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## ANALYTICAL STUDY ON LOW-CONCENTRATION GASES

### V\*. DETERMINATION OF GASEOUS NITRIC ACID IN URBAN AIR BY MICRO HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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#### SUMMARY

A method has been developed for determination of atmospheric nitric acid by micro high-performance liquid chromatography (MHPLC). Gaseous nitric acid was collected via a Millipore filter in distilled water or 0.2% sodium hydroxide solution, concentrated in a precolumn and determined by MHPLC. The method is rapid and simple with a collection efficiency of more than 90% and a coefficient of variation of less than 5%. The recovery of the precolumn concentration step was as high as 98.8% and the coefficient of variation was only 2%. The correlation coefficient between the results obtained by MHPLC and by the conventional sodium salicylate method was 0.92. The detectable range by the MHPLC method was 0.5–5.0 ng/l as nitrate nitrogen when 200 l of air were sampled. The method enabled determination of 0.18–3.3 ppb (at 0°C, 760 mmHg) of gaseous nitric acid in urban air and was found to have sufficient accuracy for environmental atmospheric determinations.

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#### INTRODUCTION

An understanding of the distribution of gaseous and aerosol constituents in the atmosphere is very important in the elucidation of the mechanisms of photochemical smog formation in urban air. The rôle of gaseous nitric acid has been regarded as particularly important in the transformation of nitrogen oxides in the air<sup>1,2</sup>. Gaseous nitric acid is often determined by the reduction<sup>3</sup>, sodium salicylate<sup>4</sup> and brucine<sup>5</sup> methods. However, these methods do not provide sufficient sensitivity for determination of the minute quantities of gaseous nitric acid in urban air. Iwamoto *et al.*<sup>6</sup> employed ion chromatography, and Gerritse<sup>7</sup> and Takahashi<sup>8</sup> determined nitrate ion in tap-water and environmental water, respectively, by high-performance chromatography (HPLC). However, no reports have been published of the determination of atmospheric nitric acid by HPLC.

I have studied the application of HPLC to atmospheric analysis. Gaseous nitric

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\* Part IV, T. Aoyama and T. Yashiro, *J. Chromatogr.*, 265 (1983) 69.

acid collected via a Millipore filter (LSWP, No. 47, pore size 5  $\mu\text{m}$ ) was concentrated to between one-tenth and one-hundredth of its original volume on an anion-exchange resin (AM-10S; JASCO, Japan) and then determined by micro high-performance liquid chromatography (MHPLC). Nitric acid could be determined sensitively and rapidly with little interference, and the method affords sufficient accuracy for environmental analysis.

## EXPERIMENTAL

### *Apparatus*

The MHPLC separation of nitric acid was carried out with an MHPLC pumping system (Familic-100; JASCO, Japan) and an ultraviolet-visible detector (Uvi-dec-100, JASCO). The PTFE column (60  $\times$  0.5 mm I.D.) was packed with the porous polymer, strongly basic anion-exchange resin AM 10S (JASCO). A 1.5 M sodium chloride solution was used as eluent at a flow-rate of 16 l/min. The wavelength of detection was 210 nm. A 1- $\mu\text{l}$  portion of the sample was introduced into the MHPLC apparatus by means of an autosampler.

### *Reagents*

All reagents used were special grade. A sodium chloride solution was prepared by dissolving 87.7 g of the salt in water and making up to 1 l. The stock solution of nitrate was prepared by dissolving 0.7218 g of potassium nitrate previously dried at 105–110°C for 4 h, in water and making up to 1 l. Standard solutions were prepared by appropriately diluting the stock solution in water.

### *Analytical procedure*

A portion (5–10 ml) of distilled water or 0.2% sodium hydroxide solution was placed in an absorption tube (Fig. 1), in which air was collected through a Millipore filter at an absorption rate of 1–2 l/min for 2–3 h (Fig. 2). A portion (1–10 ml) of the sample solution thus obtained was introduced into a concentration apparatus (Fig. 3) at a flow-rate of 2 ml/min to absorb the nitrate ion from the sample solution. The nitrate was then eluted at a flow-rate of 1 ml/min by slow injection with a microsyringe of 0.1–0.5 ml of 1.5 M sodium chloride solution at the top of the column packing material. The eluate was collected in a graduated test-tube (40  $\times$  5 mm); 1  $\mu\text{l}$  was introduced into the MHPLC apparatus by means of an autosampler.

## RESULTS AND DISCUSSION

### *MHPLC conditions*

The UV absorption wavelengths of nitrate ion have been reported to be 210 nm and 220 nm by Bastian *et al.*<sup>9</sup> and 210 nm by Hoather and Rackham<sup>10</sup>. Takahashi<sup>8</sup> determined this ion at 205 nm by means of a UV spectroscopic detector and HPLC. I have measured the absorption spectrum of nitrate ion in 1.5 M sodium chloride solution and observed an absorption maximum at about 209 nm, and so the present experiments were monitored at 210 nm. Takahashi<sup>8</sup> used potassium dihydrogen phosphate–disodium hydrogen phosphate solution as the eluent. Nakashima *et al.*<sup>11</sup> used sodium chloride and potassium chloride solutions as eluent for MHPLC

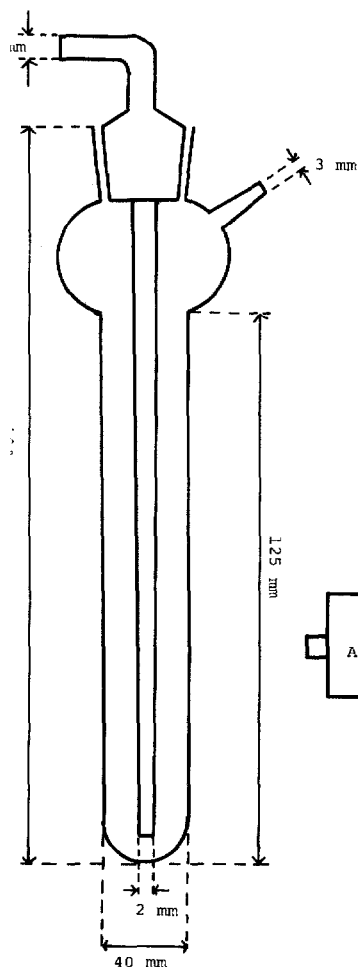


Fig. 1. Absorption tube (midget impinger).

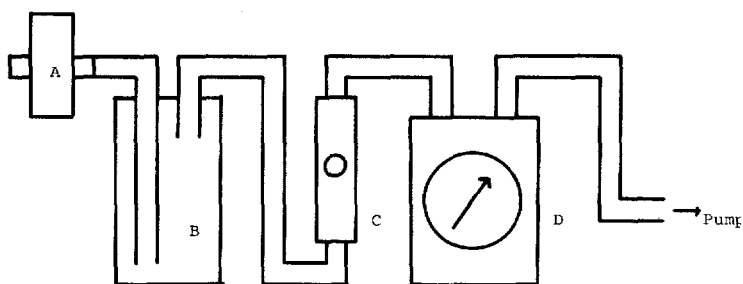


Fig. 2. Apparatus for sampling. A = filter; B = absorption tube; C = flow meter; D = gas meter.

determination of nitrate and nitrite nitrogen in water. They reported that the potassium chloride solution was better on the basis of the stability of the baseline of the chromatogram. After examining chromatograms obtained with 1.0–3.0 *M* sodium chloride solutions as eluents, I decided to use a concentration of 1.5 *M* in view of the higher peaks and shorter retention times with increasing sodium chloride concentrations. The PTFE column (0.5 mm I.D.) was packed, using a 250- $\mu$ l microsyringe, with a slurry of 0.1 g of AM-10S in about 1 ml of water. The length of the packing was 60 mm taking into consideration the decreased peak heights and increased retention times with increasing packing length. A calibration curve (Fig. 4) was prepared based on the peak heights obtained for various concentrations of nitrate nitrogen.

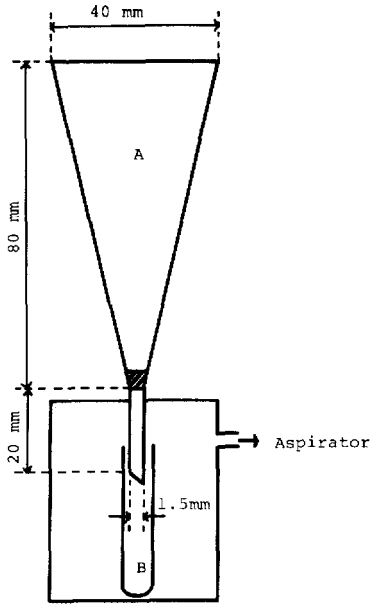


Fig. 3. Concentration apparatus. A = concentration precolumn; B = sample test-tube.

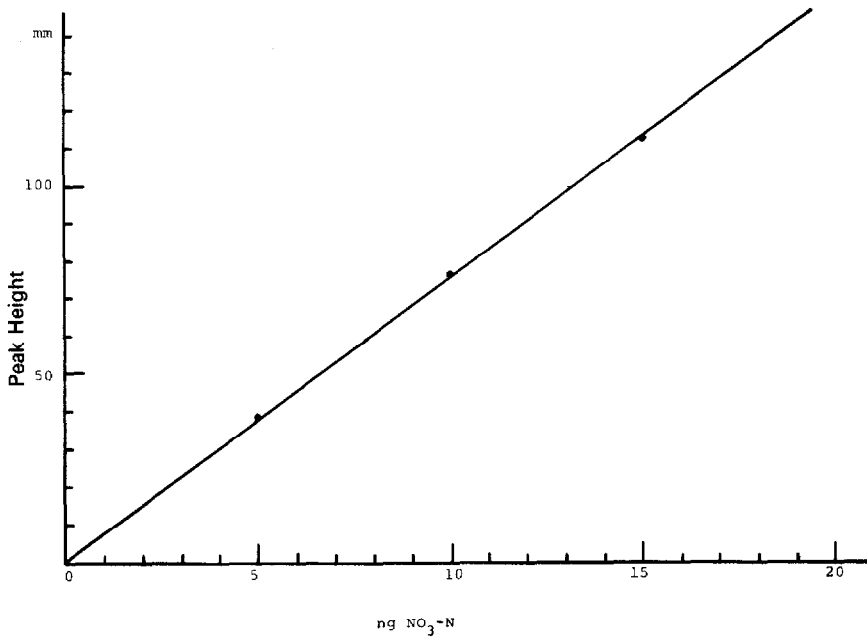


Fig. 4. Calibration curve.

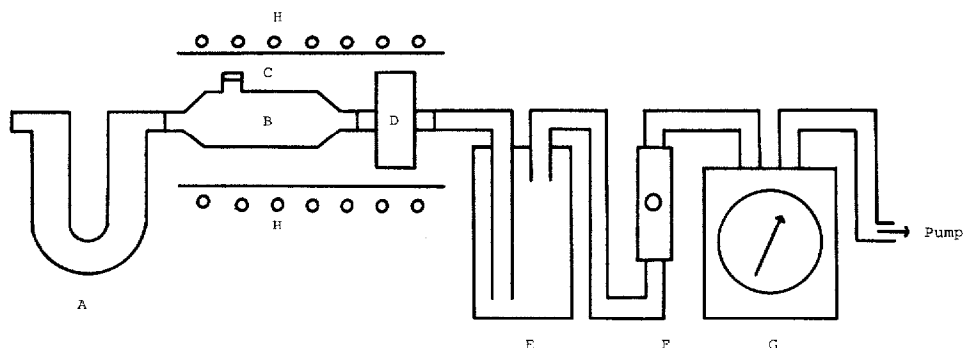


Fig. 5. Apparatus for preparation of the standard gaseous nitric acid. A = U-tube; B = nitric acid; C = inlet of nitric acid solution; D = filter; E = absorption tube; F = flow meter; G = gas meter; H = heater.

#### Absorption solution and collection efficiency

As reported by Ohta *et al.*<sup>2</sup>, atmospheric gaseous nitric acid is usually collected on a filter-paper coated with sodium chloride after passage of a sample of air through a PTFE filter. However, the method requires a pretreatment such as a uniform coating of the filter-paper with sodium chloride and is therefore unsuitable for rapid determination of photochemical smog formation. In the present method, air is collected by a wet method without pretreatment, by which a determination could be carried out immediately after the sudden occurrence of photochemical smog, and checked the collection efficiency of air and loss by aeration.

Recovery of gaseous nitric acid from water and 0.2% sodium hydroxide solution was investigated by injecting 1  $\mu$ l and 20  $\mu$ l of 13 M nitric acid into the apparatus shown in Fig. 5 and gasifying it. The results are listed in Table I in which the nitric acid collected is expressed as the percentage of the peak height in the chromatogram obtained by the above method compared to that in the chromatogram of ungasified nitric acid. When 1- $\mu$ l and 20- $\mu$ l portions of gaseous nitric acid were absorbed into water the average recoveries were 95.1% and 90.7% with coefficients of variation of 4.25% and 4.09%, respectively. When the same portions were absorbed in 0.2% sodium hydroxide the average recoveries were 97.1% and 91.4% with coefficients of variation of 4.95% and 4.02%, respectively. The recoveries of gaseous nitric acid from both solvents were thus satisfactory.

TABLE I  
COLLECTION EFFICIENCY OF GASEOUS NITRIC ACID

1- $\mu$ l and 20- $\mu$ l portions of nitric acid were gasified and then absorbed in water or 0.2% NaOH.

	Water		0.2% NaOH soln.	
	1.0 $\mu$ l	20.0 $\mu$ l	1.0 $\mu$ l	20.0 $\mu$ l
Range (max.-min.)	99.4-89.1	95.1-88.5	104-91.2	95.9-89.3
Average ( $n = 5$ )	95.1	90.7	97.1	91.4
S.D.	4.04	3.71	4.81	3.67
C.V. (%)	4.25	4.09	4.95	4.02

TABLE II  
DETERMINATION OF AERATION LOSSES

Flow-rate (l/min)	1.0	2.0
Aerated volume (l)	120	120
Recovery (%)		
max.-min.	104-95.4	101-94.5
average ( $n = 5$ )	98.8	97.1
S.D.	3.09	2.75
C.V. (%)	3.13	2.83

In actual determinations, the filter-paper was placed in a heater to prevent adsorption of water and nitric acid gas on the filter-paper and its holder. When sodium hydroxide solution was used as the absorption liquid, atmospheric nitrogen dioxide is absorbed according to



and so 1 mole of nitrogen dioxide is transformed into 0.5 mole nitrate ion. Therefore, the nitric acid concentration was obtained by making an appropriate correction for this amount. A midjet impinger used as the absorption tube gave poor recovery of  $\text{NO}_2$  gas, scarcely affecting the determination of nitric acid.

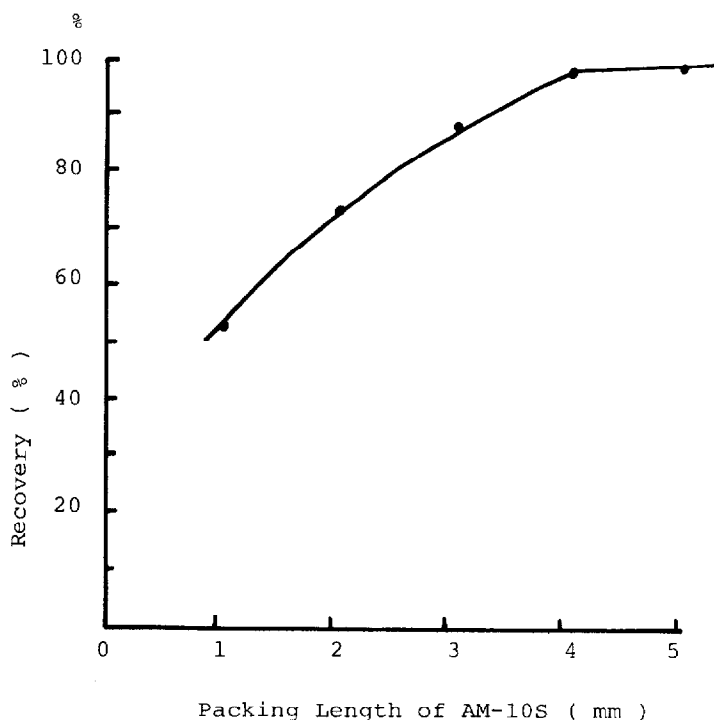


Fig. 6. Dependence of concentration recovery on packing length of AM-10S.

In order to check the loss of nitric acid collected by absorption from air, a 1-ml portion of a standard solution containing nitrate nitrogen equivalent to 10  $\mu\text{g}/\text{ml}$  was added to the 0.2% sodium hydroxide solution to give a total volume of 10 ml for the absorption liquid, which was then placed in an absorption tube (Fig. 1). A U-tube packed with activated carbon was attached to the front of the filter, A, of the apparatus shown in Fig. 2. Air was collected in the tube at an aspiration rate of 1–2 l/min for 2–3 h and then treated as described in *Analytical procedure*. Recoveries are listed in Table II as the percentages of the peak height of the aerated sample compared to that of the non-aerated standard solution. The average recoveries were 97.1–98.8% with coefficients of variation of 2.83–3.13%, showing that losses due to aeration of nitric acid once collected were negligible.

#### *Precolumn concentration*

Ishii *et al.*<sup>12</sup> have reported a method for determining phthalic acid esters in water by injecting aqueous samples in a micro-precolumn (18  $\times$  0.35 mm I.D.), adsorbing the component onto the column, desorbing it with a carrier liquid and finally injecting into an MHPLC apparatus. This method is unsuitable for large samples because of the long time needed for concentration. I have constructed a funnel-type concentration precolumn (Fig. 3A) packed with AM-10S to a length of 1–5 mm. A portion of 1–10 ml of an absorption liquid containing 1 ng/ml of nitrate nitrogen was injected at the top of the precolumn to investigate the recovery of a sample concentrated according to *Analytical procedure*. The results are shown in Fig. 6 and Table III which give the percentages of the peak height in the chromatogram compared to those of the standard solution. The average recovery was 98.8% with a coefficient of variation of 1.93% when the length of the packing AM-10S was more than 4 mm. The precolumn was found to be able to concentrate a sample within a short period of time. Fig. 7 shows a chromatogram obtained when a 1-ml portion of a nitrate nitrogen standard solution containing 1 ng/ml was concentrated to one-tenth of the original volume. In this experiment, complete recoveries could be obtained by using about 100  $\mu\text{l}$  of eluent. When 10 ml of the absorption liquid were adsorbed on the precolumn, desorption could be achieved with 100  $\mu\text{l}$  of the eluent.

#### *Interferences and comparison with sodium salicylate method*

Other substances present in urban air and which have an absorption maximum at near the UV absorption band of nitric acid are exemplified by nitrous acid and gaseous sulphuric acid. Relative to the retention value of nitric acid taken as 1.00, the retention value for nitrous acid is 0.6 and 0.36 for sulphuric acid, thus no interference from these substances is observed on the chromatogram. Table IV shows a comparison of the conventional sodium salicylate method with the present chro-

TABLE III  
RECOVERY (%) ON PRE-COLUMN CONCENTRATION

Max.-min.	101-96.2
Average ( $n = 8$ )	98.8
S.D.	1.91
C.V. (%)	1.93

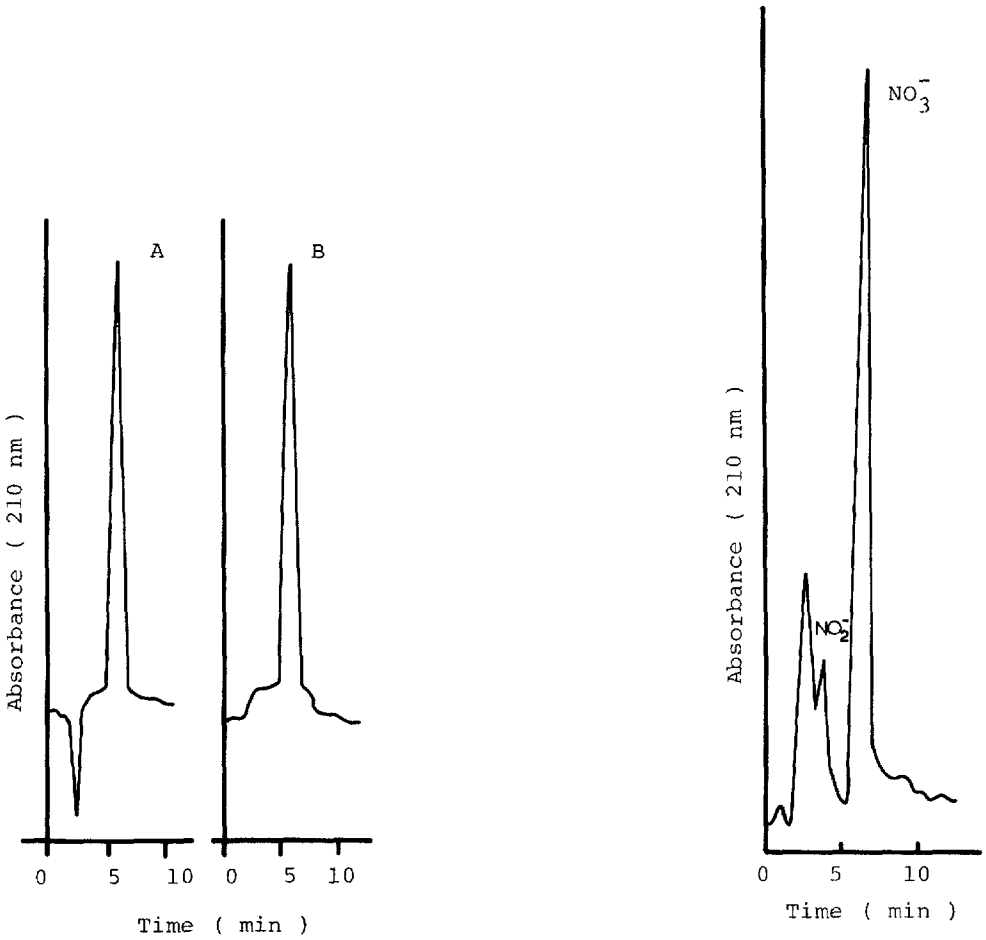


Fig. 7. Typical chromatogram. A, standard (10 ng  $\text{NO}_3\text{-N}$ ); B, after concentration and recovery (ten-fold concentration of 1 ng  $\text{NO}_3\text{-N}$ ).

Fig. 8. Typical chromatogram obtained from gaseous nitric acid in atmosphere.

TABLE IV  
COMPARISON WITH SODIUM SALICYLATE METHOD

<i>n</i>	MHPLC ( $\mu\text{g NO}_3\text{-N}$ )	Sodium salicylate method ( $\mu\text{g NO}_3\text{-N}$ )
1	0.0213	0.0217
2	0.0057	0.0071
3	0.0129	0.0169
4	0.0129	0.0139
5	0.0140	0.0120

Correlation coefficient,  $r = 0.923$



TABLE V  
EXAMPLES OF APPLICATION

Site	Sample No.	Concn. of gaseous nitric acid (0°C, 760 mmHg)
Air around the institute (January 1983)	1	0.83 ppb
	2	0.18 ppb
	3	3.30 ppb
Automotive exhausts (idling)	1	0.056 ppm
	2	0.041 ppm

matographic method. A 10-ml portion of an absorption liquid obtained by absorbing gaseous nitric acid using the apparatus shown in Fig. 4 was divided into two portions each of 5 ml. One portion was analysed by this method and the other by the sodium salicylate method. The correlation coefficient between the two sets of results was 0.923. Therefore the present method is considered to be sufficiently accurate for atmospheric environmental analyses.

#### Detection limit

The detection limit on a chromatogram was 1 ng as nitrate nitrogen when 1  $\mu$ l of a sample was injected. It was 0.5–5 ng/l as nitrate nitrogen when 200 l of air were sampled into 10 ml of an absorption liquid, which was then concentrated to between one-tenth and one-hundredth of the original volume. Although “range 0.04 a.u.f.s.” was employed in the present MHPLC determination, the maximum range of the apparatus is “range 0.005 a.u.f.s.”; accordingly the detection limit of nitrate nitrogen may be 0.125 (*i.e.* 0.005/0.04) ng.

#### Actual determination

Gaseous nitric acid in urban air and automobile exhausts was determined using the present method and the results and an example of a chromatogram obtained are shown in Table V and Fig. 8, respectively.

#### CONCLUSIONS

The results of the determination of gaseous nitric acid in urban air by MHPLC has allowed the following conclusions:

(1) The average recovery of gaseous nitric acid was 91.4–97.1% with little aeration loss.

(2) Precolumn concentration enabled simple and rapid determination of a minute quantity of gaseous nitric acid in air. The average recovery was 98.8%.

(3) The determination was not affected by gaseous NO<sub>2</sub> and sulphuric acid. The correlation coefficient between results obtained by the MHPLC method and by the sodium salicylate method was 0.923.

(4) The detection limit of the method was 0.5 ng/l as nitrate nitrogen when about 200 l (0°C, 1 atm) of air were sampled. The sensitivity of MHPLC could be improved further by increasing the sampling volume.

From the above, the method is considered to have sufficient accuracy for environmental air analysis.

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