COMPARISON OF SAMPLE EXTRACTION METHODS FOR ORGANORCHLORI NE PESTICIDES IN AMBIENT AIR

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INTRODUCTION

The organochlorines are insecticides that contain carbon (thus organo-), hydrogen, and chlorine. They are also known by other name: chlorinated hydrocarbons, chlorinated organics, chlorinated insecticides, and chlorinated synthesis. The organochlorines are mostly of historic interest, since only a few survive in today's arsenal.[1)]

9 of 12 persistent organic pollutants (POPs) are organochlorine (OC) pesticides and they are of concern because they bioaccumulate through the food chain to top predators including human beings. It is thus very important to monitor ambient air for such compounds.

The relatively low levels of OC pesticides in ambient air requires the use of high volume sampling techniques to acquire sufficient sample for analysis, but the volatility of them prevents efficient collection on filter media. Therefore, both a filter and a polyurethane foam (PUF) backup cartridge that provides for efficient collection are used for OC pesticides within same volatility range. [2)]

In this work, three sample extraction methods such as soxhlet extraction recommended by USEPA Method TO4, sonication extraction and accelerated solvent extraction (ASE) are applied to analyze OC pesticides in ambient air.

These extraction methods are compared to suggest a reliable and fast extraction method for the determination of contents of OC pesticides in ambient air. Also these extraction processes are performed with different solvent and its contents like 5%, 10%, 20% diethyl ether in n-hexane and 5%, 10%, 20% acetone in n-hexane.

MATERIALS and METHODS OF ANALYSIS

The analytical sample was prepared using both blank Quartz fiber filter and blank PUF cartridge that is spiked the mixed standard of OC pesticides by syringe. Special care taken to avoid evaporating of mixed standard during spiking.

The extracts were taken from each sample extraction process with different solvents were analyzed through both external standard and internal standard calibration by the selected ion monitoring (SIM) mode of GC/MS. The analytical condition of GC/MS for OC pesticides is presented at Table 1. And the example of mixed standard chromatogram analyzed by this

condition is shown at Fig. 1.

	Condition	
GC	column carrier gas injection port temp. injection mode	DB-5ms (30m x 0.25 ㎜ x 0.25 ㎛) He (99.999%) 260℃ splitless, 2 ㎕ injection
	oven temp.	50℃(1min.) → 280℃ → 290℃ (1min.) 10℃/min 10℃/min
MS	interface temp. ionization mode electron energy ion source temp. detecting mode	260℃ EI mode 70eV 230℃ Selected Ion Monitoring (SIM)

Table 1. Analytical condition of GC/MS for OC pesticides

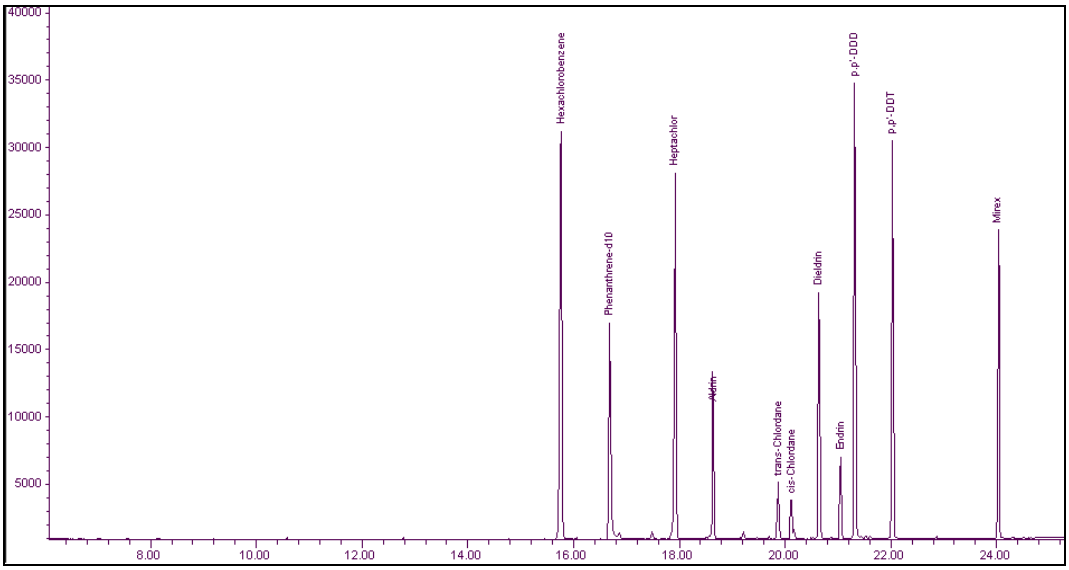

Fig. 1 Chromatogram of standard substances of OC pesticides

The recovery rate and elapsed time and efficiency were estimated at each extraction condition for the determination of OC pesticides compounds trapped into air filter and PUF cartridge. Table 2 shows the operating conditions of each extraction method.

Extraction method	Operating condition	
Soxhlet	run time solvent volume	24hours at 4cycles / hour 500ml
ASE	pressure temp. static time cell size flush volume	1500psi 150 ℃ 5 min. (2 cycles) 33 ㎖ 80%
Sonication	frequency run time solvent volume	40kHz 20 min. 250ml

Table 2. Operating conditions of each extraction method

RESULTS and DISCUSSSION

The recovery rate of each extraction method was obtained by analyzing samples spiked with same standard. Results of recovery rates are summarized in Table 3.

Compounds	Spiked level (ng)	ASE		Soxhlet		Sonication	
		recovery rate (%)	RSD (%)	recovery rate(%)	RSD (%)	recovery rate(%)	RSD (%)
Hexachlorbenzene	0.3	83.5	2.4	86.8	2.6	92.6	8.6
Heptachlor	0.5	105.1	7.3	120.1	2.1	115.6	3.7
Aldrin	0.3	69.1	2.6	63.1	7.4	67.7	5.7
trans-Chlordane	0.5	96.9	7.5	91.9	7.1	90.9	9.6
cis-Chlordane	0.5	74.2	6.9	71.3	2.7	70.7	4.6
Dieldrin	0.5	63.0	3.0	61.0	4.2	60.9	9.4
Endrin	0.5	103.2	8.9	119.0	9.1	121.1	7.6
p,p'-DDD	0.3	99.8	8.7	95.8	9.5	111.2	9.8
p,p'-DDT	0.5	115.1	6.7	121.0	8.5	122.1	9.2
Mirex	0.3	62.7	2.3	60.5	1.7	62.8	8.9

Table 3. Recovery rates of OC pesticides compounds by sample extraction method (n=15)

The recovery rates of spiked samples using ASE, Soxhlet extraction, and sonication extraction ranged from 62.7% to 115.1%, from 60.5% to 121.0%, and from 60.9% to 122.1%, respectively. Those recovery rate levels are satisfied with the criteria of recovery rate (50%~130%) for OC pesticides in Japan Speed 98 Method, [3)] therefore, these extraction methods can be used for OC pesticides only considering recovery rate. Fig.2 shows the comparison of recovery rates by three extraction methods.

In ASE, a sample is extracted for 30minutes with about 50ml of solvent, and then extract is concentrated to final volume (1ml) for 1hr. Extraction process is conducted one by one sample, but concentration is conducted a batch of samples together. In soxhlet extraction, a sample is extracted for 24hrs using about 300ml of solvent, and then extract is concentrated to final volume (1ml) for 2hrs. Extraction process is simultaneously conducted a batch of samples, but concentration is conducted one by one sample. In sonication extraction, a sample is extracted for 20minutes with about 300ml of solvent, and then an extract is concentrated to final volume (1ml) for 2hrs. Both extraction and concentration process is conducted one by one sample. The time need to obtain final volume of extracts is about 4 hours using ASE compared with 36 hours using Soxhlet extraction and 14 hours using sonication extraction with a batch of samples (6 samples). Additionally using ASE compared with using both Soxhlet extraction and sonication extraction can reduce the amount of solvent to one-sixth times. ASE is known a process performed in minutes for fast and easy extraction with low solvent consumption because of applying elevated temperature and pressure.[4)]

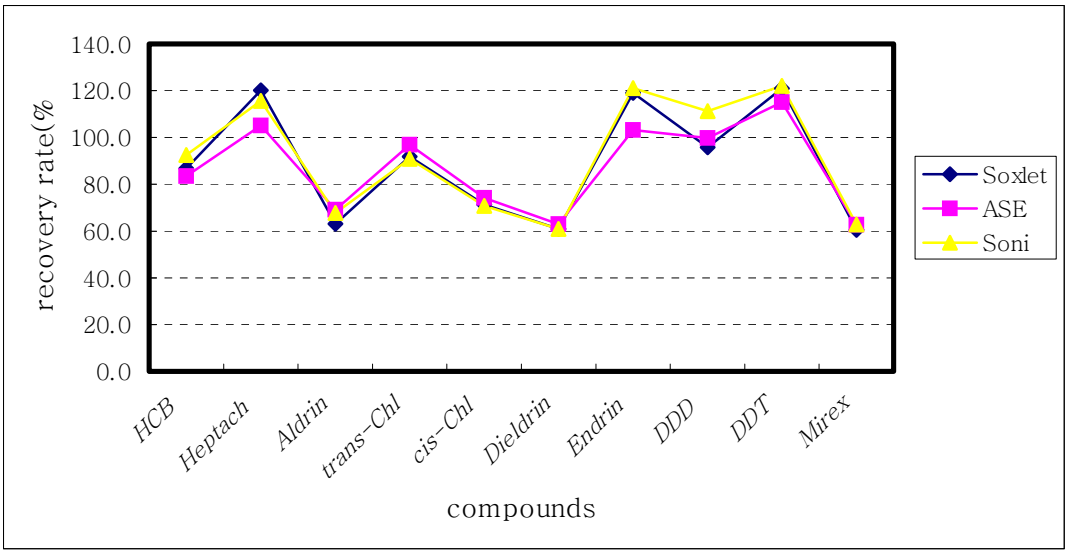

Fig. 2. Comparison of recovery rates of OC pesticides compounds by extraction methods

In order to find optimum extraction effectiveness of OC pesticides, solvents like diethyl ether in n-Hexane and acetone in n-Hexane with increasing polarity were applied to each extraction method. The recovery rates using different solvent are summarized in Table 4. The recovery rates of spiked samples using 5%, 10%, 20% diethyl ether in n-hexane solvent ranged from 63.0 %to 120.8%, from 62.4% to 120.3%, and from 63.4% to 123.1%, respectively. The recovery rates used 5%, 10%, 20% acetone in n-hexane solvent ranged from 58.2 %to 118.4%, from 62.6% to 120.1%, and from 59.1% to 116.7%, respectively.. There is a little different in

estimating recovery rate with solvent and its content ratio, but six solvents could be used as a sample extraction solvent for the determination of OC pesticides compounds in ambient air if compensating recovery rate to the calculation of compounds concentration. Fig.3 shows the comparison of recovery rates using different solvents.

Compounds	Spiked Level (ng)	5%D*		10%D		20%D	
		recovery rate (%)	RSD (%)	recovery rate(%)	RSD (%)	recovery rate(%)	RSD (%)
Hexachlorbenzene	0.3	92.4	4.8	92.1	2.4	90.6	3.4
Heptachlor	0.5	110.2	2.1	111.1	3.6	107.3	2.1
Aldrin	0.3	67.5	2.6	68.3	4.2	69.4	5.7
trans-Chlordane	0.5	95.5	9.1	96.2	9.9	96.7	9.9
cis-Chlordane	0.5	74.3	2.7	73.8	2.9	75.5	2.1
Dieldrin	0.5	63.0	4.2	62.6	4.6	66.5	3.0
Endrin	0.5	110.4	7.6	114.1	8.2	117.0	9.3
p,p'-DDD	0.3	116.4	8.7	119.4	9.1	112.4	9.8
p,p'-DDT	0.5	120.8	9.8	120.3	9.8	123.1	9.4
Mirex	0.3	63.9	2.0	62.4	3.1	63.4	4.5
Compounds		5%A**		10%A		20%A	
		recovery rate (%)	RSD (%)	recovery rate(%)	RSD (%)	recovery rate(%)	RSD (%)
Hexachlorbenzene	0.3	83.0	9.7	85.8	4.2	81.8	8.9
Heptachlor	0.5	113.1	3.5	105.3	4.6	109.5	4.9
Aldrin	0.3	63.2	6.1	67.5	4.8	63.6	5.0
trans-Chlordane	0.5	88.1	10.1	93.5	7.1	89.4	10.1
cis-Chlordane	0.5	69.3	3.4	72.2	4.3	67.3	4.6
Dieldrin	0.5	60.1	3.8	63.5	4.9	59.2	9.0
Endrin	0.5	111.3	9.7	115.0	9.9	109.9	9.5
p,p'-DDD	0.3	110.0	10.2	101.2	9.7	106.7	9.3
p,p'-DDT	0.5	118.4	9.8	120.1	9.3	116.7	6.7
Mirex	0.3	58.2	1.9	62.6	7.2	59.1	3.9

Table 4. Recovery rates of OC pesticides compounds using different extraction solvents (n=15)
(* D-diethyl ether in n-Hexane, ** A-aceton in n-Hexane)

In conclusion, although USEPA recommended Soxhlet extraction method with 5% diethyl ether in n-Hexane, [2] the comparison of extraction methods clearly showed that ASE is effective method in point of the lower solvent demand and less time consumption for the determination of OC pesticides compounds trapped into air filter and PUF cartridge in ambient air. Additionally acetone in n-Hexane could be used as a extraction solvent for OC pesticides.

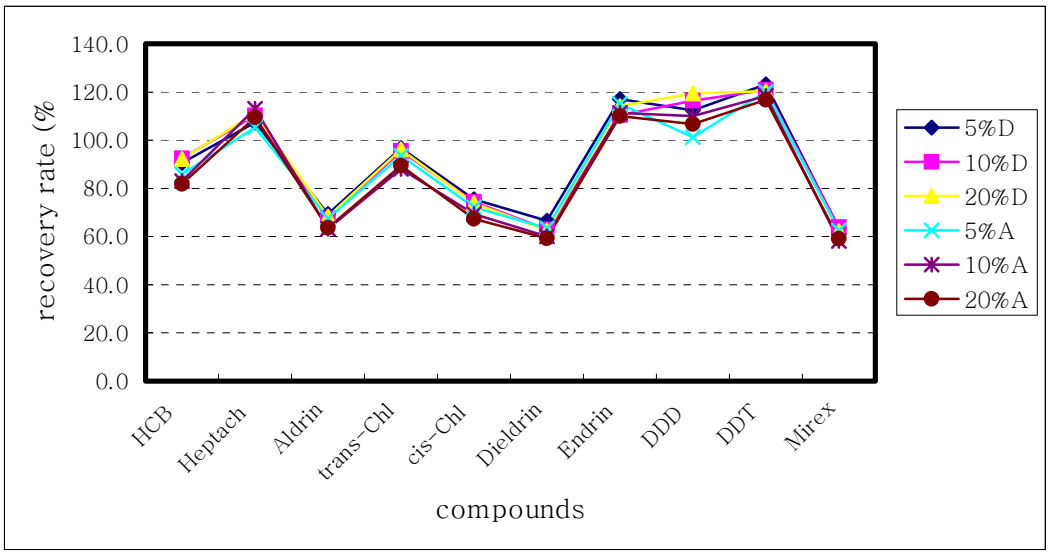

Fig. 3. Comparison of recovery rates of OC pesticides compounds with different solvents

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