

## **Oxalic Acid Enhancement of Recoveries of Organochlorine Insecticides and Polychlorobiphenyls in Estuarine Sediment Using Cyclic Steam Distillation**

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Extraction and cleanup procedures for organochlorine insecticides (OC) and polychlorinated biphenyls (PCB), formerly done by solvent extraction and column chromatography, may be much more conveniently done by cyclic steam distillation (Veith and Kiwus 1977). Cyclic steam distillation of OC and/or PCB has been applied to agricultural soils (Cooke et al. 1979a), estuarine sediments (Cooke et al. 1979b) and British birds of prey (Cooke et al. 1980). In the latter case however, recovery of OC from muscle tissue was poor, due to high lipid content.

We have experienced degradation of pp'DDT and pp'DDE during gas chromatography, which is eliminated by insertion of oxygen scrubbers in the carrier gas line. Prolonged exposure to heat and alkaline conditions may similarly lead to conversion of DDT to DDE (Nash and Harris 1972). Subsequently, ammonium chloride (Nash et al. 1973) and pH adjustment (Smith K, University of Guyana, Guyana) have been used to reduce DDT to DDE conversion and enhance recoveries of OC from soil and blood respectively. Such experience led us to the use of oxalic acid, a mildly reducing acid, during the steam distillation procedure for our estuarine sediments.

### **MATERIALS AND METHODS**

Subsamples of a composited sediment sample taken from the Caroni Swamp, Trinidad, were fortified with known amounts of either OC or Arachlor 1254, and subjected to cyclic steam distillation (see Table 1). Blank samples were analysed by a tested conventional procedure (Pesticide Analytical Manual 1977) to determine the original levels of OC and PCB in the sample.

Steam distillation units similar to those used by the Bristol workers (Cooke et al. 1979a, 1979b, 1980), topped by double surface condensers, were used with 500 ml round bottomed flasks. For this apparatus investigations into the optimal volume of distilled water and distillation time required for 50g sediment subsamples were 150 ml and 1.5 hr. respectively.

Triplicate subsamples were fortified with OC (total 3.25 ug) or PCB (1 ug), blended with 150 ml glass - distilled water and transferred to the distillation flasks. To each flask 10 ml redistilled hexane was added. Cyclic steam distillation was then carried out for 1.5 hour. Hexane extracts were drained out of the extractors which were each rinsed with a further 5 ml of hexane and the rinsings combined with the original extracts. Extracts were dried with anhydrous sodium sulphate, transferred to calibrated vials, and evaporated to 1 ml with a stream of nitrogen, at water bath temperature of 70°C. Sulfur interference was encountered during gas chromatographic analysis. This was removed by the method of Johnsen and Munsell 1977, by adding 300 mg acid-washed copper powder to each final extract.

A Pye Unicam Model 104 gas chromatograph equipped with a  $^{63}\text{Ni}$  electron capture detector was used. A 1.5 m x 4 mm i.d. glass column packed with 1.5% OV-17 + 1.95% QF-1 on 80/100 mesh Gas Chrom Q was used to analyse OC and PCB in turn. Injector, column and detector temperatures were 250, 200 and 250°C respectively. Flow rate of nitrogen carrier gas was 40 ml/min. after passage through an Oxisorb (Applied Science, PA 16801, U.S.A.) oxygen scrubbing unit.

#### RESULTS AND DISCUSSION

Results of the above investigation after correction for original levels of OC and PCB are presented in Table 1.

Table 1: Recoveries of OC and PCB from Sediment

Pesticide	Amount added (ug)	% Recovery $\pm$ Std. deviation
$\gamma$ -BHC	0.16	73 $\pm$ 3
Heptachlor	0.21	not detected
Aldrin	0.21	31 $\pm$ 4
Heptachlor epoxide	0.27	89 $\pm$ 2
pp'DDE	0.41	80 $\pm$ 3
Dieldrin	0.36	89 $\pm$ 3
op'DDT	0.62	20 $\pm$ 4
pp'DDT	1.01	13 $\pm$ 4
Arachlor 1254	1.00	79 $\pm$ 5

As can be seen however, recovery of aldrin, op'DDT and pp'DDT are unacceptably low. Heptachlor was not detected after copper treatment, in agreement with previous observation (Thompson 1972).

Aqueous solutions of 0.05, 0.1 and 0.5M oxalic acid were then used instead of distilled water to blend triplicate sets of subsamples fortified with OC and PCB similar to those used in Table 1. Steam distillation and gas chromatographic analyses were then carried out as described. The results of this study after correction for original levels of OC and PCB are presented in Table 2.

Table 2: Effect of Oxalic Acid Concentration on Recoveries of OC and PCB from Sediment

Pesticide	% Recovery $\pm$ Std. deviation		
	0.05M	0.1M	0.5M
$\gamma$ -BHC	81 $\pm$ 3	82 $\pm$ 3	80 $\pm$ 3
Heptachlor	N.D. <sup>a</sup>	N.D.	N.D.
Aldrin	83 $\pm$ 2	82 $\pm$ 2	77 $\pm$ 3
Heptachlor epoxide	85 $\pm$ 2	80 $\pm$ 2	78 $\pm$ 3
pp'DDE	83 $\pm$ 2	85 $\pm$ 2	83 $\pm$ 2
Dieldrin	80 $\pm$ 3	83 $\pm$ 3	82 $\pm$ 2
op'DDT	70 $\pm$ 3	75 $\pm$ 3	78 $\pm$ 3
pp'DDT	58 $\pm$ 4	64 $\pm$ 4	68 $\pm$ 5
Arachlor 1254	79 $\pm$ 5	82 $\pm$ 5	80 $\pm$ 5

a = Not detected

The 0.1M oxalic acid solution thus provided the greatest overall recovery of OC and PCB. The recovery of pp'DDT, although relatively low with respect to the other compounds, represents a drastic improvement over the original recovery without oxalic acid treatment. The enhanced recoveries appear to be partly due to the effect of the acidic medium on the porphyrin-type components of the sample (Smith K, University of Guyana, Guyana). The use of a reducing medium particularly to prevent conversion of pp'DDT to pp'DDE during extraction, also appears to enhance such recoveries.

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