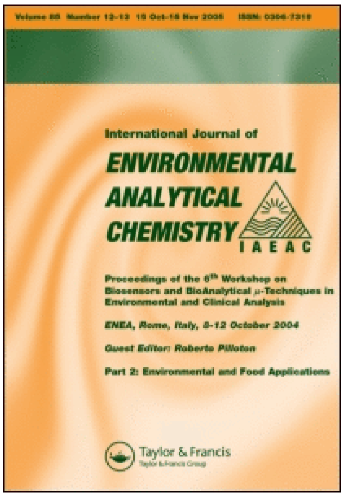

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An Approach to the Preparation of Standard Reference Material for the Analysis of Polychlorinated Biphenyls in Marine Sediments

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Using polychlorinated biphenyl (PCB) free inter-tidal marine sediments, a simple methodology for the preparation of a standard reference material has been developed for the analysis of PCB's in marine sediments. Aroclor 1254 has been used as the representative PCB analyte, since it most closely resembles the gas chromatographic characteristics of PCB's found in sediments.[1] A summary of data is presented, which shows very high PCB recoveries for the analyte and also supports the methodology to produce a well homogenized standard reference material.

KEY WORDS: Polychlorinated biphenyl analysis, marine sediments, standard reference material preparation.

INTRODUCTION

Analysis of PCB's as environmental hazards at trace levels usually calls for very accurate measurements and assessment. However, analytical methodologies for the determination of PCB's in marine sediments are on the increase[2,3] and for most of the environmental analyses there is little or no knowledge of comparability of data because of the lack of reference materials, standardized well enough by various methodologies and compared for accuracy of chemical analyses. In order for data from

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various methods to be meaningful and for analyses to be reliable, a simple approach to the preparation of a standard reference material is presented; this approach could be used for Aroclor mixtures; and also be extended to other chlorinated hydrocarbons in a marine sediment matrix.

EXPERIMENTAL

Materials and methods

a) *Gas chromatography*: (i) Hewlett Packard (HP) 5750 with an HP 7101B strip chart recorder; equipped with ^{63}Ni detector, coiled glass column, 3% SE 30 or 2250/2401 Supelco columns. Operating conditions: injection port 250°; column 230° and detector temperature at 275°; 95% argon-methane mixture used as the carrier gas at a flow rate of 75 ml/min. (ii) Perkin Elmer 910 equipped with both flame ionization (FI) and ^{63}Ni electron capture (EC) detectors; 3% OV1 glass column. Operating conditions: injection port, 250°C; column, 230°C (isothermal); detector 270°C; carrier gas is 95% argon-methane at a flow rate of 60 ml/min.

b) *Columns;* (i) 2 m glass column, packed with 3% SE 30 on 100–120 mesh Chromosorb Q (Chromatographic Specialties Ltd., Brockville, Ontario, Canada). (ii) 2 m glass column, packed with Supelco 1.5/19.5% 2250/2401 on 100–120 mesh Chromosorb Q. (iii) 2 m column, packed with 3% OV 1 on Chromosorb W.

c) Aluminum trays and stainless steel shovel for sampling of sediments.

d) Freeze dryer, (model 25 SRC, Virtis Company, New York. Division of Cence Medical/Health Supply Corp.).

e) Mortar and Pestle.

f) Metallic sieve (40 mesh).

g) Blender, consisting of a pickle jar container placed on a Norton Jar mill (Norton Chemical Process Products Division, Ohio).

h) Soxhlet extractor.

i) Deep freezer/cold room.

j) Florisil, 60–100 mesh (Fisher Scientific, Lot. 766009), activated at 120°C overnight.

k) Anhydrous sodium sulphate and potassium hydroxide pellets (Analar analytical reagent product No. 10264).

l) Distilled ethanol and hexane.

m) Elemental mercury.

n) Vortex Shaker.

Sampling procedure and storage

An inter-tidal zone was sampled using a stainless steel shovel to grab a one-shot surface scoop of sediments. Excess water was drained off, and the sediments placed in thoroughly cleaned and hexane-washed aluminum trays for quick transportation to the laboratory. The sediments were freeze dried as soon as possible and stored at $<4°C$ in hexane washed aluminum trays, covered with hexane washed perforated aluminum foil.

Physical analysis of sediments

A batch of the freeze dried sediments was ground with a mortar and pestle to a fine powder. The ground material was dry-sieved to obtain uniform size distribution for sediments which pass through 40 mesh size metallic sieve. The sieved material was then transferred into a preweighed jar and blended on a Norton mill. Subsamples (40 g) of the blended sediments were analysed to determine the background PCB and other possible organic contaminants, which might render the sediments unfit to be used to prepare the reference material.

Determination of background PCB and other interfering contaminants

A paper thimble was thoroughly cleaned by repeated soxhlet extraction with redistilled *n*-hexane, until concentrates of the extracts were found to be free from background contaminants by EC/GC. Unspiked, thoroughly blended sediments (40 g) were put into the cleaned thimble and soxhlet extracted overnight with redistilled hexane. The extract was concentrated to about 2 ml on a rotary evaporator and used in the clean-up step below.

Florisil clean-up and sulphur removal

Soxhlet extracted materials were cleaned-up on a Florisil column (topped with about half an inch of hexane-washed and oven dried anhydrous sodium sulphate) using 2×150 ml 20:80 (ether/hexane) eluants. The first fraction of 150 ml eluant was evaporated to 2 ml and background sulphur was removed with ethanolic potassium hydroxide solution according to Young and Burke,[4] and with elemental mercury according to Goerlitz and Law 1971.[5] After sulphur removal, the hexane wash was concentrated down to 1 ml for GC analysis.

Preparation of standard reference material

Having established that subsamples of the unspiked, well blended starting material showed little or no background contamination that would interfere with subsequent PCB analysis, about 120 g of this batch of contaminant free sediment was placed into a round-bottomed flask containing a known amount (375 μg) of Aroclor 1254 in hexane.

The hexane was slowly evaporated on a rotary evaporator to obtain a well coated and homogeneous batch of sediment. The round bottomed flask was emptied of its contents and the coating phase repeated with another 120 g of sediment in a hexane rinse of the flask used earlier. The two 120 g coated batches were added together to the rest of the weighed (2.76 Kg) sediment in a blender jar. The jar was then placed on a Norton mill and blended for about 48 hours.

Subsamples of this spiked and blended material were treated as described above for the unspiked starting material and the recoveries of Aroclor 1254 were determined by EC/GC of extracts concentrated after sulphur removal.

Chromatography

Hexane extracts after sulphur removal were concentrated to 1 ml and 1 μl (5.0 ng of Aroclor 1254) was injected into the GC. Quantitation was by measuring the peak heights of components of Aroclor 1254, as shown in Figure 1. Using other GC columns of different liquid phases, analyte recoveries were estimated and chromatographic inefficiencies and possible loss of analyte due to chromatographic temperature conditions were also determined.

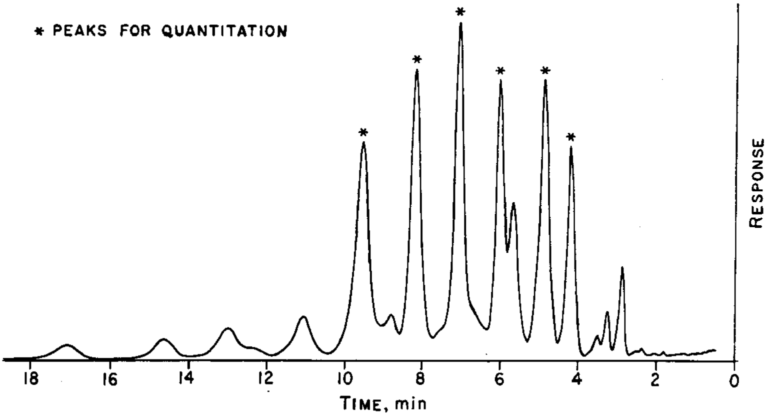

FIGURE 1 Gas Chromatogram of Standard Aroclor 1254 used as analyte.

RESULTS AND DISCUSSION

Preliminary investigation indicated that the sediment from Medford beach in the Minas Basin, Nova Scotia, was of low sulphur content and free from contaminants that might interfere with PCB analyses and therefore fit to be used for the preparation of the standard reference material. Extraction experiments for 40 g subsamples of sediment, spiked with 5.0 μg Aroclor 1254 yielded 88 to 94% recoveries. Hence very little or no PCB analyte was lost during the soxhlet extraction stage or the sulphur removal stage with ethanolic potassium hydroxide (EtOH/KOH) treatment. Comparison of the sulphur removal by EtOH/KOH[4] mixture and elemental mercury[5] showed the latter treatment to contribute to a further loss of about 10% of the analytes. Ethanolic potassium hydroxide treatment proved to be very simple and quantitative, requiring only one treatment, even on sediments of very high organic and sulphur content. It was observed that 20:80 ether/hexane mixture eluted the Aroclor analyte together with all the sulphur present. Figures 2 and 3 are typical chromatograms of extracts before and after sulphur removal. Figure 2 also indicates that the original sediment material was of low sulphur content and that very insignificant amount of PCB analyte would be lost during the sulphur removal stage of the above methodology. Quantitation of the PCB's was achieved by comparing the total height of 6 or more major components of Aroclor 1254 standard GC pattern with the corresponding peaks from the analyte extracts. Figure 1 gives a representative chromatogram of the standard Aroclor 1254 used in this work. Three GC

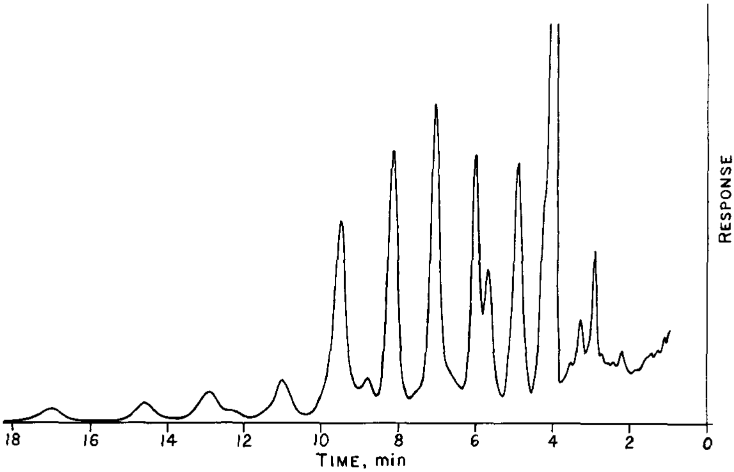

FIGURE 2 Gas Chromatogram of Aroclor 1254 extract before sulphur removal.

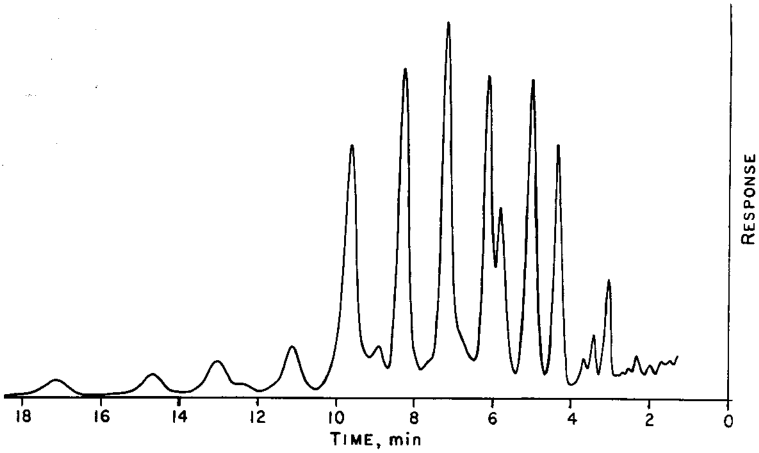

FIGURE 3 Gas Chromatogram of Aroclor 1254 extract after sulphur removal.

TABLE I
Summary of quantitation (ng of Aroclor 1254) by GC

Sample	GC liquid phases			
	3 % SE 30	2250/2401	3 % OV 1	
1	4.50	4.83	4.61	Av. 4.65
2	4.63	4.78	4.90	Av. 4.80
3	4.70	4.55	4.82	Av. 4.69

columns were used for quantitation and the results are tabulated in Table I. The results show a good agreement on all of the columns, thus no significant loss of PCB analyte occurred during chromatography. Also, the results indicate that 40 g subsamples were homogeneous enough to be used as reference material, and that the home-made blender consisting of a jar placed on a Norton mill gave a satisfactory blending, working with about 3 Kg of sediments at a time. A summary methodology for 6 subsamples is given in Table II and shows EtOH/KOH for sulphur removal to be highly recommended for PCB analysis in sulphur containing sediments.

Table II

Summary of methodology

Sample	Pre-extraction	Extraction	Clean-up	Spiked PCB per 40 g sediment (μg)	% Aroclor recovery SE 30 column
1	Freeze dry	Soxhlet (100% Hex)	Florisil /EtOH/KOH	5	90.0
2	Freeze dry	Soxhlet (100% Hex)	Florisil /EtOH/KOH	5	92.6
3	Freeze dry	Soxhlet (100% Hex)	Florisil /EtOH/KOH	5	94.0
4	Freeze dry	Soxhlet (100% Hex)	Florisil /Hg	5	80.6
5	Freeze dry	Soxhlet (100% Hex)	Florisil /Hg	5	83.0
6	Freeze dry	Soxhlet (100% Hex)	Florisil /EtOH/KOH	5	88.2

CONCLUSIONS

Polychlorinated biphenyls could be conveniently added to marine sediments and blended thoroughly enough to produce a suitable trace level standard reference material for PCB analysis in marine sediments. A wide range of analyte concentrations could be readily prepared by blending a known spiked amount of sediment with more of the unspiked original sediment. Storage at cold room temperature of <4°C, in tightly sealed aluminum cans was very satisfactory.

Acknowledgements

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References

1. O. W. Berg, P. L. Diosady and G. A. V. Rees, *Bull. Environ. Contam. Toxicol.* **7**, 338 (1972).
2. O. Hutzinger, S. Safe and V. Zitko, *The Chemistry of PCB's*, CRC Press, Cleveland, Ohio, 1974.

3. A. Walton, Editor, *Methods for Sampling and Analysis of Marine Sediments and Dredged Material,* Dept. of Fisheries and Environment Publishing Center, Hull, Quebec, Canada, 1978.
4. S. Y. Young and J. Burke, *Bull. Environ. Contam. Toxicol.* **7,** 160 (1972.
5. D. F. Goerlitz and L. M. Law, *Bull. Environ. Contam. Toxicol.* **6,** 9 (1971).