Short Communication

Determination of ammonia as its benzenesulphonyldimethylaminomethylene derivative in environmental water samples by gas chromatography with flame photometric detection

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ABSTRACT

A selective and sensitive method for the determination of ammonia by gas chromatography (GC) was developed. Ammonia was converted into its benzenesulphonyldimethylaminomethylene derivative by a convenient procedure involving benzenesulphonylation with benzenesulphonyl chloride and subsequent reaction with dimethylformamide dimethyl acetal, and was determined by GC with flame photometric detection (FPD) using a DB-1 capillary column. The derivative was very stable on standing in ethyl acetate, eluted as a single peak and provided an excellent response in the flame photometric detector. A linear calibration graph was obtained in the range 2–40 nmol of ammonia. The detection limit of ammonia was about 1.5 pmol injected. Ammonia in environmental water samples could be measured without interference from co-existing substances. The recoveries of ammonia added to environmental water samples were 95.0–97.5% and the relative standard deviations were 3.3–6.0%. Ammonia contents in several environmental water samples were 0–119.3 nmol/ml.

INTRODUCTION

Ammonia arises mainly from natural sources by decomposition of organic matter containing nitrogen and from manufacturing processes for industrial chemicals. Ammonia is irritant to the skin, respiratory tract and mucous membranes. Water pollution by ammonia often has a toxic influence on aquatic species.

The determination of ammonia in environmental water samples has been carried out by spectrophotometric methods [1–3], ammonia-selective elec-

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trode methods [4,5], gas chromatography (GC) [6–8] high-performance liquid chromatography (HPLC) [9] and flow-injection methods [10–12]. However, colour and turbidity in the sample interfere with spectrophotometric methods based on the indophenol blue reaction [1,2] or Nessler's reaction [3], and therefore a time-consuming preliminary distillation is required before analysis. The electrode methods are susceptible to intereferences from amines. GC methods based on headspace sampling give tailing peaks. HPLC and flow-injection methods based on spectrophotometric or fluorimetric detection are suitable methods, but some of them require preliminary clean-up of the sample by

using an ion-exchange column or a PTFE membrane before reaction with o-phthalaldehyde.

In this work, ammonia was analysed as its benzenesulphonyldimethylaminomethylene derivative by GC with flame photometric detection (FDP). Using this method, the content of ammonia in environmental waters was also studied.

EXPERIMENTAL

Reagents

Ammonium chloride (Nacalai Tesque, Kyoto, Japan) was dissolved in distilled water to make a stock standard solution of concentration 2 mM. p-Toluenesulphonamide (Tokyo Kasei Kogyo, Tokyo, Japan) as an internal standard (I.S.) was dissolved in 0.01 M potassium hydroxide solution to make a stock standard solution of concentration 2 mM. Benzenesulphonyl chloride (BSC) and N,N-dimethylformamide dimethyl acetal (DMF-DMA) were purchased from Nacalai Tesque. BSC was used a 20% solution in dioxane. All other chemicals were of analytical-reagent grade.

Gas chromatography

GC analysis was carried out with a Shimadzu 12A gas chromatograph equipped with a flame photometric detector (S-filter). A fused-silica capillary column (15 m × 0.53 mm I.D., film thickness 1.5 μm) of cross-linked DB-1 (J & W, Folsom, CA, USA) was used. The column temperature was 230°C, the injection and detector temperatures 260°C and the nitrogen flow-rate 10 ml/min.

Gas chromatography–mass spectrometry (GC–MS)

A Hewlett-Packard Model 5890A gas chromatograph was operated in conjunction with a VG Analytical Model 70-SE mass spectrometer and a VG-250J mass data system. The GC column was of the same type as used for GC, with an ionizing voltage of 40 eV, an ion-source temperature of 250°C and a helium flow-rate of 10 ml/min.

Derivatization procedure

An aliquot of the sample solution containing 2–40 nmol of ammonia was pipetted into a 10-ml Pyrex glass tube with a PTFE-lined screw-cap. To this solution were added 0.1 ml of 0.2 mM I.S. solution, 0.75 ml of dioxane and 0.1 ml of 2.5% sodium carbonate solution and the total reaction volume was made up to 1.5 ml with distilled water. After addition of 0.05 ml of BSC, the mixture (pH > 10) was shaken up and down at 3000 rpm for 5 min at room temperature. The reaction mixture was extracted twice with 3 ml of n-hexane in order to remove the excess of reagent. The aqueous layer was acidified to pH 1–2 with 2 M hydrochloric acid and then extracted twice with 3 ml of diethyl ether. To the pooled ethereal extracts were added 20 μl of DMF-DMA and the mixture was stood for 10 min in a hot-block bath at 80°C without a cap. After the solvent had evaporated to dryness, the residue was dissolved in 0.2 ml of ethyl acetate and then 0.5–1 μl of this solution was injected into the gas chromatograph. The derivatization process is shown in Fig. 1.

Preparation of reference compound

A reference sample of the benzenesulphonyldimethylaminomethylene derivative of ammonia, m.p. 131–132°C, was prepared from benzenesulphonamide (Tokyo Kasei Kogyo) in essentially the same manner as in the derivatization procedure. The elemental analysis was as follows: calculated for $C_9H_{12}N_2O_2S$: C 50.93, H 5.70, N 13.20; found: C 51.17, H 5.83, N 13.13%.

RESULTS AND DISCUSSION

In a previous paper on the determination of aliphatic primary amines [13], we reported that the benzenesulphonamide derived from ammonia overlapped with the benzenesulphonyl derivatives of methylamine on the chromatogram, but these derivatives could be separated by reaction with DMF-
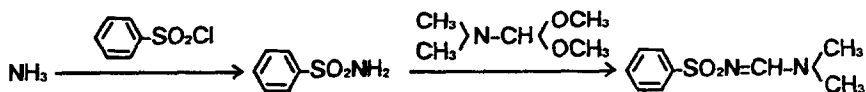

Fig. 1. Ammonia derivatization process.

DMA. The benzenesulphonamide was converted into the dimethylaminomethylene derivative, which has a longer retention time, but the benzenesulphonyl derivatives of primary amines did not react with DMF-DMA. These results indicate that ammonia could be selectively determined in samples containing low-molecular-mass primary amines such as methylamine and ethylamine. Experiments were conducted to find suitable reaction conditions for the preparation of the ammonia derivative. The benzenesulphonylation of ammonia with BSC was accomplished by shaking within 2 min at room temperature in aqueous alkaline media containing 50–70% of dioxane. By washing with hexane after benzenesulphonylation, excess of BSC and benzenesulphonyl derivatives of secondary amines were removed. The benzenesulphonyl derivative of ammonia reacted completely with DMF-DMA within 5 min at 80°C. The mean derivatization yield throughout the procedure established above was determined to be 94.6 ± 3.6% (n = 4) by comparison with the synthetic reference derivative.

The structure of the derivative was confirmed by both GC–MS and elemental analysis. As shown in Fig. 2, a molecular ion peak (M$^+$) with the postulated m/z 212 ion and prominent fragment ion peaks at m/z 141 [M$^+$ − N=CHN(CH$_3$)$_2$], 77 (C$_6$H$_5$), 71 [N=CHN(CH$_3$)$_2$] and 44 [N(CH$_3$)$_2$] were observed, and these peaks were useful for structure elucidation. The elemental analysis data agreed with the theoretical values calculated for the expected structure. These results supported the structure for the derivative shown in Fig. 1. The derivative was found to be very stable under normal laboratory conditions; no decomposition was ob-
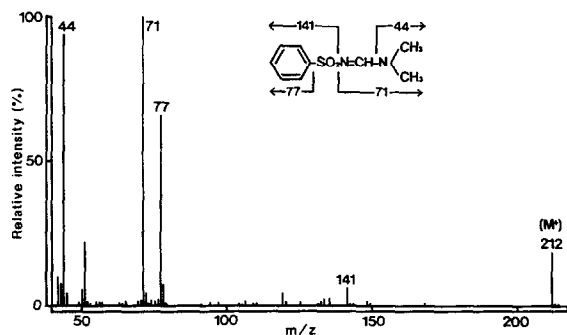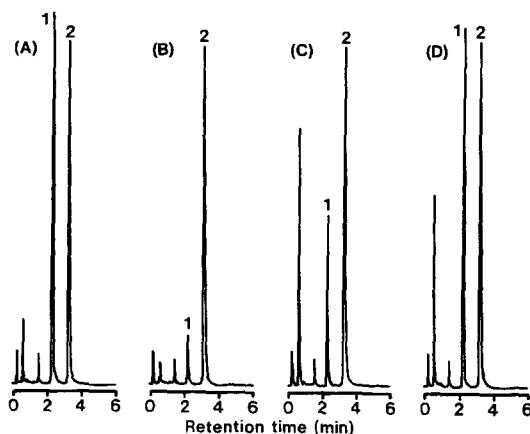

Fig. 3. Gas chromatograms obtained from a standard solution and river water samples. (A) Standard solution (containing 20 nmol of ammonia); (B–D) river waters. GC conditions are given under Experimental. Peaks: 1 = ammonia; 2 = p-toluenesulphonamide (I.S.).

served even after standing in ethyl acetate for 2 weeks at room temperature.

As shown in Fig. 3A, the ammonia derivative was eluted as a single peak and provided an excellent response in the flame photometric detector. The minimum detectable amount of ammonia required to give a signal three times as high as the noise under our instrumental conditions was *ca.* 1.5 pmol injected. To test the linearity of the calibration graph, various amounts of ammonia ranging from 2 to 40 nmol were derivatized and aliquot representing 5–100 pmol were injected. A linear relationship was obtained from both logarithmic plots, and the regression line was log y = 1.064 log x − 1.369

Fig. 2. Mass spectrum obtained by GC–MS of the benzenesulphonyldimethylaminomethylene derivative of ammonia.

TABLE I

RECOVERIES OF AMMONIA ADDED TO RIVER WATER SAMPLES

Sample	Ammonia added (nmol/ml)	Amount found^a (nmol/ml)		Recovery (%)
		Without addition	With addition	
A	10	5.9 ± 0.3	15.4 ± 0.6	95.0
B	20	42.0 ± 1.4	61.4 ± 2.1	97.0
C	40	191.3 ± 11.4	230.3 ± 9.7	97.5

^{a} Mean ± S.D. (n = 3).

TABLE II

AMMONIA CONCENTRATIONS FOUND IN ENVIRON-
MENTAL WATER SAMPLES

Sample	Concentration[a] (nmol/ml)
Subterranean water	ND[b]
River water (middle reaches)	5.9 ± 0.3
River water (lower reaches)	42.0 ± 1.4
Sewerage	119.3 ± 11.4
Irrigation water	39.9 ± 0.4
Pool water	34.6 ± 0.8
Lake water	29.4 ± 0.2
Sea water	55.6 ± 2.5

[a] Mean ± S.D. ($n = 3$).
[b] Not detectable.

($r = 0.9982$, $n = 15$), where y is the peak-height ratio and x is the amount of ammonia.

The method developed was successfully applied to environmental water without prior clean-up of the samples. As shown in Fig. 3B–D, ammonia in the river water samples could be detected without any interferences from co-existing substances. As shown in Table I, the overall recoveries of ammonia added to river water samples were 95.0–97.5% and the relative standard deviations were less than 6%, indicating that the method is accurate and precise. The ammonia contents found in several environmental water samples are given in Table II.

In conclusion, these experiments have conclusively demonstrated that trace amounts of ammonia can be successfully determined by GC–FPD as its benzenesulphonyldimethylaminomethylene derivative. The method is selective and sensitive, and complex environmental samples can be analysed directly without any interference from other substances.

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