CHROM. 5404

Effects of pesticide-grade hexanes on the silicic acid chromatography of polychlorinated biphenyls and organochlorine pesticides

Small amounts of aromatic hydrocarbons such as benzene, present in some commercial pesticide-grade hexanes, affect significantly the elution patterns of polychlorinated biphenyls (PCB) and organochlorine pesticides from silicic acid columns.

Chromatography on silicic acid has been used to clean up extracts in the determination of PCB and organochlorine pesticides[1,2]. The quality of pesticide-grade hexane is specified at best by its boiling range, and, as shown below, the results will not be reproducible when different pesticide-grade hexanes are used. It is likely that the discrepancies in the elution patterns of PCB and organochlorine pesticides from Florisil columns, reported in the literature[3,4], were observed because different pesticide-grade hexanes were used.

Experimental

Silicic acid Silicar® 100–200 mesh was activated at 130° overnight and deactivated by the addition of 3 % water as described[2]. The chromatography was carried out using 2 g of Silicar® in 45 × 0.7 cm glass columns. PCB (Aroclor® 1254) and pesticides were applied to the columns in 1.5 ml of hexane, washed into the columns with an additional 1.5 ml of hexane and the columns were eluted with hexane, collecting 10 ml (fraction I) and 20 ml (fraction II) of the effluent, and with 10 ml of 10 % diethylether in hexane (fraction III). The mixture of pesticides applied to the columns contained hexachlorobenzene (C_6Cl_6), lindane, heptachlor, aldrin, heptachlor epoxide, *p,p'*-DDE, dieldrin, *p,p'*-DDD, and *p,p'*-DDT in amounts of 6.9, 46.5, 46.5, 48.0, 90.6, 121.0, 64.8, 136.0, and 136.0 ng, respectively. The amount of Aroclor® 1254 used was 689 ng. Average recovery of the pesticides and PCB was 92 %.

A Packard A7901 gas chromatograph with a glass column (6 ft. × 4 mm), containing 4 % SE-30 on acid-washed Chromosorb W, 100–120 mesh, operated at 200°, was used. Carrier gas was nitrogen at a flow rate of 60 ml/min. Injector and detector were kept at 210°, D.C. voltage in the electron-capture detector was 80 V and the meter sensitivity for PCB and organochlorine pesticides was 3×10^{-9} and 1×10^{-8} A, respectively. Peak area determined by a disc integrator was used to quantify PCB and all pesticides except hexachlorobenzene, where peak height was used.

Pesticide-grade hexanes were supplied by the Fisher Scientific Company and by Matheson Coleman & Bell. UV spectra of both hexanes, diluted 1 to 10 with Fisher Scientific Company spectrograde hexane, were recorded on a Beckman DK2A spectrophotometer.

Results and discussion

Benzene absorption peaks at 259, 253.5, and 247.5 nm were observed in both hexanes. The absorbance increased sharply to values > 1 at shorter wavelengths in the Fisher Scientific Company hexane, while benzene peak at 242 nm was observed in the Matheson Coleman & Bell hexane. Based on the absorbance at 259 nm, the former and the latter contained 0.79 and 0.21 ml/l of benzene, respectively. Pesticide-grade

TABLE I

CHROMATOGRAPHY OF AROCLOR® 1254 AND ORGANOCHLORINE PESTICIDES ON SILICIC ACID

H = heptachlor, A = aldrin. Hexachlorobenzene was always eluted in fraction I, lindane, heptachlor epoxide, dieldrin, and *p,p'*-DDD were always eluted in fraction III.

Hexane	*Benzene added (ml/l)*	*% in fractions*[a]				
		Aroclor®	*H*	*A*	*p,p'-DDE*	*p,p'-DDT*
Fisher Scientific	—	56 (I)	100 (II)	71 (I)	100 (II)	100 (III)
Matheson Coleman & Bell	—	18 (I)	75 (II)	22 (I)	56 (II)	100 (III)
Matheson Coleman & Bell	5	69 (I)	100 (II)	16 (I)	100 (II)	100 (III)
Matheson Coleman & Bell	10	64 (I)	100 (II)	80 (I)	100 (II)	100 (III)
Matheson Coleman & Bell	20	86 (I)	33 (I)	100 (I)	31 (I)	68 (II)

[a] Balance eluted in the next fraction

hexane supplied by the Fisher Scientific Company elutes 56 % of Aroclor® 1254 in fraction I and 100 % of *p,p'*-DDE in fraction II. With pesticide-grade hexane from Matheson Coleman & Bell, only 18 % of Aroclor® 1254 and 56 % of *p,p'*-DDE appear in fractions I and II, respectively (Table I). The addition of benzene (5–10 ml/l) to the Matheson Coleman & Bell hexane makes the elution patterns practically identical with those of the Fisher Scientific Company hexane.

It is therefore necessary to characterize in more detail any commercial hexane used in the chromatography of PCB and organochlorine pesticides on silicic acid and possibly also on other adsorbents.

The most pronounced difference between the PCB peaks present in fractions I and II was the complete absence of peaks with relative retention times of 0.97 and 1.04 (*p,p'*-DDE = 1.00) from the fraction I. It is also worth noticing that hexachlorobenzene (C_6Cl_6) appears always in fraction I and lindane in fraction III. Since these two compounds have very similar retention times on gas chromatography, their separation on silicic acid is a useful confirmation technique.

Fisheries Research Board of Canada,
Biological Station, St. Andrews,
New Brunswick (Canada)

V. ZITKO

1 A. V. HOLDEN AND K. MARSDEN, *J. Chromatogr.*, 44 (1969) 481.
2 J. A. ARMOUR AND J. A. BURKE, *J. Ass. Offic. Anal. Chem.*, 54 (1970) 761.
3 L. M. REYNOLDS, *Bull. Environ. Contam. Toxicol.*, 4 (1969) 128.
4 A. BEVENUE AND J. N. OGATA, *J. Chromatogr.*, 50 (1970) 142.

Received March 15th, 1971