

Efficient Investigation of Dioxin Pollution Using Dioxin-like-Cl

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Introduction

Dioxins such as polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (Co-PCBs) in various media are currently analyzed according to a method that requires complex pretreatment techniques and expensive analytical instruments (e.g., HRGC/HRMS, hereinafter “standard method”).^{1, 2} The standard method is extremely impractical for research, monitoring, or screening of emission sources or severely dioxin-polluted areas because it is time-intensive and costly to analyze numerous samples. For that reason, we have developed a measuring method of Dioxin-like-Cl. The method is more rapid and cost-effective than the standard method using HRGC/HRMS.³

This study proposes a new investigation method of dioxin pollution using Dioxin-like-Cl – the total amounts of chlorine bonded in dioxins and dioxin-like compounds. Applicability of the new investigation method in flue gas, fly ash, soil, and sediment is also demonstrated.

Materials and methods

Flue gas samples were collected from 10 waste incineration facilities; the sampling method of flue gas was performed using a modified standard method for PCDDs, PCDFs, and Co-PCBs analyses, whose details are given elsewhere.^{4,5} Fly ash samples were collected from dry electrostatic precipitators or bag filters of 23 waste incineration facilities. Soil samples were collected at 14 sites around waste incineration facilities. The sediment samples were collected at 30 sites in six rivers using an Ekman-Birge type bottom sampler.⁶

Flue gas samples containing suspended particulates were filtered before liquid-liquid extraction with toluene; the filtered particulates were subsequently dehydrated with ethanol and extracted with toluene. The fly ash samples treated by HNO₃, along with soil, and sediment samples were also dried in air or with ethanol and extracted using a Soxhlet-extractor or a High-speed Solvent Extractor (SE-100; Mitsubishi Chemical Corp.)⁷ with toluene.

The pretreatment procedure for analysis of Dioxin-like-Cl was performed using H₂SO₄ silica/silica gel column comprised of sequential layers of sodium sulfate anhydride, 44wt% H₂SO₄ silica gel, and silica gel (AgNO₃ silica gel was added in the case of the sediment sample). Subsequently, the pretreated extracts were concentrated to exactly 500 μl.³ Concentrations of Dioxin-like-Cl in the pretreated and concentrated extracts that contained only those compounds sharing similar reactivity and polarity to dioxins were analyzed using combustion ion chromatography, which was provided by Mitsubishi Chemical Corp., according to our research.^{3, 4} The diagram of this analyzer is shown in Fig. 1; analytical conditions are given in Table 1. Pretreated extracts were set on a silica boat and put into a furnace at 900°C. Combustion of samples in a furnace converted dioxins and dioxin-like compounds into hydrogen chlorides (HCl). The HCl was absorbed into NaOH solution. Concentrations of Cl⁻ in the solution were analyzed using ion chromatography. Finally, concentrations of Dioxin-like-Cl were calculated from Cl⁻ concentrations. The total analysis time was approximately 20 min.

In addition, the pretreatment procedure for analysis of dioxins was performed using a multi-layer silica gel column and an activated alumina column according to the standard method. Concentrations of respective tetra-chlorinated to octa-chlorinated homologues and 2,3,7,8-substituted congeners of PCDDs/PCDFs and Co-PCBs were analyzed using HRGC/HRMS (JMS-700; JEOL).

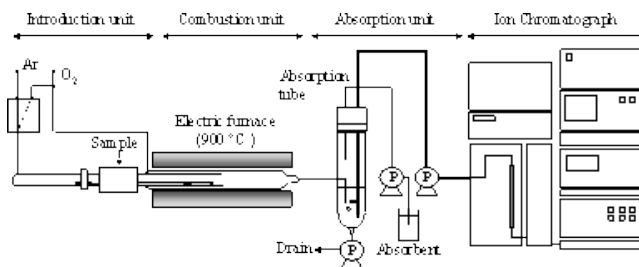


Fig. 1. Combustion Ion Chromatography Apparatus.

Table 1. Analytical conditions of Dioxin-like-Cl.

Combustion conditions		Conditions of ion chromatography	
Instrument	AQF-100, Mitsubishi Chemical Corp.	Instrument	HIC-10vp, Shimadzu Corp.
Furnace temp.	900 °C	Detector	Conductimetry detector, CDD-10vp
Ar gas	100 ml/min → inlet boat (3.5 min hold) → switchover O ₂ (3 min hold)	Column	Shim-pack IC-SA2
O ₂ gas	400 ml/min	Carrier liquid	Sodium hydrogen carbonate 1.2 × 10 ⁻³ mol/l Sodium carbonate 6.0 × 10 ⁻⁴ mol/l
Set volume	50 μl	Flow rate	1.2 ml/min
		Column oven temp.	45 °C
		Injection volume	300 μl

Results and Discussion

Correlations between concentrations of Dioxin-like-Cl and TEQ concentrations of dioxins are shown in Fig. 2; the emission or environmental criteria in Japan are also described as examples in Fig. 2. The respective coefficients of determination (r^2) in flue gas, fly ash, soil, and sediment were 0.937, 0.887, 0.900, and 0.914. For that reason, correlations between concentrations of Dioxin-like-Cl and TEQ concentrations of dioxins in flue gas, fly ash, soil, and sediment proved to be strong correlations.

On the other hand, correlations between concentrations of total semi- and non-volatile organic chlorine in concentrated raw extracts and concentrations of dioxins showed low correlation. The coefficients of determination were typically less than 0.8 because concentrated raw extracts contained numerous organohalogen compounds aside from dioxins. The contribution ratios of chlorine bonded in dioxins and Dioxin-like-Cl pretreated with H₂SO₄ silica/silica gel column in the total semi- and non-volatile organic chlorine of flue gas are shown in Fig. 3 as examples. Furthermore, concentrations of Dioxin-like-Cl pretreated with "multi-layer silica gel column" or "H₂SO₄ silica/silica gel column and activated alumina column" were nearly equivalent to concentrations of Dioxin-like-Cl pretreated with "H₂SO₄ silica/silica gel column". Therefore, we concluded that Dioxin-like-Cl pretreated with "H₂SO₄ silica/silica gel column" was suitable and useful for estimating TEQ concentrations of dioxins.

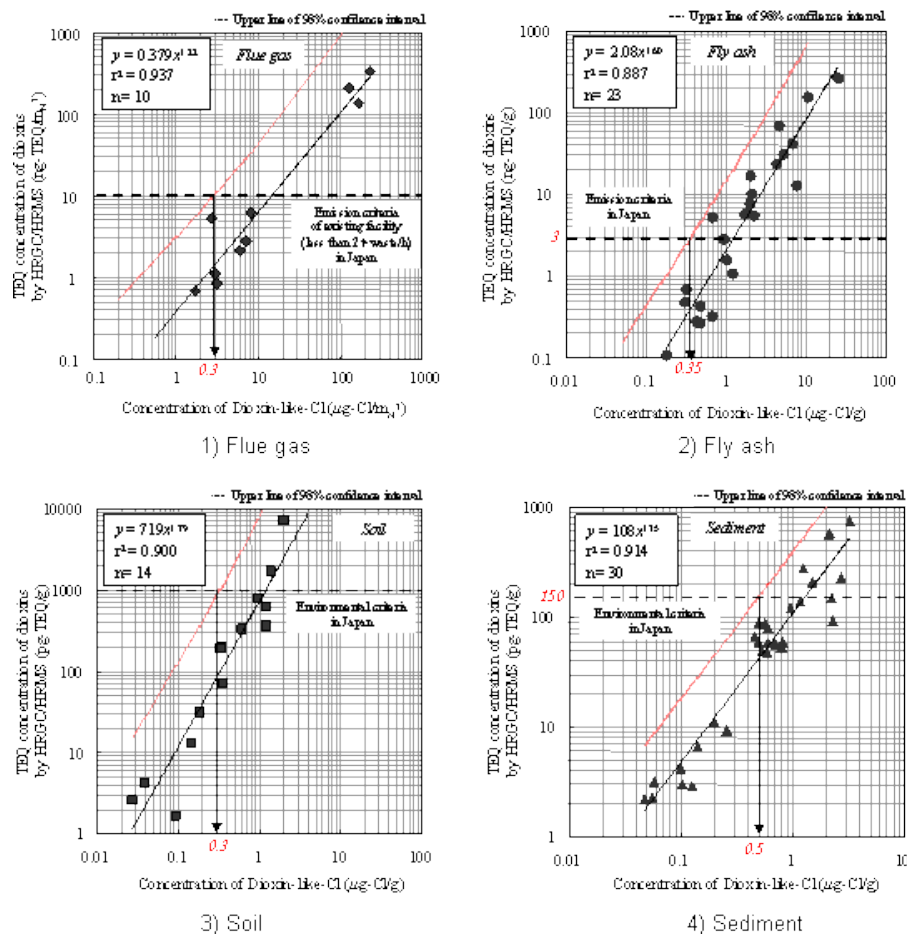


Fig. 2. Relationships between concentrations of Dioxin-like-Cl pretreated with H_2SO_4 silica/silica gel column and TEQ concentrations of dioxins using the standard method in flue gas, fly ash, soil, and sediment.

An estimation method of TEQ concentrations of dioxins from concentrations of Dioxin-like-Cl pretreated with H_2SO_4 silica/silica gel column, along with its reliability, are presented herein. The false negative rate

(i.e., false rate in the estimation that the TEQ concentrations of dioxins do not exceed the emission or environmental criteria) would be approximately 50% in usual estimation methods of TEQ concentrations of dioxins from the exponential regression lines. This study proposed an estimation method of TEQ concentrations of dioxins using upper lines of 98% confidence intervals for exponential regression lines while taking into account the data variability (Fig. 2). The estimation method would provide a smaller false negative rate than 1%, which is sufficient for judging that the TEQ concentrations of dioxins do not exceed the emission or environmental criteria. Therefore, only if the TEQ concentrations of dioxins exceed the emission or environmental criteria (i.e., the concentrations of dioxin-like-Cl exceed $0.3 \mu\text{g-Cl}/\text{m}_\text{N}^3$ in flue gas as an example), it is necessary to merely identify the TEQ concentrations of dioxins in those samples using the standard method. Therefore, our proposed method is extremely useful for research, monitoring, or screening of emission sources or highly-polluted areas of dioxins because the method provides some information regarding site contamination in only one or two days after sampling.

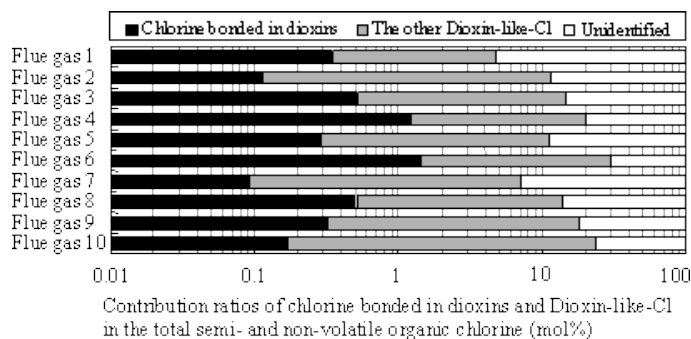


Fig. 3. Contribution ratios of chlorine bonded in dioxins and Dioxin-like-Cl pretreated with H_2SO_4 silica/silica gel column in total semi- and non-volatile organic chlorine of flue gas.

References

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