

THE UNIVERSITY OF MANITOBA

THE EXTRACTION AND RECOVERY OF PHTHALATES FROM WATER

BY THE USE OF POLYURETHANE FOAM

BY

KATHLEEN M. GOUGH

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A dissertation submitted to the Faculty of Graduate Studies of
the University of Manitoba in partial fulfillment of the requirements
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Cologne*

In Kohn, 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. In 1960, the British government established a "Toxic Chemicals and Wildlife" division, to study the effects of pesticides on wildlife. 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. 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 thereof, and personal survival kits in the case of disaster.

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-biodegradability.

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

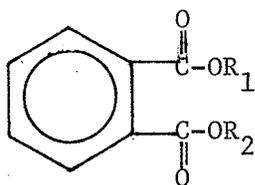
- a) legislated or voluntary control of pesticide and insecticide application, with foreknowledge of their effects
- b) the means to monitor pollutant concentration in air and water and to remove them quickly and economically.

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.

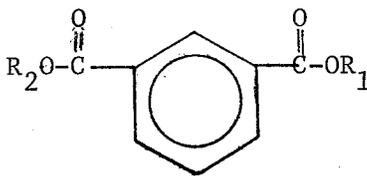
Phthalic Acid Esters

General:

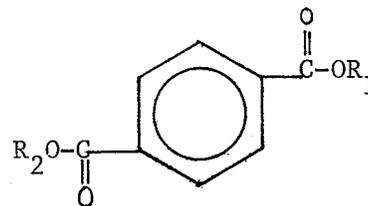
The three possible isomers of phthalic acid esters are:



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 valence forces, (Van der Waals's), 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 :	50
pesticide carriers,	
cosmetics, fragrances,	
munitions, industrial oils,	
insect repellent.	
Total:	<u>877</u>

Ubiquity of Phthalates

In 1970, Rubin and Jaegar²⁶ 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, Corcoran²⁷ 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 Merrimack Rivers during 1972. Phthalate concentrations ranged from 0.88 to 1.9 ppb, depending on proximity to suspected sources and depth of sampling.

Thomas³⁰ 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 diethyl ether, GC

and GC-MS analyses were performed. DnBP, DEHP, and BGBP were found in concentrations of up to 750 ng/m³.

Wildbrett³¹ 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 exposure of water fleas (*Daphnia magna*) to 3ug DEHP/l significantly ($P < 0.05$) reduced reproductivity by 60%.

Acute Toxicity:

Krauskopf²⁵ 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 LD₅₀ 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 Blumenthal³⁶, 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 carcinogenesis 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 Jaegar²⁶ 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 Jaegar³⁹ 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 Autian⁴¹ administered intraperitoneal doses of six phthalates to pregnant rats at levels 1/10, 1/5, and 1/3 of the acute LD₅₀. (Acute LD₅₀ - 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 (11ppm) solution, the growth of replicating cells was significantly inhibited at this level. They suggested that the low in vivo 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 olfactory 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 Middleton⁴⁴ 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.

Briedenbach⁴⁵ 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 Wayman⁴⁸ 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 -1.0 l/min)), possible loss of extracted material during the concentration 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 Jenson⁵⁰ removed PCB and OCI from water with a reversed liquid-liquid partition method, in which water is passed