

The Comparison of Derivatization Methods for the Determination of Ethylene Glycol in Lubricant Oil Sample by GC/MS

Joon-Bae Lee,^{†,‡} O-Seong Kwon,[†] Jae-Hoon You,[†] Shungkun Shon,[†] Ki-Jung Paeng,^{‡,*} and Tae-Myung Sung[§]

[†]Eastern District Office, National Forensic Service, Wonju 220-805, Korea

[‡]Department of Chemistry, Yonsei University, Wonju 220-710, Korea. *E-mail: kpaeng@yonsei.ac.kr

[§]Department of Chemistry, Criminal Investigation Command, Seoul 140-701, Korea

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Ethylene glycol (CH₂OHCH₂OH, EG) is commonly available as the main constituent of many antifreeze and coolant mixtures. EG is odorless and syrupy toxic polyhydroxy alcohol with sweet taste.¹

The EG is also a common contaminant in used lubricant oils from gasoline and diesel engines and knowledge of its concentration can yield important clues concerning engine performance and thus give early warning of impending engine trouble.²

The quantitative determination of EG in used lubricant oil that is most often performed is the ASTM Method D 2982 which is a colorimetric method using Schiff's reagent.³ However a reaction could occur with an oxidized product during the combustion as well as with the inherent aldehydes in the oil itself and for those reasons this method has considerable drawbacks.⁴

Recently, vibrational spectroscopic methods have also been employed for the determination of EG in lubricant samples, but those methods usually require expert personnel.^{5,6}

To minimizing interferences from additives, combustion products and other denatured substances, a number of gas chromatographic (GC) methods, including specific extraction and derivatization, have been developed for the determination of EG in complex matrices, such as biological fluids and used engine oil.^{2,7-13}

In order to enhance the analytical performance of the GC method, an appropriate selection of derivatization process is essential. However, most reported derivatization process of EG rely on trimethylsilylation (TMS) derivatization, which exhibited the weakness at the humidic environment.

The aim of this report is to develop a derivatization methods for the determination of EG in lubricant oil with GC/MS. Specifically, we examined the several derivatization procedures for the converting the EG to the applicable substances to GC. For this end, EG was derivatized with bistrimethylsilyltrifluoroacetamide (BSTFA), 1-butylboronic acid and cyclohexanone, and then compared with each other's results.

We presented the optimized analytical procedure for EG in lube oil samples with GC/MS including extraction and derivatization. For the analysis of alcohols by GC/MS, BSTFA is the widely used reagent for TMS derivatization.¹⁴ But we

tested 1-butylboronic acid and cyclohexanone for boration and ketalization with EG in lubricating oil respectively and compared with the BSTFA. Although BSTFA is a very powerful derivatizing agent for alcohols, it has critical weakness in moisture. This is important as in the wasted lube oil a number of degraded chemicals are present, including water. However, cyclohexanone and 1-butylboronic acid could be applied for the reaction with glycols regardless of some moisture. Also, 1-butylboronic acid was used for the analysis of EG in blood.¹⁵

In Figure 1, the procedure for the analysis of EG in the lubricating oil is described, and especially, for the complete trimethylsilylation and ketalization, the reaction was done under 80 °C for 30 min in the oven but for the boration the mixture was left for 10 min at the room temperature. The GC/MS condition was shown in Table 1.

For the extraction of EG from the oil, acetonitrile (ACN) was adopted as an extraction solvent, because it is not only polar to be miscible with EG but also aprotic not to cause column bleeding at GC column. Calibration curves were prepared for the standard lubricant oil samples containing EG of which concentration range was 10 µg/g ~ 2 × 10⁴ µg/

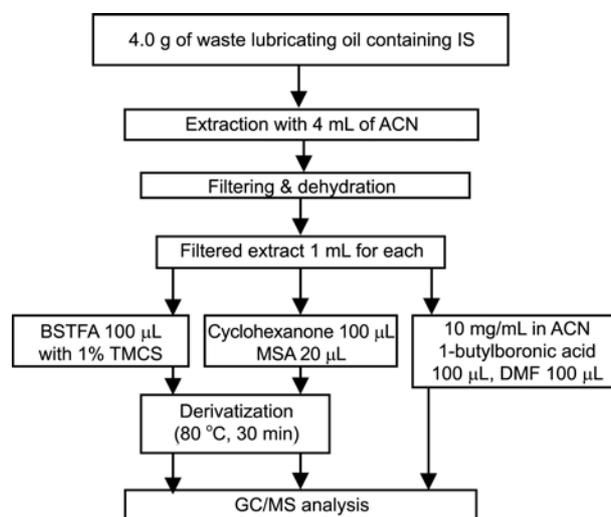


Figure 1. Pretreatment procedure for determination of EG from lubricating oil by GC/MS.

Table 1. GC/MS condition

GC/MS	Condition
Injector temp.	250 °C
Transfer line temp.	270 °C
Carrier gas	He 1 mL
Oven temp.	60 °C (3 min) → (10 °C/min) → 280 °C (5 min)
Column	DB-5MS (30 m × 0.25 mm i.d. × 0.25 μm film thickness)
Ion source temp.	230 °C

g with internal standard (deuterium substituted ethylene glycol (d_4 -EG)) added to be 1,000 μg/g.

The cleaned extract supernatant was divided into 3 aliquots to be 1 mL, and then each cleaned sample was derivatized as followed. In trimethylsilylation and ketalization, 100 μL of BSTFA with 1% trimethylchlorosilane (TMCS) and 100 μL of cyclohexanone with 20 μL of methanesulfonic acid (MSA) were added respectively. And, for the boration, 100 μL of 1% 1-butylboronic acid solution in ACN and 100 μL of dimethylformamide (DMF) were used. After the reaction, 1 μL of each derivatized sample was injected into GC/MS at the GC/MS condition of Table 1 with the solvent delay of 5.3 min for the trimethylsilylated and ketalized sample and 4.0 min for the borated sample to avoid the influence of the solvent and derivatizing reagents.

Figures 2, 3 and 4 depicted the comparisons of mass

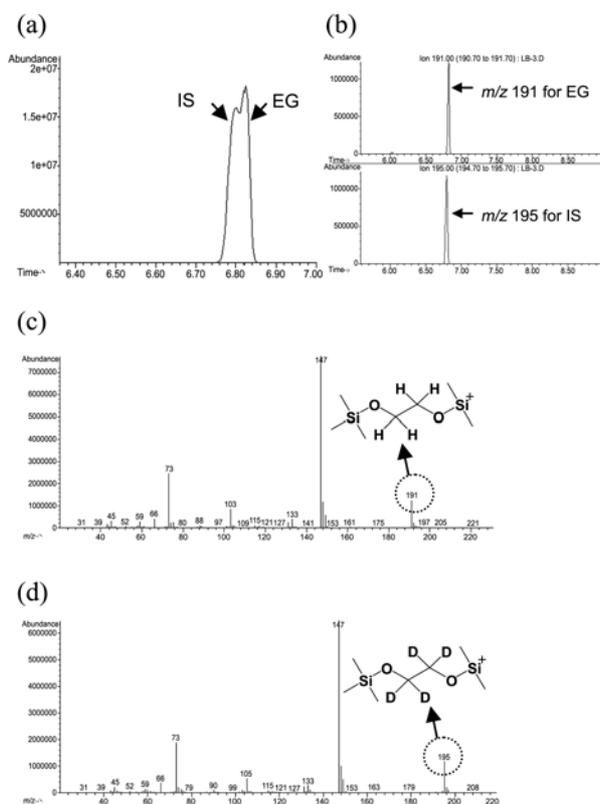


Figure 2. (a) GC/MS chromatogram for trimethylsilylated EG and IS (d_4 -EG) (b) selected ion GC/MS chromatogram for m/z 191 and 195, and mass spectrum for (c) EG-di(TMS), (d) d_4 -EG-di(TMS) and its base peak ion.

spectra for the derivatization reactions. At the figures, the characteristic ions of m/z 86 and m/z 99 are the base ions for 2-butyl-1,3,2-dioxaborolane and 1,4-dioxaspiro[4,5]decane, and it is more apparent than that of m/z 191, trimethylsilylated product of EG. Among the cycloalkanone of C4-C7 applied as a derivatization reagent in this experiment, cyclohexanone showed the best result in the view of sensitivity.

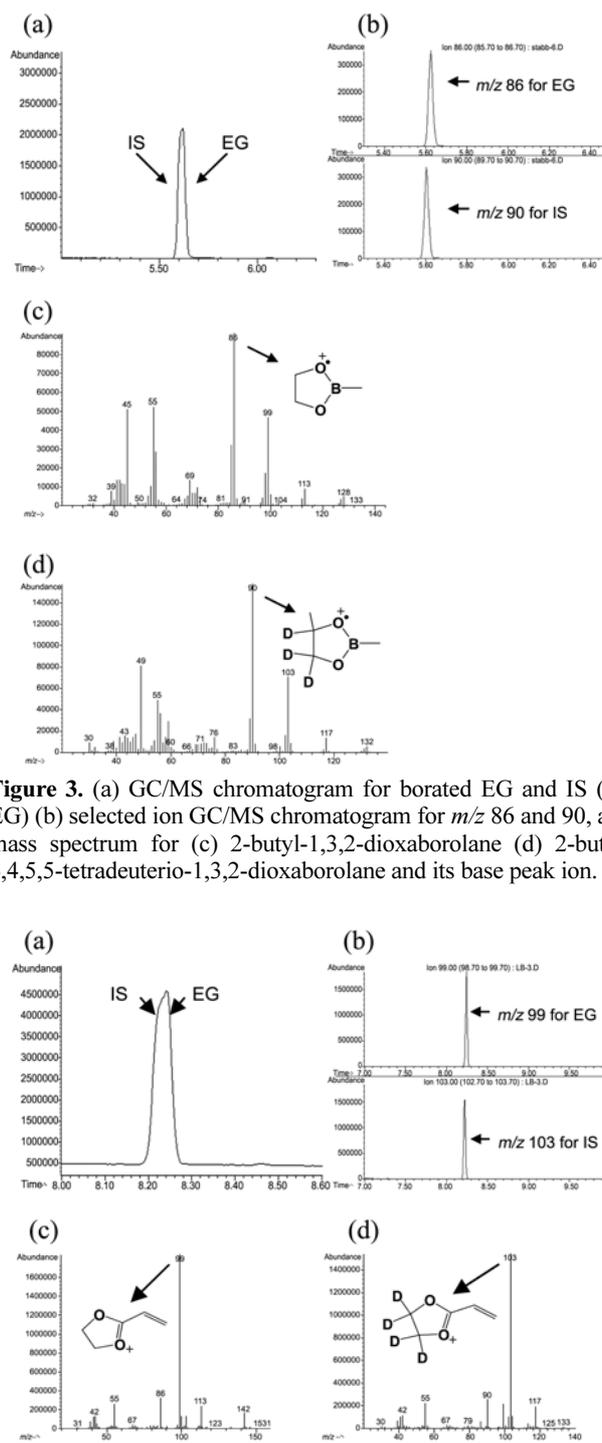


Figure 3. (a) GC/MS chromatogram for borated EG and IS (d_4 -EG) (b) selected ion GC/MS chromatogram for m/z 86 and 90, and mass spectrum for (c) 2-butyl-1,3,2-dioxaborolane (d) 2-butyl-4,4,5,5-tetradeuterio-1,3,2-dioxaborolane and its base peak ion.

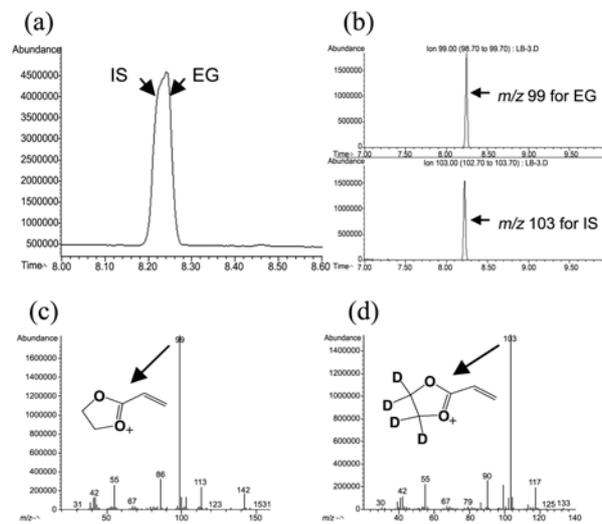
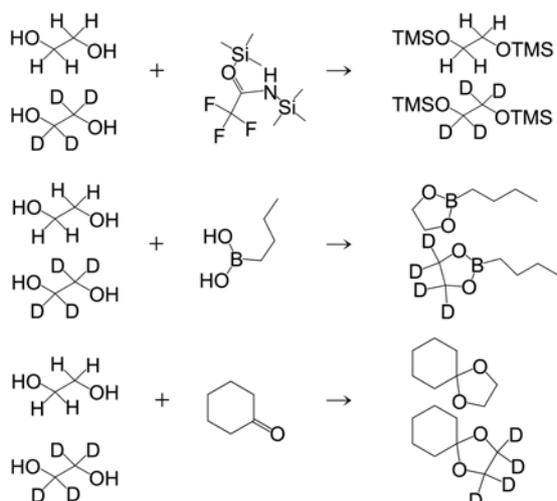


Figure 4. (a) GC/MS chromatogram for ketalized EG and IS (d_4 -EG) (b) selected ion GC/MS chromatogram for m/z 99 and 103, and mass spectrum for (c) 1,4-dioxaspiro[4,5]decane, (d) 2,2,3,3-tetradeuterio-1,4-dioxaspiro[4,5]decane and its base peak ion.



Scheme 1. Reaction of EG and IS with BSTFA, 1-butylboronic acid and cyclohexanone.

C4 and C5 cycloalkanone did not show a proper reactivity as a derivatization reagent. This can be attributed to the decrease in the *p*-character at the C=O bond due to ring strain. Cycloheptanone also shows similar result with cyclohexanone, but we only apply cyclohexanone as derivatization reagent.

The proposed derivatization reactions of EG with BSTFA, 1-butylboronic acid and cyclohexanone are shown at the Scheme 1. Also the aforementioned proposed structures of base peaks are well agreed with reaction schemes (Figs. 2, 3 and 4).

The calibration curve for EG in the ACN extract of standard lubricating oil samples is shown in Figure 5. For the reaction with BSTFA, the ratio of the area for *m/z* 191 in EG-di (TMS) at 6.82 min against that for *m/z* 195 in the *d*₄-EG-di (TMS) at 6.80 min in the derivatized extract of standard oil samples was plotted against the concentration for EG.

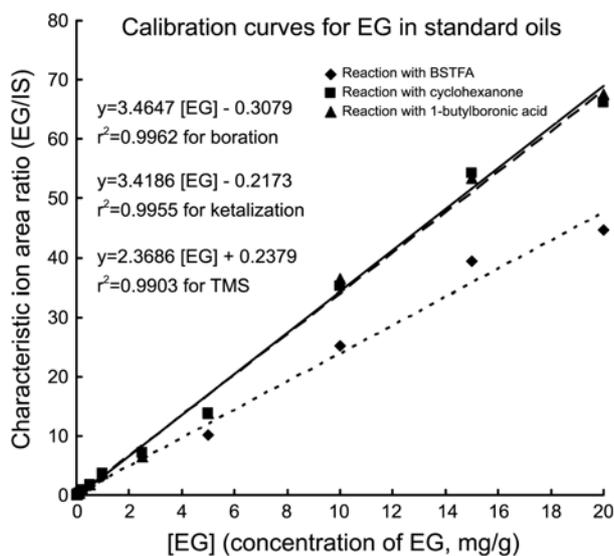


Figure 5. Calibration curves for EG in the ACN extract of standard lubricating oil samples with the reaction of BSTFA (◆), 1-butylboronic acid (▲) and cyclohexanone (■).

Likewise, for 1-butylboronic acid, *m/z* 86 in 2-butyl-1,3,2-dioxaborolane from EG at 5.62 min against that for *m/z* 90 in 2-butyl-4,4,5,5-tetradeuterio-1,3,2-dioxaborolane from IS at 5.60 min and for cyclohexanone, *m/z* 99 in 1,4-dioxaspiro[4,5]decane from EG at 8.26 min against that for *m/z* 103 in *d*₄-1,4-dioxaspiro[4,5]decane from IS at 8.24 min in the derivatized extract of standards were plotted against the concentration for EG.

The calibration curve for EG with BSTFA, 1-butylboronic acid and cyclohexanone exhibits a 0.9903, 0.9962 and 0.9955 of *r*² value and the calibration shows good linearity (Fig. 6). In Figure 6, both 1-butylboronic acid and cyclohexanone show similar behavior in calibration and the deviation from the linearity is cognate trend for all 3 kinds of derivatization sample, which means that the deviation is due to the sample preparation and extraction process.

The detection limit is defined as three times the standard deviation of signal to noise (S/N) ratio from the acetonitrile extract. The detection limit of TMS derivatization was estimated as 0.5 μg/g, and that for both boration with 1-butylboronic acid and the ketalization with cyclohexanone was to be 0.1 μg/g (Fig. 6).

It was huge improvement from previously reported results. It would be due to better ionization efficiency of 2-butyl-1,3,2-dioxaborolane and 1,4-dioxaspiro[4,5]decane because of stable structure of *m/z* 86 and *m/z* 99 ion at Figure 4(c) and 5(c). Determination results of EG in lube oil samples with both derivatization methods were exhibited the good reproducibilities as a less than 5% of RSD (relative standard deviation). Especially, the ketalized 1,4-dioxaspiro[4,5]decane is so stable that it is commercially traded, and also 1,3,2-dioxaborolane structure has been widely used for the organic reaction.

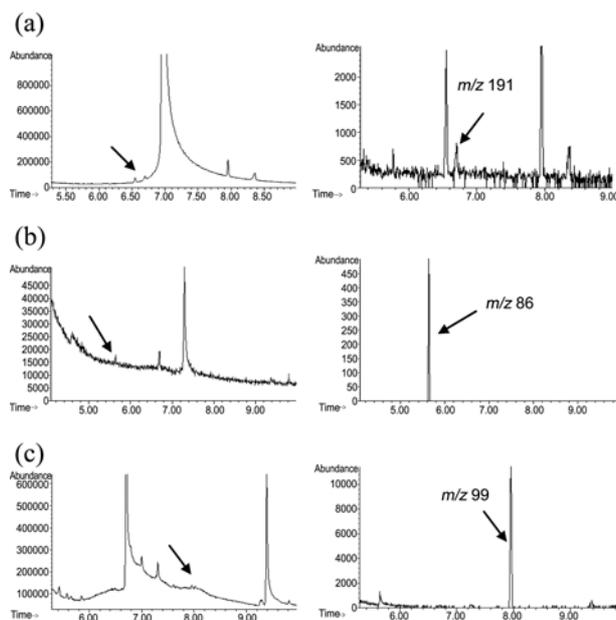


Figure 6. GC/MS chromatogram for (a) 0.5 μg/g EG with BSTFA (b) 0.1 μg/g EG with 1-butylboronic acid and (c) 0.1 μg/g EG with cyclohexanone.

In addition, the moisture removal of the TMS reaction is very important for enhancement of derivatization reaction yield because of moisture sensitivity of trimethylsilylation agent. In the derivatization, BSTFA was found to prefer moisture to EG which leads to bistrimethylsilyloxy and other white sediment. But the reaction with 1-butylboronic acid and cyclohexanone did not show significant affect by moisture in the sample.

In summary, we presented the analytical results with optimized analytical procedure for EG in lube oil samples with proposed derivatization methods and GC/MS. We can conclude that the developed derivatization methods exhibited the good results due to its validation data.

Experimental

All reagents used were of analytical grade quality or higher. Deuterium substituted ethylene glycol (d_4 -EG), internal standard (IS), ethylene glycol (EG), derivatizing agent of bistrimethylsilyltrifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) and cyclohexanone were purchased from Aldrich. Diethyl ether and acetonitrile were from Burdick & Jackson. Sodium sulfate (Na_2SO_4) was from Shinyo Pure Chemicals. Reference lubricant oil was diesel engine oil SD5000 GOLD from SK Lubricants.

The analysis was performed with 6890N GC and 5973 MSD system of Agilent Technologies with Gerstel MPS2 autosampler.

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