Gas Chromatographic–Mass Spectrometric Investigation of Aliphatic Glycols in Environmental Samples

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Abstract

A rapid, accurate method for the identification and quantitation of aliphatic glycols is described. The n-butylboronate esters of ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, and diethylene glycol are prepared by the interacton of these compounds and n-butylboronic acid. The compounds and their derivatives are analyzed using a gas chromatograph equipped with a mass spectrometric detector. The reliability of the method for routine analysis of diols in water samples is demonstrated. The method detection limits of these diols are determined. Mass fragmentation patterns of these derivatives are also reported.
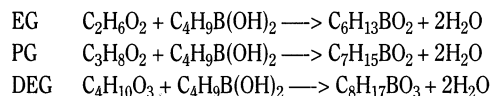
Introduction

Aliphatic diols such as ethylene glycol (EG), 1,2-propylene glycol (1,2-PG), 1,3-propylene glycol (1,3-PG), and diethylene glycol (DEG) are routinely used in antifreeze mixtures of air-craft de-icing and anti-icing fluids (1), automobile coolants, and the industrial manufacture of a variety of products (2,3). Glycols are also used as industrial feed products and in water removal systems in facilities such as gas plants. They are non-volatile, highly water-soluble, and chemically inert. These chemicals could persist and be mobile while in the environment. Therefore, they could contribute to oxygen depletion in aquatic ecosystems (4).

Gas chromatography (GC) and mass spectrometry (MS) provide the premier method for analysis of complex mixtures of compounds and provide quantitation data below the parts-per-million level. Most laboratory analysts determine glycols by direct injection of aqueous sample onto the GC column head and use a flame ionization detector (FID). This is prohib-ited for analytical data below the parts-per-million level due to an increase in baseline disturbances and in low signal responses after a few injections.

The approach to develop a sensitive method for aliphatic diols detection has been to prepare derivatives that are

amenable to GC and are detectable at the microgram level with MS. It has been shown (5) that the reaction of a particular reagent with a particular compound can significantly increase chromatographic peak resolution. The practical analytical application of n-butylboronate and phenylboronate esters for a series of diols, hydroxyacids, hydroxyamines (6,7), and amino alcohols (8) has been reported previously. In all cases, cyclic esters of n-butylboronates or phenylboronates were prepared by mixing the reagents in acetone and were analyzed by GC–MS or GC–FID.

In the present study, the diols in water solution were con-verted into the corresponding n-butyl boranate esters by reac-tion with n-butylboronic acid in chloroform according to the following reactions:

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\begin{aligned}
\text{EG} \quad & C_2H_6O_2 + C_4H_9B(OH)_2 \longrightarrow C_6H_{13}BO_2 + 2H_2O \\
\text{PG} \quad & C_3H_8O_2 + C_4H_9B(OH)_2 \longrightarrow C_7H_{15}BO_2 + 2H_2O \\
\text{DEG} \quad & C_4H_{10}O_3 + C_4H_9B(OH)_2 \longrightarrow C_8H_{17}BO_3 + 2H_2O
\end{aligned}
$$

This paper describes a fast, accurate method for the identi-fication and quantitation of ethylene, 1,2-propylene, 1,3-propylene, and diethylene glycols in environmental aqueous samples. Samples were derivatized with n-butylboronic acid solution and extracted with chloroform. They were separated on a GC column and measured using MS. Mass fragmentation patterns and method detection limits of these compounds are also presented.

Experimental

Chemicals

The compounds n-butylboronic acid (CAS #4426-47-5, 97% purity), ethylene glycol (CAS #107-21-1, +99% purity), 1,2-propylene glycol (CAS #57-55-6, 99% purity), 1,3-propylene glycol (CAS #504-63-2, 98% purity), and diethylene glycol (CAS #111-46-6, 98% purity) were obtained from Aldrich Chemical (Milwaukee, WI). All other chemicals were obtained from Caledon Laboratory Chemicals (Georgetown, ON, Canada).

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Calibration standard preparation

The diol standards were prepared by dissolving amounts of approximately 125 mg in 25 mL of deionized water in a volumetric flask. A 0.2-mL aliquot of this solution was then diluted to 100 mL with deionized water to make the diols concentration approximately 10 μg/mL.

The standard solution of n-butylboronic acid was prepared by accurately weighing 200 mg of it and dissolving it in 100 mL of chloroform to provide a concentration of 2 mg/mL.

Derivative preparation

A 2-mL aliquot of diols water solution (approximately 10 μg/mL) was transferred into a 10-mL culture tube fitted with a teflon-lined screw cap followed by the addition of 0.2 mL of the above n-butylboronic acid solution. The contents of the culture tube were shaken for 5 min and then allowed to stand for 15 min with occasional agitation at room temperature. The water mixture was extracted with three 2-mL aliquots of chloroform. The chloroform layer containing diol esters was then transferred into another culture tube. The chloroform extract was finally concentrated to 2 mL under a gentle purge stream of dry nitrogen. The final extract was dried by adding 1 g of pretreated anhydrous sodium sulfate. The concentration of diol esters in chloroform was approximately 10 μg/mL. This stock standard solution was used for calibration. The solution was further diluted with chloroform to provide the desired concentrations.

A spike composite test sample of diols was prepared separately in a manner similar to that mentioned above at a concentration of approximately 3 μg/mL for the determination of diol method detection limits (MDLs). The diethylene glycol

standard solutions were also prepared separately in a similar manner at a concentration of 10 μg/mL by adding different amounts of n-butylboronic acid reagent to make a n-butylboronate ester of diethylene glycol. The mixture of diethylene glycol and n-butylboronic acid in each case was shaken for 10 min and allowed to stand for at least an hour at room temperature to complete the reaction. The water mixture was extracted with chloroform as before. The detailed results are reported below.

Case study

In winter, when glycols are used as de-icing fluids, water samples were collected near the aircrafts by Transport Canada at Sudbury in a 40-mL vial and sent to our laboratory for the identification and quantitaion of three glycols. A 10-mL water sample was derivatized and extracted with chloroform in a manner similar to that given above. A 1-μL aliquot extract was analyzed using the selected ion monitoring (SIM) mode. The results are reported.

GC–MS system

Analyses were performed using both an HP 5890 series II GC coupled to an HP 5972A quadrupole MS (Hewlett-Packard, Palo Alto, CA) and a Varian Saturn I ion trap MS connected to a Varian 3400 GC (Varian, Walnut Creek, CA) system. The mass calibrations were performed according to the manufacturer recomendation before sample analysis. The capillary column was a J&W DB-1 (J&W Scientific, Folsom, CA) (30 m × 0.25-mm i.d., 1-μm film thickness). Helium was used as the carrier gas with a flow velocity of 40.7 cm/s and measured at 80°C.
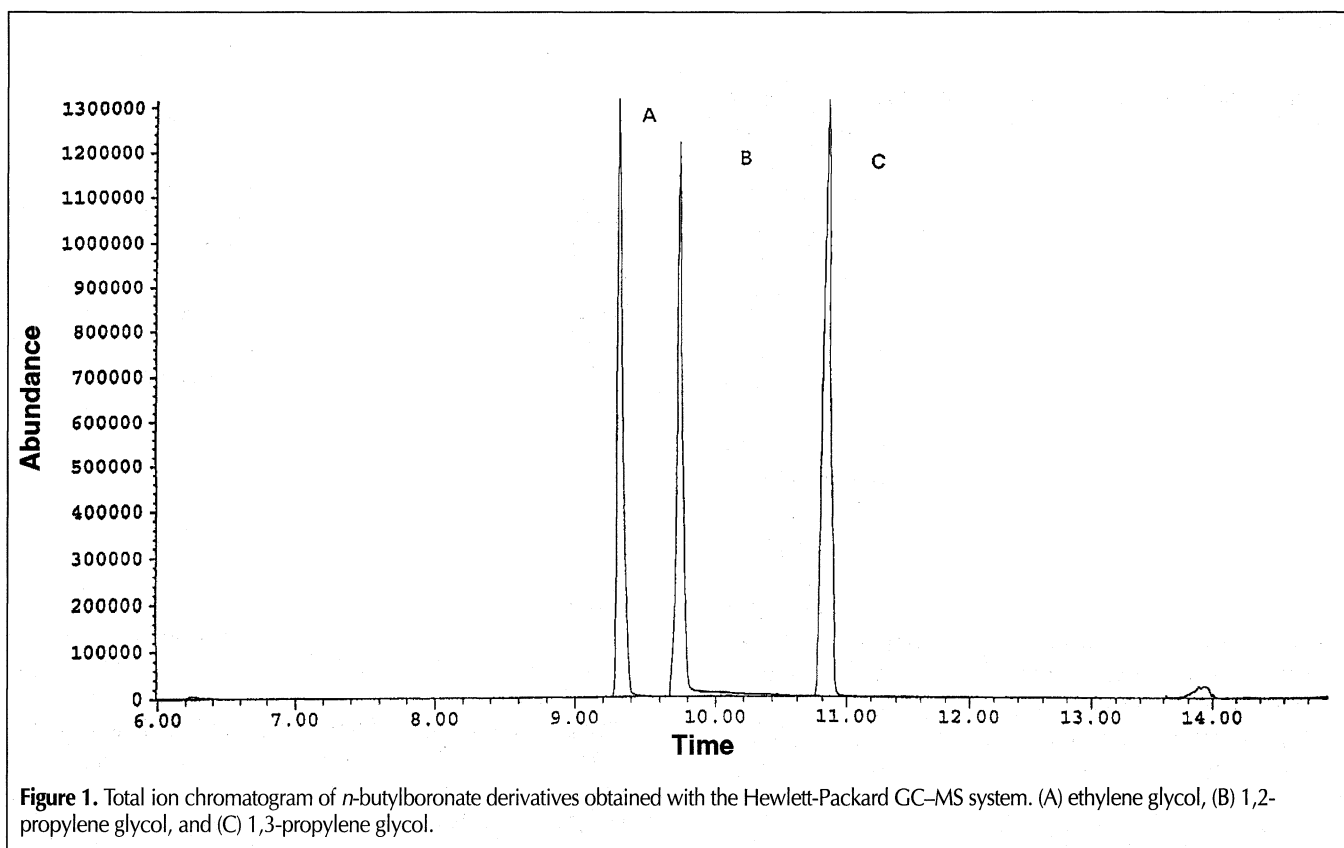

Figure 1. Total ion chromatogram of n-butylboronate derivatives obtained with the Hewlett-Packard GC–MS system. (A) ethylene glycol, (B) 1,2-propylene glycol, and (C) 1,3-propylene glycol.

The initial oven temperature was 80°C for 2 min followed by a temperature-programmed increase of 8°C/min to 180°C, then another increase of 15°C/min to 280°C. The splitless mode was used for sample injection of a 1-μL volume at an initial temperature of 80°C. All diol esters were eluted before the column temperature reached 160°C. The second programed temperature increase was used to remove unwanted com-

pounds from the column. The samples were analyzed using both full scan and SIM modes. In SIM mode, four characteristic ions were used for each glycol ester. Only the full scan mode was used for sample analysis with the Varian Saturn ion trap GC–MS system.

Results and Discussion

Mass spectral fragmentation
EG, 1,2-PG, and 1,3-PG

Before reaction with a reagent, the electron ionization spectra of EG, 1,2-PG, and 1,3-PG are very similar to those of hydrocarbons, alcohols, or amines. This presents difficulty in identifying the presence of these analytes in environmental samples. However, after the use of n-butylboronic acid as a reagent, clean GC–MS spectra of EG, 1,2-PG, and 1,3-PG derivatives were obtained. Figure 1 shows the total ion chromatogram (TIC) of n-butylboronate esters of EG, 1,2-PG and, 1,3-PG. They were well-separated with the GC column. Figures 2A–2C show the electron ionizaton mass spectra of n-butylboronate esters of EG, 1,2-PG, and 1,3-PG, respectively. The mass spectrum represents characteristic features of each glycol. The identification of molecular ions and other ions containing boron was facilitated by the characteristic isotope ratio of boron ($^{10}B^+$:$^{11}B^+$ = 1:4). The molecular ions for EG (m/z = 128, $[C_6H_{13}BO_2]^+$), 1,2-PG, and 1,3-PG (m/z = 142, $[C_7H_{15}BO_2]^+$) were observed. Their abundances were low and amounted to only 2–5%. The characteristic ions for EG were m/z = 86 ($[C_3H_7BO_2]^+$), m/z = 99 ($[C_4H_8BO_2]^+$ or $[C_5H_{12}BO]^+$), and m/z = 113 ($[C_5H_{10}BO_2]^+$), which were formed by the loss of C_3H_6 (M-42), C_2H_5 (or HCO) (M-29), and CH_3 (M-15), respectively. In the case of 1,2-PG, the characteristic ions were m/z = 100 ($[C_4H_9BO_2]^+$), m/z = 113 ($[C_5H_{10}BO_2]^+$ or $[C_6H_{14}BO]^+$), and m/z = 127 ($[C_6H_{12}BO_2]^+$). They were formed by the loss of C_3H_6 (M-42), C_2H_5 (or HCO) (M-29), and CH_3 (M-15), respectively. It is interesting to note that the observed characteristic ions for the 1,3-PG isomer were m/z = 113, 100, and 85 ($[C_3H_6BO_2]^+$). The m/z = 85 ion was formed by the loss of butyl radical C_4H_9. The m/z = 85 ion in the 1,2-PG isomer was also observed, but its abundance was very low. The m/z = 127 ion, which was the second largest ion in 1,2-PG, was only 7% abundant in 1,3-PG. The other fragment ions in the mass spectra were m/z = 41 ($[C_3H_5]^+$), m/z = 45 ($[C_2H_5O]^+$), and m/z = 55 ($[C_4H_7]^+$), etc. and were formed by stepwise degradation of the butyl side-chain.
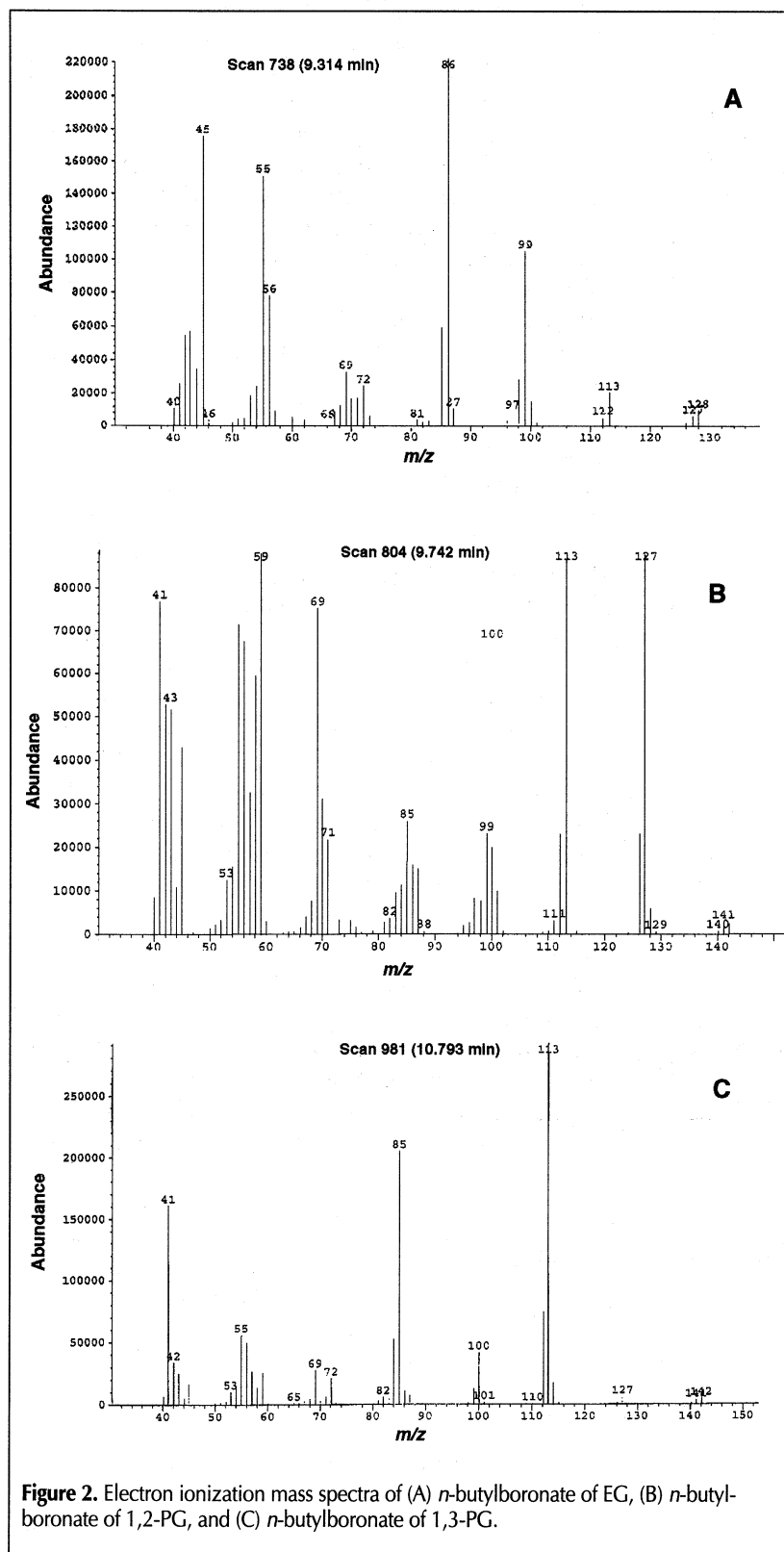
Figure 2. Electron ionization mass spectra of (A) n-butylboronate of EG, (B) n-butylboronate of 1,2-PG, and (C) n-butylboronate of 1,3-PG.
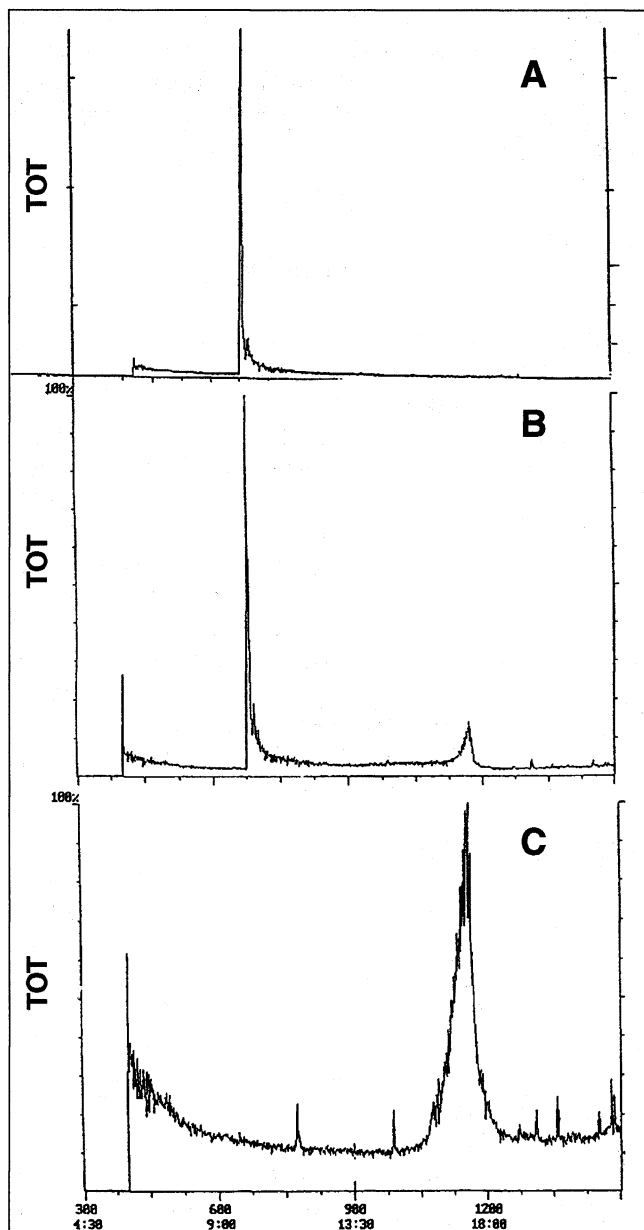
Figure 3. Total ion chromatogram of DEG and its n-butylboronate derivatives obtained with the Varian Saturn GC–MS system. (A) EG (underivatized), (B) mixture of DEG and DEG n-butylboronate, and (C) DEG n-butylboronate.

DEG

The TIC for the n-butylboronate ester of DEG was obtained using full scan mode of the Varian Saturn GC–MS system. Figure 3 shows the TIC of DEG and its derivatives. In the figure, it can be seen that the conversion of DEG to its butyl-boronate derivative was slow and needed twice the amount of reagent that EG, 1,2-PG, or 1,3-PG did to complete the reaction. The broad peak of the DEG derivative was due to coelution with the anhydrous n-butylboronic acid peak. The electron ionization mass spectrum of the DEG derivative is shown in Figure 4. The abundance of the molecular ion m/z = 172 ($[C_8H_{17}BO_3]^+$) was high, about 15% in comparison with EG or 1,2-PG and its isomer. The dominant characteristic ion in the mass spectra was m/z = 115 ($[C_4H_8BO_3]^+$) and was formed by the loss of butyl radical C_4H_9. The other fragment ions were m/z = 129 ($[C_5H_{10}BO_3]^+$) and m/z = 159 ($[C_7H_{16}BO_3]^+$) and were formed by the loss of C_3H_7 (M-43) and CH (M-13), respectively. The identity of each ion was confirmed by virtue of the characteristic isotope ratio distribution of boron.

Quantitative analysis

A four-level calibration curve at concentrations of approximately 0.50, 1.0, 2.5, and 5.0 µg/mL were prepared by diluting the above stock standard, approximately 10 µg/mL. The calibration standards were analyzed using SIM mode. For this purpose, four characteristic ions were chosen for each glycol ester. The linear response range for each glycol ester was established by plotting the peak area of the base ion (i.e., the largest peak in the spectrum) against the amount of analyte injected on the GC column. The correlation coefficients obtained were 0.989, 0.994, and 0.999 for EG, 1,2-PG, and 1,3-PG respectively, and 0.977 for DEG. These calibration curves were used in the calculation of method detection limits of glycols, and the results were used for a case study.

MDLs

The MDL for each glycol was calculated by analyzing eight 1-µL aliquots of spike composite test sample containing a concentration of glycols approximately equal to 3.0 µg/mL. The concentration of each glycol ester was then determined using above four-level calibration curves. The MDLs were calculated using the students' t-value appropriate for a 99% confidence level and a standard deviation estimated with a degree of freedom one less than the number of replicates (9). Mean measured concentration observed ranged from 95 to 102% of the true value. The MDL values and the actual concentration of each glycol used are given in Table I.

Case study from environmental sample

This proposed method was applied in our laboratory for the determination of glycols in environmental aqueous samples submitted by

Table I. Method Detection Limits of Glycols

Compound	Spike amount (ug/mL)	Mean* (ug/mL)	Standard deviation	MDL (ug/mL)	RSD[†] (%)	Replicates
Ethylene glycol	1.83	1.86	0.01	0.03	0.54	8
1,2-propylene glycol	2.51	2.44	0.02	0.06	0.82	8
1,3-Propylene glycol	2.52	2.56	0.01	0.03	0.39	8
Diethylene glycol	2.94	2.82	0.08	0.24	2.84	8

* Mean measured concentration of eight replicate analyses.

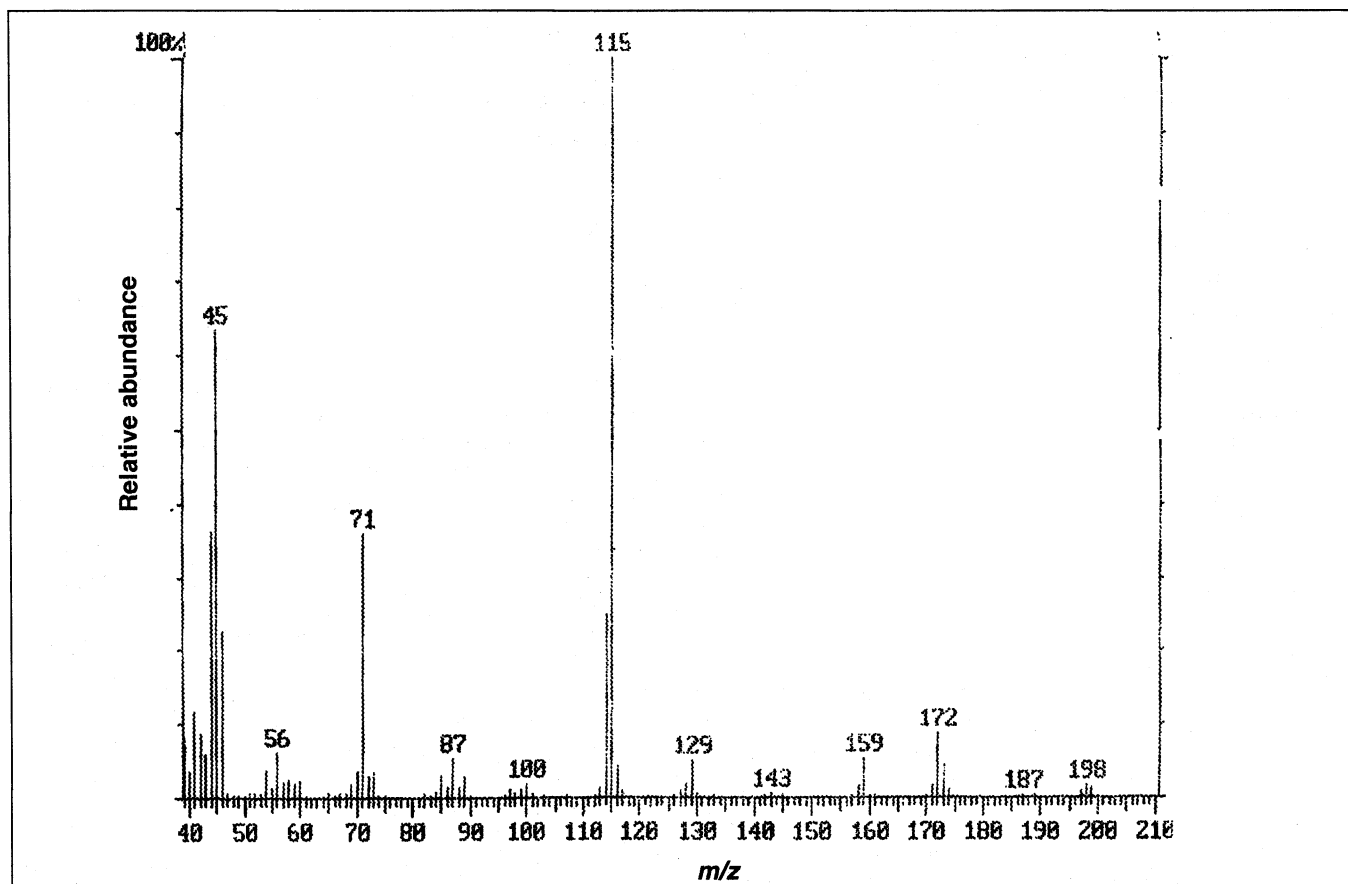† Relative standard deviation = $\dfrac{\text{Standard deviation} \times 100}{\text{Mean values}}$

Figure 4. Electron ionization mass spectra of *n*-butylboronate of diethylene glycol.
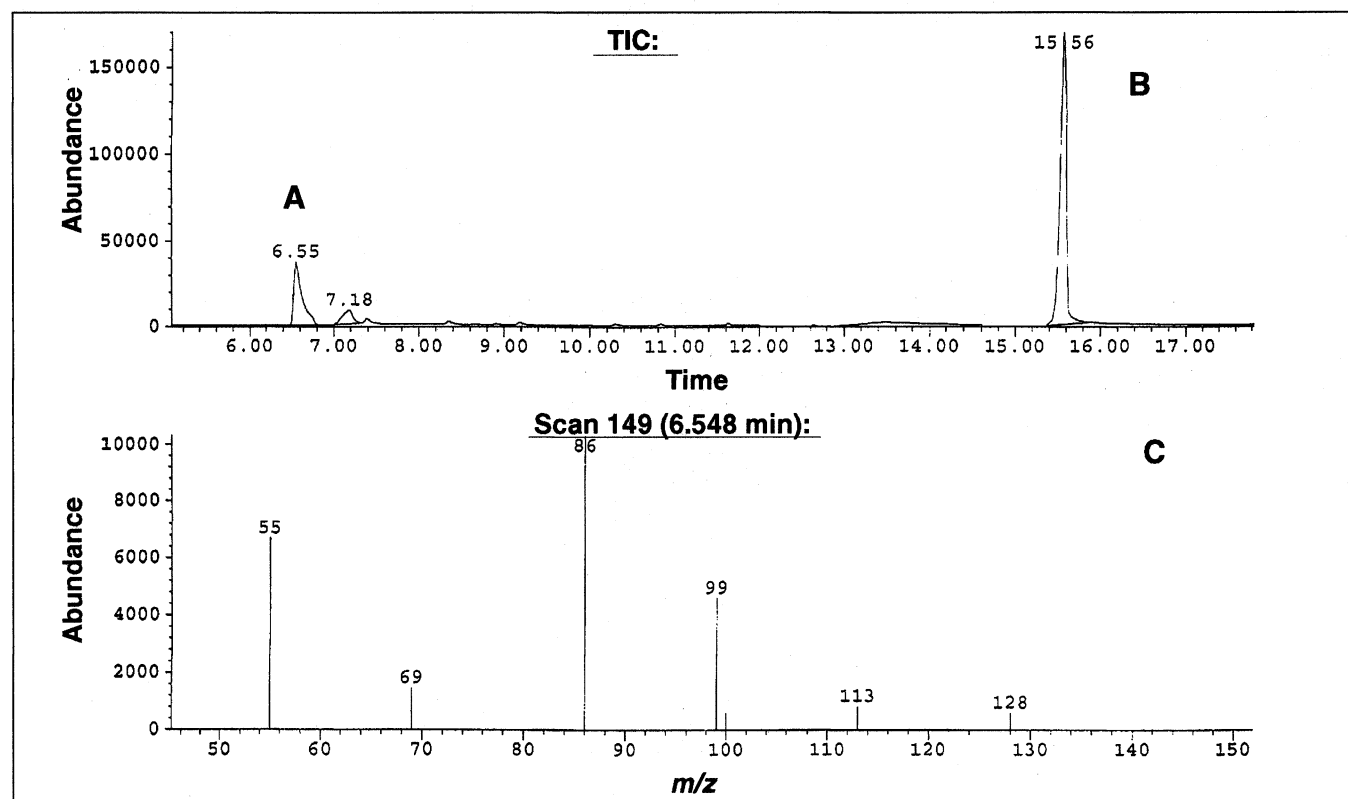

Figure 5. Total ion chromatogram of *n*-butylboronate derivatives. (A) Ethylene glycol, (B) *n*-butylboronic acid, and (C) electron ionization mass spectra of *n*-butylboronate ester of ethylene glycol.

Transport Canada. The samples were prepared in a similar manner as described previously. The samples were analyzed using the SIM mode. Figure 5 shows the TIC of *n*-butylboronate esters of glycols and the electron ionization mass spectrum of the *n*-butylboronate ester of EG because this sample contained only EG. No other glycols were detected. It should be noted that excess *n*-butylboronic acid, if present, would not interfere in the analysis of EG, 1,2-PG, or 1,3-PG. The concentration of EG in the sample was determined to be 23.8 µg/mL using the above calibration curve. A value of 49 µg/mL was determined using conventional direct aqueous sample injection into the GC–FID system. This value is about 50% higher due to interference with hydrocarbons and other compounds that were present in the aqueous sample.

Conclusion

The characteristic mass of ^{10}B and ^{11}B together with the single GC–MS peak observed in the chromatogram indicated that all these glycols were eluted from the GC column without undergoing any degradation in the column. The mass spectra of glycols show characteristic features for each glycol. The isomers of 1,2-PG and 1,3-PG were well-resolved with different mass spectra. A molecular ion was observed in all diol esters with varying relative abundances from 2 to 15%. The calculated MDLs ranged from 0.03 to 0.24 µg/mL in reagent water. The characteristic ions for each glycol can be used for SIM in GC–MS to determine their presence in complex environmental samples. The proposed analysis method for glycols makes it potentially useful for the sample of complex matrices, especially in the presence of petroleum products, amines, and alcohols, etc.

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