

## **CORRELATION OF LOW VOLATILE ORGANIC CHLORINE (LVOCI) AND PCDD/Fs IN VARIOUS MUNICIPAL WASTE INCINERATORS (MWI)**

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### **Introduction**

Formation of PCDD/Fs through combustion has been a matter of concern for a few decades. As research on the formation mechanism has advanced, it has been revealed that PCDD/Fs are only a limited fraction of the various organic chlorinated compounds. For this reason, the group parameter of “organic halogens” is considered to be a good indicator or surrogate for PCDD/Fs<sup>1,2</sup>).

However, the traditional method of halogen determination using combustion – coulometric titration is neither selective nor sensitive to the elements. This problem was overcome by the development of atomic emission spectrometry (AES) detection of halogens using radiofrequency helium plasma. This method was initially introduced by Rice et al<sup>3)</sup> in 1985 as a GC detector and improved by others<sup>4,5)</sup>. We have modified the plasma to barrier discharge and simplified the optical detection<sup>6)</sup>. Gaseous organic chlorine was determined by adsorptive collection and direct introduction of thermally desorbed sample to the plasma.

In order to examine the correlation of organic chlorine and PCDD/Fs, we have measured organic chlorine in conjunction with the legislated periodical PCDD/Fs inspections of MWI stack gas emissions in Osaka City, Japan. From data collected during 2001, a fairly good correlation between low-volatile organic chlorine

(LVOCl) and PCDD/Fs was found, while semi-volatile organic chlorine (SVOCl) gave a poor correlation with PCDD/Fs<sup>7</sup>).

However, a study conducted in 2002 resulted in some shift of the regression line of LVOCl – PCDD/Fs. As the determination of LVOCl involves fractionation based on boiling points (b.p.), it is expected that removal of PCDD/Fs with adsorptive devices influences the regression. In this paper, the experimental results are summarized and the effect of the gas treatment condition on the correlation between LVOCl and PCDD/Fs is discussed.

## Methods and Materials

### *Sampling and determination*

Stack gas from MWI was sampled as shown in Fig. 1. Drawn gas was introduced to a drain trap to remove moisture and sampled in two adsorption tubes. The front tube contained 0.3 g of 20/40 mesh Carbotrap C, while the latter contained 0.3 g of 20/40 mesh Carbotrap B. The flow rate and the sampled gas were 2 L/min and 10~40 L, respectively.

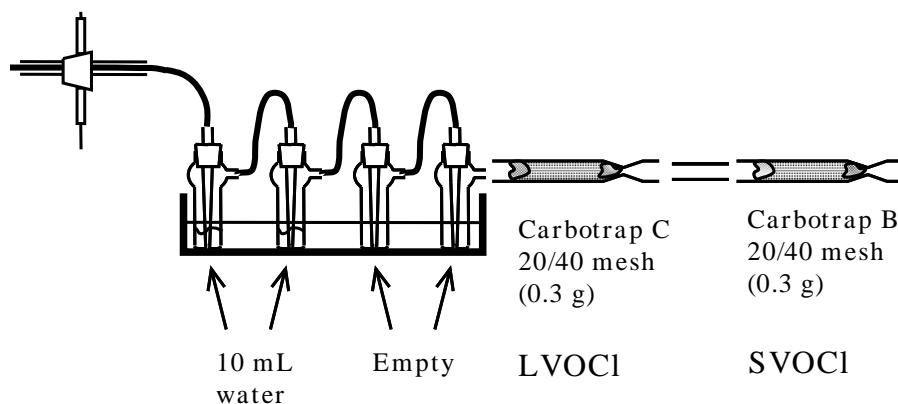


Fig. 1 Sampling apparatus

The fractionation conditions<sup>8)</sup> of SVOC and LVOC are summarized in Table 1. The organic chlorinated compounds collected in the front tube were LVOC with boiling points ranging about 150~270 °C. As more volatile organic compounds were not adsorbed in the front tube, the compounds with boiling points around 70~150 °C, SVOC, was collected in the latter tube. The tubes were brought to the laboratory and thermally desorbed chlorine was quantified by helium barrier discharge – AES<sup>6,7)</sup>.

| Group parameter                          | Fraction conditions  | Boiling point (°C) |
|--|--|--------------------|
| SVOC<br>(Semi volatile organic chlorine) | Not captured in drain trap<br>Not adsorbed to Carbotrap C<br>Adsorbed to Carbotrap B | ca. 70 ~ ca. 150   |
| LVOC<br>(Low volatile organic chlorine)  | Not captured in drain trap<br>Adsorbed to Carbotrap C                                | ca. 150 ~ ca. 270  |

### *Municipal waste incinerators*

In conjunction with legislated periodical PCDD/Fs inspections of gas emitted from MWI stacks in Osaka City, Japan, LVOC and SVOC were measured in 2001 and 2002. All MWIs in Osaka City were stoker furnace types, but the gas treatment lines could be categorized into 4 types, A to D (Fig. 2).

1. Type A: the MWI consisted of an activated carbon (AC) injected electrostatic precipitator (ESP) and a wet scrubber.
2. Type B: the MWI had an ESP, a wet scrubber and a bag filter in which AC was circulated for PCDD/Fs removal.
3. Types C and D: MWI were equipped with a lime-injected bag filter, a catalytic NO<sub>x</sub> removal device and a wet scrubber. The order of those devices differed between types C and D.

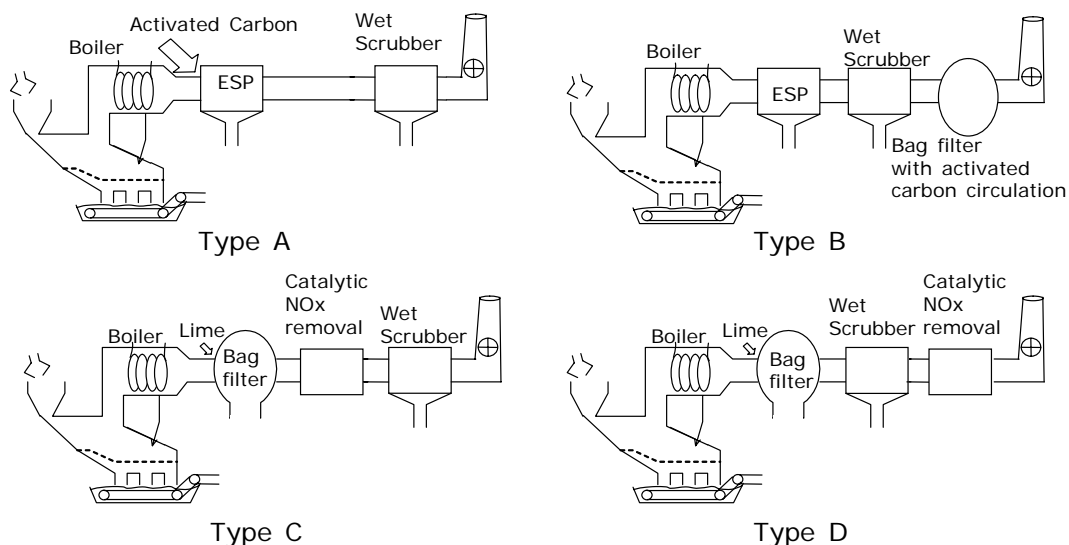


Fig. 2 Gas treatment lines of the municipal waste incinerators (MWI) studied

## Results and Discussion

### *Correlation between LVOCl and PCDD/Fs*

Collected data are tabulated in Table 2. As expected, LVOCl correlated with PCDD/Fs better than SVOC1. The plots of LVOCl versus PCDD/Fs are given in Fig 3. The regression lines of 2002 differed from those of 2001, however, and the following tendencies were observed.

1. In type A MWIs, LVOCl and SVOC1 both increased greatly in 2002 compared with 2001, even though the PCDD/Fs level hardly changed.
2. In the type B MWIs, although SVOC1 and LVOCl levels were constant through 2001 and 2002, the PCDD/Fs level of 2002 was consistently lower than that of 2001.

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Table 2 SVOC1, LVOCl and PCDD/F levels measured in stack gas from MWIs

|        |   | SVOC1( $\mu\text{gCl}/\text{Nm}^3$ ) |      | LVOCl( $\mu\text{gCl}/\text{Nm}^3$ ) |      | PCDD/Fs (ng-TEQ/ $\text{Nm}^3$ ) |          |
|--------|---|--------------------------------------|------|--------------------------------------|------|----------------------------------|----------|
|        |   | 2001                                 | 2002 | 2001                                 | 2002 | 2001                             | 2002     |
| Type A | J | 7.3                                  |      | 6.1                                  |      | 0.36                             |          |
|        |   | 30                                   |      | 13                                   |      | 0.59                             |          |
|        |   | 72                                   |      | 13                                   |      | 1                                |          |
|        |   | 18                                   |      | 5.6                                  |      | 0.15                             |          |
|        |   |                                      | 92   |                                      | 628  |                                  | 1.6      |
|        |   |                                      | 13   |                                      | 138  |                                  | 0.13     |
|        | D | 6.6                                  |      | 15                                   |      | 0.081                            |          |
|        |   |                                      | 33   |                                      | 31   |                                  | 0.51     |
|        |   |                                      | 262  |                                      | 418  |                                  | 0.72     |
| Type B | E | 6.4                                  |      | 9.8                                  |      | 0.22                             |          |
|        |   | 27                                   |      | 3.7                                  |      | 0.064                            |          |
|        |   |                                      | 19   |                                      | nd   |                                  | 0.000088 |
|        |   |                                      | 35   |                                      | 15   |                                  | 0.0031   |
|        | G |                                      | 8.1  |                                      | 2.7  |                                  | 0.00012  |
|        |   |                                      | 1.8  |                                      | 0.95 |                                  | 0.00015  |
|        | A |                                      | 12   |                                      | 4    |                                  | 0.00017  |
|        |   |                                      | 20   |                                      | 7.2  |                                  | 0.000031 |
|        | B | 7.8                                  |      | 2.9                                  |      | 0.0049                           |          |
|        |   | 9.6                                  |      | 4                                    |      | 0.0008                           |          |
|        |   | 13                                   |      | 6.3                                  |      | 0.0024                           |          |
|        |   | 45                                   |      | 13                                   |      | 0.00017                          |          |
| F      |   | 38                                   |      | 5.5                                  |      | 0.013                            |          |
|        |   | 7.4                                  |      | 2.9                                  |      | 0.00018                          |          |
| Type C | C | 6.8                                  |      | 24                                   |      | 0.17                             |          |
|        |   | 5.2                                  |      | 10                                   |      | 0.16                             |          |
|        |   |                                      | 7.7  |                                      | 26   |                                  | 0.0068   |
|        |   |                                      | 15   |                                      | 20   |                                  | 0.045    |
| I      |   | 5.5                                  |      | 3.5                                  |      | 0.05                             |          |
|        |   | 4.7                                  |      | 2.7                                  |      | 0.036                            |          |
| Type D | H |                                      | 2.2  |                                      | 3.3  |                                  | 0.0022   |
|        |   |                                      | 24   |                                      | 13   |                                  | 0.00086  |

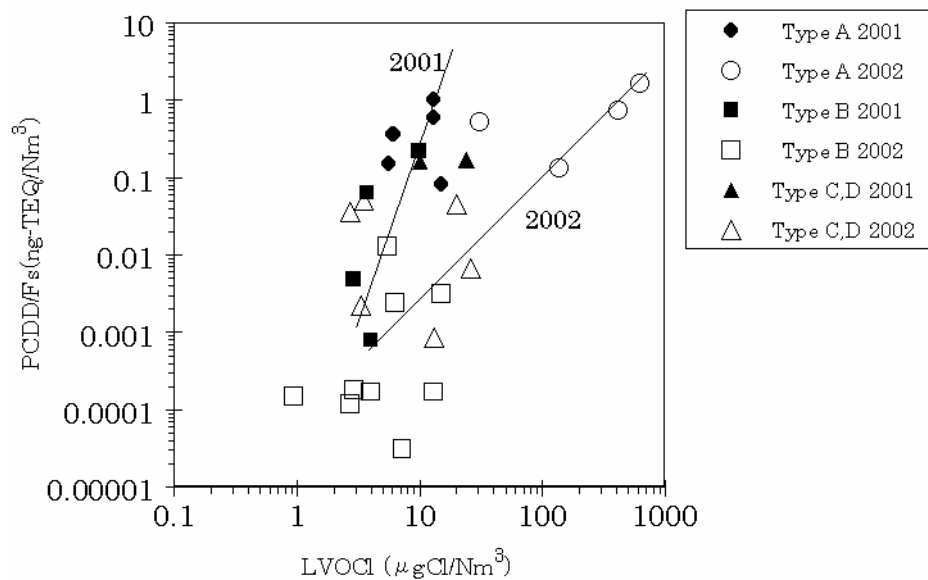


Fig. 3 Plots of LVOCI versus PCDD/Fs

#### Activated carbon-injected ESP

The injection of AC before the ESP was started in 2001. The temperature and the injected AC were controlled at 200~220 °C and 100 mg/Nm<sup>3</sup>, respectively. Since the purchase contract of AC is annually determined by bidding, the quality of AC had presumably changed in 2002. Although PCDD/Fs can be adequately captured by any AC, compounds that are more volatile may be missed depending on the properties of the AC.

#### Activated carbon circulated bag filter

Since the operation temperature of the AC-circulated bag filter was 150~170 °C, the PCDD/Fs removal efficiency was expected to be higher than that for AC-injected ESP. The AC-circulated bag filter was installed in 2001 and the measurement of S/LVOCI and PCDD/Fs levels was conducted just after the installation. The measurement in 2002 was conducted one year later. The PCDD/Fs removal efficiency in 2002 seemed higher than in 2001, although the S/LVOCI level did not change. The difference could occur from the bag filter's performance improvement because of formation of a layer of AC through usage.

Organic compounds with high boiling points such as PCDD/Fs were thought to be removed more efficiently than LVOCl compounds.

#### *Monitoring of organic halogenated compounds by SLVOX*

Since LVOCl measurement only monitors organic chlorine in a certain range of boiling points, which does not include PCDD/Fs, the correlation of LVOCl and PCDD/Fs levels must rely on the boiling point spectrum (Fig. 4). However, since the spectrum is influenced by the conditions of the gas treatment, the correlation is not a rigid line.

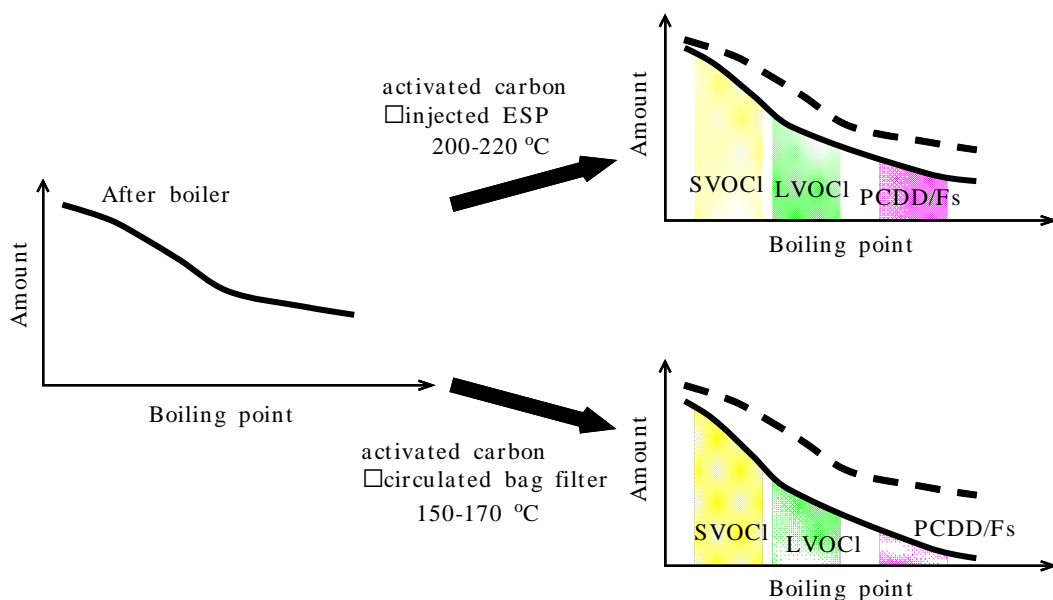


Fig. 4 Influence of gas treatment devices on LVOCl - PCDD/F level correlation

Nevertheless, the versatility of S/LVOX as an element-selective organic halogen monitor is noteworthy. PCDD/Fs were the first organic halogenated compounds which gained public attention in MWI flue gas. However, tremendous varieties of organic halogenated compounds are emitted from MWI through either *de novo* synthesis or incomplete decomposition of organic halogenated compounds. A method using helium barrier discharge-AES, is now being developed for further investigation of organic halogenated compounds.

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