

## Simplified Determination of Organic Chlorine Pesticides in Water Samples Using Activated Carbon Filter Papers

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### Introduction

Recently, there is concern about organochlorine pesticides (OCPs) such as lindane and DDT, which have been accused of having an environmental hormone effect. The analytical method for measuring these substances up to a concentration of ng/L should be accurate and easy to process, as well as cheap. An extraction method using a solid phase extraction disk (ED) has recently come into popular use for the extraction of lipid-soluble pollutants like PCDD/Fs from water. Compared to liquid-liquid extraction, this method can prevent the formation of emulsions and reduce the amount of solvent needed. However, care must be taken for the ED method to keep the water suction speed within 200ml/min and to avoid the disk's dry. In the event that the sample has a large amount of particulate matter, clogging of the disk can become a problem. The price of the ED is also a problem when analyzing many samples.

Active carbon has widely been utilized as a depurator for tap water and a scavenger of odor due to its strong adsorption power. Active carbon has been used for the analysis of water samples; there are instances in which it has been used for measuring VOC in water<sup>1</sup> or collecting water-soluble chemicals<sup>2</sup>, but such application is rare. Authors have found activated carbon filter paper (ACFP) to be effective for collecting pesticides in air<sup>3</sup>. ACFP has the ability to adsorb many kinds of chemicals strongly, as well as to desorb them easily, and it has the added benefit of being very cheap. Therefore, we examined whether ACFP could be used for the collection of OCPs in water samples. OCPs were efficiently collected by inserting the ACFP into a bottle of water and stirring it. OCPs adsorbed on the ACFP were easily removed by ultrasonic solvent extraction. In order to optimize the collection efficiency, the stirring time and the amount of ACFP used were examined. The applicability for real samples was also tested.

### Materials and Methods

*Reagents and materials:* 18 kinds of organochlorine pesticides and their metabolites were obtained from Spelco (USA). These were diluted and mixed into 2µg/ml (5 µg/ml of methoxychlor) acetone solution as a mixing standard solution. DDT-<sup>13</sup>C<sub>12</sub>, HCB-<sup>13</sup>C<sub>6</sub> and α-HCH-d<sub>6</sub> acetone solution were also obtained from Spelco and mixed into 10µg/ml of acetone solution, used as a surrogate solution. ACFP (KF paper P-175), which was created as an industrial adsorbent, was supplied by TOYOBO Co.(Japan). It was cut into 5cm square pieces and extracted over 8 hours by Soxhlet extractor using toluene and acetone, respectively. The cleaned sheets of ACFP were dried and stored in a desiccator before use. The weight of one sheet was 0.173g (6.92mg/cm<sup>2</sup>).

*Collection and extraction procedure:* The sheets of ACFP were dampened by methanol and cut into

chips 7mm square just before use. The chips were added to 3L of a water sample in a gallon bottle and stirred for a few days at room temperature (ca.20°C). When the sample become ripe for algae to grow in, copper sulfate was added to depress their growth. After the adsorption was complete, the water sample was filtrated by quartz fiber filter paper under reduced pressure, and all carbon chips and suspended particles contained in the sample were collected on the quartz fiber filter paper. After the filtrate was washed with methanol to remove the water, the filtration residue and methanol cleaner were each extracted separately. The methanol cleaner was dissolved into 100ml of purified water including 3%NaCl and extracted 3 times by dichloromethane. The dichloromethane extract was dehydrated by sodium sulfuric anhydride and concentrated by a rotary evaporator. Filtration residue including the ACFP was extracted ultrasonically with 20ml of toluene-ethanol (4:1) 3 times. The extract was filtered through quartz wool and combined with the extract of the methanol cleaner. The extract was spiked with 2 $\mu$ l of surrogate solution, concentrated again, purified in a Sep-Pak Plus Florisil, and eluted with 10ml of dichloromethane. Afterwards, the eluate was spiked with 10 $\mu$ l of PEG solution (0.5%) and carefully concentrated to just before dryness under nitrogen stream. The concentrate was dissolved into 100 $\mu$ l of acetone and spiked with 2 $\mu$ l of 9-bromoanthracene solution (50 $\mu$ g/ml) for GC/MS analysis.

*GC/MS analysis:* The samples containing a high concentration level of OCP were analyzed by quadruple GC/MS in an HP 6890 gas chromatograph coupled to a JEOL Automass15, operating in the scan mode. The samples containing a low concentration level of OCP were analyzed by HRGC/HRMS in an HP 5890 gas chromatograph coupled to a JEOL SX-102A, at 5,000 resolving power of SIM mode. The OCPs that had surrogate compounds were determined by an internal standard method using surrogate compounds, and the other OCPs, by an internal standard method using 9-bromoanthracene.

*Samples analyzed:* The rain waters were collected with a humid deposition sampler in Niigata city from February to April 2001. The river waters were sampled from Nishi river in March 2001.

## Results and Discussions

*Collection time:* First, stirring time was checked with 3L of spiked (with 250 $\mu$ l of the mixed standard solution) pure water using 2 sheets of ACFP at 20°C for 0.3~4 days. As shown in Fig. 1, over a 70% recovery rate was obtained for HCB, DDT and its metabolites (DDTs) in the 0.3 day time period, showing that sufficient recovery can be obtained in even a short time. The recovery rate of the other OCPs at 0.3 days was less than 70%, but the adsorption of all OCPs became equilibrium after 1 day. Therefore, the collecting time was set to 2 days.

*Sheets of ACFP:* The number of ACFP was changed from 0.5~4

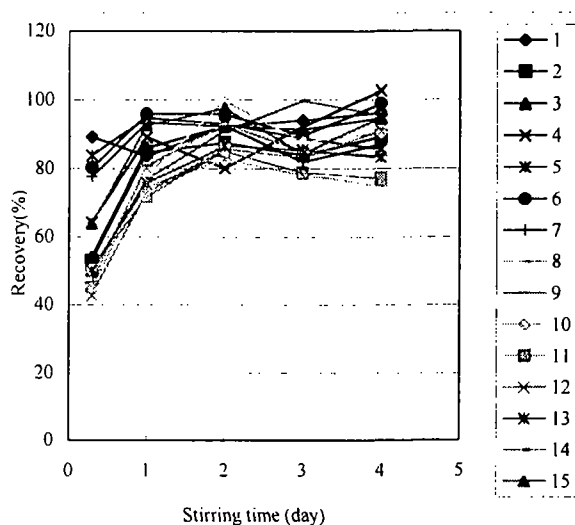


Fig. 1 Effect of stirring time on adsorption  
\* Number of OCP is the same in Table 1.

sheets, and the collection efficiency of the OCPs was then examined. The results, shown in Fig. 2, indicated that recovery rates of over 80% were obtained for HCB and DDTs even at 0.5 sheets. The recovery rates of other OCPs increased as the amount of the ACFP was increased, but they leveled out at over 2 sheets. So, we decided to use 3 sheets of ACFP for collection.

*Effect of OCP content:* In order to examine the effect of the OCP content, we examined the collection efficiency when we changed the dosage from 0.05 to 50 $\mu$ g of HCB. The results, shown

in Fig. 3, indicated that the collection efficiency was constant and was not influenced by the dosage.

*Recovery test for actual samples:* In accordance with the time of the experiment, we performed a recovery test using a pure water, a rain water and a river water at a high concentration level (spiked with 250 $\mu$ l of the mixed standard solution). Since there was a lot of suspended matter contained in the river sample, the filtration was carried out using 3~5 sheets of quartz fiber filter papers. Simultaneously, the spiked river water was analyzed by the ED method<sup>4</sup>. As shown in Table 1, the recovery rates of OCPs by this method were over 80%, and the coefficients of variation were within 10% for every kind of sample. These results show that the accuracy and reproducibility of this method are nearly the same as with the ED method.

*OCP concentrations in actual samples:* This method was applied to the actual rain water and river water samples. The results are shown in Table 2. In the river water, the results of the duplicate measurement showed good agreement and satisfied the criteria of precision. The concentrations in environmental water obtained here were rather low compared to the concentrations reported in Japan<sup>5</sup>.

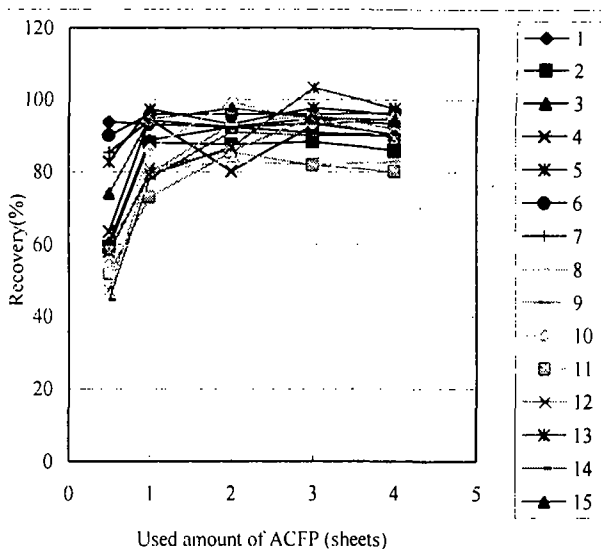


Fig. 2 Effect of used amount of ACFP

\* Number of OCP is the same in Table 1.

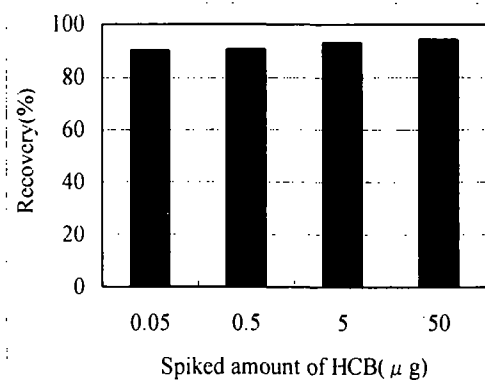


Fig. 3 Effect of spiked amount on recovery

## Conclusion

In this method, an adsorption time of 2 days is generally necessary. But, compared to the ED method, (1) the adsorption procedure is very easy and does not involve much work, (2) it is not necessary to control the flow of the water conduction for filtration, (3) the filtration speed is very fast, (4) there is no worry of a breakage by excessive water conduction, and (5) the cost of the adsorbent is very cheap. We can conclude that the collection method of OCPs in water using ACFP reduces labor and

Table 1 Recovery test using water samples

No.	Compounds	This method						ED method***	
		Pure water		Rain water		River water		River water	
		Rec <sup>*</sup>	CV <sup>**</sup>	Rec <sup>*</sup>	CV <sup>**</sup>	Rec <sup>*</sup>	CV <sup>**</sup>	Rec <sup>*</sup>	CV <sup>**</sup>
1	HCB	91	1	91	1	79	5	85	2
2	$\alpha$ -HCH	89	3	91	2	80	5	81	4
3	$\gamma$ -HCH	93	2	94	4	81	5	93	8
4	$\delta$ -HCH	95	6	102	7	75	7	83	5
5	<i>p,p'</i> -DDE	91	5	84	4	93	4	78	7
6	<i>p,p'</i> -DDD	98	5	89	3	89	5	88	6
7	<i>p,p'</i> -DDT	89	2	87	4	84	4	81	4
8	Aldrin	74	7	84	4	80	4	80	5
9	Dieldrin	91	5	83	4	90	5	97	3
10	Endrin	94	1	87	4	88	3	91	6
11	Heptachlor	74	8	84	3	93	11	86	6
12	Heptachlor epoxide	83	4	93	7	90	4	96	2
13	$\alpha$ -Endosulfan	85	8	95	6	88	7	90	8
14	$\beta$ -Endosulfan	87	5	82	4	91	11	89	3
15	Methoxychlor	95	1	88	7	86	4	83	6

\*: Recovery rate(%), \*\*: coefficient of variation (%), \*\*\*: extraction disk method

is exceptional in the area of cost as well. In the future, we would like to look into expanding the targets of this method to include compounds such as dioxins.

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Table 2 Concentration of actual samples measured by this method (ng/L)

OCPs	River water*		Rain water		LOD**
	No.1	No.2	2/22-28	3/1-4/4	
HCB	nd	nd	0.3	nd	0.2
$\alpha$ -HCH	0.54	0.45	0.66	0.83	0.08
$\beta$ -HCH	0.33	0.30	0.14	0.21	0.03
$\gamma$ -HCH	0.25	0.18	0.37	0.52	0.05
$\delta$ -HCH	0.04	0.04	0.07	0.08	0.03
Heptachlor	nd	nd	nd	nd	0.04
Heptachlor epoxide	0.01	0.01	0.017	0.008	0.003
<i>trans</i> -Chlordan	0.06	0.05	0.10	nd	0.04
<i>cis</i> -Chlordan	0.04	0.04	0.05	nd	0.02
<i>p,p'</i> -DDE	0.18	0.19	0.04	0.04	0.02
<i>p,p'</i> -DDD	0.07	0.09	nd	nd	0.02
<i>p,p'</i> -DDT	0.21	0.26	0.08	0.12	0.07
Aldrin	nd	nd	nd	nd	0.03
Dieldrin	0.21	0.15	0.20	nd	0.08
Endrin	nd	nd	nd	nd	0.08
$\alpha$ -Endosulfan	nd	nd	nd	nd	0.2
$\beta$ -Endosulfan	nd	nd	nd	nd	0.4
Methoxychlor	nd	nd	nd	nd	0.07

\*: Duplicate measurement, \*\*: limit of detection (ng/L)

nd: not detected