

Behavior of Extractable Organic Halogens in a Municipal Solid Waste Incinerator and the Relationship with That of Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans

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Organic halogens (OX) extractable with a water-miscible organic solvent in samples from municipal solid waste incinerators (MSWIs) were determined quantitatively using apparatus for measuring total organic halogens in drinking water. Besides OX, polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in samples from MSWI were analyzed separately to compare their behavior in MSWI. OX was generated both in flue gas and the electrostatic precipitator and exhibited a linear correlation with both PCDD and PCDF, implying that PCDD and PCDF were derived from OX. These results show that OX is a useful surrogate marker for PCDD and PCDF in MSWIs.

Key words — organic halogen, municipal solid waste incinerator, polychlorinated dibenzo-*p*-dioxin, polychlorinated dibenzofuran

INTRODUCTION

Because highly toxic organic compounds such as polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are well known to be generated in municipal solid waste incinerators (MSWIs),¹⁾ a large number of studies have been carried out the

behavior of PCDD, PCDF and their precursors, such as polychlorinated biphenyls, chlorobenzenes and chlorophenols in MSWIs. Apart from these well known members, many other organic halogens (OX) have also been detected in MSWI samples,^{2–6)} although little is known about their toxicity and behavior. The detection of OX in MSWIs during operation is important for controlling the environmental pollution ascribed to these compounds. In fact, it has been reported that, in the case of PCDD and PCDF, the amount and composition of OX discharged from MSWIs depend on the incineration conditions.⁷⁾ Although it is difficult to monitor the behavior of individual OX components, they can be represented as a whole by OX. Furthermore, if there is a correlation between the behavior of PCDD/PCDF and OX, the latter could also act as a surrogate marker of the former.

Usually, organic compounds in samples from MSWIs, such as gaseous samples collected on XAD-2 resin and fly ash, are extracted with water-immiscible organic solvents (WIOS), such as benzene and toluene. Determination of OX in WIOS has been examined using total OX analyzers for drinking water (TOX analyzers).^{8,9)} For gaseous samples collected on a dodecyl sulfuric acid-bound DEAE-Sephadex (DS-Sephadex) column,¹⁰⁾ on the other hand, organic materials are eluted out with water-miscible organic solvents (WMOS), such as ethanol and acetone. When WMOS samples are applied to the TOX analyzer, the effect of polar organic solvents on the sample-retaining capacity of granular activated carbon columns is a major concern.

In this paper, we first investigated the effect of WMOS concentration on the determination of OX in WMOS samples. Then, OX, PCDD and PCDF in flue gas and fly ash samples were analyzed separately to compare their behavior in MSWI.

MATERIALS AND METHODS

Reagents — Pesticide-analysis grade hexane, benzene, ethanol, dichloromethane and anhydrous sodium sulfate (Na₂SO₄), and HPLC and IR grade toluene and carbon tetrachloride were obtained from WAKO Pure Chemical Ind. Ltd., Japan (WAKO). 1,2,3,4,5-Pentachlorobenzene (P5CBz) was used as an authentic material and an internal standard was obtained

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from Tokyo Chemical Industries, Japan. 2,3,7,8-Substituted tetra- to octachlorinated dibenzo-*p*-dioxins (T4 to O8CDDs) and tetra- to octachlorinated dibenzofurans (T4 to O8CDFs), $^{37}\text{Cl}_4$ -2,3,7,8-T4CDD, $^{13}\text{C}_6$ -2,3,7,8-T4CDF and $^{13}\text{C}_{12}$ -O8CDD were from Cambridge Isotope Laboratories Co. Ltd. Silica-gel 60, 70–230 mesh, and neutral alumina 90 active I, 70–230 mesh, were obtained from Merck. Granular activated charcoal (GAC, 100/200 mesh) for TOX analysis was obtained from Dohrmann Division Envirotech Corp. U.S.A. Other chemicals were of reagent grade and obtained from WAKO. Water was used after being deionized, distilled and extracted twice with hexane.

Apparatus—The DX-20 Total Organic Halide Analyzer System was obtained from Dohrmann Division Envirotech Corp. for OX analysis.

The GC-MS system for the analysis of PCDD and PCDF consisted of an MS (JMS SX-102A/JMA 7000 data system, JEOL) and GC (5890 Series 2, Hewlett-Packard) equipped with a capillary column SP-2331 (Supelco, 0.25 mm i.d. \times 60 m, 0.2 μm film) for T4 to hexachlorinated (H6C) DDs and T4 to H6CDFs, or SPB-5 (Supelco, 0.32 mm i.d. \times 30 m, 0.25 μm film) for heptachlorinated (H7C) DDs, O8CDD, H7CDFs and O8CDF.

Analytical Conditions—The pressure of O_2 for combustion and CO_2 as carrier gas for the TOX analyzer were both set at 1.8 kg/cm². The furnace was operated at $800 \pm 20^\circ\text{C}$ and the other conditions were those described in the TOX analyzer manual. The weight of GAC used as adsorbent was 40 ± 2 mg and three samples or more were measured.

The analytical conditions for GC-MS analysis for PCDD and PCDF have been described previously.¹⁰⁾

Incinerator—The continuous-system incinerator used in this study was equipped with a fluidized bed and an electrostatic precipitator (EP), with a capacity of 150 t per 24 h. The refuse was made homogeneous by mixing and incinerated under the routine operating conditions of the MSWI.

Sampling—Samples were collected independently for each experiment. Approximately 500 g fly ash samples were collected from the conveyor of the EP at intervals of 30 min during the gas sampling period, and made homogeneous by mixing, while approximately 1.4 to 2 Nm³ gaseous samples were collected at the boiler outlet, EP inlet and EP outlet by the gas sampling system connected to DS-Sephadex columns.¹⁰⁾

Determination of OX in WMOS—The organic compounds including OX, such as PCB, PCDD and

PCDF, trapped on the DS-Sephadex column were eluted with 200 ml ethanol as previously reported.¹⁰⁾ The eluates were combined and diluted to 1000 ml with ethanol in a volumetric flask (WMOS sample). A 50 ml portion of each WMOS sample was diluted with 500 ml water and extracted twice with 100 ml benzene. The extract was dried over Na_2SO_4 and concentrated using a Kuderna-Danish (KD) concentrator and the residue was weighed after solvent evaporation.

To investigate the effect of a polar organic solvent on the sample-retaining capacity of the GAC columns, two serially-connected GAC columns, *ca.* 40 mg each, were flushed with 100 ml sample solution containing 2.5 or 5% WMOS sample in an aqueous solution of 5, 10, 20, 30, 40 or 50% ethanol. OX was determined by the procedures used for drinking water.

To test the reliability of this method for the determination of OX in WMOS, 100 ml samples of aqueous 10% ethanol solutions containing 0, 1, 5, 10 and 25 μg P5CBz as Cl^- , with or without 50 μg WMOS sample, were individually passed through the dual GAC columns before the determination of OX.

To test the efficacy of this method for the determination of OX in actual samples in WMOS, 0, 25, 50, 100 or 200 ml WMOS sample diluted 10-fold with water (*ca.* 10% ethanol at final) was passed through the columns in the absence or presence of 2 μg P5CBz as Cl^- .

Comparative Study of the Behavior of OX, PCDD and PCDF—The gaseous samples collected on DS-Sephadex columns were eluted with 200 ml ethanol and diluted 10-fold with water. To remove metallic compounds and water-soluble materials for efficient extraction of organic compounds, 3000 ml 2 N hydrochloric acid was added to 300 g fly ash, and the mixture was allowed to stand with stirring at room temperature for 2 h and then filtered under reduced pressure. The filtrate was extracted twice with 200 ml benzene. The residue was extracted with 300 ml benzene using a Soxhlet extractor for 24 hours. The benzene extracts were combined and washed twice with 100 ml water. The extract was dried over Na_2SO_4 and concentrated using a KD concentrator. The drain water from the gaseous samples was extracted with 50 ml benzene. The filters and the dust on them were treated with 200 ml 2 N HCl and the organic compounds were extracted by the same procedures used for fly ash.

Each extract was divided into two equal volumes. One was used for OX analysis with P5CBz equivalent to 2 μg Cl^- . OX in WMOS samples was analyzed by

previous methods^{8,9)} with some modifications and that in WMOS samples was processed as described in the previous section. The second half was used for the analysis of PCDD and PCDF as previously described.¹⁰⁾

RESULTS AND DISCUSSION

Determination of OX in WMOS from MSWI Samples

Fairly constant OX values were obtained for both 2.5 and 5% WMOS samples prepared in 5 and 10% aqueous ethanol solutions as shown in Fig. 1. However, the samples in the aqueous solutions containing more than 10% ethanol gave reduced OX values compared with those in the aqueous solutions containing less than 10% ethanol. This phenomenon could be caused by a reduced retaining capacity of the GAC column for organic compounds with an increased ethanol concentration, part of the OX in the solutions passing through the columns. Therefore, the ethanol content in the sample solution should be kept at 10% or lower.

Using aqueous 10% ethanol samples, a linear correlation was obtained between the amounts of OX and P5CBz added to the assay system in the presence of 50 μg WMOS samples with satisfac-

tory R^2 values, in parallel with their correlation in the absence of WMOS samples, as shown in Table 1. OX determination by the column method does not seem to be affected by unknown substances in the gaseous sample extract. The correlation between the amounts of OX and those of added WMOS samples is linear, irrespective of the presence of 2 μg P5CBz as Cl^- (Table 2). The difference in the y-axes intercepts, *i.e.*, 2.0 μg , was equal to the amount of internal standard. It was confirmed that OX in WMOS from MSWI samples could be directly determined after being diluted with water using the TOX analyzer and the internal standard method.

Behavior of EOX, PCDD and PCDF in MSWIs and Their Relationship

Table 3 shows the concentrations of OX, PCDD and PCDF in flue gas and fly ash, their hourly converted amounts and the abundance ratios of PCDD and PCDF to OX, where the hourly amount was calculated by [concentration] \times [gas volume passed at sampling point for 1 h] or [weight of fly ash generated in EP for 1 h]. The hourly amount at EP was the sum of that in the flue gas at the EP outlet and in the fly ash per 1 h of the sampling period.

The concentrations of PCDF were higher than those of PCDD in both the flue gas and fly

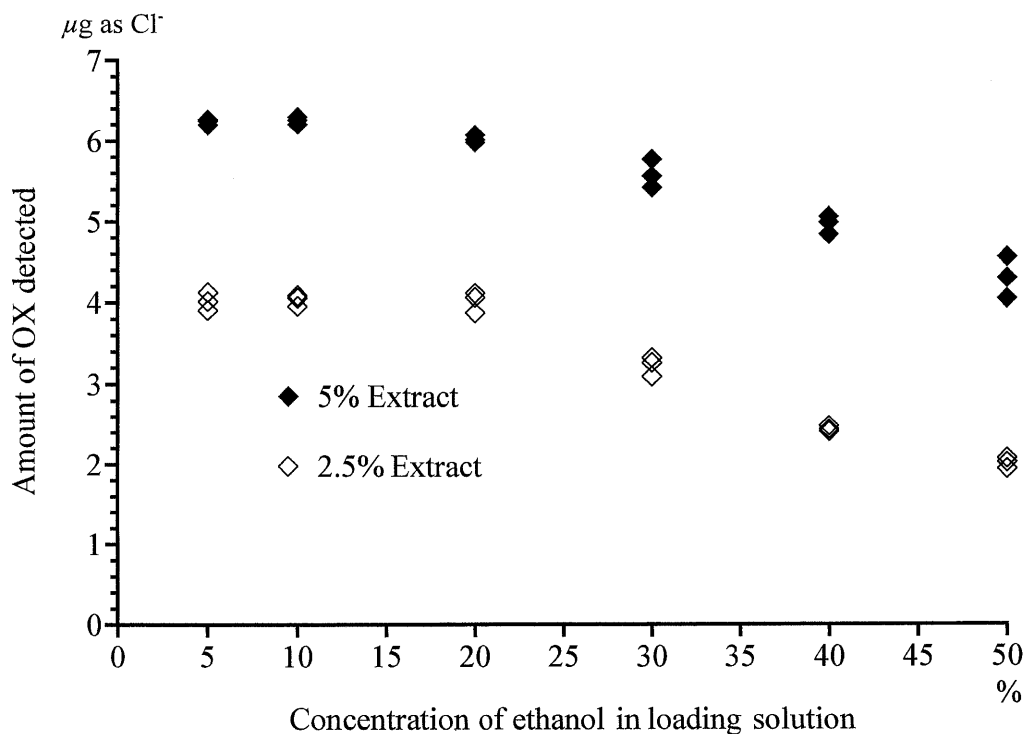


Fig. 1. Effect of Ethanol Concentration in Loading Solution on OX Measurement in the Column Method

Table 1. Effect of a 50 μg WMOS Sample on the Correlation between the Amount of OX Detected and That of P5CBz Loaded on Activated Carbon Columns

Amount of P5CBz as Cl^- loaded	Amount of OX detected (μg as Cl^-)				
	Exp. ^{a)} 1	Exp. 2	Exp. 3	Average	S.D. ^{b)}
0 μg	1.29	1.45	1.30	1.35	0.09
+50 μg WMOS sample	3.18	3.28	3.37	3.28	0.10
1 μg	2.14	2.18	2.20	2.17	0.03
+50 μg WMOS sample	4.31	4.21	4.09	4.20	0.11
5 μg	5.90	6.10	6.01	6.00	0.10
+50 μg WMOS sample	7.76	8.33	8.63	7.91	0.37
10 μg	10.29	10.95	10.28	10.51	0.38
+50 μg WMOS sample	11.92	12.06	11.86	11.95	0.10
25 μg	24.54	24.41	23.9	24.28	0.34
+50 μg WMOS sample	26.15	25.91	26.25	26.10	0.17
Correlation between amount of OX detected and Amount of P5CBz (as Cl^-) loaded	Equation [$f(x)=ax+b$] ^{c)} and contribution ratio (R^2) calculated by least square method				
+50 μg WMOS sample	$f(x)=0.91x+1.33$ $R^2=0.9991$ $f(x)=0.91x+3.22$ $R^2=0.9994$				

a) Exp. is experiment. b) S.D. is standard deviation. c) The "a" value is the slope of the line meaning the ratio of the OX amount to the loaded amount of P5CBz, and the "b" value is the y-axis intercept meaning the sum of the amount of OX in the carbon columns, as the blank value, and that of 50 μg WMOS sample.

Table 2. Effect of P5CBz (2 μg as Cl^-) on the Correlation between the Amount of OX Detected and That of WMOS Sample in 10% Ethanolic Solution Loaded on Activated Carbon Columns

Volume of WMOS sample solution loaded	Amount of OX detected (μg as Cl^-)				
	Exp. ^{a)} 1	Exp. 2	Exp. 3	Average	S.D. ^{b)}
0 ml	1.85	1.66	1.79	1.77	0.10
+2 μg P5CBz as Cl^-	3.78	3.88	3.65	3.77	0.12
25 ml	4.01	3.96	4.08	4.02	0.06
+2 μg P5CBz as Cl^-	5.98	6.03	5.82	5.94	0.11
50 ml	6.21	6.40	6.11	6.24	0.15
+2 μg P5CBz as Cl^-	8.33	8.19	8.33	8.28	0.08
100 ml	11.14	10.85	10.97	10.99	0.15
+2 μg P5CBz as Cl^-	13.32	12.99	13.05	13.12	0.18
200 ml	20.85	21.06	20.96	20.96	0.11
+2 μg P5CBz as Cl^-	22.99	22.85	22.67	22.84	0.16
Correlation between amount of OX detected and Volume of WMOS sample solution	Equation [$f(x)=ax+b$] ^{c)} and contribution ratio (R^2) calculated by least square method				
+2 μg P5CBz as Cl^-	$f(x)=0.096x+1.58$ $R^2=0.9993$ $f(x)=0.096x+3.60$ $R^2=0.9995$				

a) Exp. is experiment. b) S.D. is standard deviation. c) The "a" value is the slope of the line meaning the ratio of the OX amount to the loaded volume of WMOS sample, and the "b" value is the y-axis intercept meaning the sum of the amount of OX in the carbon columns, as the blank value, and that of added P5CBz.

ash, as already well known for fluidized bed incinerators. The hourly amounts of OX, PCDD and PCDF could be ranked as follows: boiler inlet < EP inlet < EP and this also reflected the abundance ratios of PCDD and PCDF to OX. Based on these findings, OX including PCDD and PCDF were considered to be generated in the gas flow route and EP, and PCDD and PCDF were

converted from OX. Furthermore, the fact that the abundance ratios of PCDD and PCDF to OX were the lowest in flue gas at the EP outlet and the highest in fly ash suggests that most of the PCDD and PCDF in the flue gas is removed with dust in EP as fly ash. This might result from the difference in the vapor pressures of materials in the flue gas, resulting in condensation of lower

Table 3. Concentrations and Hourly Converted Amount of OX, PCDD and PCDF and Abundance Ratio of PCDD and PCDF to OX in Flue Gas and Fly Ash

	Concentration (/Nm ³ , g)			Amount converted per hour ^{a)}			Abundance ratio (%)	
	OX (μg)	PCDD (ng)	PCDF (ng)	OX (mg)	PCDD (μg)	PCDF (μg)	PCDD	PCDF
Flue gas at boiler inlet	610	234	409	17.1	6.6	11.5	0.039	0.067
Flue gas at EP inlet	780	423	614	23.6	12.8	18.6	0.054	0.079
Flue gas at EP outlet	491	83	151	15.3	2.6	4.7	0.017	0.031
Fly ash	31.9	34.2	54.1	10.6	11.3	17.9	0.107	0.169
at EP ^{b)}	—	—	—	25.9	13.9	22.6	0.054	0.087

a) These values were calculated from concentrations, gas volumes passed at sampling points and fly ash weight accumulated per hour.

b) Amount at EP is the sum of that in flue gas at the EP outlet and fly ash.

vapor pressure OX, such as PCDD and PCDF, onto dust.

A linear correlation with good R^2 values was observed between the concentration of OX and that of PCDD and PCDF in flue gas (Fig. 2) and the hourly amount of OX and that of PCDD and PCDF at each point of the MSWI (Fig. 3). These findings show for the first time that there are proportional relationships between the behavior of OX and that of PCDD and PCDF in MSWI. Although it remains to be confirmed, it may be possible to deduce the behavior of highly toxic OX, such as PCDD and PCDF, by using OX as a surrogate marker.

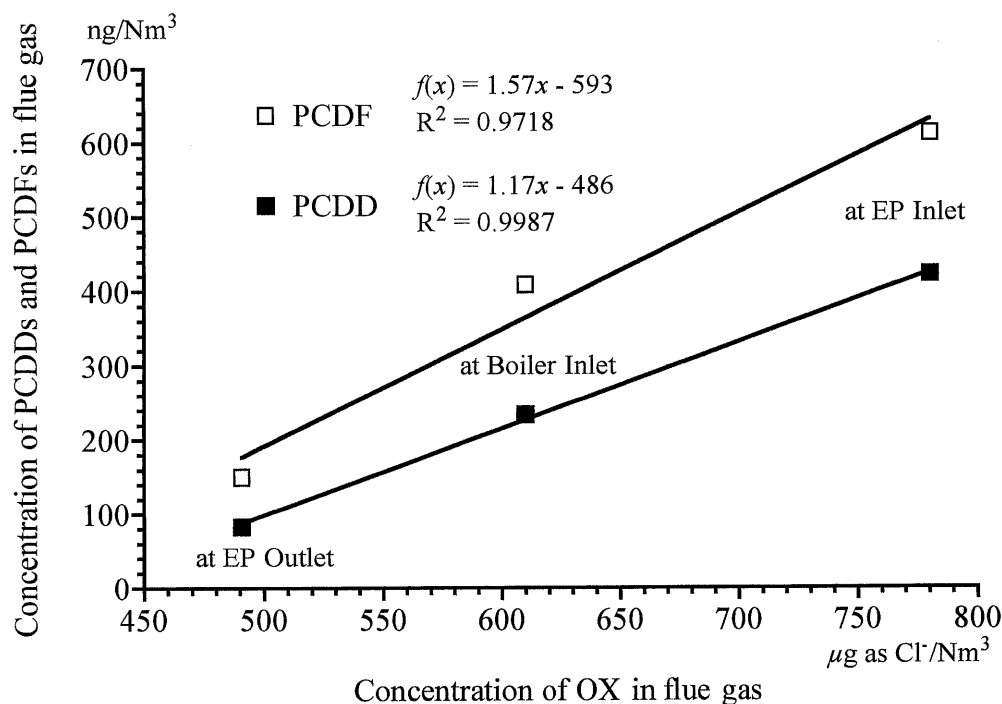
In conclusion, the monitoring of OX in MSWIs is useful in studies of the generation of

OX, including PCDD and PCDF, and monitoring environmental pollution involving the operation of MSWIs.

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**Fig. 2.** Correlation between Concentration of OX and That of PCDD and PCDF in Flue Gas

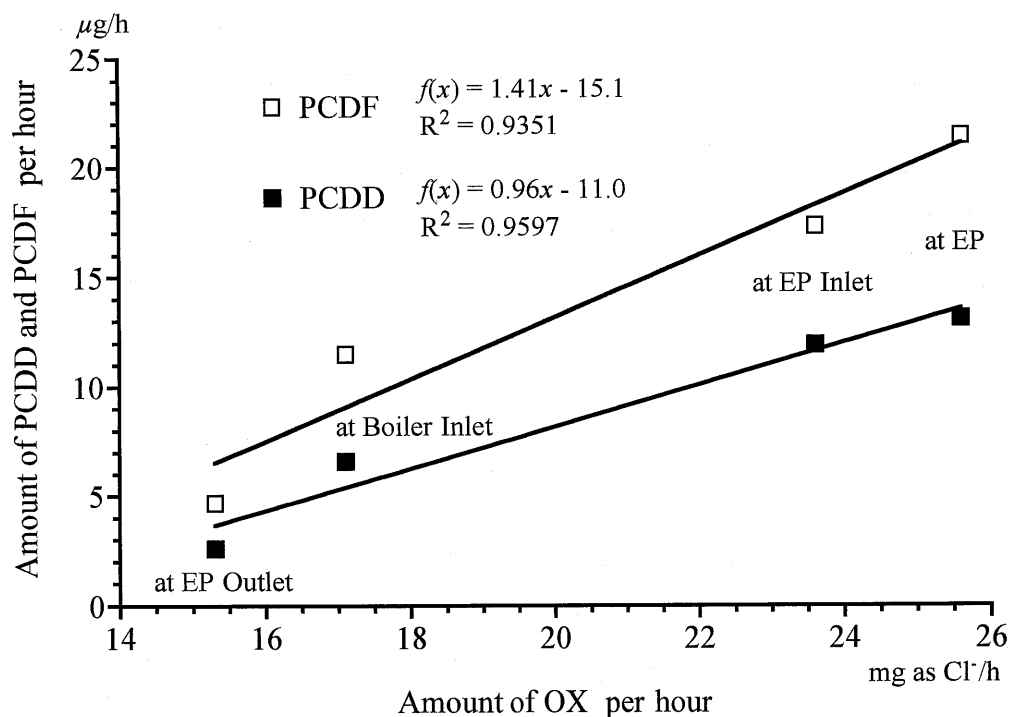


Fig. 3. Correlation between Amount of OX per Hour and That of PCDD and PCDF in MSWI

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