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Journal of Chromatography A, 739 (1996) 301–306

JOURNAL OF
CHROMATOGRAPHY A

Ion chromatographic determination of nitrogen monoxide and nitrogen dioxide after collection in absorption bottles

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Abstract

A facile collection procedure for nitrogen dioxide (NO₂) was developed by using an absorption bottle equipped with a fritted glass bubbler containing 2,2',2''-nitrilotriethanol (triethanolamine) absorbing solution followed by direct determination by ion chromatography (IC). When a 5% TEA absorbing solution is used, NO₂ is completely collected in the first absorption bottle and NO₂⁻ and NO₃⁻ are detected in the absorbing solution. Although hardly any nitrogen monoxide is absorbed in the TEA solution, it is collected and can be determined by IC after oxidation to NO₂ by using a liquid oxidizing agent or UV irradiation.

Keywords: Nitrogen oxides; Triethanolamine

1. Introduction

Sulfur dioxide and hydrogen chloride in stationary sources are easily collected in an absorption bottle containing hydrogen peroxide solution or dilute sulfuric acid, and then determined by ion chromatography (IC) [1–3]. However, nitrogen monoxide (NO) and nitrogen dioxide (NO₂) are not collected in the absorbing solution because of their low Henry's constants. Therefore, nitrogen oxides (NO_x) are collected in a syringe or an evacuated flask containing

dilute sulfuric acid and can be determined by IC after oxidation with oxygen or ozone [4,5].

In the EPA methods [6,7], NO_x is collected in an evacuated flask containing dilute sulfuric acid–hydrogen peroxide absorbing solution or collected in an impinger containing alkaline permanganate solution, and then determined by IC. However, these methods are time consuming and troublesome.

This paper describes the facile collection of NO₂ in an absorption bottle equipped with a fritted glass bubbler containing 2,2',2''-nitrilotriethanol (triethanolamine; TEA) solution; NO₂ is then determined directly by IC. Nitrogen monoxide is determined by IC after oxidation to

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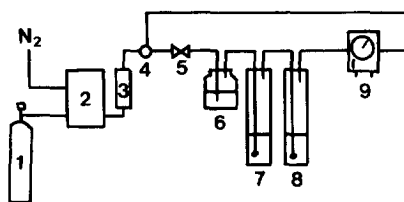


Fig. 1. Sampling system for the oxidation of NO by liquid oxidizing agent. 1 = NO + N₂; 2 = gas divider; 3 = rotameter; 4 = three-way glass stopcock; 5 = needle valve; 6 = liquid oxidizing agent; 7 = first absorption bottle; 8 = second absorption bottle; 9 = wet gas meter, thermometer.

NO₂ by using a liquid oxidizing agent or UV irradiation in the presence of oxygen.

2. Experimental

2.1. Apparatus

In order to evaluate the ability of an absorbing solution to collect NO₂, three absorption bottles (50 or 100 ml) equipped with a fritted glass bubbler (pore size 40–50 μm) were used in series. The collection apparatus for NO after oxidation with liquid oxidizing agent or UV irradiation is shown in Figs. 1 and 2. The UV irradiation apparatus (Hamamatsu) consisted of a power supply (Model C-940) and low-pressure mercury vapour lamp (L-937-02, quartz).

Ion chromatography was performed on a Dionex Model 2010i ion chromatograph

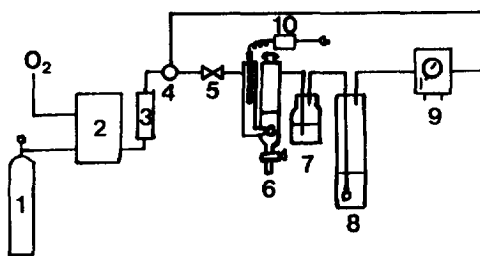


Fig. 2. Sampling system for the oxidation of NO by UV irradiation. 1 = NO + O₂ or NO + air; 2 = gas divider; 3 = rotameter; 4 = three-way glass stopcock; 5 = needle valve; 6 = first absorption bottle with UV lamp; 7 = liquid oxidizing agent; 8 = second absorption bottle; 9 = wet gas meter, thermometer; 10 = UV irradiation apparatus

equipped with a conductivity detector and UV-Vis detector. The sample loop size was 50 μl. A separation column (IonPac AS4A) with a guard column (IonPac AG4A) and an anion micro membrane suppressor (AMMS-II) were used. The eluent was 1.8 mM Na₂CO₃–1.7 mM NaHCO₃ at a flow-rate of 1.5 ml/min. The suppressor regenerant was 12.5 mM sulfuric acid.

2.2. Reagents

All chemicals were of the highest grade commercially available.

Standard nitrogen dioxide (NO₂; 211 ppm in nitrogen) and standard nitrogen monoxide (NO; 180 or 96.0 ppm in nitrogen) were obtained from Takachiho Chemical Industry. The standard NO₂ gas was diluted with nitrogen and NO was diluted with oxygen or air by using a gas divider (STEC).

Hydrogen peroxide from Mitsubishi Gas Chemical Industry and TEA from Kanto Chemical were used as absorbing solutions. High-purity water obtained with an Elgastat UHQ system (Sena) was used.

To prepare the liquid oxidizing agent, equal amounts of 5% potassium permanganate and 5% phosphoric acid were mixed and then 100 ml of the solution were placed in a 250-ml oxidizing bottle. In the case of UV irradiation, oxygen or air was used as the carrier gas.

2.3. Procedure

Various kinds of absorbing solutions (water, H₂O₂, TEA) were used to evaluate the absorption efficiency of NO₂. A 25-ml volume of absorbing solution was placed in the three absorption bottles and standard NO₂ gas was passed through. Subsequently the bottles were washed and separately diluted to 50 ml with deionized water in a volumetric flask. An aliquot of sample solution was injected into the ion chromatograph and nitrite and nitrate ions were determined. At the same time temperature and pressure were measured, and then the absorption efficiency of NO₂ was calculated.

The sampling trains shown in Figs. 1 and 2 were used to evaluate the oxidation efficiency of NO by using a liquid oxidizing agent or UV irradiation. A 25-ml volume of 5% TEA absorbing solution was placed in each of two absorption bottle (100 ml), then standard NO gas was passed. The absorbing solution was also analysed by IC.

3. Results and discussion

3.1. Absorption of NO₂ by various kinds of absorbing solution

The efficiency of absorption of NO₂ by the water, H₂O₂ and TEA absorbing solutions are shown in Table 1. The chromatograms obtained by IC are shown in Figs. 3 and 4.

When water (pH 6, pH 12) was used as the absorbing solution, the sum of the absorption efficiencies of the three bottles was 57.6% (pH 6)–59.3% (pH 12). Even though three absorption bottles were used, NO₂ was not collected completely. When 0.03% H₂O₂ (pH 6) was used, the sum of the absorption efficiencies of the three bottles was 62.3%. A high concentration of NO₃⁻ and a low concentration of NO₂⁻ were

detected when 0.03% H₂O₂ (pH 6) was used as the absorbing solution (Fig. 3a). When 0.03% H₂O₂–sodium hydroxide mixed solution (pH 12) was used, the sum of the absorption efficiencies of the three bottles was 71.3%, and a high concentration of NO₂⁻ compared with NO₃⁻ was detected (Fig. 3b).

On the other hand, when >5% TEA absorbing solution was used, NO₂ was completely collected in the first absorption bottle, and the sum of the absorption efficiencies was 98.1–100%. In this case, a high concentration of NO₂⁻ was detected in the absorbing solution (Fig. 4). NO₂⁻ and NO₃⁻ were also detected by the UV detector. Both ions can be identified. A high absorption efficiency of NO₂ can be obtained in alkaline TEA solution using an absorption bottle equipped with a fritted glass bubbler. However, NO was also collected in absorption bottles containing 5% TEA solution, as it was not absorbed in the TEA solution.

3.2. Absorption of NO₂ by TEA solution

The collection of atmospheric NO₂ on TEA-impregnated firebrick [8] or a TEA-impregnated filter [9–11] has already been reported.

Table 1
Collection of NO₂ by various kinds of absorbing solution

NO ₂ (ppm)	Absorbing solution (25 ml)	Absorption efficiency (%)			
		1	2	3	Total
211	H ₂ O (pH 6)	29.0	17.2	11.6	57.8
211	H ₂ O (pH 12)	30.4	17.3	11.6	59.3
211	0.03% H ₂ O ₂ (pH 6)	31.7	18.0	12.6	62.3
211	0.03% H ₂ O ₂ (pH 12)	38.5	20.6	12.2	71.3
211	1% TEA (pH 9.7)	97.2	0.9	0.0	98.1
211	1% TEA (pH 11.8)	96.2	0.0	0.0	96.2
211	1% TEA + 0.03% H ₂ O ₂	98.6	1.0	0.0	99.6
211	5% TEA (pH 10.3)	98.1	0.0	0.0	98.1
211	10% TEA (pH 10.7)	100.	0.0	0.0	100.
42.2	0.1% TEA + 0.03% H ₂ O ₂	44.3	19.9	11.4	75.6
42.2	1% TEA (pH 9.7)	94.3	2.1	0.0	96.4
42.2	1% TEA + 0.03% H ₂ O ₂	95.2	3.8	0.0	99.0

Absorption bottles, 50 ml with fritted glass bubbler; gas volume, 5 l; gas flow-rate, 0.3–0.4 l/min.

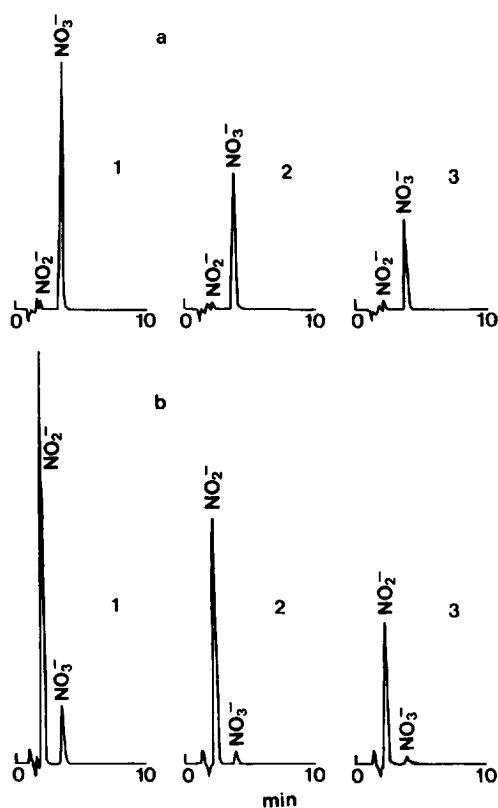


Fig. 3. Ion chromatograms obtained after the collection of NO₂. NO₂ concentration, 211 ppm. 1, 2, 3 = Absorption bottles, 50 ml with fritted glass bubbler. Absorption solution, (a) 0.03% H₂O₂ (pH 6) and (b) 0.03% H₂O₂ (pH 12); column, IonPac AG4A, AS4A; suppressor, AMMS-II; sample, 50 μl; detector, conductivity, 30 μS full-scale; eluent, 1.8 mM Na₂CO₃-1.7 mM NaHCO₃; flow-rate, 1.5 ml/min; suppressor regenerant, 12.5 mM H₂SO₄.

In the reaction of NO₂ and TEA, Levaggi et al. [8] reported that nitrite and nitrate ester formation or HNO₂·TEA salt formation occurred. On the other hand, Okita et al. [9] reported that the collection of NO₂ in TEA was not through the reaction of HNO₂ and HNO₃ with TEA as reported by Levaggi et al. [8], but by direct absorption and reaction of NO₂ with TEA.

From our results obtained by IC, NO₂ was easily absorbed in TEA solution and showed NO₂⁻ and NO₃⁻ ions.

We consider the reaction mechanism of the

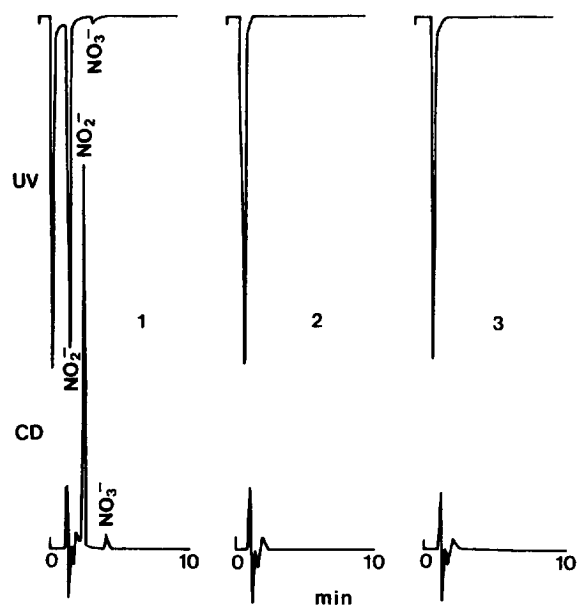
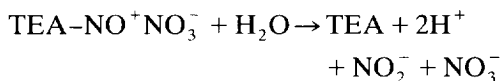
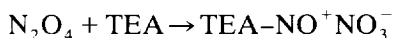
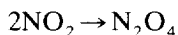


Fig. 4. Ion chromatograms obtained after the collection of NO₂. NO₂ concentration, 42.2 ppm. 1, 2, 3 = Absorption bottles, 50 ml with fritted glass bubbler. Absorption solution, 5% TEA (pH 10.3); column, IonPac AG4A, AS4A; suppressor, AMMS-II; sample, 50 μl; detector, conductivity, 30 μS full-scale; UV, 215 nm; eluent, 1.8 mM Na₂CO₃-1.7 mM NaHCO₃; flow-rate, 1.5 ml/min; suppressor regenerant, 12.5 mM H₂SO₄.

NO₂ with TEA solution to be as described by Cee and Ku [12]:



3.3. Oxidation of NO by liquid oxidizing agent

The sampling system described in Fig. 1 was used to oxidize NO by a liquid oxidizing agent and the products were absorbed in 5% TEA solution. The results are given in Table 2.

This oxidizing solution has an efficiency of 58.0–58.9% (average 58.6%) at 36 ppm NO and 60.6–61.1% (average 60.9%) at 180 ppm NO. The NO₂ formed was collected in the first

Table 2
Oxidation of NO by liquid oxidizing agent and collection

NO (ppm)	Absorbing solution (25 ml)	Oxidation and absorption efficiency (%)		
		1	2	Total
180	5% TEA	61.1	0.0	61.1
		61.1	0.0	61.1
		60.6	0.0	60.6
				Av. 60.9
36	5% TEA	58.0	0.0	58.0
		58.9	0.0	58.9
		58.9	0.0	58.9

Liquid oxidizing agent, 5% KMnO_4 + 5% H_3PO_4 mixed solution; absorption bottles, 50 ml with fritted glass bubbler; gas volume, 5 l; gas flow-rate, 0.3 l/min.

Table 3
Oxidation of NO by UV irradiation and collection

NO (ppm)	Absorbing solution (25 ml)	Oxidation and absorption efficiency (%)		
		1	2	Total
57.6	5% TEA	100.7	0.0	100.7
		100.3	0.0	100.3
		100.3	0.0	100.3
		97.4	0.0	97.4
		92.2	0.0	92.2
		97.4	0.0	97.4
				Av. 98.0 (RSD 3.0%)
19.2	5% TEA	96.9	0.0	96.9
		99.0	0.0	99.0
		98.4	0.0	98.4
		99.0	0.0	99.0
		92.7	0.0	92.7
		101.6	0.0	101.6
				Av. 97.9 (RSD 2.8%)

First absorption bottle, 70 ml with UV lamp and fritted glass bubbler; second absorption bottle, 100 ml with fritted glass bubbler; carrier gas, oxygen; gas volume, 5 l; gas flow-rate, 0.3 l/min.

absorption bottle and a stable oxidation efficiency was obtained.

3.4. Oxidation of NO by UV irradiation

The sampling system described in Fig. 2 was used to oxidize NO in the presence of oxygen or air by UV irradiation, and the products were collected in 5% TEA absorbing solution. In order to check the oxidation by UV irradiation, a liquid oxidizing agent (2.5% KMnO_4 + 2.5% H_3PO_4) was used following the first absorption bottle.

When oxygen was used as the carrier gas, NO was oxidized to NO_2 by UV irradiation and the products were collected completely in the first absorption bottle, (Table 3). The absorption efficiency was 92.2–100.7% (average 98.0%) at 57.6 ppm NO and 92.7–101.6% (average 97.9%) at 19.2 ppm NO.

However, when air was used as the carrier gas, oxidation of NO was not achieved and NO_2^- and NO_3^- were detected in the second absorption bottle.

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