

## Flow Injection Analysis for the Determination of Ammonia in Exhaust Gas of Thermal Power Plant

Tomonori Tsuboi<sup>1\*</sup>, Yoshio Hirano<sup>1</sup>, Mitsuko Oshima<sup>2</sup> and Shoji Motomizu<sup>2</sup>

<sup>1</sup> The Chugoku Electric Power Co., Inc. Technical Research Center, 3-9-1, Kagamiyama, Higashi-Hiroshima-shi 739-0046

<sup>2</sup> Department of Chemistry, Faculty of Science, Okayama University, 3-1-1, Tsushima-naka, Okayama-shi, Okayama 700-8530

---

### Abstract

Flow injection method for the spectrophotometric determination of ammonia contained in the exhaust gas of a thermal power plant was developed on the basis of a indophenol blue coloration reaction. Prior to the FIA determination, Ammonia in the exhaust gas was absorbed into a boric acid solution, and the absorption solution was analysed by the proposed FIA. The optimal conditions for the formation of the indophenol blue were examined by using a three-line flow system. The limit of detection corresponding to the signal to noise ratio(S/N) of 3 was 0.002 mg l<sup>-1</sup> (= 2 ppb) of NH<sub>4</sub><sup>+</sup>, and ammonium ion above 5 ppb could be determined. A calibration graph was linear from 0.005 ppm to 10 ppm of ammonium ion. The relative standard deviations(n=7) for 0.01 ppm and 0.1 ppm of ammonium ion were 5.2% and 3.3%, respectively. The proposed method was applied to the determination of ammonia in the exhaust gas of the thermal power plant.

*Keywords*: ammonia; exhaust gas of a thermal power plant; flow injection analysis; spectrophotometry; indophenol blue.

---

### Introduction

Nitrogen oxides (NOx) can be formed by a thermal power plant boiler, when it works under the combustion of oil or coal fuel. Therefore, ammonia is commonly added to exhaust gas of the thermal power plant boiler to remove NOx, which reacts with ammonia to give nitrogen and water in a denitrification

system. Though the efficiency of the denitrification system can be improved with increasing ammonia added in the gas, residual ammonia, which is not used for the denitrification reaction, can leak out of the denitrification system and causes the blockade and the corrosion of an air heater. Also when the ammonia is released from the stack of the system, it pollutes the atmospheric environment. Therefore, the concentration of ammonia in the exhaust gas must be controlled. The determination of

---

\* Corresponding author.

E-mail: 595184@pnet.energia.co.jp

ammonia in the exhaust gas has been carried out by the method consisting of such procedures as gas sampling, dissolution of ammonia in an absorption solution, and the determination of ammonium ion in the absorption solution by a batchwise absorptiometry. These procedures have been carried out by manual methods, which are very tedious and time-consuming.<sup>1</sup>

It is an urgent need to develop a real-time feed back system for the ammonia addition to and the ammonia determination in the exhaust gas, and for the proper control of the denitrification system. For the development of a novel feed back system, a rapid and simple system for the sensitive determination of ammonia, as well as an ammonia sampling system, must be developed. The ammonia sampling system, which consists of a gas sampling device and an absorption solution, has already developed in our thermal power plant. One of the next problems is to obtain the analytical data of ammonia contents in the absorption solution rapidly and simply, as well as automatically and on site of the denitrification system near the thermal power plant. In order to automate the on-site determination of ammonia in the absorption solution, a flow injection analysis (FIA) was investigated in this work.

Several methods for the determination of ammonium ion by FIA have been proposed so far, and some of the typical representatives are based on the spectrophotometric measurement with Nessler's reagent and phenol-hypochlorite reagents.<sup>2,3</sup> The reactions with the phenol-hypochlorite reagents show relatively high sensitivity and selectivity for ammonia determination. Of the phenol-

hypochlorite reagents, a salicylic acid-hypochlorite reagent seems to be most promising with respect of the chemical stability of the reagent and the sensitivity for ammonium ion. As an automated system for the rapid and simple determination of ammonium ion, a spectrophotometric method coupled with FIA seems to be the best in these days. The spectrophotometric FIA using sodium salicylate was applied to the determination of ammonium ion in sea water sample.<sup>4</sup> However, the more examination must be advanced to improve the sensitivity of the determination of ammonia at the site of a thermal power plant.

In this work, the concentrations of reagent composition, reaction conditions and flow conditions were examined in detail for improving the sensitivity of ammonia determination. Under the experimental conditions of higher temperature slower flow rate and longer reaction tubing than the reported method<sup>4</sup>, and newly adopted concentration of nitroprusside, the sensitivity was much more improved than the method.<sup>4</sup> The established FIA method was found to be applicable to the exhaust gas of the thermal power plant.

## Experimental

### Apparatus

A flow diagram for the determination of ammonium ion is shown in Fig.1. The FIA system was mainly composed of a Hitachi FIA system (Model K-1000), a Hitachi plunger pump (Model L-6320), a Hitachi spectrophotometric detector (Model L-4200 ; optical path

length : 10 mm of flow cell; the capacity : 17.7  $\mu$ l; measurement wavelength: 665 nm), and a GL Sciences data-processing software (Vstation).

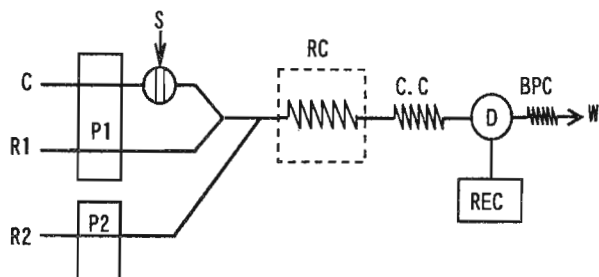


Fig.1 FIA system for ammonia determination based on an indophenol blue method.

C: carrier( $H_2O$  or 0.5% w/v boric acid aqueous solution); R1: reagent solution I (sodium salicylate, sodium nitroprusside, potassium sodium tartrate, and sodium hydroxide); R2: reagent solution II (sodium hypochlorite); P1: pump ( $0.5 \text{ ml min}^{-1}$ ); P2: pump( $0.2 \text{ ml min}^{-1}$ ); S: sample (0.5 mm i.d.  $\times$  1.5 m, 300  $\mu$ l); RC: reaction coil (0.5 mm i.d.  $\times$  6 m); CC: cooling coil (0.5 mm i.d.  $\times$  1 m); D: detector(665 nm); REC: recorder; BPC: back-pressure coil(0.25 mm i.d.  $\times$  1 m); W: waste.

## Reagents

All solutions used were prepared using a highly pure water of  $18.3 \text{ M}\Omega \text{ cm}^{-1}$ , which was prepared with a Milli Q system(Millipore Milli-Q SP TOC), and chemicals used were of analytical reagent grade.

## Reagent solution I and II

Reagent solution I was prepared by dissolving sodium salicylate, potassium sodium tartrate, and a small amount of a catalyst

in water. Reagent solution II was prepared by dissolving sodium hypochlorite in sodium hydroxide solution (0.5 M) to give a 0.5 M solution.

## Standard ammonium ion solution

A stock solution containing  $100 \text{ mg l}^{-1} \text{ NH}_4^+$  was prepared by dissolving 0.297 g of ammonium chloride in 1 l of highly pure water. Working solutions were prepared daily by diluting the stock solution of ammonium chloride accurately.

## Results and Discussion

### Effect of reagent concentrations on sensitivity of ammonia detection

The effect of concentrations of sodium salicylate in the reagent solution I on peak height was examined by varying them from 80 to  $280 \text{ g l}^{-1}$ . The peak height increased with increasing the concentration of sodium salicylate. In the concentration ranges above  $200 \text{ g l}^{-1}$ , the peak height became decreased gradually;  $200 \text{ g l}^{-1}$  was adopted.

Sodium nitroprussid acts as a catalyst for the formation of indophenol derivatives. However, sodium nitroprussid has toxicity. Therefore, other chemicals, such as manganese chloride, copper sulfate, cobalt chloride and iron chloride, as well as potassium ferrocyanide and potassium ferricyanide, were examined; each chemical ( $2.5 \times 10^{-3} \text{ M}$ ) was added to the reagent solution I in the place of sodium nitroprussid. and its effect on peak height was examined. The accelerating effect of these chemicals, however, was less than that of sodium

nitroprussid. Therefore, sodium nitroprussid was adopted in the further experiments. The effect of concentrations of sodium nitroprusside in the reagent solution I was examined by varying its concentration from  $0.025 \times 10^{-3}$  M to  $2.5 \times 10^{-3}$  M. The peak height increased with increasing the concentrations of sodium nitroprusside. In the concentration ranges lower than  $0.25 \times 10^{-3}$  M, the peak height became decreased abruptly, as is shown in Fig.2. In the further experiments,  $1.25 \times 10^{-3}$  M was adopted as a compromise, considering sensitivity and lowering of concentration.

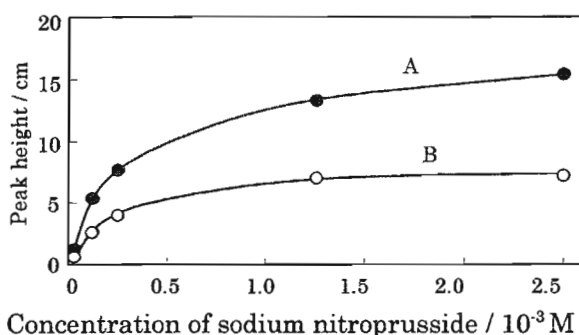


Fig.2 Effect of concentration of sodium nitroprusside on peak height  $\text{NH}_4^+$ (mg l<sup>-1</sup>): (A) 0.1, (B) 0.05.

#### Effect of reaction coil length on sensitivity of ammonia detection

The length of a reaction coil was examined by varying the tubing length from 2 to 10 m. As the tubing length was increased to more than 5 m, peak height was increased, and became almost constant by using the tubing of 6 m or more, as is shown in Fig.3.

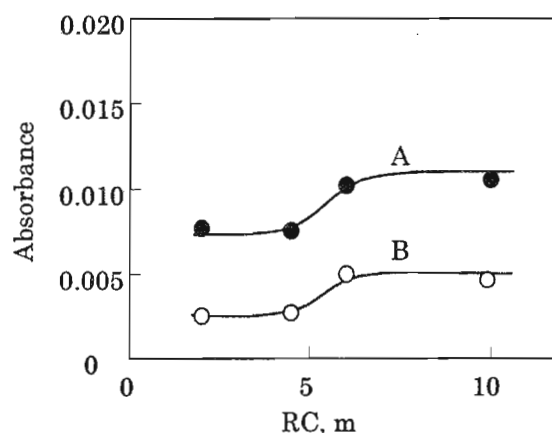


Fig.3 Effect of reaction coil length on the absorbance of peaks.  $\text{NH}_4^+$  (mg l<sup>-1</sup>): (A) 0.1, (B) 0.05.

#### Effect of reaction temperature on sensitivity

The effect of the reaction temperature at the reaction coil was examined by varying the temperature from 40 °C to 100 °C with the reaction coil length of 2 m and 6 m. The results obtained are shown in Fig.4. In the case of 2 m length of the reaction coil, the peak height increased with an increase in the temperature. In 6 m length, peak height increased till 80 °C and fell above 80 °C. At the temperature higher than 90 °C, a generation of gas bubbling was occurred.

As the result, the length of the reaction coil was fixed at 6 m, and the temperature was fixed at 80 °C.

#### Effect of sample volume on sensitivity

The effect of sample volume on peak height was examined by varying it from 100  $\mu\text{l}$  to 600  $\mu\text{l}$ . Peak height was increased with increasing the volume, and approached to almost identical height

when more than 300  $\mu\text{l}$  was injected; 300  $\mu\text{l}$  of the sample was adopted.

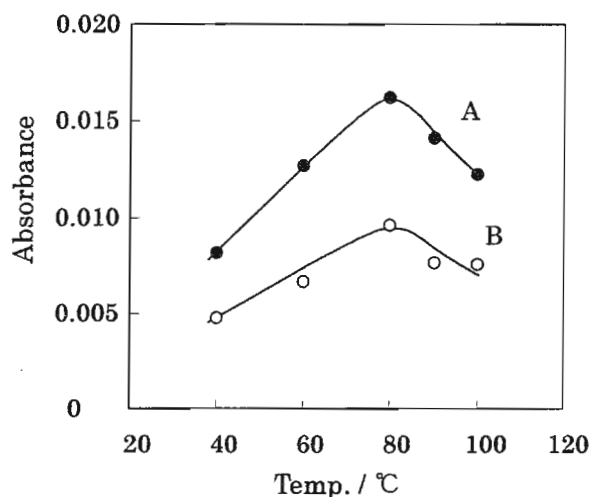


Fig4. Effect of reaction temperature on the absorbance.

$\text{NH}_4^+$  ( $\text{mg l}^{-1}$ ): (A) 0.1, (B) 0.05.

#### Effect of flow rate on sensitivity

The effect of the flow rate of the reagent solution II containing sodium hypochlorite was examined by varying it from 0.08 to 0.7  $\text{ml min}^{-1}$ . Peak height decreased with increasing the flow rate. As a compromise of the stability of a pump, the flow rate of 0.2  $\text{ml min}^{-1}$  was adopted.

#### Effect of the order of reagent mixing on sensitivity

The effect of the order of the mixing of the reagent solution I (sodium salicylate) and II (sodium hypochlorite) with the sample stream was investigated. Three mixing orders were examined: (1) the reagent solution I was mixed with the sample stream, and later the

reagent solution II was mixed with the stream; this order was abbreviated as R1/R2, (2) a reverse order of R1/R2(R2/R1) and (3) the premixed stream of the reagent solution I and II was mixed with the sample stream (R1+R2). Of these, the addition order (R1/R2) gave the highest peaks. In the proposed FIA system, R1/R2 order was adopted.

#### Calibration graph

Under the optimal conditions, a calibration graph was prepared using the flow system in Fig.1. Flow signals obtained using standard solutions of ammonium ion are shown in Fig.5. The calibration graph showed good linearity in the range of 10–100 ppb (ppb =  $\text{ng ml}^{-1}$ ) of  $\text{NH}_4^+$ . The relative standard deviations for seven measurements of 10 and 100 ppb  $\text{NH}_4^+$  were 5.2% and 3.3%, respectively. The detection limit, corresponding to a signal to noise ratio of 3, was 2 ppb.

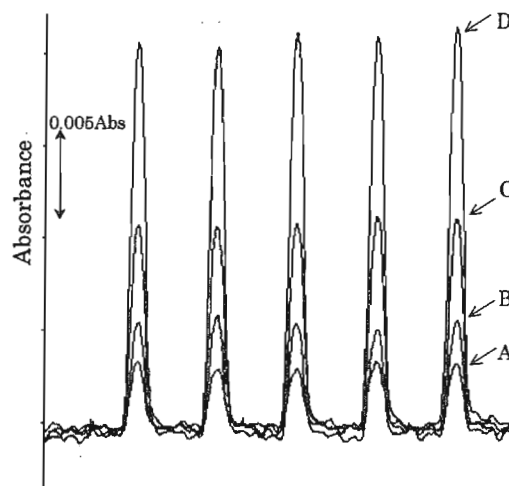


Fig.5 Flow signals for standard ammonium ion solutions.

$\text{NH}_4^+$  ( $\text{ng ml}^{-1}$ ): (A) 10; (B) 20; (C) 50; (D) 100.

Application of the proposed method to practical samples

In order to apply the proposed method to the determination of ammonia in practical exhaust gas samples obtained in a thermal power plant, 0.5% (0.082 M) boric acid aqueous solution, which is currently used as an absorption liquid of ammonia in exhaust gas, was used as a carrier solution in FIA method. In this case, sodium hydroxide was added to the reagent solution I to neutralize boric acid in the carrier and to keep the pH of the reaction mixture to be alkaline. It was found that the linearity of a

calibration graph was good and the peak height of the standard solutions of ammonium ion was almost the same as in the procedure with water as a carrier, when sodium hydroxide was added to the reagent solution I to give 0.08 M.

The determination of ammonium ion in the absorption liquid (0.5% boric acid), which dissolved ammonia in the boiler exhaust gas, was performed by the proposed method. Flow signals are shown in Figs. 6 and 7. The concentrations of ammonium ion in the absorption liquids were summarized in Table 1.

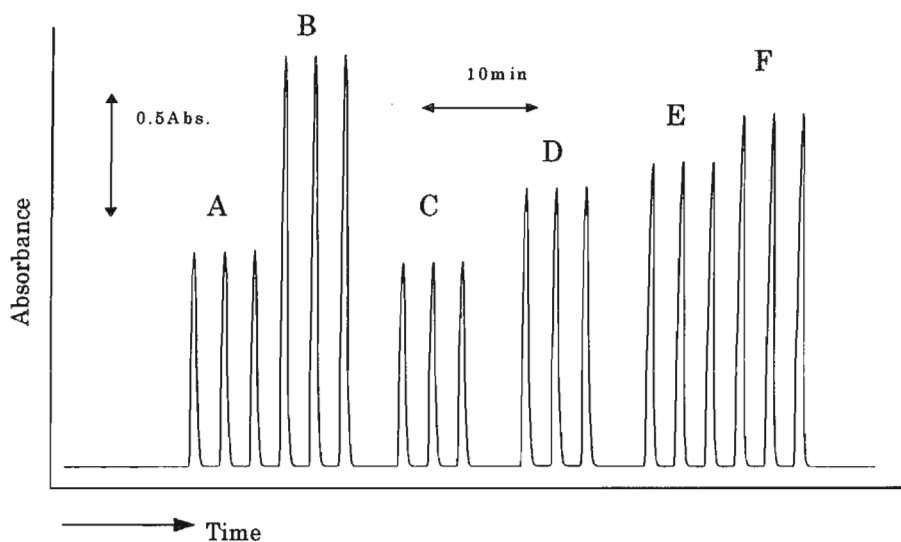


Fig.6 Flow signals for standard solutions and practical samples (high-level contents of ammonia) A and B: standard solutions of  $\text{NH}_4^+$  ( $\mu\text{g ml}^{-1}$ ) in 0.5% boric acid, (A) 5, (B) 10; C-F: practical samples (absorption liquid of 0.5% boric acid, which dissolves ammonia in boiler exhaust gas).

The analytical values obtained by the graphy. The proposed method was found to proposed method are in good agreement be sensitive enough for the determination with the values obtained by ion chromato- of ammonia at the contents of 1 ppm(1 ml m<sup>-3</sup>)

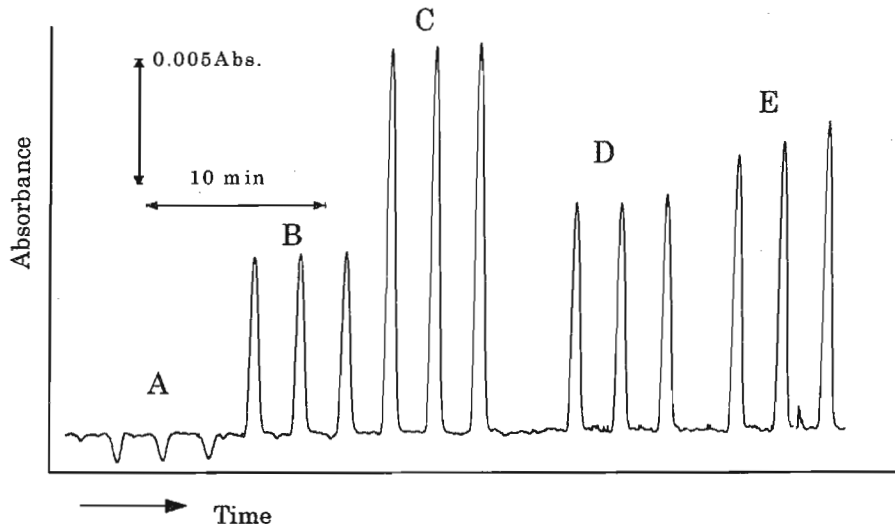


Fig.7 Flow signals for standard solutions and practical samples(low-level contents of ammonia)  
 A-C: standard solutions of NH<sub>4</sub><sup>+</sup> (ng ml<sup>-1</sup>) in 0.5% boric acid, (A) 0, (B) 50, (C) 100;  
 D and E: practical samples (absorption liquid of 0.5% boric acid, which dissolves ammonia in boiler exhaust gas).

Table 1 Analytical results for ammonium ion in absorption liquids which dissolved ammonia in the real boiler exhaust gas

Sample	This method				Other method <sup>d)</sup>	
	NH <sub>4</sub> <sup>+</sup> <sup>a)</sup> ppm	SD <sup>b)</sup> ppm	RSD <sup>c)</sup> %	NH <sub>3</sub> contents* ppm	NH <sub>4</sub> <sup>+</sup> ppm	NH <sub>3</sub> contents* ppm
A	0.0629	0.0010	1.6	0.55	0.068	0.60
B	0.0779	0.0040	5.2	0.68	0.059	0.52
C	4.90	0.01	0.3	168	4.66	160
D	7.32	0.03	0.4	198	7.09	192
E	6.70	0.02	0.2	228	6.49	220
F	8.51	0.03	0.4	224	8.32	219

a) Mean values of three determinations.

b) Standard deviations of three determinations. c) Relative standard deviations.

d) Values obtained by ion chromatography.

\* Ammonia contents in the real boiler exhaust gas.

or more in the exhaust gas, when ammonia in 5 l of exhaust gas was absorbed in 250 ml of the absorption liquid by using the ammonia sampling system, which has already developed and used in our thermal power plant. Furthermore, there are some advantages in the proposed FIA: shortening of measurement time, simple and automatical procedure, and a versatile sensitive method for the determination of ammonia.

## References

- 1) JIS 0099 Methods for Determination of Ammonia in Exhaust Gas(1983).
- 2) T.Kuroishi and N.Iwamura, *J.Flow Injection Anal.*,2000,16(Supplement),44.
- 3) K.Higuchi and Y.Ogawa, *J.Flow Injection Anal.*, 2000, 16(Supplement),48.
- 4) H.Muraki, K.Higuchi, M.Sasaki, T.Korenaga and K.Tôei, *Anal.Chim.Acta*, 1992, 261,345.

(Received May 26, 2000)

(Accepted June 15, 2000)