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ADSORPTION–DERIVATIZATION GAS CHROMATOGRAPHIC–MASS SPECTROSCOPIC DETERMINATION OF AQUEOUS 1,6-HEXANEDIAMINE AT THE LOW AND SUB-PPM LEVEL

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SUMMARY

An adsorption–derivatization gas chromatographic–mass spectrometric procedure has been developed for the determinations of low and sub-ppm levels of aqueous 1,6-hexanediamine. The amine from a 50-ml aqueous sample is adsorbed on Ambersorb XE-348 and recovered by trifluoroacetylation to give consistent recoveries of about 50, 40 and 35% respectively for 0.1, 0.5 and 1.0 ppm concentrations.

INTRODUCTION

The detection and determination of primary aliphatic amines and diamines at low concentrations by gas chromatography (GC) is difficult at best because of the polar nature of these compounds.

In order to enhance their GC performance, primary amines have been subjected to a variety of derivatization schemes[1–5] by which their polarity has been suppressed.

In this work, a simple combined adsorption–derivatization procedure (followed by GC and/or GC–mass spectrometric (MS) analysis) is described for determining trace 1,6-hexanediamine in water which not only reduces amine polarity but considerably enhances detectability.

EXPERIMENTAL

Reagents

1,6-Hexanediamine (HMDA) was purchased from Aldrich (Metuchen, NJ, U.S.A.); N-methyl-bis-(trifluoroacetamide) (MBTFA) was purchased from Pierce (Rockford, IL, U.S.A.); Ambersorb XE-348 was obtained as a complimentary sample from Rohm & Haas (Philadelphia, PA, U.S.A.).

Adsorption procedure

A small plug of glass wool was placed at one end of a 15 cm × 4 mm O.D.

(2.3 mm I.D.) glass tube and 100 mg Ambersorb XE-348 (as received) was added to the tube followed by another plug of glass wool. The tube was connected at the empty end by means of a short piece (or pieces) of suitable PTFE tubing to a 50-ml burette equipped with a PTFE stopcock. The beveled section of the burette delivery tip was cut off in order to facilitate attachment of the PTFE connecting piece as well as to improve liquid flow characteristics.

Approximately 5–10 ml of distilled water was poured into the burette and a flow-rate of about 1.5 ml/min was established by adjusting the stopcock while applying gentle air pressure at the top of the burette.

When the flow-rate was established and before the burette ran dry, the air pressure source at the top of the burette was momentarily disconnected, and 50 ml of aqueous sample was poured into the burette. Pressure was reestablished and the sample was passed through the scrubber. The apparatus is shown in Fig. 1.

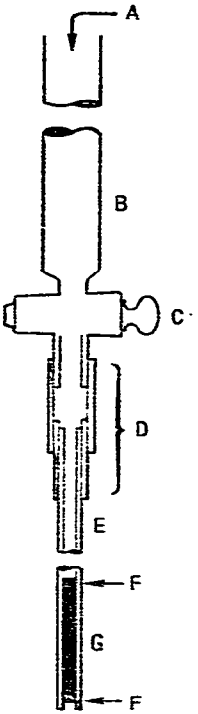

Fig. 1. Apparatus for adsorption of HMDA from water. A = slight applied pressure; B = burette (abbreviated delivery tube); C = PTFE stopcock; D = PTFE connecting tube(s); E = glass tube; F = glass wool plugs; G = Ambersorb XE-348.

Desorption–derivatization procedure

The scrubber tube was removed from the burette and attached via rubber tubing to a light vacuum source so that a gentle flow (approx. 10 ml/min) of room air was drawn through the scrubber in the same direction as the original liquid flow. After a period of 20 min, the air dried Ambersorb XE-348 was poured out of the

tube into a 4-ml vial and 250 μl of MBTFA was added via a 500-μl syringe. The contents of the vial were sealed with a PTFE-lined screw cap and heated at 110 °C for 15 min. Upon cooling to room temperature, the sample was ready for GC and/or GC–MS analysis.

Gas chromatography

A Hewlett-Packard 5750B Series research chromatograph equipped with a flame-ionization detector (FID) was used. The derivatized sample (4 μl) was injected onto a 1.5 m × 2 mm I.D. glass column packed with 3% QF-1 + 3% OV-17 on Chromosorb W HP using a temperature program of 100 to 200 °C at 20 °C/min with a 4-min hold at upper limit. Carrier gas was helium at 50 ml/min, detector temperature 275 °C, injector (on column) temperature 240 °C, retention time was approximately 7 min. Chromatogram peak heights were used for quantitation. Calibration of the detector was accomplished by the analysis of known solutions (in MBTFA) of previously prepared N,N′-hexamethylene-bis-(trifluoroacetamide). Fig. 2 (a and b) shows typical chromatograms.

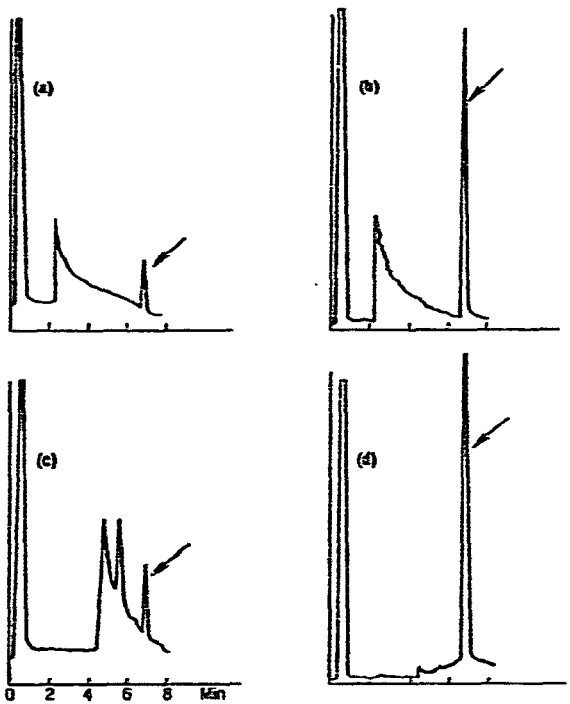

Fig. 2. Chromatograms of N,N′-hexamethylene-bis-(trifluoroacetamide) HMDA–TFA. (a) 20 ppm standard $10^2 \times 2$; (b) 200 ppm standard $10^2 \times 4$; (c) 0.11 ppm sample run, $10^2 \times 2$; (d) 1.1 ppm sample run, $10^2 \times 4$. All 4 μl.

Mass spectrometry

A Finnigan 3200 mass spectrometer equipped with a Finnigan 9600 gas chromatograph and Finnigan 6000 data acquisition and reduction system was used. The derivatized sample (1 μl) was injected onto a 1.8 m × 2 mm I.D. glass column

containing 10% OV-225 on Chromosorb W HP (80–100 mesh). Under an isothermal column temperature of 225 °C the retention time was 2.40 ± 0.03 min. The injection port, separator oven, and transfer line were 250 °C. Approximately 10 ml/min of 99.99% purity methane was used as the carrier gas and the methane became the MS reagent gas for chemical ionization.

The chemical ionization spectrum of the derivatized HMDA (HMDA–TFA) was obtained by using a 1-μl injection of a 200-ppm standard. A scan from *m/e* 500 to *m/e* 70 in 2 sec gave the spectrum shown in Fig. 3. For identification and quantitation single ion monitoring of *m/e* 309.2 was used. This *m/e* value was the pseudo-molecular ion produced by a proton transfer from CH_5^+ to the derivatized hexamethylene diamine. The peak area produced by the single ion monitoring technique was used for quantitation. Calibration was accomplished by the analysis of known solutions of HMDA–TFA.

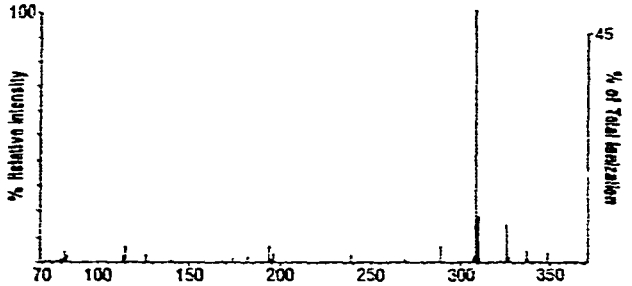

Fig. 3. Methane-chemical ionization mass spectrum of N,N′-hexamethylene-bis-(trifluoroacetamide) HMDA–TFA.

RESULTS AND DISCUSSION

Recovery of HMDA by Ambersorb XE-348

In this work, aqueous solutions of 1.1, 0.55 and 0.11 ppm (w/v) HMDA were prepared from a stock solution of 110 ppm (w/v) HMDA in distilled water. Four separate 50-ml portions of each of the 1.1, 0.55 and 0.11 ppm solutions were put through the sorption–reaction-desorption procedure and analyzed by GC. Recoveries are shown in Table I, section A.

In as much as recoveries are acceptably consistent but less than 100% over the concentration ranges examined, an attempt was made to account for the unrecovered HMDA. Accordingly, single backup scrubbers (also 100 mg) were used and analyzed in the same way. This procedure showed that incomplete retention by the initial scrubber is responsible for at least some of the lost HMDA. Results of the analyses of the backup scrubbers are shown in Table I, section B.

The reason for the decreasing efficiency of HMDA recovery as concentration increases from 0.11 ppm to 1.1 ppm is believed to be attributable to the relative availability of retentive sites on the Ambersorb surface under the conditions of analysis. Thus, for a given amount of active sites, an increase in the concentration of aqueous HMDA results in a decrease of scrubber efficiency.

TABLE I

RECOVERY PERCENTAGE OF 1,6-HEXANEDIAMINE FROM 50-ml AQUEOUS SAMPLES BY XE-348

Analysis No.	*Concentration (ppm)*		
	1.1	*0.55*	*0.11*
Section A			
1 (Front 100 mg)	35	40	53
2 (Front 100 mg)	31	38	53
3 (Front 100 mg)	36	38	50
4 (Front 100 mg)	35	44	48
Section B			
1 (Back 100 mg)	4	*	11
2 (Back 100 mg)	3	*	11
3 (Back 100 mg)	3	*	15
4 (Back 100 mg)	4	*	11

* Not determined.

A theoretical 100% recovery of HMDA from an aqueous solution would afford a 200-fold increase in final concentration (*i.e.*, 50 ml of aqueous sample resulting in 0.25 ml of reaction mixture). In addition, a 2.65-fold increase in molecular weight is also achieved (HMDA, mol.wt. 116 *vs.* HMDA–TFA, mol.wt. 308). Combining the two factors gives a 530-fold increase in mass for an ideal recovery. However, even a 50% recovery for a 0.1 ppm HMDA solution results in a final concentration of about 27 ppm as HMDA–TFA. Thus, sub-ppm levels of original HMDA are easily detected using a flame-ionization gas chromatograph. Fig. 2 (c and d) shows typical chromatograms.

Sample reaction mixtures that were analyzed after 24 h or so of standing were observed to develop several small artifact peaks that were not originally present. These peaks eluted prior to the HMDA–TFA peak and therefore were not interferences. This procedure was developed for an application where HMDA was the only expected aqueous contaminant. It is certainly possible that aqueous contaminants other than HMDA could be determined by the same procedure.

Calibration standards

For calibration, a stock solution of HMDA–TFA (pure, previously prepared) in methanol (typically 1%, w/w) was made up. From this, very small aliquots were taken and placed in vials. The appropriate amount of MBTFA was added to provide the final desired concentration. The small amounts of methanol were consumed by the excess MBTFA.

Repeated injections of calibration standards (*e.g.*, 20 ppm, 200 ppm, etc., HMDA–TFA in MBTFA) over several days of analysis time exhibited variations of $\pm$ 2.5–3.0% in the average FID peak response (hand measured) for a given day. Repeated injections into the GC–MS single-ion monitoring conditions gave variations of $\pm$ 4–7% in average peak area (computer measured). In both methods the response was linear over the range of 20 to 200 ppm for FID and 0.25 to 200 ppm for GC–MS. The detection limit for FID was at least 20 ppm and 0.25 ppm for the

GC–MS single-ion monitoring method of analysis at a signal to noise ratio of 5:1. No degradation of the standard solutions was apparent over several weeks time when stored at room temperature.

The GC–MS single-ion monitoring method coupled with the adsorption–desorption–derivatization technique described in this paper will give quantitative analysis of 1,6-hexanediamine in water down to 1 ppb (10^9).

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