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Note

Determination of polychlorinated biphenyls in commercial silica gel by capillary gas chromatography

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Polychlorinated biphenyls (PCBs) are environmental pollutants of global significance and have been determined in air, water, sediments and biota¹⁻³. The use of PCBs in open systems was strongly restricted in many countries during the 1970s after these compounds were found to be accumulated by a number of species and also to be biomagnified. PCBs are still manufactured, but at least in western countries, they are mainly used in closed systems such as in transformers and capacitors⁴. However, contamination of the environment from these sources does occur, *e.g.*, via a slow continuous leakage or by accidents such as transformer fires. Another source of the environmental contamination by PCBs may be the thermal degradation of chlorinated paraffins⁵.

In order to identify the constituents of complex mixtures from various environmental sources, more or less complicated clean-up procedures must be followed. The isolation of PCBs in such samples may involve separations on silica gel, in columns or on thin-layer plates. Several batches of silica gel were found to be contaminated by PCBs during methodological development of the analysis of PCBs^{6,7}. Furthermore, silica gel coated plates for thin-layer chromatography (TLC), were reported to contain up to 40 ppm contaminants, including several polychlorinated aromatic compounds⁸. The present report concerns the qualitative and quantitative determination of PCBs as contaminants of commercial silica gel used for liquid chromatography.

EXPERIMENTAL

Four silica gel products from Merck were investigated: Kieselgel 60, particle size <0.063 mm (batch no. 9034314), 0.040-0.063 mm (batch no. 2665636), 0.063-0.100 mm (batch no. 2739041) and Kieselgel 60 reinst, 0.063-0.200 mm (batch no.

2632096). A silica gel product from Woelm Pharma, Silica Woelm 63-200 (particle size 0.063–0.200 mm, batch no. 2230), was also studied. The silica gel was obtained from the supplier in Sweden and the containers were opened directly before analysis. The silica gel (30.0 g) was wet packed (<0.063 mm) or dry packed (0.040–0.063, 0.063–0.100, 0.063–0.200 mm) in a glass column. Each silica gel was analyzed in triplicate. The silica gel was treated with methylene chloride (p.a. Merck) and the first 100 ml eluted from the column were collected. 2,2',5,6'-Tetrachlorobiphenyl (IUPAC no. 53), used as the internal standard, was added to give a final concentration of 20 $\mu\text{g}/\mu\text{l}$. The methylene chloride was evaporated (Rotavapor) and the residue was redissolved in *n*-hexane (5 ml, glass distilled). The hexane solutions were treated with concentrated sulphuric acid (Merck, density 1.84 g/ml), in order to determine persistent contaminants⁹. The hexane was subsequently dried on a sodium sulphate (Merck) column and the solvent was evaporated. The samples were dissolved in *iso*-octane (3.0 ml) prior to the gas chromatographic (GC) analysis. All solvents and chemicals were tested for impurities in a blank procedure.

The analyses were carried out on a Hewlett-Packard 5880 gas chromatograph fitted with a ⁶³Ni electron-capture detector and an automatic liquid sampler. A BP-1 (SGE) fused-silica capillary column (25 m \times 0.22 mm I.D.) was used. The helium carrier gas flow was 0.3 ml/min. The column temperature was programmed from 70°C (7 min) at 30°C/min to 180°C (2 min), then at 2°C/min to 260°C (2 min). The detector temperature was 320°C and the injector temperature was 270°C. Argon-methane (90:10) was used as the detector make-up gas (30 ml/min). The quantitative analyses were carried out in the splitless mode (valve opened after 6 min) with a reference mixture of twelve polychlorinated biphenyls and by comparison to the technical PCB product that best resembled the sample, as described elsewhere^{9,10}.

Gas chromatography-mass spectrometry (GC-MS) was performed by negative chemical ionization on a Finnigan 4000 mass spectrometer with a Finnigan Inco 400 data system. The gas chromatograph was equipped with a BP-1 (SGE) fused-silica capillary column (25 m \times 0.22 mm I.D.). The flow-rate of the helium carrier gas was 0.5 ml/min. The column was programmed from 70°C (2 min) at 20°C/min to 300°C (20 min). The ion source temperature was 200°C, the reactant gas was methane and the ionization energy was 70 eV.

RESULTS AND DISCUSSION

Gas chromatograms of the persistent contaminants obtained from the silica gel (particle sizes <0.063 and 0.063–0.100 mm) are shown in Fig. 1, together with a chromatogram of a highly chlorinated commercial PCB mixture, Aroclor 1260. Even though differences can be seen between the chromatograms of the silica gel samples and of Aroclor 1260, the general patterns are quite similar. The eluates from silica gel of particle sizes 0.040–0.063 and 0.063–0.200 mm gave similar chromatograms. In order to further characterize the contaminants, GC-MS was performed and mass chromatograms corresponding to PCBs containing 5–9 chlorine atoms were determined as shown in Fig. 2. No PCBs were detected in the blank samples.

Evidently, PCBs are present in the silica gel batches tested. The content of PCBs in the different Merck products are given in Table I. The results were determined by the use of two different reference mixtures as described under Experimental.

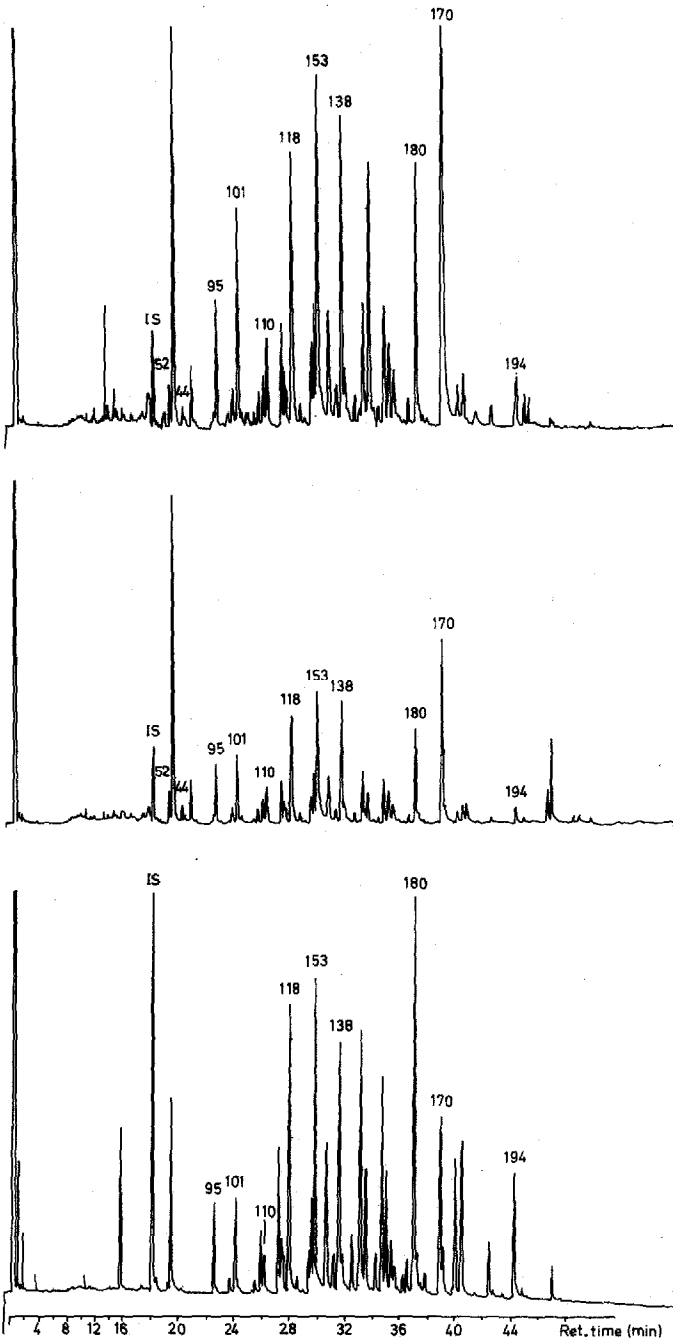


Fig. 1. Gas chromatograms of the persistent contaminants obtained from silica gel (Kieselgel 60), particle sizes <0.063 mm (upper), $0.063\text{--}0.100$ mm (middle) and of Aroclor 1260 (bottom). PCB numbers according to IUPAC^{1,5} are superimposed on the chromatograms. The internal standard (IS) was 2,2',5,6'-tetrachlorobiphenyl.

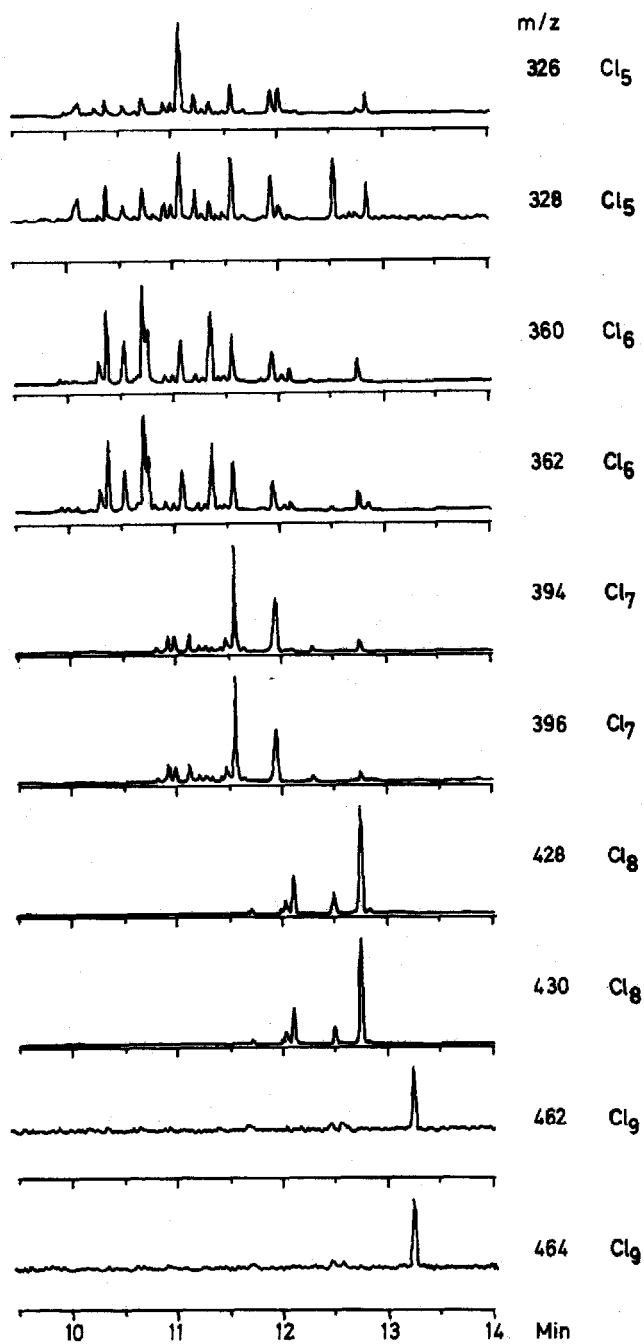


Fig. 2. Mass chromatogram with M^+ and $(M+2)^+$ of the persistent contaminants obtained from silica gel (Kieselgel 60), particle size <0.063 mm. The number of chlorine atoms substituted on the biphenyl is indicated.

TABLE I

AVERAGE CONCENTRATION AND STANDARD DEVIATIONS (S.D.) OF PCBs IN SILICA GEL (MERCK) FOR LIQUID CHROMATOGRAPHY ANALYZED IN TRIPPLICATE

The quantitative analyses were performed with: A, a standard of twelve polychlorinated biphenyls* and B, Aroclor 1254 or 1260 as a standard.

Silica gel particle size (mm)	Concentration (ng/g)			
	A	± S.D.	B	± S.D.
0.063**	37	6.2	40	1.3
0.040-0.063***	17	1.1	18	0.6
0.063-0.100***	16	2.2	18	1.2
0.063-0.200***	9	2.3	13	3.7

* PCB numbers according to IUPAC¹⁵: 44, 52, 95, 101, 110, 118, 128, 138, 153, 170, 180 and 194.

** Aroclor 1260 used as a standard in method B.

*** Aroclor 1254 used as a standard in method B.

The major constituents of the PCB contaminants were tentatively identified (*cf.*, IUPAC numbers in Fig. 1) and also found to correspond to the major homologues and isomers of the technical PCBs, Aroclor 1254 and 1260. The silica gel from Woelm Pharma (0.063-0.200 mm) was not included in the initial study but was later shown to contain PCBs at a level of 10-20 ng per g silica gel. For comparison, the PCB level in silica from Mallinckrodt (Silicar) was reported to be 31 ng/g (lot TEE) and 163 ng/g (lot PXR)⁶.

Silica gel is commonly obtained by the addition of mineral acid to sodium silicate and the product formed is ground, washed, dried and activated¹¹. If PCBs are present in the starting material, the amounts of PCBs in the resulting silica gel preparations should be at approximately the same level. Since this is not the case and the highest concentrations of PCBs in the present study were found in gels with smaller particle sizes (Table I), it is reasonable to assume that the contamination takes place either during the latter part of the preparation process or by the adsorption of ambient PCBs. Silica gel columns have been used to sample airborne organochlorines^{12,13}. Furthermore, indoor air levels of PCBs are known to be at least ten times higher than outdoor levels¹⁴.

The present results demonstrate that PCBs may generally be present as a contaminant of commercial silica gel, and as a precautionary measure, such gels should be purified before use in trace analysis, *e.g.*, by use of methylene chloride as described above. The amount of silica gel used for separations by liquid chromatography is at least ten times the amount of sample. This means that the presence of contaminants from the gel must be considered but should not play a significant rôle if proper analytical techniques are used. However, since clean silica gel is especially important for trace analysis, it is important to determine at what stage the PCB contamination occurs during manufacture.

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