Determination of Polychlorinated Biphenyl (PCB's) Residues in Grades of Pulp, Paper and Paperboard

by
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Polychlorinated biphenyls (PCB's, Aroclor® 1242 and 1254) are of widespread use in the manufacturing of electrical insulators, varnishes, paints, lubricants and heat transfer fluids. They are also used as plasticizers. JENSEN, et al, (1,2) and WIDMARK (3) identified a group of PCB's in the Swedish environment through the use of gas chromatography and mass spectroscopy. This was the first time that PCB's were recognized as environmental pollutants.

The purpose of this study was to determine residues of PCB's in different grades of pulp, paper and paperboard samples. These grades included both food packaging and non-food packaging grades. The samples were procurred from members of The American Paper Institute from various geographic locations throughout the country during the months of November and December of 1971.

Materials and Methods

Ten grams of sample were weighed, shredded into small pieces, and transferred to a 500-ml round bottomed flask. One-hundred milliliters of 2% methanolic potassium hydroxide were added to the sample and refluxed for 30 minutes. The hydrolized sample was filtered and 40 ml were taken for extraction with petroleum ether.

The 40-ml aliquot (4.0 gm sample) from the extract was transferred to a 250-ml separatory funnel. The aliquot was shaken vigorously with 20 ml of petroleum ether and 40 ml of distilled water. The aqueous layer was drained into a second separatory funnel containing 40 ml of petroleum ether, the separatory funnel was shaken vigorously, and the aqueous layer discarded. The petroleum ether extracts were combined and washed with three 20-ml portions of distilled water. The petroleum ether extract was taken through a column of anhydrous sodium sulfate into a 100-ml volumetric flask. The volume was adjusted to the mark with petroleum ether.

A 10-ml aliquot (0.4 gm sample) was taken from the above-mentioned 100-ml sample, and concentrated to a known volume. A 1- to 5-µl sample was injected into a gas chromatograph equipped with an Ni^{63} electron capture detector system. A standard curve was plotted each day for Aroclors 1242 and 1254.

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Gas Chromatographic Conditions

Gas chromatographic column, 6' x 1/4" O.D. glass, packed with 3% OV-17 on 100/200 mesh Gas-chrom Q

Column Temperature: 200 C

Detector Temperature: 245 C

Inlet Temperature: 275 C

Carrier Gas (Nitrogen): 86 ml/min flow

TABLE 1

Summary of Aroclor 1242 and 1254 residues detected in pulp, paper and paperboard.

Sample Identification	Aroclor 1242 Found ppm	Aroclor 1254 Found ppm	Total* Aroclor Found ppm
	Unbleached Kraft Pulp		
81	<0.50	<0.50	<0.50
3	<0.50	<0.50	<0.50
39	<0.50	<0.50	<0.50
	Bleached Kraft Pulp		
44	<0.50	<0.50	<0.50
11	1.33	<0.50	1.33
82	<0.50	<0.50	<0.50
55	<0.50	<0.50	<0.50
	Virgin Newsprint		
47	<0.50	<0.50	<0.50
15	0.58	0.42	1.00
48	<0.50	<0.50	<0.50
	Recycled Newsprint		
45	<0.50	<0.50	<0.50
86	<0.50	<0.50	<0.50
36	1.38	<0.50	1.38
	Recycled Bond Paper		
35**	91.00	-	113.50
35**	-	22.50	
17	265.00	25.00	290.00
	Bleached Kraft Linerboard		
54	<0.50	<0.50	<0.50

* 1242 and 1254

** Aroclor 1242 was assayed from a 50-ml final volume. Aroclor 1254 was assayed from a 4-ml final volume. The total of 1242 and 1254 is indicated in column labeled Total ppm.

TABLE 1 (contin.)

Sample Identification	Aroclor 1242 Found ppm	Aroclor 1254 Found ppm	Total* Aroclor Found ppm
	Unbleached Kraft Linerboard		
33	<0.50	<0.50	<0.50
23	<0.50	<0.50	<0.50
41	<0.50	<0.50	<0.50
72	<0.50	<0.50	<0.50
51	<0.50	<0.50	<0.50
61	<0.50	<0.50	<0.50
40	<0.50	<0.50	<0.50
	Solid Bleached Sulfate Board Nonclay Coated		
25	<0.50	<0.50	<0.50
75	<0.50	<0.50	<0.50
83	<0.50	<0.50	<0.50
32	<0.50	<0.50	<0.50
30	1.92	<0.50	1.92
50	<0.50	<0.50	<0.50
	Solid Bleached Sulfate Board Clay Coated		
84	<0.50	<0.50	<0.50
80	<0.50	<0.50	<0.50
38	<0.50	<0.50	<0.50
49	<0.50	<0.50	<0.50
71	<0.50	<0.50	<0.50
31	<0.50	<0.50	<0.50
74	<0.50	<0.50	<0.50
	Solid Unbleached Sulfate Board Clay Coated		
73	<0.50	<0.50	<0.50
	Patent White Newsback Paperboard (also known as White Lined, White Lined News, and White Lined Manila Back)		
87	10.70	<0.50	10.70
69	3.21	1.29	4.50
66	2.42	1.67	4.09
64	18.80	4.17	23.00
28	<0.50	10.35	10.35
13	35.00	7.50	42.50
26	1.55	0.22	1.77
52	<0.50	<0.50	<0.50
9	1.50	1.00	2.50
	Patent White Newsback Clay Coated Paperboard (Also Known as Clay Coated News and Clay Coated White Back)		
88	2.75	<0.50	2.75
68	2.92	0.92	3.84
65	2.83	1.50	4.33

* 1242 and 1254

TABLE 1 (contin.)

Sample Identification	Aroclor 1242 Found	Aroclor 1254 Found	Total* Aroclor Found
	ppm	ppm	ppm
62	5.42	1.46	6.88
27	1.55	0.30	1.85
12	28.40	2.20	30.60
6	7.50	1.10	8.60
53	<0.50	<0.50	<0.50
7	1.71	0.67	2.38
	Shell Stock (Any Dry Food Packaging Grade Which Will Be Overwrapped with a Printed Wrapper, May be a Lined Sheet such as Manila Lined News)		
89	23.12	<0.50	23.12
70	2.46	1.09	3.55
67	2.29	1.25	3.54
63	1.63	0.08	1.71
29	8.40	2.40	10.80
14	41.00	8.00	49.00
58	3.25	<0.50	3.25
8	3.10	3.84	6.94
	Unbleached Kraft Bag or Wrapper Stock		
59	<0.50	<0.50	<0.50
2	<0.50	<0.50	<0.50
	Bleached Kraft Bag, Wrapper or Tag Stock		
57	<0.50	<0.50	<0.50
78	<0.50	<0.50	<0.50
77	<0.50	<0.50	<0.50
19	1.00	<0.50	1.00
	Glassine		
20	1.10	0.25	1.35
60	<0.50	<0.50	<0.50
5	<0.50	<0.50	<0.50
	Greaseproof		
10	<0.50	<0.50	<0.50
37	<0.50	<0.50	<0.50
76	<0.50	<0.50	<0.50
	Publication Paper		
42	<0.50	<0.50	<0.50
43	<0.50	<0.50	<0.50
22	<0.50	<0.50	<0.50

* 1242 and 1254

TABLE 1 (contin.)

Sample Identification	Aroclor 1242 Found ppm	Aroclor 1254 Found ppm	Total* Aroclor Found ppm
	Virgin Bond Paper		
79	<0.50	<0.50	<0.50
21	8.50	<0.50	8.50
4	<0.50	<0.50	<0.50
1	<0.50	<0.50	<0.50
16	2.10	<0.50	2.10
85	<0.50	<0.50	<0.50
34	1.60	<0.50	1.60

* 1242 and 1254

TABLE 2

Recovery of Aroclor 1242 and Aroclor 1254 from pulp, paper and paperboard samples.

Sample Identification	Paperboard Grade	Spike Level 1242 ppm	Spike Level 1254 ppm	Recovery 1242 %	Recovery 1254 %
50	Solid Bleached Sulfate Board Nonclay Coated	0.61		92.2	
45	Recycled Newsprint	1.21		93.0	
52	Clay Coated Unbleached Patent White Newsback	2.42		88.0	
5	Glassine	4.85		75.0	
1	Virgin Bond Paper	9.70		88.0	
10	Greaseproof	14.54		80.5	
3	Unbleached Kraft Pulp	29.10		86.0	
63	Shell Stock	121.10		82.0	
52	Patent White Newsback		2.065		99.0
63	Shell Stock		103.250		97.0
10	Greaseproof		14.450		82.5
1	Virgin Bond Paper		10.330		108.5

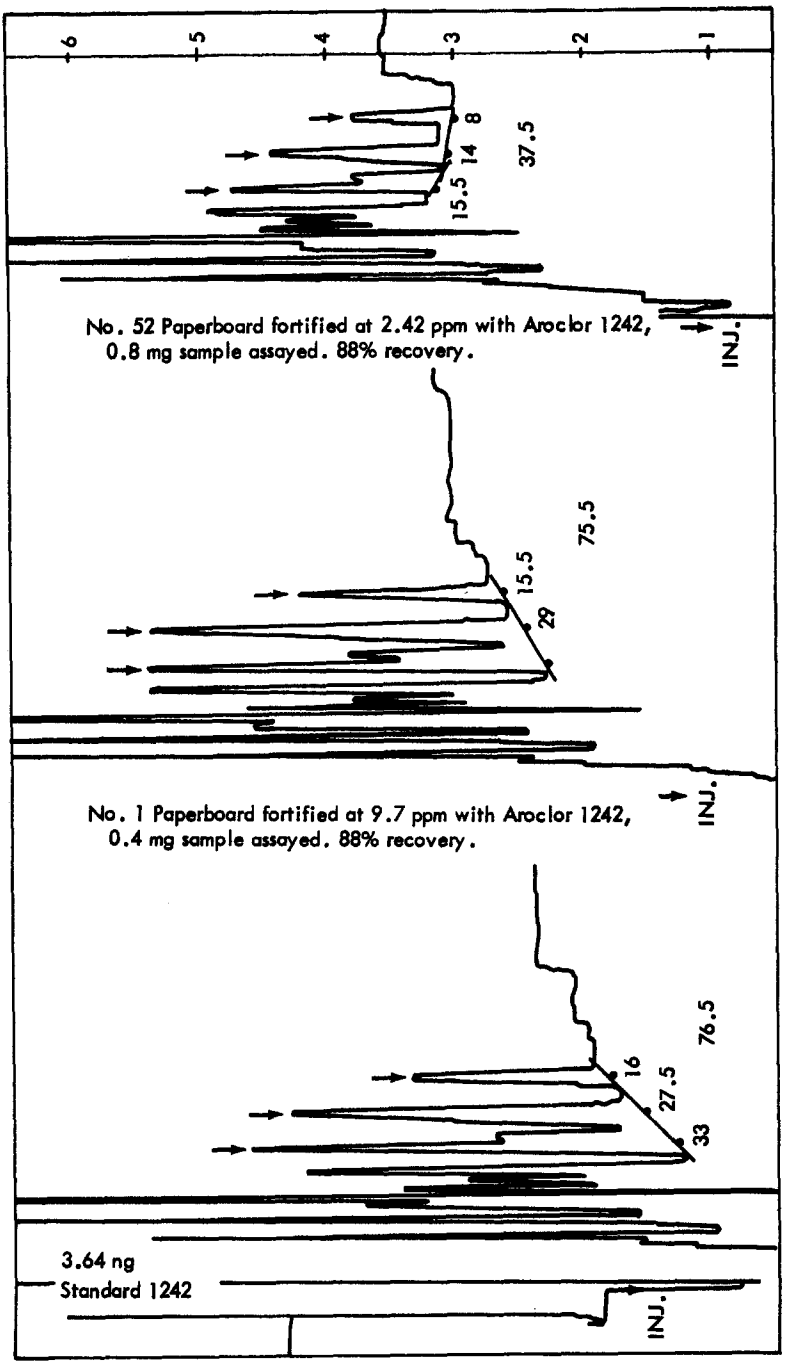

Figure 1 - REPRESENTATIVE CHROMATOGRAMS OF A STANDARD (AROCLOR 1242) AND FORTIFIED SAMPLES

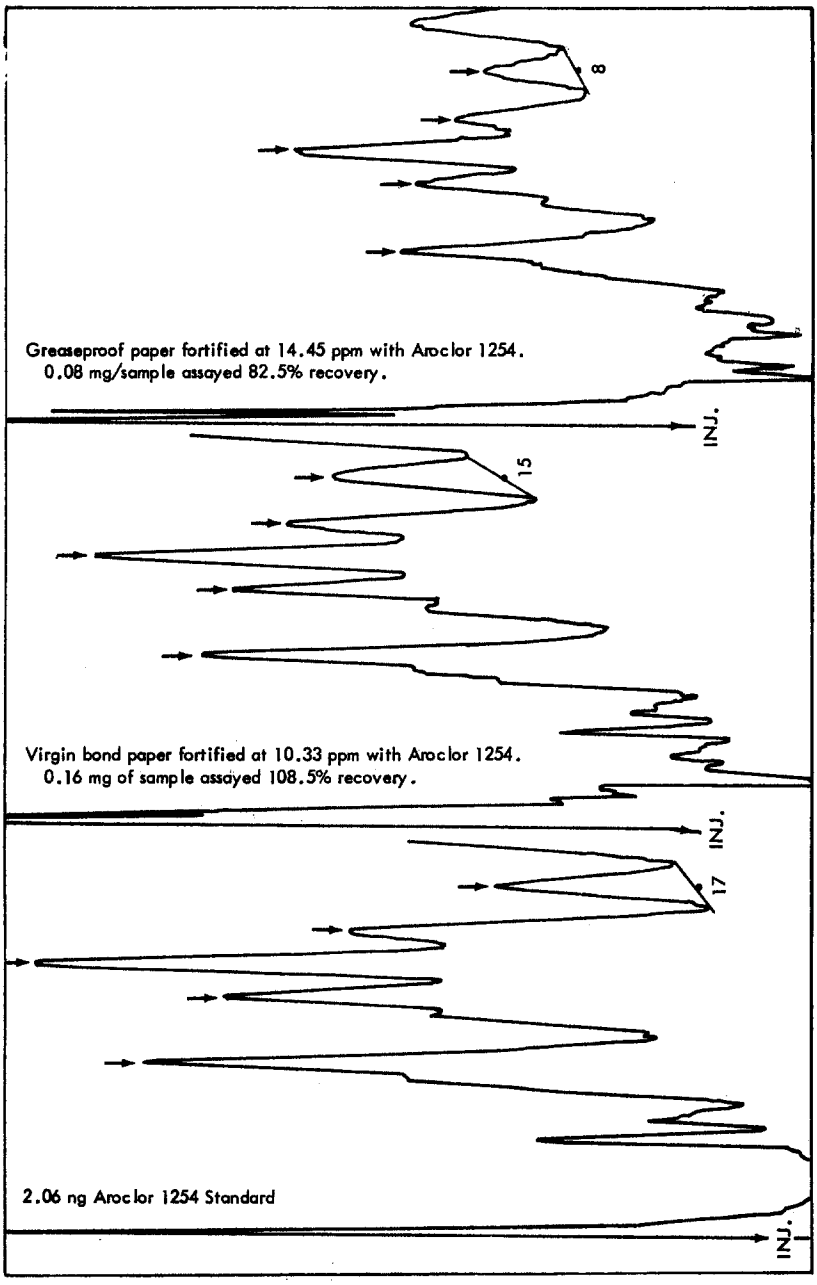

Figure 2 - REPRESENTATIVE CHROMATOGRAMS OF A 1254 AROCLOR AND FORTIFIED PAPERBOARD SAMPLES.

Results and Discussion

The results obtained for the survey are summarized in Table 1. The sensitivity of the method for PCB's is 0.50 ppm. Recovery data to validate the method are presented in Table 2. The average recovery for Aroclor 1242 is 86% and that for Aroclor 1254 is 98%.

Typical chromatograms for a standard (Aroclor 1242) and fortified samples are presented in Figure 1. In addition, typical chromatograms for a standard (Aroclor 1254) and fortified paperboard samples are shown in Figure 2.

We found that 11% of the different grades of pulp, paper, and paperboard samples contained PCB residues higher than 10.0 ppm, 4% of the samples contained PCB residues of 6.0 to 10.0 ppm and 25% of the samples contained PCB residues in the range of 1.0 to 5.0 ppm. However, PCB residues were found to be less than 0.50 ppm in 58% of all samples analyzed. It should be noted, however, that this survey was conducted during the November-December 1971 period, and if a new survey is made, levels of PCB residues in samples would most likely be lower due to the effort put forth by the paper industry.

As shown in Table 1, PCB residues were also found in virgin newsprint and virgin bond paper. However, it is suspected that the manufacturing processes may be the cause of the residues.

Acknowledgments

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