Adsorption of PCB's and DDT's on Membrane Filters—A New Analysis Method

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Numerous methods for the analysis of trace amounts of PCB mixtures and DDT isomers in water have been used and reported. EPA methods utilize pure hexane (BERCK 1953, KAHN and WAYMAN 1964, and EPA 1971). Several adsorption systems have been used to extract such compounds from water. They include activated carbon (ROSEN et al. 1959 and BREIDENBACH et al. 1966), urethane foam plugs (GESSER et al. 1971, UTHE et al. 1972, and UTHE et al. 1974) and Carbowax 4000 monostearate and undecane-coated Chromosorb W (AHLING et al. 1970). These methods have adsorption efficiencies from 80-100%. The foam plug method has given excellent recoveries from distilled water. However, when knowns were added to natural lake waters containing fine silt, lower recoveries were obtained (BEDFORD 1974). The PCB's were found to be adsorbed to the silt which passed through the plugs. This finding led to the work of this paper.

Adsorption methods have also been used in analyzing air samples for these compounds. Florisil packing has been used to collect PCB's and phthalates (GIAM et al. 1975), and urethane plugs also have been used for PCB's (BIDLEMAN et al. 1974). The urethane plugs in this latter study separated tri-, tetra-, and pentachlorobiphenyls from air at a 96-99% efficiency as compared to a 1-4% efficiency for glass fiber-A plugs.

The need still exists to analyze large quantities of water for PCB's and DDT's in ocean seas (CRAMER 1973, JENSEN et al. 1969, RISEBROUGH et al. 1968, and WOODWELL et al. 1971), state waters (EPA 1975a), and private ponds. Methods of increased sensitivity with convenient field sampling will be required (EPA 1975a).

This paper describes a new adsorption method by which PCB mixtures and DDT isomers and other chlorinated hydrocarbon residues can be efficiently separated from water sources. The adsorption medium is a membrane filter made from cellulose triacetate material. Field methods with simple apparatus can be used. The membrane system can be used both for analytical

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purposes and for purifying contaminated sources. There is potential for its use in analyzing air samples.

MATERIALS AND METHODS

Metricel filter circles (Gelman, GA-6) with a pore size of 0.45 μ and diameter of 47 mm were used without further treatment to separate PCB's and DDT's from water. These circles contained a small amount of starch cellulosic material used as a wetting agent. The flow of water through these was about 200 ml/min via water aspirator pumping. The filter holders were either stainless parabella (Gelman #4230, 1 liter capacity) or glass cone (VWR Scientific #28153020, 0.5 liter capacity). Hexane, acetone, cyclopentane, and acetonitrile (Burdick and Jackson distilled-in-glass) were used as received. Sodium sulfate (MCB, anhydrous, gran. reagent, lot 59) was heated at 400°C. Glassware was cleaned with a 5% solution of Contrad 70 cleaning agent (Scientific Products) heated to 70°C. Measuring pipets for dispensing standards were of the disposable type (Drummond microcap tubes). Column cleanup utilized 60/100 PR florisil (The Floridin Co.), activated at 1250°F and stored at 130°C.

Gas chromatographic analyses were accomplished with a Microtek MT-220 GLC fitted with a 5.5 foot ¼ inch o.d. glass "U" column packed with 1.5% SP-2250/1.95% SP-2401 (similar to OV-17/QF-1) on 100/120 Supelcoport packing (Supelco, Inc.), operated at 215°C oven temperature, 240°C inlet and nitrogen flow of 60 ml/min. The ^{63}Ni electron capture detector was held at 330°C and had a 20 ml/min nitrogen purge. The column gave from 3000 to 6000 theoretical plates efficiency for p,p'-DDT. The electrometer sensitivity was 1.6×10^{-9} amps full recorder scale background current. Analyses were quantified with an Infotronics Model CRS-100 area integrator.

Standards were prepared by adding μl quantities (10-100) of Aroclor (PCB) mixtures and DDT isomers dissolved in isooctane directly on 3.00 liters of double-distilled water contained in one-gallon Burdick and Jackson solvent bottles. Each standard was shaken eight times for one min each and used the next day. The three spiking levels were obtained by using 30 ml, 150 ml, and 750 ml of the water standard. All spikes were 750 ml in volume; the lower two levels required make-up water to achieve this volume.

Analysis of aqueous solutions prepared as PCB mixture or DDT isomer spikes. Separately prepared spiking solutions were analyzed for total available spike content as a methods check. The 3.00 liter

aqueous solution prepared as above was divided into 4 equal aliquots. Each aliquot was extracted three times with 75 ml cyclopentane each time. The solvent was dried with anhydrous Na_2SO_4, concentrated, and analyzed by GLC.

Recovery of PCB or DDT from the membrane filter following spiking with aqueous solutions. Each spiked water sample was filtered through a membrane filter with water aspirator suction. Double-distilled water (100 ml) was used to wash down the walls of the funnel. The filter was extracted in a screw-capped 200-ml bottle with 3 portions of hexane (100, 10, and 10 ml) by mechanically shaking (30, 10, and 10 min each) in the presence of anhydrous Na_2SO_4. The samples were concentrated and put through florisil columns utilizing the methylene chloride method (MILLS 1972) adapted to 1/10 size. GLC analyses followed.

Recovery of PCB or DDT from membranes spiked directly. The membranes to be dosed directly were wetted with water and rolled up in the mouth of a 200-ml extraction bottle. Standards of µl quantities (10-100) were dropped on the filters. Extraction with hexane, etc. was the same as that described above.

All spiking was done in triplicate and at three levels for each PCB mixture or DDT isomer tested. Levels were in multiples of five, the lowest giving full recorder scale detection at 100% recovery.

RESULTS AND CONCLUSIONS

Aroclor 1242 and Aroclor 1254 as well as p,p'-DDT were found to be efficiently adsorbed onto the surface of a cellulose triacetate membrane filter. Table 1 shows results of the extraction of the eluted water spikes passing through the filter. The filter removed up to 60 µg of these species. The membrane shows promise for rapid removal of these chemical species from contaminated supplies not only for research or testing purposes but also for community water supplies. While a mechanical pump would be required for cleaning up large quantities of water, a simple gas sampling syringe with attached filter holder would suffice for testing purposes. Either a pure water sample would be taken or the purity could be checked in this manner in the field. The membrane filter could easily be stored and transported to the laboratory for analytical testing.

TABLE 1

Analysis of Membrane Effluent From a Water Spike

Compound or Mixture	Applied Quantity[1] ng	Adsorption %
Aroclor 1242	40,000	98.0
Aroclor 1254	60,000	99.1
p,p'-DDE	2,000	97.9
p,p'-DDT	4,000	99.1

[1]Dissolved in 750 ml water, flow rate of 200 ml/min.

On the other hand, desorption of these constituents from the membrane was found to be inefficient and inconsistent. Filter discs were first extracted with hexane in the presence of anhydrous Na_2SO_4. Low recoveries were obtained. The same discs were then extracted with acetonitrile in a tissue grinder. However, even with this dual treatment, the extraction ranged from 41 to 118% recovery (Table 2). Generally speaking, a higher recovery was obtained with the latter treatment. It is clear that additional work needs to be done to improve the consistency and efficiency of the extraction process if membrane filters are to be used for analytical purposes.

The water standards prepared as a spike were quantitatively analyzed. The Aroclor 1242 recovery averaged 79% for the 4 aliquots. Aroclor 1254 was recovered in two trials on an average of 82 and 79%. The p,p'-DDE and p,p'-DDT recoveries averaged 107 and 110%, respectively. Apparently, the Aroclors were adsorbed to the glass surface of the jug to a reasonably high degree (BELLAR et al. 1975). A subsequent hexane extraction of the jug for one trial for Aroclor 1254 gave a 7% recovery. These data were used to correct the quantity of PCB and DDT's present in the water spikes of the membrane filters.

These spikes were also applied directly to wetted membrane circles. The hexane extractions indicated a similar difficulty for recovering them (Table 3). Recoveries of individual samples of Aroclor 1242 ranged from 16 to 66% over the three levels of application, those of Aroclor 1254 from 32 to 92%. Those of Aroclor 1254 were higher at all spiking levels than those of Aroclor 1242. Data for the individual DDT isomers and aldrin are also given in Table 3. The

isomers p,p'-DDE and p,p'-DDT were studied at three levels while those of p,p'-TDE, o,p'-DDT, and aldrin were studied at only two. In all cases, recovery results were lower and even less consistent than those for the Aroclors.

TABLE 2

Recovery of Aroclors and DDT's from Membrane After Filtration of a Water Spike. Extraction of Membrane with Hexane and then Acetonitrile (1).

Extractn Solvent (2)	Applied Quant ng	Recovery Trials 1	2	3	Ave %	Applied Quant ng	Recovery Trials 1	2	3	Ave %
Compound: Aroclor 1242						Aroclor 1254				
Hexane	400	43	13	31		600	31	25	59	
Aceton.		97	62	109			26	33	32	
Total		140	75	140	118		57	58	91	69
Hexane	2000	62	35	35		3000	26	3	46	
Aceton.		21	64	64			39	81	37	
Total		83	99	99	94		65	84	83	77
Hexane	10,000	43	61	47		15,000	26	6	18	
Aceton.		31	21	30			18	36	21	
Total		74	82	77	78		44	41	39	41
Compound: p,p'-DDE						p,p'-DDT				
Hexane	20	25	18	45		40	10	5	24	
Aceton.		42	59	33			34	51	53	
Total		67	77	78	74		44	56	77	59
Hexane	100	17	27	25		200	23	22	21	
Aceton.		56	lost	45			66	lost	59	
Total		73	-	70	72		89	-	80	85
Hexane	500	44	1	7		1000	27	4	6	
Aceton.		13	72	24			15	49	33	
Total		57	73	31	54		42	53	39	45

(1) Data corrected for recovery of spikes from aqueous solutions.

(2) Aceton. is acetonitrile.

TABLE 3

Recovery of Aroclors and DDT's from Membrane After Direct Spiking. Extraction of Membrane with Hexane.

Applied Quantity ng	Recovery Trials, % 1	2	3	Ave	Applied Quantity ng	Recovery Trials, % 1	2	3	Ave
Aroclor 1242					Aroclor 1254				
400	16	66	45	42	300	53	32	52	46
2000	31	44	46	40	3000	65	58	63	62
10,000	38	48	22	36	30,000	92	56	75	71
p,p'-DDE					p,p'-DDT				
15	lost	48	80	64	40	lost	16	22	19
75	13	9	45	22	200	8	4	27	13
400	26	30	24	27	1000	36	33	22	30
p,p'-TDE					o,p'DDT				
40	lost	26	35	31	40	lost	17	23	20
200	8	3	29	13	200	9	5	27	14
Aldrin									
5	lost	107	183	145					
25	5	0	11	5					

Cellulose triacetate membrane filters exhibit a high degree of adsorption of organochlorine compounds. This quality provides potential uses in two areas, analysis and purification.

This work has shown that the use of cellulose triacetate membrane filters is an excellent adsorption method for the analysis of PCB's and DDT isomers in water. Using the method in the field would be simple with a minimum of equipment required. The used filters could easily and cheaply be stored and shipped to a laboratory for analysis. While desorption methods are not now efficient, further studies for their improvement are under investigation.

Purification of waters from PCB and organochlorine insecticides is of current ecological interest. SHTANNIKOV (1972) has studied flocculation, coagulation, and filter agents to this end. The use of aluminum sulfate and ferric sulfate as flocculating agents or

sand as a filtering medium were not successful even at higher pH's. The combination of aluminum sulfate, sand, and polyacrylamide did give water of high purity. Water plants gave limited results as a purification method. Ionites were more effective than activated carbon, while ion exchange polymers were fairly effective. SCHOLZ and ALTMANN (1971) studied the use of packed columns for removal of chlorinated hydrocarbons from drinking water. They reported removal of up to 73% applied DDT by activated carbon and polyethylene (both 2000 and 300,000 mol wt). Polyiosbutylene (10-15,000 mol wt) removed 88% of the applied DDT. On the other hand, this study has shown that cellulose triacetate membrane filters were very effective.

There are possibilities this type of filter could be applicable to air pollution problems.

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