

ANALYSIS

THE SAMPLING AND ANALYSIS OF PCDDs/PCDFs IN WATER SAMPLE BY MEANS OF CO-PRECIPIATION

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INTRODUCTION

During recent years a series of reports have shown the presence of PCDDs/DFs in various water samples, including drinking water^{5,8,9,13,14}, waste water^{1,6,7,11,13}, sea water⁴, lake and river water^{3,10}.

It is difficult to determine PCDDs/DFs in water sample for the very low concentration on account of the low solubility.²⁾ Many reports have shown data of PCDDs/DFs partitioned in the water sample between the dissolved phase and the particulate phase. Material that passes through a filter, usually of 0.45um pore size, is defined as dissolved phase. However, the presence of minute particulates less than 0.45um pore size has been recognized. PCDDs/DFs adsorbed to those particulates can not be trapped with XAD2 resin and not be extracted by organic solvents. A number of researchers have used PUF(Polyurethane foam), glass or paper filters and XAD2 resin for the determination. The figures of presence of PCDDs/DFs such as "dissolved", "colloidal" and "adsorbed" in water sample make the determination the discussion of result difficult.

Table 1 The advantage and the fault of PCDDs/DFs collection in water sample

Fraction	Particle-Bound		Dissolved		
	● Filtration	● Centrifugal Separation	● Liquid-Liquid Partition	● XAD-2	● PUF
Large Volume Treatment	△	×	△	⊙	⊙
Minute Particles Collection	×	⊙	×	×	△
Simple	⊙	△	⊙	○	○
Comment	Choking		High Extraction Efficiency		

Dioxin '97, Indianapolis, Indiana, USA

Lamparski, L.L., et al ^{6,7} reported that 80-99% of the 2378-TCDD in waste incinerator water adsorbed particulates larger than 1.2 μ m D. Some sampling methods have advantages and faults to partition PCDDs/DFs into both of "dissolved phase" and "particulate phase" (Table 1).

Accordingly, we have an idea to collect minute particles such as "colloidal" in water sample. In the present paper, we'll explain this method and report the results of determination of PCDDs/DFs in water samples using this method.

SAMPLING AND ANALYTICAL METHODS

Principle of sampling method is shown in Figure 1. At the beginning, Fe^{3+} is added to water sample collected at the rate 2g/20L in polypropylene container. Then $Fe(OH)_3$ precipitation is generated by addition of 5N- NH_4OH . This precipitation is treated by first filtration (No.1 paper filter) and redissolved with 2N-HCl. This residue is dried with acetone and extracted with dichloromethane by Soxhlet for 16 hours. The filtrate is extracted with Hexane at 2 times. Both solvents are combined and followed by reduction of its volume to 50-100 ml by a Kuderna-Danish (KD) concentrator. Cleanup procedure were described earlier¹². (Figure 2)

Seawater samples were taken from Seto Inland Sea on October 1994 and freshwater samples from some ponds in Matsuyama plain on October 1995.

★ Suspended particles were included in, adsorbed on floc and precipitated in water

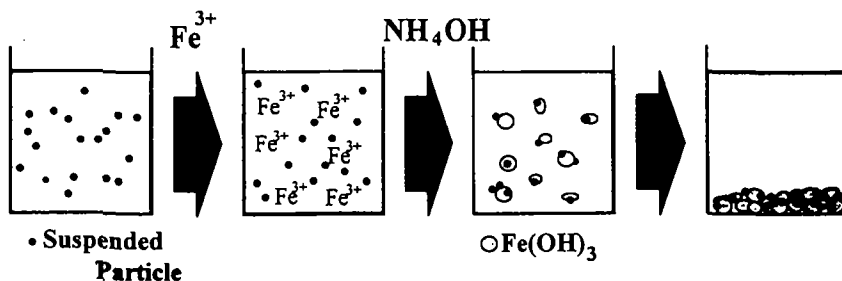


Fig.1 Definition of "Co-precipitation"

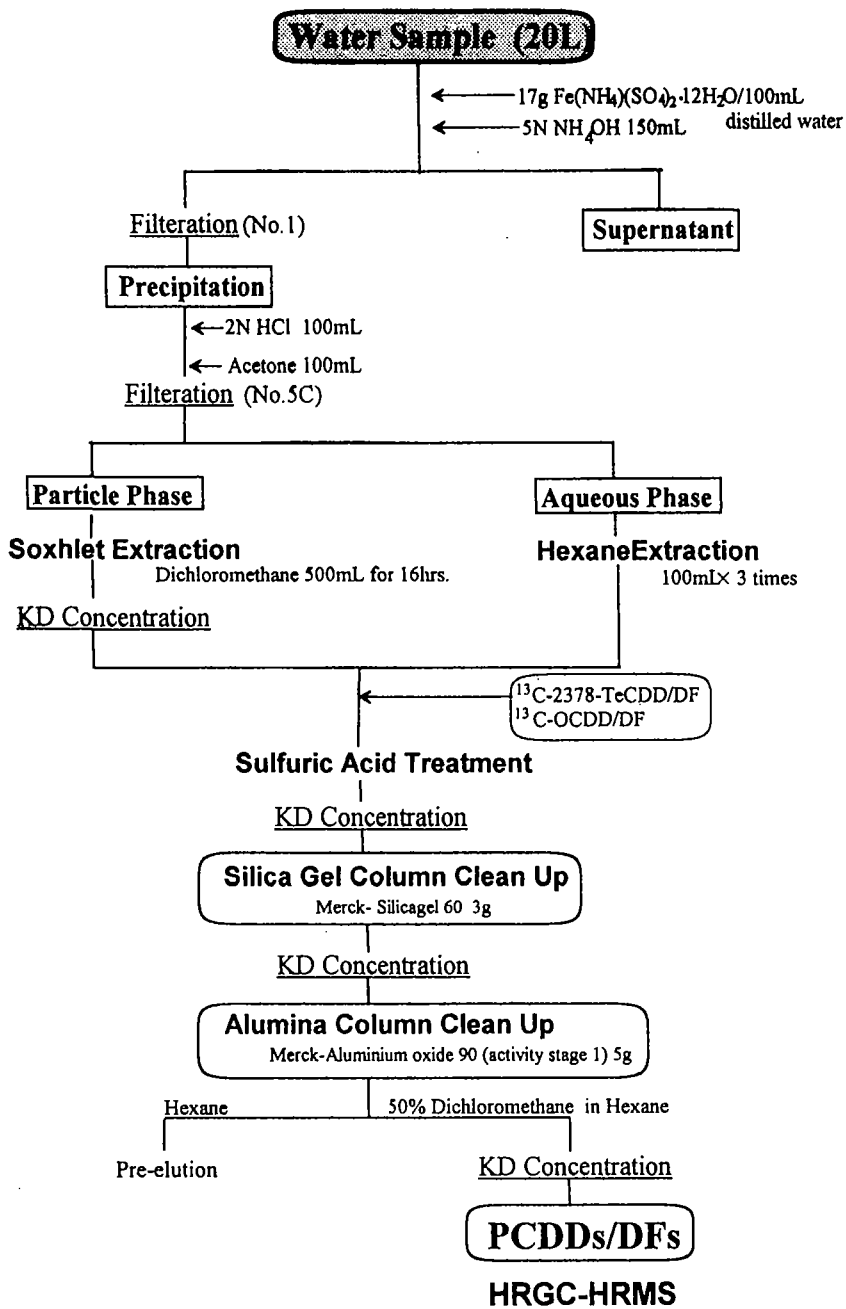


Fig. 2 Analytical procedure of PCDDs/DFs in water sample

Dioxin '97, Indianapolis, Indiana, USA

RESULT AND DISCUSSION

All results of PCDDs and PCDFs in water samples are shown in Table 2. Concentrations of them in seawater ranged from 8.3 to 168.2 pg/L. Isomer composition of PCDDs and PCDFs in this report showed to be originated from combustion such as fly ash of incinerator or herbicides such as CNP and PCP.

In fresh- water samples , PCDDs/DFs were detected higher levels than seawater.

CONCLUSION

1. Minute particles such as "colloidal" were collected efficiently from water sample by means of co-precipitation with $\text{Fe}(\text{OH})_3$.
2. For water samplee sampling volume of 20 L will allow a detection limit of 0.1pg/L.
3. The coagulation was held in spite of redissolving $\text{Fe}(\text{OH})_3$ precipitation by 2N-HCl and extracted with dichloromethane for 16 hours. This procedure gave an improvement for extraction efficiency of PCDDs/DFs.

Table 2 Concentrations(pg/L) of PCDDs/DFs in water sample

	Sea Water (n=8)		Fresh Water (n=4)	
	Range	Mean	Range	Mean
TeCDDs	<0.04 - 20.8	4.9	7.5 - 90	29
PeCDDs	<0.02 - 2.4	0.3	0.51 - 5.2	2.3
HxCDDs	<0.07 - 25.3	5.8	1.2 - 9.2	4.3
HpCDDs	<0.07 - 27	4.5	4.0 - 61	21
OCDD	2.1 - 48.5	20	25 - 340	190
Total PCDDs	11.4 - 124	35	39 - 505	250
TeCDFs	<0.04 - 8.1	1.7	0.77 - 2.6	1.6
PeCDFs	<0.04 - 21.3	4.5	0.81 - 3.1	1.6
HxCDFs	<0.02 - 6.8	1.9	0.80 - 6.0	2.6
HpCDFs	<0.03 - 8.1	1.3	0.81 - 6.5	2.7
OCDF	<0.1	0.1	<0.1 - 6.8	2.1
Total PCDFs	<0.1 - 44.3	9.4	3.5 - 25	11

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