MEASUREMENT OF THE COLLECTION EFFICIENCY AND ADSORPTIVE DISTRIBUTION OF SEMI AND LOW VOLATILE ORGANIC CHLORINE (SLVOCI) IN FLUE GAS

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Introduction

Municipal waste incineration (MWI) flue gas includes various organic halogen compounds, which show a close correlation between PCDD/Fs concentration and organic halogen group parameters, e.g. TOX[1)] and SNVOX[2)].

Last year, we reported a newly developed sampling method and atomic emission spectrophotometry system equipped with barrier discharge radio-frequency helium plasma[3)], which detect organic halogen compounds with the advantages of elemental selectivity, high sensitivity and robustness. In this sampling system, flue gas was directed to a two-drain trap and two empty impingers, which removed drain water, hydrochloric acid and moisture (Fig. 1). After those four impingers, semi and low volatile organic halogens (SLVOX) were captured with two different adsorbents. Carbotrap C was the adsorbent for LVOX and Carbotrap B was for SVOX. The flow rate and the sampled gas were 2 L/min and 10-40 L, respectively.

In this paper, in order to investigate the passage efficiency through the drain trap and the adsorptive distribution to Carbotrap C and B of various organic chlorinated compounds, chlorinated benzenes (CBs) and chlorinated phenols (CPs) were tested in the sampling system as model organic halogen compounds.

Methods and Materials

Passage efficiency through the drain trap

A standard solution of CBs and CPs (listed in Table 1) in methanol was utilized in the experiments. The drain trap consisted of two impingers that contained 10 mL of water each. The adsorbent column was connected to the second impinger. The standard solution was injected into the inlet of the first impinger and a helium gas flow was supplied (4 L/min x 2 min) (Fig. 2). Water temperature was kept at 17 or 2-4 ^{o}C, while pH was adjusted at 1, 4, 12, 14 with HNO_3 and KOH.

Adsorptive distribution between columns
Adsorptive distribution was investigated with two serially connected columns: Carbotrap C and B (Fig. 3). The standard solution was injected into the inlet of the first column (Carbotrap C), and afterwards a helium gas flow was supplied (1 L/min x 2 min, 2 L/min x 2 min, 4 L/min x 2 min).

Results and Discussion
Passage efficiency of tested compounds through the drain trap
The passage efficiency of CBs through the drain traps is presented in Fig 4. The passage efficiency of CBs was high enough for adsorptive collection in the Carbotrap column independent of the number of impingers and water temperature. On the other hand, passage efficiency of CPs (except for pentachlorophenol (PeCP)) was much influenced by pH (Fig. 5). The passage efficiency was 20% with pH 1 and gradually decreased with alkalinity. This result indicates that dissolution of CPs occurs through ionization in water.

Mechanism of capture in the drain trap
The capture and dissolution of compounds in the drain trap can be induced by condensation with gas cooling. Considering the boiling point with the experimental results, the capture mechanism can be described as follows. The passage efficiency of TeCB, which has a boiling point (b.p.) of 250 ^{o}C, was almost 100%. On the other hand, CPs that have boiling points lower than 250 ^{o}C displayed low passage efficiency and were affected by pH. In short, the capture of CPs is governed by the dissolution mechanism. On the other hand, since the passage efficiency of PeCP was consistently low regardless of pH, the mechanism of its capture in the drain trap is thought to be condensation instead of dissolution, which suggests that compounds with boiling points higher than 300 ºC cannot pass through the gas drain trap. As TeCBs could pass through the drain trap almost completely, the boundary of passage/capture ranges between ca. 250-300 ºC.

Adsorptive distribution in Carbotrap columns
Compounds were classified into the following 6 patterns according to their adsorption behavior characteristics.

1. Adsorbed in Carbotrap C and did not continue to Carbotrap B
2. Adsorbed in Carbotrap C, but gradually continued to Carbotrap B as the flow rate was increased
3. Evenly adsorbed in Carbotrap C and Carbotrap B
4. Not adsorbed in Carbotrap C, but adsorbed in Carbotrap B
5. Not adsorbed in Carbotrap C, but partially adsorbed in Carbotrap B with increasing loss corresponding to flow volume increase
6. Not at all adsorbed in either Carbotrap C or Carbotrap B

Comparing these classifications with a molecular mass – b.p. plot (Fig. 6), it turns out that classification with b.p. is more suitable than with molecular mass. Broadly speaking, under the conditions of a gas volume of 8 L and 0.3 g of adsorbent, the compounds with a b.p. higher than 170 ºC distributed to Carbotrap C, while the compounds with b.p. of 70 – 120 ºC distributed to Carbotrap B.

Conclusions

The passage efficiency of CBs through the drain trap was high enough for adsorptive collection in the Carbotrap column. On the other hand, CPs (except for PeCP) dissolved in the drain trap water and compounds with b.p. higher than 300 ºC, such as PeCP, could not pass through the gas drain trap.

This adsorptive distribution experiment under the conditions of gas flow volume of 8 L and 0.3 g of adsorbent showed that the compounds with b.p. higher than 170 ºC distributed to the adsorbent column of Carbotrap C, while the compounds of b.p. 70 - 120 ºC distributed to Carbotrap B.

Acknowledgements

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References

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Fig.1 Sampling device

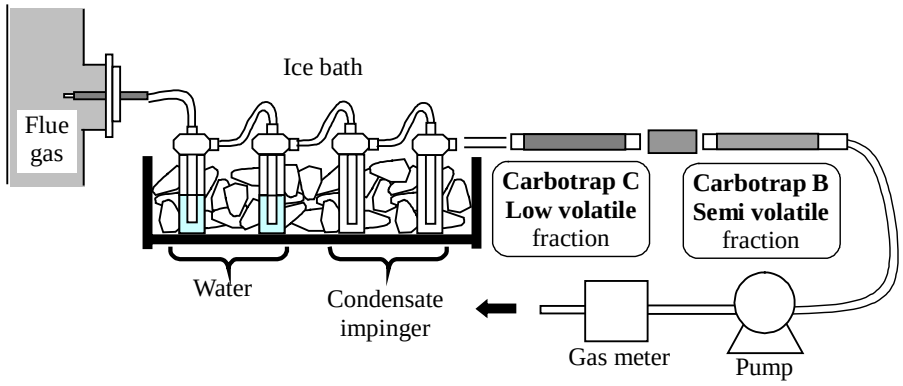

Table.1 Model compounds for experiments

compounds	abbreviation	molecular mass (g/mol)	boiling point(°C at 760 mmHg)	log K_{ow}
Dichloromethane	Dichloromethane	84.94	39.75	-
Chloroform	Chloroform	119.37	61.2	-
1,1,1 - Trichloroethane	1,1,1 - TriCE	134	74.1	-
1,1,2,2 - Tetrachloroethane	1,1,2,2 - TeCE	167.9	146.5	-
Monochlorobenzene	MCB	112.56	131.6	2.84
o - Dichlorobenzene	*o* - DiCB	147	180.5	3.38
m - Dichlorobenzene	*m* - DiCB	147	173	3.38
p - Dichlorobenzene	*p* - DiCB	147	174.1	3.39
1,2,3 - Trichlorobenzene	1,2,3 - TriCB	181.4	221	4.02 -4.11
1,2,4 - Trichlorobenzene	1,2,4 - TriCB	181.4	213	4.18
1,2,4,5 - Tetrachlorobenzene	1,2,4,5 - TeCB	215.9	244	4.52
1,2,3,5 - Tetrachlorobenzene	1,2,3,5 - TeCB	215.9	246	4.5
1,2,3,4 - Tetrachlorobenzene	1,2,3,4 - TeCB	215.9	254	4.46
2 - Monochlorophenol	2 - MCP	128.56	175	2.17
2,4,5 - Trichlorophenol	2,4,5 - TriCP	197.44	253	3.72
2,4,6 - Trichlorophenol	2,4,6 - TriCP	197.44	246	3.49
2,3,4 - Trichlorophenol	2,3,4 - TriCP	197.44	246	-
2,3,5,6 - Tetrachlorophenol	2,3,5,6 - TeCP	231.98	115	-
Pentachlorophenol	PeCP	266.32	310	5.01

Fig. 2 Experimental device for testing passage efficiency

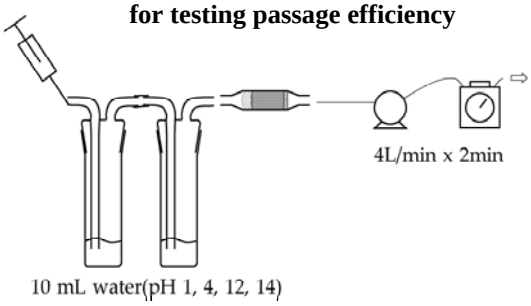

Fig. 3 Experimental device for testing adsorptive distribution

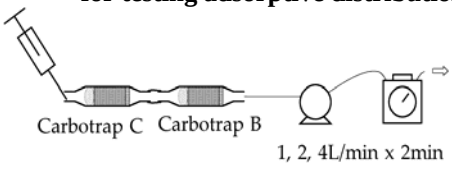

Fig. 4 Passage efficiency of CBs

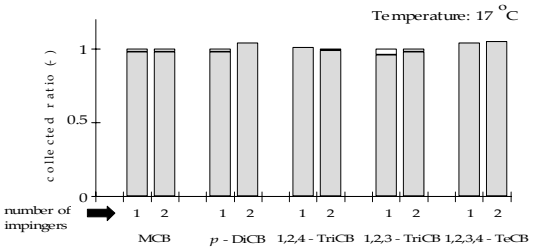

Fig. 5 Passage efficiency of CPs

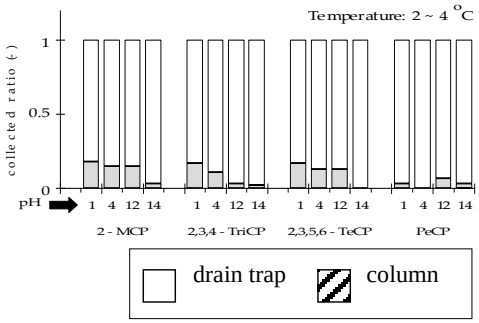

Fig. 6 Adsorptive classification by molecular mass – boiling point plot