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## Note

# Separation and analysis of ethylenediamines as their *tert.*-butyldimethylsilyl derivatives by gas–liquid chromatography and mass spectrometry

LAY-KEOW NG
*Laboratory & Scientific Services Directorate, Revenue Canada, Customs & Excise, Ottawa, Ontario K1A 0L5 (Canada)*

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Ethylenediamines are frequently used as reactive hardeners in epoxy resin formulations employed for protective coatings, adhesives etc.[1]. We are particularly interested in the ethylenediamine family of products consisting of ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). The separation and identification of these ethylenediamines in imported products is of importance for tariff classification purposes.

$H_2N(CH_2CH_2NH)_nH$

$n$ = 1: EDA
$n$ = 2: DETA
$n$ = 3: TETA
$n$ = 4: TEPA

In this family of compounds, EDA and DETA are available in pure form (>98% purity), whereas the higher-molecular-weight members, TETA and TEPA contain, as impurities, branched isomers and cyclic products such as piperazines. The assay of the lower ethylenediamines, especially EDA and DETA, is frequently accomplished by conventional gas chromatography (GC)[2]. For the higher ethylenediamines, severe tailing is often encountered due to their high polarity. To counteract this, the use of silane-treated[3] or alkaline hydroxide-treated[4] columns or the use of PTFE powder as a support[5] were recommended. TETA and TEPA have also been chromatographed on uncoated, porous column packings based on poly(2,6-diphenyl-*p*-phenylene oxide)[6]. These techniques, however, required the use of larger amount of sample than usual in order to avoid loss of components by adsorption. For this reason, it is often desirable to work with derivatives. Ethylenediamines have been chromatographed as trifluoroacetyl (TFA) derivatives using a neopentyl glycol succinate packed column and a flame ionization detector[7]. The method required separation of the TFA derivatives before GC analysis.

For GC analysis of organic compounds containing active hydrogen, such as alcohols, carboxylates, thiols, amines etc., silylation[8] has long been used to improve

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resolution and peak symmetry, or to decrease adsorption on the column. The amino group is generally more difficult to silylate than hydroxyl or carboxyl functions and few studies on the silylation of ethylenediamines have been reported. Only DETA has been treated with N-(trimethylsilyl)-dimethylamine to yield mono-, di- and tri-silylated derivatives depending on the substrate–silylating agent ratio[9]. Recently a very versatile silylating agent, N-methyl-N-(*tert.*-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA), has been developed and found to quantitatively (97% yield) and rapidly silylate alcohols, carboxylates, as well as thiols and amines[10]. In the present investigation we report on the silylation with MTBSTFA, separation and analysis of the EDA, DETA, TETA and TEPA by GC using OV-7 packed column, and combined gas chromatography–mass spectrometry (GC–MS) using a capillary DB-5 column. Each of the resulting *tert.*-butyldimethylsilyl (*t*-BDMS) derivatives of the ethylenediamines displays a sharp and symmetrical chromatographic peak by GC and yields a characteristic mass spectrum. This method has the advantage over TFA derivatization[7] in that the silylation mixtures were analysed directly, without product isolation before GC analysis.

## EXPERIMENTAL

### *Reagents*

MTBSTFA and acetonitrile (HPLC grade) were purchased from Pierce Chemical Company (Rockford, U.S.A.) and Caledon Labs. (Ontario, Canada) respectively. EDA and DETA were obtained from Akzo Zout Chemie (Amsterdam, The Netherlands) and Kodak (U.S.A.) respectively. Commercial polyamines containing TETA (called polyamine A) and TEPA (called polyamine B) were obtained from commercial sources. Mixture A was prepared by mixing by weight 10% EDA, 16% DETA, 21% polyamine A and 53% polyamine B. All these amines were used for derivatization without further purification.

### *Derivatization procedure*

The *t*-BDMS derivatives of EDA, DETA, polyamine A, polyamine B and mixture A were prepared by adding 100 $\mu$l of acetonitrile and 100 $\mu$l of MTBSTFA into a PTFE-faced silicone-rubber septum capped reaction vial containing 3–4 mg of each of the ethylenediamine samples. After standing at room temperature for 30 min, 1 $\mu$l and 0.4 $\mu$l of the solution was injected into the gas chromatograph and the gas chromatograph–mass spectrometer respectively.

### *Gas chromatography*

A Hewlett-Packard Model 5480 A gas chromatograph was employed equipped with a flame ionization detector and a 3% OV-7 on Chromosorb W HP, 80–100 mesh, 4 ft. × 0.125 in. I.D. nickel column. The injector temperature was 250°C and the *t*-BDMS derivatives were injected at an oven temperature of 80°C, after an initial hold time of 2 min at 80°C, the oven temperature was programmed at 10°C/min until 250°C, flow-rate of nitrogen as carrier gas was 35 ml/min.

### *GC–MS*

The gas chromatograph–mass spectrometer (Finnigan Model 1020) was equipped with an electron impact source and a Nova 4 data system. The scanning

rate was 1 sec/scan in the range 40–650 a.m.u. The ion source temperature was held at 80°C. Electron impact (EI) spectra were obtained at 75 eV. The GC instrument (Perkin-Elmer Sigma-3B) was fitted with a 15 m × 0.242 mm O.D. DB-5 capillary fused-silica column used in a splitless mode. The oven temperature was kept at 80°C for 3 min, then programmed at 20°C/min until 280°C and held at this temperature for 10 min. The injector temperature was set at 250°C and the flow-rate of the carrier gas (helium) was 1 ml/min.

## RESULTS AND DISCUSSION

### *Derivatization*

The degree of silylation of each *t*-BDMS derivative was determined by the molecular weight derived from the [M − 15] and [M − 57] peaks in its EI spectrum. *tert.*-Butyldimethylsilylation of EDA, DETA, TETA in polyamine A, and TEPA in polyamine B yielded predominantly the disilylated derivatives with less than 1% of the trisilylated derivative under the reaction conditions as described in the Experimental section. For the disilylated derivatives, presumably one *t*-BDMS group was introduced to each of the two primary amino groups since primary amines are known to be much more readily silylated than the secondary[10]. Prolonged standing over several days at room temperature resulted in an increase in the amount of trisilylated

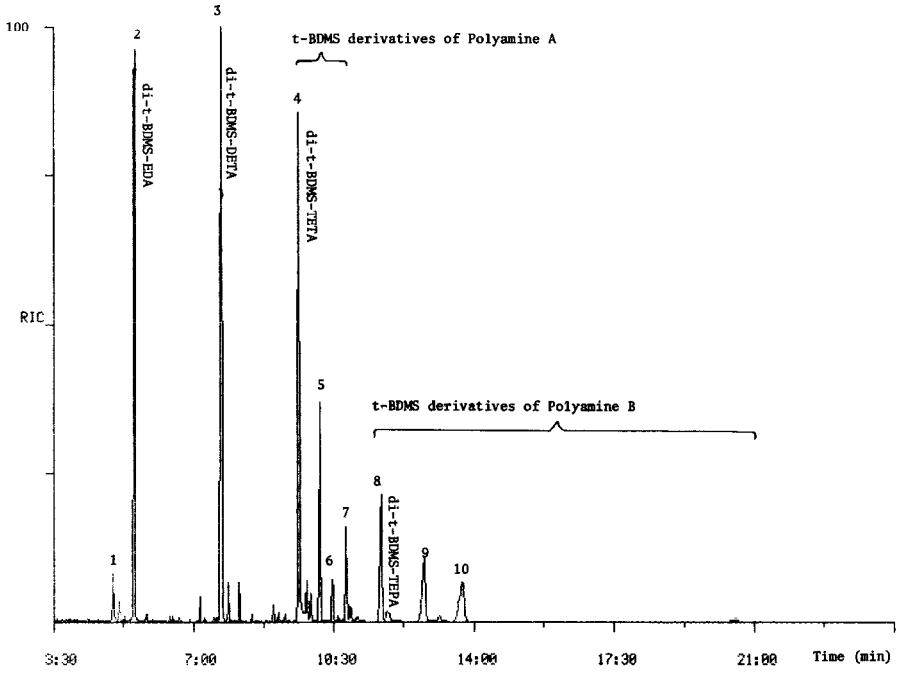



Fig. 1. Reconstructed ion chromatogram of *t*-BDMS derivatives of mixture A: di-*t*-BDMS derivatives of EDA, DETA, TETA and TPA (peaks 2, 3, 4 and 8 respectively), various *t*-BDMS derivatives of piperazines (peaks 1, 5, 6 and 9) and tri-*t*-BDMS derivatives of branched TETA and TEPA (peaks 7 and 10 respectively). Other minor peaks, though not identified, are not *t*-BDMS derivatives of linear ethylenediamines.

TABLE I

RELATIVE INTENSITIES OF PROMINENT FRAGMENT IONS IN THE MASS SPECTRA OF THE DI-*tert.*-BUTYLDIMETHYLSILYLATED DERIVATIVES OF ETHYLENEDIAMINES

| *Ethylenediamine* | *m/e (relative intensity, %* | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $M^+$ | *[M−15]* | *[M−57]* | *[M−144]* | *[M−187]* | | | | | |
| EDA | 288 (0.05) | 273 (2.8) | 231 (25) | 144 (100) | 101 (10) | 73 (96) | 115 (12.5) | 144 (100) | 158 (1) | 187 (0) |
| DETA | 331 (0) | 316 (0.6) | 274 (0.9) | 187 (57) | 144 (36) | 73 (100) | 115 (10) | 144 (36) | 158 (25) | 187 (57) |
| TETA | 374 (0) | 359 (0.8) | 317 (1.2) | 230 (2.6) | 187 (34) | 73 (100) | 115 (6) | 144 (34) | 158 (33) | 187 (34) |
| TEPA | 417 (0) | 402 (0.4) | 360 (0.6) | 273 (15) | 230 (9) | 73 (100) | 115 (6) | 144 (27) | 158 (38) | 187 (25) |

derivative and a corresponding reduction in the amount of the disilylated diamine. We limited our study to the disilylated derivatives because the more highly silylated derivatives are less favorable for GC and GC–MS analysis in view of their higher retention times.

*GC–MS*

Separation of *t*-BDMS derivatives of mixture A (made up of EDA, DETA, Polyamines A and B) on GC–MS is shown in the reconstructed ion chromatogram (RIC) in Fig. 1. All peaks were well separated and each *t*-BDMS derivative displayed a very sharp single chromatographic peak and exhibited no peak tailing on the fused-silica DB-5 column. Retention times for the di-*t*-BDMS derivatives of EDA, DETA, TETA and TEPA were 5.25, 7.41, 9.37 and 11.41 min respectively. The observed retention times appear to be directly related to the molecular weights of the derivatives.

All synthesized *t*-BDMS derivatives were each subjected to EI analysis. Generally the molecular ions were not discernible. Fragments resulting from loss of $CH_3$, $-C(CH_3)_3$ and $-CH_2NHSi(CH_3)_2C(CH_3)_3$ were usually present with their relative intensities increasing in the order $[M-15] < [M-57] < [M-144]$. These fragments were used to derive the molecular weights of the derivatives. The EI results of the di-*t*-BDMS derivatives of ethylenediamines are presented in Table I. Loss of $-CH_2NHCH_2CH_2NHSi(CH_3)_2C(CH_3)_3$ yielded the fragment $[M-187]$ of appreciable relative intensity in cases where such fragmentation is desirable such as in the derivatives of DETA, TETA and TEPA. Characteristic of each mass spectrum are the fragment ions at *m/e* 73, 115 and 144 which are the silicone-containing ions. Other fragments at *m/e* 158 and 187 are also very intense except in the case of EDA.

$[HNSi(CH_3)_2]^+$ *m/e* 73

$[Si(CH_3)_2C(CH_3)_3]^+$ *m/e* 115

$[CH_2{-}NHSi(CH_3)_2C(CH_3)_3]^+$ *m/e* 144

$[CH_2CH_2NHSi(CH_3)_2C(CH_3)_3]^+$ *m/e* 158

$[CH_2NHCH_2CH_2NHSi(CH_3)_2C(CH_3)_3]^+$ *m/e* 187

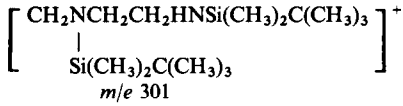
Since a piperazine has a molecular weight different from an ethylenediamine having the same number of N atoms, its *t*-BDMS derivatives could be easily recognized by the molecular weights derived from the $[M-15]$ and $[M-57]$ fragments present in their EI spectra. A *t*-BDMS derivative of a piperazine generally gives characteristic fragments at *m/e* 73 and *m/e* 115. Other fragments characteristic of linear ethylenediamines were also observed when the N atom in the piperazine ring is substituted with $(CH_2CH_2NH)_nH$.

The tri-t-BDMS derivatives of branched TETA and TEPA formed in appreciable amount (peaks 7 and 10 in Fig. 1) under the described experimental conditions are believed to have the *t*-BDMS groups introduced to the primary amino functions only.

$N[CH_2CH_2NHSi(CH_3)_2C(CH_3)_3]_3$
tri-*t*-BDMS-branched TETA

$[(CH_3)_3C(CH_3)_2SiHNCH_2CH_2]_2N(CH_2CH_2NH)_2Si(CH_3)_2C(CH_3)_3$
tri-*t*-BDMS-branched TEPA

Although these derivatives have the same molecular weights as the tri-*t*-BDMS derivatives of their respective linear isomers, the isomeric tri-*t*-BDMS derivatives could be differentiated by the peak at *m/e* 301 present only in the EI spectra of the trisilylated derivatives of the linear isomers. These derivatives having a secondary amino function silylated were formed only when the reaction mixture was allowed to stand at room temperature for several days.



*m/e* 301

*GC*

GC separation of *t*-BDMS derivatives of mixture A on packed OV-7 column is shown in Fig. 2. The di-*t*-BDMS derivatives of EDA and DETA were confirmed by standard addition. Since the chromatogram was basically the same as the RIC obtained on GC–MS (Fig. 1) except that peaks were better resolved on the capillary DB-5 column, peaks 3 and 4 are tentatively assigned to be due to the di-*t*-BDMS derivatives of TETA and TEPA respectively.

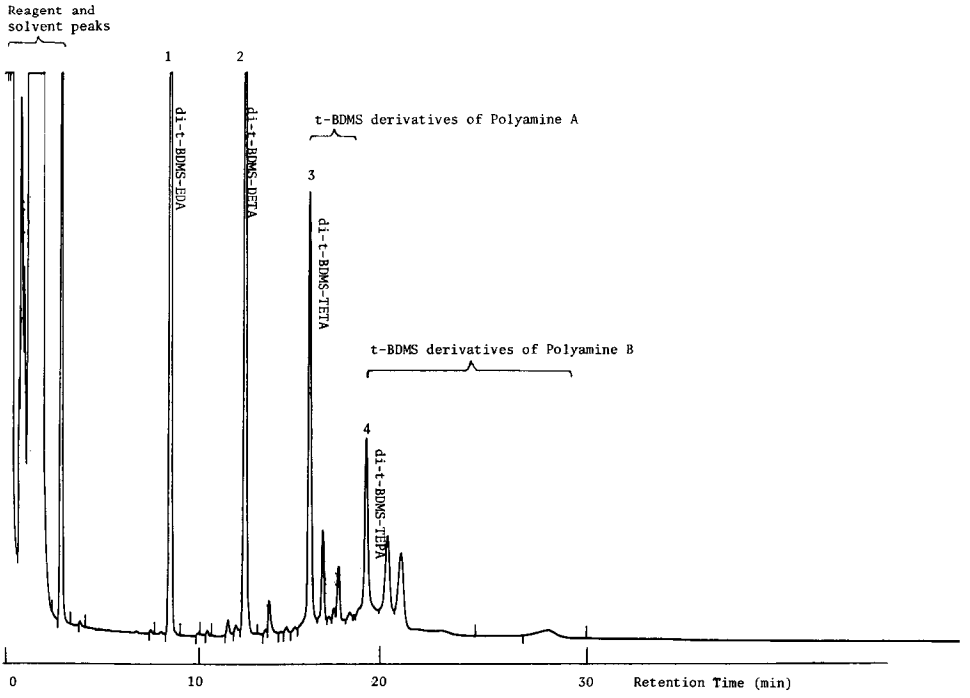



Fig. 2. GC chromatogram of *t*-BDMS derivatives of mixture A containing EDA, DETA, TETA and TEPA. 3% OV-7 on Chromosorb W HP, 80–100 mesh; column: nickel 4 ft. × 0.125 in. I.D.; program: 80°C for 2 min, increased at 10°C/min to 250°C; flow-rate of nitrogen (carrier gas) 35 ml/min.

## CONCLUSIONS

In conclusion, the *t*-BDMS derivative preparation of the ethylenediamines is simple and rapid, the *tert*-butyldimethylsilylation proceeds smoothly under mild reaction conditions and can be controlled to produce disilylated derivatives that are amenable to both GC and GC–MS analysis.

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