A FAST SCREENING METHOD FOR THE DETERMINATION OF POLYCHLORINATED BIPHENYLS IN DRY DIARYLIDE PIGMENTS AND IN DRY PHTHALOCYANINE PIGMENTS

Prepared and Developed
by the

ANALYTICAL COMMITTEE OF THE

DRY COLOR MANUFACTURERS ASSOCIATION

This method is divided into five (5) parts:

A. SCOPE AND PRINCIPLE

B. REAGENTS, STANDARDS, SAFETY, APPARATUS

C. SAMPLE EXTRACTION AND PREPARATION

D. SAMPLE ANALYSIS AND QUANTITATION

E. QUALITY ASSURANCE

A.1 SCOPE:

A procedure is described for the determination of polychlorinated biphenyls (PCBs) in dry diarylide yellow pigments and in dry phthalocyanine blue and green pigments, or crude, using gas chromatography with electron capture detector (GC/EC).

There are 209 possible PCBs. Their molecular formula is \(C_{12}H_XCl_Y\), where

\[X = 0 \text{ to } 9 \quad \text{and} \quad Y = 10 - X.\]

In diarylide yellow pigments only 3,3'-dichlorobiphenyl is determined since this is the only PCB found in these pigments.

In phthalocyanine green pigments and crude, only decachlorobiphenyl is determined since this is the only PCB found in these pigments.

In phthalocyanine blue pigments and crude, only pentachloro- and hexachlorobiphenyls are determined since these are the only PCBs found in these pigments.

Quantitation is effected by the external standard method. In the case of phthalocyanine blue pigments and crude, the isomeric structures of pentachlorobiphenylns and hexachlorobiphenyls found are unknown. The quantitation of these PCBs is based on the response factor of a single pentachlorobiphenyl standard and a single hexachlorobiphenyl standard which were chosen based on their availability at the time this study was undertaken.

Since GC/EC is not an absolute identification technique, this method can only be used to screen samples. It is recommended that samples having PCB levels above the allowed limits, as determined by this method, be reanalyzed by capillary GC/MS, in order to verify the presence and the amounts of PCB congeners in the pigment.
A.2 PRINCIPLE:

Diarylide yellow pigments are dispersed with hexane in a culture tube. Concentrated sulfuric acid is added and the mixture is shaken until the pigment is dissolved. The 3,3'-dichlorobiphenyl is extracted quantitatively by shaking with hexane. The hexane layer is removed after centrifugation and analyzed by GC/EC.

Phthalocyanine blue and green pigments and crude are dissolved in concentrated sulfuric acid in a culture tube. The PCBs are extracted quantitatively by shaking with hexane. The hexane layer is removed after centrifugation and analyzed by GC/EC.

Quantitation is by the external standard method using $^{63}$Ni electron capture detector.

B. REAGENTS, STANDARD, SAFETY, APPARATUS

B.1 Reagents and Standards

B.1.1 Concentrated sulfuric acid (98%).

B.1.2 Hexane, Burdick and Jackson, distilled in glass grade or equivalent.

B.1.3 Anhydrous sodium sulfate, granular, (Mallinckrodt, Cat. #8024, or equivalent.)

B.1.4 Standard solution of DCMA - PCB mixture in hexane

This DCMA-PCB standard mixture is available from:

Foxboro/Analabs, North Haven, Conn. (203-288-8463)
Supelco Inc., Bellefonte, Pa. (814-259-2784)
Ultra Scientific, Hope, R.I. 02831 (401-828-9400)

Individual PCBs can also be purchased from the same companies.

The DCMA-PCB mixture contains the following PCB congeners at the given concentrations in hexane:

<table>
<thead>
<tr>
<th>PCB</th>
<th>Concentration ug/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-chlorobiphenyl</td>
<td>100</td>
</tr>
<tr>
<td>3,3'-Dichlorobiphenyl</td>
<td>100</td>
</tr>
<tr>
<td>2,4,5-Trichlorobiphenyl</td>
<td>10</td>
</tr>
<tr>
<td>2,2',4,4'-Tetrachlorobiphenyl</td>
<td>10</td>
</tr>
<tr>
<td>2,3',4,5',6-Pentachlorobiphenyl</td>
<td>10</td>
</tr>
<tr>
<td>2,2',3,3',6,6'-Hexachlorobiphenyl</td>
<td>10</td>
</tr>
<tr>
<td>2,2',3,4,5,5',6-Heptachlorobiphenyl</td>
<td>5</td>
</tr>
<tr>
<td>2,2',3,3',4,4',5,5',6-Octachlorobiphenyl</td>
<td>5</td>
</tr>
<tr>
<td>2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl</td>
<td>5</td>
</tr>
<tr>
<td>2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl</td>
<td>5</td>
</tr>
</tbody>
</table>

B.2 Safety

B.2.1 Sulfuric acid causes burns, avoid skin contact.

B.2.2 PCBs are suspected animal carcinogens. Avoid skin contact with these compounds and their solutions. Perform evaporations and other manipulations in a hood.

B.2.3 Hexane is extremely flammable. Use in a hood and away from ignition sources.
B. REAGENTS, STANDARD, SAFETY, APPARATUS (Continued)

B.3 Apparatus

B.3.1 Gas Chromatograph equipped with a $^{63}\text{Ni}$ detector.
B.3.2 1.5% SP 2250 Glass 6 ft x 1/4" OD x 2 mm ID column or fused silica capillary SP 2100, 15m x 0.2mm i.d., 0.25μm df.
B.3.3 Wrist action shaker.
B.3.4 Centrifuge, capable of working at 2,500 RPM.
B.3.5 Glass boiling beads - 4.0mm diameter.
B.3.6 Culture tubes - 150 x 16mm, 20 ml.
B.3.7 Pasteur capillary pipets.
B.3.8 Assorted laboratory glassware.

C. SAMPLE EXTRACTION AND PREPARATION

All glassware should be precleaned with sulfuric acid and should be free of abrasions. Heating glassware to 400°C eliminates interfering contaminants.

C.1 Extraction and Preparation of Diarylide Yellow Pigments

C.1.1 Weigh approximately 0.5g (to the nearest milligram) of sample and transfer to a 20ml culture tube.
C.1.2 Add about 5 boiling beads and 8 ml of hexane.
C.1.3 Secure tube to the wrist action shaker, place in a horizontal position and shake for 5 minutes at a rate of about 150 jolts per minute.
C.1.4 Remove tube from shaker and immediately add 8ml of concentrated sulfuric acid. Immediate addition of the acid is necessary to prevent the pigment from settling which makes its dissolution more difficult.
C.1.5 Replace tube on the shaker. Shake for 5 minutes at about 150 jolts per minute. Remove the shaker. With the tip of a narrow stirring rod, remove a small portion of the sample and examine under the microscope to ensure complete dissolution. If pigment particles are still visible, shake for an additional 3 minutes and recheck for total dissolution. Repeat shaking until all pigment particles are in solution.
C.1.6 Centrifuge at about 2500 RPM for 5 minutes. If separation does not occur, shake gently by hand for about 10 seconds and recentrifuge.
C.1.7 Using a Pasteur pipet transfer the hexane layer into a small beaker containing at least 2g of anhydrous sodium sulfate. (Alternatively the sample may be dried by passing it through a small column, of anhydrous sodium sulfate.) Repeat the hexane extractions two additional times using 5ml each time. Combine extracts, mix well and dilute to 25ml in a volumetric flask.

C.2 Extraction and Preparation of Phthalocyanine Pigments and Crudes

C.2.1 Weigh approximately 0.5g (to the nearest milligram) of sample and transfer into a 20 ml culture tube.
C. SAMPLE EXTRACTION AND PREPARATION

C.2 Extraction and Preparation of Phthalocyanine Pigments and Crudes (Continued)

C.2.2 Add about 5 boiling beads and 10ml of concentrated sulfuric acid to the culture tube. Secure tube to the wrist action shaker, place in a horizontal position and shake for 15 minutes at a rate of about 150 jolts per minute.

C.2.3 Remove from the shaker. With the tip of a narrow stirring rod, remove a small portion of the sample and examine under the microscope to ensure complete dissolution. If pigment particles are still visible, shake for an additional three minutes and recheck for total dissolution. Repeat shaking until all pigment particles are in solution.

C.2.4 Remove tube from shaker and add 6ml of hexane. Replace tube on the shaker and shake for 5 minutes at about 150 jolts per minute. Remove from shaker.

C.2.5 Centrifuge at about 2500 RPM for 5 minutes. If separation does not occur, shake gently by hand for about 10 seconds and recentrifuge.

C.2.6 Using a Pasteur pipet, transfer the hexane layer into a 50 ml beaker containing at least 2g of anhydrous sodium sulfate. (Alternatively, the sample may be dried by passing it through a small column of anhydrous sodium sulfate.) Repeat the hexane extraction two additional times using 5ml each time. Combine extracts, mix well and dilute to 25 ml in a volumetric flask.

D. SAMPLE ANALYSIS AND QUANTITATION

D.1 Instrumentation

Tracor Model 560 gas chromatograph, or equivalent, equipped with $^{63}$Ni electron capture detector. Other detectors which give similar results can also be used. FID has given acceptable results with extracts of Diarylide Yellow pigments when the final volume of the sample is concentrated tenfold.

D.2 G.C. Conditions

D.2.1 Conditions for packed column G.C.

Column: Supelco, 6 ft x 2mm ID 1/4" OD glass column packed with 1.5% SP 2250 on 100/120-mesh Supelcoport.

Conditions:

<table>
<thead>
<tr>
<th>Injection Port Temperature</th>
<th>280°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interface Temperature</td>
<td>270°C</td>
</tr>
<tr>
<td>ECD Detector Temperature</td>
<td>350°C</td>
</tr>
<tr>
<td>Carrier Gas: argon:methane</td>
<td>95:5</td>
</tr>
<tr>
<td>Carrier Flow:</td>
<td>20ml/min.</td>
</tr>
<tr>
<td>Temperature Program:</td>
<td>4 min. hold at 175°C followed by a 4°C/min. program to 270°C. Hold for 4 min.</td>
</tr>
<tr>
<td>Injection Volume</td>
<td>3 microliters</td>
</tr>
<tr>
<td>Run Time</td>
<td>Approx. 40 min.</td>
</tr>
</tbody>
</table>
D.2 G.C. Conditions

D.2.1 Conditions (Continued)

NOTE: It was found that small differences in column loading have a major effect on column performance. Lower loading causes adsorption and tailing and higher loading increases the retention time. The column performance should be similar to Figure 1 and the resolution should be as follows: for the di- and tri-chlorobiphenyl 2.9-3.0 and for the octa- and nona-chlorobiphenyl 2.5-2.7.

D.2.2 Conditions for Capillary Column G.C.

Column: Supelco, SP 2100 fused silica capillary 15m x 0.20mm i.d., 0.25um df.

Injection Port Temperature: 270°C
E.C. Detector Temperature: 350°C
Carrier Gas: Helium
Column Head Pressure: 50 psi
Make Up Gas: argon:methane, 95:5
Make Up Gas Flow Rate: 40ml/min.
Injection Mode: splitless
Injection Volume: 2.5 ul

Temperature Program:

Initial Temperature: 140°C
Initial Hold: 2 minutes
Heating Rate: 8°C/min.
Final Temperature: 270°C
Final Hold: 2 minutes

NOTE: For 3,3'-dichlorobiphenyl use a 5 min. initial hold and heat to 270°C at 20°C/min.

D.3 Calibration of the Instruments

The DCMA-PCB mixture listed in section B.1.4 should be purchased from the vendors indicated in the same section. After opening, this standard should be kept sealed in the freezer to prevent evaporation.

D.3.1 Prepare a working standard solution by diluting 1 ml of the purchased DCMA-PCB mixture to 50ml in a volumetric flask. This standard is stable for at least six months if kept refrigerated.

D.3.2 Optimize the GC and integrator conditions by injecting approximately 3 microliters of the working standard solution.

D.3.3 Dilute the concentrated DCMA standard solution with hexane by the following factors: 1 to 25 ml, 1 to 50 ml, 1 to 100 ml, and 1 to 500 ml. Determine the linearity of the electron capture detector by injecting approximately 3 microliters of each of the solutions and plotting the response versus the amount (nanograms) injected. A straight line denotes linearity.
D.3 Calibration of the Instruments (Continued)

D.3.4 Typical retention times of PCB congeners in the DCMA standard, using the packed column, are as follows:

<table>
<thead>
<tr>
<th>Time (Min.)</th>
<th>PCB</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>monochlorobiphenyl</td>
</tr>
<tr>
<td>6.0</td>
<td>dichlorobiphenyl</td>
</tr>
<tr>
<td>7.5</td>
<td>trichlorobiphenyl</td>
</tr>
<tr>
<td>10.0</td>
<td>tetrachlorobiphenyl</td>
</tr>
<tr>
<td>12.5</td>
<td>pentachlorobiphenyl</td>
</tr>
<tr>
<td>16.0</td>
<td>hexachlorobiphenyl</td>
</tr>
<tr>
<td>20.5</td>
<td>heptachlorobiphenyl</td>
</tr>
<tr>
<td>26.0</td>
<td>octachlorobiphenyl</td>
</tr>
<tr>
<td>27.5</td>
<td>nonachlorobiphenyl</td>
</tr>
<tr>
<td>28.5</td>
<td>decachlorobiphenyl</td>
</tr>
</tbody>
</table>

A typical chromatogram is shown in Figure 1.

D.3.5 Calculate a response factor, \( F \), for each PCB:

\[
F = \frac{\text{Response (area count)}}{\text{Volume Injected (ul)}} \times \left( \frac{\text{Attenuation}}{\text{Conc. (ng/ul)}} \right)
\]

D.4 Selection of PCB Standards

D.4.1 GC/MS analysis has shown that 3,3'-dichlorobiphenyl is the only PCB present in diarylide yellow pigments. Therefore, for these pigments only the peak corresponding to 3,3'-dichlorobiphenyl is used for determining the PCB content.

D.4.2 For phthalocyanine green pigments and crudes, GC/MS analysis has shown only the presence of decachlorobiphenyl. Therefore, only the peak corresponding to decachlorobiphenyl should be used for the determination of the PCB content in these pigments.

D.4.3 In the case of phthalocyanine blue pigments and crudes, GC/MS analysis has shown the presence of several pentachlorobiphenyls and hexachlorobiphenyls. Most pentachlorobiphenyls were found to elute prior to the hexachlorobiphenyls, however, some were found to elute after certain hexachlorobiphenyls. Therefore, retention time alone is not adequate for identifying all the peaks as penta- or hexachlorobiphenyls. It has also been shown that even isomeric PCBs may differ considerably in their response factors (by ECD or MSD).

Since the structure of all the pentachlorobiphenyls and hexachlorobiphenyls found in phthalocyanine blue pigments is not known, the accuracy of the results is curtailed due to the variation in their response factors.

In this method, for the purpose of consistency among laboratories, only one pentachlorobiphenyl and one hexachlorobiphenyl standard is used. The choice of these PCB standards was based on their availability at the time the study was undertaken. All peaks having retention times near the 2,3',4,5',6-pentachlorobiphenyl standard are calculated based on the response factor of this PCB. All peaks having retention times near the 2,2',3,3',6,6'-hexachlorobiphenyl standard are calculated based on the response factor of this PCB. The exact retention time windows are specified in section D.5.4.
D. SAMPLE ANALYSIS AND QUANTITATION

D.4 Selection of PCB Standards

D.4.4 It is recommended that samples found to exceed the allowed limit of PCBs, as determined by this method, be analyzed by capillary GC/MS in order to identify and quantify more accurately the total PCB content. The higher value may be due to interfering compounds with the same retention time as PCBs.

D.5 Sample Analysis and Calculation

D.5.1 Inject approximately 3 microliters of the sample solution obtained in steps C.1.7 or C.2.6. If the response is outside the linear range of the detector, dilute or concentrate the extract to bring the response within the linear range. Concentration of the sample must be done over low heat under a stream of air or nitrogen.

D.5.2 For diarylide yellow pigments record the response (peak area or peak height) of the peak eluting within ± 0.2 minutes of the retention time of the 3,3'-dichlorobiphenyl standard. Obtain the concentration of this PCB (ng/ul) by dividing the sample response by the response factor (F) of the 3,3'-dichlorobiphenyl standard and by the volume of sample injected (microliters) as shown below:

\[
\text{ng/ul} = \frac{\text{area count or peak height}}{(F) \times \text{(microliters injected)}}
\]

Calculate the 3,3'-dichlorobiphenyl content (ppm) by the sample as follows:

\[
\text{ng/ul found} \times \frac{\text{initial volume of sample (ml)}}{\text{sample weight (g)} \times \text{dilution or concentration factor}} = \text{ppm}
\]

D.5.3 For phthalocyanine green pigments and crudes, record the response (peak area or peak height) of the peak eluting within ± 0.2 minutes of the retention time of the decachlorobiphenyl standard. Obtain the concentration (ng/ul) of this PCB by dividing the sample response by the response factor (F) of the decachlorobiphenyl standard and by the volume of sample injected (microliters) as shown below:

\[
\text{ng/ul} = \frac{\text{area count or peak height}}{(F) \times \text{(microliters injected)}}
\]

Calculate the decachlorobiphenyl content (ppm) of the sample as follows:

\[
\frac{(\text{ng/ul found}) \times \left[\frac{\text{initial volume of sample (ml)}}{\text{sample weight (g)}} \times \text{dilution or concentration factor}\right]}{\text{ppm}}
\]
D.5 Sample Analysis and Calculation (Continued)

D.5.4 For phthalocyanine blue pigments and crudes, record the response (peak area or height) of all the peaks eluting from 0.2 minutes prior to the 2,3',4,5',6-pentachlorobiphenyl standard up to 0.3 minutes prior to the 2,2',3,4,5,5',6-heptachlorobiphenyl standard.

The peaks eluting up to 0.3 minutes prior to the 2,2',3,3',6,6'-hexachlorobiphenyl are calculated as 2,3',4,5',6-pentachlorobiphenyl.

The peaks eluting from 0.2 minutes prior to the 2,2',3,3',6,6'-hexachlorobiphenyl standard up to 0.3 minutes prior to the 2,2',3,4,5,5',6-heptachlorobiphenyl standard are calculated as 2,2',3,3',6,6'-hexachlorobiphenyl.

Obtain the concentration (ng/μl) of each PCB by dividing the sample response by the response factor (F) of the corresponding PCB standard and by the volume of sample injected (ml) as shown below:

\[
\text{ng/μl} = \frac{\text{area count or peak height}}{(F) \times (\text{microliters injected})}
\]

Add the concentrations (ng/μl) of all the PCBs found and calculate the total PCB content (ppm) of the sample as follows:

\[
\frac{\text{sum of PCBs found (ng/μl)}}{\text{[initial volume of sample (ml)]}} \times \frac{\text{[sample weight (g)]}}{\text{[dilution or concentration Factor]}}
\]

D.5.5 Example

If PCB Concentration = 0.5 ng/μl
Initial Volume = 25 milliliters
Weight of Sample = 0.5 g

a) Concentration of Sample Volume = 25 ml to 5 ml

Then PCB Content = \(\frac{0.5 \times 25}{5} = 5.0 \text{ ppm}\)

b) Dilution of Sample Volume = 1 ml to 25 ml

Then PCB Content = \(\frac{0.5 \times 25}{1} = 625 \text{ ppm}\)
This program involves the validation of the procedure described above. This includes GC/MS analysis, determination of the efficiency of recovery from spiked samples and the analysis of blind and spiked samples. Repetitive analysis of a retained sample (blind sample) should be one of the tools used to train new analysts and to check the performance of already trained analysts. Spiked samples should also be analyzed periodically. Although spiking cannot be done by adding known amounts of PCBs within the ultimate pigment particle, the experiments are still necessary in order to prove that once the PCBs are released from the pigments by dissolution they are carried through the other steps quantitatively.

E.1 Verification of the Method

Whenever a significant process change has occurred, including a change in a raw material, or the amount of PCBs found exceeds the allowable limit, the type of sample affected should be analyzed by capillary GC/MS to demonstrate that no PCBs, other than the ones previously present, are being generated by the process change and that the distribution is still consistent with previous data.

E.2 Quality Assurance (Blind Sample)

A sample typical of each of the manufactured pigments should be available. The sample must be analyzed by trained analysts, as a blind sample, once every 50 samples or at least once every six months. The sample should also be used to train new analysts until they develop a sufficiently good level of analytical expertise.

E.3 Spiking Experiments

Several spiking experiments with the standard PCB mixture, or with other PCBs, depending on the pigment analyzed, should be done when the methods are first established. After that, these experiments should be repeated whenever significant procedure changes have taken place. In the absence of any significant changes, such experiments are to be done once every 50 samples but not less than once every six months.


DCMA MEMBER COMPANIES THAT PARTICIPATED IN THE STUDY WERE:

Hoechst Celanese Corporation
BASF Corporation
Hilton Davis Chemical Company
Sun Chemical Corporation