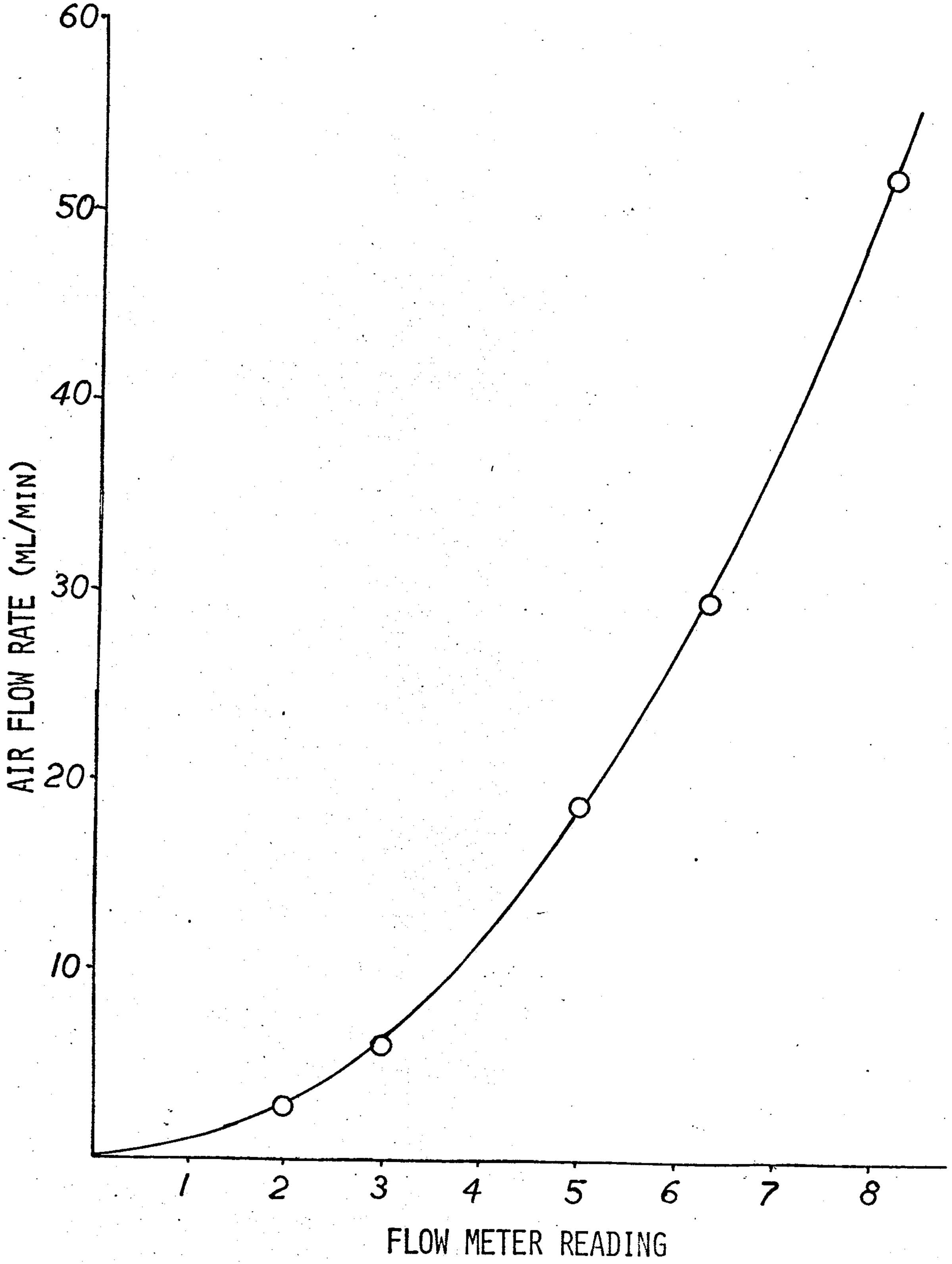
Experiment XLV : DnOP was collected for 48 hours, at a flow rate of 10 ml/min.

Experiment XLVI : DMP was collected for 24 hours, at a flow rate of 10 ml/min.

Experiment XLVII : DnBP was collected for 48 hours, at a flow rate of

Figure 23

Calibration Curve for Air Flow Meter,Used in Studies with Air-Borne Pollutants.


60
50
40
30
20
10
AIR FLOW RATE (ML/MIN)
1
2
3
4
5
6
7
8
FLOW METER READING

10 ml/min.

Experiment XLVIII : DnOP was collected for 48 days, at a flow rate of 30 ml/min. Only four foams were used in the trap.

The results of these experiments are shown in Table 18. The phthalate content of each foam is given in μg. The foams are numbered from the entrance of the column to the exit as 1 to 5. Only the results from the trap column are given.

Table 18 : Recovery of Phthalates from Air with Small DiSPo Foam Plugs

Exp't	Flow rate (ml/min)	Duration (hours)	Foam No.	µg of Phthalate	
				DnBP	DnOP
XLIII	10	2	1	36	
			2	1	
			3	24	
			4	0	
			5	0	
XLIV	30	3	1	49.5	
			2	5	
			3	0	
			4	0	
			5	0	
XLV	10	48	1		0
			2		0
			3		0
			4		0
			5		0
XLVI	10	24	1	145	
			2	0	
			3	0	
			4	0	
			5	0	

continued

Table 18 : continued

Exp't	Flow rate (ml/min)	Duration (hours)	Foam No.	µg of Phthalate DMP	DnBP	DnOP
XLVII	20	48	1		0	
			2		0	
			3		0	
			4		0	
			5		0	
XLVIII	30	1152	1			113
			2			44
			3			25
			4			11

Discussion

No interfering or extremely large amounts of material were found in the pre-cleanup column, therefore the results of the extractions of these foams were not shown in Table 18. The identity of the materials recovered by the first foams of the pre-cleanup column was not investigated.

The amount of DMP recovered in experiment XLIII was quite small, but apparently the removal of phthalate was complete, as the last foams in the column did not contain any phthalate. As the vapour pressure of the various phthalates at room temperature was not known (Appendix C), the concentration of phthalates in air was not known, and the minimum duration of an experiment required for a detectable amount of phthalate to be collected had to be found by trial and error.

In the next experiment, XLIV, which ran for three hours, at 30 ml/min, DMP was recovered in easily measureable quantities. The most part of the material was found in the first foam, with only a trace in the second, and none in the rest of the column. Given the flow rate, the duration, and the amount recovered, the initial concentration of DMP in the air can be estimated to have been about 1.0 ppb.

In experiment XLV, a total of 145 μg of DMP was recovered from air, and all was found in the first foam. From the flow rate, the duration, and the amount recovered, the concentration of DMP in air could again be estimated to be about 1.0 ppb, consistent with experiment XLIV. The foam was evidently not yet saturated, but no experiments were done to determine the breakthrough point. From the quantity of DMP recovered either diffusion of DMP into the bulk of the foam, or formation of multilayers on the foam surface (condensation) must be assumed. The latter was shown to be unlikely from later studies. (experiment XLVIII)

From experiment XLV, it appeared that either the DnOP could not be recovered from air in this system, or the quantity collected was not measureable. The latter was seen to be the case from experiment XLVII, for DnOP must have a lower vapour pressure than DnBP, yet after collecting DnBP for 48 hours at 20 ml/min, no measureable quantity was recovered.

In experiment XLV, the air flow system was operated for an extended period of time to ensure the collection of a measureable quantity of DnOP. At the end of this time, a slight mist on the lower half of the inner walls of the glass tubing between the phthalate reservoir and the trap column indicated that condensation had taken place. The foams were removed from the column through the other end, to avoid contamination. The amount of DnOP found on the four foams corroborated the theory that condensation was occurring, as greater amounts of DMP had been collected on a single foam of equal size without any breakthrough, in experiment XLVI. In the case of the DMP, had the process been one of adsorption only, breakthrough to the second and third foam would have been expected to occur much earlier, as it did for DnOP.

Section 2 : Removal of PVCM from Air with Polyurethane Foam, Coated and Uncoated

The air flow apparatus was altered so that the removal of polyvinylchloride monomer (PVCM or VCM) from air could be studied. The toxicity of this compound has recently been the topic of much interest.[102-107] The volume of air between C and D, (see figure 3b, experimental section), was estimated to be about 125 ml, and therefore, the presence of an equal amount of PVCM in air at points C and at D after 125 ml had passed through that space, was taken to indicate non-retention of PVCM by the foams.

Experiment XLIX : Initial concentration of PVCM in the 2 litreservoir was 75 ppm. Five diSPo foams were placed in the trap column, and the apparatus was assembled. The amount of PVCM in the air at points C and D was measured, and the air flow was started, at 30 ml/min. The amount of PVCM in the air at points C and D was monitored continuously to determine the extent of the retention of PVCM.

The results of this experiment are not tabulated. Breakthrough of PVCM was immediate, and no detectable retention of the PVCM could be observed.

Experiment L : Five diSPo foam plugs, each coated with approximately 25 mg of mineral oil, were placed in the trap column. The initial concentration in the reservoir was 150 ppm. The concentration of PVCM in air at points A, B, C, and D, was checked, and then the air flow was started, at 30 ml/min. The concentration of PVCM in air at points C and D was again monitored to determine the retention of the PVCM.

The results of this experiment are again not tabulated, as breakthrough of PVCM was again immediate.

Experiment LI : Five diSPo foams were placed in the trap. Initial concentration of PVCM in the reservoir was 150 ppm. Flow rate was 6 ml/min. A sharp increase in the concentration of PVCM at point D was observed after 20 minutes, which is the amount of time required for the first of the PVCM-carrying air to travel from point C to point D, at that flow rate, if there was no retention.

Experiment LII : The amount of mineral oil coating on the foams was increased to 30 mg, and the initial concentration of PVCM in the air was 50 ppm PVC Five coated foams were used. The flow rate was 10 ml/min. Breakthrough was again immediate.

Discussion

The concentrations of PVCM in air used in these experiments were the same as those reported in the air at the PVC factories before the standards were ordered to be changed. The new permissible level set by the U. S. Occupational Safety and Health Administration was 1.0 ppm averaged over an eight hour period, and a maximum of 5.0 ppm for a period of no greater than 15 minutes.[107] It was evident from experiments XLIX to LII that PVCM cannot be removed from air by polyurethane foam plugs or by mineral oil-coated polyurethane foam plugs. It is possible that the reason for this is the high volatility of the PVCM combined with a low solubility in polyurethane foam. If foamed PVC could be obtained, the desired removal might be effected, as the polymer structure would be more compatible with the PVCM. In any case, the polyurethane foam was not successful in removing the PVCM from air. Similar lack of success in the removal of halothane from air has also been found.[111]

Part 3 : Measurement of the Relative Surface Areas of Various Foams by Adsorption of Methylene Blue Dye

Introduction

Musty and Nickless[69] described a method for the measurement of the relative surface areas of different polyurethane foams. Pieces of foam, of the same size and type, were each placed in an aqueous solution of methylene blue dye. The volume of each solution was the same, but the concentration of the dye varied from 0.02 to 0.20 mM/1. The foams were left in the dye solution for 24 hours, at the end of which time, the amount of dye left in solution was measured by optical absorption at 664 nm. The amount adsorbed by the foam was found from the change in concentration of each solution. It was found that if the number of mM/kg adsorbed was plotted against the initial concentration of dye in solution, a plateau was reached at about 0.12 mM/kg, and the amount adsorbed per kilogram remained constant, despite further increases in the initial concentration of the dye solution. The maximum amounts of dye adsorbed by the foams ranged from 28 to 260 mM/kg. This method of determining the relative surface areas was applied to the foams used in this thesis, to determine whether there was a relationship between surface area and the percent recovery of phthalates. Musty and Nickless[69] were able to correlate surface area and recovery of PCB for one type of foam - that which adsorbed the most dye was also the most efficient in the removal of PCB from water. The same correlation did not exist for the five other types of foam tested.

Section 1 : Adsorption of Methylene Blue Dye by Various Types of Foam

Experiment LIII : As no data had been given in the original paper[69] regarding the weights of foam used or the volumes of solution, the data on the maximum adsorption was used to determine these factors. The highest maximum adsorption found by Musty and Nickless was about 260 mM/kg. Assuming this value would not be exceeded by the foams to be tested here, a large #1338 foam plug, weighing about 1.6 g would not adsorb more than 0.416 mM of dye, and a solution of 200 ml of 1.0 mM/l of dye , (containing a total of 0.400 mM of dye), was considered to be sufficient. The solution was poured into a static extraction beaker, and a large #1338 foam plug placed in the beaker, and squeezed to expel air bubbles. The beaker with the foam was then placed under the glass plunger of the static extraction system, and the motor was started. The system was allowed to operate for 19 hours, then the motor was stopped and 1 ml of the solution was removed and analyzed by optical absorption at 664 nm, along with suitable standards. (Calibration curve : Figure 24)

A change in the dye concentration of less than 1% was recorded. The experiment was then repeated, using a lower range of concentrations and a number of different types of foam.

Experiment LIV : Five different types of foam : diSPo, #1115, #1338, Union Carbide type "A", and Union Carbide type "B", were tested, using the same procedure as was used in the above experiment. The concentrations of the dye solutions tested were varied from 0.03 to 0.122 mM/l. The duration of the experiment was 24 hours in each case.

The results of these studies are shown in Table 19.

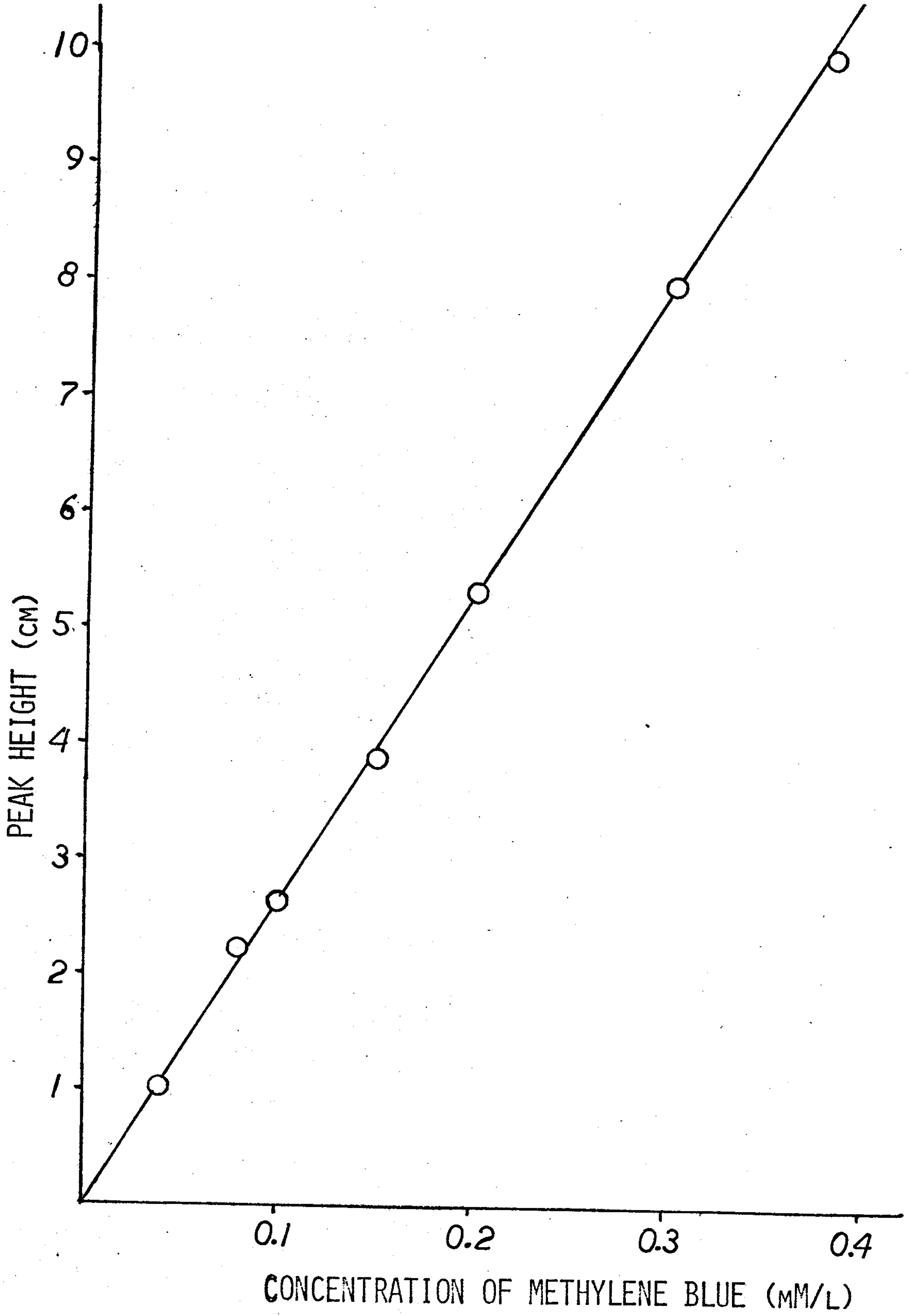
Table 19 : Amounts of Methylene Blue Adsorbed

Experiment LIV
Volume of Solution : 100 ml
Duration : 24 hours

Foam Type	Init. Conc. (mM/l)	Final Conc. (mM/l)	Wt. of Foam (g)	mM/kg of Dye Adsorbed (x 10)
DiSPo	0.030	0.020	2.436	4.1
	0.050	0.046	1.253	3.2
	0.080	0.054	2.471	10.5
	0.120	0.088	2.435	13.1
#1338	0.030	0.025	1.566	3.0
	0.050	0.038	1.612	7.4
	0.080	0.064	1.604	10.0
	0.120	0.080	1.635	24.5
U.C."A"	0.030	0.021	5.841	1.5
	0.050	0.037	5.056	2.6
	0.080	0.061	5.163	3.7
	0.120	0.010	6.125	3.3
U.C."B"	0.030	0.025	5.351	0.9
	0.050	0.045	2.857	1.7
	0.080	0.065	4.484	3.3
	0.120	0.010	5.124	3.9
#1115	0.030	0.023	2.172	3.2
	0.050	0.046	2.264	1.8
	0.080	0.072	2.337	3.4
	0.120	0.011	2.323	3.9

Figure 24

Calibration Curve for Methylene Blue UV Absorption at 664 mu.


10
9
8
7
6
5
4
3
2
1
PEAK HEIGHT (CM)
0.1
0.2
0.3
0.4
CONCENTRATION OF METHYLENE BLUE (MM/L)

Discussion

No evidence of a plateau was found in the plot of mM/kg adsorbed vs initial concentration of the dye solution for any of the five types of foam tested. Further information from Musty[112] showed that the wrong amounts of foam and solution had been used. The volume of the solutions used in these tests was 100 ml, and the weights of foam were about 5 g. Musty and Nickless had used 25 ml of solution, and about 0.2 g of foam. Therefore, it was possible that the solutions that were used had been too dilute for any plateau to have been reached. The experiments were repeated using the recommended amounts of foam and dye solution. Only the diSPo and #1338 foams were tested.

Experiment XLV : The relative surface areas of diSPo and #1338 foams were measured by allowing the foams to sit in the methylene blue solutions for 24 hours, and determining the amount of dye adsorbed. The weights of the foams were all about 0.2 g; the volume of the solutions tested was 25 ml; and the range of concentrations studied was from 0.04 to 0.50 mM/l. The results are shown in Table 20.

Discussion

Once again, no plateau was reached in the plot of mM/kg adsorbed vs the initial concentration of the dye solution, although the amounts measured were higher than before. On reconsideration of the data given in the paper by Musty and Nickless, and that given later by private communication,[69,70,112] a discrepancy was found to exist between the experimental data and the maximum amounts reported to have been adsorbed. If 0.2 g of foam were used, and if the maximum amount adsorbed was 260 mM/kg, then the test solution had to contain at least 0.052 mM of dye. However, 25 ml of solution, at a concentration of 0.12 mM/l, which was the concentration given in the original paper[69] for the maximum adsorption of 260 mM/kg, contains only 0.003 mM of dye. Whatever the explanation for this discrepancy may be, in the tests conducted here, it was not possible to achieve a plateau over the range of concentrations suggested using the prescribed amounts of foam. It was thus not possible to attempt to correlate the relative surface areas as measured with the methylene blue dye and the efficiency of recovery of phthalates.

Table 20 : Amounts of Methylene Blue Dye Adsorbed

Experiment XLV
Duration : 24 hours
Volume of Solution : 25 ml

Foam Type	Wt. Foam (g)	Init. Conc. (mM/1)	Final Conc. (mM/1)	Dye Adsorbed (mM/kg)
DiSPo	.203	0.040	0.0094	3.08
	.197	0.080	0.036	2.91
	.200	0.100	0.046	3.25
	.196	0.150	0.081	2.56
	.198	0.200	0.103	3.04
	.196	0.400	0.237	2.29
	.197	0.500	0.272	8.24
#1338	.175	0.040	0.0095	4.00
	.188	0.080	0.039	2.39
	.181	0.100	0.038	5.39
	.185	0.150	0.069	5.41
	.174	0.200	0.063	8.62
	.183	0.300	0.163	5.45
	.196	0.400	0.237	2.29

Conclusion

The recovery of a homologous series of phthalates from water at the ppm level was studied by absorption of the phthalates into a column of five small diSPo polyurethane foam plugs under flow conditions. The efficiency of recovery and the distribution of the phthalates down the length of the column varied with the length of the alkyl side-chain of the phthalate. (see Table 7) Only a few per cent of the smallest phthalate, DMP, was extracted, and the amount of DMP in the foam plugs increased down the length of the column. This effect was also seen with the second smallest phthalate, DEP, but it was less pronounced. About 80% of the DEP was recovered, distributed unevenly down the column as a broad band, with a maximum at about the middle of the column. It appeared that this phthalate was moving down the column, its progress partly retarded by the foam. The next phthalates studied, DnBP and DiBP, were recovered entirely, with the major portion being found in the first foam, and traces in the second and third foams. The phthalates DAP and DnHxP showed profiles similar to those of DnBP and DiBP, but the recovery was much lower, though the recovery of DAP was greater than that of DnHxP. Only small amounts of DnHpP were recovered, and this was evenly distributed down the column. The largest phthalates studied in this series, DEHP, DEHiP, DnOP, and DiDP, were not recovered at all. Two phthalates with aryl-alkyl and aryl-aryl diester side-chains, BBP and DPP, were recovered quite efficiently, having column profiles similar to those of DnBP and DiBP.

The same column profiles and approximately the same efficiency of recovery of each phthalate was found when this series of phthalates was tested on another type of open-pore polyurethane foam, #1338.

Rough calculations of the surface area showed that the phthalates were being removed by absorption, not adsorption. It was concluded that the amount of phthalate absorbed depended on two major factors : the distribution coefficient , K_D, and the rate at which the phthalate molecules diffused away from the foam-water interface and into the bulk of the foam. The first parameter, K_D, gives the ratio of the phthalates in the foam to the phthalates in the water at equilibrium. K_D should be independent of the concentration, and would be expected to increase with increasing length of the side-chains. The second parameter is also dependent on the length of the side-chains, but would be expected to decrease as chain length increases. Other factors which could affect the amount absorbed are: flexibility of the chains of the polymer network, flow rate, initial concentration of the phthalate in water, and, possibly, the chemical composition of the foam.

This does not explain the unusual profiles found for DMP and DEP. Because the sample was followed by 100 ml of distilled water, it is easy to account for the maximum to be displaced downward from the top foam plug. An experiment where clean water was passed through a foam plug spiked with DEP, and then was passed through a column of five clean foam plugs, showed that desorption on DMP and DEP could be a significant factor. However, the same profiles, though with slightly higher recovery, were observed when the sample solution was passed through a column of either small DISPO or small #1338 foams, without "wash" water. A plausible, consistent explanation cannot be offered.

It is thought that the removal of phthalates from water with polyurethane foam follows a two-step path:

1)

1) adsorption of the phthalate onto the foam surface
2) diffusion of the phthalate molecules away from the foam surface and into the foam matrix, if such diffusion is possible.

Step one would be achieved more rapidly by the by the large phthalates;
step two
step two, by the smaller phthalates.

The recovery of the phthalates under static conditions was investigated to determine whether the value for K_D varied as had been predicted. For the larger phthalates, DnHxP, DnHpP, DnOP, recovery was usually greater than 50% of the initial spike, but reproducibility was poor, Extraction and recovery was greatest after two hours o operation of the extraction system. The material balance for the static extraction of the phthalates DMP, DnHxP, DnHpP, and DnOP was not established. The three larger phthalates are evidently tending toward complete removal, but some may have been lost, either by irreversible adsorption onto the glass surfaces of the container, or by some other way. Values for K_D calculated for these experiments would be variable.

Static extraction of DMP showed that the K_D for DMP would be much lower than those of the larger phthalates, as had been expected. (see Table 12) While this explains why the recovery of DMP is very low, it does not explain the shape of the DMP and DEP column profiles under flow conditions.

Recoveries of phthalates on coated foams , using either DC 200 silicone oil or mineral oil, were generally lower than [illegible]

Recoveries of phthalates on coated foams, using either DOW-200 silicone oil or mineral oil, were generally lower than those for uncoated foams. In terms of equilibria, (supported by the findings of Musty and Nickless in PCB studies[69]), the equilibrium is probably established more quickly between the uncoated foam and water than between the coated foam and the water. Musty and Nickless[69] found that when they used higher flow rates the coated foams performed better than the uncoated foams, though the performance did not equal that of the uncoated foam at lower flow rates. They concluded that the coated foam retained the PCB more strongly, though equilibrium was established at a lower rate.

DnOP was recovered to a small extent using coated foam, under flow conditions. It was concluded that the DnOP was dissolving in the oil but probably not penetrating into the foam. This could not be proved.

Of the variety of other foams tested under static conditions, only Union Carbide type "A" performed similarly to the #1338 foams. The Union Carbide type "B", under static conditions, removed the large phthalates almost completely, but under flow conditions, recovery was very poor. It is possible that the recovery was due to an adsorption process which was too slow to be of any value under flow conditions.

The type #1115 foam, a very soft, flexible foam, did not remove the large phthalates from water to any great extent under static conditions. This was thought to indicate that the foam had either such great flexibility that even the largest phthalates were not retained, or such poor solvent characteristics that the phthalates could not diffuse into the foam fast enough for significant removal. The flexibility of the polymer network should allow for higher diffusion rates of the phthalates within the foam, and if this were the case, the smaller phthalates would not be retained at all. That is, the column profiles observed with the smaller phthalates on the diSPo and # 1338 foam columns could be produced by the larger phthalates when the flexibility of the foam is increased. Studies on the recoveries of the smaller phthalates on columns of #1115 foams under flow conditions showed no recovery of DMP or DEP, and very poor recovery of DnBP. This was interpreted as being due to the high flexibility of the foams. It is possible that these foams could be used for the reocvery of phthalates with side-chains which are more than eight carbons long.

The recovery of the full series of phthalates already tested under flow conditions at concentrations of 1.0 ppm, with small diSPo and #1338 foams, was studied at the ppb level. It was found that DMP and DEP were not recovered, while the column profiles of the other phthalates had changed markedly. The profile of each phthalate was similar to that of its next smallest homolog at the ppm level. This is believed to be consistent with the two step absorption process postulated earlier. After adsorption on the surface, a certain amount of time is required before the molecule has diffused into the polymer network. The length of time required decreases with decreasing phthalate size. If the phthalate is large, the entire surface could become blocked with adsorbed phthalate molecules, so that the next phthalate molecules pass through the foam, in aqueous solution, without being adsorbed. Thus, the profile is lowered, and the phthalate is spread through the column. (see DAP and DnHxP, ppm level, Figure 19) Lowering the concentration has the effect of allowing more time for the phthalate molecules to be absorbed, after their adsorption, before fresh phthalate solution enters the column. The net result of lowering the concentration, then, is a shift in the type of profile obtained, and the larger phthalates behave similarly to the next smaller phthalates at higher concentration.

The removal of phthalates from air with polyurethane (diSPo) plugs was studied for DMP, DnBP, and DnOP. The removal of DMP was complete: .14 mg of DMP were collected in one foam without breakthrough to the next foam. The DMP concentration in air was estimated to be about 1.0 ppb. DnBP and DnOP could not be detected after running the collection apparatus for 48 hours. After 1152 hours, at a flow rate of 30 ml/min., DnOP was collected in easily measureable amounts, but the removal appeared to be due to condensation only, Breakthrough had occurred after only a small amount of phthalate had been collected, and a mist was observed on the walls of the glass between the phthalate reservoir and the foam column.

Attempts to remove polyvinylchloride monomer (PVCM) from air with both coated and uncoated foams were unsuccessful. Concentrations of PVCM tested were 50, 75, and 150 ppm, at flow rates of from 6 to 30 ml/min..

Attempts to measure the relative surface areas of the foams by the adsorption of methylene blue dye were unsuccessful, though the method followed was identical to one which had been reported for the measurement of polyurethane foam surface areas.[69] A discrepancy in the results from this paper indicated that this method may not have been reported correctly.

Appendix A : Acute Toxicity of Some Phthalates to Rats[101]

Phthalate	LD_{50} (ml/kg)*
di-methyl phthalate	3.3751
di-methoxyethyl phthalate	3.7355
di-ethyl phthalate	5.0579
di-n-butyl phthalate	3.0496
di-iso-butyl phthalate	3.7498
butyl carbobutoxymethyl phthalate	6.8892
di-octyl phthalate	>50
di-2-ethylhexyl phthalate	>50

*The numbers given here are those listed by the authors. No explanation is given for the questionably high number of significant digits reported.

Appendix B : Abbreviations for Phthalates Used in this Thesis

Phthalate	Abbreviation
di-methyl phthalate	DMP
di-methoxyethyl phthalate	DMEP
di-methyl isophthalate	DMiP
di-ethyl phthalate	DEP
di-n-butyl phthalate	DnBP
di-iso-butyl phthalate	DiBP
di-amyl phthalate	DAP
di-n-hexyl phthalate	DnHxP
di-n-heptyl phthalate	DnHpP
di-2-ethylhexyl phthalate	DEHP
di-2-ethylhexyl isophthalate	DEHiP
di-n-octyl phthalate	DnOP, DOP
di-n-nonyl phthalate	DnNP
di-iso-decyl phthalate	DiDP
di-phenyl phthalate	DPP
butyl benzyl phthalate	BBP
butyl glycolylbutyl phthalate	BGBP
glycolylbutyl phthalate	GBP

Appendix C : Some Physical Properties of Phthalates[108-110]

PAE	M. W. (g)	V. P. (mm Hg)	Boiling Range* (°C)	Solubility in Water † (%)	Evaporation Rate (g/cm^2/hr, @ 100°C)	S.G. @20°C/20°C
DMP	194	$\sim .01^{25^\circ C}$	282-285	0.4	0.001925	1.190-1.194
DEP	222	$< .01^{25^\circ C}$	294-296	0.1	0.000617	1.117-1.121
DnBP	278	$1.1^{150^\circ C}$	330-340(s.d.)	$<$ 0.01	0.000221	1.047-1.050
DiBP	278		300-320(s.d.)			1.048-1.050
DAP	306	$.0001^{25^\circ C}$	336-342	0.01		1.022-1.025
DnHxP	334		340-350	$<$ 0.025		1.007-1.008
DnHpP	362	$2.0^{200^\circ C}$		$<$ 0.01		0.985-0.991
DEHP	390	$1.32^{200^\circ C}$	370	$<$ 0.01	0.00002	0.986
DEHiP	390	$0.69^{200^\circ C}$	$241^{5\text{ mm Hg}}$			
DnOP	390	$< 0.01^{25^\circ C}$	340	$<$ 0.01		0.978
DiDP	446	$0.3^{200^\circ C}$	356			0.966-0.968
BBP	312		370	0.0003		1.117-1.119
DPP	318		405	$<$ 0.01		1.28

* at 760 mmHg, unless noted

† %by volume, at 20°C

s.d.=with some decomposition

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