Journal of Chromatography, 144 (1977) 113–117

CHROM. 10,252

Note

Determination of polychlorinated biphenyls in a polymer matrix by gel permeation chromatography using micro-Styragel® columns

JEANNE M. PACCO and ANIL K. MUKHERJI*

Analytical Services Section, Materials Analysis Area, Xerox Corporation, Webster, N.Y. 14580 (U.S.A.)

(Received April 29th, 1977)

Polychlorinated biphenyls (PCBs) have been used extensively in industrial applications and are marketed in the United States under the trade name of Arochlor® by Monsanto (Dayton, Ohio, U.S.A.). Recently their primary use has been as dielectric and heat transfer fluids for capacitors and transformers. They have, however, been extensively used as plasticizers, as hydraulic and lubricating fluid and as components of carbonless copying paper. Some of their properties such as stability, non-flammability and high dielectric constant which make them desirable industrial compounds also make them environmental contaminants by their resistance to degradation with consequent accumulation in the biosphere.

PCBs have been used as secondary plasticizers in a large number of polymer systems. Gas chromatography (GC) is widely used for their analysis and Fishbein[1] has summarized all the important chromatographic data quite thoroughly. Drawbacks with the GC procedures are twofold; first, mixtures yield multi-component peaks making quantitation more complex and second, PCBs have to be isolated from the polymer matrix with an appropriate solvent before injection into the GC system. In most cases, however, a small amount of the polymer dissolves and extra precautions have to be taken to avoid plugging the column. Qualitative separation of PCBs has been studied by Brinkman and co-workers[2] using silica gel–dry *n*-hexane system with UV detection at 205 nm. Seven to twelve peaks for Arochlor 1221–1261 are reported.

The procedure described here evolved out of a need for a more rapid method entailing minimal steps in sample preparation, *i.e.*, dissolution of the sample, subsequent separation of PCBs from the polymer matrix, and finally quantitation. Gel permeation chromatography (GPC) offers the advantage that several species, varying little in molecular size but having commonality of structure, would elute at the same point. This allows for a simplified calibration procedure since only a single calibration curve need be determined. Stalling *et al.*[3] and Stalling[4] have described GPC procedures to isolate pesticide and PCB residues from fish, plant lipid and adipose tissue samples. These classical GPC methods are relatively slow. However, the recently developed micro-Styragel® columns (Waters Assoc., Milford, Mass., U.S.A.) can be operated at higher pressures, consequently reducing analysis time with no loss in resolution.

* To whom correspondence should be addressed.

The proposed method describes the separation and quantitation of PCBs in one homopolymer system and could readily be adapted to other polymer systems if warranted.

EXPERIMENTAL

A Model 502 ALC/GPC high-speed liquid chromatograph (Waters Assoc.) equipped with a Model 6000 solvent delivery system, a UV detector fixed at 254 nm, and a Model U6K valve injector were utilized for this study. The column set consisted of four 100-Å micro-Styragel columns also obtained from Waters Assoc. Sample injections were made using Precision Sampling pressure-10k series C syringes, both 10- and 100-μl capacity.

Calibration standards were prepared using a 10-mg sample of Arochlor 1248 in 10 ml of spectro grade chloroform, and subsequent serial dilutions were made from this solution to obtain the very low concentration levels of interest to us. Arochlor 1248 from Monsanto has the designation 12 for biphenyl and 48 for percent chlorine.

This sample is composed of many PCBs; it is not a pure material, but elutes in a single peak by GPC techniques.

RESULTS

Replicate injections of 10 μl and 100 μl were made at various known levels of PCB concentration. Spectro grade chloroform, the mobile phase was set at a constant flow-rate of 0.8 ml/min. A Texas Instruments recorder was utilized to monitor the UV response at 254 nm operating at 12 in./h chart speed. A calibration curve for 10-μl injections of PCB concentrations of 0.1–1.0 mg in 10 ml was prepared first, giving adequate detection of PCB levels from approximately 10–100 ppm. Fig. 1 illustrates the relationship obtained for multiple injections at four concentration levels. Detector response is linear throughout the entire range of interest. Peak area measurements were obtained by the method of height times width at half-height in inches. Table I contains the replicate area values for each of the four concentration

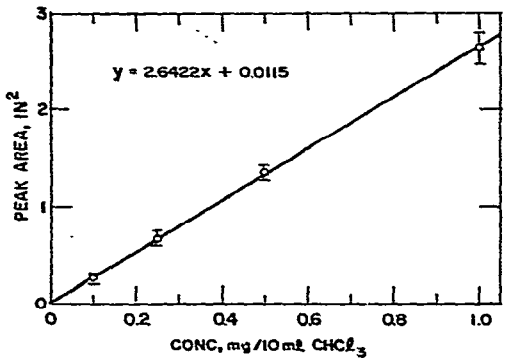

Fig. 1. Calibration curve for amount of PCB in 10 ml of chloroform, range 0–1.0 mg. Each point is the average of at least six analyses at 10-μl injection quantities. Error bars represent highest and lowest values obtained.

TABLE I

AREA RESULTS OF 10-μl INJECTION CALIBRATION SERIES

Run	*Concentration (mg per 10 ml)*			
	0.1	*0.25*	*0.50*	*1.0*
1	0.2580	0.6510	1.3671	2.6598
2	0.2688	0.7471	1.2710	2.5740
3	0.2580	0.7316	1.4353	2.4679
4	0.2716	0.6206	1.3547	2.6164
5	0.2790	0.6750	1.3733	2.7156
6	0.2635	0.6525	1.3423	2.8148
7	0.2079	0.6913	1.3113	2.6610
$\bar{x} \pm (S_m \times t)$	0.2581 ± 0.0216	0.6816 ± 0.0421	1.350 ± 0.0476	2.6442 ± 0.1009

levels studied. Confidence limits of the means, at the 95% confidence coefficient were determined using the following statistical expression:

$$\bar{X} \pm (S_m \times t)$$

where $\bar{X}$ = average area (in.^{2}), S_m = standard deviation of the mean S/n, and $t = 2.447$ (95% confidence level at $n - 1$ degrees of freedom, $n = 7$).

$$y = 2.6422x + 0.0115$$

If one increases the sample injection volume by a factor of 10, one can lower the detection levels by a factor of 10, to the more desired 1–10 ppm range. Fig. 2 illustrates the calibration curve determined for multiple 100-μl injections at the four concentration levels indicated. Table II contains the replicate area measurements from the height times width at half-height method for each concentration level. The areas are in square inches. The similarity of these data to those in Table I are as one might have predicted since the injection volume was increased by the same factor as the decrease in detection level.

The 95% confidence limits of the means were established as explained earlier.

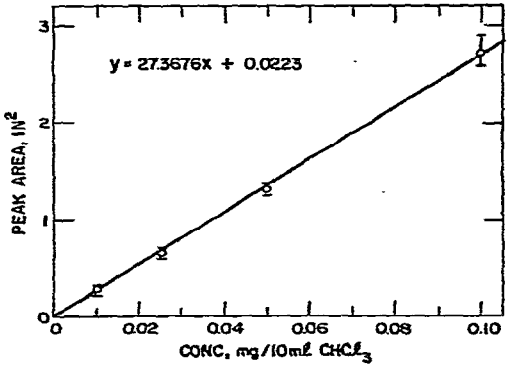

Fig. 2. Calibration curve for amount of PCB in 10 ml of chloroform, range 0–0.10 mg. Each point is the average of at least six analyses at 100-μl injection quantities. Error bars represent highest and lowest values obtained.

TABLE II

AREA RESULTS OF THE 100-μl INJECTION CALIBRATION SERIES

t Value of 2.306 for 8 degrees of freedom used in calculations.

Run	*Concentration (mg per 10 ml)*			
	0.01	*0.025*	*0.05*	*0.10*
1	0.2940	0.6975	1.3268	2.7838
2	0.3162	0.6690	1.2586	2.6490
3	0.2880	0.6789	1.3423	2.7621
4	0.3050	0.6003	1.3609	2.7652
5	0.2968	0.6119	1.2870	2.9120
6	0.2759	0.6510	1.3082	2.5890
7	0.2639	0.6390	1 3175	2.6430
8	0.2380	—	—	—
9	0.2352	—	—	—
$\bar{x} \pm (S_m \times t)$	0.2792 ± 0.0219	0.6496 ± 0.0325	1.3144 ± 0.0315	2.730 ± 0.1004

This yields a worst case precision limit of 7.8% at the 1-ppm level and a best case precision limit of 2.4% at the 5-ppm level.

With calibration curves established, the procedure was tested with a polymer sample containing a known amount of PCB material. A mixture of polystyrene homopolymer containing 0.1 mg of PCB was analyzed repeatedly and the amount of PCB determined using the regression equation given in Fig. 2. A typical LC chromatogram of the PCB separation from the homopolymer is shown in Fig. 3.

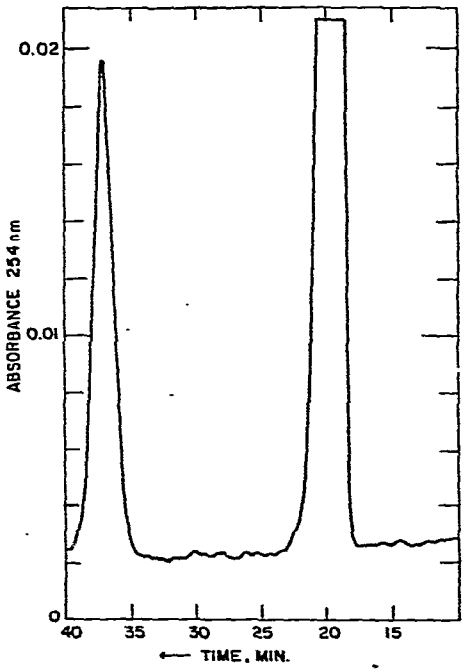

Fig. 3. Typical GPC chromatogram of a 0.10-mg standard solution. The polystyrene peak elutes around 20 min followed by the PCB-containing fraction.

The homopolymer having a molecular weight of 33,000 eluted at the interstitial volume, not being resolved by the small-Ångstrom column system. The PCB containing fraction eluted at a later point, the entire separation taking place in nearly 40 min. The calculated amounts of PCB in the artificial mixture using the calibration curve in Fig. 2, based on eight injections, are shown in Table III.

Statistical analysis of these data shows a $96.25 \pm 2.026 \times 10^{-4}$ percent recovery at the 95% confidence level.

TABLE III

PCB RECOVERED FROM 10-mg SAMPLES

Run	*% Recovered*
1	97.05
2	96.48
3	95.80
4	95.47
5	95.92
6	96.26
7	96.03
8	97.05

DISCUSSION

The proposed method offers a straightforward approach to quantitating the amount of PCB present in homopolymers. Precision levels are as good as or better than classical GC methods. A round robin experiment of PCB analysis in water using GC with electron capture resulted in a recovery of $87.5 \pm 55.2\%$ (at 500-ppb* level) at a 95% confidence limit[5]. Webb and McCall[6] using a similar GC procedure report a standard deviation of 1.1–23.9 for Arochlor 1248. The longer analysis time of the GPC technique is offset by the minimal sample preparation time. Modifications of the technique could provide a separation vehicle for quantitation in more complex polymer systems.

REFERENCES

1 L. Fishbein, *J. Chromatogr.*, 68 (1972) 345.
2 U. A. T. Brinkman, J. W. F. L. Seetz and H. G. M. Reymer, *J. Chromatogr* , 116 (1976) 353.
3 D. L. Stalling, R. C. Tidle and J. L. Johnson, *Anal. Chem.*, 55 (1972) 32.
4 D. L. Stalling, *3rd Int. Conf. Pesticide Chem., Helsinki, Finland, 1974*; *Pure Appl. Chem.*, 42, No. 1–2 (1975).
5 *Standard Methods for Analysis of Environmental Materials*, ASTM-D3304, April 1974.
6 R. G. Webb and A. C. McCall, *J. Chromatogr. Sci.*, 11 (1973) 366.

* The American billion (10^9) is meant.