

Determination of primary and secondary aliphatic amines in the environment as sulphonamide derivatives by gas chromatography–mass spectrometry

AKIKO TERASHI*, YOSHIFUMI HANADA, AZUMA KIDO and RYOTA SHINOHARA

Kitakyusyu Municipal Institute of Environmental Health Sciences, 1-2-1, Shin-ike, Tobata-ku, Kitakyusyu-shi, Fukuoka 804 (Japan)

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SUMMARY

A gas chromatographic–mass spectrometric (GC–MS) method for the determination of primary and secondary aliphatic amines in water and sediment was developed. A standard solution of amines was added to river water, sea water and sea sediment, and distilled under alkaline conditions. The distillate was reacted with benzenesulphonyl chloride to form the corresponding sulphonamides. After extracting the derivatives into dichloromethane, the organic layer was concentrated to a definite volume. The determination was carried out by GC–MS with selected-ion monitoring. The detection limits of amines in water and sediment were 0.02–2 µg/l and 0.5–50 µg/kg, respectively. The recoveries were 68.4–98.8%.

INTRODUCTION

Aliphatic amines are broadly distributed in the environment, reflecting the fact that they are produced in living bodies as metabolites. Amine compounds have also been widely used as raw materials for pesticides, medicines, dyestuffs, etc. Not only are some amines themselves hazardous to human health, but some may form nitrosamines, known to be carcinogenic by reaction with nitrates^{1–3}. It is therefore important to determine the concentration levels of amines in the environment.

Amines are usually determined by gas chromatography (GC) or high-performance liquid chromatography (HPLC), but methods have some problems⁴. Handling of low-molecular-weight amines is difficult because of their high water solubility and volatility. Moreover, in GC analysis, they are likely to be adsorbed and decompose in the column, and readily give tailed elution peaks. LC analyses also have the problem of low detection sensitivity and selectivity on ultraviolet (UV) detection. Derivatizations are popular methods for overcoming these problems.

In recent years, there have been many reports concerning HPLC analyses of amines by using UV^{5–7}, fluorescence^{8–12}, chemiluminescence excitation¹³ or electro-

chemical detection (ED)^{14,15} with appropriate derivatization. Some of them are very sensitive, but it needs to be examined whether their selectivities are satisfactory for environmental samples with complicated matrices.

Many derivatization reagents for GC analyses of amines by using electron-capture detection (ECD)¹⁶⁻¹⁸, flame thermionic detection (FTD)¹⁹, flame photometric detection (FPD)^{20,21} or GC-mass spectrometry with selected-ion monitoring (GS-MS-SIM)²² have also been reported. Benzenesulphonyl chloride (BSC)^{19,20} and 2,4-dinitrofluorobenzene (DNFB)^{4,23} have proved to be very useful for low-molecular-weight aliphatic amines because they can convert the amines into hydrophobic and non-volatile derivatives in water. The reaction procedures are simple, but DNFB irritates the skin and occasionally cause allergic dermatoses.

In this study, BSC was used as a derivatization reagent and the GC-MS-SIM determination of some aliphatic primary and secondary amines in environmental samples was examined.

EXPERIMENTAL

Chemicals

n-Propylamine (nPA), isopropylamine (iPA), *n*-butylamine (nBA), allylamine (AA), *n*-octylamine (nOA), di-*n*-propylamine (DPA), diisobutylamine (DBA), di(2-ethylhexyl)amine (DEHA), [²H₁₀]fluoranthene [as an internal standard (IS)] and BSC were purchased at the highest purity available and used without further purification. Dichloromethane and hexane were of pesticide grade and all other reagents were of analytical-reagent grade.

Apparatus

A Model DX303 mass spectrometer (JEOL) coupled with a Model 5890A gas chromatograph (Hewlett-Packard) was used under the following conditions: column, 25 m × 0.53 mm I.D., SE-54; column temperature, 200°C (1 min), increased at 10°C/min to 280°C, held for 3 min; injection temperature, 280°C; carrier gas, helium at 13.0 ml/min; GC-MS interface temperature, 280°C; ionization voltage, 70 eV; and sample size, 2 µl of diluted samples.

For GC-FID, A Model JGC-20K gas chromatograph (JEOL) equipped with a 1-m 3% OV-17-1% PZ179 packed column and a Model G-3000 gas chromatograph (Hitachi) equipped with a 25 m × 0.53 mm I.D. SE-54 column were used for preliminary examinations to determine the optimum conditions.

Procedure

A water sample (500 ml) was placed in a round-bottomed flask, adjusted to pH 10 with 0.2 *M* sodium hydroxide solution and distilled. The distillate (100 ml) was collected in a separating funnel. The condenser was washed with 0.1 *M* hydrochloric acid. To the distillate, 3 g of sodium hydroxide and 7 ml of BSC were added and the mixture was shaken vigorously for 30 min, then a further 3 g of sodium hydroxide were added and the mixture was shaken for 10 min to decompose the excess of BSC. This solution was adjusted to pH 5 with 50% hydrochloric acid and extracted twice with 10 ml of dichloromethane. The organic layer was separated and concentrated to 1 ml with a Kudema-Danish evaporator. After 10 µl of 10 ppm [²H₁₀]fluoranthene

(I.S.) solution had been added, 2 μ l were injected into the GC system. A series of standard solutions were treated using the same procedure, except for the distillation process, and calibration graphs were constructed by comparing their peak heights with that of the internal standard.

If an interference was observed on the GC-MS-SIM trace, the sample solution was treated as follows. Hexane was added to the sample solution to a total volume of *ca.* 2 ml. A silica gel column (10 cm \times 10 mm I.D.) was prepared by washing with hexane, then the sample solution was placed on it. The column was washed with 20 ml of hexane-dichloromethane, then the amines were eluted with 30 ml of dichloromethane. The eluate was concentrated to 1 ml with a Kuderna-Danish evaporator.

RESULT AND DISCUSSION

Reaction conditions

The reaction yield depends on the amounts of BSC and sodium hydroxide. When 7 ml of BSC (0.055 mol) and 3 g of sodium hydroxide (0.075 mol) were added, the rate was found to be optimum.

Distillation conditions

The recovery of the distillation procedure was maximum at pH 10. Sodium chloride as a salting-out reagent had a negative effect on the recovery efficiency.

Individual amine standards (1000 μ g) were added to 500 ml of water and distilled at pH 10. The distillate was fractionated every 10 ml, and each fraction was treated in the same way as above. The washing solution from the condenser was combined with the last fraction (90–100 ml). The amine concentrations were determined by GC-FID.

The distillation curves are shown in Fig. 1. All amines were eluted within 100

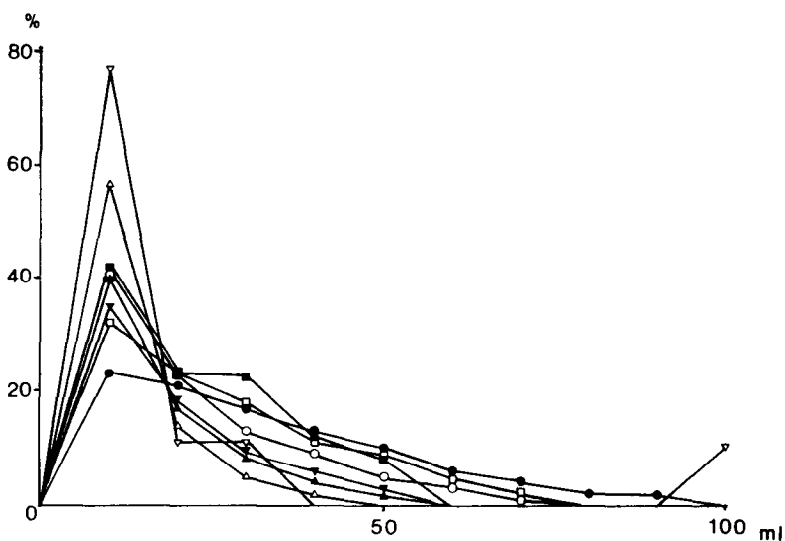


Fig. 1. Distillation curves for aliphatic amines. \circ = iPA; \bullet = AA; \square = nPA; \blacksquare = nBA; \triangle = DPA; \blacktriangle = DBA; ∇ = nOA; \blacktriangledown = DEHA.

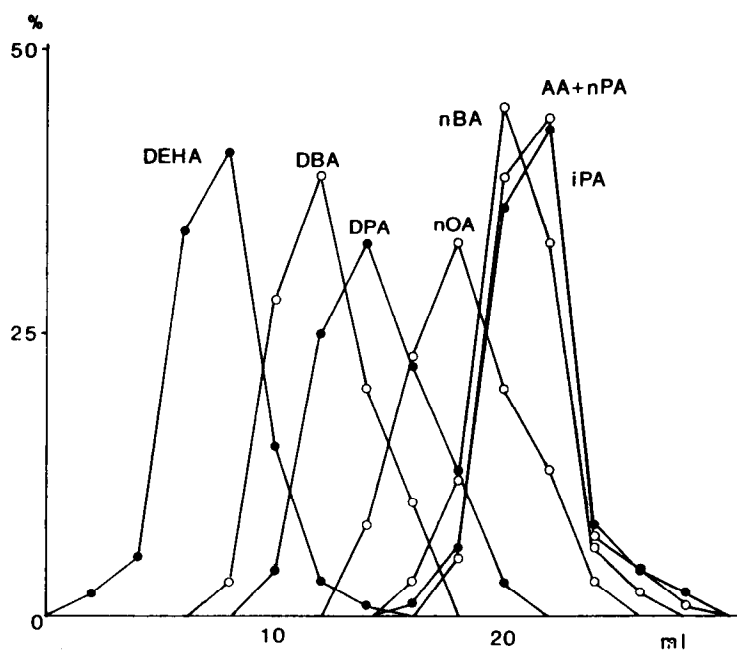


Fig. 2. Elution curves for amine-BSC derivatives obtained by silica gel column chromatography.

ml. Detection of *n*-octylamine in the last fraction can be attributed to the 0.1 *M*-hydrochloric acid washing of the condenser. *n*-Octylamine seems to be easily adsorbed on the glass wall and may fail to be recovered without washing.

Silica gel column chromatography

Clean-up was examined with a silica gel column because environmental samples usually contain many interfering substances. A standard mixture in dichloromethane

TABLE I

DETECTION LIMITS OF AMINES FOUND BY GC-MS-SIM

Water sample, 500 ml; sediment sample, 10 g (dry base).

Compound	<i>m/z</i>	Detection limit	
		Water ($\mu\text{g/l}$)	Sediment ($\mu\text{g/kg}$)
iPA	184	0.06	3
AA	170	2	100
nPA	170	0.07	3.5
nBA	170	0.06	3
DPA	212	0.01	0.5
DBA	226	0.01	0.5
nOA	170	0.05	2.5
DEHA	184	0.03	1.5
I.S.	212.1	—	—

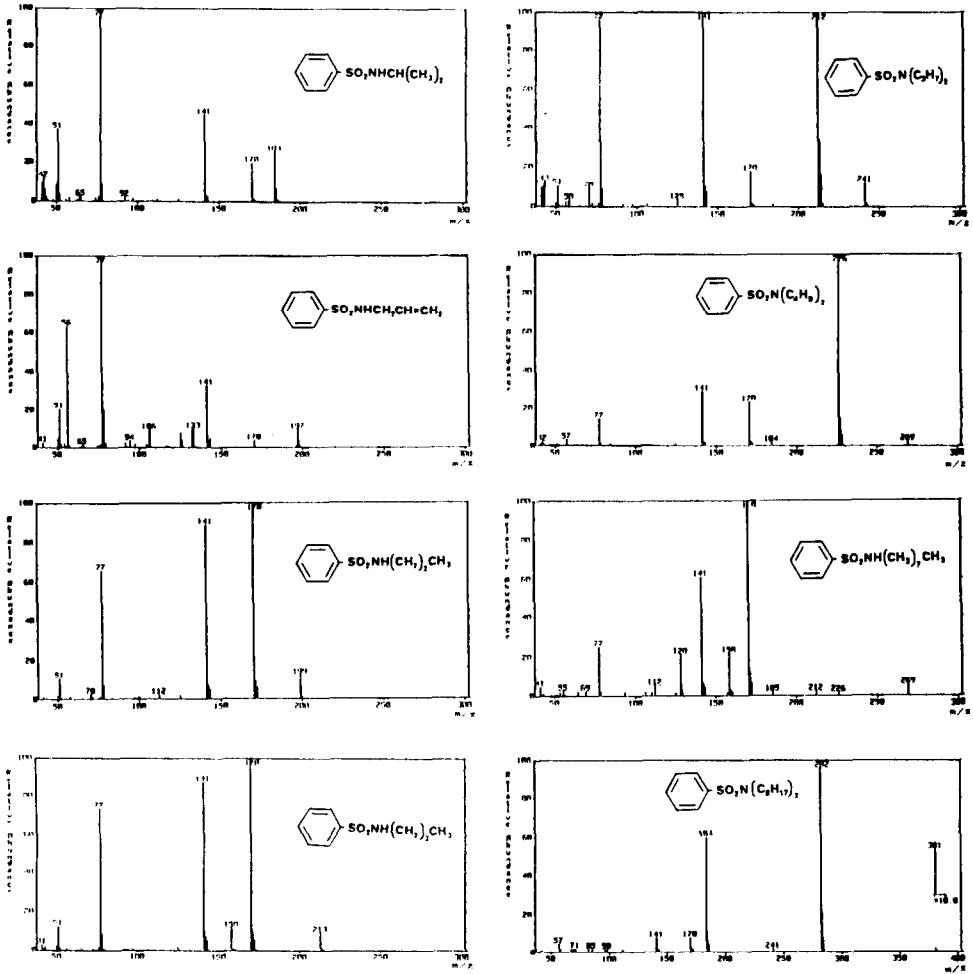


Fig. 3. Mass spectra of amine-BSC derivatives.

containing 100 ppm of each amine-BSC derivative was prepared. This solution (5 ml) was concentrated to 1 ml and diluted with same volume of hexane. Silica gel column chromatography was then carried out by the procedure mentioned above. The eluate was fractionated every 2 ml and the concentration of each amine in each fraction was determined by GC-FID. Fig. 2 shows the elution curves. No amines were eluted with hexane-dichloromethane (1:1), and all of them were completely eluted with 30 ml of dichloromethane.

Derivatization

The reaction of amines and BSC is

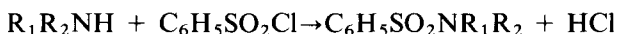


TABLE II

RECOVERIES OF AMINES FROM ENVIRONMENTAL SAMPLES ($n=4$)

R.S.D. = Relative standard deviation.

Compound	River water		Sea water		Sea sediment	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
iPA	98.8	4.5	92.3	3.8	89.7	5.2
AA	90.2	2.4	87.2	3.6	68.4	3.8
nPA	87.6	4.3	84.9	7.2	85.5	3.8
nBA	97.2	5.1	73.0	4.6	68.5	3.6
DPA	92.4	3.3	98.0	5.1	69.0	1.0
DBA	90.8	5.6	92.1	3.4	96.2	5.3
nOA	94.2	3.9	88.9	9.1	73.7	2.2
DEHA	91.9	3.4	88.3	4.5	72.3	9.3

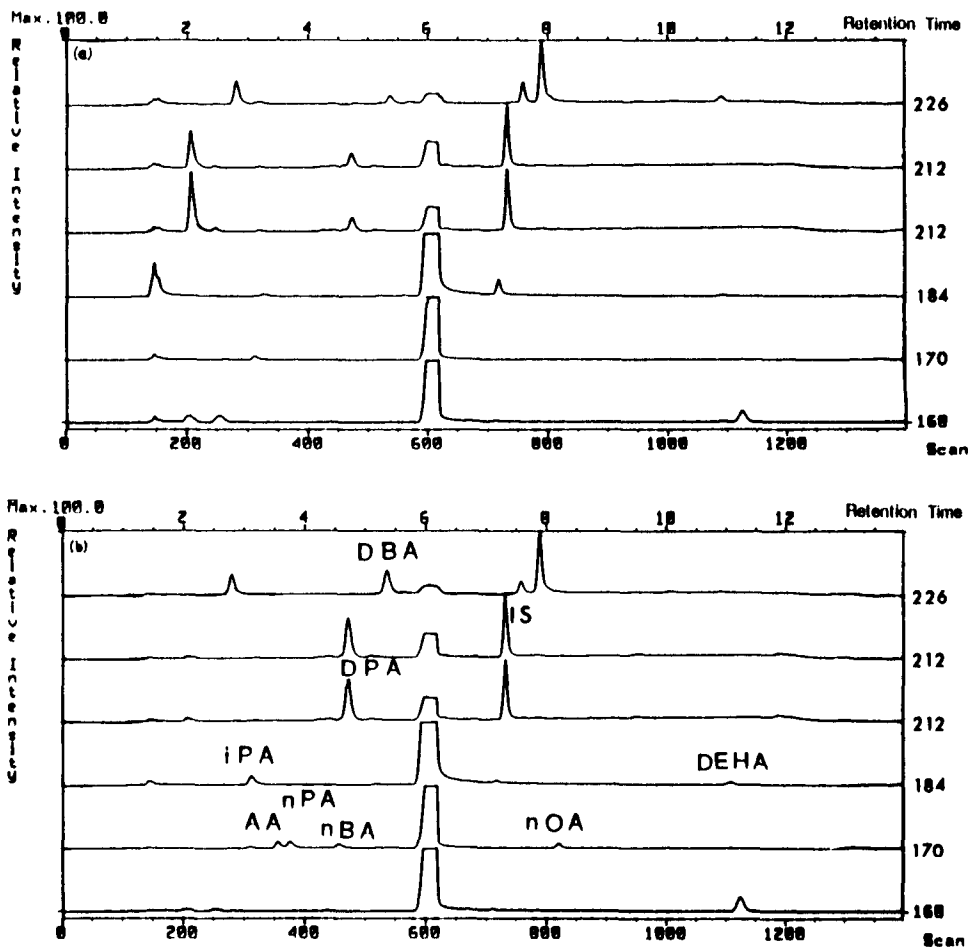


Fig. 4. SIM chromatograms of amine-BSC derivatives in a sea-water sample: (a) unspiked; (b) spiked.

where R = alkyl or H. This reaction can be performed in an early step in the analysis in water. It is reasonable to derivatize the amines prior to the concentration procedure in order to prevent the loss of some low-molecular-weight amines that are liable to volatilize.

Mass spectra of amine-BSC derivatives are shown in Fig. 3. From these mass spectra, suitable fragment ions were chosen for GC-MS-SIM.

The detection limits of the amines are shown in Table I (signal-to-noise ratio = 3). Allylamine has a relatively high detection limit because it has few intensive fragment ions (see Fig. 3).

Recovery tests were carried out by using river water, sea water and sea sediment spiked with amounts of each amine representing about ten times the detection limits. The results are given in Table II and representative chromatograms are shown in Fig. 4. nBA, DPA and DBA were detected in trace amounts in unspiked samples.

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