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**INTERLABORATORY STUDY OF THE DETERMINATION OF POLYCHLORINATED
BIPHENYLS IN A PAPER MILL EFFLUENT**

JOSEPH J. DELFINO AND DWIGHT B. EASTY

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INTERLABORATORY STUDY OF THE DETERMINATION OF POLYCHLORINATED

BIPHENYLS IN A PAPER MILL EFFLUENT

Joseph J. Delfino*
Laboratory of Hygiene
465 Henry Mall
University of Wisconsin - Madison
Madison, WI 53706

and

Dwight B. Easty
The Institute of Paper Chemistry
P.O. Box 1039
Appleton, WI 54912

ABSTRACT

Six laboratories collaboratively studied a method for determining polychlorinated biphenyls (PCBs) in paper mill effluent. In preliminary studies, the recovery and relative standard deviation (RSD) for the PCB Aroclor 1242 added to and extracted from distilled water were 95.6% and 14.7%, respectively. Because the RSD of data from direct injection of Aroclor 1242 solutions into the gas chromatograph was of similar magnitude, 15.6%, gas chromatographic analysis appeared to provide the principal source of variation in the overall determination. Participating laboratories achieved an average 93.7% recovery of Aroclor 1242 added to a paper mill effluent; their data had a RSD of 16.0%. The results indicate that the method is satisfactory for use with paper mill effluents having PCB concentrations above 2 $\mu\text{g/L}$ and it compares favorably with findings from studies in other environmental matrices. Greater variation might be expected from effluents containing significant interferences.

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BRIEF

A method for determining PCBs in paper mill effluent was found to be satisfactory for effluents having greater than 2 $\mu\text{g/L}$ PCB content and easily removed interferences.

INTRODUCTION

Polychlorinated biphenyls (PCBs) were formerly used in carbonless copy papers, but this practice was terminated in 1971 (1,2). Small amounts of PCBs, particularly the Aroclor 1242 mixture, are still entering paper mills which recycle used paper fibers as part of their manufacturing process. It has not been logistically nor economically feasible to completely separate carbonless copy paper from the other waste papers that are being recycled (1). Thus, until all of the PCB-containing papers still in circulation cease to appear in recycled fiber, small quantities of PCBs will continue to be discharged in the mills' aqueous effluents. The amounts of PCBs discharged can be lowered by reducing the suspended solids in the effluents from the mill (3).

A procedure for determining PCBs in industrial effluents has been issued by the Environmental Protection Agency (EPA) (4). In our collaborative investigation, we modified the EPA method to apply specifically to paper mill effluents and aimed to document the precision of the modified method when used in several laboratories. However, the modified method described here has not been submitted to the EPA for approval — an action that would be necessary if the data were to be included in an EPA-required monitoring program. Participants in the study included industry, universities, independent laboratories, and government agencies.

The promulgated EPA method for determining PCBs in industrial effluents involves liquid-liquid extraction, Florisil cleanup (Florisil is a registered Trade Mark of the Floridin Company, Pittsburgh, PA 15235), and electron capture gas chromatography. Previous work has revealed deficiencies when this procedure is used on in-mill process streams containing large amounts of cellulose fibers (2). Complete removal of the PCBs from cellulose fiber suspensions required alcoholic KOH reflux of the isolated fibers subsequent to liquid-liquid extraction. Samples of paper mill

effluent for PCB monitoring are typically taken following waste treatment. Because a large percentage of the suspended fibers are removed in the treatment system, these samples should not require PCB isolation procedures beyond those specified in the EPA method (4). Therefore, the procedure used in this investigation retained many features of the EPA method (4) and was judged suitable by the collaborators for the purposes of this study. As described below, some modifications were incorporated to make the method easier to use on effluents in which organochlorine pesticides were not expected nor generally observed in previous analyses.

EXPERIMENTAL

The interlaboratory study was performed in two parts. Phase 1 was designed to determine the comparability of PCB methodologies in use in each laboratory and to assess the ability of the participating analysts to perform the basic operations employed in PCB determinations. Phase 2 consisted of application of the modified method to determination of Aroclor 1242 in a paper mill effluent.

Phase 1. Each participating analyst was provided with septa-sealed vials containing acetone solutions of Aroclor mixtures. Each laboratory was asked to analyze the PCB mixture by (a) direct injection into a gas chromatograph (GC) employing an electron capture detector, and (b) addition of 1 mL of the unknown to 1000 mL distilled water followed by solvent extraction, concentration, and then injection into the GC. Procedures for these operations were left to the discretion of the analysts.

Phase 2. Validation of Sample Preparation Procedure. Prior to collection of paper mill effluent samples to be used for the PCB determinations, a separate study was performed to evaluate the study coordinator's ability to provide equivalent effluent samples to each participant. Because PCBs tend to sorb onto

suspended solids, samples for collaborative study must contain equivalent suspended solids contents. A large volume of paper mill effluent was placed in a metal container and was mechanically stirred. Aliquots (250 mL) were removed and sequentially added to each of ten separate 2.5-L glass containers. (Bottles were rinsed with hexane several times to remove possible contaminants before being used for paper mill effluent samples. The hexane was drained and the bottles air dried prior to use. Aluminum foil was used to line the bottle caps.) The process was repeated ten times until each 2.5-L container was filled. Suspended solids were determined on the contents of each container.

Instructions to Analysts. Each analyst received two 2.5-L paper mill effluent samples and three sealed glass ampules containing Aroclor 1242. Two of the three ampules contained Aroclor 1242 in isooctane; one ampule was designated a "known" and contained 13.6 $\mu\text{g}/10\text{ mL}$; the second ampule was an "unknown" and contained 35.2 $\mu\text{g}/10\text{ mL}$. Participants were asked to analyze each solution by direct injection into the GC. The third ampule contained an unknown concentration of Aroclor 1242 in methanol and was to be added directly to one of the two paper mill effluent sample bottles. The ampule was designed to deliver 6.8 μg of Aroclor 1242 directly into the paper mill effluent sample bottle.

The study plan called for each participant to divide the contents of one of the paper mill effluent samples into two equal portions. Then, each portion was to be extracted and the Aroclor 1242 concentration of each portion determined by GC. Each analyst was also instructed to add the ampule containing the 6.8 μg of Aroclor 1242 to the second 2.5-L sample container, break the ampule inside the container, mix well and let this "spiked" sample stand for 24 hr before beginning extraction and analysis by GC. As before, this "spiked" effluent sample was also to be analyzed in duplicate by dividing the 2.5-L sample into two equal portions with each one being analyzed separately.

Determination of PCBs in Paper Mill Effluent. In the promulgated method for PCBs in industrial effluents (4), PCBs and organochlorine pesticides are coextracted from the sample by liquid-liquid extraction. A silica gel microcolumn procedure and standard Florisil column cleanup are prescribed for separating PCBs from pesticides and for dividing the pesticides into subgroups. Because pesticides are unlikely constituents of paper mill effluents and were not of concern here, the EPA method (4) was modified for use in this study by removing from the procedure those steps necessary for extraction, separation, and determination of pesticides. The features of the EPA method (4) which were modified for application to paper mill effluent in this investigation are:

- (1). Hexane and petroleum ether (30-60°) were independently shown by the collaborators to be suitable alternates to 15% methylene chloride in hexane for separatory funnel extraction of effluent. Hexane extraction has been shown to recover PCBs almost quantitatively from effluents with low fiber contents (2). Solvents of higher polarity, such as methylene chloride in hexane, extract excessive amounts of non-PCB materials without improving PCB recovery.
- (2). To assure consistent performance of the electron capture detector and to minimize downtime for detector cleaning, all extracts were subjected to Florisil column cleanup prior to gas chromatographic analysis.
- (3). In addition to the specifications for Florisil columns (4), other column sizes and amounts of Florisil and eluting solvent were acceptable for PCB determination provided that (a) all PCBs were completely eluted, and (b) chromatogram quality signified that samples had been adequately cleaned up. Elution of PCBs from the Florisil column with hexane or petroleum ether as well as with 6%

ethyl ether in petroleum ether was permitted. Use of petroleum ether alone for elution is standard practice in determining PCBs in paper and paperboard (5).

- (4). The silica gel microcolumn procedure for separating PCBs from pesticides was deleted from the method.
- (5). Gas chromatographic column liquid phases specified in the EPA method (4) include SE-30 or OV-1, and OV-17/QF-1. Other silicone liquid phases used successfully for determining PCBs in Phase 1 of this study included OV-17, OV-210, DC-200, OV-101, OV-225, and equivalent SP phases. An earlier collaborative study has indicated that several column materials are useful for PCB determinations (6). Therefore, the phases listed above were considered acceptable for this study. Also accepted were stainless steel as well as glass columns.
- (6). Unknown Aroclors were identified by matching retention times and relative peak heights with peaks in reference Aroclors. To ensure valid quantitation, amounts were injected such that the size of the peaks from the sample and the standard were within $\pm 25\%$. When quantitation was based upon peak heights, at least four peaks were used.

RESULTS AND DISCUSSION

Phase 1. The results of the GC analyses of Aroclor 1242 in acetone are presented in Table I. The average PCB concentration (as Aroclor 1242) based on direct injection into the GC was 1.47 ng/ μ L, representing an average recovery of 98% of the 1.5 ng/ μ L present in the acetone solution. Therefore, on the average, the results indicated that the eight participants in Phase 1 had good GC technique and could quantify PCBs.

While the results of the direct injection experiment were good, some variation among the analysts was evident as shown by the standard deviation (0.23 ng/ μ L), relative standard deviation (RSD) (15.6%) and range (1.05-1.76 ng/ μ L). While this indicated more variation than might be desired in an interlaboratory study, it is shown later that a RSD of 15.6% is typical for PCB determinations involving environmental matrices.

The extraction of Aroclor 1242 added to distilled water resulted in an average recovery of 95.6%. This was satisfactory, although the variation was again relatively high as indicated by the RSD (14.7%) and the range (70-114%). Because this sample was free from interferences, the precision represents that which is attainable under unusually favorable analytical conditions.

The RSDs obtained in the direct injection experiment and in determination of Aroclor 1242 added to distilled water were of similar magnitude. This suggests that GC analysis provided the major sources of between-laboratory variation in the overall analytical scheme. Likely contributors to this variation included: (a) use of different Aroclor 1242 standards with slightly different PCB isomeride composition, and (b) use of different quantitation methods, including measurement of peak heights, peak areas, or weight percentages of individual peaks (7-9). The contribution of different GC columns and conditions is difficult to assess, although it was possibly advantageous for the analysts to use their own columns which produced familiar Aroclor chromatograms.

Phase 2. This phase of the study again involved determination of Aroclor 1242 by direct injection of solvent solutions into the GC and, of greater importance, also included determination of Aroclor 1242 in a paper mill effluent. The effluent was studied as collected and after addition of a known amount of an Aroclor 1242 standard.

The ability of the proposed sample collection procedure to supply equivalent mill effluent samples for collaborators was tested by determining if the procedure could provide samples of equivalent suspended solids content. Results are given in Table II. One analyst removed aliquots from each of ten different 2.5-L sample bottles, filled as described earlier, and performed the standard suspended solids measurement (10). The data indicate that representative suspended solids distribution could be achieved by the sampling technique, since the RSD experienced was 3.3%. The published RSD for suspended solids determinations ranges from 0.76 to 33% depending on the actual suspended solids concentration present in the sample (10).

Known and unknown Aroclor 1242 concentrations were determined by direct GC injection from glass ampules. The results are shown in Table III. The known solution allowed participating analysts to check their in-house standards with one prepared by the coordinating laboratory and also provided a reference standard to be used for the spiking, extraction, and recovery experiment involving the paper mill effluent sample.

The determination of the known and unknown PCB concentrations by direct injection into the GC yielded essentially the same average calculated recovery data, i.e., 98% and 97%, respectively (Table III). However, the variation among seven reporting analysts was somewhat greater for the unknown standard solution (RSD = 12.6%) than for the known standard solution (RSD = 7.5%). There is no immediate explanation for this except that the unknown solution was ca. 2.5 times more concentrated than the known solution. This resulted in an additional dilution step to keep the unknown Aroclor on scale. This could have introduced additional error and the slightly higher RSD.

The PCB concentration in the paper mill effluent was determined in duplicate by six analysts according to the modified analytical procedure. The results are given in Table IV. The paper mill effluent was also analyzed in duplicate following addition of a methanol-based Aroclor 1242 standard. These data appear in Table V. Relative standard deviations of the PCB determinations performed on the effluent as collected and following addition of Aroclor 1242 were 19.0% and 16.0%, respectively.

The variations in the results for the determination of Aroclor 1242 in the paper mill effluent among the six analysts who completed Phase 2 were not very different from the variations noted for the direct GC injection of Aroclor 1242 solutions (Tables I and III). This suggests, as did the Phase 1 findings, that only small additional errors were introduced by the sample extraction and Florisil cleanup steps.

As indicated in Table V, the average recovery of the added Aroclor 1242 was 93.7%. This average is slightly misleading since three results clustered near 100% and the remainder ranged from 84 to 88%.

Following Florisil cleanup of the paper mill effluent used in this study, all collaborators obtained characteristic Aroclor 1242 chromatograms. Some other paper mill effluents contain interfering materials that cannot be removed on Florisil and which produce badly distorted chromatograms (11). Between-laboratory variation in PCB determinations conducted on effluents containing intractable interferences would undoubtedly be greater than that experienced in the current investigation.

Other observations reported by the collaborators in Phase 2 included (a) formation of emulsions during solvent extraction of the effluent, and (b) small differences in peak ratios between the individual laboratory's Aroclor 1242

standards and the standard provided by the coordinating laboratory. Emulsions were broken by centrifugation or addition of Na_2SO_4 . The problem of variations in PCB standards could be obviated by providing Aroclor standards from a common source to all laboratories conducting PCB determinations.

Considering the nature of the paper mill effluent matrix, the results of this interlaboratory study were good. This can be substantiated by comparison of the RSDs reported in this study with those reported for PCB collaborative studies involving other complex environmental matrices (Table VI). It is clear, however, that analysts desiring to compare their results for the determination of PCBs in environmental samples must anticipate variations within the range of 15-20% expressed as the RSD.

CONCLUSIONS

Based on this interlaboratory study, the method described herein for PCBs in paper mill effluents appeared satisfactory. However, the statistics developed in this work were derived from determination of Aroclor 1242 mixtures in the concentration range of 2-6 $\mu\text{g}/\text{L}$ and on an effluent from which interferences were readily removed. Different precision and accuracy findings could occur when the method is applied to paper mill effluents having different contents of PCBs and of materials which interfere in the determination. Gas chromatographic standards and techniques appear to have been the principal sources of variation in this study. It is important that regulatory officials seeking to establish effluent standards for PCBs in discharge media such as paper mill effluent take the findings of this and other related studies into consideration, so that the standards may be enforced rationally in light of analytical variability.

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Table I. Determination of PCBs as Aroclor 1242 in Acetone Solution by Direct Injection and Extraction From Distilled Water (Phase 1)

Analyst	PCB by Direct Injection, ng/ μ L ^a	PCB Extraction From Distilled Water, %
1	1.52	90.0
2	1.41	99.3
3	1.46	89.6
4	1.70	>100 ^c
5	1.59	114
6	1.26	106
7	1.76	70.1
8	1.05	100
Average	1.47 ng/ μ L ^b	95.6% ^d
Range	1.05-1.76 ng/ μ L	70.1-114%
Standard deviation	0.23 ng/ μ L	14.1%
Rel. std. deviation	15.6%	14.7%

^aConcentration of Aroclor 1242 = 1.50 ng/ μ L.

^bRepresents average finding by direct injection = 98%.

^cTreated as outlier as analyst was unable to quantitate recovery except as reported.

^dData from analyst No. 4 excluded in statistical calculations.

Table II. Test for Determining Suspended Solids Concentrations in Representative Samples

<u>Run</u>	<u>Suspended Solids, mg/L</u>
1	73.2
2	80.8
3	74.8
4	74.8
5	75.6
6	73.6
7	77.6
8	77.6
9	74.4
10	72.4
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Average	75.5 mg/L
Range	72.4-80.8 mg/L
St. deviation	2.53 mg/L
Rel. std. deviation	3.3%

Table III. Determination of PCBs as Aroclor 1242 in Isooctane Solution by Direct Injection (Phase 2)

Analyst	PCB Concentration as Aroclor 1242			
	Known (13.6 $\mu\text{g}/10\text{ mL}$)		Unknown (35.2 $\mu\text{g}/10\text{ mL}$)	
	Concentration Reported, $\mu\text{g}/10\text{ mL}$	Calculated Recovery, %	Concentration Reported, $\mu\text{g}/10\text{ mL}$	Calculated Recovery, %
1	14.2	104	37.0	105
2	13.6	100	34.0	97
3	12.5	92	36.0	102
5	12.5	92	27.3	78
6	12.8	94	31.0	88
7	15.0	110	40.7	116
8	12.5	92	33.4	95
Average	13.3 $\mu\text{g}/10\text{ mL}$	98%	34.2 $\mu\text{g}/10\text{ mL}$	97%
Range	12.5-15 $\mu\text{g}/10\text{ mL}$	92-110%	27.3-40.7 $\mu\text{g}/10\text{ mL}$	78-116%
Std. dev.	1.0 μg	7.2%	4.3 μg	12.2%
Rel. std. dev.		7.5%		12.6%

Table IV. Determination of PCBs as Aroclor 1242 in a Paper Mill Effluent (Phase 2)

Analyst	Replicate, $\mu\text{g/L}$		Average PCB Concentration Reported by Each Analyst, $\mu\text{g/L}$
	No. 1	No. 2	
1	2.70	2.09	2.40
2	3.48	3.88	3.36
3	2.45	2.89	2.67
6	2.26	2.32	2.36 ^a
7	2.33	2.73	2.53 ^a
8	2.98	2.84	2.95 ^a
Average (n=12)	2.74 $\mu\text{g/L}$		2.71 $\mu\text{g/L}$ ^b
Range	2.09-3.88 $\mu\text{g/L}$		2.36-3.36 $\mu\text{g/L}$
St. dev.	0.52 $\mu\text{g/L}$		0.39 $\mu\text{g/L}$
Rel. std. dev.	19.0%		14.4%

^a Includes small additional amount of PCB obtained by rinsing sample bottle with solvent after removal of sample.

^b Statistics developed by considering only the average PCB concentration reported by each analyst.

Table V. Determination of PCBs as Aroclor 1242 in a Paper Mill Effluent to Which a Standard Solution of Aroclor 1242 was Added

Analyst	Replicate, $\mu\text{g/L}$		Average PCB Concentration Reported by Each Analyst, $\mu\text{g/L}$	Calculated Recovery of Std. PCB ^b , %
	No. 1	No. 2		
1	4.30	4.90	4.60	88
2	6.26	5.95	6.10	100
3	6.56	4.50	5.53	103
6	4.32	4.15	4.32 ^a	84 ^a
7	5.80	4.96	5.42 ^a	101 ^a
8	4.64	5.17	4.96 ^a	86 ^a
Average (n=12)	5.13 $\mu\text{g/L}$		5.16 $\mu\text{g/L}$ ^a	93.7% ^c
Range	4.15-6.56 $\mu\text{g/L}$		4.32-6.10 $\mu\text{g/L}$	84-103%
Std. dev.	0.82 $\mu\text{g/L}$		0.63 $\mu\text{g/L}$	8.53%
Rel. std. dev.	16.0%		12.2%	9.1%

^aIncludes small additional amount of PCB obtained by rinsing sample bottle with solvent after removal of sample.

^bBased on average PCB concentration reported by analysts in Table IV.

^cStatistics developed by considering only the average PCB concentration reported by each analyst.

Table VI. Some Examples of Interlaboratory Variation Based on Collaborative Studies Involving PCBs

Sample Matrix	Rel. Std. Dev., %	No. of Analysts	Reference
Paperboard	15-22	11	(6)
Milk	18-31 ^a	10	(9)
Chicken fat	6-16 ^a	10	(9)
Marine wildlife	21	14	(12)
Shark liver homogenate	27	6	(13)
Marine sediments	22	10	(14)
Fish	27-37	7-13	(15)
Paper mill effluent	15-19	6	This study

^aRSD varied with method used for GC quantitation.