Clean Up Procedures for PCB Analysis on River Water Extracts

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PCB analyses are carried out mainly on biological samples and to some extent on sediment samples. The clean up procedures are worked out to meet requirements from these types of samples. Water extracts have been found to require a somewhat different procedure. There are two reasons for this. First, the concentration of PCB in water usually is very low. Concentrations below 1 ppt have been reported (AHLING and JENSEN 1970, AHNOFF and JOSEFSSON 1973, AHNOFF and JOSEFSSON 1974). This makes it necessary to consider interfering substances that occur even in very small amounts. Second, water samples from polluted rivers may contain in addition interfering substances, which are not present in biological materials. Such a compound is elemental sulphur which appears in extracts from polluted river water and sediment. It seriously interferes with the gas chromatographic determination of PCB with an electron capture detector.

Interfering substances are eliminated by utilizing differences between the PCBs and interfering compounds in physical and chemical properties:

a) Degradation by sulphuric acid. This method removes most interferences of biological origin such as different lipids. It does not remove all oil and other chemically stable pollutants which may be present in river water.
b) Polarity. Since the PCBs are extremely non-polar many interferences can be eliminated by adsorption on a polar adsorbent like Florisil or silica gel using a non-polar eluting solvent.
c) Special reagents. To remove interferences which remain after the coarse procedures mentioned above more specific reagent are used. Sulphur may be removed by treatment with alkali. Nonactivated Raney copper, a copper aluminium alloy, has also been used for this purpose (SCHUTZMANN et al. 1971). Chromic acid has been used to eliminate DDE (WESTÖÖ and NORÉN 1970, MILES 1972).

In this work clean up procedures including treatment with Florisil, sulphuric acid, potassium hydroxide and activated Raney nickel were tested on river water extracts.

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METHODS

Reagents

Cyclohexane and n-hexane were purified by distilling technical grade qualities on a 1m bubble cap plate column with a reflux ratio of 12:1. Tap water and distilled acetone were used for washing the glassware. Florisil 600-100 mesh (Matheson, Coleman & Bell) and sodium sulphate AR were heated to 500°C for 5 hours and kept at 130°C in glass stoppered vials. Highly active Raney nickel (Bohus Electrochemical Co., Sweden) which is delivered in xylen as protective medium, was thoroughly washed with hexane until no significant trace of impurities appeared in a blank test. The catalyst was stored in hexane. For the sulphuric acid treatment sulphuric acid AR and fuming sulphuric acid AR containing 30% SO_3 were mixed just prior to use to give a mixture containing 10% SO_3. Potassium hydroxide pellets (AR) were pulverized for the potassium hydroxide treatment.

Extraction of river water samples

Because of the low concentrations of PCB in water large sample volumes are required. For this a continuous liquid-liquid extractor was used (AHNOFF and JOSEFSSON 1974). Two volumes of 400 liters each were extracted with 300 ml of cyclohexane in two separate extractions. The extracts were mixed giving a 500 ml "stock solution" from 800 liters of river water. This was divided into four equal portions and used in clean up methods a to d (see below). Extract from another 200 l was used to compare clean up procedures d and e.

Clean up procedures

The five procedures tested were:

a) treatment with sulphuric acid

b) treatment with sulphuric acid followed by treatment with Raney nickel

c) treatment on Florisil column

d) tratment on Florisil column followed by treatment with Raney nickel

e) treatment on Florisil column followed by treatment with potassium hydroxide.

Concentration of sample

All methods included concentration of the sample to a final volume of 1.0 ml. The samples were concentrated to 10 ml in a Kuderna-Danish concentrator. The same apparatus was used to concentrate the Florisil column eluate to 10 ml. Concentration from 10 to 1 ml was carried out in a tube heater (Kontes K 720000).

Treatment with sulphuric acid

After concentration to 1.0 ml the concentrate was shaken with 2 ml of sulphuric acid containing 10% SO_3 in a teflon lined screw capped centrifuge tube for 30 minutes. The emulsion was centrifuged and the two phases were separated.

Treatment on Florisil column

The sample was initially concentrated to 10 ml. The concentrate was applied to the top of a column packed with Florisil to a height of 10 cm (i.d. 20 mm) and covered with 1 cm of anhydrous sodium sulphate. The column had initially been washed with 100 ml of hexane. PCB was eluted with 200 ml of hexane and the eluate was concentrated to 1.0 ml. (Under these conditions DDT and its metabolites are not completely eluted).

Treatment with Raney nickel or potassium hydroxide

Samples which had been treated with sulphuric acid or Florisil and concentrated to 1.0 ml were placed in teflon lined screw capped reaction tubes together with a small amount of Raney nickel (0.02 g) or potassium hydroxide powder (0.1 g). The tubes were placed with their tips dipped into a hot oil bath (120°C) and were shaken for 20 minutes.

Recovery

The recovery in all stages of the clean up procedure was checked with standard PCB samples containing about the same amount of PCB as an actual sample, i.e. about 100 ng.

Control of contamination

The handling of minute quantities of PCB requires much attention to contamination risks at all stages of the analysis. Contaminating materials including all plastic materials except PTFE must be avoided. The use of PTFE calls for special attention that it be properly cleaned. The clean glassware is kept in an oven at 130°C and is washed three times with pure solvent directly before use. The purity of the solvents and other reagents must be controlled by running adequate blanks. The overall contamination is controlled by running blanks through the whole procedure including sampling, extraction, clean up and concentration.

Gas chromatography

A Hewlett-Packard 7620-A instrument equipped with a tritium electron-capture detector was used. The 2 m glass column with 2 mm i.d. was silanized with dimethyldichlorsilane and packed with Chromosorb W DMCS coated with 3% OV-1. Helium was used as the carrier gas with a flow rate of 25 ml/min. Argon with 10% methane was used as the purge gas with a flow rate of 45 ml/min. The column, injector and detector temperatures were 200°C, 230°C and 215°C respectively. The standing current of the tritium detector was 0.5×10^{-9}A. The injected sample volume was 10 µl.

RESULTS AND DISCUSSION

The four gas chromatograms resulting from the four clean up procedures a,b,c and d are shown in Fig. 1. From chromatogram D the PCB content was quantitated at 0.68 ng per 10 µl injected sample by comparing the peak height sums for five peaks in the sample and the standard (the five peaks are indicated in Fig. 1). This corresponds to 0.34 ppt PCB in the sampled water. The total background of contamination was below 0.02 ng per 10 µl of the blank corresponding to 0.01 ppt in water. The chromatograms in Fig. 1 clearly show that for the river water used in this study (Göta river) treatment with sulphuric acid is insufficient for a PCB determination. For comparison Fig. 2 shows the chromatogram of a sediment extract treated with sulphuric acid and potassium hydroxide. On water extracts Florisil clean up is more effective. Apparently there are compounds present in the water extract which are resistant against sulphuric acid but are sufficiently polar to be retained on the Florisil column.

Sulphur is removed by neither of these two treatments. That sulphur was in fact present in the extract was shown by both gas chromatography and UV spectrophotometry. The sulphur content, determined by the method of Maurice (MAURICE 1957), was roughly 10 ppm in the untreated extract corresponding to 6 ppb in the water. Thus sulphur exceeds the PCB content by about four orders of magnitude. The sulphur was easily removed by treatment with activated Raney nickel. Sulphur and sulphur containing compounds are known to be strong catalyst poisons. The sulphur is mainly bound as sulphide to the nickel.

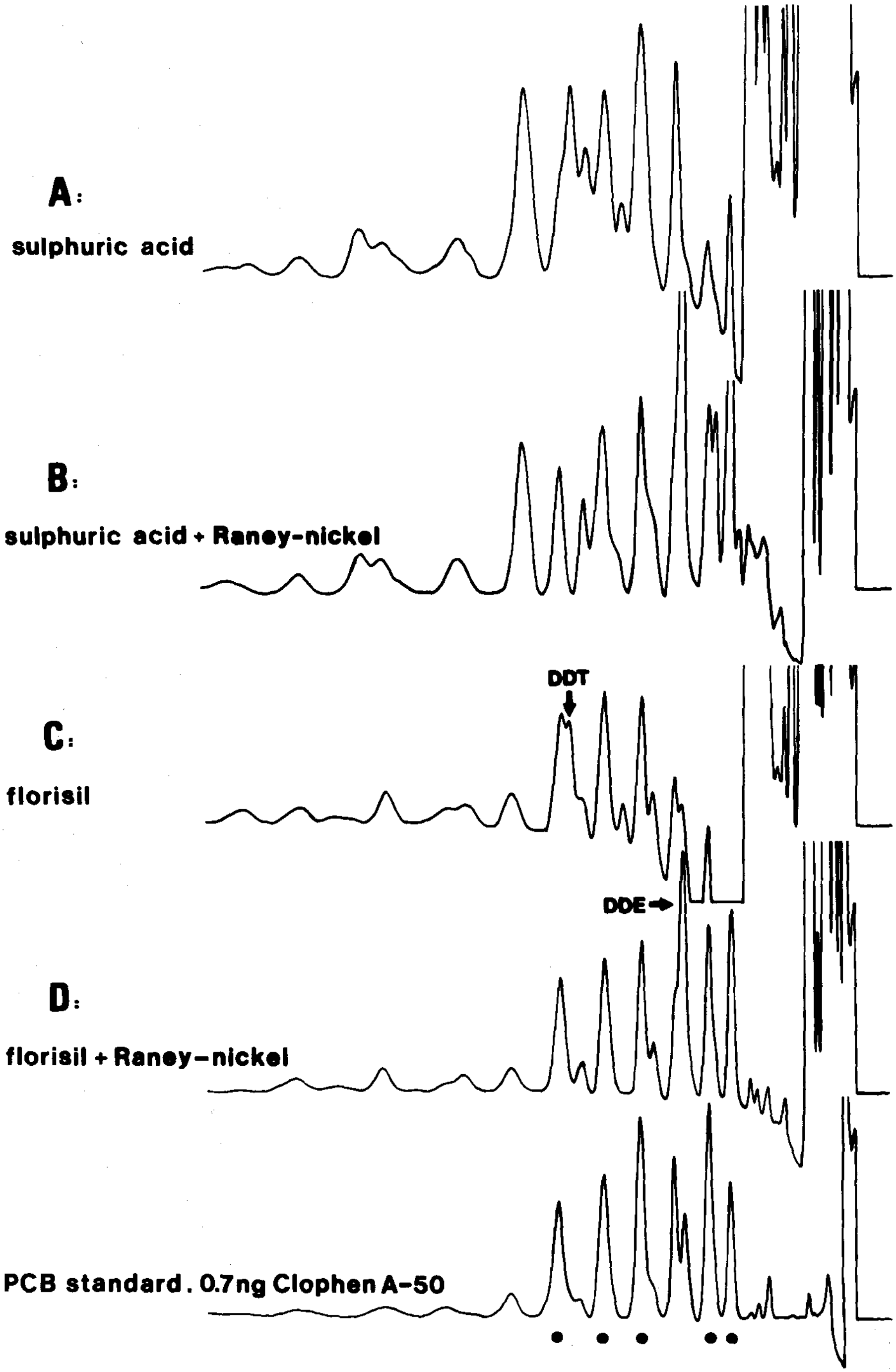

Fig. 1. Gas chromatograms of the same river water extract treated by four different clean up methods.

The two chromatograms resulting from clean up procedures d and e are compared in Fig. 3. They show that Raney nickel can be replaced by potassium hydroxide for the removal of sulphur. The sulphur probably is reduced to S_n^{2-} and removed from the organic phase (PESCHANSKI 1949 and MARONNY 1959). However, the figure also shows that there are compounds which are removed by the Raney nickel catalyst but not by potassium hydroxide. These non-PCB compounds have not been identified.

The procedures with Raney nickel and potassium hydroxide were also tested on a solution of chlorine containing pesticides. According to the resulting gas chromatograms they gave equal results, including the transformation of DDT to DDE.

Two other methods of potassium hydroxide treatment were also tested. Treatment with alkali dissolved in water gave incomplete reactions. Alkali dissolved in ethanol added to the hexane extract was just as effective as solid alkali. However, the latter was chosen because of its simplicity.

The activated Raney nickel did not affect PCB. While chlorine bound to aliphatic structures often is removed under mild conditions, chlorine bound to unsaturated or aromatic structures is more strongly held (BALTZLAY 1946).

With the Florisil-Raney nickel clean up only one non-PCB peak was found in the gas chromatogram which elutes later than 2 minutes after injection (see Fig. 3), namely the DDE peak. Consequently this method may be considered the best of those tested. DDE can be removed by treatment with chromic acid (WESTÖÖ and NORÉN 1970, MILES 1972). If it is possible to evaluate the PCB content in the presence of DDE, this is preferred since the chromic acid treatment involves several steps which may cause partial loss or contamination of the sample.

The Raney nickel procedure has a disadvantage. The activity of a catalyst may be difficult to control. It was noticed that the reactions with some chlorinated pesticides were affected by changes in catalyst activity. However, this has less importance when only PCB is analyzed. Raney nickel was used for routine analysis of PCB in river water for several months without problems.

The Florisil-potassium hydroxide clean up can not be generally employed. However, depending on the water quality and on the quantitation method used, this procedure may be adequate.

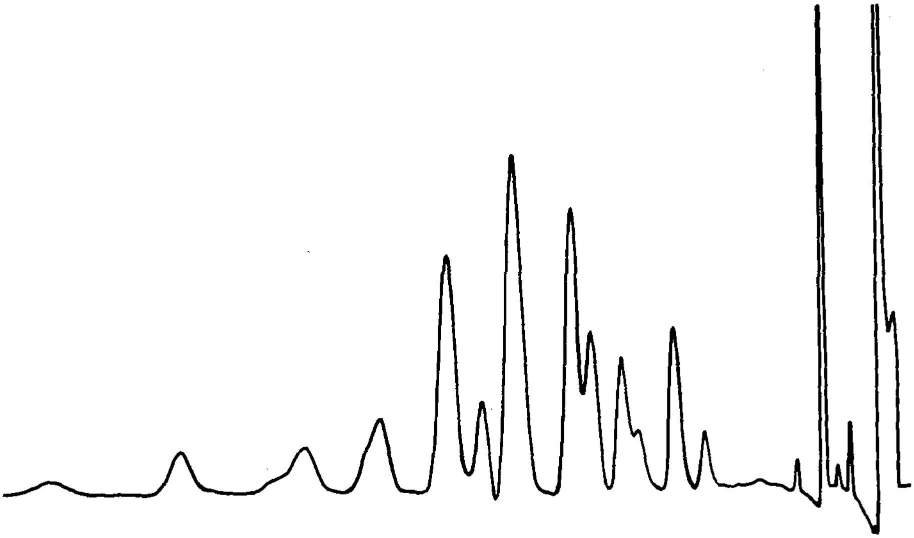

Fig. 2. Gas chromatogram of a sediment extract treated with sulphuric acid and potassium hydroxide.

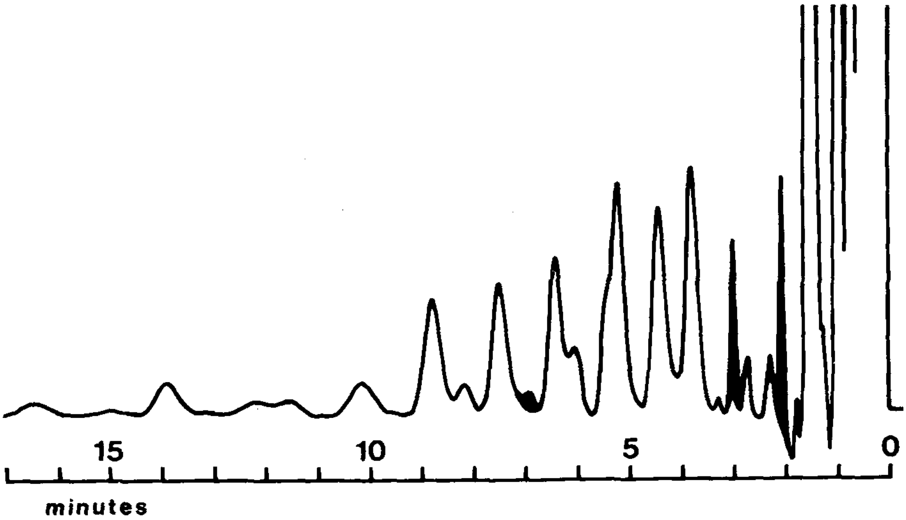

Fig. 3. Gas chromatograms of a river water extract treated a) with Florisil and potassium hydroxide (all peaks) and b) with Florisil and Raney nickel (all except black peaks).

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