Note

A Simple Method for Sampling and Analysis of Particulate, Inorganic Gaseous and Organic Gaseous Halogens in the Atmosphere

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A simple method for simultaneous sampling and analysis of particulate, inorganic and organic gaseous halogens, Cl, Br and I, in the atmosphere was reported. The sampling system consisted of three kinds of filters of 47 mm ϕ which were supported in a Norwegian Institute for Air Research (NILU) filter holder system connected in series. Fine and coarse particulate halogens were collected on separate fluoropore filters with a cascade impactor. Inorganic gaseous halogens were sampled with three cellulose filters impregnated with 1 M LiOH in a 10% glycerol water mixture. Organic gaseous halogens were absorbed in three activated charcoal paper filters. An outdoor air sample was passed at a flow rate of 10 L min^{-1} every two weeks. After sample collection, each filter sample was separately sealed in a polyethylene bag, and analyzed for Cl, Br and I with an instrumental neutron activation analysis (NAA) using the Kyoto University Research Reactor (KUR). Recoveries of inorganic and organic gaseous halogens in this system were greater than 80%. Atmospheric I concentrations of coarse and fine particulate, inorganic and organic gaseous were between 0.17 - 0.52, 0.46 - 1.38, 1.50 - 3.44 and 1.66 - 5.94 ng m^{-3}, respectively. Those of Br were between 6.94 - 14.03, 1.74 - 3.92, 8.59 - 12.68 and 6.65 - 17.05 ng m^{-3}, respectively. And those of Cl ranged between 1980 - 4600, 5.72 - 23.16, 318 - 647 and 25.0 - 115 ng m^{-3}, respectively.

Key words: halogen, inorganic gaseous, organic gaseous, NAA analysis

1. Introduction

Atmospheric halogen (Cl, Br, I) compounds are important constituents that affect the concentrations of ozone and hydrocarbons, and cloud condensation nuclei through several chemical reactions[1, 2]. The main natural source of Cl, Br and I in the atmosphere is the ocean, they are also released from the combustion of fossil fuels[3,4]. Physicochemical fractions of atmospheric halogens are classified into particulate, inorganic gas and organic gas forms. It is expected that the behavior of halogens in each fraction in the atmosphere is different. Cicerone[5] has summarized an overview of research on halogens in the atmosphere (species, transformation and global cycles). However, reported values about the chemical forms of halogens in the atmosphere are limited[6, 7]. We applied a simple method for determination of particulate, inorganic

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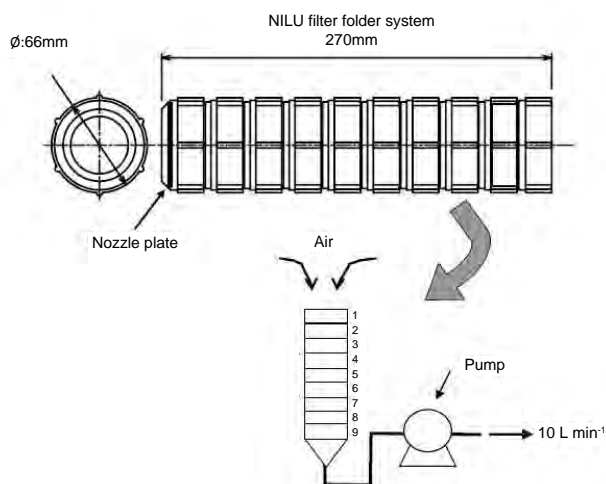E-mail: akata.naofumi@lhd.nifs.ac.jp

Fig. 1. Configuration figure of routine air sampling system by NILU filter folder with preseparator.

and organic gaseous halogens in the atmosphere by simultaneously sampling three kinds of filters in Norwegian Institute for Air Research (NILU) filter holder systems, and determined the contents of halogens in the fine and coarse particles, and in inorganic and organic gaseous forms.

2. Experimental

2.1. Sampling system
Configuration of the air sampling system is shown in Fig. 1. The sampling system consisted of nine stages supporting NILU filter holders (NL-O-09, NILU Products AS)[8]. It is made of polycarbonate and silicon O-rings, and the opening diameter is 47 mm with an effective diameter of 40 mm. Recently, fine airborne particulates less than 2.5 μm, $PM_{2.5}$, used as air quality standards for environmental and health effects[9]. Generally, it is well known that the mass concentration of atmospheric aerosols shows a bimodal distribution pattern between approximately 1.0 - 2.0 μm[10,11]. Here, we classified airborne particulate greater than 2.0 μm according to Hara *et al.*[12] Coarse (> 2.0 μm, CP) and fine (< 2.0 m, FP) particulates were collected with a cascade impactor (stage 1) and backup stages (stage 2 + 3) on poreflon membrane filters (AF07P, Sumitomo Electric; DOP (performance test using a powder made by Dioctyl Phthalate): 0.3 μm, collection efficiency: 99.99%), respectively. Inorganic gaseous halogens were collected with three cellulose filters (No. 41, Whatman) impregnated with 1.0 M LiOH in a 10% glycerol water mixture (F_{WHAT}; stage 4, 5, 6; Inorg). Rahn *et al.*[6] reported that these impregnated filters have a high retaining efficiency for inorganic gaseous halogens (HX and X_2). Atmospheric halogens, except particulates and inorganic gases, were absorbed in two activated charcoal

Table 1. Nuclear data for NAA

Element	Process	Half-life(min)	Gamma-ray(keV)
I	^{127}I(n, γ)^{128}I	24.99	443
Br	^{79}Br(n, γ)^{80}Br	17.4	616
Cl	^{37}Cl(n, γ)^{38}Cl	37.3	1642

paper filters (STV-505, Kynol) for each stage (F_{STV}: stage 7, 8, 9; Org). The F_{STV} filters were used after heating (at 150 °C for 4 hours) for degassing under a vacuum. In this study, we assumed that the atmospheric halogens, with the exception of particulates and inorganic gases, were organic gases. There was no pressure loss during the sampling period.

2.2. Air sampling
We installed the sampling system on the roof of building (approximately 13 m from ground level) on Pacific Ocean side of Northern Japan (40°57'N, 141°21'E) a rural area of the Tohoku region. The distance from the Pacific Ocean to the building is approximately 1.5 km. Outdoor air sample was passed at a constant flow rate of 10 L min⁻¹ and the filters were replaced every two weeks from September to December 2006 (*n* = 5).

Local meteorological data such as atmospheric temperature were collected using meteorological observation equipment (AWA2700, Aanderaa Instruments) at the ground level near the sampling point (a distance of approximately 60m). We estimated the average atmospheric temperature during the entire sampling period.

2.3. Instrumental neutron activation analysis of halogens
Details of the analytical method have already been reported[13, 14]. Each filter sample was individually sealed in a small polyethylene bag. Several polyethylene bags were placed together into a polyethylene capsule, and irradiated in the KUR (flux rate: 4.6 x 10¹² n m⁻² s⁻¹) of Kyoto University for 20 seconds. After cooling, the samples were counted with a Ge γ-ray detector connected to a multichannel analyzer (GEM30-70, GEM-25185P and GEM-30105P, ORTEC). The γ-ray energies used for the determination of Cl, Br and I were shown in Table 1. Standard samples were adjusted according to Tsukada *et al.*[14] The data of blank filters were summarized by Tsukada *et al.*[14] The blank filter values were subtracted from the sample values.
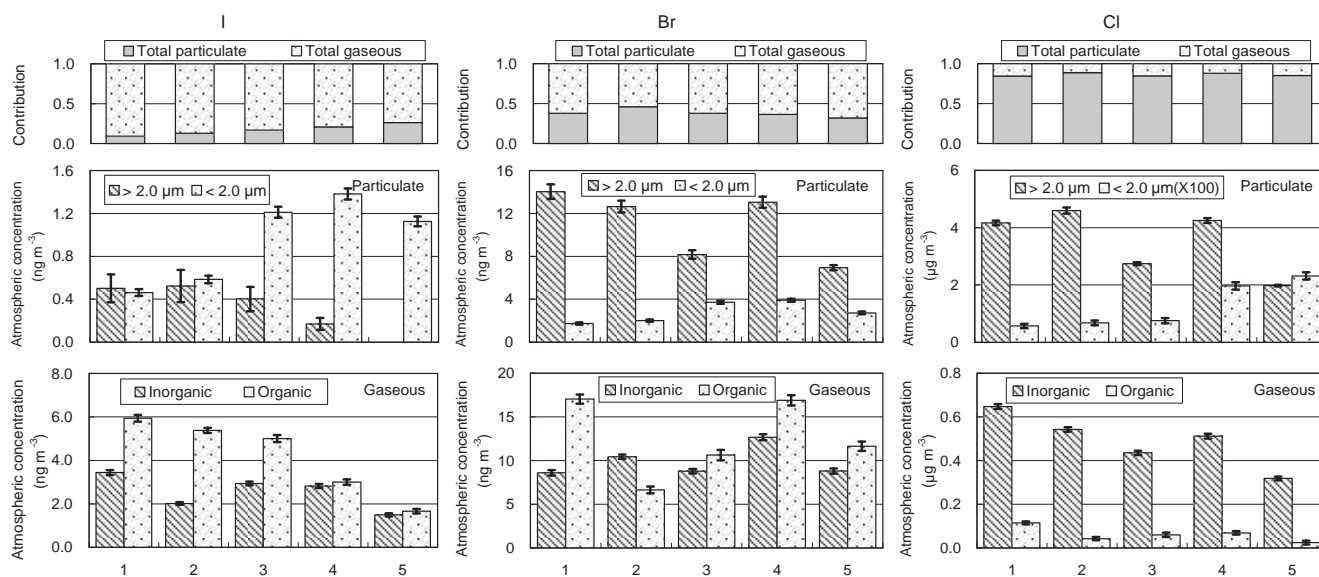
3. Results and Discussion

3.1. Evaluating of the collection efficiencies of gaseous halogens
The collection efficiency (η) was obtained by a nonlinear

Table 2. Collection efficiencies (%) of inorganic and organic gaseous halogens ($n = 5$)

	Inorganic		Organic	
	Range	Mean ± S.D.	Range	Mean ± S.D.
I	82.1 - 93.4	87.5 ± 4.9	91.3 - 100.0	96.6 ± 3.6
Br	100.0 - 101.7	100.3 ± 0.8	80.2 - 93.4	88.5 ± 5.4
Cl	100.0	100.0	100.0	100.0

Fig. 2. Atmospheric concentrations of particulate, inorganic and organic gaseous halogens (sampling period; 1: Aug. 31 - Sep. 15 2006, 2: Sep. 15 - Oct. 2 2006, 3: Oct. 2 - Oct. 16 2006, 4: Oct. 16 - Nov. 1 2006, 5: Nov. 15 - Dec. 1 2006).

least-squares fitting of the analytical result of the collection efficiency at each stage. Table 2 shows the collection efficiencies of inorganic and organic gaseous halogens calculated at three stages. The collection efficiencies of inorganic and organic I ranged from 82.1 to 93.4% with a mean of 87.5 ± 4.9% and from 91.3 to 100.0% with a mean of 96.6 ± 3.6%, respectively. And collection efficiencies of inorganic and organic Br ranged from 100.0 to 101.7% with a mean of 100.3 ± 0.3% and from 80.2 to 93.4% with a mean of 88.5 ± 5.4%, respectively. Inorganic and organic Cl demonstrated a collection efficiency of 100% for this system, as Cl in each of the third stages wasn't detected. Although the collection efficiency of I is the lowest among halogens, recoveries of inorganic and organic gaseous I in this system were more than 80%. In this paper, we discuss the atmospheric concentration and percentage of each fraction using the data that have not been corrected for collection efficiencies.

3.2. Concentration level of particulate, inorganic and organic gaseous halogens in the atmosphere
Atmospheric concentrations of particulate, inorganic and organic gaseous halogens are shown in Fig. 2. Atmospheric concentrations of coarse and fine particulate

I, inorganic and organic gaseous I are between 0.17 - 0.52, 0.46 - 1.38, 1.50 - 3.44 and 1.66 - 5.94 ng m^{-3}, respectively. Those of Br are between 6.94 - 14.03, 1.74 - 3.92, 8.59 - 12.68 and 6.65 - 17.05 ng m^{-3}, respectively. And those of Cl are between 1980 - 4600, 5.72 - 23.16, 318 - 647 and 25.0 - 115 ng m^{-3}, respectively. The average concentration of I in the fractions was in the order of CP< FP< Inorg (Inorganic) < Org (Organic) due to the element being very volatile. However, the concentration Br in the fine particulate fraction was the lowest. The concentration of Cl in the coarse particulate fraction was the highest among all of the fractions as it is derived from sea-salt particles. The results show the percentage distribution among I, Br and Cl in the fractions were different as the result of their characteristics. Yoshida et al.[8] reported atmospheric concentrations of these species I in Ibaraki, Japan (April 1990 to May 1991) ranged 0.3 - 3.4 (particulate), 1.2 - 3.3 (inorganic gas) and 7.8 - 20.4 ng m^{-3} (organic gas), respectively, which were comparable to our results. Tsukada et al.[12] reported atmospheric concentration of particulate and inorganic gaseous halogens in Chiba, Japan (June 1991 to February 1992). Our results of inorganic halogens were comparable to the reported values, and those of particulate halogens were lower than
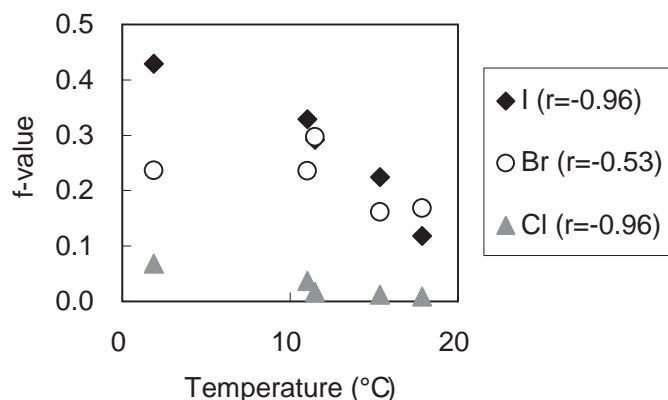
Fig. 3. Temperature dependence of *f*-values for I, Br and Cl.

the results at Chiba.

It is known that atmospheric halogens change phase as a result of the physicochemical factor[5]. Tsukada *et al.*[15] has demonstrated the gas-to-particle conversion of gaseous I. The gas and particle distribution factor of halogens, the *f*-value[12] was defined as follows:

$$f - \text{value} = \frac{P_{\text{fine}}}{P_{\text{fine}} + G_{\text{inorganic}}} \qquad (1)$$

where P_{fine} and $G_{\text{inorganic}}$ are the concentrations of fine particulate and inorganic gaseous halogens, respectively. The plot in Fig. 3 demonstrates a clear negative correlation between the air temperature and *f*-values. This suggests that the gas-to-particle conversion of halogens is dependent on air temperature. The *f*-values of Br and I are slightly higher than that of Cl. It seems that gas-to-particle conversion from homogeneous gas-phase reaction and particulate-phase reaction process is different in Cl, Br and I. And it would be the reason of the observed complementary seasonal variation of halogen concentrations in the particulate and gaseous phase.

4. Conclusion

A simple method for sampling and analysis of particulate, inorganic and organic gaseous halogens, Cl, Br and I, in the atmosphere was examined. The sampling system consisted of three kinds of filters which were supported over nine stages in NILU filter holders. The concentrations of I, Br and Cl in the sample filters were determined by instrumental neutron activation analysis. The results indicate that the recoveries of inorganic and organic gaseous halogens in this system were greater than 80%. This collecting system is utilized for sampling

of physicochemical fractions in atmospheric halogens.

Conflict of Interest Disclosure

The authors declare that they have no conflict of interest.

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