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MONITORING STUDY OF SEMI AND LOW VOLATILE ORGANIC HALOGEN AS THE INDICATOR OF PCDD/Fs IN THE STACK GAS AT A MUNICIPAL WASTE INCINERATION PLANT

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) have been recently one of the biggest public concerns in the municipal waste incineration plant. In Japan, since Dec. 1st, 2002, the emission standard has been strictly enforced, and it has led the necessity of stack gas monitoring.

On the other hands, the analysis of PCDD/Fs needs much time and cost because of many steps e.g. sampling, extraction, clean-up and HRGC-HRMS operating, which make daily gas monitoring difficult to perform. Recently, TOX (Total Organic halogen) has been suggested as one of the promising indicators of PCDD/Fs[1, 2].

However, TOX involves various organic halogen compounds of molecular mass in a wide range. Semi volatile organic halogen compounds like chlorinated benzenes are considered to be a good indicator of PCDD/Fs, on the other hand volatile organic halogen compounds of low molecular like chloroform cannot be a sufficient PCDD/Fs surrogate.

Consequently an effort for a separate determination of organic halogen compounds according to the volatility should be undertaken. Kato et al. established semi- and non-volatile organic halogen (SNVOX) determination method and gave a good correlation with PCDD/Fs [3]. An alternative speciation technique is to utilization of two adsorption - thermal desorption columns of different surface area.

The detection of halogen elements is also a critical point. Traditional TOX and SNVOX measurement employed a combustion – coulometric titration or ion chromatograph, the detection level of which are in the range of μg. In order to make the detection more sensitive and element-selective, a small instrument for Cl and Br detection was developed using plasma – optical emission spectroscopic method, which accepts gaseous sample.

In this paper, the newly developed semi and low volatile organic halogen (SLVOX) determination method is presented, accompanied by SLVOX value from the emission gas at municipal waste incineration plants in Osaka.

Methods and Materials

Stack gas was led to two bottles of water, which removed drain water and hydrochloric acid (Fig.1). After moisture was eliminated in two condensate impingers, SLVOX was captured with two columns of adsorbents. Column 1 is adsorbent for low volatile compounds and column 2 is for semi volatile compounds. Flow rate was 2L/min, amount of sampling gas was 10~40L.

Analysis was performed with our emission spectrophotometer system equipped with barrier discharge radio-frequency helium plasma (Fig.2). This system has two-sample transfer lines, Line A is for standard injection and Line B is for sample. The quartz tube, wrapped with two copper films electrodes, flowed with helium gas, is discharged with high radio-frequency voltage. The spectrum by halogen's excitation (Cl: 837nm, Br: 827nm) is focused by lenses and led to spectrophotometer (USB2000, Ocean Optics, USA).

Results and Discussion

Samplings were performed at municipal waste incineration plants (7 facilities) in Osaka in 2001. Some SLVOX and PCDD/Fs samplings were simultaneously carried out.

SLVOX in the stack gas was analyzed and the correlations with PCDD/Fs were examined (Fig.3). As low volatile chlorinated compound (LVOCl), the correlation coefficient (r^2) was 0.55, which was higher than 0.19 as semi volatile compound (SVOCl). The range of molecular mass for adsorbents filled in column 1 is approximately over 200 (C12~C20), which covers the mass of chlorinated benzene, PCDD/Fs and Co-PCBs.

SLVOX concentration at 7 municipal waste incineration plants in Osaka city is given in Figure 4. The comparison of SLVOX value at the inlet and the outlet of the gas-cleaning system clearly revealed the decrease. At plant No.4, the removal efficiency of SLVOX by activated carbon injection was higher than 99% (LVOCl), and 84~98% (SVOCl). At plant No. 1 & 6, bag filter with circulation system of activated carbon removed 98~99% of LVOCl, 50~84% of SVOCl. SLVOX level after gas cleaning system was 10~80µgCl/Nm3. Analyses of SLVOBr were also performed, and the results yielded the less level compared with SLVOCl, and SVOBr was higher than LVOBr in most cases. At plant No.3, SVOBr level reached 250µg-Br/Nm3, which was particularly high. It seems to be due to the incomplete combustion of brominated organic compounds like flame retardant e.g. PBDEs.

Conclusions

Stack gas sampling at the municipal waste incineration plant was performed to study the level and behavior of SLVOX. The following conclusions were made.

1) The monitoring of low volatile organic halogen seems to be effective in incineration control. In view of this sampling being performed under good incineration control, the correlation ($r^2 = 0.55$) could be high.
2) SLVOCl has decreased at electrostatic precipitator and bag filter system with activated carbon injection, and after the gas-cleaning system, the level was 10~80µgCl/Nm3.
3) SLVOBr level was less than SLVOCl, and SVOBr was higher than LVOBr in most cases.

Acknowledgements

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References

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Fig.1 Sampling device

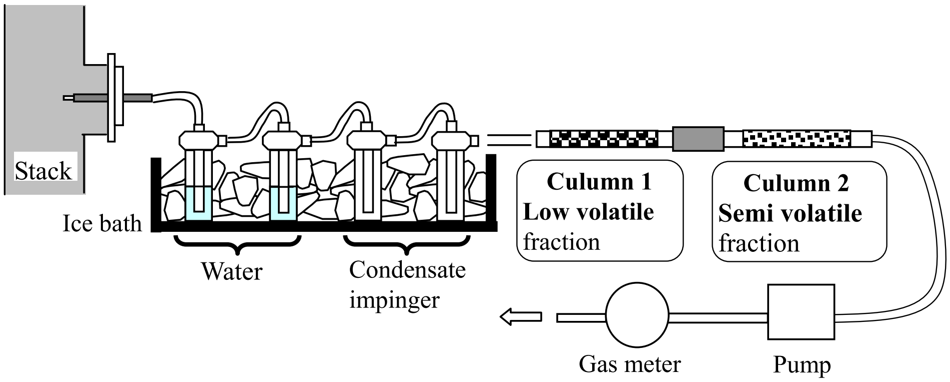


Fig.2 Barrier discharge radio-frequency helium plasma system

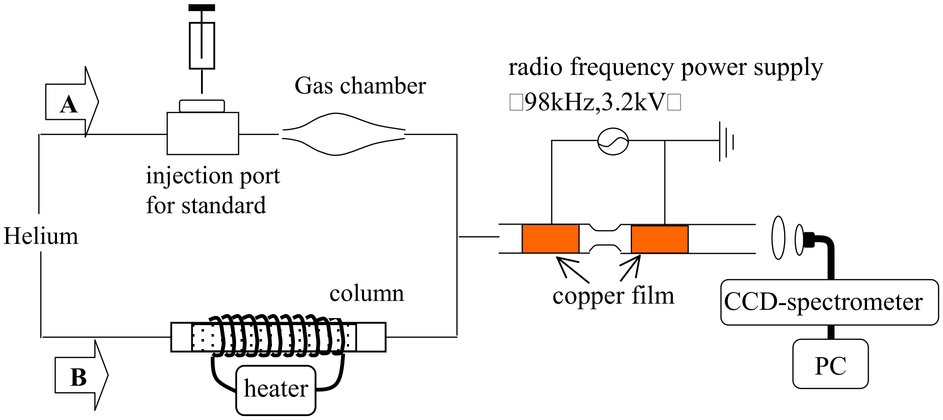


Fig.3 Correlation between SLVOX and PCDD/Fs

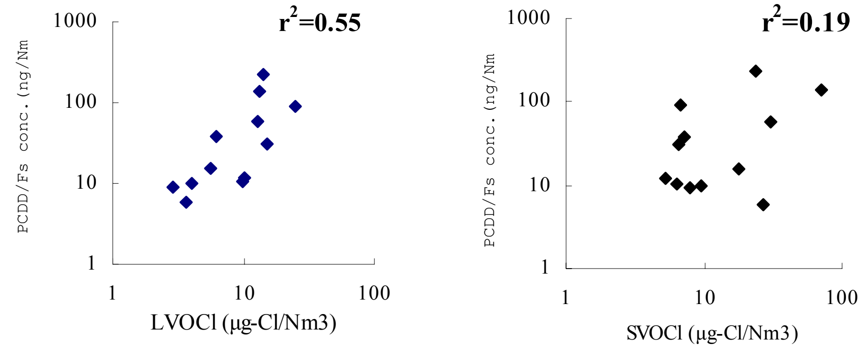
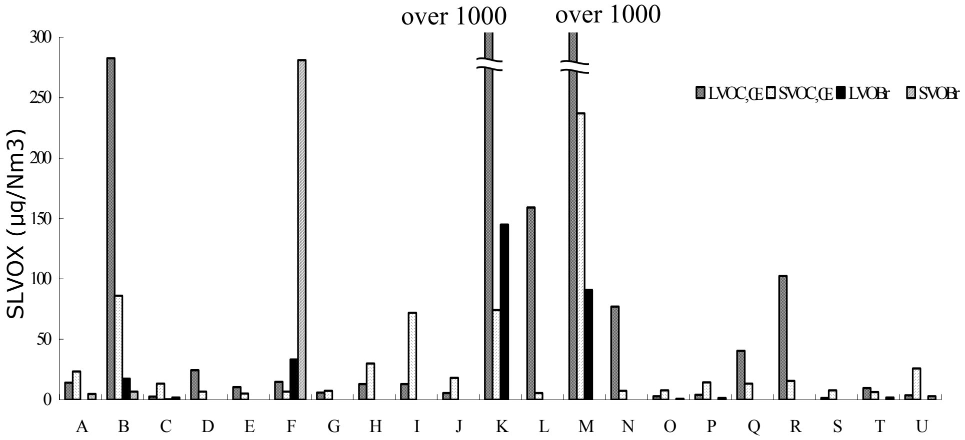


Fig. 4 SLVOX concentration at various points of the gas cleaning system



	Facility No.	Sample Point □combustion unit No.□	Date□1	Remarks
A	No. 1	after spray absorber (2)	1	BF without A.C
B		after EP (1)	2	before BF with A.C
C		after BF with A.C□□(1)	3	
D	No. 2	after spray absorber (1)	4	
E		after spray absorber (2)	4	
F	No. 3	after spray absorber (combine of 1,2,3)	5	after A.C injection
G	No. 4	after EP (1)	6	after A.C injection
H		after EP (2)	6	
I		after EP (3)	6	
J		after spray absorber (combine of 1,2,3)	6	
K		before EP (3)	7	before A.C injection
L		after EP (3)	7	after A.C injection
M		before EP (3)	8	before A.C injection
N		after EP (3)	8	after A.C injection
O	No. 5	after BF with A.C (1)	9	
P		after BF with A.C (2)	9	
Q		after EP (1)	10	before A.C injection
R	No. 6	before BF with A.C (1)	11	no SVOBr data
S		after BF with A.C (1)	12	
T	No. 7	after BF with A.C (1)	13	
U		after BF with A.C (2)	13	

□1 □□□ Same number shows same sampling date

□2 □□□ Activated Carbon