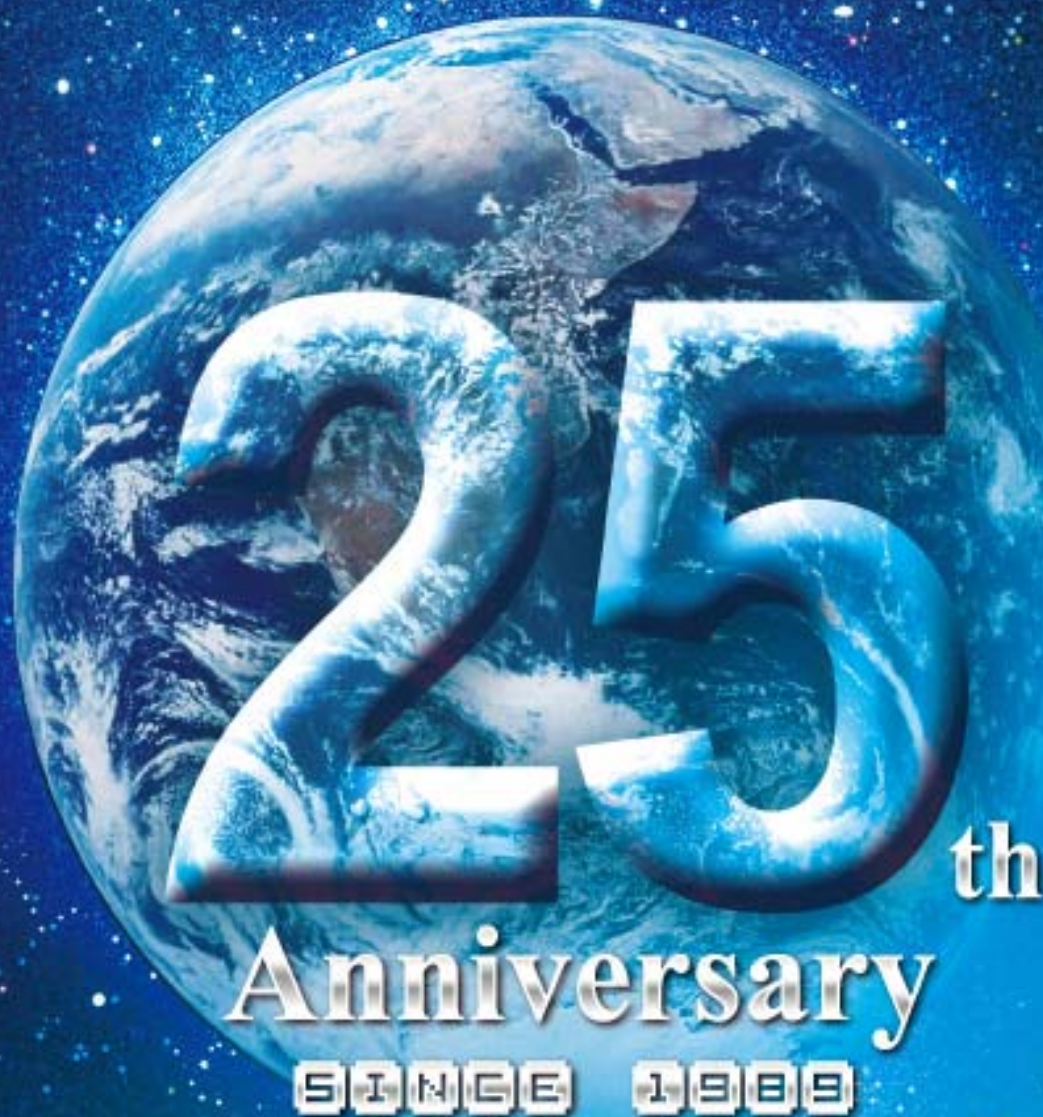


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Determination of gaseous semi- and low-volatile organic halogen compounds by barrier-discharge atomic emission spectrometry

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Abstract

A group parameter approach using “total organic halogen” is effective for monitoring gaseous organic halogen compounds, including fluorine, chlorine, and bromine compounds, generated from combustion. We described the use of barrier-discharge radiofrequency-helium-plasma/atomic emission spectrometry, for the detection of semi- and low-volatile organic halogen compounds (SLVOXs), which can be collected by CarbotrapTM adsorbents and analyzed using thermal desorption. The optimal carrier gas flow rates at the injection and desorption lines were established to be 100 mL/min. The detection range for SLVOXs in the gaseous samples was from 10 ng to tens of micrograms. Measuring F was more difficult than measuring Cl or Br, because the wavelength of F is close to that of air. The barrier-discharge radiofrequency-helium-plasma/atomic emission spectrometry measured from 85% to 103% of the SLVOXs in the gas sample. It has been found that Carbotrap B is appropriate for high-boiling-point compounds, and Carbotrap C is suitable for the determination of organic halogen compounds with lower boiling points, in the range 200–230°C. Under optimal analysis conditions, a chlorine-containing plastic was destroyed using different oxygen concentrations. Lower oxygen concentrations resulted in the production of lower amounts of organic halogen compounds.

Key words: organic halogen; semi- and low-volatile organic halogen; radiofrequency helium plasma; desorption

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Introduction

Socioeconomic development and increased standards of living involving mass-production, mass-consumption, and mass disposal have led to the generation of increased amounts of wastes. MSW incinerators (MSWIs) can significantly reduce the volume of waste to be landfilled and can be used to recover energy. For example, approximately 78% of 51 million tons of MSW is estimated to have been incinerated each year in Japan since the 1990s (Ministry of the Environment of Japan, 2006). With current technology, where incinerators separate the environmentally harmful compounds from MSW and concentrate them in air pollution control residues, this could become an attractive method for detection, control, and disposal of pollutants.

Many types of hazardous semi- and low-volatile organic halogen (SLVOX) compounds, including dioxins, dioxin-like polychlorinated biphenyls (PCBs), polychlorinated benzenes (CBzs), and polychlorinated phenols (CPs),

which are precursors of dioxins, have been found during *de novo* processes (Karasek and Dickson, 1987; Stieglitz et al., 1989, 1990, 1991; Gullett et al., 1990; Jay and Stieglitz, 1991; Froese and Hutzinger, 1996); concentrations of dioxin precursors (Shaub and Tsang, 1983; Karasek, 1995), as well as those of dioxin-like PCBs, have been shown to be strongly correlated with dioxin levels (Sakai et al., 2001). In addition, in the disposal by combustion of electrical and electronic plastics wastes, and of fluorine compounds such as chlorofluorocarbons or poly(tetrafluoroethylene), completely or partly substituted compounds of fluorine and bromine have been detected in flue gases from MSWIs (Rittmeyer et al., 1994; Vehlow et al., 2000; Tange and Drohmann, 2005). However, it is difficult to quantify the potential risks from flue gases because organic halogen compounds contain many different isomers. It is also costly and labor- and time-intensive to determine the main compounds individually.

The current method of measuring organic halogen compounds in wastewater is called the adsorbable organic

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halogen (AOX) method, and it is widely applied to gaseous organic halogen compounds (Kato et al., 2000). Flue gas is introduced to water after removal of hydrogen halides, and organic halogen compounds are absorbed by activated carbon. The activated carbon is then introduced to a potassium nitrate solution and analyzed by coulometric titration or ion chromatography, which are labor-intensive, or by combustion-water ion-trap chromatography, which can be contaminated before and during adsorption by the activated carbon.

Many types of plasmas have been developed as excitation sources for elemental analysis. High excitation-efficiency, low matrix-effects, and the possibility of simultaneous determination of elements are the basic requirements. One of the most important is inductively coupled plasma (ICP). However, elemental analysis of non-metallic materials by ICP with an Ar carrier gas is not possible, because the ionization potential of Ar is too low to excite the atoms of non-metallic elements. The ionization potential of helium (24.6 eV) is higher than that of Ar (15.8 eV) and of halogens (Kagaku Binran (II), 1999), and the ionization potential of F is 17.4 eV, thus F can be excited by helium. Moreover, ICP spectrometers are very expensive, and have high operating and maintenance costs. Recently, several alternative methods to ICP systems have been proposed; one of these is microwave-induced plasma (MIP). This source is inexpensive, easily generates plasma, and has low gas consumption (Hayashi et al., 2001). However, if the pressure changes, the plasma will be disturbed at the sample-introduction site.

In this study, we developed a technical system for monitoring or controlling the total SLVOX compounds from MSWIs. The developed radiofrequency-plasma technique could be carried out under normal pressure and low carrier gas flow. It is also easy to use, and has excellent sensitivity. Radiofrequency-plasma/atomic emission spectrometry (AES), which was developed as a detector for gas chromatography (GC) by Pedersen-Bjergaard and Greibrokk (1993), is used in this technique. A barrier discharge radiofrequency-helium-plasma/AES system was used to determine the total organic chlorine generation from combustion (Watanabe et al., 2002).

1 Material and methods

1.1 Instrumentation

The instrumentation for barrier helium discharge has been described in a previous article (Watanabe et al., 2007). A schematic illustration of the experimental system is given in Fig. 1. Briefly, helium gas was introduced into a discharge tube (ceramic tube, i.d. 4 mm × o.d. 6 mm, SSA-S, Nikkato Corp., Japan), which was equipped with two external film electrodes, and was converted to a plasma using a high-voltage radiofrequency generator (Haiden, Japan).

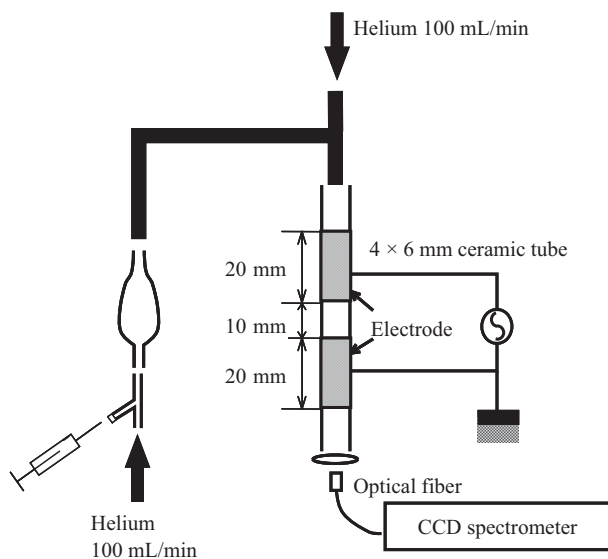


Fig. 1 Schematic diagram of the barrier-discharge radiofrequency-helium-plasma system coupled with a CCD-spectrometer.

The gas sample was introduced via a sample injection line using a helium gas stream with a flow rate of 100 mL/min. The emissions from the discharge tube were monitored using a collimated lens, which was connected to a spectrometer (HR 2000, Ocean Optics, Dunedin, FL, USA), the resolution of which was 0.2 nm in the range 700–870 nm. The data from the spectrometer were processed using SpectraSuite software (Ocean Optics, Dunedin, USA). Three peak positions were monitored, i.e., the elemental lines of F (739.9 nm), Cl (837.6 nm) and Br (827.2 nm).

1.2 Standard chemicals and materials

A sample of 2,2,2-trifluoroethanol (Tokyo Kasei, Japan) was used as the standard compound for fluorine, and 16 μL of this reagent were injected into a gas chamber (522.3 mL) filled with helium. A sample of 50 μL of gas from the gas chamber was equivalent to 1205 ng of F. In the same manner, bromochloromethane (Tokyo Kasei, Japan) was used as the Cl and Br standards, and 2 μL of bromochloromethane were diluted in the gas chamber (522.3 mL), resulting in 60.8 ng of Cl and 137.0 ng of Br in 30 μL of gas (20 μL of gas from the gas chamber are equivalent to 482 ng of F. In the same manner, bromochloromethane (Tokyo Kasei, Japan) was used as the Cl and Br standard. 2 μL of bromochloromethane were diluted in a gas chamber (522.3 mL), resulting in 40.5 ng of Cl and 91.3 ng of Br in 20 μL of gas.)

Organohalogen compounds including fluorobenzene, hexafluorobenzene, chlorobenzene (MonoCBz), *p*-dichlorobenzene (*p*-diCBz), 1,2,3-trichlorobenzene (1,2,3-triCBz), 1,2,3,5-tetrachlorobenzene (1,2,3,5-tetraCBz), pentachlorobenzene (pentaCBz), bromobenzene (monoBBz), *o*-dibromobenzene (*o*-diBBz), *p*-dibromobenzene (*p*-diBBz), and 1,3,5-tribromobenzene

(1,3,5-triBBz) were provided by Wako Pure Chemicals Industries, Ltd. (Japan). All of the organic halogen compounds were prepared in ether or methanol (Wako) for analysis.

1.3 Gas-sampling and analysis system

The gas-sampling and analysis system is shown in Fig. 2. The length and inner diameter of the quartz tube were 70 and 5 mm, respectively. A total of 5000 ng of F and 500 ng of 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. The gas-sampling process was allowed to proceed for 10 min under an Ar gas stream with a flow rate of 50 mL/min. To wash the gas, the exhaust gas was introduced into two impingers, each filled with 10 mL of water. After removing moisture using an empty gas impinger, gaseous organic F, Cl and Br compounds were collected using a non-porous adsorbent consisting of 0.3 g of Carbotrap C and Carbotrap B 20/40 mesh (Supelco, Sigma-Aldrich, St Louis, USA).

1.4 Data evaluation and quantification

The monitored signal at a specific wave-length was evaluated by emission intensity and detection limit. The evaluation concept is shown in Fig. 3. The emission intensity was expressed as the amount of F, Cl or Br equivalent to a value of $S/B = 1$, where S and B are the elemental and background signals, respectively. The smaller the amounts of F, Cl, or Br equivalent to $S/B = 1$, the higher the emission intensity is. The other evaluation aspect, detection limit, is expressed by the amount of F, Cl, or Br equivalent to an S/N value of 3, where N is the mean noise.

The instrumentation for barrier helium discharge has been described in a previous article (Watanabe et al., 2007; Nakui et al., 2011). The amounts of F, Cl, and Br collected in the Carbotrap C and B tubes were determined using 2,2,2-trifluoroethanol or bromochloromethane as a standard. The amount of F, Cl, or Br (W_s) in the standard substance was calculated as follows:

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

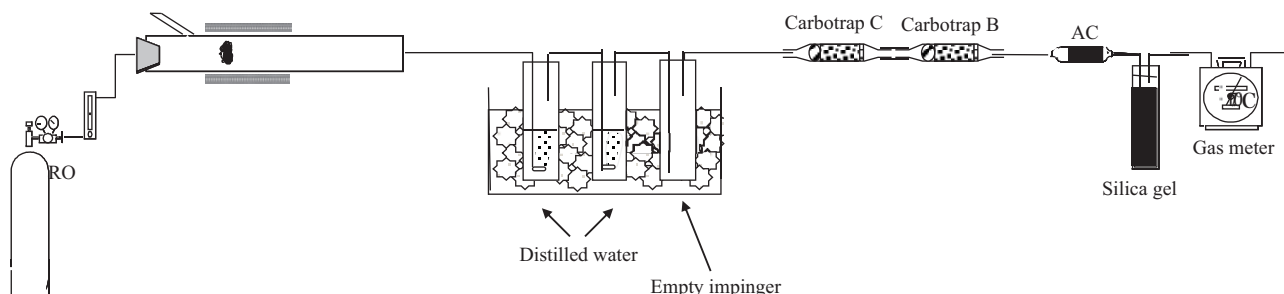


Fig. 2 Schematic illustration of the gas-sampling and analysis system.

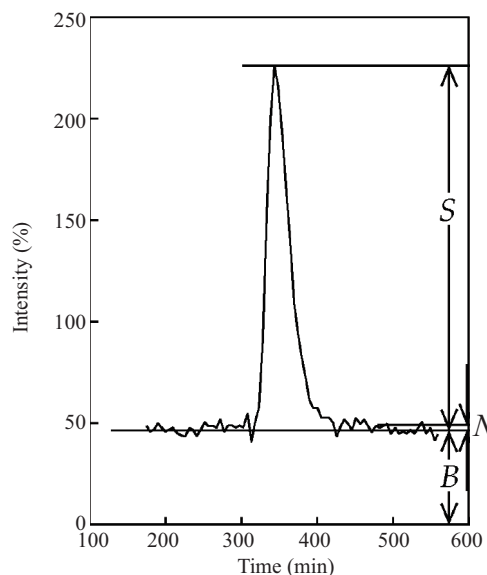


Fig. 3 Signal (S), background (B), and noise (N) in a graphic representation of the emission signal of F at 739.9 nm.

where, ρ is the density of the standard solution, which is 1.38 g/mL for 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.

After injection of the standard, the thermally desorbed organic halogen compound was introduced into the plasma. Comparison of the peak areas gave the amount of halogen (mg).

The amount of organic halogen, W_0 , after gas sampling was calculated using Eq. (2):

$$W_0 = W_s \times \frac{S_0}{S_s} \quad (2)$$

where, S_s is the peak area of the standard, which was 2,2,2-trifluoroethanol or bromochloromethane in this study, and S_0 is the peak area of the organic halogen in Carbotrap B or C.

1.5 Plastic decomposition process

A chlorine-containing plastic was burned under different oxygen concentrations, namely 2%, 5%, 10%, 20%, 50%

and 100%, in a system consisting of electric furnaces, one of which was movable. The organic chlorine was measured at a decomposition temperature of 800°C, under the optimal conditions determined using barrier discharge radiofrequency-helium-plasma/AES.

2 Results and discussion

2.1 Emission intensity and detection limit

The results of the S/B studies are shown in **Table 1**. About 200 ng of F, 10 ng of Cl, and 5 ng of Br gave a signal emission intensity equal to the background ($S/B = 1$) for an electric power from 32 to 46 W. The detection limit was 10 ng of F, 2 ng of Cl and 1.5 ng of Br. However, these values are significantly affected by the optical conditions. A recent study by Ohba et al. (2006) using a DC microplasma achieved detection limits in the 10 pg region. However, practical detection ranges are more important in actual applications. The present discharge was maintained for injections of microgram levels of F, Cl, and Br.

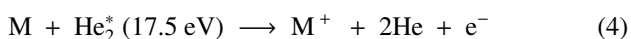
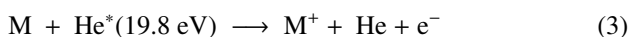
Table 1 Amounts of F, Cl, or Br in barrier-discharge radiofrequency-helium-plasma/atomic emission spectrometry

	Halogen elements amounts (ng)*		
	32 W	40 W	46 W
F	185	181	185
Cl	12.5	8.9	7.1
Br	6.5	5.2	4.7

* Emission intensity in barrier discharge radiofrequency plasma-atomic emission reach $S/B = 1$.

The amounts of F needed to reach an emission intensity of $S/B = 1$ were much larger than those needed for Cl and Br. One reason why determination of F is more difficult than determination of Cl and Br is that the emission wavelength of F, 739.9 nm, is close to that of emissions from air, 700–800 nm, which leaks into the system via the outlet of the discharge tube (**Fig. 4**). The background in F determination is therefore not stable. In contrast, as the emission wavelengths of Cl and Br are 837.6 nm and 827.2 nm, respectively, this problem does not occur with Cl and Br.

As the He_2^* molecule is in a metastable triplet state, it has a relatively long life and can interact with and ionize foreign atoms in a helium plasma. Foreign atoms (M) are ionized by collisions with molecular helium particles and collisions with metastable helium atoms:



After ionization, the foreign atoms are excited by the capture of slow electrons (Houpt, 1976):

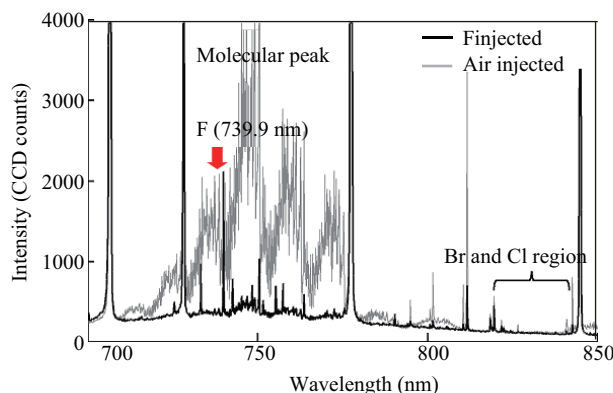
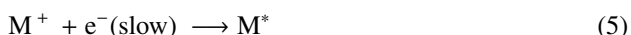


Fig. 4 Spectra of F, Cl, Br, and air.



2.2 Influences of carrier gas flow rate and discharge tube

To clarify the influence of the carrier gas flow rate on the detection sensitivity and limit, the gas flow rate at the injection line was set at 50, 100, 150, or 200 mL/min, with an electric power of 32 W. The amounts of F, Cl, or Br needed in barrier-discharge radiofrequency-helium-plasma/AES for a detection limit of $S/N = 3$ (Cooper, 1970), which revealed detection sensitivity (**Fig. 5**).

The F sensitivity was found to be independent of power consumption, but power consumption affected the Cl and Br sensitivities. The difference between F and Cl and Br is a result of the reaction products formed with the ceramic tube material. Although the SSA-S ceramic tube is very stable, partial reaction with elemental halogens can occur. AlCl_3 and AlBr_3 are gaseous at 300°C, but AlF_3 is in the condensed phase. Interaction is enhanced at higher temperatures, which might therefore reduce the amount of F in the gas, although the plasma density increased with

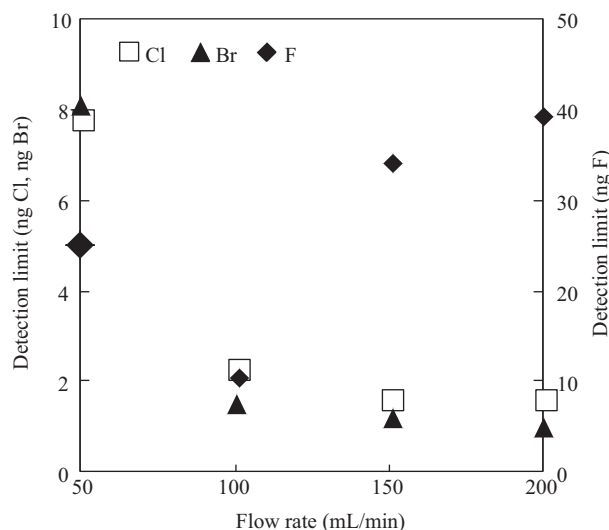


Fig. 5 Required amounts of F, Cl or Br in barrier discharge radiofrequency helium plasma AES at detection limit of $S/N = 3$ with electric power of 32 W.

temperature. In our first report of this type of plasma, although the F peak decreased rapidly, the Cl and Br peaks decreased smoothly (Lepkojus et al., 1999). In that instrumentation, the temperature of the discharge tube was high enough to soften the Teflon support screw. However, in the present work, a smooth decrease in the F peak was obtained because the efficient plasma production emitted little heat. The temperature of the electrode surface was about 250°C, and the temperatures of the supporting parts were low enough for the parts to be touchable after the plasma was extinguished. **Figure 6** shows the barrier-discharge radiofrequency-helium-plasma for F.

2.3 Recovery efficiencies and distributions of SLVOXs

The analytical recoveries and distributions of SLVOXs using different desorption tubes were examined using organic F, organic Cl, and organic Br compounds. **Table 2** gives information on the organic halogen compounds used in this study, and their recoveries using barrier-discharge radiofrequency-helium-plasma/AES. Recoveries for organic F were 90% and 92% for a total added F concentration of 5000 ng. Recoveries for organic Cl ranged from 82% to 99%, and for organic Br ranged from 91% to

110% for total added Cl or Br concentrations of 500 ng and a gas quantity of 30 L.

Figure 7 shows the analytical chart for Br in a monoBBz gas that was measured using barrier-discharge radiofrequency-helium-plasma/ AES with a gas quantity of 9 L. The concentrations of organic Br collected by Carbotrap B or C were calculated from the peak area and concentration of the standard (bromochloromethane), and the peak areas of the desorbed organic Br at Carbotrap B or C, using Eq. (2). The distributions of these organic halogens with different desorption tubes containing Carbotrap B or C are shown in **Fig. 8**. With a gas quantity of 30 L, the distribution of organic halogens in Carbotrap B and C were as follows: 57% and 43% of monoCBz were absorbed by Carbotrap C and B, respectively; more than 94% of *p*-DiCBz, 1,2,3-TriCBz, 1,2,3,5-TetraCBz, *o*-DiBBz, *p*-DiBBz, and 1,3,5-TriBBz were absorbed by Carbotrap C; 49% and 51%, respectively, of pentaCBz, 54% and 46%, respectively, of MonoBBz, were absorbed by Carbotrap C and B.

For mono-BBz, when the gas quantity increased from 9 L to 15 L and 30 L, the distribution ratio for Carbotrap C changed from 100% to 70% and 54%. The organic Cl in mono-CBz and *p*-diCBz showed the same tendency when

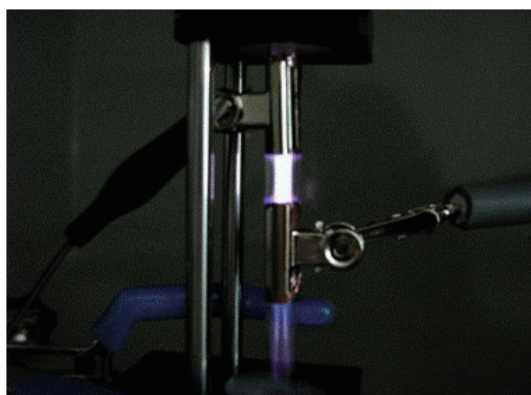


Fig. 6 Photograph of the barrier-discharge radiofrequency-helium-plasma with organic fluorine.

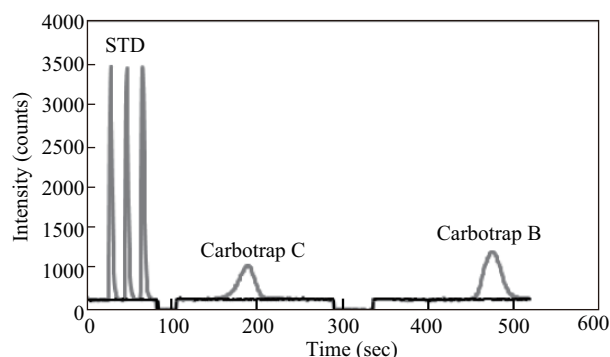


Fig. 7 Analytical chart of Br in mono-BBz gas sample using barrier-discharge radiofrequency-helium-plasma/atomic emission spectrometry.

Table 2 Organic halogen compounds and their recoveries using barrier-discharge radiofrequency-helium-plasma/atomic emission spectrometry

Classification	Compound	Molecular weight	Boiling point (°C)	Recovery (%)		
				9 L	15 L	30 L
Fluorine compounds	Fluorobenzene	96.1	85			90
	Hexafluorobenzene	186.1	82			92
	Chlorobenzene	112.6	132			83
Chlorine compounds	<i>p</i> -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
	Bromobenzene	157	156	82	92	110
Bromine compounds	<i>o</i> -Dibromobenzene	235.9	224			92
	<i>p</i> -Dibromobenzene	235.9	218			91
	1,3,5-Tribromobenzene	314.8	271			104

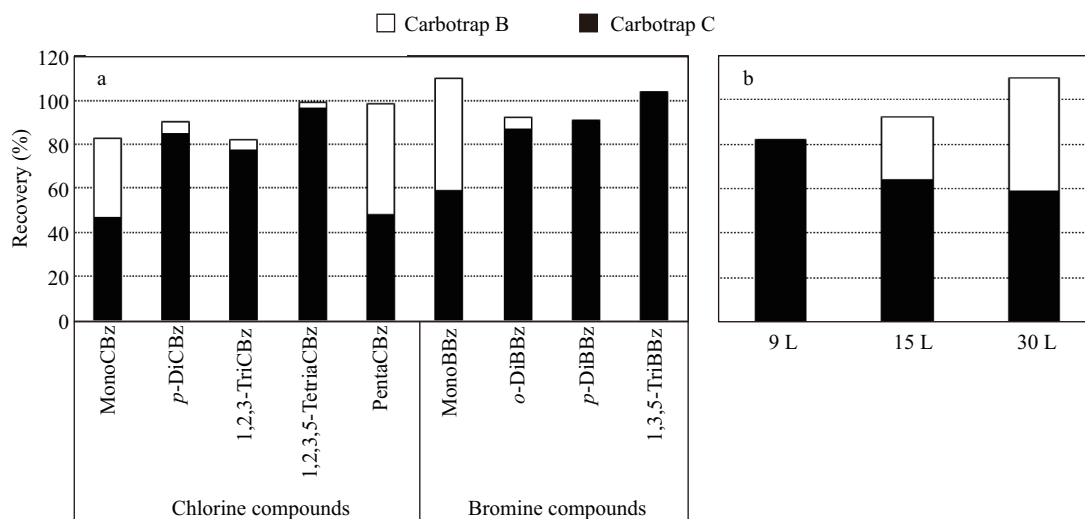


Fig. 8 (a) Distribution of organic Cl and organic Br at Carbotrap B or C with gas quantity of 30 L and (b) organic Br in bromobenzene at Carbotrap B or C for different gas quantities.

the gas quantity increased to more than 30 L. Carbotrap C first absorbs the organic Cl and Br, and then some of the absorbed halogens are transferred to Carbotrap B. This was due to the boiling points of these compounds, which are in the range 130–170°C. Carbotrap C, with its small surface area of 10 m²/g, was appropriate for the determination of organic halogens with boiling points in the range 130–170°C. However, pentaCBz was different: 49% and 51% were respectively absorbed by Carbotrap C and B. Carbotrap B was suitable for the determination of organic halogens with boiling points below 130°C. These results indicate that if Carbotrap B and C are used properly, based on the characteristics of the analyzed compounds, the SLOVXs of flue gases from MSWIs can be measured with high sensitivity.

2.4 Analytical application

The developed method has been used to study the influence of oxygen concentration on chlorine production during decomposition of a polymer. **Figure 9** shows the generation ratio of organic chlorine to total chlorine at different oxygen concentrations. As the oxygen concentration increased, the relative amount of organic chlorine also increased. Except for the data point for an oxygen concentration of 2.5%, subject to the detection limit, the correlation is linear. At a 5% oxygen concentration, the generation ratio of organic chlorine was lowest at only 0.2%. When the oxygen concentration reached 100%, all of the chlorine was converted to organic chlorine.

3 Conclusions

The barrier discharge radiofrequency-helium-plasma/AES system could determine organic halogens in SLVOXs with a detection limit with 10.4 ng of F, 2.3 ng of Cl, and 1.5 ng of Br at $S/N = 3$ with electric power of 32 W, and emission

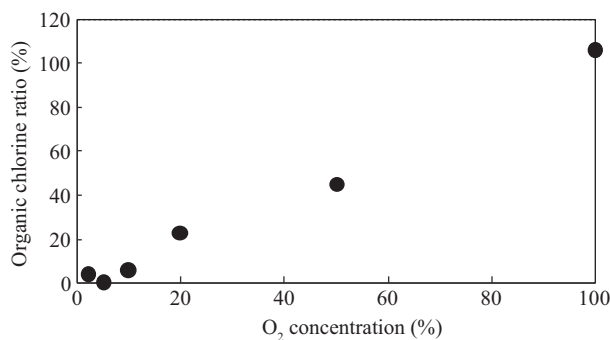


Fig. 9 Organic chlorine generation ratios for different oxygen concentrations.

intensity with 180 ng of F, 10 ng of Cl, and 10 ng of Br for tens of micrograms. Moderate power consumption was sufficient to achieve a good F line signal. The interaction of F with the inner surface of the discharge tube was minimized by a low temperature of operation.

As the carrier gas flow rate at the injection line was increased, the amount of standards or samples per unit time increased and the detection sensitivity of Cl and Br increased, while the detection limit of Cl and Br decreased. However, as the flow rate was increased from 100 to 200 mL/min, F could not be thoroughly excited by helium. Therefore, the detection limit of F became weaker. A slower rate for the carrier gas at the injection lines was established at 100 mL/min.

The gas sampling and analysis system showed high recoveries (80%–110%) of SLVOX detected by the barrier discharge radiofrequency-helium-plasma/AES system. The Carbotrap B or Carbotrap C adsorbents were suitable for collection, and thermal desorption was an efficient analysis method. Carbotrap C was appropriate for high boiling point compounds, while Carbotrap B was suitable for the determination of organic halogens with low boiling points below 130°C. The compounds with intermediate

boiling points ranging from 130 to 170°C distributed between Carbotrap B and C.

The barrier discharge radiofrequency-helium-plasma/AES system could be applied for real-time detection of flue gas from MSWIs. The results showed that the concentration of SLVOC had a good linear relationship with dioxins (Watanabe et al., 2007). In addition, the gas quantity of 20 L was sufficient for the radiofrequency helium plasma AES system, which is about 1/15 of that required for the AOX system.

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References

- Cooper J A, 1970. Factors determining the ultimate detection sensitivity of Ge(Li) gamma-ray spectrometers. *Nuclear Instruments and Methods*, 82: 273–277.
- Froese K L, Hutzinger O, 1996. Polychlorinated benzene, phenol, dibenzo-*p*-dioxin, and dibenzofuran in heterogeneous combustion reactions of acetylene. *Environmental Science & Technology*, 30(3): 998–1008.
- Gullett B K, Bruce K R, Beach L O, 1990. Formation of chlorinated organics during solid waste combustion. *Waste Management & Research*, 8(3): 203–214.
- Hayashi H, Tanaka T, Hiraide M, 2001. Electrothermal vaporization on a tungsten filament for the determination of arsenic in chloride solutions by low-pressure helium ICP-MS. *Analytical Sciences*, 17(1): 171–173.
- Houpt P M, 1976. Physical phenomena and analytical applications of helium microwave discharges. *Analytica Chimica Acta*, 86: 129–138.
- Jay K, Stieglitz L, 1991. On the mechanism of formation of polychlorinated aromatic compounds with copper(II) chloride. *Chemosphere*, 22(11): 987–996.
- Kagaku Binran (II), 1999. The Chemical Society of Japan, Maruzen, Tokyo, Japan. 764.
- Karasek F, 1995. An overview of dioxin formation in combustion processes. *Organohalogen Compounds*, 23: 315–317.
- Karasek F W, Dickson L C, 1987. Model studies of polychlorinated dibenzo-*p*-dioxin formation during municipal refuse incineration. *Science*, 237(4816): 754–756.
- Kato M, Urano K, Tasaki T, 2000. Development of semi-and nonvolatile organic halogen as a new hazardous index of flue gas. *Environmental Science & Technology*, 34(19): 4071–4075.
- Lepkojus F, Watanabe N, Buscher W, Cammann K, Bohm G, 1999. A simple radiofrequency helium discharge plasma (RFP) for spectroscopic purposes. *Journal of Analytical Atomic Spectrometry*, 14(9): 1511–1513.
- Ministry of the Environment of Japan. http://www.env.go.jp/recycle/waste/ippan/ippan_h16.pdf.
- Nakui H, Koyama H, Takakura A, Watanabe N, 2011. Online measurements of low-volatile organic chlorine for dioxin monitoring at municipal waste incinerators. *Chemosphere*, 85(2): 151–155.
- Ohba G, Miyahara H, Watanabe M, Hotta E, Okino A, 2006. Development of microplasma source for trace elemental analysis and its application to AES measurement of halogen. *Bunseki Kagaku*, 55(8): 555–560.
- Pedersen-Bjergaard S, Greibrokk T, 1993. On-column bromine- and chlorine-selected detection for capillary gas chromatography using a radio frequency plasma. *Analytical Chemistry*, 65(15): 1998–2002.
- Rittmeyer C, Kaese P, Vehlow J, Vilöhr W, 1994. Decomposition of organohalogen compounds in municipal solid-waste incineration plants. 2. Co-combustion of CFC containing polyurethane foams. *Chemosphere*, 28(8): 1455–1465.
- Sakai S I, Hayakawa K, Takatsuki H, Kawakami I, 2001. Dioxin-like PCBs released from waste incineration and their deposition flux. *Environmental Science & Technology*, 35(18): 3601–3607.
- Shaub W M, Tsang W, 1983. Dioxin formation in incinerators. *Environmental Science & Technology*, 17(12): 721–730.
- Stieglitz L, Vogt H, Zwick G, Beck J, Bautz H, 1991. On formation conditions of organohalogen compounds from particulate carbon of fly-ash. *Chemosphere*, 23(8-10): 1255–1264.
- Stieglitz L, Zwick G, Beck J, Bautz H, Roth W, 1989. Carbonaceous particles in fly-ash – a source for the de-novo-synthesis of organochlorocompounds. *Chemosphere*, 19(1-6): 283–290.
- Stieglitz L, Zwick G, Beck J, Bautz H, Roth W, 1990. The role of particulate carbon in the de-novo synthesis of polychlorinated dibenzodioxins and-furans in fly-ash. *Chemosphere*, 20(10-12): 1953–1958.
- Tange L, Drohmann D, 2005. Waste electrical and electronic equipment plastics with brominated flame retardants – from legislation to separate treatment-thermal processes. *Polymer Degradation and Stability*, 88(1): 35–40.
- Vehlow J, Bergfeldt B, Jay K, Seifert H, Wanke T, Mark F E, 2000. Thermal treatment of electrical and electronic waste plastics. *Waste Management and Research*, 18(2): 131–140.
- Watanabe N, Buscher W, Böhm G, 2002. Determination of fluorine, chlorine, bromine and iodine by barrier discharge radiofrequency helium plasma. *Analytical Sciences*, 18(11): 1191–1194.
- Watanabe N, Takakura A, Minami Y, Mizutani S, Takatsuki H, 2007. Correlation of low-volatile organic chlorine (LVO-Cl) and PCDD/Fs in various municipal waste incinerators (MWIs). *Chemosphere*, 67(9): S198–S204.

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