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Short communication

Simultaneous determination of sulphur oxides, nitrogen oxides and hydrogen chloride in flue gas by means of an automated ion chromatographic system

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Abstract

An automated ion chromatographic (IC) system has been developed for the simultaneous determination of sulphur oxides, nitrogen oxides and hydrogen chloride in flue gas. The sample gas was collected in a hollow cylindrical absorption bottle with a fritted glass bubbler containing 5% triethanolamine (TEA)-absorbing solution and was then determined by IC. Nitrogen monoxide was also collected in a TEA solution after oxidation to nitrogen dioxide by UV irradiation. A designed IC apparatus was operated automatically for sampling and determination. The time required for one cycle was about 55 min. The detection limits of SO₂, NO₂ and HCl were 0.3 ppm, 0.1 ppm and 0.1 ppm (all v/v) with a 5-l gas volume, respectively. The interference of carbonate ion was eliminated by using a separation column of IonPac AS7 and an anion self-regeneration suppressor. © 1998 Published by Elsevier Science B.V.

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1. Introduction

Acid components such as sulphur oxides (SO₂, SO₃), nitrogen oxides (NO, NO₂) and hydrogen chloride (HCl), which are discharged from boilers and incinerators at stationary sources, are causing air pollution and acid rain. It is important to analyze the acid components for the evaluation and the prevention of air pollution. Therefore, these components are determined by official methods such as those of the Japanese Industrial Standard (JIS) [1–3], the US Environmental Protection Agency (EPA) [4–6] and the International Organization for Standards (ISO) [7].

Recently, the concentration of the acid components in flue gas has declined with the use of low sulphur fuel, improvement of the combustion process and exhaust gas treatment by desulphurisation, denitration and gas washing. It is therefore difficult to determine low concentrations of acid components by conventional titrimetry and ion-selective electrode methods. In addition, spectrophotometry does not determine these acid components simultaneously.

Ion chromatography (IC) is a suitable analytical technique for the simultaneous determinations of low concentration of anions and cations. It is applied not only to water but also to gas analysis. IC methods for the determination of sulphur oxides [1,7], nitrogen oxides [3–5] and hydrogen chloride [2,6] in flue gas have been adopted in the official methods.

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Although SO_2 and HCl are easily collected in an absorbing solution, nitrogen oxides are not collected in an absorbing solution because of their low Henry's law constants. The nitrogen oxides are usually collected in an evacuated flask containing dilute sulphuric acid–hydrogen peroxide solution [3,4] or collected in an impinger containing alkaline permanganate solution [5] and then determined by IC. However, these methods are time-consuming and troublesome. A facile collection procedure for nitrogen oxides has already been reported using absorption bottles containing 5% triethanolamine (TEA), followed by UV irradiation [8].

The aim of the work described here is to develop an automated IC system for the simultaneous determination of sulphur oxides, nitrogen oxides and hydrogen chloride in flue gas.

2. Experimental

2.1. Analytical instrumentation

A systematic diagram of the gas sampling and ion chromatograph apparatus, which is produced by Denki Kagaku Keiki Corporation, is shown in Fig. 1.

IC was performed on a Yokogawa Analytical Systems (Model IC-7000) ion chromatograph equipped with a conductivity detector. The sample loop size was 50 μl . A separation column (IonPac AS4A, Dionex) with a guard column (IonPac AG4A, Dionex) and an anion membrane suppressor (HPS-SA1, Yokogawa Analytical Systems) were used. The eluent was 1.8 mM Na_2CO_3 –1.7 mM NaHCO_3 at a flow-rate of 1.5 ml/min . The regenerant was 12.5 mM sulphuric acid.

In the case of carbonate ion interference in the separation of anions, another separation column (IonPac AS7, Dionex) with a guard column (IonPac AG7, Dionex) and an anion self-regeneration suppressor (ASRS, Dionex) was used. The eluent was 20 mM NaOH –10 mM *p*-cyanophenol at a flow-rate of 1.0 ml/min . The regenerant was 12.5 mM sulphuric acid.

A work station (CDS, Ver.4.2, LA Soft) was used.

The ultraviolet (UV) irradiation apparatus (Hamamatsu) consisted of a power supply (Model

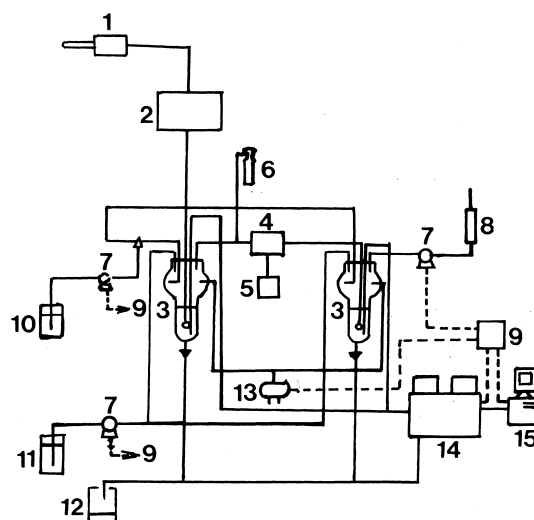


Fig. 1. Systematic diagram for gas sampling and ion chromatograph. 1=Sampling probe; 2=connecting tube; 3=absorption bottles; 4=UV lamp; 5=UV irradiation generator; 6=oxygen cylinder; 7=pump; 8=flow meter; 9=time sequencer; 10=absorbing solution tank; 11=deionized water tank; 12=waste solution tank; 13=compressor; 14=IC apparatus; 15=work station.

C-940) and a low pressure mercury vapor lamp (L937-02, quartz).

2.2. Reagents

All chemicals were of the highest grade commercially available.

Standard sulphur dioxide (SO_2 ; 98 ppm in nitrogen), standard hydrogen chloride (HCl ; 95 ppm in nitrogen), standard nitrogen dioxide (NO_2 ; 98 ppm in nitrogen) and standard nitrogen monoxide (NO ; 95 ppm in nitrogen) were obtained from Takachiho Chemical Industry, in pressurized cylinders, and were diluted with air using a gas divider (STEC).

Oxygen (99.9%) was used for the oxidation of NO .

Absorbing solution: 5% 2,2',2''-nitrilotriethanol (triethanolamine, TEA) was used.

2.3. Procedures

In order to evaluate the collection and determination of the designed automated IC apparatus, standard gases of SO_2 , HCl , NO_2 and NO were used.

The gas sampling and analytical procedures are as follows.

The apparatus is automatically operated by a time sequencer (9) and a work station (15).

Absorption bottles (3) were washed with deionized water (11) and exhausted to a waste solution tank (12). Ten ml of absorbing solution (10) was delivered to two absorption bottles (3). The UV irradiation apparatus (4) was operated with oxygen (6) at a flow-rate of 50 ml/min for the oxidation of NO to NO₂. Sample gas was drawn for 10 min at a flow-rate of 0.5 l/min. Two absorbing solutions were analysed separately by the IC, and chromatograms obtained. The concentration of anions in the absorbing solutions were calculated, and then the print-out of the chromatograms and analytical results. The time required for the sampling and determination is about 55 min.

3. Results and discussion

3.1. Collection and determination of NO₂ and NO

Suitable absorption bottles for the designed IC apparatus were studied using NO₂ standard. The bottles contained 5% TEA solution.

When cylindrical and conical absorption bottles were used, bubbles of the TEA absorbing solution flowed out from the outlet because of frothing. A hollow cylindrical absorption bottle shown in Fig. 1 was good for the designed IC apparatus, and NO₂ was completely collected in the first absorption bottle. A high concentration of nitrite ion (NO₂⁻) and a low concentration of nitrate ions (NO₃⁻) were observed.

Nitrogen monoxide was also collected in the same absorbing solution when the UV irradiation was operated before the second absorption bottle. Although almost no NO was collected in the first absorption bottle, NO was collected in the second absorption bottle giving NO₂⁻ and NO₃⁻ ions. When the UV irradiation lamp was used, NO was oxidized to NO₂ completely up to a concentration of 60 ppm NO. Air and N₂O were not oxidized by the UV irradiation lamp.

3.2. Collection and determination of SO₂ and HCl

A mixed gas of SO₂ and HCl standard was also collected in the same absorption bottles, which contained 5% TEA absorbing solution.

Although chloride (Cl⁻), sulphite (SO₃²⁻) and sulphate (SO₄²⁻) ions were detected in the first absorption bottle, these ions were not detected in the second absorption bottle. Therefore, SO₂ and HCl were easily collected in the first absorption bottle.

3.3. Collection and determination of a mixed gas of NO₂, SO₂ and HCl

A mixed gas of NO₂, SO₂ and HCl was collected in the absorption bottles of the designed IC apparatus. The chromatograms are shown in Fig. 2. A mixed gas was prepared using NO₂, SO₂ and HCl standards. Air was used as the carrier gas. An absorbing solution of 5% TEA was used.

The Cl⁻, NO₂⁻, NO₃⁻, SO₃²⁻ and SO₄²⁻ ions were detected in the first absorption bottle, and almost no peaks were detected in the second bottle. The retention time of Cl⁻, NO₂⁻, NO₃⁻, SO₃²⁻ and SO₄²⁻ ions were 3.1 min, 3.6 min, 5.8 min, 10.1 min and 11.1 min, respectively. The concentrations of NO₂, SO₂ and HCl gas were calculated from the concentration of anions in the absorbing solution. The

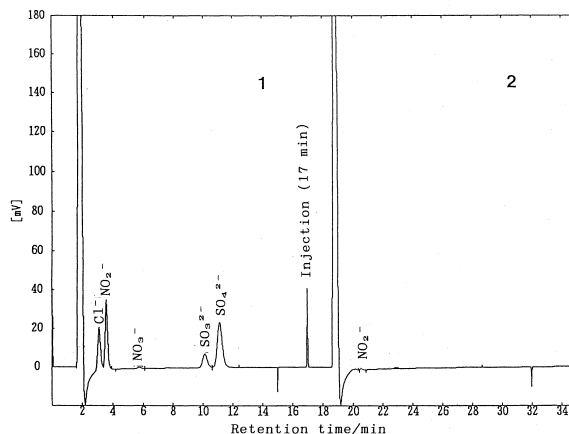


Fig. 2. Chromatogram after the collection of NO₂, SO₂ and HCl gas (1) First absorption bottle, (2) second absorption bottle. Absorbing solution: 5% TEA, 10 ml each, column: IonPac-AG4A, IonPac-AS4A. Suppressor: HPS-SA1 Eluent: 1.8 mM Na₂CO₃ + 1.7 mM NaHCO₃.

results for NO_2 , SO_2 and HCl were 8.0 ppm (v/v) (ppmv), 7.2 ppmv and 3.5 ppmv, respectively.

3.4. Collection and determination of a mixed gas of NO , SO_2 and HCl

A mixed gas of NO , SO_2 and HCl was collected in the absorption bottles of the designed IC apparatus after the UV irradiation was carried out before the second absorption bottle. The chromatograms are shown in Fig. 3. A mixed gas was prepared using NO , SO_2 and HCl standard. Air was used as the carrier gas, and 50 ml/min of oxygen was added at the UV lamp. An absorbing solution of 5% TEA was used.

The chromatogram in the first absorption bottle represents the collection of SO_2 and HCl gas and also a low concentration of NO_2 in NO gas. The chromatogram in the second bottle represents the collection of NO after the UV irradiation.

The concentrations of NO , SO_2 and HCl gas are 7.9 ppmv, 8.7 ppmv and 3.8 ppmv, respectively.

These results are shown that NO_2 , NO , SO_2 and HCl are collected in the absorption bottle with a fritted glass bubbler containing 5% TEA solution and are simultaneously determined by IC. When UV irradiation is carried out before the first absorption bottle, the sum of NO_2 and NO will be determined,

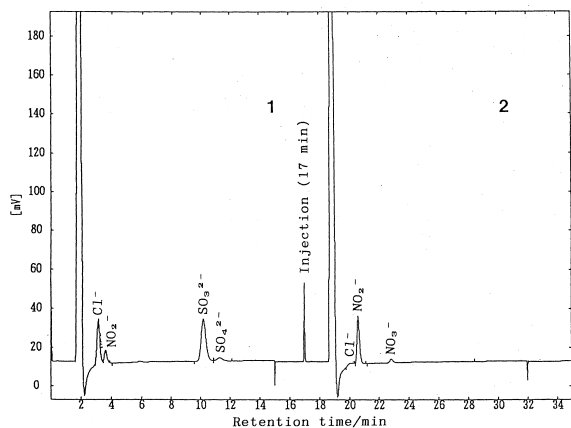


Fig. 3. Chromatogram after the collection of NO , SO_2 and HCl gas (1) First absorption bottle, (2) second absorption bottle. Absorbing solution: 5% TEA, 10 ml each. Column: IonPac-AG4A, IonPac-AS4A. Suppressor: HPS-SA1. Eluent: 1.8 mM Na_2CO_3 + 1.7 mM NaHCO_3 .

and when carried out before the second absorption bottle, NO_2 and NO will be determined, separately.

When 10 ml of absorbing solution and 5 l of mixed gas were used, the lower detection limits of SO_2 , NO_2 and HCl for the designed IC apparatus were 0.3 ppmv, 0.1 ppmv and 0.1 ppmv, respectively.

3.5. Real sample analysis

A real sample of boiler flue gas was collected and determined by the designed IC apparatus. The chromatograms are shown in Fig. 4, when the UV irradiation was carried out before the second absorption bottle.

In this case, NO_2 and SO_2 were collected in the first absorption bottle, and NO was collected in the second bottle. Almost no chloride ion was detected because the sample gas was boiler flue gas.

In the real sample analysis, carbon dioxide in the flue gas interferes with the chromatogram, and the retention times of NO_2^- and NO_3^- were changed. This occurs because carbon dioxide is also collected in the 5% TEA solution.

In order to eliminate the interference of carbonate ion, the same absorbing solution was determined using a Dionex ion chromatograph with a separation column (IonPac AS7) and an anion self-regeneration

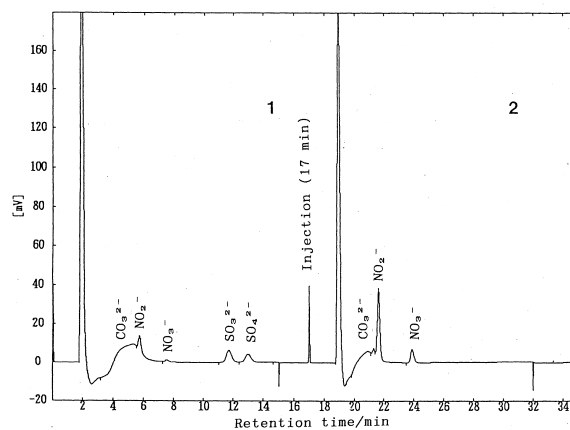


Fig. 4. Real sample analysis of boiler flue gas. (1) First absorption bottle, (2) second absorption bottle. Absorbing solution 5% TEA, 10 ml each. Column: IonPac-AG4A, IonPac-AS4A. Suppressor: HPS-SA1. Eluent: 1.8 mM Na_2CO_3 + 1.7 mM NaHCO_3 .

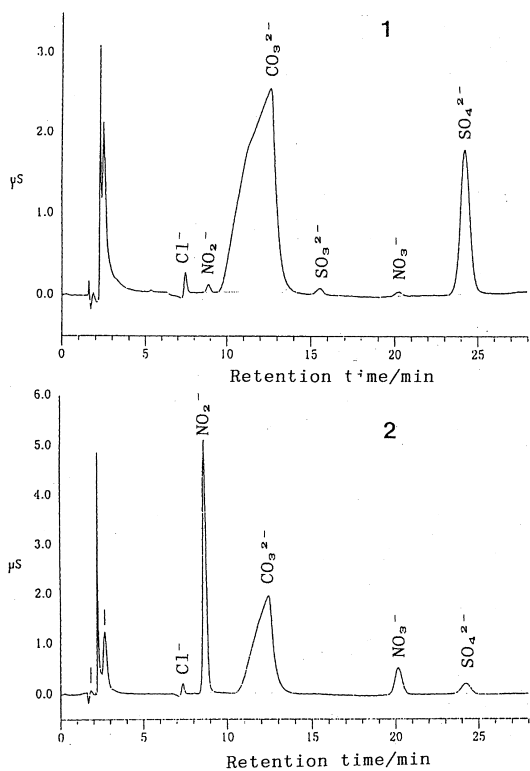


Fig. 5. Real sample analysis of boiler flue gas. (1) First absorption bottle, (2) second absorption bottle. Absorbing solution: 5% TEA, 10 ml each. Column: IonPac-AG7, IonPac-AS7. Suppressor: ASRS. Eluent: 20 mM NaOH+10 mM *p*-cyanophenol.

suppressor (ASRS). The chromatograms are shown in Fig. 5.

The results showed that Cl⁻, NO₂⁻, CO₃²⁻, SO₃²⁻, NO₃⁻ and SO₄²⁻ were clearly separated. The concentrations of NO₂, NO and SO₂ in real flue gas were 0.5 ppmv, 9.3 ppmv and 3.5 ppmv, respectively.

4. Conclusion

An automated sampling and IC apparatus has been designed for simultaneous measurement of sulphur oxides, nitrogen oxides and hydrogen chloride in flue

gas. The SO₂, NO₂ and HCl gases are collected at one time in an absorption bottle containing 5% TEA solution and then simultaneously determined by IC. These gases are present as Cl⁻, NO₂⁻, NO₃⁻, SO₃²⁻ and SO₄²⁻ ions in the solution. NO is also determined after the oxidation to NO₂ by UV irradiation in the presence of a small amount of oxygen.

The designed IC apparatus can determine low concentrations of SO₂, NO_x and HCl in flue gas and is easy to operate and rapid compared to the conventional analytical methods.

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