TOX AS A NOVEL ALTERNATIVE INDEX OF DIOXINS IN FLUE GAS

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Introduction

The formation and emission of PCDDs and PCDFs (dioxins) is an increasingly serious issue in Japan where incineration is the most important method for the disposal of municipal solid waste. Although criteria for dioxins emission in incineration plants were established, monitoring of dioxins has been problematic due to the high cost and time-consuming nature of the measurement. Therefore, a more cost- and time-efficient measurement technique is strongly needed. Alternative flue gas indices such as chlorobenzenes and chlorophenols were already proposed and many data were accumulated [1]. A novel index for dioxins in flue gas is proposed in this paper, which enables rapid, easy and safe measurement.

Material and methods

Activated carbon

A measurement method proposed in this study is based on adsorption of gaseous organo-halogen compounds by a special grade activated carbon. The properties of the activated carbon are shown in Table 1. It is very important to minimize the halogen constituents (both of organic and inorganic) in the activated carbon. The distinctive feature of the carbon in this study is that the halogen blank is very low. Proper particle size and amount of needed for gas sampling was also taken into account. A column with an inner diameter of 15 mm contains 500 mg of carbon that is derived from combustible amount.

Table 1 Activated carbon used as adsorbent

Item	Value
Specific surface area (m^2/g)	1100
Volume of micropore (ml/g)	0.7 (<30 nm)
	0.2 (<1 nm)
Halogen blank (μg-Cl/g)	< 2
Particle diameter (mm)	1.00~1.68

Sampling of flue gas

Figure 1 shows a sampling train of flue gas, which is sampled via a probe from the stack and drain is collected in glass bottles. It does not include a dust collector and is made as simple as possible. A gas stream that goes through the bottles enters a sequence of 3 ~ 5 activated carbon columns at a gas flow rate of 3 ~ 5 l/min. The sampling time is set to four hours which is the same time used for dioxin measurements in field sampling at incineration plants. The total sampling volume of gas is 0.7 ~ 1.2 m^3 per four hours.

Two terms are defined here in relation to the sampling method. TOX (Total Organic Halogen) is defined as organo-halogen compounds collected both in the water drain and in the activated carbon columns. VTOX (Volatile Total Organic Halogen) is defined as only components collected by activated carbon columns. The contents of VTOX are considered to be volatile and water insoluble compounds such as low molecular chlorobenzenes; whereas, TOX includes water soluble or low volatile compounds such as chlorophenols and minor dioxins.

Flue gas samplings were conducted at incineration plants of municipal solid waste and of industrial wastes in Japan.

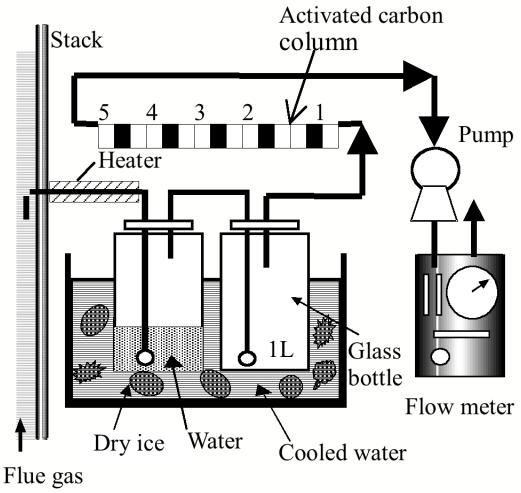

Fig.1 Sampling train of TOX in flue gas

Determination of TOX

Figure 2 shows a schematic of the TOX measurement system. Activated carbon particles are rinsed with a nitrate solution to eliminate inorganic chlorine. This is an essential process because incineration flue gas includes gaseous hydrogen chloride. The carbon particles are moved to a silica glass boat and burned completely in an electric furnace that is kept 900 °C. Halogenated organics are transformed to halogenated hydrogen and the generated amount is determined by electrochemical titration, which leads to TOX expressed as chlorine amount (μg-Cl/m^3).

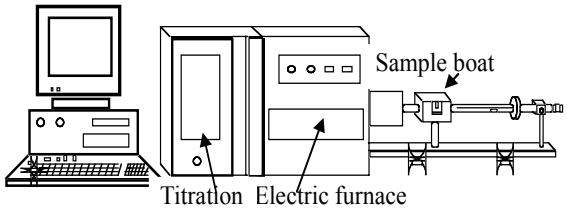

Fig. 2 TOX measurement system

Results and discussion

Activated carbon column in sampling train

Figure 3 shows the determined TOX in each of the columns in two different plants. Amounts collected by the four columns reached almost 100 % in the case of plant A; whereas, amounts collected by three columns reached 99 % in the case of plant B. There should be as few columns as possible to minimize the measurement time. As a consequence, the number of activated carbon columns needs to be at least three or four.

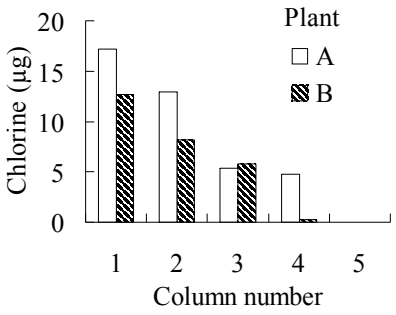

Fig. 3 Collection of TOX by each column

Pre-procedure for the determination of TOX

Figure 4 shows the removal of chloride ion derived from hydrogen chloride added to columns artificially.

Ammonium nitrate was used in this experiment. Nitrate solution removed chloride ion faster and more effectively than distilled water. In each case, 20 ml was enough to completely elute the chloride ion. From these experiments, we determined that the optimum rinse was 20 ml of 0.8 % KNO_3 followed by distilled water.

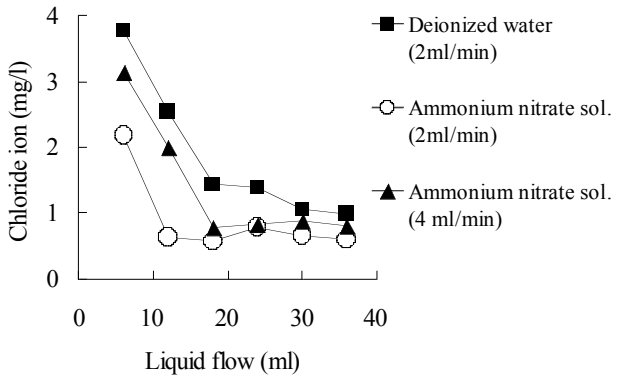

Fig.4 Effect of rinse of chloride ion

TOX and VTOX in incineration flue gas

Table 2 shows examples of measurement data of TOX, VTOX and dioxins in incineration plants that we continuously operated (24 h/d) by some large local governments. Plant No. 5 employs recently developed bag filter process for removing dust, acid gas and dioxins. Although the concentration of dioxins was very low (0.0011 ng-TEQ/m^3_N), the TOX and VTOX were not too low. This fact suggests that the contents expressed by TOX or VTOX includes more volatiles than dioxins and that the pollutants behave in a different manner in the gas filtration process. Furthermore, the VTOX/TOX ratio which varies from 0.54 ~ 0.89 shows that the major constituents of TOX are volatile halogenated organics. Most of halogen content is recognized to be chlorine in another investigation.

Table 2 VTOX, TOX and DXNs in incineration flue gas*

Plant No.	VTOX ($\mu g/m^3_N$)	TOX ($\mu g/m^3_N$)	VTOX / TOX (-)	DXNs (ng/ m^3_N)	DXNs (ng-TEQ/ m^3_N)
1	132	166	0.79	88	1.4
2	170	200	0.85	41	0.65
3	366	410	0.89	41	0.68
4	48.1	82.0	0.59	44	0.81
5	28.2	52.6	0.54	0.77	0.0011
6	124	165	0.75	240	5.1

* All concentration values are translated to ones at 12% O_2.

Correlation between TOX/VTOX and dioxins

A correlation between TOX/VTOX and dioxins would have great practical utility. Figures 5, 6 and 7 show the correlations we have found in this study. The figures suggest that there are good correlations and that there are many halogenated organic compounds in the samples than dioxins [1,2]. The results lead to the following correlation equations :

$$\text{PCDDs/PCDFs} = 6.33 \times 10^{-2} \, (\text{VTOX})^{1.34} \qquad (1)$$

Where, Correlation coefficient R = 0.627

PCDDs/PCDFs : ng/m^3_N @12% O_2

VTOX :μ g/m^3_N @12% O_2

$$PCDDs/PCDFs = 2.80 \times 10^{-2} (TOX)^{1.45} \quad (2)$$
$$R = 0.811$$
$$TOX : \mu g/m^3_N @12\% O_2$$

$$PCDDs/PCDFs\ (TEQ) = 1.20 \times 10^{-4} (TOX)^{1.66} \quad (3)$$
$$R = 0.783$$
$$PCDDs/PCDFs : ng\text{-}TEQ/m^3_N$$

These equations enabled simple and rapid estimate of dioxins and emphasis was placed on the usefulness as an alternative index of daily operation in incineration plants.

Acknowledgement
The author thanks Mitsubishi Chemical Corporation for the generous offer of activated carbon and TOX measurement apparatus.

References

1. Kawamoto K; *J. Japan Soc. Air Pollut.* **1993**, 28, 266
2. Abed E, Caixach J and Rivera J; *Chemosphere* **1999**, 38, 109

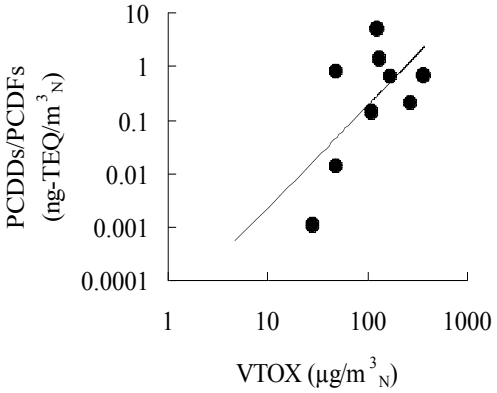

Fig.5 Relationship between VTOX and dioxins

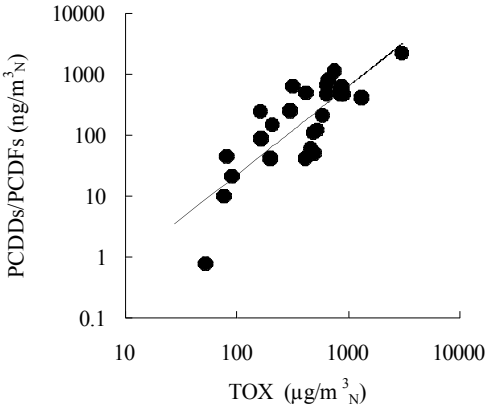

Fig.6 Relationship between TOX and dioxins

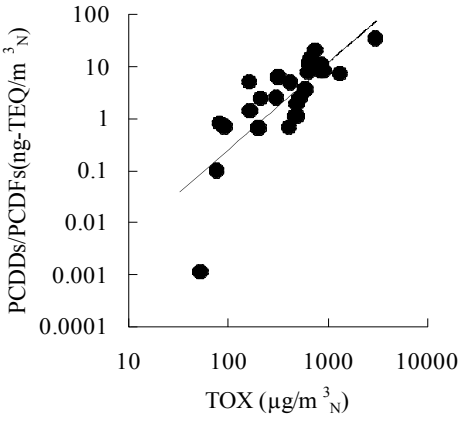

Fig.7 Relationship between TOX and dioxins toxic equivalent