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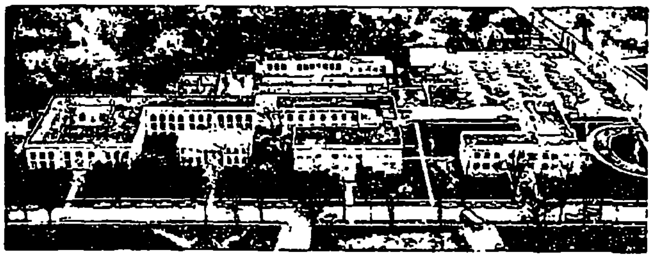

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# DETERMINATION OF POLYCHLORINATED BIPHENYLS IN PAPER MILL EFFLUENTS AND PROCESS STREAMS

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# DETERMINATION OF POLYCHLORINATED BIPHENYLS IN PAPER MILL EFFLUENTS AND PROCESS STREAMS

Polychlorinated biphenyls, Analytical methods, Chemical analysis,
Cellulose fibers, Effluents, Reclaimed fibers, Paper mills,
Gas chromatography, Volatilization, Stability, Storage

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## ABSTRACT

Special techniques have been found necessary for isolating PCB's from cellulose fiber-containing effluents and process streams and for determining PCB's in effluents from paper mills using recycled fiber. Sources of potential PCB loss from aqueous solutions are revealed and means of avoiding these losses are proposed.

Significant amounts of PCB remained on cellulose fibers following separatory funnel extraction of a fiber-water suspension with hexane or methylene chloride-hexane. Reflux of the fibers with alcoholic KOH was necessary to remove the PCB's. PCB losses due to volatilization from aqueous solution occurred during analysis, but this

was minimized by working in a cool environment and covering the sample with a layer of hexane. The presence of cellulose fibers in PCB-containing effluents enhanced the effluents' stability during storage.

Chromium trioxide oxidation was found to be valuable in cleaning up extracts from paper mill effluents. Perchlorination is apt to yield misleading results.

## INTRODUCTION

Polychlorinated biphenyls (PCB's) are commonly determined in industrial effluents by a method involving liquid-liquid extraction, Florisil cleanup, and electron capture gas chromatography, as prescribed by the U.S. Environmental Protection Agency[1]. The utility of this and other methods was evaluated for use on paper mill effluents and process streams within the mill.

## ISOLATION OF PCB's FROM FIBER-WATER SUSPENSIONS

Known amounts of Aroclor 1242, 100 µg/l., were added to 1% suspensions of cellulose fibers in water. Incomplete recoveries were experienced when these suspensions were subjected to triple separatory funnel extractions with petroleum ether, hexane, or 15% methylene chloride in hexane. Following the separatory funnel extraction, the fibers were filtered from the sample and the residual PCB was removed from the fibers by reflux in 2% alcoholic KOH, as is normally used for determining PCB's in paperboard.[2] Removal of all residual PCB by the alcoholic KOH was demonstrated by dissolving the fibers in 72% $H_2SO_4$, diluting with water, and extracting with hexane.

Data in Table 1 resulted from a study designed to determine whether alcoholic KOH reflux of the fibers subsequent to separatory funnel extraction was needed to remove PCB's from fiber-water suspensions with low fiber contents. The results indicate that fibers, even at low concentrations in the sample, retained some PCB's, and that alcoholic KOH reflux was needed for complete PCB removal. However, in analysis of effluents containing less than 0.01% suspended hardwood fibers, the amount of PCB retained by the fibers was small compared with other reported sources of error in PCB determinations (e.g., 20% relative standard deviation for chromatogram quantitation[3]). Somewhat smaller amounts of Aroclor 1242 were retained by softwood fibers.

TABLE 1

Recovery of Aroclor 1242 from Hardwood Fiber Suspensions

| Fiber Content, % | Recovery by Extraction, % | Recovery from Fibers, % | Total Recovery, % |
|---|---|---|---|
| 0.005 | 97.0 | 0.9 | 97.9 |
| 0.01 | 96.4 | 2.4 | 98.8 |
| 0.05 | 91.8 | 8.4 | 100.2 |
| 0.10 | 91.8 | 10.8 | 102.6 |
| 0.16 | 84.2 | 9.0 | 93.2 |
| 0.40 | 80.2 | 15.8 | 96.0 |
| 0.60 | 80.0 | 15.5 | 95.5 |
| 0.80 | 80.4 | 15.6 | 96.0 |

Thus, it may be concluded that the EPA liquid-liquid extraction technique should be adequate for most effluents containing low amounts of suspended solids and that it is inadequate for fiber-water suspensions within the mill. Because of their high suspended solids contents, the fiber-water suspensions require a separate alcoholic KOH reflux to remove all of the PCB's from the fibers.

## MINIMIZING PCB LOSSES DUE TO VOLATILIZATION

Low recoveries (60-80%) of known amounts of Aroclor 1242 added to aqueous samples were experienced in the summer. Volatilization of PCB's from aqueous solution, as described by Mackay and Wolkoff[4] and Paris, et al.[5], during analysis of the samples seemed to be a possible explanation for the low values. Trapping of the Aroclor 1242 from the gas phase, as shown by the data in Table 2, demonstrated that volatilization could occur from aqueous solutions and fiber-water suspensions. A stream of nitrogen entered through a stopper in the top of a suction flask, impinged upon (but did not bubble through) the sample, and exited via the side arm of the flask into a trap containing deactivated Florisil.[6]

TABLE 2

Volatilization and Trapping of Aroclor 1242

| Sample | Start, µg | Remaining, µg | Trapped, µg |
|---|---|---|---|
| Aqueous solution | 10 | 4.0 | 3.9 |
| Softwood suspension | 10 | 5.8 | 2.9 |

Conditions: One hundred ml solution or 0.5% fiber-water suspension in 125-ml suction flask. $N_2$ flow: 600 ml/min across surface for 2 hours at 23°C. Trap: 0.3 g deactivated Florisil in 5 mm glass tube.

Losses of Aroclor 1242 from fiber-water suspensions in stirred beakers under simulated summer and winter laboratory conditions are shown in Table 3. A comparison of total recoveries from the open, cool (Condition B) and open, warm (Condition D) samples suggests that Aroclor 1242 was lost by volatilization during 5 minutes stirring under summer conditions but not under winter conditions. It may be speculated that PCB loss from the closed, warm beaker (Condition C) occurred because the aluminum foil cover formed an imperfect seal or that some PCB escaped into the air space between the foil and the solution.

TABLE 3

Effect of Temperature and Exposure on PCB Spike Recovery

| Conditions[1] | Recovery by Extraction, % | Recovery from Fibers, % | Total Recovery, % |
|---|---|---|---|
| Closed, cool (A) | 88.4 | 11.0 | 99.4 |
| Open, cool (B) | 87.0 | 13.4 | 100.4 |
| Closed, warm (C) | 76.9 | 15.2 | 92.1 |
| Open, warm (D) | 73.4 | 12.2 | 85.6 |

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[1] One percent hardwood suspension, 57.1 μg/l. Aroclor 1242, 5 minutes stirring with magnetic stirrer. Warm = 30-32°C. Cool = 22-23°C.

These studies have provided the basis for the recommendations listed below for minimizing PCB volatilization losses during sample handling and analysis:

1. Minimize air space in sample container.
2. Keep glassware, hexane, distilled water, and sample below 23°C.

3. Pour hexane into separatory funnel before introducing sample.
4. Maintain layer of hexane on top of aqueous phase.
5. Filter fibers as soon as possible.
6. Avoid pulling air through fibers during filtration.
7. Cook fibers in alcoholic KOH promptly.

Steps 1 through 4 should be of value in isolating PCB's from any aqueous sample. The layer of hexane seals the air-water interface from which volatilization can occur. Steps 5 through 7 are critical if the sample contains suspended fibers from which PCB must be extracted separately. Over half of the Aroclor 1242 has been lost from fibers when they were permitted to air dry before being placed in alcoholic KOH.

## SAMPLE STABILITY DURING STORAGE

The need for special extraction procedures to remove PCB's from cellulose fibers suggests that the PCB's are sorbed onto the fibers. Table 2 shows less Aroclor 1242 volatilization from the softwood suspension than from the aqueous solution without fibers. Perhaps sorption of the PCB onto the fibers protected the PCB against volatilization. Sorption would also explain the improved stability of Aroclor 1242 during storage of fiber-water suspensions, compared with aqueous solutions, demonstrated in Figure 1. In that study, the spiking level was 86 µg/l. Aroclor 1242 in river water, and the suspensions contained 1% softwood fibers. Samples were stored in daylight at ambient temperature. Half of the samples contained formaldehyde at 15 ml/l. In a separate investigation, no stability differences were observed between Aroclor 1242 solutions stored for 10 days in daylight vs. in the dark.

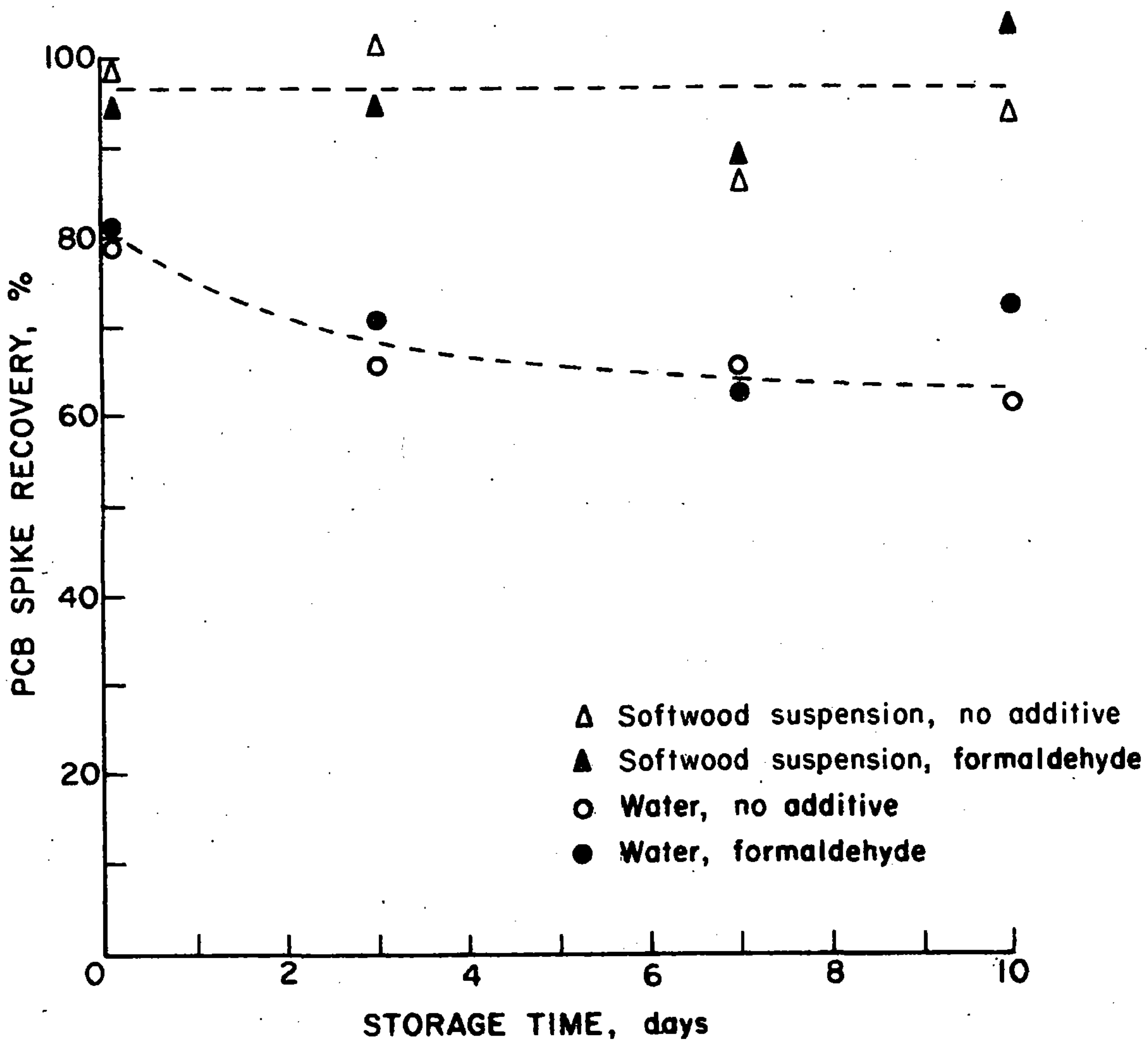

FIG. 1

Stability During Storage of Water and Fiber Suspensions Containing Aroclor 1242

This study did not confirm the finding of Bellar and Lichtenberg that formaldehyde was an effective preservative for PCB's.[7] However, an indirect benefit from adding formaldehyde to industrial effluents and fiber suspensions has been experienced: Formaldehyde inhibits decomposition of non-PCB organics which degrade to liberate sulfur, a common interference on PCB gas chromatograms.

## REMOVAL OF INTERFERING PEAKS FROM CHROMATOGRAMS

### Perchlorination

Extracts from paper mill effluents should always be cleaned up on a Florisil column prior to gas chromatography. However, it does not remove all interferences. It was hoped, therefore, that the PCB's in paper mill effluents could be perchlorinated to decachlorobiphenyl (DCB), whose long retention time would move it well away from interfering peaks.

The perchlorination procedure used was essentially the method of Huckins, et al.[8], modified in order to promote complete perchlorination with minimized volatilization loss of Aroclor 1242. The principal modification consisted of concentrating the extract containing the suspected PCB at room temperature in a culture tube by directing a stream of nitrogen at the top of the tube.

Perchlorination was attempted on authentic effluents from recycling mills as well as on distilled water containing Aroclor 1242 plus other suspected high-boiling components of recycled carbonless copy paper (alkyl biphenyls and alkyl napthalenes). Reaction mixtures consistently charred, and low DCB yields were obtained on these spiked samples. Aroclor 1242 is thought to occur in paper mill effluents because of the recycling of carbonless copy paper made prior to mid-1971. If pre-1971 carbonless copy paper (with PCB's) is present in a mill's raw material, newer carbonless paper (with alkyl biphenyls, alkyl naphthalenes, or other high-boilers, but not PCB's) is probably also present. Consequently, a mill effluent containing PCB's would quite likely also contain the alkyl biphenyls, alkyl naphthalenes, or other high-boiling compounds. Because these non-PCB components of modern carbonless copy paper reduce the DCB yield, perchlorination of paper mill effluents is apt to give incorrect estimates of the effluents' PCB contents.

Alkyl biphenyls and naphthalenes were also subjected to perchlorination in the absence of PCB. Reaction products were analyzed by FID gas chromatography using temperature programming to improve peak resolution. All samples yielded a peak with the same retention time as DCB. Thus, effluent analysis using perchlorination might incorrectly identify these originally nonchlorinated compounds as PCB's. Consequently, perchlorination is <u>not</u> recommended for determining or confirming PCB's in paper mill effluents.

## Mercury and Chromium Trioxide

Interferences due to sulfur may be removed with mercury[1] or, as an alternative, chromium trioxide oxidation[9] followed by a second Florisil cleanup, as shown in Fig. 2. Recoveries of Aroclor 1242 spikes carried through the chromium trioxide treatment have been

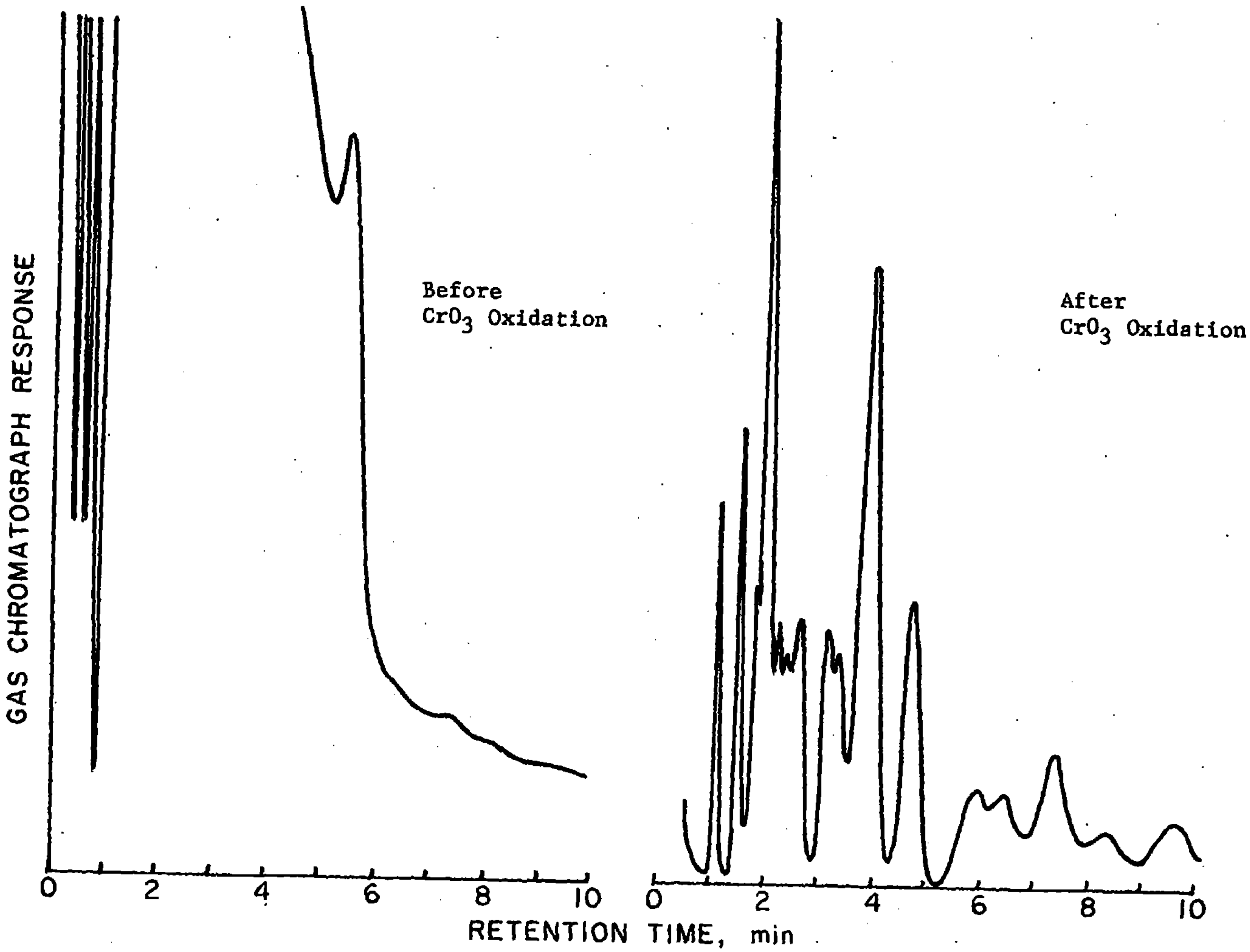

FIG. 2

Pulp Mill Effluent Spiked with Aroclor 1242 approximately 90%. Gentle concentration of the sample extract in the presence of acetic acid is required to prevent loss of the more volatile Aroclor 1242 constituents.

Alkyl naphthalenes, a possible component of newer carbonless copy paper, were removed by the chromium trioxide oxidation, but alkyl biphenyls were not affected. Figure 3 shows the result of using the chromium trioxide oxidation on an extract whose original chromatogram contained large unidentified interferences.

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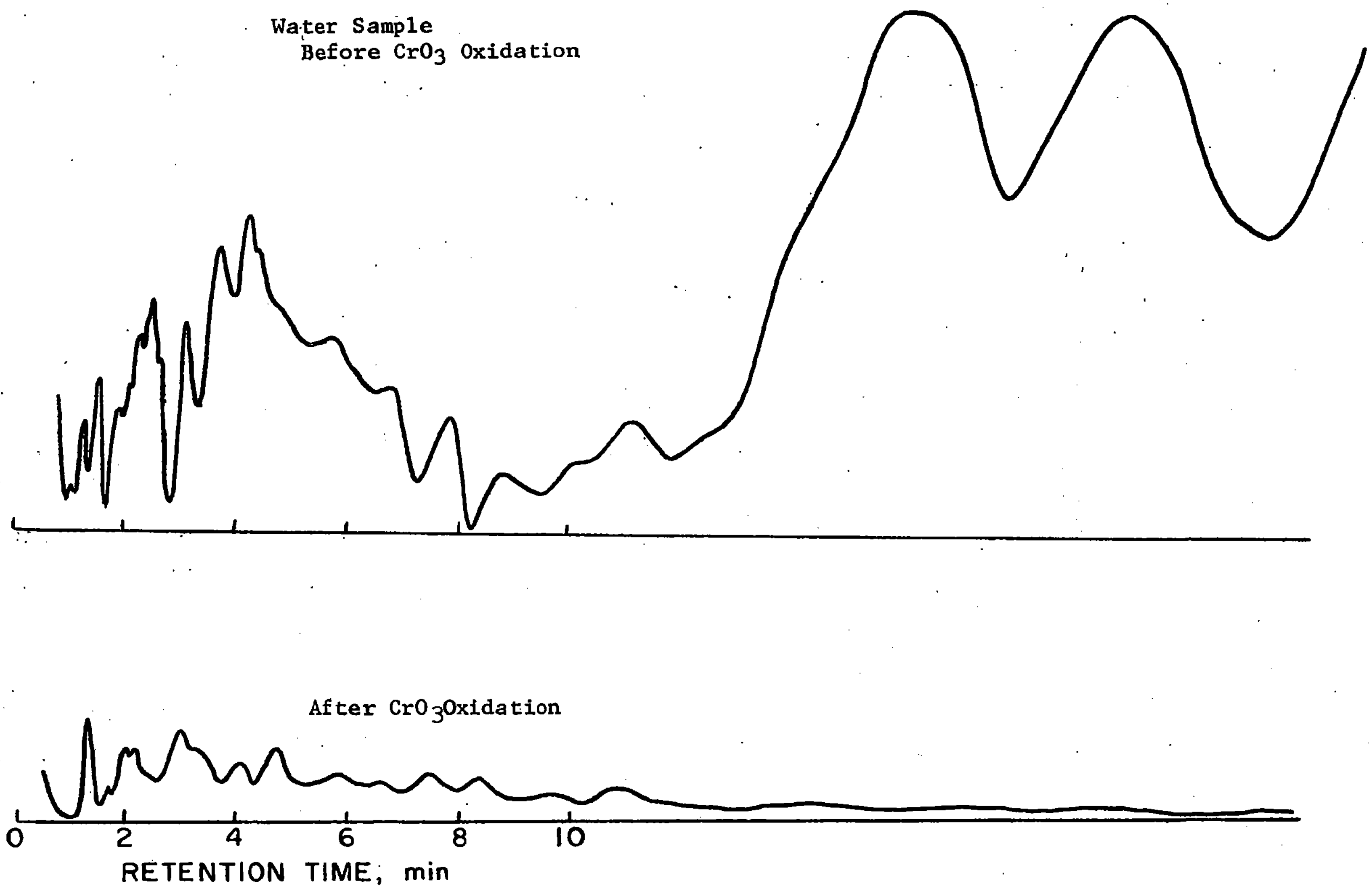
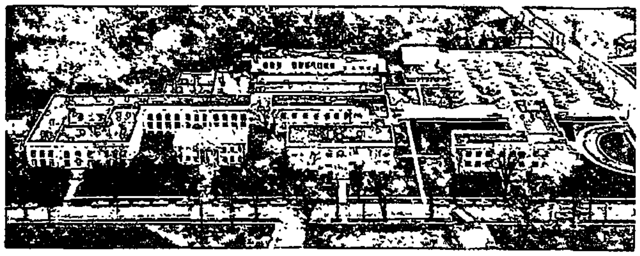


FIG. 3

Effect of Chromium Trioxide Oxidation on Water Sample Containing Interferences



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NUMBER 45

# DETERMINATION OF POLYCHLORINATED BIPHENYLS IN PAPER MILL EFFLUENTS: THE INFLUENCE OF SUSPENDED SOLIDS

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OCTOBER, 1977

# DETERMINATION OF POLYCHLORINATED BIPHENYLS IN PAPER MILL EFFLUENTS: THE INFLUENCE OF SUSPENDED SOLIDS

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Polychlorinated biphenyls (PCB's) are organic contaminants found in some grades of waste paper used as a fiber source by paper mills. As a consequence of the reported toxicity of PCB's and the resultant proposed or promulgated regulations pertaining to these compounds, accurate methods for determining PCB's in mill effluents are needed.

This report describes the need for and development of improved procedures for determining PCB's in effluents containing suspended solids. PCB's have been found to sorb onto cellulose fibers but not onto several other components of a typical papermaking furnish. Determination of PCB's in effluents containing fibers requires alcoholic KOH reflux of the fibers to remove sorbed PCB's. This step is in addition to the solvent extraction procedure now recommended by the Environmental Protection Agency. Failure to remove the PCB from the fibers has resulted in errors as high as 15% in analysis of samples with high fiber contents. Another consequence of PCB sorption onto fibers was the apparent reduction of volatilization loss of the PCB mixture, Aroclor 1242, from fiber-containing samples.

These investigations of polychlorinated biphenyls in pulp and paper mills have been conducted under Institute Project 3295. Initial results from the analytical methodology phase of the project were included in Progress Report One, issued in September, 1976. Distribution and removal studies were described in Progress Report Two in July, 1977. The current paper completes the planned investigation of analytical methods.

This paper is to be presented at the TAPPI Printing and Reprography/Testing Conference, Atlanta, Georgia, November 14-16, 1977.

Regulations designed to minimize the entry of PCB's into the environment via aqueous effluents have been or soon will be promulgated by both federal and state agencies. Consequently, accurate methods for PCB determinations are needed for effluent monitoring and for in-plant use in evaluation of control technology. The method prescribed by the Environmental Protection Agency (EPA) for determining PCB's in industrial effluents[1] involves liquid-liquid extraction, Florisil cleanup, and electron capture gas chromatography, as summarized in Table I. In the current investigation, the effectiveness of this methodology in analysis of paper mill effluents and process streams containing suspended solids has been evaluated. Of principal interest has been the retention of PCB's by suspended cellulose fibers during separatory funnel extraction.

TABLE I

EPA PROCEDURE FOR PCB'S IN INDUSTRIAL EFFLUENTS

1. Extraction: Three times in separatory funnel with 15% methylene chloride in hexane
2. Cleanup of extract: Florisil column adsorption chromatography
3. Identification and quantitation: Gas chromatography with electron capture detector

## ISOLATION OF PCB's FROM SAMPLES CONTAINING SUSPENDED SOLIDS

### TECHNIQUES REQUIRED BY SAMPLES CONTAINING CELLULOSE FIBERS

Known amounts of Aroclor 1242, 100 μg/ℓ., were added to 0.7-1.0% suspensions of several hardwood and softwood pulps in water. Incomplete recoveries were usually experienced when these suspensions were subjected to triple separatory funnel extractions with hexane, as indicated by the data in Table II. Improvements in recovery did not occur when 15% methylene chloride in hexane was used as extracting solvent. Following the separatory funnel extraction, the fibers were filtered from the samples, and the residual PCB was removed from the fibers by reflux in 2% alcoholic KOH, as is normally used for determining PCB's in paperboard[2]. Amounts of PCB recovered in this manner are also shown in Table II. Removal of all residual PCB by the alcoholic KOH was demonstrated by dissolving the fibers in 72% $H_2SO_4$, diluting with water, and extracting with hexane.

TABLE II

RECOVERY OF AROCLOR 1242 FROM SPIKED WOODPULPS
AND FROM SUBMITTED FIBER SUSPENSIONS

| Sample | Consistency, % | Recovery by Separatory Funnel Extraction, % | Recovery by Alcoholic KOH Reflux, % |
|---|---|---|---|
| Hardwood A | 1.0 | 84.6 | 11.6 |
| Hardwood B | 0.7 | 91.0 | 8.6 |
| Hardwood C | 0.7 | 82.2 | 11.2 |
| Softwood A | 0.8 | 101.0 | ~0 |
| Softwood B | 0.7 | 83.0 | 5.8 |
| Softwood C | 0.7 | 84.2 | 7.2 |
| Mill sample | 0.4 | 91.5 | 8.5 |
| Mill sample | 0.06 | 94.4 | 5.6 |
| Mill sample | -- | 85.0 | 15.0 |

Included also in Table II are extraction data obtained on typical fiber suspensions submitted by a paper mill for PCB determination. Results in that table indicate that complete removal of Aroclor 1242 from suspensions of cellulose fibers required a two-step procedure. The steps are (1) triple separatory funnel extraction, and (2) subsequent alcoholic KOH reflux of the isolated fibers.

Data in Tables III and IV resulted from a study designed to determine whether alcoholic KOH reflux of the fibers subsequent to separatory funnel extraction was needed to remove PCB's from fiber-water suspensions with low fiber contents. The results indicate that fibers, even at low concentrations in the sample, retained some PCB's, and that alcoholic KOH reflux was needed for complete PCB removal. However, in analysis of effluents containing less than about 0.05% hardwood or 0.5% softwood fibers, the amount of PCB retained by the fibers was small compared with other reported sources of error in PCB determinations (e.g., 20% relative standard deviation for chromatogram quantitation[3]).

TABLE III

RECOVERY OF AROCLOR 1242 FROM HARDWOOD FIBER SUSPENSIONS

| Fiber Content, % | Recovery by Extraction, % | Recovery from Fibers, % | Total Recovery, % |
|---|---|---|---|
| 0.005 | 97.0 | 0.9 | 97.9 |
| 0.01 | 96.4 | 2.4 | 98.8 |
| 0.05 | 91.8 | 8.4 | 100.2 |
| 0.10 | 91.8 | 10.8 | 102.6 |
| 0.16 | 84.2 | 9.0 | 93.2 |
| 0.40 | 80.2 | 15.8 | 96.0 |
| 0.60 | 80.0 | 15.5 | 95.5 |
| 0.80 | 80.4 | 15.6 | 96.0 |

Thus, it may be concluded that the EPA liquid-liquid extraction technique should be adequate for most effluents containing low amounts of suspended solids and that it is inadequate for process streams containing large amounts of cellulose fibers. Because of their higher fiber contents, the process streams would require the two-step procedure for complete PCB removal.

## TABLE IV

### RECOVERY OF AROCLOR 1242 FROM SOFTWOOD FIBER SUSPENSIONS

| Fiber Content, % | Recovery by Extraction, % | Recovery from Fibers, % | Total Recovery, % |
|---|---|---|---|
| 0.005 | 95.3 | 0.5 | 95.8 |
| 0.01 | 94.2 | 0.5 | 94.7 |
| 0.05 | 93.8 | 1.1 | 94.9 |
| 0.10 | 98.8 | 1.5 | 100.3 |
| 0.16 | 85.4 | 2.6 | 88.0 |
| 0.40 | 84.4 | 2.6 | 87.0 |
| 0.60 | 81.4 | 5.6 | 87.0 |
| 0.80 | 82.2 | 5.9 | 88.1 |

## EFFECTS OF FIBER PROPERTIES ON PCB DISTRIBUTION

The hardwood pulp in Table III apparently retained more Aroclor 1242 during separatory funnel extraction than did the softwood pulp in Table IV. Perhaps that result was influenced by the higher hydrodynamic specific surface area of the hardwood (19,880 vs. 15,100 $cm^2/g$). Those findings prompted consideration of the impact of fiber properties on distribution of PCB's between fibers and water.

For initial studies of PCB distribution, a bleached softwood pulp was beaten and classified. Using the constant rate filtration technique, the hydrodynamic specific surface of the on-10 mesh fibers and the through-65 mesh fines was found to be 9,580 and 120,000 $cm^2/g$, respectively. Identical alcohol-benzene extractives, 0.2%, were measured on each of the two fractions. Suspensions, 0.78% consistency for the long fibers and 0.425% for the fines, were spiked with 100 μg/ℓ. Aroclor 1242 and stirred for three minutes. The samples were filtered, and the PCB was removed from the filtrate by separatory funnel extraction with petroleum ether and from the fibers by alcoholic KOH reflux.

Data on these samples in Table V indicate that the fines sorbed more PCB than did the long fibers. If the fines consistency had been as high as that of the fibers, that trend would quite likely have been even more emphatic. The PCB sorbed by the long fibers and fines was computed to be 1,580 and 13,700 ng/g o.d. fiber, respectively. Thus, the ratio of the amounts of PCB sorbed by the two fractions was roughly proportional to the ratio of their hydrodynamic specific surfaces (about 1:10). Subsequent to this investigation, sorption of Aroclor 1242 by cellulose fibers was found to continue for several hours[4]. If these suspensions had been stirred longer before filtration, amounts of PCB on the fibers and fines would probably have been greater.

### TABLE V

### DISTRIBUTION OF AROCLOR 1242 ON FIBERS AND FINES BEFORE AND AFTER SEPARATORY FUNNEL EXTRACTION

| | On 10 Mesh | Through 65 Mesh |
|---|---|---|
| Filtration before extraction | | |
| Recovery from filtrate, % | 78.2 | 12.3 |
| Recovery from fibers, % | 21.8 | 87.7 |
| Filtration after extraction | | |
| Recovery by extraction, % | 100 | 81.8 |
| Recovery from fibers, % | 0 | 18.2 |

Portions of these same suspensions were filtered after separatory funnel extraction with petroleum ether, yielding results also shown in Table V. Methodology for these analyses was, therefore, identical with that used to obtain data in Tables II-IV. These data show that the separatory funnel extraction removed all of the sorbed PCB from the long fibers and most, but not all, of the PCB from the fines. The PCB not extracted from the fines was in some manner resistant or inaccessible to the extracting solvent. It might be speculated that a portion of the porous structure of the fines was not penetrated by droplets of petroleum ether during separatory funnel extraction of the aqueous slurry. It is because of this resistant or inaccessible PCB that the two-step extraction procedure must be used in order to remove all of the PCB from suspensions containing cellulose fibers and fines.

Additional insight into ease of extraction of PCB's from wood pulps was obtained from studies involving unbleached and bleached hardwood and softwood pulps made in the same mill. Alcohol-benzene extractive contents of the unbleached pulps were both 0.36%; they were 0.45% and 0.23% for the bleached hardwood and softwood, respectively. The pulps had generally similar hydrodynamic specific surface areas, ranging from 10,000 to 13,600 $cm^2/g$. Aqueous suspensions of 0.1% consistency were prepared from each of the pulps as received and following removal of alcohol-benzene extractives. Aroclor 1242 amounting to 10 μg/ℓ. was dispersed in each sample, and the suspensions were allowed to stand for 1/2 hour. PCB's were then isolated from the samples using the two procedures employed previously: (1) Filtration before extraction, with the filtrate extracted in a separatory funnel, and the fibers refluxed in alcoholic KOH. (2) Filtration after the suspension had been extracted in the separatory funnel, with subsequent reflux of the fibers in alcoholic KOH (the two-step extraction procedure).

Data are shown in Tables VI and VII. These data confirm earlier results indicating that separatory funnel extraction of fiber suspensions removed most but not all of the PCB sorbed onto the fibers. With the exception of the unbleached softwood pulp, removal of alcohol-benzene extractives reduced the apparent tendency of Aroclor 1242 to sorb onto fibers (Table VI) and to be retained by fibers during separatory funnel extraction of the suspension (Table VII). Thus, resin content of the pulp usually affected PCB sorption and retention. Because PCB's have low polarity, their sorption was probably facilitated by the low polarity resins.

TABLE VI

DISTRIBUTION OF AROCLOR 1242 BETWEEN WATER AND FIBERS, FILTERED BEFORE ANALYSIS

| | Recovery from Filtrate, % | Recovery from Fibers, % |
|---|---|---|
| As received | | |
| Bleached softwood | 52.0 | 37.5 |
| Bleached hardwood | 37.0 | 57.5 |
| Unbleached softwood | 24.0 | 62.5 |
| Unbleached hardwood | 31.0 | 52.0 |
| Preextracted | | |
| Bleached softwood | 70.4 | 18.8 |
| Bleached hardwood | 71.4 | 12.6 |
| Unbleached softwood | 33.0 | 59.6 |
| Unbleached hardwood | 56.0 | 29.0 |

## TABLE VII

## RECOVERY OF AROCLOR 1242 USING TWO-STEP EXTRACTION PROCEDURE

| | Recovery by Extraction, % | Recovery from Fibers, % |
|---|---|---|
| As received | | |
| Bleached softwood | 90.9 | 9.1 |
| Bleached hardwood | 89.4 | 13.4 |
| Unbleached softwood | 92.7 | 4.6 |
| Unbleached hardwood | 87.3 | 11.0 |
| Preextracted | | |
| Bleached softwood | 89.8 | 2.4 |
| Bleached hardwood | 96.0 | 2.2 |
| Unbleached softwood | 94.4 | 4.4 |
| Unbleached hardwood | 88.6 | 4.8 |

In Table VII it is shown that significant amounts of Aroclor 1242 were retained on the fibers during separatory funnel extraction even after resinous materials were removed from the pulps by preextraction. This suggests that pulp structure or chemical makeup, in addition to resin content, affected PCB inaccessibility or resistance to extraction. The greater amounts of PCB retained by the unbleached, pre-extracted pulps suggest a possible effect of lignin. With the unbleached softwood pulp, features other than resin content appeared to be predominant in PCB distribution and retention; preextraction of this pulp had little effect in either Table VI or VII.

## EFFECT OF SURFACTANTS

A survey of several surfactants revealed that the nonionic surfactant, Triton X-100 (Rohm & Haas Co.) shifted the distribution of Aroclor 1242 so that more PCB was in the aqueous phase and less on the cellulose fibers. Therefore, it was hoped that addition of this surfactant to fiber suspensions would permit all of the PCB to be removed during separatory funnel extraction and would obviate the second step of the two-step extraction.

Suspensions of three bleached pulps at 0.7% consistency were spiked with 80 μg/ℓ. Aroclor 1242 and were extracted using the two-step procedure. Samples of each pulp were prepared with and without 0.02% Triton X-100, based on the total suspension. Data in Table VIII indicate that surfactant addition reduced the amount of PCB retained by the fibers. However, the alcoholic KOH reflux of the fibers was still needed for complete PCB removal.

TABLE VIII

EFFECT OF SURFACTANT IN EXTRACTION OF AROCLOR 1242 FROM FIBER SUSPENSIONS

| | Recovery by Separatory Funnel Extraction, % | Recovery by Alcoholic KOH Reflux, % |
|---|---|---|
| Softwood B | 83.0 | 5.8 |
| Softwood B + surfactant | 89.4 | 3.4 |
| Softwood C | 84.2 | 7.2 |
| Softwood C + surfactant | 87.8 | 3.0 |
| Hardwood C | 82.2 | 11.2 |
| Hardwood C + surfactant | 86.6 | 7.0 |

## OTHER SUSPENDED SOLIDS

The effectiveness of separatory funnel extraction for removal of PCB's from noncellulosic suspended solids in paper mill effluents and process streams was also evaluated. Materials studied and percentages of the 10 μg/ℓ. Aroclor 1242 spike recovered in each step of the two-step extraction procedure are noted in Table IX. Although no cellulose fibers were present in these samples, the amounts of the materials added were what might be found in a furnish containing 5 g/ℓ. cellulose.

TABLE IX

EXTRACTION OF AROCLOR 1242 FROM SUSPENSIONS OF NONCELLULOSIC MATERIALS

| Sample | Concentration, g/ℓ. | Recovery by Separatory Funnel Extraction, % | Recovery by Alcoholic KOH Reflux, % |
|---|---|---|---|
| Starch | 0.15 | 94.6 | ∿0 |
| Kaolin clay | 1.25 | 93.8 | Interference |
| $TiO_2$ | 0.25 | 96.4 | ∿0 |
| Talc | 1.25 | 94.2 | Interference |

Gas chromatograms of materials isolated from the solids by alcoholic KOH reflux did not indicate PCB's, although the non-PCB interferences from the clay and talc might have obscured small amounts of Aroclor 1242. Recoveries of less than 100% by separatory funnel extraction probably reflect manipulative and volatilization losses, to be discussed below. The apparent low retention of PCB's by the pigments is consistent with the comparatively low affinity of PCB's for kaolin clay and other inorganics[5]. These data, of course, do not preclude a small amount of irreversible sorption of the PCB onto the solids. They do indicate, however, that the cellulose fibers, rather than the noncellulosic materials, are the components of paper mill effluents and process streams which require the two-step extraction.

## EFFECT OF CELLULOSE FIBERS ON SAMPLE STABILITY DURING STORAGE AND ANALYSIS

### SAMPLE STABILITY DURING STORAGE

Aqueous solutions and 1% softwood suspensions in river water were spiked with 86 μg/ℓ. Aroclor 1242. Samples were stored in daylight at ambient temperature. Half of the samples contained formaldehyde at 15 ml/ℓ. In a separate investigation, no stability differences had been observed between Aroclor 1242 solutions stored for 10 days in daylight _vs_. in the dark.

Results in Fig. 1 indicate that Aroclor 1242 was more stable during storage in fiber-water suspensions than in aqueous solution. The need for special extraction procedures to remove PCB's from cellulose fibers suggests that the PCB's were sorbed onto the fibers. This quite likely contributed to the suspensions' stability during storage.

This study did not confirm the finding of Bellar and Lichtenberg that formaldehyde was an effective preservative for PCB's[6].

### MINIMIZING PCB LOSSES DURING ANALYSIS

Low recoveries (60-80%) of known amounts of Aroclor 1242 added to aqueous samples were experienced in the summer. Volatilization of PCB's from aqueous solution, as described by Mackay and Wolkoff[7] and Paris, _et al_.[8], during analysis of the samples seemed to be a possible explanation for the low values. The system shown in Fig. 2 was designed to test that possibility. A stream of nitrogen entered through a stopper in the top of a suction flask, impinged upon (but did not bubble through) the sample, and exited via the side arm of the flask into a trap containing deactivated Florisil[9]. Trapping of the Aroclor 1242 from the gas phase, as shown by the data in Table X, demonstrated that volatilization could occur from fiber-water suspensions as well as from aqueous solutions.

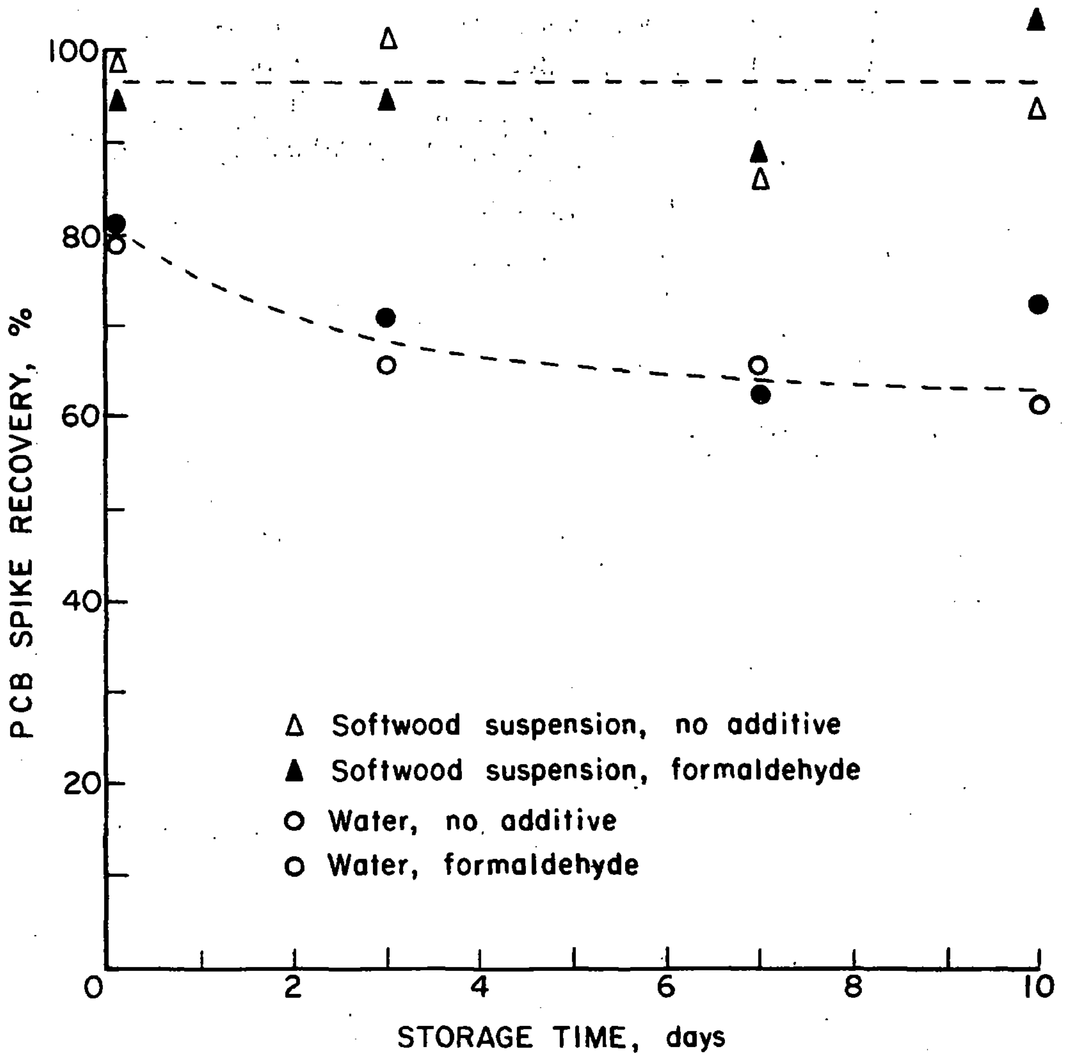

Figure 1. Stability During Storage of Water and Fiber Suspensions Containing Aroclor 1242

A study was conducted to gain a better understanding of the apparent volatilization losses and to provide a basis for minimizing their impact on the analysis. Losses of Aroclor 1242 from fiber-water suspensions in stirred beakers under simulated summer and winter laboratory conditions are shown in

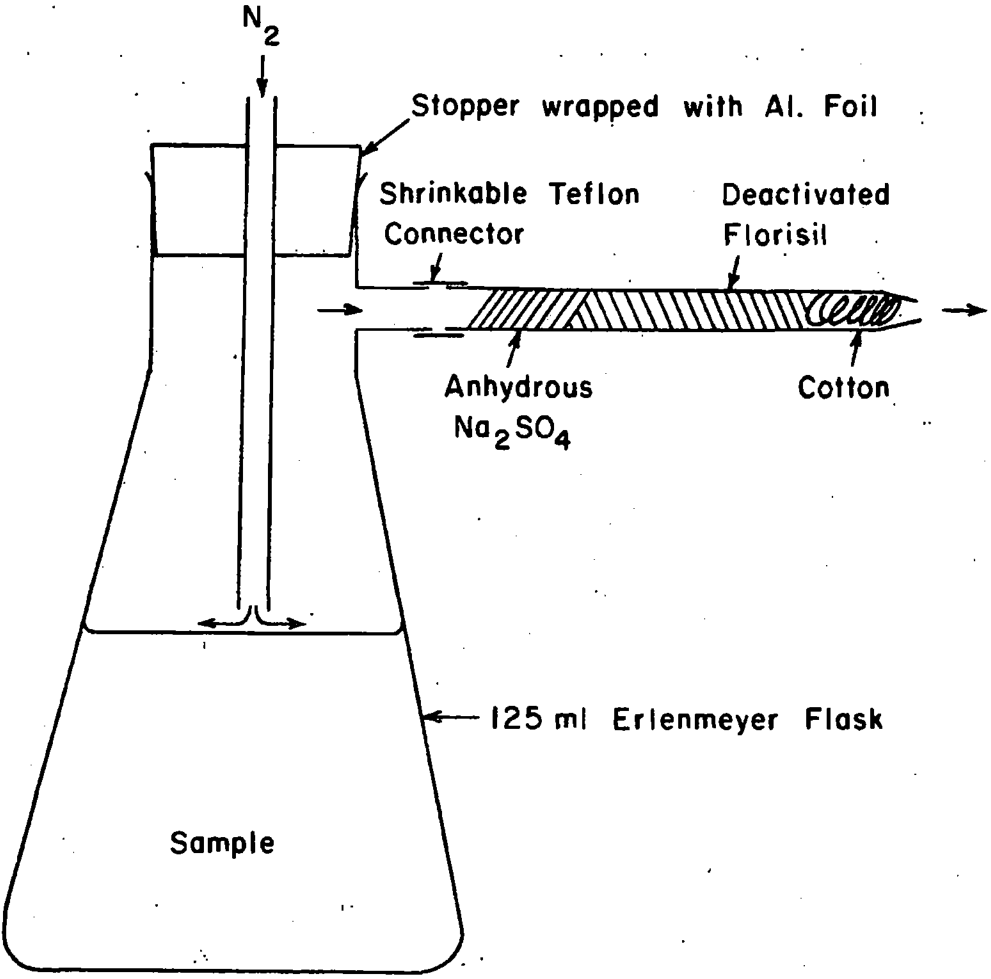

Figure 2. System for Testing Volatilization and Trapping of Aroclor 1242 from Aqueous Samples

TABLE X

VOLATILIZATION AND TRAPPING OF AROCLOR 1242

| Sample | Start, µg | Remaining, µg | Trapped, µg |
|---|---|---|---|
| Aqueous solution | 10 | 4.0 | 3.9 |
| Softwood suspension | 10 | 5.8 | 2.9 |

---

Conditions: One hundred ml solution or 0.5% fiber-water suspension in 125-ml suction flask. $N_2$ flow: 600 ml/min across surface for 2 hr at 23°C. Trap: 0.3 g deactivated Florisil in 5 mm glass tube.

Table XI. A comparison of total recoveries from the open, cool (Condition B) and open, warm (Condition D) samples suggests that Aroclor 1242 was lost by volatilization during 5 minutes stirring under summer conditions but not under winter conditions. It may be speculated that PCB loss from the closed, warm beaker (Condition C) occurred because the aluminum foil cover formed an imperfect seal or that some PCB escaped into the air space between the foil and the solution.

### TABLE XI

### EFFECT OF TEMPERATURE AND EXPOSURE ON PCB SPIKE RECOVERY

| Conditions[a] | Recovery by Extraction, % | Recovery from Fibers, % | Total Recovery, % |
|---|---|---|---|
| Closed, cool (A) | 88.4 | 11.0 | 99.4 |
| Open, cool (B) | 87.0 | 13.4 | 100.4 |
| Closed, warm (C) | 76.9 | 15.2 | 92.1 |
| Open, warm (D) | 73.4 | 12.2 | 85.6 |

---

[a] One percent hardwood suspension, 57.1 μg/ℓ. Aroclor 1242, 5 minutes stirring with magnetic stirrer. Warm = 30-32°C. Cool = 22-23°C.

Results of this investigation have indicated that the low Aroclor 1242 spike recoveries were caused by volatilization losses occurring in a warm laboratory. Subsequent routine conduct of PCB determinations in a cool environment has confirmed the importance of temperature in obtaining near-quantitative recoveries. Volatilization losses are also reduced by keeping aqueous samples covered with a layer of hexane whenever they are open to the air during analysis. The hexane seals the air-water interface from which volatilization can occur.

PCB losses can also occur during the second step of the two-step extraction. Over half of the Aroclor 1242 has been lost from fibers when they were permitted to air dry before being placed in the alcoholic KOH. This problem is avoided by placing the wet fibers in the alcoholic KOH immediately following filtration.

## RECOMMENDED ANALYTICAL PROCEDURES

Procedures recommended for isolating PCB's from paper mill effluents and process streams containing suspended solids consist essentially of the EPA-prescribed liquid-liquid extraction technique[1] followed by alcoholic KOH reflux of the suspended solids. The alcoholic KOH treatment has been recommended by the Food and Drug Administration for determining PCB's in paperboard[2]. In this report these combined methods have been termed the "two-step extraction procedure." Omission of the second step of the procedure may be considered, depending upon the amount and type of suspended solids in the sample and the degree of accuracy required in the analysis. It is recommended that the analyst evaluate the need for the second extraction step on the types of samples which he routinely analyzes. Other features of the procedure summarized in Table XII are points of technique which should minimize volatilization or other losses of Aroclor 1242.

### TABLE XII

### STEPS IN RECOMMENDED ANALYTICAL PROCEDURE

1. Minimize air space in sample container.
2. Keep glassware, extracting solvent, and sample below 23°C.
3. Pour extracting solvent into separatory funnel before introducing sample. Maintain layer of solvent on top of aqueous phase.
4. Perform triple extraction with hexane, petroleum ether, or 15% $CH_2Cl_2$ in hexane as prescribed in EPA method.
5. Break emulsions by centrifugation or anhydrous $Na_2SO_4$. Retain any unbroken emulsion for subsequent reextraction.

## TABLE XII (Continued)

### STEPS IN RECOMMENDED ANALYTICAL PROCEDURE

6. Filter fibers promptly following separatory funnel extraction. Avoid pulling air through fibers during filtration.
7. Cook fibers in alcoholic KOH promptly.
8. Clean up extracts on Florisil. Analyze by electron capture gas chromatography.

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