Limitation on the Use of Antimony Pentachloride for Perchlorination of Polychlorinated Biphenyls

WILLIAM J. TROTTER and SUSAN J. V. YOUNG
Division of Chemistry and Physics, Food and Drug Administration, Washington, DC 20204

Two contaminants are present in commercially available antimony pentachloride ($SbCl_5$) used to perchlorinate polychlorinated biphenyls (PCBs) to decachlorobiphenyl (DCB). DCB is found in the $SbCl_5$ perchlorination reaction blank in which no PCBs were added. Bromononachlorobiphenyl (BNCB) is found after use of $SbCl_5$ to perchlorinate PCBs. Levels of DCB found in the $SbCl_5$ reaction blanks from various distributors ranged from 8 to 972 ng DCB/ml $SbCl_5$. The relationship of the formation of BNCB to amounts of various PCB Aroclors perchlorinated is examined.

Polychlorinated biphenyl (PCBs) residues are extracted, cleaned up, and detected by methods similar to those used for organochlorine pesticides. PCB residues are quantitatively determined by comparing the gas-liquid chromatographic (GLC) response of the multicomponent residue and commercial PCBs (Aroclor®) or a mixture of Aroclors producing a GLC response pattern similar to that of the residue (1). This approach is limited because the multicomponent PCB residue may not have the same proportional composition as the Aroclor or Aroclors used as the quantitation reference. Residues can be composed of mixtures of chlorobiphenyl components from more than 1 Aroclor. Metabolic and other environmental factors complicate the description of the PCB residue composition.

There has been considerable work to develop methods to convert the multicomponent PCBs to a single derivative on which to base the residue determination. Procedures have been reported to catalytically dechlorinate PCBs with hydrogen over palladium or platinum to biphenyl, cyclohexylbenzene, and bicyclohexyl (2, 3). A principal disadvantage with that procedure is that the hydrocarbon product is determined with a GLC flame ionization detector, resulting in low sensitivity. Attempts have been made to convert PCBs to the fully chlorinated decachlorobiphenyl (DCB) (3–5). Armour (6) reported optimum conditions for perchlorinating PCBs with antimony pentachloride ($SbCl_5$). The method provides a qualitative confirmatory procedure for PCB determination. The GLC electron capture detector response is enhanced because total PCBs are manifested as a single peak for DCB. In measuring the single peak for DCB the analyst is not faced with analytical judgments such as baseline correction, method of integration, or discrimination between PCBs and non-PCB components. However, it is necessary to be aware that the various Aroclors give rise to different equivalents of DCB (6) and that the nonchlorinated biphenyl (also used as a fungicide) is perchlorinated by $SbCl_5$ to DCB. Nonetheless, using the perchlorination derivatization can reinforce the residue value determined by measuring a multicomponent PCB residue.

During attempts to apply the perchlorination derivatization in determining low residue levels of PCB and make use of the increased electron capture response to DCB, 2 contaminants were indicated which led to erratic recoveries of DCB.

Experimental

Reagents and Apparatus

(a) *Antimony pentachloride.*—Hooker Chemical, Niagara Falls, NY 14302 (received in glass bottle with lead-lined cap); Matheson Coleman & Bell (MCB), Norwood, OH 45212 (reagent grade); B&A (Allied Chemical), Morristown, NJ 07960 (reagent grade, 99%); Research Organic-Inorganic Chemical (ROC-RIC), Belleville, NJ 07109 (99.99%); and J. T. Baker Chemical, Phillipsburg, NJ 08865 (Baker Analyzed Reagent).

(b) *Gas chromatograph.*—Searle-Analytic (Des Plaines, IL 60088) Model 5360 with 6′ × 4 mm id glass column containing 1% OV-101 on 80–100 mesh Chromosorb W (HP). Operating conditions: column flow, 60 ml nitrogen/min; column, 202°C; detector, 202°C; injector, 225°C; pin-cup design electron capture detector with titanium ^3H foil; detector voltage (constant dc) adjusted to cause one-half full scale recorder deflection for 0.7 ng DCB when full scale deflection is 1×10^{-9} amp.

(c) *Mass spectrometer.*—Varian MAT (25 Route 22, Springfield, NJ 07081) CH5-DF mass spectrometer (MS) coupled to Varian Aerograph 2740 gas

chromatograph via all-glass system using Watson-Biemann 2-stage separator. GLC operating conditions: 6' × 4 mm id glass column containing 3% OV-1 on 80-100 mesh Chromosorb W (HP); column flow, 60 ml helium/min; column 240°C. MS operating conditions: electron energy, 70 ev; emission current, 300 μa; multiplier voltage, 2.2 kv.

Results and Discussion

A peak identical to that of DCB was found in the reaction blank for the Armour perchlorination procedure (6) with the described GLC operating conditions. The identification of DCB was confirmed by GLC-MS of a hexane extract of a hydrolyzed sample of $SbCl_5$ which had not been subjected to the perchlorination procedure. Various quantities (0.2–2.0 ml) of $SbCl_5$ from the 5 commercial sources were examined to determine the presence of DCB. $SbCl_3$ alone was carried through the perchlorination reaction (6) except that no $CHCl_3$ was present with $SbCl_5$ in the reaction vessel. DCB was determined by GLC. Table 1 lists the amounts of DCB found.

After perchlorinating PCBs with $SbCl_5$, a secondary peak with a GLC retention time relative to DCB of 1.31 was observed similar to that reported by Huckins *et al.* (7). This later eluting peak is seen in Fig. 1, the chromatogram from the 0.2 ml $SbCl_5$ (Hooker Chemical) perchlorination of 0.50 μg Aroclor 1221. This peak was found when $SbCl_5$ from each supplier was used. The peak was determined by GLC-MS to be due to bromononachlorobiphenyl (BNCB). BNCB was assumed to be a competing product with DCB arising from a small amount of $SbCl_4Br$ in $SbCl_5$, so parameters relating to possible limitations of the perchlorination procedure were studied. Various quantities (0.5–10 μg) of Aroclors 1221, 1242, 1254, and 1260 in $CHCl_3$ were perchlorinated. Recoveries of DCB and estimates of the relative amounts of BNCB formed are given in Table 2. Calculation of the relative amounts of BNCB product formed was based on comparison of the electron capture GLC peak height of BNCB with that of a DCB reference.

Table 1. DCB (ng/ml) formed from various amounts of $SbCl_5$

Supplier	$SbCl_5$, ml			
	0.2	1.0	2.0	Av.
Hooker Chemical	37	44	47	43
MCB	35	42	38	38
B&A	960	1042	913	972
ROC-RIC	12	13	12	12
J. T. Baker	9	7	7	8

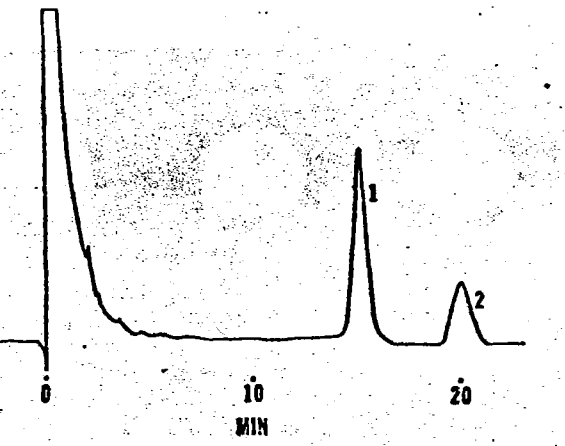

FIG. 1—Electron capture GLC curve from the 0.2 ml $SbCl_5$ (Hooker Chemical) perchlorination of 0.50 μg Aroclor 1221; 0.51 ng equivalent Aroclor 1221 injected. Peak 1 represents 0.81 ng DCB. Peak 2 represents 0.28 ng BNCB.

The amount of DCB determined in the reaction blank was directly proportional to the amount of $SbCl_5$ used (Table 1). This indicates $SbCl_5$ was the source of the DCB and that contamination from other possible sources during the perchlorination was negligible. The procedure for perchlorinating PCBs specifies the use of 0.2 ml $SbCl_5$. $SbCl_5$ producing 8–972 ng $SbCl_5$/ml in the reaction blank would add 0.5–65 ppb, based on a 3 g sample.

DCB produced in the reaction blank was assumed to come from PCB contamination of $SbCl_5$. In an effort to locate the origin of this contamination, $SbCl_5$ bottle closures were investigated. GLC analysis of hexane, in which the plastic caps were soaked for 4 days, did not reveal PCBs. Hooker Chemical, the sole domestic source of $SbCl_5$, supplied $SbCl_5$ in glass bottles with lead-lined caps. This bulk supplier of $SbCl_5$ indicated that the production of chlorine in carbon anode half-cells with linseed oil or other organic binders forms certain organic compounds; however, the destructive oxidative environment in the electrolytic cells would make the production of PCB unlikely as a result of this pathway. On the other hand, antimony metal is commonly obtained as a metallurgical by-product by carbon reduction of its oxide; therefore,

Table 2. DCB and BNCB from perchlorination of various Aroclors with 0.2 ml $SbCl_5$[a]

Aroclor	Amt, μg	DCB recd, %	BNCB[b] recd, %	DCB + BNCB[b] combined rec, %
1260	10	86	0	86
1254	10	84	0	84
1242	10	88	4	92
1221	10	67	16	83
1260	4	81	0	81
1254	4	80	0	80
1242	4	78	8	86
1221	4	70	18	88
1260	0.5	89	2	91
1254	0.5	78	6	84
1242	0.5	72	10	82
1221	0.5	60	19	79

[a] Hooker Chemical $SbCl_5$.
[b] Quantity calculated by comparison of electron capture GLC response to BNCB vs. response to DCB reference standard.

it is conceivable that PCBs could be associated with the antimony metal employed in the $SbCl_5$ process. No heat transfer systems containing PCBs are used in either the chlorine or $SbCl_5$ production facilities, and $SbCl_5$ does not come into contact with plastics in the manufacturing operation or in shipping containers (Hooker Chemical and Plastics Corp., 1974, private communication).

Two parameters (various quantities and various Aroclors) were studied in relationship to the production of BNCB as a competing product of DCB during the perchlorination of PCBs. BNCB was calculated by comparison of the electron capture GLC response to BNCB vs. the response to DCB. Several factors are considered: (*1*) In this reaction bromination is kinetically favored over chlorination. With perchlorination of lower amounts of PCBs the relative yield of BNCB to DCB is greater because the brominating agent is the limiting quantity in contaminated $SbCl_5$. (*2*) Bromination occurs to a larger degree for a given quantity of the less chlorinated PCBs such as Aroclors 1221 and 1242, rather than for 1254 and 1260. This likely is due to a greater number of reactive sites and less steric hindrance. (*3*) In the range of PCBs perchlorinated (0.5–10 μg) in the above study, it is likely that with lower amounts of PCBs and/or less chlorinated Aroclors the decrease in DCB recovery is principally due to the increase of BNCB formed.

One of the major advantages of perchlorination in determining minute quantities of PCBs is the inherent increase in effective GLC detector response. Contaminated $SbCl_5$, as described here, would preclude its use in many of these cases.

References

(1) *Official Methods of Analysis* (1975) 12th Ed., AOAC, Washington, DC, secs. 29.001-29.007
(2) Asai, R., Gunther, R., Westlake, W., & Iwata, Y. (1971) *J. Agr. Food Chem.* 19, 396–398
(3) Berg, O. W., Diosady, P. L., & Rees, G. A. V. (1972) *Bull. Environ. Contam. Toxicol.* 7, 338–347
(4) Hutzinger, O. W., Safe, S., & Zitko, V. (1972) *Int. J. Environ. Anal. Chem.* 2, 95–106
(5) Hutzinger, O. W., Jamieson, D., Safe, S., & Zitko, V. (1973) *JAOAC* 56, 982–986
(6) Armour, J. A. (1973) *JAOAC* 56, 987–993
(7) Huckins, J. N., Swanson, J. E., & Stalling, D. L. (1974) *JAOAC* 57, 416–417

Received August 21, 1974.
This paper was presented at the 88th Annual Meeting of the AOAC, Oct. 14–17, 1974, at Washington, DC.