

INFLUENCE OF OXYGEN CONCENTRATION DURING SEMI- AND LOW-VOLATILE ORGANIC HALOGEN COMPOUNDS DECOMPOSITION PROCESS BY BARRIER DISCHARGE ATOMIC EMISSION SPECTROMETRY

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Abstract

A group parameter approach using “total organic halogen” is effective for monitor gaseous organic halogen compounds including bromine, chlorine and fluorine from combustion. We developed barrier discharge radiofrequency helium plasma - atomic emission spectrometry (AES) for detecting semi- and low-volatile organic halogens (SLVOXs), which are amenable to collection by Carbotrap™ or Carboxen™ and analysis using thermal desorption. The optimal carrier gas flow rates at the injection and desorption lines were established at 100 mL min⁻¹. The detection range for these SLVOX compounds in the gaseous samples was from 10 ng to tens of micrograms. Compared to Cl or Br, measuring F was difficult because its wavelength is near that of air. The barrier discharge radiofrequency helium plasma AES measured from 85 to 103% of the SLVOX in the sampling gas. Carbotrap B was appropriate for high boiling point compounds, while Carbotrap C was suitable for the determination of organic halogens with middle boiling points ranging from 200 to 230 °C. Carboxen 1000 was suitable for the determination of organic halogens with boiling points below 100 °C. Base on the optimal analysis condition, plastic which containing chlorine was destructed under different oxygen concentration. The lower oxygen concentration showed the lower organic halogen production.

Introduction

Beginning in the 1990s, approximately 78% of 51 million tons of municipal solid waste (MSW) is estimated to have been incinerated each year in Japan. To achieve a sustainable society, MSW incinerators (MSWIs) must produce solid residues that do not pose any environmental concerns. With current technology, incinerators separate the environmentally harmful compounds from MSW and concentrate them in air-pollution control residues, which could become an attractive method for detection, control, and disposal.

Many kinds of hazardous semi- and low-volatile organic halogen compounds including dioxins, dioxin-like polychlorinated biphenyls (PCBs), polychlorinated benzenes (CBzs), polychlorinated phenols (CPs), which are precursors of dioxins during the *de novo* process. and their completely or partly substituted compounds of fluorine, bromine and iodine are detected from flue gas of MSWI. However, it is not possible to estimate the potential risk in flue gas because organic halogen compounds contain a lot of isomers. On the other hand, it takes much labor, long time, and high cost to measure the main compounds individually.

So far, measurement method of organic halogen compounds in wastewater called adsorbable organic halogen (AOX) is also applied widely to the gaseous organic halogen compounds. Flue gas was introduced to water, after removing the hydrogen halide, organic halogen compounds were absorbed by activated carbon. This activated carbon was introduced to potassium nitrate solution, and measured by coulometric titration and ion chromatography, which is much labor; or analyzed by combustion-water trap-ion chromatography method, which has a contamination before and during adsorption process by activated carbon.

In this study, we develop the technical systems to monitor or control the total semi- and low-volatile organic halogen (SLVOX) compounds from MSWIs. Radiofrequency helium plasma - atomic emission spectrometry is proposed as an effective technique for SLVOX determination.

Many types of plasmas have been developed as excitation sources for elemental analysis over many years. High excitation efficiency, low matrix effects and the possibility of simultaneous determination of elements are the basic requirements of an excitation source. One of the most important sources is the inductively coupled plasma (ICP). Nevertheless, the ICP has some disadvantages. The price of ICP spectrometers is still very high and the operating costs are also high because of the high consumption of carrier gas mostly used argon (Ar) and high maintenance costs. On the other hand, elemental analysis of nonmetallic by ICP with carrier gas of Ar is not useful because organic materials generally evaporate explosively in an arc or spark discharge and also because the ionization potential of argon is too low to excite the atoms of nonmetallic elements. The ionization potential of He is obviously higher than that of Ar. F ionization potential of 17.4 eV can be excited by He whose ionization potential is 24.6 eV [1]. Conversely, Ar (15.8 eV) cannot excite F. Recently, several alternatives to ICP systems have been proposed, one of which is the

microwave-induced plasma (MIP). This source has the advantages of low cost, simplicity of the generator and low gas consumption [2]. However, when the pressure changed, plasma will be damaged at the sample introduction.

In this study, we tried to use a new excitation source called radiofrequency plasma (RFP), which had been developed as a detector for gas chromatography (GC) by Pedersen-Bjergaard and Greibrokk [3]. We described the practical capability of this method followed by a preliminary study on organic F emission from PTFE combustion.

Materials and Methods

Gas sampling and analysis system

The gas sampling and analysis system is shown in Fig. 1. The length and inner diameter of the quartz tube were 70 and 5 mm, respectively. A total of 500ng of F, Cl, or Br from fluorobenzene, hexafluorobenzene, MonoCBz, p-diCBz, 1,2,3-triCBz, 1,2,3,5-tetraCBz, pentaCBz, monoBBz, o-diBBz, p-diBBz, and 1,3,5-triBBz was injected and vaporized at the inlet of the gas sampling system, respectively. The gas sampling process was allowed to proceed for 10 min under an Ar gas stream, which was provided at 50 mL min⁻¹. To wash the gas, exhaust gas was introduced to two impingers filled with 10 mL of water each. After removing moisture with an empty gas impinger, gaseous organic halogens of Cl and Br were collected by a non-porous adsorbent of 0.3 g Carbotrap C and Carbotrap B 20/40 mesh (Supelco, USA), while gaseous organic halogens of F were collected by two columns of Carbotrap C and B and porous adsorbents of Carboxen 1000 (60/80 mesh, micro-, meso-, macro-porous) (Supelco, USA).

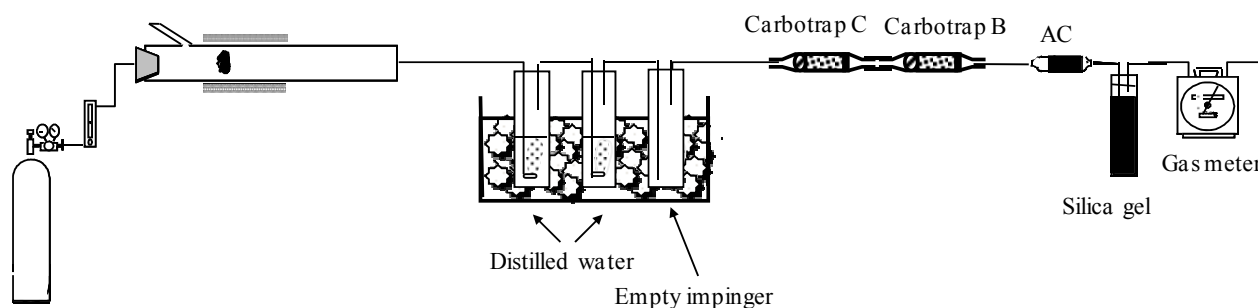


Fig. 1. Schematic illustration of the gas sampling and analysis system.

SLVOX quantification

The instrumentation of the barrier helium discharge is described in the previous paper [4]. The amount of F, Cl, and Br collected in Carbotrap C and B or Carboxen 1000 tubes was determined using 2,2,2-trifluoroethanol or bromochloromethane as a standard, respectively. The F, Cl, or Br amount (W_s) in the standard substance was calculated as follows:

$$W_s = \frac{\rho \times V_L}{V} \times V_G \times \frac{M_X}{M_S} \quad (1)$$

In Eq. (1), ρ is the density of the standard solution, which is 1.38 g mL⁻¹ of 2,2,2-trifluoroethanol and bromochloromethane; V_L is the standard volume used; V is the gas chamber volume; V_G is the volume of standard gas used from the gas chamber; M_X is the molecular weight of the total halogens in the standard gas; and M_S is the molecular weight of the standard, which was 2,2,2-trifluoroethanol or bromochloromethane.

After the injections of the standard, thermally desorbed organic halogen was introduced to the plasma. The comparison of the peak area gave the amount of halogen (μ g).

The amount of organic halogen after gas sampling was calculated by Eq. (2), which is shown as W_o :

$$W_o = W_s \times \frac{S_o}{S_s} \quad (2)$$

In Eq. (2), W_s shows the organic halogen amount of the standard solution, which was calculated by Eq. (1); S_s is the peak area of the standard, which was 2,2,2-trifluoroethanol or bromochloromethane in this study, and S_o is the peak area of the organic halogen in Carbotrap B and C or Carboxen 1000.

Influence of Oxygen Concentration During Decomposition Process

Plastic containing chlorine was used. Under the condition of different oxygen concentration of 2%, 5%, 10%, 20%, 50% and 100%, plastic was burned in a electric furnace which has two furnaces, one of them could shift. With the decomposition temperature of 800°C, organic chlorine was measured under the optimal condition determined using barrier discharge radiofrequency helium plasma – AES.

Results and Discussion

Recovery efficiencies and distribution of SLVOXs

The analytical recovery and distribution of SLVOXs with different desorption tubes were examined using three kinds of organic F, organic Cl, and organic Br compounds. Table 1 lists the information of organic halogen compounds used in this study, and their recoveries using barrier discharge radiofrequency helium plasma AES. Recoveries for organic Cl ranged from 82 to 99%, and organic Br ranged from 91 to 110% with the gas quantity of 30 L. However, organic compound of fluorobenzene was not detected.

Table 1 Organic halogen compounds and their recoveries using barrier discharge radiofrequency helium plasma AES.

Classification	Compound	Molecular weight	Boiling point (°C)	Recovery (%)		
				9 L	15 L	30 L
Fluorine compounds	Fluorobenzene	96.1	85	-	-	-
	Hexafluorobenzene	186.1	82	-	-	-
Chlorine compounds	Chlorobenzene	112.6	132	-	-	83
	p-Dichlorobenzene	147	174	-	-	90
	1,2,3-Trichlorobenzene	181.5	219	-	-	82
	1,2,3,5-Tetrachlorobenzene	215.9	246	-	-	99
	Pentachlorobenzene	250.3	275	-	-	98
Bromine compounds	Bromobenzene	157	156	82	92	110
	o-Dibromobenzene	235.9	224	-	-	92
	p-Dibromobenzene	235.9	218	-	-	91
	1,3,5-Tribromobenzene	314.8	271	-	-	104

Fig.2 shows the analytical chart of Br in mono-bromobenzene of gas sample using barrier discharge radiofrequency helium plasma AES with the gas quantity of 9 L. The concentration of organic Br collected by Carbotrap B or C were calculated by the peak area and concentration of standard (bromochloromethane), and peak areas of desorption organic Br at Carbotrap B or C using Eq. (2).

The distributions of these organic halogens with different desorption tubes of Carbotrap B or C were shown in Fig.3. With the gas quantity of 30 L, the distribution of organic halogen in Carbotrap B and C were as follows: 57% and 43% of MonoCBz were absorbed by Carbotrap C and B; More than 94% of p-DiCBz, 1,2,3-TriCBz, 1,2,3,5-TetraCBz, o-DiBBz,

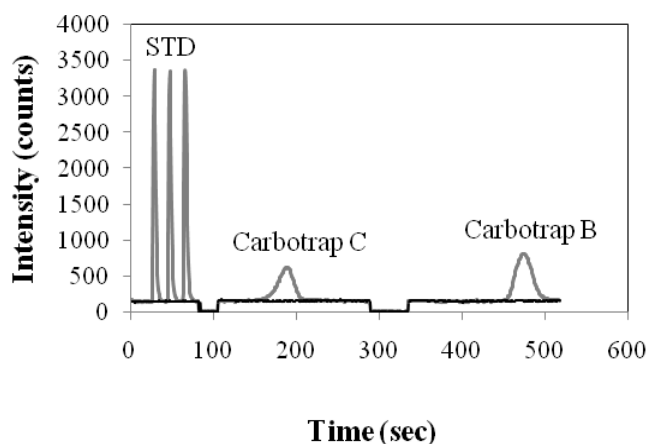


Fig. 2 Analytical chart of Br in monoBBz gas sample using barrier discharge radiofrequency helium plasma AES.

p-DiBBz, and 1,3,5-TriBBz were absorbed by Carbotrap C; 49% and 51% of pentaCBz, 54% and 46% of MonoBBz were absorbed by Carbotrap C and B, respectively.

For monoBBz, when the gas quantity increased from 9 L to 15 L and 30 L, the distribution ratio of Carbotrap C was changed from 100% to 70% and 54%. Organic Cl of monoCBz and p-diCBz have the same tendency when gas quantity increased more than 30 L. Carbotrap C absorbs the organic Cl and Br first, and then parts of the absorbed halogens were transferred to Carbotrap B. This was concern to the boiling points, which are from 130 to 170 °C. Carbotrap C with its small surface area of 10 m² g⁻¹, was appropriate for the determination of organic halogens with middle boiling points ranging from 170 to 270 °C. However, pentaCBz was different, that 49% and 51% were absorbed by Carbotrap C and B. Carbotrap B was suitable for the determination of organic halogens with low boiling points below 130 °C. Carboxen 1000 was not suitable for the organic halogens in this study. These results indicate that if Carbotrap B and C are used properly according to the characteristics of the analyst compounds, the SLOVXs of flue gases from MSWIs can be measured with a high sensitivity.

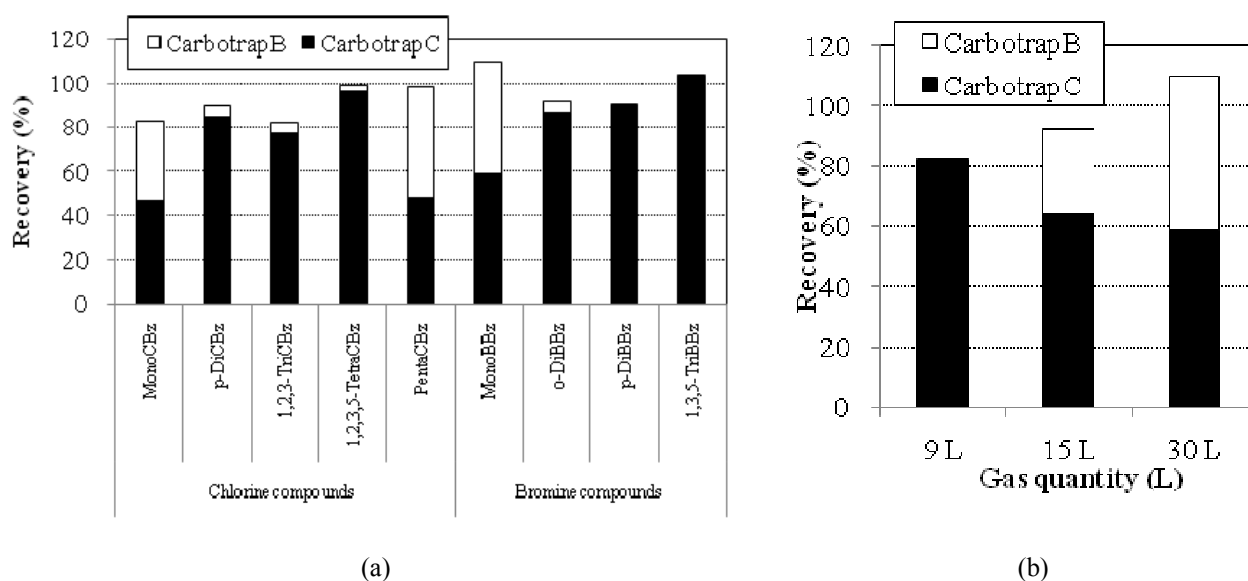


Fig.3 Distribution of organic Cl and organic Br at Carbotrap B or C with the gas quantity of 30 L (a); and organic Br in monobromobenzene at Carbotrap B or C under different gas quantities (b).

Influence of Oxygen Concentration During Decomposition Process

As the oxygen concentration increased, the organic chlorine increased too (Shown as Fig.4). When the O₂ concentration was 100%, all of the chlorine was generated to organic chlorine. When the O₂ concentration was 5%, the generated organic chlorine ratio was the lowest, which was 0.2%.

Acknowledgements

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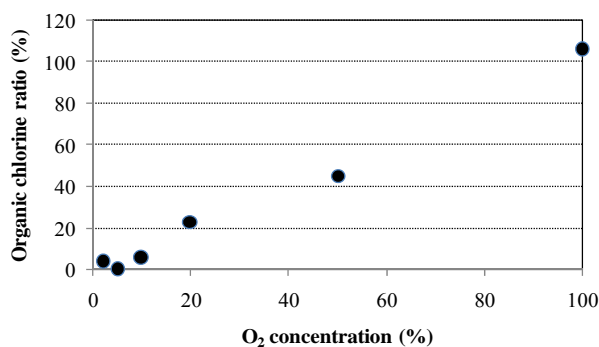


Fig.4 Organic chlorine generation ratio with different O₂ concentration.