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To cite this article: Liangliang Tian *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **237** 022053

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# Method for the Analysis of 7 Indicator Polychlorinated Biphenyls (PCBs) and 13 Organochlorine Pesticide Residues in Sediment by Gas Chromatography (GC)

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**Abstract.** This study described the development of a multiresidue method based on gas chromatography (GC) for the detection of 7 indicator polychlorinated biphenyls (PCBs) and 13 organochlorine pesticide (OCPs) residues in sediment with electron capture detector (ECD). The samples were extracted by n-hexane/dichloromethane (1/1, v/v) by ultrasonic extraction. The extracts were desulfurization with copper powder and purification with concentrated sulfuric acid. The method was validated by the analysis of spiked Tai lake sediment. Analytical performances were evaluated in terms of linearity, quantification limits, accuracy, and precision. Good linearity responses with coefficients of determination higher than 0.9945 were obtained. Methodological limit of quantitation (LOQ) was 0.5-5.0 $\mu$ g/kg for OCPs and PCBs. The recovery and RSDs of three-level spiked samples were in the ranges of 71.6%-105% and 3.2-11.2%. This method is highly effective to reduce the cost and time for the pretreatment of sample, and offers the ability to detect and quantify the PCBs and OCPs in sediments.

## 1. Introduction

The polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) researched in this paper were listed in the Stockholm Convention as persistent organic pollutants (POPs) which came into force on May 2004. Very large numbers of Stockholm POPs were manufactured during the last century and used in numerous industrial applications as pesticides and flame retardants<sup>[1]</sup>. The PCBs and OCPs are ubiquitous in the environment, in continents, deserts, oceans and even in the Arctic and Antarctic regions<sup>[2]</sup>. They have the characteristics of high toxicity, persistence, bio-accumulative and are prone to long-range transport.

Sediments represent the integration of biological, physical and chemical processes that occur in an aquatic ecosystem. Sediments may differ in form and composition and are considered to be pollutant accumulation compartments from the water column<sup>[3]</sup>. Persistent organic pollutants (POPs) are prone to accumulate in sediment. Conventionally, different techniques such as soxhlet extraction<sup>[4]</sup>, accelerated solvent extraction (ASE)<sup>[1, 5]</sup>, microwave-assisted extraction (MAE)<sup>[6]</sup> and ultrasound assisted extraction (UAE)<sup>[7]</sup> have been performed for the extraction of PCBs or OCPs in sediments. Some methods, such as soxhlet extraction and ASE, have high recovery, but over solvent depletion and extraction time or cost. Another methods, such as UAE and MAE, have been used because of their speed, simplicity and low solvent depletion. Moreover, the extraction step is generally followed by a



clean-up step to remove any interfering substances, which involves a time consuming step commonly performed by solid phase extraction (SPE)<sup>[4,7,8]</sup>. With the development of new technology, some methods were used for purification, such as quick, easy, cheap, effective, rugged, safe (QuEChERS) method<sup>[3]</sup> and gel permeation chromatography (GPC)<sup>[9]</sup>. The objective of this present study was to establish a reliable, simple, time saving and cost-effective extraction procedure based on ultrasound and effective purification for the analyses of multiple groups of PCBs and OCPs in sediment.

## 2. Materials and method

### 2.1. Materials and instrument

The GC system consisted of an Agilent 7890A GC (Agilent Technologies, Shanghai, China), equipped with an electron capture detector (ECD). The GC was fitted with a HP-5MS fused silica capillary column (5% phenyl polysiloxane as non-polar stationary phase, 30 m, 0.25 mm i.d. and 0.25  $\mu$ m film thickness) from Agilent (J&W Scientific, Folsom, CA, USA).

PCB 28, PCB 52, PCB101, PCB 118, PCB 152, PCB 138, PCB 180 were purchased from Dr.Ehrenstorfer GmbH and had purities >98%.  $\alpha$ -hexachlorocyclohexane ( $\alpha$ -HCH),  $\beta$ -hexachlorocyclohexane ( $\beta$ -HCH),  $\gamma$ -hexachlorocyclohexane ( $\gamma$ -HCH),  $\delta$ -hexachlorocyclohexane ( $\delta$ -HCH), hexachlorobenzene (HCB), heptachlor, aldrin, dis-chlordane, 4,4'-DDE, 2,4'-DDT, 4,4'-DDD, 4,4'-DDT, mirex were purchased from A ChemTek INC and had purities >98%. Stock solutions were prepared for all standard substances were 1.0  $\mu$ g/mL in n-hexane. Spiking mixtures was obtained by mixing appropriate amounts of each individual PCBs and OCPs stored at -20°C. Calibration mixtures at various concentration levels were obtained by combing aliquots of stock solutions with n-hexane and stored at -20°C.

N-hexane and dichloromethane were purchased from J.T.Baker (Avantor Performance Materials, Inc.) and all solvents were HPLC grade. Copper powder and concentrated sulfuric acid were purchased from sinopharm chemical reagent Co.,Ltd.

### 2.2. Sample collection and handling

The sediment used in the present study was collected from Tai lake across the jiangsu province and zhejiang province in China. Sediment samples were placed in amber glass bottles on ice after collection and were held at 4 °C in the laboratory. Sediments were air dried, homogenized, sieved to less than 1 mm, and stored in amber glass bottles at 4 °C until extracted.

### 2.3. Sediment extraction and cleanup

Five grams of prepared sediment were weighed into a 50 mL centrifuge tube. The samples were added 30 mL aliquots of extraction solvent mixture of n-hexane/dichloromethane (1/1, v/v) and soaking for 15 min. Then they were ultrasonically extracted at room temperature for 20 min. The each mixture was centrifuged at 8000 r/min for 8 min. The extraction procedure was repeated twice and the extracts from each time were combined into a pear-shaped bottle and evaporated in a rotary evaporator to dry at a low temperature and weak vacuum. The residue was dissolved by 20 mL n-hexane twice and then the dissolved solution was subjected to clean up.

The dissolved solution was added five grams copper and shocked for 5 min, then centrifuged at 8000 r/min for 5 min. The supernatant was added 3mL concentrated sulfuric acid and fully shocked for 2min, then the mixture was centrifuged at 2000 r/min for 5 min. The supernatant was added 1mL concentrated sulfuric acid and fully shocked for 2min, then the mixture was centrifuged at 2000 r/min for 5 min. The supernatant solvent was dried by a rotary evaporator. The residue was reconstituted with 1 mL n-hexane and mixed in a vortex stirrer.

### 2.4. Instrumental analysis

The final samples were detected on an Agilent 7890A GC, coupled to an electron capture detector (ECD). Nitrogen with a purity of 99.999% was used as the carrier gas. The column temperature

program was as below: 150°C hold for 1 min, ramp at 25°C/min to 230°C, hold for 2 min; ramp at 20°C/min to 240°C, hold for 1 min; ramp at 20°C/min to 260°C, and hold for 5 min; ramp at 3°C/min to 280°C, and hold for 5 min; ramp at 2°C/min to 285°C, and hold for 10 min. The carrier gas (nitrogen) flow rate was 2.5 mL/min, injection port temperature was 240°C, and injection volume was 1  $\mu$  L. The injection was made in the splitless mode with purge on after 0.75 min.

### 3. Results and Discussion

#### 3.1. Extraction method

The extraction methods of the PCBs and OCPs widely used are soxhlet extraction, ASE, MAE and UAE at present. The extraction time of soxhlet is so long that needs more than 10 h. ASE instruments are expensive that the popularization of the method is limited. MAE can rapidly increase the temperature of the extract solvent that volatilize the reagents used. So UAE was used in this study because of its short extraction time and low solvent depletion. The recovery of UAE in the research could reach 85%, so this extract method was chosen.

#### 3.2. Sulfide removal method

Sulphide in sediment is an important interference in determination of POPs in sediment, and addition of copper to extracts is a common method removing interfering materials [10]. In this study, it was found that it could completely remove the interference of sulphide with 5 gram copper at 10 minutes incubation with room temperature oscillation. So this method of desulfurization was used.

#### 3.3. Purification method

The composition of the sediments is very complex. It is advantageous to eliminate any possible interference from samples in order to trace analysis of the PCBs and OCPs. Purification with concentrated sulfuric acid [11] is an effective method to remove impurities. But at the same time, it should be confirmed that concentrated sulfuric acid would not cause the loss of the target substance. In this study, it was found that concentrated sulfuric acid had no effect on 7 PCBs and 13 OCPs we researched, but caused low recovery of dieldrin and endrin. Therefore the purification method with concentrated sulfuric acid was not applicable to dieldrin and endrin. The result was in line with the previous studies [9].

In this paper, the purification effects of silica SPE column, florisil SPE column and concentrated sulfuric acid were compared. The result showed that the recoveries of  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH,  $\delta$ -HCH, 4,4'-DDD, 4,4'-DDT after the silica SPE column were less than 70%, and the recoveries of  $\beta$ -HCH and  $\delta$ -HCH after the florisil SPE column were less than 70%. The purification effect of concentrated sulfuric acid was good, and the recoveries of all compounds were more than 70%. So the concentrated sulfuric acid was used to purification.

#### 3.4. Method performance

The calibration curves for detection of the target compounds were obtained by performing a linear regression analysis using the standard area against the concentrations ranging from 5 to 150 ng/mL for PCBs,  $\beta$ -HCH, 2, 4'-DDT, 4, 4'-DDT, 4, 4'-DDD, mirex, and from 0.5 to 150 ng/mL for  $\alpha$ -HCH,  $\gamma$ -HCH,  $\delta$ -HCH, 4, 4'-DDE, HCB, heptachlor, aldrin, dis-chlordane. The chromatogram was shown in Figure 1. Good linearity was obtained for all analytes with correlation coefficients of  $R^2$  ranged from 0.9945 to 0.9997. The limit of quantification (LOQ), defined as the concentration which yield an S/N equal to 10, ranged from 0.5  $\mu$  g/kg to 5.0  $\mu$  g/kg (Table 1). The recovery of this procedure was evaluated by spiking 2.0, 10.0 and 20.0  $\mu$  g/kg of each standard analyte to sample at three levels in replicates of six. The results are listed in Tables 2. The average recoveries of each compound ranged from 71.6% to 105%. The reproducibility of this method was represented by percent relative standard

deviation (RSD) and these values were also summarized in Table 2. The results show that the method's precision was within 15%, which is satisfactory.

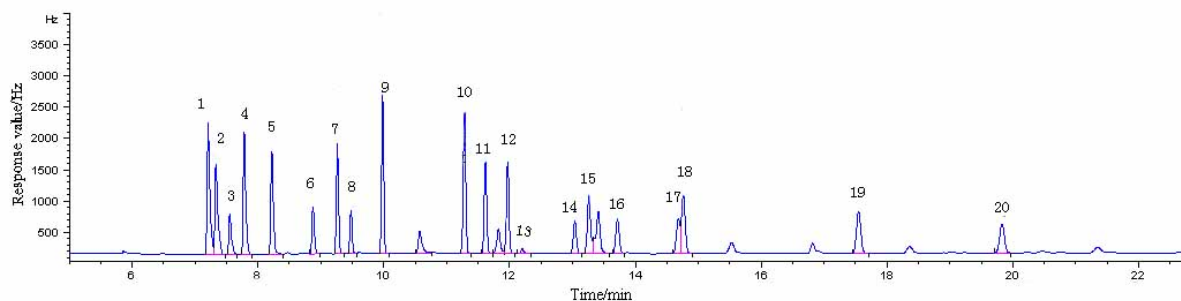


Figure 1. Chromatograms of 7 PCBs and 13 OCPs standard

(1.  $\alpha$ -HCH 2.HCB 3.  $\beta$ -HCH 4.  $\gamma$ -HCH 5.  $\delta$ -HCH 6.PCB 28 7.heptachlor 8.PCB 52 9. aldrin 10.PCB 101 11.dis- chlordane 12.4,4'-DDE 13 2,4'-DDT 14.PCB 118 15.4,4'-DDD 16.PCB 153 17.4,4'-DDT 18.PCB 138 19.PCB 180 20. mirex

Table 1. Regression equations, linear ranges, correlation coefficient and the limit of quantification (LOQs) for the 7 PCBs and 13 OCPs.

Compounds	Regression equation	Linear range $\rho/(ng/mL)$	Correlation coefficient ( $r$ )	LOQ ( $\mu g/kg$ )
PCB28	$Y=36.7547X+189.6812$	5~150	0.9991	1.5
PCB52	$Y=27.3825X+225.6785$	5~150	0.9945	1.5
PCB101	$Y=38.0214X+199.4556$	5~150	0.9989	1.5
PCB118	$Y=40.2541X+132.5687$	5~150	0.9992	1.5
PCB153	$Y=36.9981X+222.3215$	5~150	0.9994	1.5
PCB138	$Y=53.0986X+120.9124$	5~150	0.9997	1.5
PCB180	$Y=68.0916X+24.6461$	5~150	0.9996	1.5
$\alpha$ -HCH	$Y=102.8564X+545.3212$	0.5~150	0.9982	0.5
$\beta$ -HCH	$Y=48.8986X+51.2107$	5~150	0.9990	1.5
$\gamma$ -HCH	$Y=149.7657X-246.6524$	0.5~150	0.9988	0.5
$\delta$ -HCH	$Y=121.9481X-298.2384$	0.5~150	0.9985	0.8
2,4'-DDT	$Y=31.7564X+31.2625$	5~150	0.9984	5.0
4,4'-DDT	$Y=41.0165X+12.7825$	5~150	0.9991	1.5
4,4'-DDE	$Y=114.0513X+12.3564$	0.5~150	0.9996	0.8
4,4'-DDD	$Y=65.7851X+4.3438$	5~150	0.9984	1.5
HCB	$Y=112.9124X+1278.9145$	0.5~150	0.9983	0.8
Heptachlor	$Y=90.0817X+845.7642$	0.5~150	0.9992	0.5
Aldrin	$Y=40.8266X+2058.1452$	0.5~150	0.9951	0.5
Dis-chlordane	$Y=118.5468X+1401.4327$	0.5~150	0.9947	0.8
Mirex.	$Y=48.1582X+44.6725$	5~150	0.9979	1.5

Table 2. Recoveries of PCBs and OCPs in sediment n= 6.

Compounds	2.0 µg/kg		10.0 µg/kg		20.0 µg/kg	
	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %
PCB28	81.7	5.6	83.5	4.7	80.2	6.1
PCB52	88.5	4.4	90.1	4.9	86.3	5.2
PCB101	91.6	4.2	89.6	5.4	85.7	7.5
PCB118	83.5	3.8	87.5	4.2	90.1	6.7
PCB153	87.6	4.6	83.7	4.8	86.4	5.7
PCB138	90.2	3.2	93.5	5.1	88.4	7.1
PCB180	89.7	6.1	87.9	5.4	82.1	6.7
α-HCH	82.5	5.2	80.8	6.7	78.9	8.6
β-HCH	84.1	6.0	85.1	8.4	80.8	11.2
γ-HCH	76.1	4.3	74.8	3.8	71.6	6.4
δ-HCH	80.4	4.8	79.7	4.4	81.3	7.2
2,4'-DDT	74.3	10.8	80.1	8.7	77.9	8.1
4,4'-DDT	87.6	6.8	84.3	7.5	75.4	9.2
4,4'-DDE	84.2	6.4	86.8	7.3	81.6	6.7
4,4'-DDD	86.2	5.3	82.3	4.6	83.3	6.5
HCB	91.7	4.2	93.7	3.9	87.7	5.7
Heptachlor	89.8	3.8	91.4	4.1	88.7	8.4
Aldrin	98.4	3.6	105	4.5	94.1	6.8
Dis-chlordane	86.7	6.7	88.7	5.4	82.9	10.1
Mirex	87.5	5.7	86.3	6.2	84.5	7.1

#### 4. Conclusion

A laboratory procedure was developed for detecting of 7 PCBs and 13 OCPs in the sediment. The procedure includes ultrasound assisted extraction (UAE) and one step cleanup with concentrated sulfuric acid and multiple runs for all compounds using GC. The entire methodology developed can be used to assess the levels of pollutants in the sediments in an attempt to enhance the aquatic ecosystem monitoring strategies.

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