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Note

Chromatography of chlorinated paraffins on alumina and silica columns

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High-molecular-weight chlorinated paraffins (C_{20}–C_{24}, 40–70% chlorine) are incorporated as plasticizers, extenders, and fire retardants into many industrial products[1]. In 1968 the U.S.A. annual production of chlorinated paraffins was 26×10^6 kg (ref. 2). It is possible that chlorinated paraffins leak into the environment in a manner similar to polychlorinated biphenyls (PCB). However, no method is available for the determination of chlorinated paraffins in environmental samples.

Paraffins were determined gravimetrically in chlorinated paraffins after elution with petroleum ether from an alumina column[3], and chlorinated paraffins were separated from a mixture of commonly used plasticizers by elution with carbon tetrachloride from a silica–Celite column[4].

This paper describes the chromatography of chlorinated paraffins on alumina and silica columns, used to clean up biological samples for the determination of chlorinated hydrocarbon pesticides and PCBs[5,6], and the determination of chlorinated paraffins in spiked environmental samples.

EXPERIMENTAL

Materials

Alumina for chromatography (Fisher Scientific A-540), Silicar® (Mallinckrodt CC7), pesticide-grade hexane (Fisher Scientific H-300), pesticide-grade benzene (Fisher Scientific B-426), and diethyl ether (Fisher Scientific E-134) were used. The activation of alumina and silica, column dimensions, and the amount of adsorbents were described in ref. 6. PCB-contaminated batches of silica were purified before activation by washing with hexane and dried under reduced pressure in a rotatory evaporator. Batches of hexane contained varying amounts of benzene (0–0.59 ml/l) and were adjusted to a final benzene concentration of 5.00 ml/l (ref. 7).

Methods

Chlorinated paraffins Cereclor 42 (I.C.I., 42% chlorine) and Chlorez 700 (Dover Chemical, 70% chlorine), in an amount of 3–5 μg were applied to alumina and silica columns and the columns were percolated with hexane, followed by 10% diethyl ether in hexane, to collect 20 ml of each fraction. The fractions were evaporated

to dryness in 25-ml round-bottom flasks on a rotatory evaporator under reduced pressure. The residue was taken up in 0.3–0.5 ml of a 20 w/v% solution of di-(2-ethylhexyl) phthalate (DEHP, practical grade, Matheson Coleman & Bell) in hexane, or in a 20 w/v% hexane solution of Nujol (U.S.P., Plough Canada Limited). An aliquot of this solution (3–9 μl) was injected into the "total" inlet of a Dohrmann microcoulometric system MCTS-20. A Glenco 10-μl syringe, fitted with a 3 in. × 24GA screw-hub needle and a Hamilton repeating dispenser PB-600-1 was used. The injections were carried out in 0.2 μl/2 sec pulses. Each sample was injected at least three times. The standard deviation was 7–11% of the mean. The temperatures were 720, 810, and 810° in the inlet, center, and outlet of the pyrolysis furnace, respectively. Oxygen and nitrogen flow-rates were 173 and 21 ml/min, respectively. The microcoulometer gain was 2400 Ω and the range was 300 Ω. Under these conditions 2 ng of chloride were detectable. The concentration of standards and samples and the volume injected were chosen to yield 10–80 ng of chloride. The recovery of the microcoulometric system was checked periodically by injecting hexane solutions of chlorobenzene (Dohrmann standard), 1-chlorohexane, 1-chlorohexadecane, 1,1,1,2,3,3,3-heptachloropropane (Eastman Kodak 4988, 6152, and 6668, respectively), and solutions of 2,2′,4,4′,6,6′-hexachlorobiphenyl, decachlorobiphenyl, and tetradecachloro-*p*-terphenyl (all prepared by Dr. O. Hutzinger, National Research Council, Halifax, Nova Scotia, Canada) in 20 w/v% DEHP or Nujol in hexane. Standards of Cereclor 42 and Chlorez 700 in 20 w/v% DEHP or Nujol in hexane were injected daily to determine recovery, and all analyses were corrected accordingly. Solvent blanks were injected frequently to check the needle for possible contamination.

Hexane extracts of common seal *(Phoca vitulina)* blubber and herring gull *(Larus argentatus)* yolk, prepared as described[6], were spiked with hexane solutions of chlorinated paraffins. The hexane-extractable lipid content of blubber and yolk was 76.5 and 30.6% of wet weight, respectively. From 10 to 80 mg of lipid was applied to the alumina column. Chlorinated paraffins were added as described[8] to dry fish food (Trout Chow, Purina), the food was extracted[6] and analysed. Hexane-extractable lipid content of the food was 2.73%.

RESULTS AND DISCUSSION

Microcoulometric system recovery. The recovery of chloride from chlorobenzene, 1-chlorohexane, 1-chlorohexadecane, and 1,1,1,2,3,3,3-heptachloropropane is 92–97% of the theoretical amount. The recovery of chloride from the other compounds of higher molecular weight is only 40–60%, when hexane solutions are injected, and improves significantly when DEHP–hexane solutions are used. The low recovery is probably due to a very rapid evaporation of hexane in the needle. The recovery of chloride from Cereclor 42 is 54.8, 80.8, and 86.7%, when 5, 10, and 20 w/v% solution of DEHP, respectively, are injected. The average recovery of chloride from Chlorez 700, 2,2′,4,4′,6,6′-hexachlorobiphenyl, and tetradecachloro-*p*-terphenyl, injected as 20 w/v% DEHP in hexane solutions, are 78.3, 95.5, 94.0, and 70.0%, respectively. Practically equal recoveries are achieved using 20 w/v% Nujol solutions.

Chromatography on alumina. Chromatography on alumina is used to remove lipids from hexane extracts of biological samples. PCB and common chlorinated hydrocarbon pesticides are eluted with hexane and lipids remain adsorbed on the

TABLE I

DETERMINATION OF CHLORINATED PARAFFINS IN SPIKED SAMPLES AFTER CHROMATOGRAPHY OF THE EXTRACTS ON ALUMINA

Sample	*Chlorinated paraffin*			*Recovery (%)*
	Type	*μg/g wet weight*		
		Added	*Found*	
Herring gull yolk	Cereclor 42	13.9	13.7	98.6
	Chlorez 700	21.6	17.3	80.2
Common seal blubber	Cereclor 42	85.0	85.0	100
	Chlorez 700	26.6	22.0	82.8
Fish food	Cereclor 42	1.06	1.02	96.2
	Cereclor 42	10.2	11.7	115
	Cereclor 42	101	99.8	98.7
	Chlorez 700	0.99	1.01	102
	Chlorez 700	10.1	10.4	103
	Chlorez 700	101	102	101

column[5,6]. In the absence of lipids, chlorinated paraffins are partly eluted with hexane (37–38 and 22–23% of the applied amount of Cereclor 42 and Chlorez 700, respectively), and the balance is eluted with 10% ether in hexane, the overall recovery being 90–94%. The presence of up to approximately 20 mg of lipids per application does not change the elution pattern. However, if the applied amount of lipid is more than 40 mg, chlorinated paraffins are completely eluted with hexane. This change of the elution pattern is probably due to the deactivation of alumina by lipids. A similar effect of lipids on the elution of phthalate plasticizers from alumina columns has been described[9].

Chromatography on silica. Chromatography on silica is used to separate PCB and *p,p'*-DDE, eluted with hexane, from other chlorinated hydrocarbon pesticides, eluted with 10% ether in hexane[5,6]. In this system chlorinated paraffins are eluted only with the latter solvent and the recovery of both Cereclor 42 and Chlorez 700 is 95–100%. Since the silica column is used only for essentially lipid-free solutions, the effect of lipids on the chromatography of chlorinated paraffins was not investigated. The results indicate that chromatography on silica may be used to separate chlorinated paraffins from PCB.

Determination of chlorinated paraffins in spiked samples. Sulfur and nitrogen compounds interfere with direct microcoulometric determination of chlorinated compounds in hexane extracts of biological samples. At least some of the interference is removed by chromatography of the extracts on alumina. Thus the level of "apparent chlorine" decreases from 214 μg/g wet weight in the hexane extract of herring gull yolk to 17.6 μg/g in the hexane fraction from the alumina column. Similarly 3.00 and 1.11 μg/g is found in the hexane extract of fish food before and after chromatography on alumina, respectively. The level of chlorine in the seal blubber extract, 94 μg/g, is, however, not changed by chromatography on alumina. PCB and DDT and metabolites accounted for 57% of chlorine in herring gull yolk, for 71% in seal blubber, and for 20% in fish food, all chromatographed on alumina. The origin of the remaining chlorine is under investigation.

The recovery of chlorinated paraffins from spiked samples is in most cases practically quantitative (Table I). However, the microcoulometric determination of chlorine is obviously not specific for chlorinated paraffins and specific methods for the detection or confirmation of these compounds have to be developed. The described chromatography of chlorinated paraffins may be used for a preliminary clean-up of biological samples and for the separation of chlorinated paraffins from PCB.

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