Reversed Liquid–Liquid Partition in Determination of Polychlorinated Biphenyl (PCB) and Chlorinated Pesticides in Water

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A new method based on an application of the common reversed liquid–liquid partition method is described for the extraction of chlorinated pesticides from water. In this method the water is passed through a filter (3 grams) containing a mixture of *n*-undecane and Carbowax 4000 monostearate on Chromosorb W, and the absorbed pesticides are eluted with petroleum ether (10 ml). When detected by means of a gas chromatographic system with an electron capture detector, the sensitivity is 10 ng/m³ of lindane with a sample size of 200 liters. The recovery of added pesticides was 50–100% (DDT, 80%) and for PCB, 93–100%.

DURING RECENT YEARS, many attempts have been made to determine the presence of chlorinated hydrocarbons in water. The two methods most often used are based either on continuous extraction with an organic solvent (*1*, *2*) or adsorption on a filter containing activated carbon (*3*). These methods are, however, rather time consuming owing to a long extraction time, both from the water and from the carbon.

The sensitivity of the different methods depends mostly on the way of detection and the used volume of water. Thus Kahn and Wayman (*1*) extracted several hundred liters of water with petroleum ether. The speed of extraction was 0.5–1 liter/hour and recovery of added pesticide was 83–100%. A range of compounds was detected with an electron affinity detector at the 0.2–340 ppb level. Rosen and Middleton (*2*) used activated carbon and 2000 liters of water and extracted the chlorinated hydrocarbons from the carbon with chloroform. The recovery was 75–86% and the 2.5-ppm level was reached with infrared detection. Breidenbach (*3*) found that 35 hours' extraction with chloroform was necessary for complete recovery of the chlorinated hydrocarbons from the carbon after previously drying the filter material for two days at 40 °C.

Recent progress of these two methods will be found in an excellent review by Thornburg and Beckman (*4*).

Our intention in the present work has been to develop an easier method than the above mentioned, in which it could be possible to reach the proposed level of chlorinated hydrocarbons in natural water in Sweden.

Because of the oleophilic character of the chlorinated pesticides, a possible method might be based on the commonly used reversed phase partition method.

Partition of organic material from water by means of Amberlite XAD (a cross-linked polymer) was first used by Rohm and Haas (*5*) and also found to be highly efficient for the extraction of chlorinated pesticides from water. Re-extraction of the filter material gave, however, poor recovery.

Good results both in extraction and recovery from filter material were found in a method based on the reversed liquid–liquid partition method with partition from water to hydrophobized carrier coated with a lipophilic stationary phase followed by recovery from the column by means of a small amount of petroleum ether (10 ml).

EXPERIMENTAL

Reagents and Equipment. *n*-Undecane, (purum, b.p. 195–196 °C) is shaken with portions of concentrated sulfuric acid (p.a.) until the acid is colorless. The undecane is then passed through a column of activated alumina (12 hours at 250 °C).

Petroleum ether (Skellysolve B, b.p. 60–70 °C) and acetone (p.a.) are distilled through a 1-meter column filled with sadels and insulated with glass-wool and aluminum foil. The head of the column is fitted to a still-head condenser adjusted for 90% reflux. The solvents are tested on the gas chromatograph after evaporation to the same degree as in the analysis. Carbowax 4000 monostearate (GP 27) was obtained from Analytical Engineering Laboratories Inc. Chromosorb W was 60–80 mesh, HMDS treated, and acid washed (Johns-Manville). Sulfuric acid was p.a. (Merck).

The filter column was 30 cm × 1 cm i.d. with a glass-filter disk G 1 (100–120 μ). A 10-ml graduated centrifugation tube was used. The gas chromatographic column was borosilicate glass, 160 cm × 0.20 cm.

All the glassware is washed with detergent, heated in a mixture of sulfuric acid–nitric acid (4:1) to 70 °C and rinsed with distilled water. After cleaning, the glassware is checked by shaking with *n*-hexane from which 10 μl is injected on the gas chromatograph. The gas chromatograph with EC-detector was a Varian Aerograph 204, with a Speedomax G-1 mV recorder. Paper speed was 12 inches/hour.

Gas Chromatography. The columns are HMDS-treated and filled with 80–100 mesh HMDS-treated Chromosorb W covered with either 4% methyl silicone oil (SF 96), or 8% fluorsilicone oil (QF I). The carrier gas is nitrogen purified with a 6-inch molecular sieve. Gas speed is about 30 ml per minute. Detector and injector temperature is 205 and 220 °C, respectively. The column temperature was chosen to give DDT a retention time of 20 minutes (about 190 °C).

Preparation of Column Material. Ten grams of Carbowax 4000 monostearate and 30 grams of undecane are dissolved in 100 ml of acetone in a one-liter round-bottomed flask. One hundred grams of Chromosorb W is added followed by additional acetone to cover all support. The acetone is evaporated in a rotavapor apparatus under slightly diminished pressure.

Partition and Precipitation Procedure. Three grams of the column material are weighed into the column which is then fitted to the outflow of the water container by means of an all-glass fitting. In laboratory work, the lower end of the column is connected to a water suction pump and in the field work, to any other kind of vacuum pump. The vacuum

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(1) L. Kahn and C. H. Wayman, ANAL. CHEM., **36,** 1340 (1964).
(2) A. A. Rosen, and E. M. Middleton, *ibid.*, **31,** 1729 (1959).
(3) A. W. Breidenbach *et al.*, "The Identification and Measurement of Chlorinated Hydrocarbon Pesticides in Surface Waters," U. S. Department of the Interior Federal Water Pollution Control Administration, November 1966.
(4) W. Thornburg and H. Beckman, ANAL. CHEM., **41,** 149R (1969).
(5) Rohm & Haas, *Chem. Eng. News*, **44,** 54 (Jan. 17, 1966).

Table I. Results from Recovery Experiments

Filter	Filter, g	Water, l.	Flow speed, ml/min	Standard µl/l. Pesticides[a]	Petroleum ether, ml	Recoveries BHC	Lind.	Aldrin	Dieldr.	DDE	DDD	DDT	PCB
Chromosorb W + *ca.* 80% Undecane	1.5	6	65	5[a]	10	trace	20	40	80	56	69	50	
10% Carbowax	1.5	6	65	5	10	trace	trace	28	[b]	37	37	63	
10% Carbowax + *ca.* 80% Undecane	1.5	6	65	5	10	41	51	44	75	75	77	70	
10% Carbowax + 30% Undecane[b]	2	6	65	5	5	45	30	34	[b]	31	66	38	
10% Carbowax + 30% Undecane[b]	2	6	130	5	5	45	30	34	[b]	31	70	38	
10% Carbowax + 30% Undecane	3	6	65	5	5	68	46	59	97	65	104	80	
10% Carbowax + 30% Undecane	4	6	65	5	8	88	67	56	69	100	100	90	
10% Carbowax + 30% Undecane	2.5	18	65	1.33	5	64	42	43	62	100	100	68	
10% Carbowax + 30% Undecane	5	44	65	0.18 PCB[a]	5	156	111	100	100	90	86	93	
10% Carbowax + 30% Undecane	1	5	65	10	5								53–80
10% Carbowax + 30% Undecane	3	5	65	10	5								93–100

[a] The standard had the following composition and concentration in ng/µl: BHC 1.0, Lindane 1.0, Aldrin 2.0, DDE 4.0, Dieldrin 5.0, DDD 8.0, DDT 12.0, and PCB (Clophen A50) 10.0.
[b] The extract was treated with sulfuric acid which destroyed the dieldrin.

is adjusted to give an outflow between 65 and 130 ml of water per minute. For analysis of waste waters and other waters with high particle content, the residue is estimated separately in the particles and in the water. Before filtering such waters, 300 mg of aluminum sulfate per liter is added and after sedimentation of the solid, the water is decanted and passed through the filter. For extraction of the solid, see below. This two-step method will also avoid blockages in the column.

Elution of Chlorinated Hydrocarbons from the Column. When the filtration is finished, the suction is continued for a few minutes. Petroleum ether is then added to elute the pesticides; 10 ml of the effluent is collected in a graduated centrifugation tube. The extract is further prepared and analyzed as described below.

Extraction of Solid from Aluminum Sulfate Precipitation. The sediment is air dried and two grams or less is extracted with 6 ml of acetone in a small column (30 cm × 1 cm) followed by 5 ml of petroleum ether. The extract is collected in a 25-ml bottle filled with distilled water and shaken. The petroleum ether is then treated as described below.

Treatment of Extract before Gas Chromatography. One ml of the extract is transferred to a 3-ml test tube containing 1 ml of concentrated sulfuric acid. The tube is covered with aluminum foil, shaken carefully, and then centrifuged. The sulfuric acid is chilled in a mixture of carbon dioxide ice and acetone. After decantation of the petroleum ether, a 10-µl portion is injected on the gas chromatograph. If the injection gives too low peaks, the remaining 9 ml is concentrated to 0.9 ml in a 50 °C water bath with a stream of purified nitrogen and treated with sulfuric acid as above.

Gas Chromatographic Procedure. The extract is injected on two columns, one SF 96 and one QF 1. Neither of these columns gives a full separation of the chlorinated hydrocarbons present in the water. The combination, however, gives a rather good possibility for calculations.

RESULTS AND DISCUSSION

Development of Column Material. The most critical point in this investigation was to develop the best composition of the filter material, both with regards to absorption and to desorption.

In addition to the column materials mentioned in Table I, two others were tested (*5*, *6*). Amberlite XAD-2 a cross-linked non-ionic copolymer of styrene and divinylbenzene absorbed the chlorinated hydrocarbons from the water with high efficiency but the desorption from the filter was not very easy. From Porapak, 100–120 mesh, with a similar composition as Amberlite, some pesticides could be eluted with recoveries over 50%, but impurities in the support were very difficult to remove.

As shown in Table I, Chromosorb W, 60–80 mesh, covered with a mixture of Carbowax 4000 monostearate and *n*-undecane gave good results, while any of them alone gave bad recoveries for the pesticides used. When the amount of undecane was higher than 25–30 grams per 100 grams of solid support, it ran out of the filter during the filtration procedure and the filter material was difficult to handle.

Besides Chromosorb W, Chromosorb P, 35–80 mesh, and Silica gel HMDS-treated, 50–72 mesh, were tried. These materials could not maintain the necessary amount of stationary phase to give a satisfactory recovery.

No diminished recovery could be seen after increasing the waterflow through the filter from 65 to 130 ml per minute, but if the amount of filter material was doubled from 2 to 4 grams, the recovery was increased. With 4 grams, however,

(6) W. A. Winsten, ANAL. CHEM., **34,** 1334 (1962).

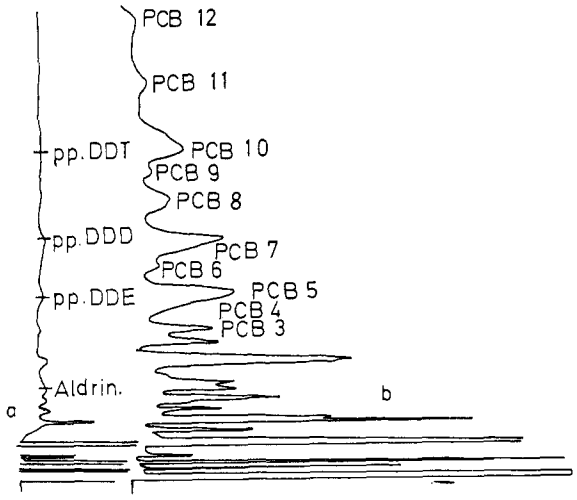

Figure 1*a*. Gas chromatogram from SF 96 column of extract from distilled water
***b*. Gas chromatogram from SF 96 column of extract from natural water**

it was difficult to reach the 65 ml/min necessary to give 100 liters in 24 hours.

Recovery Experiments. The efficiency of the over-all procedure was tested by adding known amounts of chlorinated insecticides or polychlorinated biphenyl (PCB) to the water. The recoveries are found in Table I.

Recovery experiments at the ppq-level (parts per quadrillion, ng/m^3) are difficult to verify, because a true blank in this range hardly exists. For instance, it was impossible to find distilled water to fortify because the water itself gave peaks on the gas chromatograph in this method (Figure 1*a*). These peaks most often correspond to BHC and lindane on both the GC columns. Where they come from, and if they really are BHC and lindane has not been further examined. These peaks are responsible for the recoveries over 100% when a very small amount (180 ppq or lower) of standard is added to distilled water. A blank made by elution of the filter without any water passing through was totally free from peaks.

The identification of the peaks and the calculation of the amount present became very difficult because peaks from some of the 14 peaks of PCB overlapped those from the chlorinated pesticides even when using the mentioned double column system. This made it impossible to get a true calculation of DDE and DDD in the waste waters even when detectable amounts were present. The calculation of PCB is possible in this case because of the similarity between the sample chromatogram and chromatograms from known standards

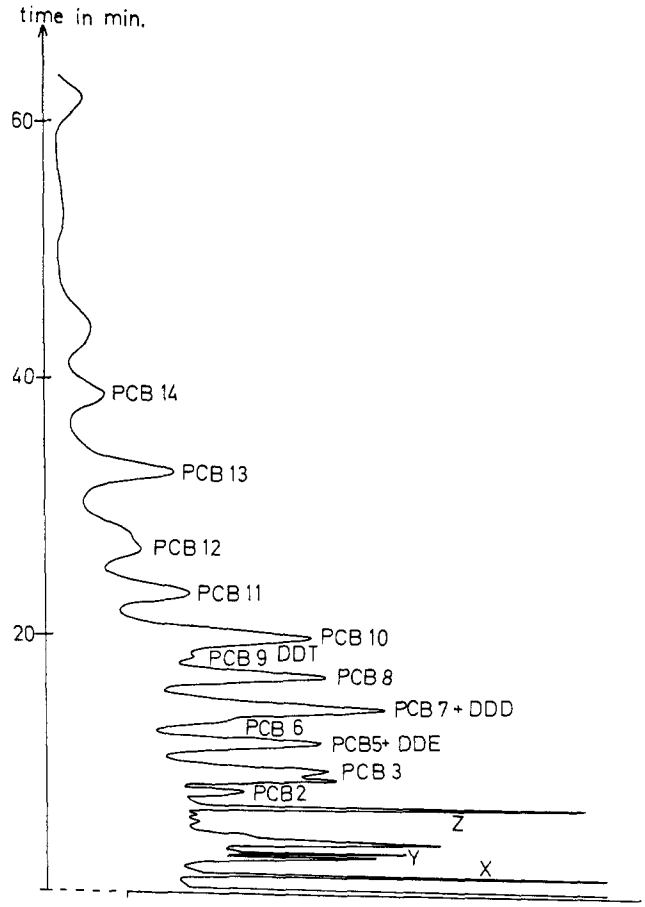

Figure 2. Gas chromatogram from SF 96 column of extract from sewage sludge

solutions (Chophen A 40 and A 50, Bayer). Because of the thorough clean up with sulfuric acid, all epoxy-containing pesticides, such as dieldrin, will be destroyed. This method can be justified because epoxy-containing pesticides are very rare in Sweden.

Sensitivity. With a range setting of $^1/_8$ of highest sensitivity, 10 ng/m^3 of lindane can be detected if the size of the sample is 200 liters, the extract is concentrated to 2 ml and 10 μl is injected.

Results from Analyses of Water. Natural and tap water from the water-works in Lovö on Lake Mälaren taken April 24 and 22, 1968, were analyzed for the presence of BHC, lindane, aldrin, DDE, DDD, DDT, and PCB (Figure 1*b* shows the chromatogram from natural water). Table II shows that the values are of the same magnitude in both samples.

Table II. Chlorinated Hydrocarbans in Tap- and Waste Waters

Sample	Sampling date	Sampling place	Water l.	Sediment, g	ng per kg water, ppt BHC	Lindane	DDE	DDD	DDT	PCB
Tap water	22/4/68	Lovö	176		0.05	0.07	0.07	0.22	0.20	0.33
Incoming water	24/4/68	Lovö	166		0.12	0.16	0.06	0.24	0.33	0.50
Waste water without sediment	24/4/68	Henriksdal	10		22	38				
Sediment	24/4/68	Henriksdal		2.65	38	146	Present		100	1350
Waste water with sediment	24/4/68	Henriksdal	10	2.65	60	184			100	1350

Analysis conditions for water analyses:
Filter: 3 g 10–30 (10% Carbowax, 30% undecane on Chromosorb W).
Flow speed: 65 ml/min.

Waste water leaving the purification plant in Henriksdal near Stockholm was analyzed April 24, 1968. The sediment and the water were analyzed separately as described above. The results, given in Table II, show that the water itself was almost free from residues in relation to the amount found in the aluminium sulfate sediment, indicating the good effect if the plant used the aluminium sulfate precipitation in the cleaning procedure. The weight of sediment plus aluminium hydroxide was 265 mg per liter of water.

A sample of 10 liters of waste water taken April 16 was impossible to analyze because serious artifacts were present. The amount of the artifacts was so large that the 10-ml extract from the water had to be diluted 100 times to give peaks with the same height as 0.1 ng of aldrin. In the same way the extract from one-fifth or 0.6 gram of the solid had to be diluted to 1500 ml to give the peak height corresponding to 0.1 ng of aldrin. The artifacts gave three peaks, (see Figure 2, peaks *X*, *Y*, and *Z*) with the last peak having a retention time almost equal to aldrin on the SF 96 column and exactly equal to lindane on the QF 1 column. An acetonitril/*n*-hexane partition (*7*) followed by elution with hexane from a silica gel column did not remove the artifacts from the chlorinated hydrocarbon fraction.

When treating the extract with potassium hydroxide in methanol, the artifacts disappeared. Analysis of highly concentrated extract on a combined gas chromatograph–mass spectrometer (LKB 7 000) did not give any result. When this extract was cooled in carbon dioxide ice, crystals appeared which could be analyzed on the mass spectrometer (*via* the direct inlet) and shown to be elemental sulfur as S_8 molecules. Finally the three artifact peaks appeared on the gas chromatograph when a sulfur solution was injected giving proof that sulfur was responsible for these peaks.

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(7) R. W. Storrherr and P. A. Mills, *J. Ass. Office Agr. Chemists*, **43,** 81 (1966).

Variable Selectivity Stationary Phases for Gas Chromatography

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The performance of a new class of chromatographic stationary phases is described. Their selectivity can be manipulated over a wide range merely by changing the column temperature. By combining substances differing in melting point and solute selectivity, a stationary phase mixture is produced exhibiting an extended range of melting. Since both the effective volume and composition of the melt are strongly temperature dependent, absolute and relative retention volumes of the solutes are altered markedly by temperature over the transition region, resulting in varying degrees of specificity through choice of the appropriate column temperature. Positive relative retention shifts on the order of 100% have been observed with a 20 °C increase in temperature. It is shown that the ability of the novel stationary phase to identify various classes of solutes by a retention index method is as good as the two-column method, and possesses the additional advantage that its specificity can be varied at will to obtain the best resolution of a complex sample.

A NUMBER OF gas chromatographic procedures have been devised which owe their success to the use of two different stationary phases, either singly or in combination. For example, a widely used technique for solute identification has been the determination of retention behavior of the unknown sample on two columns of different selectivity (*1*, *2*). For quantitative analysis, the separation of complex mixtures has been accomplished by combining different stationary phases either as series columns or in a single column (*3–5*).

All of these methods reflect a need for a stationary phase whose selectivity can be varied over a large range by manipulating some convenient parameter such as the column temperature. A recently reported method for peak identification (*6*) relies on variations in the temperature dependences of the Kovats Indices (*7*) for various classes of solutes. These changes in selectivity with temperature, however, are relatively small for conventional stationary phases.

This paper describes a class of stationary phases which undergo reversible temperature-dependent compositional changes to produce large variations in selectivity for various classes of solutes. These systems are not to be confused with the use of liquid crystals (*8*) or conventional liquid sorbents operated near their freezing point (*9*), where alterations in selectivity for different solutes can be attributed primarily to a change in the physical state of the solvent.

(1) D. A. Leathard and B. C. Shurlock, in "Progress in Gas Chromatography," J. H. Purnell, Ed., Interscience, New York, N. Y., 1968, pp 18, 23.
(2) G. Schomburg, in "Advances in Chromatography," Vol. 6, J. C. Giddings and R. A. Keller, Ed., M. Dekker, New York, N. Y., 1968, p 211.
(3) R. A. Keller and G. H. Stewart, ANAL. CHEM., **36,** 1186 (1964).
(4) G. P. Hildebrand and C. N. Reilley, *ibid.*, p 47.
(5) A. B. Littlewood and F. W. Willmott, *ibid.*, **38,** 1031 (1966).
(6) N. C. Saha and G. D. Mitra, *J. Chromatogr. Sci.*, **8,** 84 (1970).
(7) E. Kovats, in "Advances in Chromatography," Vol. 1, J. C. Giddings and R. A. Keller, Ed., M. Dekker, New York, N. Y., 1965.
(8) H. Kelker and E. Von Schivizhoffen, in "Advances in Chromatography," Vol. 6, J. C. Giddings and R. A. Keller, Ed., M. Dekker, New York, N. Y., 1968, p 247.
(9) R. Claeys and H. Freund, *J. Gas Chromatogr.*, **6,** 421 (1968).