

# Gas chromatographic–mass spectrometric determination of lower aliphatic tertiary amines in environmental samples

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## ABSTRACT

A method is described for determining lower aliphatic tertiary amines in environmental samples such as river water and bottom sediments. The method consists of distillation of aliphatic tertiary amines and determination by headspace gas chromatography–mass spectrometry. The detection limits for final 40-ml samples were 50 ng for trimethylamine, 10 ng for triethylamine, 5 ng for triallylamine, 10 ng for tripropylamine and 5 ng for tributylamine. The recoveries were over 70% and the relative standard deviations of the recoveries were below 12% ( $n = 5$ ). The method is easy to operate, shows excellent sensitivity and selectivity and is applicable to environmental samples.

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## INTRODUCTION

Lower aliphatic tertiary amines are important as industrial raw materials for agricultural medicines, medicines, surfactants, dyes, etc., and are used in vast quantities. These compounds have such an unpleasant smell and high toxicity that working environmental standards are imposed on many of them. Tripropylamine in particular is included among high-toxicity chemical substances in Japan. For such reasons, it is necessary to develop a microanalytical method for aliphatic tertiary amines in order to monitor their concentration levels in environmental samples.

Analysis for aliphatic tertiary amines have frequently been reported [1–12], mainly involving analytical methods for trimethylamine in the atmosphere and for trimethylamine in tissues to determine the freshness of fish and shellfish. A few reports have appeared on triethylamine, triallylamine, tripropylamine and tributylamine [13–19]. However, little has been reported on these amines in aqueous or bottom sediment samples; only Prokopenko *et al.* [15], Yamamoto [20] and Selyutina and Vinnikov [18] have presented some methods. Prokopenko *et al.*'s method, for the analysis of amines in industrial waste waters at  $\mu\text{g/ml}$  concentrations directly by GC with flame ionization detection (FID), is too low in sensitivity to apply directly to environmental samples. In Yamamoto's method the sample water is acidified and concentrated to make

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it strongly alkaline, amines are vaporized by purging with nitrogen and trapped in water, then the aqueous solution is subjected to GC with flame thermionic detection (FTD). The drawbacks of this method are that a large amount of sodium hydroxide is used and the detector has low sensitivity. In Selyutine and Vinnikov's method, potassium hydroxide solution is added directly to the sample water to make it alkaline, then it is purged with nitrogen and amines are trapped in sulphuric acid. The solution obtained is concentrated and made alkaline, then the headspace gas is subjected to GC-FID. As with Yamamoto's method, this method also uses large amounts of alkali and is low in sensitivity.

With the above in mind, we report here the development of a method with a detection limit for amines below the  $\mu\text{g/l}$  level using a headspace analysis method that minimizes solvent and reagent use and analysis by capillary column GC-MS that has increased selectivity.

## EXPERIMENTAL

### Reagents

Sodium hydroxide and sodium chloride were of analytical-reagent grade. Trimethylamine (TMA), triethylamine (TEA), triallylamine (TAA), tripropylamine (TPA) and tributylamine (TBA) were purchased at the highest purity available. [ $^2\text{H}_{15}$ ]Triethylamine (TEA- $\text{d}_{15}$ ) was obtained from MSD Isotopes.

Sodium chloride was heated for 3 h at  $600^\circ\text{C}$  before use. Water was distilled and passed through a cation-exchange resin for purification.

### Apparatus

The gas chromatograph was a Hewlett-Packard Model 5890 and the mass spectrometer was a JEOL Model JMA-AX505W.

### GC-MS measurement conditions

The conditions for GC-MS with selected ion monitoring (SIM) were as follows: column, TC-1, 5- $\mu\text{m}$  film thickness 30 m  $\times$  0.53 mm I.D. (GL Science); column temperature, initially  $40^\circ\text{C}$  for 2 min, increased to  $180^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$  and held at  $180^\circ\text{C}$  5 min; injection port temperature,  $180^\circ\text{C}$ ; separator and ion source temperatures,  $250^\circ\text{C}$ ; ion-

ization voltage, 70 V; ionization current, 300  $\mu\text{A}$ ; carrier gas (helium) linear velocity, 75 cm/s; monitored ions ( $m/z$ ), 59 (TMA), 86 and 101 (TEA), 110 and 137 (TAA), 114 and 143 (TPA), 142 and 185 (TBA) and 98 (TEA- $\text{d}_{15}$ ).

### Standard procedure

**Aqueous samples.** A water sample of 500 ml is placed in a 1 l distillation flask, 5 ml of 2.5 M sodium hydroxide solution and 1.0  $\mu\text{g}$  of TEA- $\text{d}_{15}$  are added and 40 ml of the sample solution are distilled out into 5 ml of 0.025 M sulphuric acid as absorption solution at a distillation rate of about 1 ml/min. The 40-ml distillate is transferred into a 75-ml vial containing 8 g of sodium chloride, 10 ml of 15 M sodium hydroxide solution are added and immediately the vial is stoppered. The vial is shaken well and kept in a water-bath at  $40^\circ\text{C}$  for 1 h, then 1 ml of the headspace gas is injected into the GC-MS system for analysis.

**Bottom sediment samples.** A 50-g wet sediment sample is placed in a 1-l distillation flask containing 300 ml of purified water, 1.0  $\mu\text{g}$  of TEA- $\text{d}_{15}$  and 5 ml of 2.5 M sodium hydroxide solution are added and 40 ml of the sample solution are distilled out into 5 ml of 0.025 M sulphuric acid as absorption solution at a rate of about 1 ml/min. The 40-ml distillate is treated in the same way as for aqueous samples.

## RESULTS AND DISCUSSION

### Examination of distillation conditions

Lower aliphatic amines can be distilled out relatively easily under alkaline conditions, so in the present method distillation is used for both clean-up and concentration.

For the examination of recovery, each of the standard substances was placed in 500 ml of purified water 5 ml of 2.5 M sodium hydroxide solution were added and distillation was conducted to give 10-ml fractions. As the results in Table I show, the tertiary amines may be almost 100% recovered when 20 ml have been distilled; a 40-ml distillation is sufficient even for TBA, which is lowest to distil. For bottom sediment samples, 300 ml of purified water were added to 50 g of bottom sediment and the recovery was measured in the same way as for aqueous samples. The results were similar to those

TABLE I

RELATIONSHIP BETWEEN RECOVERY AND PORTIONS OF DISTILLATE FROM AQUEOUS SAMPLE

Portion of distillate (ml)	Recovery (%)					
	TMA	TEA-d <sub>15</sub>	TEA	TAA	TPA	TBA
0–10	95.8	98.0	97.8	92.6	96.7	83.6
10–20	3.5	1.5	1.6	5.4	2.5	11.9
20–30	0.7	0.5	0.6	1.3	0.6	3.2
30–40	0	0	0	0.7	0.2	1.3
40–50	0	0	0	0	0	0

for the aqueous samples. For this reason, the present method adopts the addition of 5 ml of 2.5 M sodium hydroxide solution and the 40-ml distillate into 5 ml of 0.025 M sulphuric acid as adsorption solution. In addition, a distillation rate as slow as 1 ml/min has been found to be suitable.

#### Examination of headspace conditions

As the present method involves a headspace procedure, which is simple to be operate and not susceptible to interfering substances, the optimum vaporization conditions were examined.

**Effect of sodium chloride concentration on vaporization efficiency.** Into five 75-ml vials, 0, 2.5, 5.0, 7.5 and 10 g of sodium chloride were placed, followed by 40 ml of purified water, 5 µg of each standard substance and 10 ml of 15 M sodium hydroxide solution. The vials were immediately stoppered and kept in a water-bath at 40°C for 1 h, then the headspace gases were analysed by GC-MS.

The relationship between the sodium chloride concentration and the vaporization efficiency was thus examined. The results (Fig. 1) show that the vaporization efficiency at saturation increased *ca.* 5 times for TMA, TEA and TEA-d<sub>15</sub>, *ca.* 3 times for TAA and TPA and *ca.* 1.5 times for TBA relative to no addition of sodium chloride. The salting-out effect increased as the molecular size decreased. For this reason, saturation with sodium chloride was adopted.

**Effect of temperature on vaporization efficiency.** For the headspace method, it was expected that higher temperatures would increase the vaporization efficiency. The vaporization efficiency was ex-

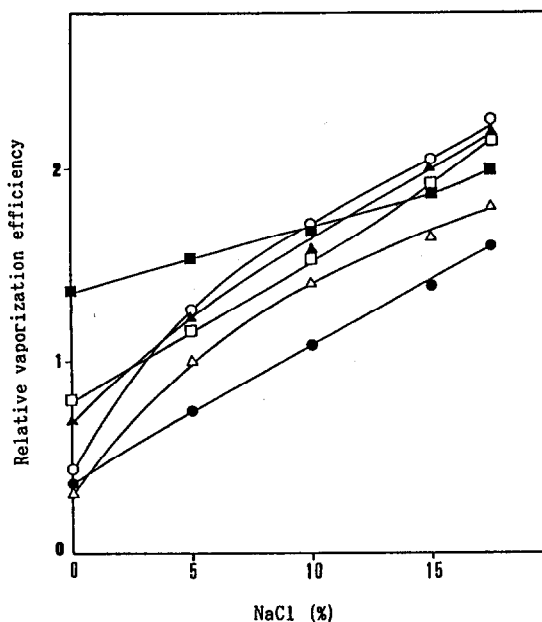


Fig. 1. Relationship between vaporization efficiency and sodium chloride concentration. ● = TMA; ○ = TEA; ▲ = TAA; □ = TPA; ■ = TBA; △ = TEA-d<sub>15</sub>.

amined by adding sodium chloride to saturation under the above-mentioned conditions and varying the water-bath temperature from 20 to 50°C at intervals of 10°C. For TMA, the vaporization efficiency increased *ca.* 4 times at 50°C relative to that at 20°C, and for the other substances 1.5–2 times (Fig. 2). In addition, it was found that higher temperatures tended to increase the variation in the measured values, so that 40°C was adopted.

**Effect of sodium hydroxide concentration on vaporization efficiency.** Conventionally, potassium hydroxide, sodium carbonate or sodium hydroxide has been used for the vaporization of aliphatic amines. On the precondition that the present method should use the cheapest salt, vaporization at different sodium hydroxide concentrations in the range 0–6 M, was examined, with saturated sodium chloride and the water-bath temperature kept at 40°C.

As the results in Fig. 3 show, the relationship between the alkali concentration and the vaporization efficiency was linear for TMA without giving any maximum vaporization efficiency, but TEA, TAA, TPA and TBA yielded maximum vaporization effi-

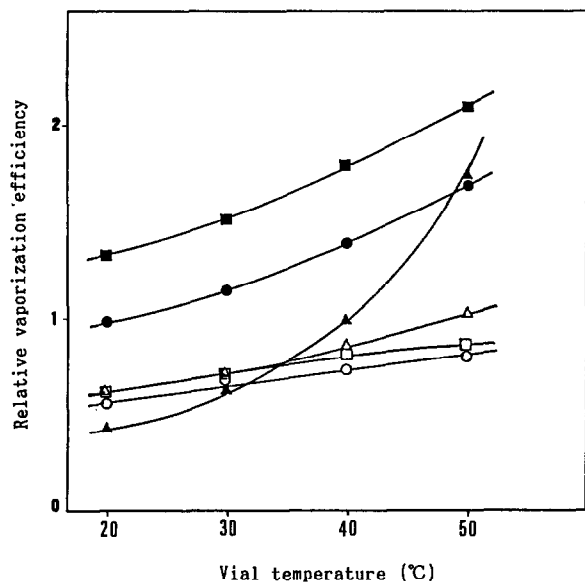


Fig. 2. Relationship between vaporization efficiency and vial temperature. ▲ = TMA; ● = TEA; ○ = TAA; □ = TPA; ■ = TBA; △ = TEA-d<sub>15</sub>.

ciencies 4, 3, 2.5-3 and 1 *M*, respectively. This indicates that the alkali concentrations for the maximum vaporization efficiency tend to decrease with increasing length of the alkyl group. Based on this result, an intermediate concentration of 3 *M* for the sodium hydroxide solution was adopted.

#### Examination of GC-MS measurement conditions

The columns used for analyses for aliphatic amines are typically packed columns in which Tenax GC or Chromosorb 103 is coated with potassium hydroxide. These columns are low in efficiency and induce adsorption at low concentrations and therefore, have been considered inapplicable to the microanalysis of environmental samples. In this work, satisfactory separations were obtained with a wide-bore capillary column using a thick layer of a non-polar liquid phase such as OV-1 rather than a high-polarity phase such as PEG or FFAP.

To select the monitoring ions for SIM measurement, MS measurements were made in the electron impact mode. It was found that, except for TMA, monitoring can be effected with base ions. For TMA, no selective fragments were found except *m/z*

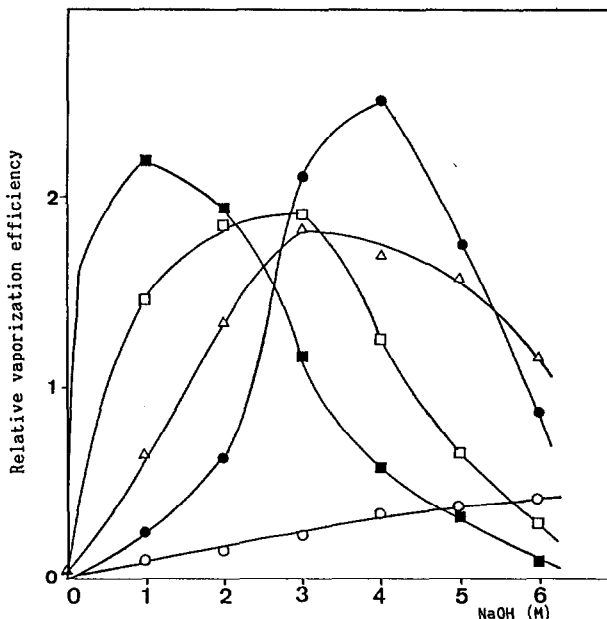


Fig. 3. Relationship between vaporization efficiency and sodium hydroxide concentration. ○ = TMA; ● = TEA; △ = TAA; □ = TPA; ■ = TBA.

= 59, which was therefore adopted for monitoring. The SIM chromatograms of the standard substances are shown in Fig. 4.

#### Calibration and detection limits

To construct the calibration graphs, 8-g amounts of sodium chloride were placed in 75-ml vials, then 40 ml of purified water, 1.0  $\mu\text{g}$  of TEA-d<sub>15</sub> and varying amounts of a standard substance were added, finally 10 ml of 15 *M* sodium hydroxide solution were added. The vials were immediately stoppered, shaken well and kept in a water-bath at 40°C for 1 h, then 1 ml of the headspace gas was injected into the GC-MS system. The peak-area ratios with respect to the internal standard were used to construct calibration graphs. The detection limits for the final 40-ml sample solution were found to be 50, 10, 4, 10 and 5 ng for TMA, TEA, TAA, TPA and TBA, respectively.

#### Recovery experiments and application to real samples

The recovery obtainable by the method was examined by adding 0.5  $\mu\text{g}$  of a standard substance

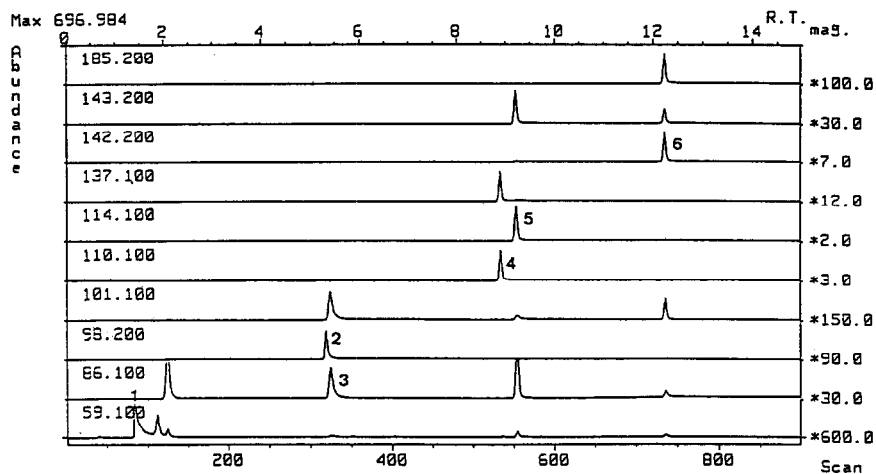


Fig. 4. SIM chromatogram of aliphatic amines. Peaks: 1 = TMA; 2 = TEA- $d_{15}$ ; 3 = TEA; 4 = TAA; 5 = TPA; 6 = TBA. R.T. = Retention time in min.

TABLE II

RECOVERY OF ALIPHATIC TERTIARY AMINES FROM RIVER WATER AND BOTTOM SEDIMENT

Compound	River water			Bottom sediment		
	Added ( $\mu\text{g}$ )	Recovery (%)	R.S.D. <sup>a</sup> (%)	Added ( $\mu\text{g}$ )	Recovery (%)	R.S.D. <sup>a</sup> (%)
TMA	0.5	69.4	11.7	50	85.3	4.9
TEA	0.5	89.0	9.3	0.5	87.6	10.2
TAA	0.5	80.4	8.3	0.5	73.7	12.2
TPA	0.5	81.0	8.7	0.5	84.3	7.3
TBA	0.5	73.4	12.0	0.5	82.3	5.1

<sup>a</sup>  $n = 5$ .

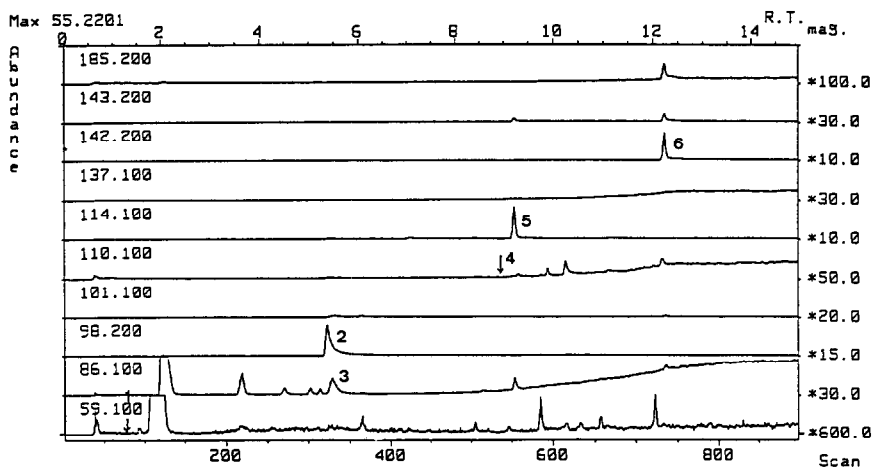


Fig. 5. SIM chromatogram of pond water from Suwa Lake. Peaks as in Fig. 4.

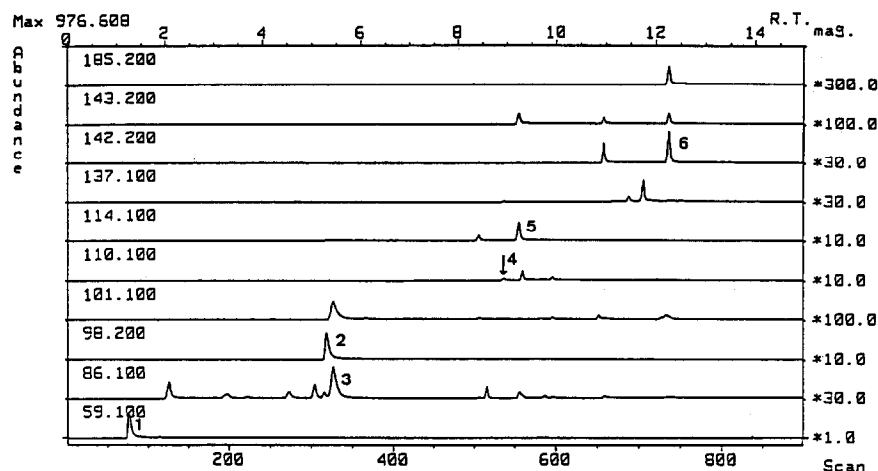


Fig. 6. SIM chromatogram of bottom sediment from Tokyo Bay. Peaks as in Fig. 4.

(50  $\mu\text{g}$  of TMA for bottom sediment samples having high blank TMA values) to either 500 ml of water from the Susobana River in Nagano City or 50 g of bottom sediment from Tokyo Bay. As the results in Table II shows, the recovery was over 70% with a relative standard deviation below 12%.

As application examples, the method was applied to waters and bottom sediments from rivers, lakes and marshes in Nagano Prefecture and bottom sediment from Tokyo Bay ( $n = 12$ ). Fig. 5 shows the results for water from Suwa Lake and Fig. 6 those for bottom sediment from Tokyo Bay. The water from Suwa Lake contained 0.25  $\mu\text{g}/\text{l}$  of TEA and 0.23  $\mu\text{g}/\text{l}$  of TBA and the bottom sediment from Tokyo Bay contained 0.53  $\mu\text{g}/\text{g}$  of TMA, 4.0  $\mu\text{g}/\text{kg}$  of TEA, 0.26  $\mu\text{g}/\text{kg}$  of TPA, 1.0  $\mu\text{g}/\text{kg}$  of TBA and no TAA.

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