

ANALYSIS OF WATER AND SEDIMENT FOR
POLYCHLORINATED BIPHENYLS

SCOPE

This methodology was developed for the determination of the amount and type of polychlorinated biphenyls (PCB) in water and sediment samples. Absolute confirmation of PCB structures is not obtained with this method. Structure proof can be obtained using additional techniques such as mass spectrometry to further identify the GC fractions.

PRINCIPLE

The PCB(s) in water and sediment samples are extracted into an organic solvent. Interfering components are then removed from the extracts by chemical treatment and column adsorption chromatography. The amount and type of PCB present is determined by electron capture gas chromatography (EC/GC).

REAGENTS

Hexane	Nanograde, Mallinckrodt Chemical Works, Catalog No. 4159.
Acetonitrile	Nanograde, Mallinckrodt Chemical Works, Catalog No. 2442.
Sodium Sulfate	Anhydrous, granular: AR grade, Mallinckrodt Chemical Works, Catalog No. 8042. Heat at 400°C for one hour prior to use.
Alumina Adsorption	(for chromatographic analysis) 80/200 mesh, Fisher Scientific Co., Catalog No. A540. Heat at 400°C for a minimum period of 4 hrs. and deactivate with 5% (w/w) distilled water. Alumina column preparation: Fill a chromatographic column with hexane up to the point where the reservoir joins the column and push a glass wool plug to the bottom with a glass rod. In a 50 ml beaker measure 35 ml of deactivated alumina (~30g), and pour this slowly into the column. Tap or vibrate the column to settle the alumina and top the alumina with 2-3 cm of anhydrous sodium sulfate. Wash the column with 50-100 ml of hexane prior to the addition of the sample.
Distilled Water	Extracted with hexane to remove hexane soluble electron capturing impurities.

PLAINTIFF'S
EXHIBIT

697

ADM 005749

SAMPLING

It is to be assumed that a rather wide variety of sampling techniques were employed in collecting the samples submitted for analysis. In general the procedures used were probably selected for ease of adaption to the local situation. For this reason water and sediment samples were usually treated as follows:

Water

Where possible the entire water sample, including the container in which it was collected, was extracted with hexane. With larger samples, where this was not physically possible, the containers were simply agitated and a 250 ml portion used for analysis.

Sediment

Any excess water was decanted and the entire sediment transferred to a glass baking dish to air dry at room temperature. The dried material was transferred from the dish into a mortar and pestle and ground. The ground sediment was sieved, remixed, and a 250g portion taken for analysis.

PROCEDURES

Extraction of Water Samples

1. Extraction of water samples - after agitating, transfer the entire aqueous sample or a 250 ml aliquot into a graduated glass cylinder. Record the volume of the sample and quantitatively transfer it to a separatory funnel with distilled water.
2. Rinse the graduated cylinder with two 50 ml portions of hexane and add each to the separatory funnel.
3. Stopper the separatory funnel and shake vigorously for at least 1 minute. Allow the layers to separate and transfer the lower aqueous phase to a second separatory funnel.
4. Extract the water sample a second time with a 50 ml portion of hexane. After the layers have separated, add the first hexane extract to the second separatory funnel and transfer the aqueous layer to the original separatory funnel.
5. Repeat the extraction with a third 50 ml portion of hexane. Discard the aqueous layer and combine the hexane extracts.
6. Filter the combined extracts through a 4" funnel plugged with glass wool which is covered with sodium sulfate. Collect the filtrate in a Kunderna-Danish evaporative concentrator, add a small boiling chip, put the Snyder column in place, and reduce the hexane volume to less than 5 ml by heating the apparatus in a 80-90°C water bath. (CAUTION: SOLVENT VAPORS MUST BE VENTED TO A HOOD.)

8. Evaporate the extract just to dryness with a gentle stream of dry filtered nitrogen and add 25 ml of 2.5% alcoholic potassium hydroxide.
9. Add a boiling chip, put a water condenser in place, and allow the solution to reflux for 45 minutes.
10. After cooling, transfer the solution to a 250 ml separatory funnel with the aid of 25 ml of distilled water.
11. Rinse the extraction flask with 25 ml of hexane and add it to the separatory funnel.
12. Stopper the separatory funnel and shake vigorously for at least 1 minute. Allow the layers to separate and transfer the lower aqueous phase to a second separatory funnel.
13. Extract the saponification solution with a second 25 ml portion of hexane. After the layers have separated add the first hexane extract to the second separatory funnel and transfer the aqueous alcohol layer to the original separatory funnel.
14. Repeat the extraction with a third 25 ml portion of hexane. Discard the saponification solution and combine the hexane extracts.
15. Carefully add 25 ml of the sulfuric acid solution (9:1 concentrated sulfuric acid/water) to the hexane extracts.
16. Stopper the separatory funnel and shake vigorously for at least one minute. Allow the layers to separate and discard the lower aqueous - acid layer. Repeat this step until the acid layer is colorless.
17. Wash the hexane with 25 ml portion of water. Discard the water wash.
18. Filter the hexane extract through a 4" funnel plugged with glass wool which is covered with a layer of sodium sulfate into a Kunderna-Danish evaporative concentrator.
19. Add a small boiling chip, put the Snyder column in place and reduce the hexane volume to less than 5 ml by heating the apparatus in a 80-90°C water bath.
20. After cooling, remove the 5 ml graduated tube and transfer the hexane extract to an alumina adsorption column washing it in with several 5 ml portions of hexane.
21. Carefully add 100 ml of hexane to the column reservoir and collect the total eluent in either a 250 ml volumetric flask or a Kunderna-Danish evaporative concentrator.

The average recovery and deviation achieved substantiated the applicability of the method for the quantitative recovery and analysis of PCB's from water at the ppb-ppm level.

No PCB recovery experiments from spiked sediment and soil samples have been performed. Instead, several of the residual solids representative of some of the types of sediment or soil analyzed were re-extracted with hexane/acetone (40/60) in a soxhlet extractor to test for the efficiency of the acetonitrile extraction step. The hexane, after isolation by dilution with distilled water was then carried through the purification steps. Recoveries by soxhlet extraction have indicated that the acetonitrile extraction of PCB's was essentially quantitative in the cases checked.

Sample Concentration

Concentration of sample extracts is necessary, prior to clean up by chromatographic or chemical means, to reduce sample size and increase sensitivity. The preferred method of concentrating allows minimum loss through volatilization or chemical decomposition and requires a minimum time. The three methods of solvent volume reduction most commonly used are evaporation by exposure to a stream of air, evaporation employing a Kunderna-Danish evaporative concentrator equipped with a Snyder column, and evaporation under reduced pressure. We have used all three techniques and have not encountered any significant losses from volatilization or chemical alternation. However, the Kunderna-Danish evaporative concentrator and the stream of air were employed because of the ease of use.

Column Adsorption Chromatography and Chemical Clean Up

Silica gel, Florisil and Alumina deactivated with 0, 1.0, 1.5, 2.0 and 5% water were investigated as adsorbants for the elimination of interferences. Alumina (5% water) was found to be more effective and reproducible than either silica gel or Florisil. The activity of alumina varies with age and lot, therefore, 5% water was added to the alumina, after heating for a minimum of 4 hours at 400°C, to insure a reproducible activity.

Saponification and subsequent extraction of the sample with sulfuric acid is an effective way to remove a number of chlorinated hydrocarbon interferences as well as other matrix interferences. PCB's are not affected.

Electron Capture Gas Chromatography

Columns:

Column performance is the key to effective gas chromatographic analysis and as such the choice of column materials is particularly important. Ideally, the support employed should be inert, mechanically strong, and of high surface area. For these reasons, Chromosorb W, HP, AW-DMCS was used in all of our work.

at higher temperatures prevents maintenance problems due to contamination from high boiling components. Glass columns should also be employed.

Detection and Measurement

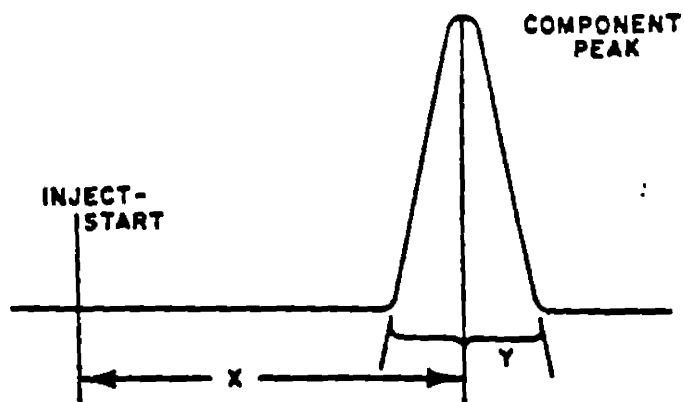
Quantitative determinations employing the electron capture detector are non-stoichiometric measurements made by comparing peak heights or areas for known concentrations with those for unknown compositions. Four variations of the peak height or area quantification procedures have been employed.

- Case I EC gas chromatogram of PCB unknown unchanged with respect to standard PCB with no evidence of interferences.
- Case II EC gas chromatogram of PCB unknown altered with respect to standard PCB with no evidence of interferences.
- Case III EC gas chromatogram of PCB unknown unchanged with respect to standard PCB with evidence of interference.
- Case IV EC gas chromatogram of PCB unknown altered with respect to standard PCB with evidence of interference.

The PCB level in a Case I sample can be determined by comparison of the height of the major peak in the unknown with a calibration curve prepared by plotting the height of the major peak in the electron capture chromatogram of the corresponding standard vs the number of ng of the standard injected. With a Case II sample because of the alteration, the maximum PCB level is estimated by comparison of the total area of the electron capture envelope of the unknown to a calibration curve prepared by plotting the total area of the electron capture envelope of the most similar standard vs the number of ng of the standard injected. Case III and IV samples are initially subjected to the chemical clean up procedure followed by chromatography as outlined on alumina. If the interferences are removed by this treatment the PCB levels are calculated for Case III and IV in the same manner as Case I and II, respectively. If dominant interference(s) is (are) still present, then the height of a different analytical peak, free from obvious interference, is employed to calculate the PCB level in Case III. With Case IV samples, the maximum PCB level is estimate as in Case II after correcting the total area for that of the interfering peak(s).

In all cases, the response of the electron capture must be linear for quantitative analysis.

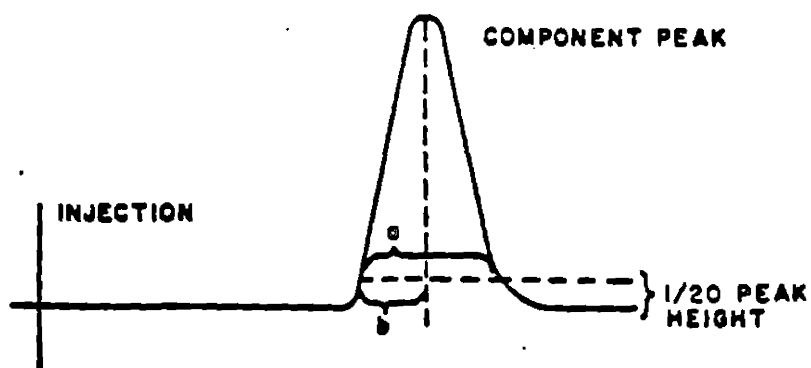
COLUMN PERFORMANCE INDICATORS



Calculating Column Efficiency

1. Theoretical Plates, N

$$N = 16(x/y)^2$$



Calculating the Tailing Factor

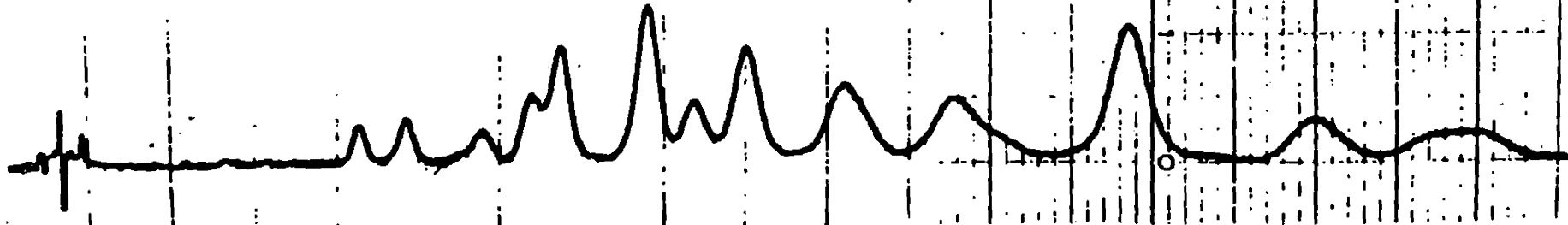
2. Tailing, T

$$T = a/2b$$

500 FIVE MIX B TREATED

See Profile Mr B Treated
(SAP, Saturated, Aluminous)

File Section 1260



100% Chloroform TMS

100% CHLOROFORM TMS

511 5106 m/e 76470

511 5106 m/e 76470

Soil Pesticide Mix 9

HEPTACHLOR

ALDRIN

DDT
DDT

TDE

MIREX

DDT(TDE)

METHOXYCHLOR

FM 402
6' x 6mm glass 4 for
Packed on 8/100 mesh
Chromasorb W, W.P. RW-DVCS
FH 185
Det 160
Det 300 4163 open
Pulse 150
8x10
QV: HE 2.60 m/min
Pulse 400, 2.10 m/min

Sul. Pesticide Mix B

PERTANE

BNC

BNC

ENDOSULFAN (BNC)

BNC

PERTANE

DIELDRIN

PERTANE
ENDRIN

ENDOSULFAN

ADM 005777 038

3rd Above 1259

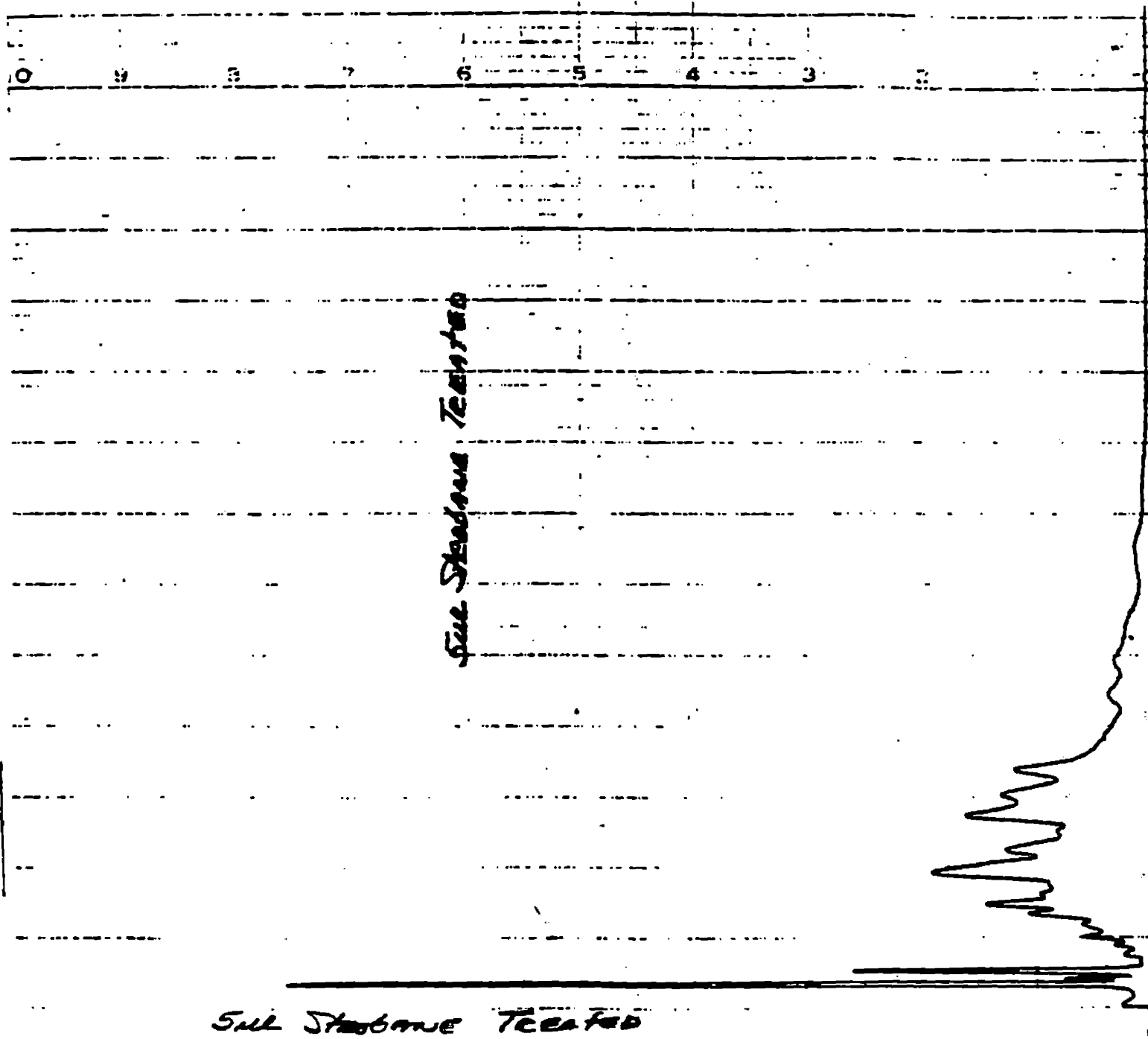


10% CHLOROPANE
Treated

10 ml Ditto

5ml. Tolaphene Treated

5ml. TOLAPHENE TREATED



Sue Stabone Treated

APOLAR 1292

FM 5750. B

6'x6mm square glass column

1% XE-60 on Chromosorb W₃ HP₃

AW-DNICS

FI 200°C

Col 190°C

Det 300°C

N₂ 65 pulse 150

242 HE ~ 60 m/min

Purge Ar/CH₄ ~ 120 m/min

AF 8x10

Scale (1.00 x 10⁻⁹ g/ml)

DDE (6.8')

