

Simultaneous Determination of Halogen Compounds and Sulfur Oxides in Flue Gas by Ion Chromatography

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Abstract: Ion chromatography (IC) is a suitable analytical method for the determination of anions. As analytical methods for the halogen compounds in flue gas, those of bromine compound, fluorine compound, chlorine (Cl₂) and hydrogen chloride (HCl) are listed in JIS. However, IC has not been adopted in JIS except for HCl and Cl₂. Because the carbon dioxide in flue gas is absorbed in a 0.1 M sodium hydroxide solution as an absorber, it is interfered with the measurement of F⁻ and Cl⁻ ions. This paper describes the development of the pretreatment equipment for the flue gas analysis by IC, and its applications to real flue gas analysis. The F⁻, Cl⁻, Br⁻ and SO₄²⁻ in the absorbing solution can be clearly separated by IC using the pretreatment equipment. The halogen compounds and sulfur oxides in flue gas can be simultaneously determined by IC.

Key word: Fluorine compound, chloride compound, sulfur oxide, flue gas analysis, ion chromatography.

1. Introduction

Sulfur oxides (SO_x), nitrogen oxides (NO_x) and hydrogen chloride (HCl) from stationary sources such as factories and waste incineration plants, are causative substances of air pollution and acid rain, therefore, the emissions of these compounds are strictly regulated. Titrimetry, spectrophotometry and ion selective electrode methods for the determination of the components in flue gas are described in JIS [1-3]. Since the concentration of these components was lower so far because of the regulation and treatment of emission gases, it can not be measured by the conventional methods described in JIS.

Ion chromatography (IC) is a suitable analytical method for the determination of ions at low concentration. It has been adopted for the determination of SO_x [1, 4], NO_x [2, 5, 6], HCl [3, 7], Cl₂ [8] and ammonia [9] in flue gas. We have already

reported the simultaneous determination of SO_x, NO_x and HCl in flue gas [10-12], and cyanide compounds in wastewater [13, 14] by IC.

On the other hand, it is thought that halogen compounds in emission gases are related to the formation of dioxin-like substances. Precise determination of halogen compounds in flue gases is highly expected. As analytical methods for the halogen compounds in flue gas, those for bromine compound [15], fluorine compound [16], chlorine [8] and HCl [3] are listed in JIS. However, IC has not been adopted in JIS except for HCl [3] and Cl₂ [8].

This paper describes the development of the pretreatment equipment for the analysis of halogen compounds in flue gas by IC, and its applications to the simultaneous determination of halogen compounds and sulfur oxides in flue gas.

2. Experiment

2.1 Apparatus

The chromatographic measurements were performed using a Dionex system DX 500 ion

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chromatograph equipped with a conductivity detector. The sample loop size was 25 μL . A separator column (IonPac AS12A) with a guard column (IonPac AG12A) and an anion self regenerating suppressor (ASRS- II) were used at 35 $^{\circ}\text{C}$. The eluent was 2.7 mM Na_2CO_3 + 0.3 mM NaHCO_3 at the flow rate of 1.3 $\text{mL}\cdot\text{min}^{-1}$. The suppressor regenerant was prepared from the eluent at 50 mA (Recycle mode).

In order to remove the sodium and carbonate ions in the absorbing solution, so the pretreatment equipment has been developed (Fig. 1). It consists of a gas washing bottle containing a 0.1 M sodium hydroxide (NaOH) solution, a neutralization-degassing bottle, a pump and a flow meter.

2.2 Reagents

All chemicals used in this study were commercially available highest grade.

As the absorbing solution, a 0.1 M NaOH solution is commonly used for the collection of HCl, fluorine and bromine compounds in the official methods [3, 15, 16]. Therefore, a 0.1 M NaOH solution was also used for the collection of the halogen compounds in the flue gases in these experiments. In addition, a 0.1 M NaOH and 0.1% H_2O_2 mixed solution is preferable for the collection of

halogen compounds and SO_x in the flue gases.

A mixed standard solution containing seven different anions from Kanto Chemical Co., Ltd., was used.

2.3 Procedures

An aliquot of the absorbing solution and H^+ formed cation exchange resin (Amberlite IR124HAG) were added to the neutralization-degassing bottle in Fig. 1, and followed by an aeration of air or nitrogen at 0.25 $\text{L}\cdot\text{min}^{-1}$ for 10 min through the bottles. The solution was then analyzed by IC.

3. Result and Discussion

3.1 Effects of NaOH Absorbing Solution and Carbonate Ion for the Separation of Anions

The problem about interference of carbonate ion has been studied by using a 0.1 M NaOH absorbing solution for the collection of the halogen compounds in the flue gas and analyzing it by IC.

A mixed standard solution containing seven different anions was added to the 0.1 M NaOH absorbing solution and analyzed by IC using a carbonate eluent (Fig. 2).

As a result, the alkaline peak and large water dip

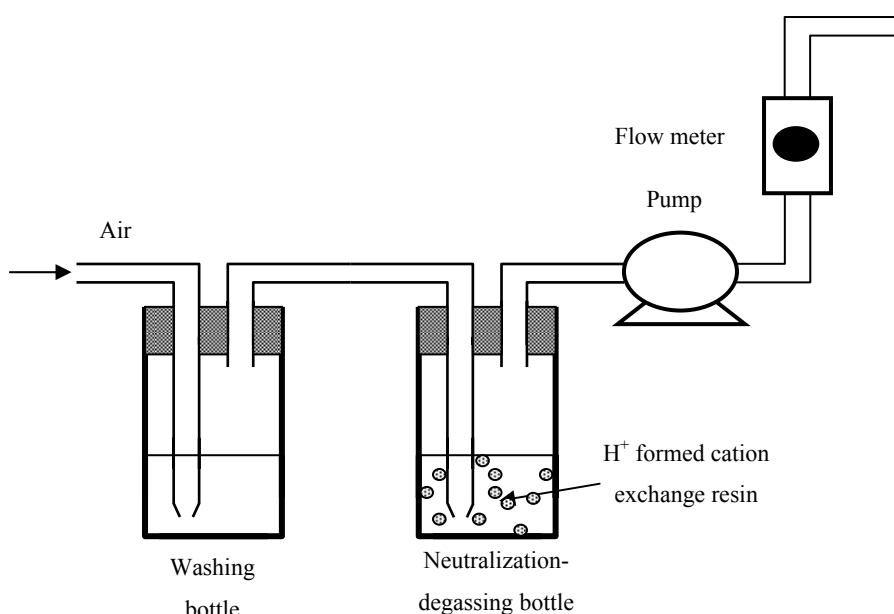


Fig. 1 Pretreatment equipment.

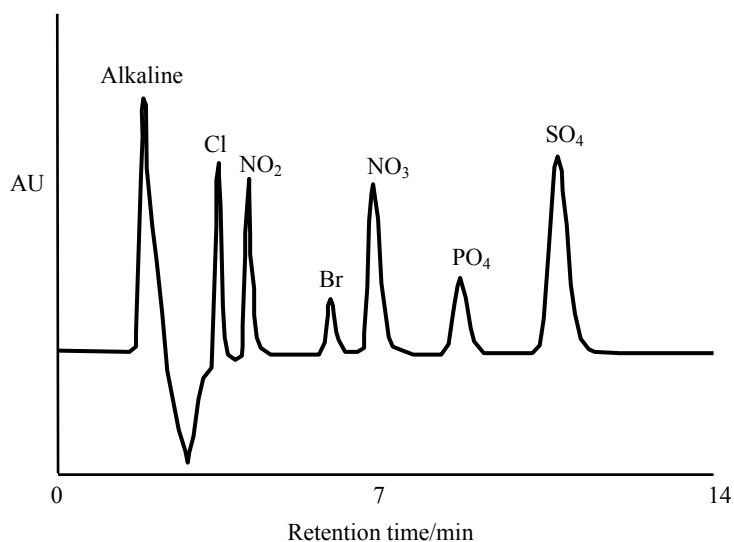


Fig. 2 Separation of seven anions in 0.1 M NaOH solution using carbonate mixed eluent. Sample: seven anions in a 0.1 M NaOH solution. Column: Ion Pac AG12A + Ion Pac AS12A. Suppressor: ASRS-II. Eluent: 2.7 mM Na_2CO_3 + 0.3 mM NaHCO_3 . Detector: conductivity.

appeared on the chromatogram, because the absorbing solution had a higher concentration of alkaline than the carbonate eluent. Therefore, it interfered with the measurement of the fluoride ion (F^-).

3.2 Addition of Cation Exchange Resin

In order to remove the water dip due to the alkaline absorbing solution containing the seven anions, an aliquot of the H^+ formed cation exchange resin (1 g) was added to the solution (10 mL), and the chromatogram was improved (Fig. 3).

As a result, the alkaline peak disappeared and big water dip became smaller, then the F^- peak appeared. This is because the sodium ion in the absorbing solution was adsorbed and neutralized with H^+ formed cation exchange resin.

3.3 The Removal of Carbonate Ion

When a 0.1 M NaOH absorbing solution was used, high concentration of carbon dioxide (CO_2) in the flue gas was collected in the solution at the same time.

In order to remove the CO_3^{2-} in an absorbing solution, 0.1 M Na_2CO_3 solution containing the seven anions was used, and air was pumped for a definite time after the addition of H^+ formed cation exchange resin into

the solution. These results are shown in Fig. 4(a) and Fig. 4(c).

In Fig. 4(a), the F^- and Cl^- peaks overlapped with the large alkaline and CO_3^{2-} peaks, therefore, these ions could not be determined. When 1 g of the H^+ formed cation exchange resin was added to the 10 mL of the 0.1 M Na_2CO_3 solution containing the seven anions in Fig. 1, the large alkaline peak disappeared, and the F^- and Cl^- peaks appeared. However, the CO_3^{2-} peak remained between the F^- and Cl^- peaks, and interfered with the separation of the F^- and Cl^- peaks (Fig. 4(b)).

Furthermore, when air was pumped at $0.25 \text{ L}\cdot\text{min}^{-1}$ into the solution for 10 min, the CO_3^{2-} peak disappeared, and the F^- and Cl^- peaks were clearly separated (Fig. 4(c)).

In order to remove CO_3^{2-} from the absorbing solution, the aeration time and the behavior of the seven anions in the 0.1 M Na_2CO_3 (20 mL) after the addition of the H^+ formed cation exchange resin (2 g) were studied. These results are shown in Fig. 5.

The CO_3^{2-} peak disappeared by a 15-min aeration and the separation of the F^- and Cl^- peaks was improved. Although the nitrite ion (NO_2^-) concentration was decreased by aeration, the other anions remained stable during the 60-min aeration. The following pretreatment

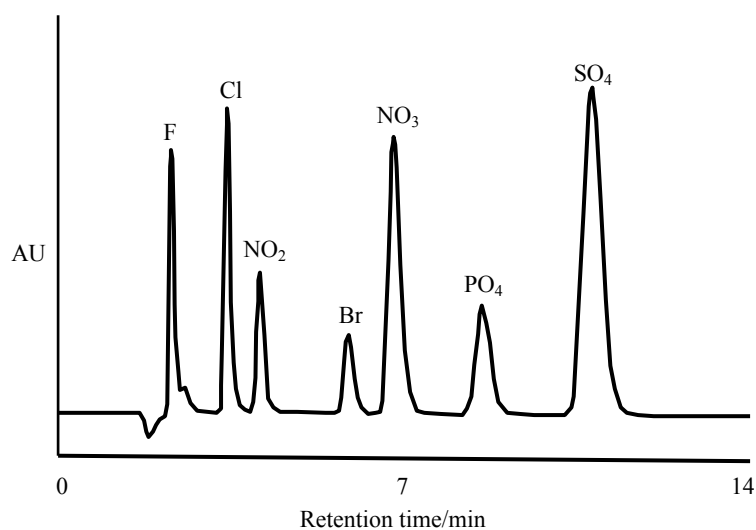


Fig. 3 Effects of cation exchange resin on the separation of seven anions in 0.1 M NaOH solution. Sample: seven anions in a 0.1 M NaOH solution. Column: Ion Pac AG12A + Ion Pac AS12A. Suppressor: ASRS-II. Eluent: 2.7 mM Na₂CO₃ + 0.3 mM NaHCO₃. Detector: conductivity.

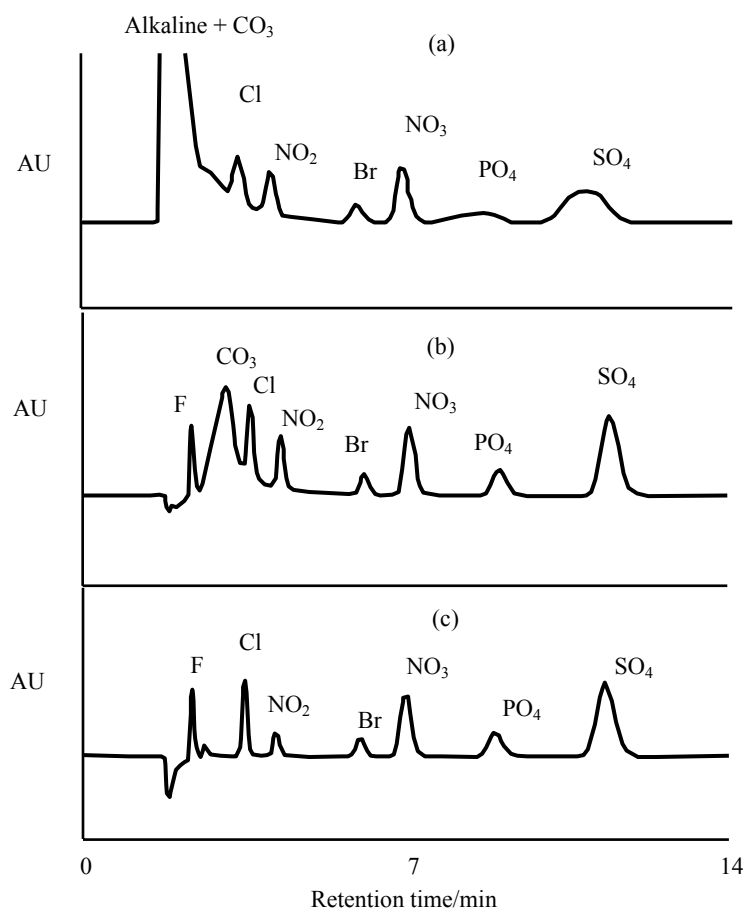


Fig. 4 Chromatogram of seven anions in 0.1 M Na₂CO₃ solution. (a): Seven anions in a 0.1 M Na₂CO₃ solution; (b): Addition of cation exchange resin in a 0.1 M Na₂CO₃ solution containing seven anions; (c): After aeration for 10 min. Column: Ion Pac AG12A + Ion Pac AS12A. Suppressor: ASRS-II. Eluent: 2.7 mM Na₂CO₃ + 0.3 mM NaHCO₃. Detector: conductivity.

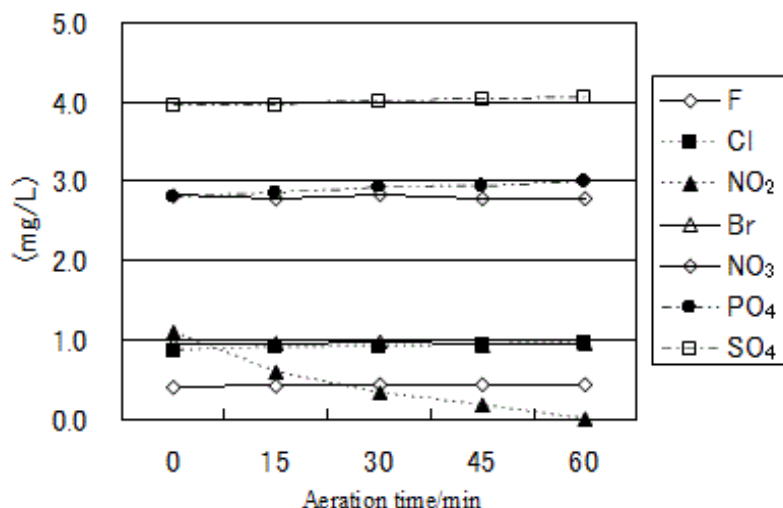


Fig. 5 Effects of anions after the addition of cation exchange resin and aeration. Sample: 0.1 M Na₂CO₃ solution containing seven anions (20 mL) + cation exchange resin (2 g). Column: IonPac AG12A + IonPac AS12A. Suppressor: ASRS-II. Eluent: 2.7 mM Na₂CO₃ + 0.3 mM NaHCO₃. Detector: conductivity.

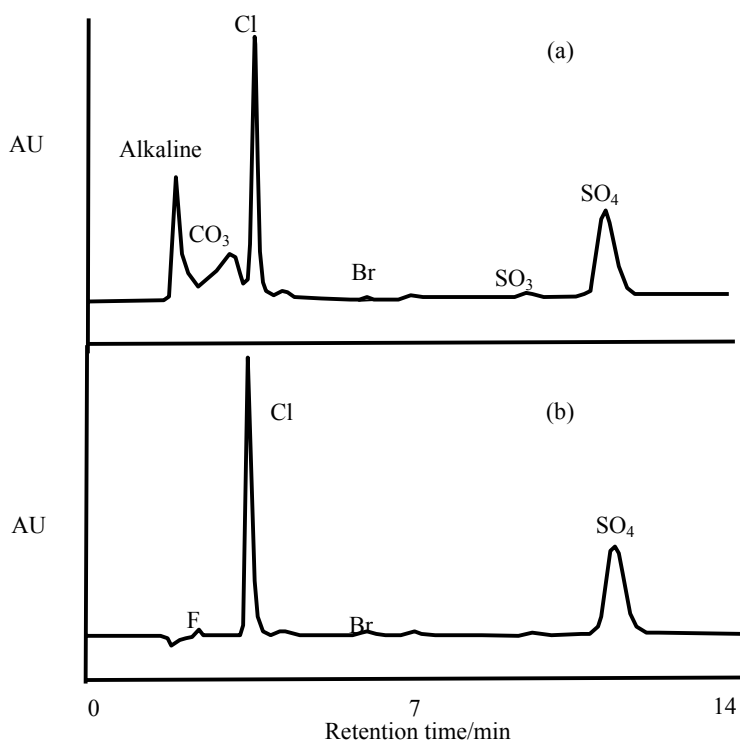


Fig. 6 Real flue gas analysis. (a): Flue gas analysis directly by IC; (b):Flue gas analysis after the pretreatment. Column: Ion Pac AG12A + Ion Pac AS12. Suppressor: ASRS-II. Eluent: 2.7mM Na₂CO₃+ 0.3 mM NaHCO₃. Detector: conductivity.

is recommended; after the collection of the halogen compounds in the flue gas, an H⁺ formed cation exchange resin (1 g) is added to the absorbing solution (10 mL) and air is pumped at 0.25 L·min⁻¹ for 10 min. using the pretreatment equipment in Fig. 1.

3.4 Real Flue Gas Analysis

The flue gases from a waste incineration plant were absorbed in 0.1 M NaOH absorbing solutions four times. The pretreatments were performed by using the H⁺ formed cation exchange resin and aeration, and then the

ions were determined by IC. The chromatograms are shown in Fig. 6, and the concentrations are shown in Table 1. As a result, the alkaline and CO_3^{2-} peaks disappeared by the pretreatment, and the F^- , Cl^- , Br^- and SO_4^{2-} in the absorbing solution were clearly separated and could be simultaneously determined.

The concentration of HF, HCl, HBr and SO_x in the real flue gases were 0.2-0.6 ppmv, 16.5-65.6 ppmv, 0.0-0.2 ppmv and 10.8-38.4 ppmv, respectively.

In addition, the F^- and Cl^- in the absorbing solution were determined by Lanthanum-alizarin complexone absorptiometry (LAC) [16] and mercury (II) thiocyanate absorptiometry (MTC) [3] of JIS (Table 2).

Almost the same results were obtained for HCl between the proposed IC and MTC of JIS. However, HF was not determined by LAC, because the concentrations were below the determination limit of JIS.

4. Conclusions

The halogen compounds and sulfur oxides in the flue gas were collected in 0.1 M NaOH absorbing solution. A cation exchange resin (1 g) was added to the absorbing

Table 1 Determination of halogen compounds and sulfur oxides in real flue gas by IC sulfur Column: Ion Pac AG12A + Ion Pac AS12A.

Sampling No.	HF	HCl	HBr	SO_x
1	0.2	16.5	0.0	38.4
2	0.5	35.5	0.1	20.2
3	0.2	27.9	0.0	10.8
4	0.6	65.6	0.2	24.6

Concentration unit: ppmv.

Table 2 Comparison of HF and HCl with IC and absorptiometry.

Sampling No.	HF IC ¹	HF LAC ²	HCl IC ¹	HCl MTC ²
1	0.2	< 1.0	16.5	17.0
2	0.5	< 1.0	35.5	36.3
3	0.2	< 1.0	27.9	28.4
4	0.6	< 1.0	65.6	64.9

Concentration unit: ppmv,

IC: Ion chromatography,

LAC: Lanthanum-alizarin complexone absorptiometry,

MTC: Mercury (II) thiocyanate absorptiometry,

¹: Analyzed at TMIRI,

²: Analyzed at ECC.

solution (10 mL) and air was pumped at $0.25 \text{ L} \cdot \text{min}^{-1}$ for 10 min using the pretreatment equipment. The F^- , Cl^- , Br^- and SO_4^{2-} in the absorbing solution could be clearly separated. By this treatment, low concentrations of halogen compounds (HF, HCl, HBr) and SO_x in the flue gas could be simultaneously determined by IC. This is expected to shorten the time for gas sampling and analysis and reduce the cost of analysis.

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References

- [1] JIS K 0103, Methods for Determination of Sulfur Oxides in Flue Gas, Japanese Standards Association, Tokyo, 2005.
- [2] JIS K 0104, Methods for Determination of Nitrogen Oxides in Flue Gas, Japanese Standards Association, Tokyo, 2000.
- [3] JIS K 0107, Methods for Determination of Hydrogen Chloride in Flue Gas, Japanese Standards Association, Tokyo, 2002.
- [4] ISO 11632, Stationary Source Emissions—Determination of Mass Concentration of Sulfur Dioxide—Ion Chromatography Method, International Organization for Standards, 1998.
- [5] EPA Method 7A, Determination of Nitrogen Oxide Emissions from Stationary Sources—Ion Chromatographic Method, US Environmental Protection Agency, p. 626.
- [6] EPA Method 7D, Determination of Nitrogen Oxide Emissions from Stationary Sources—Alkaline/Permanganate/Ion Chromatographic Method, US Environmental Protection Agency, p. 637.
- [7] EPA Method 26, Determination of Hydrogen Chloride Emissions from Stationary Sources, US Environmental Protection Agency, p. 865.
- [8] JIS K 0106, Methods for Determination of Chlorine in Flue Gas, Japanese Standards Association, Tokyo, 2010.
- [9] JIS K 0099, Methods for Determination of Ammonia in Flue Gas, Japanese Standards Association, Tokyo, 2004.
- [10] M. Nonomura, T. Hobo, E. Kobayashi, T. Murayama, M.

Satoda, Ion chromatographic determination of nitrogen monoxide and nitrogen dioxide after collection in absorption bottle, *J. Chromatogr. A* 739 (1996) 301.

- [11] M. Nonomura, T. Hobo, Simultaneous determination of sulfur oxides, nitrogen oxides and hydrogen chloride in flue gas by means of an automated ion chromatographic system, *J. Chromatogr. A* 804 (1998) 151.
- [12] M. Nonomura, Determination of carbon dioxide and acid components in exhaust gas by suppressed ion chromatography, *Anal. Sci.* 20 (2004) 219.
- [13] M. Nonomura, Indirect determination of cyanide

compounds by ion chromatography with conductivity measurement, *Anal. Chem.* 59 (1987) 2073.

- [14] M. Nonomura, T. Hobo, Ion chromatographic determination of cyanide compounds by chloramine-T and conductivity measurement, *J. Chromatogr. A* 465 (1989) 395.
- [15] JIS K 0085, Methods for Determination of Bromine in Flue Gas, Japanese Standards Association, Tokyo, 1998.
- [16] JIS K 0105, Methods for Determination of Fluorine Compounds in Flue Gas, Japanese Standards Association, Tokyo, 1998.