

Note

Determination of polychlorinated biphenyls in copper phthalocyanine pigments*

R. C. BUCHTA**, H. F. WYLES*, C. J. HENSLER, F. J. VAN LENTEN, R. B. WESTERBERG***
and L. A. WILLIAMS

Chemicals and Pigments Department, Jackson Laboratory, E. I. du Pont de Nemours & Company, Wilmington, DE (U.S.A.)

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Polychlorinated biphenyls (PCBs) have been determined in blue and green (chlorinated) copper phthalocyanine (CPC) pigments using a direct hexane extraction of solid pigment followed by gas chromatography-electron-capture detection (GC-ECD) and GC-mass spectrometry (GC-MS)¹. This procedure¹ assumes that all the PCBs in the solid pigments are extracted by hexane. To minimize the potential problem of incomplete extraction, we dissolved the pigment in concentrated sulfuric acid and then extracted with hexane. The sulfuric acid-hexane extraction method was compared to the direct hexane extraction method and found to provide higher recoveries of PCBs from some blue and green CPC pigments.

Hexane extracts were first analyzed by GC-ECD which has been used extensively in PCB analyses². GC-MS normally was used when the total PCBs by GC-ECD in a sample exceeded a regulatory maximum PCB level such as the 25-ppm maximum (annual average) with a less than 50-ppm maximum specified by the Environmental Protection Agency³. GC-MS analysis involved a limited mass scan multiple ion detection approach which was a modification of a published procedure^{4,5}. PCBs were detected in CPC pigments manufactured using trichlorobenzene but not those made with non-chlorinated solvents.

EXPERIMENTAL

Extraction procedures

Unchlorinated blue pigment (3 g, ground) was slowly added to 150 ml of stirred concentrated sulfuric acid (95-98%) in an 8-ounce wide-mouth, screw-capped glass jar. Magnetic stirring was continued for 15 min, and then 20 ml of UV grade *n*-hexane (Burdick & Jackson) was added by pipet. The jar was well-capped and heat-sealed in a polyethylene bag as a safety precaution. The bagged jar was shaken for 15 min using a mechanical shaker (GCA/Precision Scientific, 265 cycles per minute). The contents of the jar were allowed to settle, and about 15 ml of the hexane phase

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** Present address: Petrochemicals Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, DE 19898, U.S.A.

*** Present address: Biology Department, Battelle Northwest, Richland, WA 99352, U.S.A.

was easily recovered with a disposable pipet. Hexane extracts were analyzed by GC-ECD, and the reagents were checked by this procedure for the absence of PCBs. All pigment solubilities herein were determined using ultrafine porosity, glass-fritted filters.

The procedure for extracting green pigments was identical to that for the blue CPCs except that a 0.3-g sample was used due to limited solubility. In addition, some samples required a 15 min mechanical shaking in sulfuric acid before adding hexane to obtain the best recovery of PCBs. The use of 0.1% hydrogen peroxide in sulfuric acid for dissolving green pigments also was evaluated.

The procedure described by Uyeta *et al.*¹ was used with the exception of the Florisil column clean-up treatment. The means for extract concentration was not specified, but in this study a Kuderna-Danish evaporative concentrator was used.

GC-ECD and GC-MS procedures

A Perkin-Elmer 3920 chromatograph equipped with a ⁶³Ni electron-capture detector at 325°C was used with a 6-foot × 2-mm I.D. glass column packed with 3% SP-2250 on 80–100 mesh Supelcoport. The column temperature was programmed at 4°C/min from 150 to 260°C. The injector was at 270°C and 1- μ l samples were injected by a Hewlett-Packard Model 7670A automatic sampler. Argon-methane (95:5) carrier gas was used at 20 ml/min.

Table I shows the PCB standards (Analabs, and Ultra Scientific) used and retention times determined by GC-ECD. Response factors were obtained for each PCB using the external standard calibration technique. Peak areas were determined for all sample components eluting between the retention times of monochloro- and decachlorobiphenyl. The response factor for a particular PCB standard was assigned to any compound eluting within ± 0.25 min of it. Compounds eluting outside this designated "window" were assigned the factor of the PCB immediately preceding it in retention time. For example, based upon the retention times shown in Table I, a peak eluting at 16 min would be assigned the response factor for tetrachlorobiphenyl. All other peaks were assigned similarly and a total PCB concentration was obtained.

A capillary GC column was used in the GC-MS analysis and all conditions have been reported previously⁵.

TABLE I
PCB STANDARDS AND CORRESPONDING RETENTION TIMES

<i>PCB</i>	<i>Retention time (min)</i>
2-Chlorobiphenyl	5.9
3,3'-Dichlorobiphenyl	11.3
2,4,5-Trichlorobiphenyl	12.8
2,2',4,4'-Tetrachlorobiphenyl	15.3
2,3',4,5',6-Pentachlorobiphenyl	17.6
2,2',3,3',6,6'-Hexachlorobiphenyl	21.2
2,2',3,4,5,5',6-Heptachlorobiphenyl	25.7
2,2',3,3',4,4',5,5'-Octachlorobiphenyl	31.2
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	32.8
2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	34.0

RESULTS AND DISCUSSION

Blue CPC pigments were found to be completely (>99%) soluble in concentrated sulfuric acid at the concentration used. This complete solubility eliminated the problem encountered sometimes with direct hexane extraction of pigment crystals which contained inaccessible PCBs possibly due to occlusion or the presence of certain finishing agents. GC-MS detected only pentachloro- and hexachlorobiphenyls in hexane extracts of some blue CPCs (those made using trichlorobenzene solvent) which were dissolved in sulfuric acid. These results agree with those of Uyeta *et al.*¹. The recoveries of PCB standards of this type from sulfuric acid in the presence of the blue CPC pigment were 97–101%. The recovery of other PCB standards from sulfuric acid was also studied to check for PCB stability in sulfuric acid and extraction efficiency. The recoveries of tetrachloro- through decachlorobiphenyl were good (100 ± 5%). These PCBs are stable in sulfuric acid which agrees with the published study in which concentrated sulfuric acid was used to remove interferences from hexane extracts of animal tissues⁶. However, the recovery from sulfuric acid of PCBs with less than four chlorine substituents varied and depended upon the isomer used. For example, the recoveries of 2-chlorobiphenyl, 2,2'-dichlorobiphenyl and 4,4'-dichlorobiphenyl from sulfuric acid were 55, 70 and 99%, respectively. A 104% recovery of 2,2',5-trichlorobiphenyl was obtained compared to 55–75% for 2,4,5-trichlorobiphenyl. Based upon results of multiple extraction experiments, the low recovery in the latter case is apparently due to a problem with stability of the PCB in sulfuric acid and not with extraction efficiency. Blue CPC pigments do not contain these less halogenated biphenyls, but this stability problem is a possible limitation of the use of concentrated sulfuric acid for the determination of these PCBs in other types of samples.

Table II shows PCB results obtained for blue CPCs using the sulfuric acid-hexane and the direct hexane extraction methods¹. Commercial pigment samples 1 and 2 in the table were made using trichlorobenzene solvent and contained pentachloro- and hexachlorobiphenyls by GC-MS. A typical reconstructed ion chromatogram of a blue CPC pigment (sample 1) is shown in Fig. 1. In addition, the retention time ranges over which each PCB congener group was found are indicated. Triplicate injections of a single sample preparation yielded a standard deviation, σ , of 3 ppm

TABLE II

COMPARISON OF GC-ECD AND GC-MS PCB RESULTS FOR BLUE CPC PIGMENTS BY SULFURIC ACID-HEXANE AND DIRECT HEXANE EXTRACTION METHODS

ND = none detected (<0.01 ppm).

Blue CPC	PCBs (ppm, w/w)			
	Sulfuric acid-hexane extraction		Direct hexane extraction	
	GC-ECD	GC-MS	GC-ECD	GC-MS
1	69	72	40	34
2	121	65	51	31
3	ND	ND	ND	ND

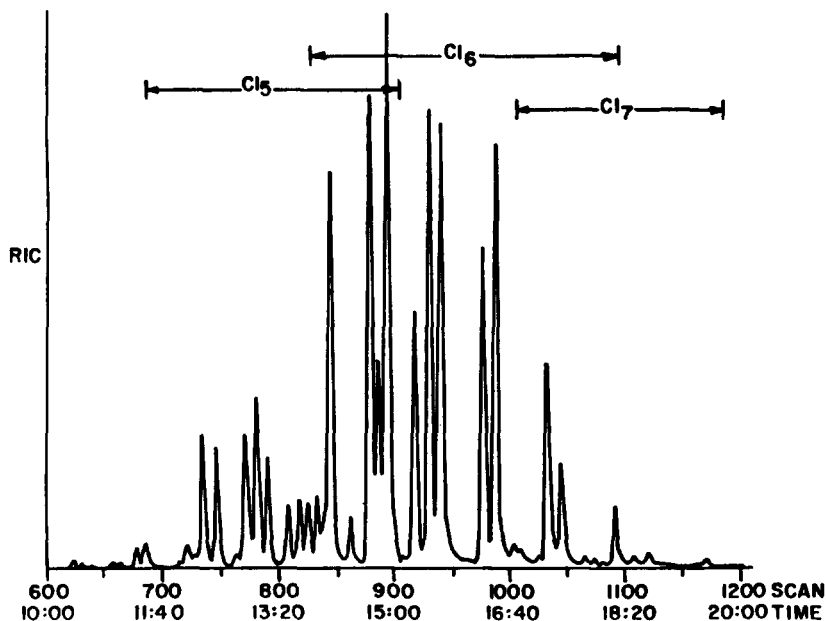


Fig. 1. Reconstructed ion chromatogram of the hexane extract of a blue CPC pigment dissolved in sulfuric acid.

at the 72-ppm mean PCB level. Sample 3 did not contain PCBs and is a Du Pont pigment made using a non-chlorinated solvent. The GC-ECD results represent an average of at least triplicate analyses. Pigment sample 1 was analyzed six times using the sulfuric acid-hexane extraction method to obtain a mean PCB ppm value by GC-ECD of 69 ($\sigma = 4$).

The GC-ECD and GC-MS results obtained for pigment sample 1 using the sulfuric acid-hexane extraction method differ by only 4% which indicates an absence of GC-ECD interferences. This is unlike the case of pigment sample 2 which by GC-MS contained interferences such as bis-2-ethylhexylphthalate. Although the sulfuric acid-hexane and direct hexane extraction methods gave the same results for some blue CPC pigments, Table II shows two exceptions. For samples 1 and 2, the direct hexane extraction provided results which were about one-half those by the sulfuric acid-hexane extraction method. These pigments apparently contain PCBs which are inaccessible in the direct hexane extraction method. Another advantage of the sulfuric acid-hexane extraction procedure is that the hexane extracts of the blue CPC pigments are more concentrated which minimizes the need for concentration.

Chlorinated green CPC pigments were not as soluble in sulfuric acid as the blue CPCs, and a sample size equal to one-tenth that of the blues was used. However, the solubility in sulfuric acid of the green CPCs tested varied from 30 to 70% under the conditions used. GC-MS detected only decachlorobiphenyl in hexane extracts of some green CPCs (those made from PCB contaminated blue CPCs) in sulfuric acid which agrees with the work of Uyeta *et al.*¹. A doubling of the contact time for green CPCs in sulfuric acid increased the recovery of decachlorobiphenyl by as much as 15% for some of the more insoluble green, but there was essentially no change for

others. The sulfuric acid contact time should be determined for the particular green CPC pigments to be analyzed. The recoveries of decachlorobiphenyl, 2,3',4,5',6-pentachlorobiphenyl and 2,2',3,3',6,6'-hexachlorobiphenyl standards from sulfuric acid containing green CPC pigment were 101, 99 and 104%, respectively.

Results indicated that, at least in sulfuric acid, the green CPC pigment may not have to be completely soluble to obtain complete recovery of decachlorobiphenyl. Seven green CPC pigments of varying solubility were analyzed using the sulfuric acid-hexane extraction, and the ppm decachlorobiphenyl results agreed within 5% of those obtained using a hexane extraction from 0.1% hydrogen peroxide in sulfuric acid. This medium dissolved or decomposed at least 80-90% of each pigment. The sulfuric acid-hexane extraction method provided greater recovery of decachlorobiphenyl from some green CPCs than the direct hexane extraction method. The use of sulfuric acid with the green CPCs may minimize problems associated with finishing agents which might inhibit the contact of hexane with decachlorobiphenyl in the pigment.

The hydrogen peroxide-sulfuric acid-hexane extraction method was evaluated for use with greens because CPC pigments in sulfuric acid are easily oxidized by various oxidizing agents⁷. However, the hydrogen peroxide-sulfuric acid-hexane extraction method cannot be recommended for two reasons. First, although decachlorobiphenyl was completely stable in the hydrogen peroxide-sulfuric acid mixture, the recoveries of other PCBs such as pentachloro- and hexachlorobiphenyl were less than 50%. These results indicate some potential for complications in the medium. Secondly, the 0.1% hydrogen peroxide in sulfuric acid can be a safety hazard if it is not stored in a vented container, especially when the solution is not freshly prepared. A sealed glass container ruptured apparently from the build up of gases resulting from the decomposition of hydrogen peroxide due to trace reagent impurities.

Table III shows decachlorobiphenyl results obtained for green CPCs using the sulfuric acid-hexane and the direct hexane extraction methods¹. Commercial pigment samples 1A and 2A in the Table III were made from PCB-contaminated blue CPCs and contained only decachlorobiphenyl as detected by GC-MS. Sample 3A was made from a Du Pont blue CPC and did not contain PCBs. The GC-ECD results represent an average of at least triplicate analyses. Pigment sample 1A was analyzed six times

TABLE III

COMPARISON OF GC-ECD AND GC-MS PCB RESULTS FOR GREEN CPC PIGMENTS BY SULFURIC ACID-HEXANE AND DIRECT HEXANE EXTRACTION METHODS

ND = none detected (<0.01 ppm).

<i>Green CPC</i>	<i>Decachlorobiphenyl (ppm, w/w)</i>			
	<i>Sulfuric acid-hexane extraction</i>		<i>Direct hexane extraction</i>	
	<i>GC-ECD</i>	<i>GC-MS</i>	<i>GC-ECD</i>	<i>GC-MS</i>
1A	65	58	31	29
2A	77	73	79	84
3A	ND	ND	ND	ND

using the sulfuric acid-hexane extraction method to obtain a mean decachlorobiphenyl ppm value by GC-ECD of 65 ($\sigma = 3$).

In all cases in Table III, there is good agreement between GC-ECD and GC-MS results obtained for any one sample using one extraction method. These results indicate an absence of GC-ECD interferences which is usually the case when determining the later eluting decachlorobiphenyl. The agreement of results by both extraction methods is good for pigment sample 2A. However, for sample 1A, the sulfuric acid-hexane extraction method result was about twice the result obtained with the direct hexane extraction method. This is another example where the sulfuric acid-hexane extraction is superior to the direct hexane extraction method.

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