# INVESTIGATION OF PCDD/FS INDICATORS IN FLUE GAS FROM MUNICIPAL SOLID WASTE INCINERATORS(MSWIS)

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**Introduction**

Incineration technology can reduce the volume and quantity of solid waste easily and quickly, but also produce secondary pollution,including dioxins (PCDD/Fs), chlorobenzene (CBz), polycyclic aromatic hydrocarbons (PAHs) and heavy metals, etc. What's more, these organic pollutants can deposit into the surrounding environment with the flue gas. Therefore, pollution control has become the foremost constraint for promoting incineration technology.Rapid detection of pollutant emissions is an important subject to emission control especially the on-line detection technology of PCDD/Fs. At present, the controlling and monitoring of PCDD/Fs is seriously restricted because of high cost and time consuming by using off-line detection technology. The current detection technology can't achieve on-line detection because the dioxin exists in the complex flue gas and have many complex structure homologues. A relative feasible technology to achieve online detection is monitoring the indicator which has high corrleation with dioxin concentration. [1]This study focus on the correlation of PCDD/Fs and the chlorobenzene, which are considered of PCDD/Fs indicators.

**Materials and methods**

The flue gas samples were collected from three different MSWIs, set as A,B,C. They have the same gas cleaning system including electrostatic precipitator, semi-dry reaction tower, activated carbon adsorption and bag filter. A and B are grate incinerators with 400tons / day design treatment capacity in the same waste incineration power plant. The date of sampling is August 2011. C is a circulating fluidized bed waste incinerator with 500tons / day design treatment capacity. The date of sampling is March 2012.Nine flue gas samples (A1~A3, B1~B3, C1~C3) were collected at the tail flue gas, Three flue gas samples (C4~C6) were collected before the gas cleaning system. More than 2.0 $Nm^3$ of flue gas was collected for about 1.5 h. They were sampled by M5 type flue gas sampler (Korea, KNJ Engineering Company), according to USEPA23 standard isokinetic sampling method.

The CBz analysis was conducted using GC-ECD (GC6890N, Agilent, USA) with a DB-5 column (30 m × 0.25mm × 0.25 μm). The temperature program for GC oven was as follows: initial temperature 80°C, held for 4 min,increased at 5°C/min to 106°C, held for 0.5 min; increased at 8°C/min to 250°C and held for 15 min.

Pretreatment was according to the state standard method of HJ/T74-2001 and GB 7492-87. After the clean up procedure according the EPA1613 Method,high-resolution gas chromatography with high resolution mass spectrometry (HRGC/HRMS) (JMS-800D, JEOL, Japan) with a DB-5MS column (60 m × 0.25mm × 0.25 μm) was applied to analyze the PCDD/Fs concentration.All statistical analysis was performed using the SPSS 16.0 software package and OriginPro8.0.

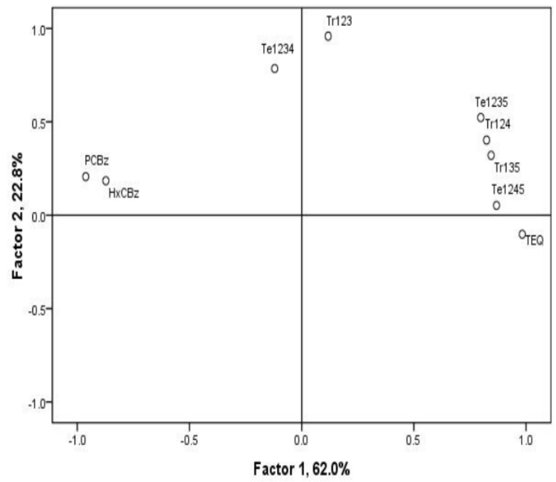
**Results and discussion**

Table 1 shows the concentration of CBz and I-TEQ of dioxins in flue gas.Table 2 shows the concentration of 17 isomers in flue gas.The concentration of chlorobenzene in flue gas of furnace A ranges from 20.43 to 878.93ng $Nm^{-3}$, while the concentration of dioxins ranges from 0.09 to 0.13 ng I-TEQ $Nm^{-3}$. It ranges from 48.49 to 554.09ng $Nm^{-3}$ in furnace B,while the dioxins ranges from 0.06 to 0.09 ng I-TEQ $Nm^{-3}$. As for the furnace C, the concentration of chlorobenzene and dioxins are very different between before and after gas cleaning system, the concentration of chlorobenzene ranges from 43.69 to 5834.14ng $Nm^{-3}$ before the gas cleaning system, while it reduced to ranging from 3.85 to 577.73ng $Nm^{-3}$ after the gas cleaning system, the concentration of dioxins also reduced and the range is ,from 13.56 to 0.66 ng I-TEQ $Nm^{-3}$(average value ). We could find that the concentration of dioxins in tail flue gas of all furnaces are lower than national emission standards(1.0 ng I-TEQ $Nm^{-3}$).

Table 1 The concentration of CBz and I-TEQ of dioxins in flue gas（ng $Nm^{-3}$）

| | 135TrCBz | 124TrCBz | 123TrCBz | 1235TeCBz | 1245TeCBz | 1234TeCBz | PCBz | HxCBz | 23478-PeCDF | I-TEQ |
|---|---|---|---|---|---|---|---|---|---|---|
| A1 | 20.43 | 312.92 | 111.91 | 237.30 | 173.41 | 175.43 | 299.26 | 116.76 | 0.04 | 0.09 |
| A2 | 86.85 | 771.99 | 234.00 | 330.17 | 228.52 | 198.93 | 254.72 | 81.87 | 0.05 | 0.12 |
| A3 | 106.76 | 878.93 | 289.63 | 317.75 | 217.62 | 184.91 | 252.90 | 79.68 | 0.07 | 0.13 |
| B1 | 48.49 | 529.74 | 320.55 | 299.56 | 175.13 | 261.31 | 306.06 | 111.17 | 0.04 | 0.09 |
| B2 | 57.03 | 539.92 | 243.73 | 232.99 | 113.66 | 180.44 | 309.54 | 141.19 | 0.04 | 0.08 |
| B3 | 49.68 | 554.09 | 291.10 | 272.50 | 155.49 | 204.09 | 344.75 | 190.18 | 0.02 | 0.06 |
| C1 | 3.85 | 10.24 | 7.95 | 5.03 | 4.88 | 4.95 | 19.18 | 5.86 | 0.18 | 0.32 |
| C2 | 16.76 | 24.17 | 29.86 | 41.68 | 23.39 | 46.43 | 115.32 | 188.36 | 0.61 | 0.99 |
| C3 | 5.84 | 371.88 | 240.19 | 311.88 | 157.38 | 280.81 | 577.73 | 159.24 | 0.43 | 0.67 |
| C4 | 43.69 | 1049.09 | 886.12 | 1209.65 | 539.02 | 1128.63 | 2021.75 | 563.14 | 6.49 | 10.68 |
| C5 | 89.83 | 1916.32 | 2000.08 | 1937.29 | 3184.11 | 3099.70 | 5834.14 | 2605.10 | 15.68 | 27.94 |
| C6 | 224.57 | 3466.68 | 3854.70 | 1955.26 | 680.46 | 2335.74 | 2486.24 | 522.49 | 1.10 | 2.07 |

Principal components analysis (PCA) is a multivariate statistical method that is frequently employed in environmental science. The purpose of PCA was to reduce the multidimensional data set to a few significant principal components, describing as completely as possible the variation in the original data.Fig.1 and Fig.2 show the patterns of chlorobenzene and I-TEQ in flue gas after PCA. As seen in Fig.1, we could find that there is a strong negative correlation between PCBz, HxCBz andI- TEQ,1234TeCBz and 123TrCBz nearly have no correlation with I-TEQ.Fig.2 shows that 1245TeCBz,PCBz,HxCBZ and I-TEQ have a strong positive correlation. In order to further evaluate the correlation of chlorobenzene and I- TEQ in flue gas, Correlation analysis was employed.



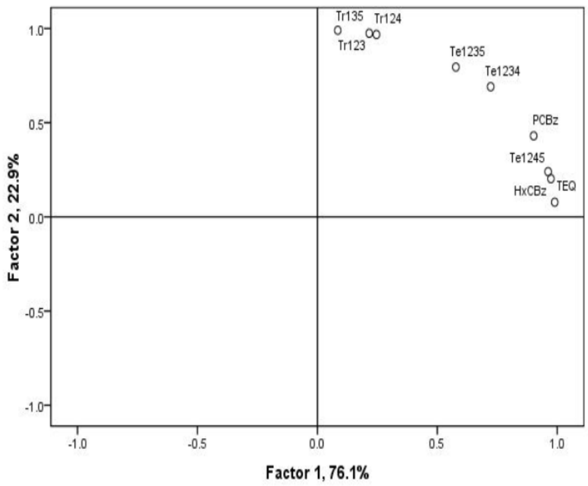




**Fig.1** Principal Components Analysis of furnace A and B **Fig.2** Principal Components Analysis of furnace C

The correlation analysis is a statistical method for studying close degree of two variables. Pearson correlation coefficient is employed. It is mostly used to describe the linear correlation. Samples of A and B were analyzed together, because they have the same incineration system and also in the same waste incineration power plant, the samples of furnace C were analyzed separately.

Fig.3 and Fig.4,5,6 shows the correlation analysis of chlorobenzene and I- TEQ in flue gas of furnace A,B and C. They indicate that there is quite obvious correlation between chlorobenzene and I- TEQ in Flue gas. The $R^2$ is 0.950 and 0.829 respectively of pentachlorobenzene, hexachlorobenzene and I- TEQ in flue gas of furnace A and B.As for furnace C, it is 0.859 and 0.940 respectively, in addition, there is a good correlation between tetrachlorobenzene and I-TEQ in flue gas, $R^2$ is 0.894.These results are consistent with Kaune et al.[2,3]researches.There is a phenomenon that can't be ignored, chlorobenzene concentration was negatively correlated with I- TEQ in flue gas of furnace A and B, but it is positively correlated in flue gas of furnace C. This may be caused by the different sampling points. More work should be done to get more information.It was found that good correlation exist between the I-TEQ values with the concentration of 2,3,4,7,8-P5CDF when 17 PCDD/Fs toxic congeners was analyzed(Fig.7), the correlation coefficient of the 2,3,4,7,8-P5CDF concentration to the I-TEQ in the flue gas was $R^2$ = 0.999, This result is consistent with Fiedler et al.[4] and Kato and Urano [5]researches.

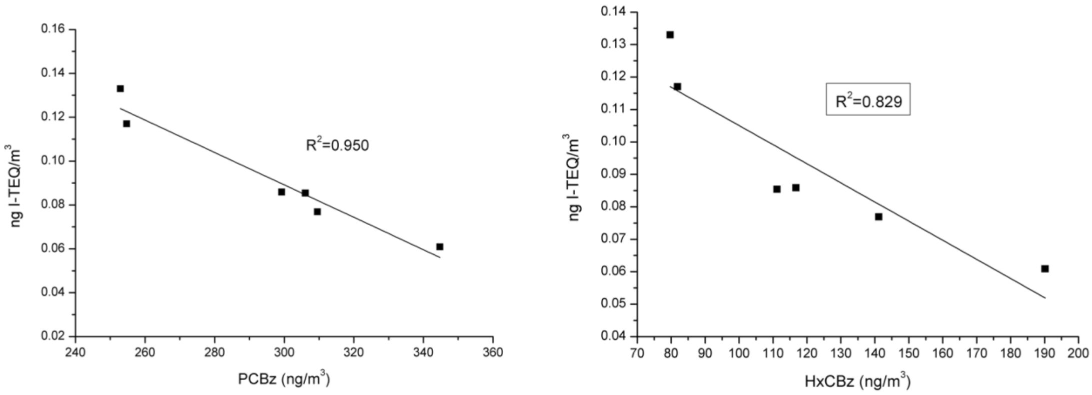



Fig.3 The correlation between PCBz ,HxCBz and TEQ in flue gas of furnace A and B

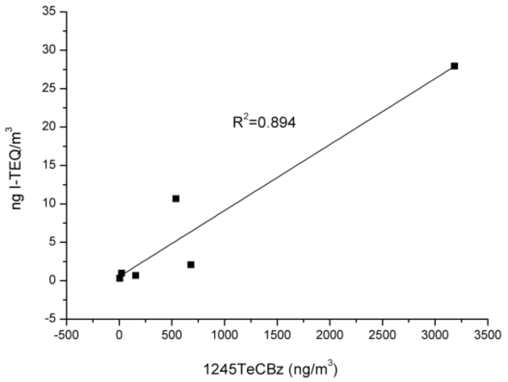



Fig.4 The correlation between1245TeCBz and I-TEQ in flue gas of furnace C

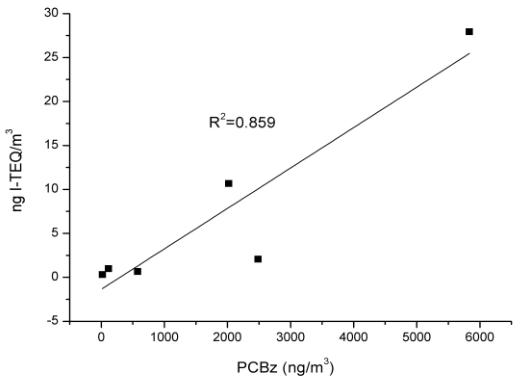



Fig.5 The correlation between PCBz and I-TEQ in flue gas of furnace C

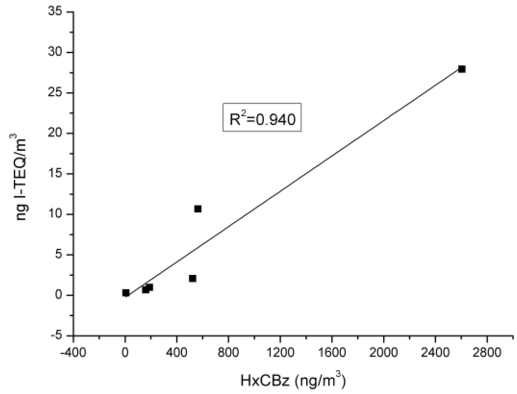



Fig.6 The correlation between HxCBz and I-TEQ in flue gas of furnace C

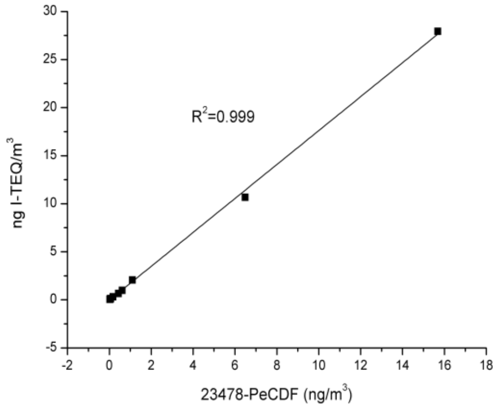



Fig.7 The correlation between 23478-PeCDF and I-TEQ in flue gas

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Table 2 The concentration of dioxins in flue gas（ng I-TEQ $Nm^{-3}$）

| PCDD/Fs | 2378-TCDD | 12378-PeCDD | 123478-HxCDD | 123678-HxCDD | 123789-HxCDD | 1234678-HpCDD | OCDD | 2378-TCDF | 12378-PeCDF | 23478-PeCDF | 123478-HxCDF | 123678-HxCDF | 123789-HxCDF | 234678-HxCDF | 1234678-HpCDF | 1234789-HpCDF | OCDF | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A1 | 0.01 | 0.01 | ND | ND | ND | ND | ND | 0.01 | ND | 0.04 | 0.01 | ND | 0.01 | ND | ND | ND | ND | 0.09 |
| A2 | 0.01 | 0.01 | ND | 0.01 | ND | ND | ND | 0.01 | ND | 0.05 | 0.01 | 0.01 | 0.01 | ND | ND | ND | ND | 0.12 |
| A3 | 0.01 | 0.01 | ND | ND | ND | ND | ND | 0.01 | 0.01 | 0.07 | 0.01 | ND | 0.01 | ND | ND | ND | ND | 0.13 |
| B1 | 0.01 | 0.01 | ND | ND | ND | ND | ND | 0.01 | ND | 0.04 | 0.01 | ND | 0.01 | ND | ND | ND | ND | 0.09 |
| B2 | 0.01 | 0.01 | ND | ND | ND | ND | ND | 0.01 | ND | 0.04 | 0.01 | ND | ND | ND | ND | ND | ND | 0.08 |
| B3 | 0.01 | 0.01 | ND | ND | ND | ND | ND | 0.01 | ND | 0.02 | 0.01 | ND | ND | ND | ND | ND | ND | 0.06 |
| C1 | 0.01 | 0.01 | ND | 0.01 | ND | ND | ND | 0.01 | 0.01 | 0.18 | 0.02 | 0.02 | 0.04 | 0.01 | ND | ND | ND | 0.32 |
| C2 | 0.02 | 0.03 | 0.01 | 0.01 | 0.01 | 0.01 | ND | 0.05 | 0.03 | 0.61 | 0.05 | 0.05 | 0.08 | 0.02 | 0.01 | ND | ND | 0.99 |
| C3 | 0.02 | 0.02 | ND | 0.01 | 0.01 | ND | ND | 0.02 | 0.01 | 0.43 | 0.03 | 0.03 | 0.06 | 0.02 | 0.01 | ND | ND | 0.67 |
| C4 | 0.46 | 0.51 | 0.06 | 0.08 | 0.07 | 0.04 | 0.01 | 0.54 | 0.33 | 6.49 | 0.51 | 0.45 | 0.72 | 0.29 | 0.09 | 0.03 | 0.01 | 10.68 |
| C5 | 0.57 | 1.22 | 0.27 | 0.37 | 0.22 | 0.17 | 0.02 | 0.53 | 0.66 | 15.68 | 1.95 | 1.93 | 2.82 | 0.89 | 0.44 | 0.15 | 0.04 | 27.94 |
| C6 | 0.02 | 0.06 | 0.02 | 0.03 | 0.02 | 0.01 | ND | 0.03 | 0.03 | 1.10 | 0.15 | 0.15 | 0.31 | 0.08 | 0.04 | 0.01 | ND | 2.07 |