On-fiber Derivatization for Determination of Ethylene Glycol Concentration in Lubricant oil By SPME-GC/MS

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Lubrication of the moving parts in machinery is required for their proper function, because it reduces friction and aids in cooling, while cleaning and sealing the mechanical contacts. In particular, internal combustion engines cannot be operated properly without lubricant oil, because the thermal load is too high. However, lubricant oil is deteriorated by high temperature, combustion products, and extraneous impurities. Oil can also be contaminated by ethylene glycol (EG) leaking from the cooling systems of the equipments. Ethylene glycol (CH_2OHCH_2OH, EG) is the main component of coolant used in internal combustion engines. In many cases, coolant from the cooling system could leak into the lubricating system, particularly in machinery under harsh and overloaded conditions. Contamination of oil with EG reduces its tribological properties, which lead to engine cylinder fusion. Thus, the periodic examination of lubricant oil is necessary to prevent this phenomenon. To this end, ASTM Method D 2982 is a commonly used local test method to inspect oil.[1] However, this method applies colorimetric measurement using a Schiff's reagent, which may lead to inexact determination of the state of the oil. Incorrect results may be generated because the color developing reaction may occur for inherent aldehydes in the oil as well as oxidized combustion products.[2,3]

Therefore, methods using gas chromatography (GC)[4] or gas chromatography/mass spectrometry (GC/MS) are recommended to overcome this flaw. However, GC/MS analysis requires a cumbersome pretreatment step including solvent extraction from the complex matrix of contaminated lubricant oil. For enhanced GC performance, an extra-pretreatment process in addition to extraction, purification, and concentration is often required. The highly polar target compounds must be converted into less polar, more volatile, and stable compounds to increase their analytical performance, which is accomplished by derivatization. Trimethysilylation (TMS) is generally used for alcohol samples to protect hydroxyl group (−OH) by converting to the trimethylsilyloxy ($-OSi(CH_3)_3$) group.[5] In this study, we employed the ketalization of EG with cyclohexanone (CH-one) for polluted lubricant oil, because it is less vulnerable to ambient moisture than that of trimethylsilylation. The ketalization or acetalization reaction is usually used in organic synthesis for protecting the aldehyde and ketone carbonyl groups, because dioxolane is stable against chemically active reagents.[6,7]

We adopted CH-one among the C4–C7 cycloalkanone reagents, following our previous report.8 EG reacts with CH-one to form a spiro-dioxolane, 1,4-dioxaspiro [4.5]decane (CAS no.: 177-10-6; MW, 142 g/mol). The dioxolane is so stable that it is traded commercially for use in intermediate organic synthesis. The intensity of the base ion in the product is higher than that of the base ion in trimethylsilylized EG.

The EG and internal standard (IS) derivatization reaction scheme with CH-one is described in Figure 1.

The mass spectra of the derivatized products are described in Figure 2(a) and (b). The base ions for each case were the m/z 99 and 103 ions.

Moreover, combining derivatization and extraction using solid-phase microextraction (SPME) makes it possible to conduct the pretreatment process with easier and faster way. In addition, this method needs no solvent, so it is an environment friendly analysis.

SPME fiber is composed of silica rods coated with adsorbent. It looks like the syringe needle, so it can be easily injected into a GC. The SPME principle is the extraction on the fiber as the respective partition ratio between the fiber polymers and the target compound in the sample. Polymers on commercial SPME fibers are polydimethylsiloxane (PDMS), polyacrylate (PA), and copolymers of divinylbenzene (DVB), polyethylene glycol (PEG), or carboxen (CAR).[9–11] These compounds have different polarities, which is distinguished by the hub color in SPME fibers, as shown in Table 1.

The extraction by SPME and derivatization has been widely applied to complex matrix samples as urine, algae, and wine.[12–14]

The mass spectra for EG and CH-one are obtained. The average area response of each fiber for the EG (*m*/*z* 31), CH-one (*m*/*z* 55), and derivatized EG (*m*/*z* 99) base ions is shown in Figure 3. Based on these results, we adopted CAR/PDMS fiber to measure EG in the lubricant oil.

The area response of EG was smaller in all fibers compared to that of CH-one and spiro-dioxolane. This was probably due to the ionic stability of EG in the MS and its extraction ability on SPME fiber. CAR/PDMS fiber showed the best performance for spiro-dioxolane and ketalized EG among the five kinds of fibers, which may have been due to the excellent adsorption properties of carboxen with various pore sizes.

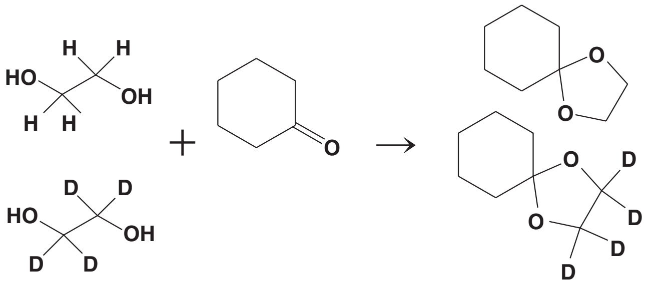

Figure 1. Reaction scheme of EG and the IS with CH-one.

This result could be compared to the calculated area response value of EG and CH-one by multiplying the area response of *m*/*z* 31 for EG and are a response of *m*/*z* 55 for CH-one and the calculated results are shown in Figure 4.

The spiro-dioxolane area response measured by GC/MS was similar to that of the multiplied area response of *m*/*z* 31 for EG and *m*/*z* 55 for CH-one in its tendency to be absorbed through the SPME fibers.

Therefore, the adsorption abilities of the analyte and the derivatizing reagent on the fiber should be similar in capacity to obtain the best performance when combining adsorption and derivatization on SPME fibers using GC/MS analysis.

The area response for the *m*/*z* 99 and 103 ions is depicted in Figure 5 for the standard oil sample containing 0.01–20 mg/g of EG. The IS concentration added was the same for all samples.

As the concentration of EG increased, the area response for the derivatized IS showed a decreasing trend in contrast to that for derivatized EG. This was probably due to mass detector saturation and competition of EG and IS for the

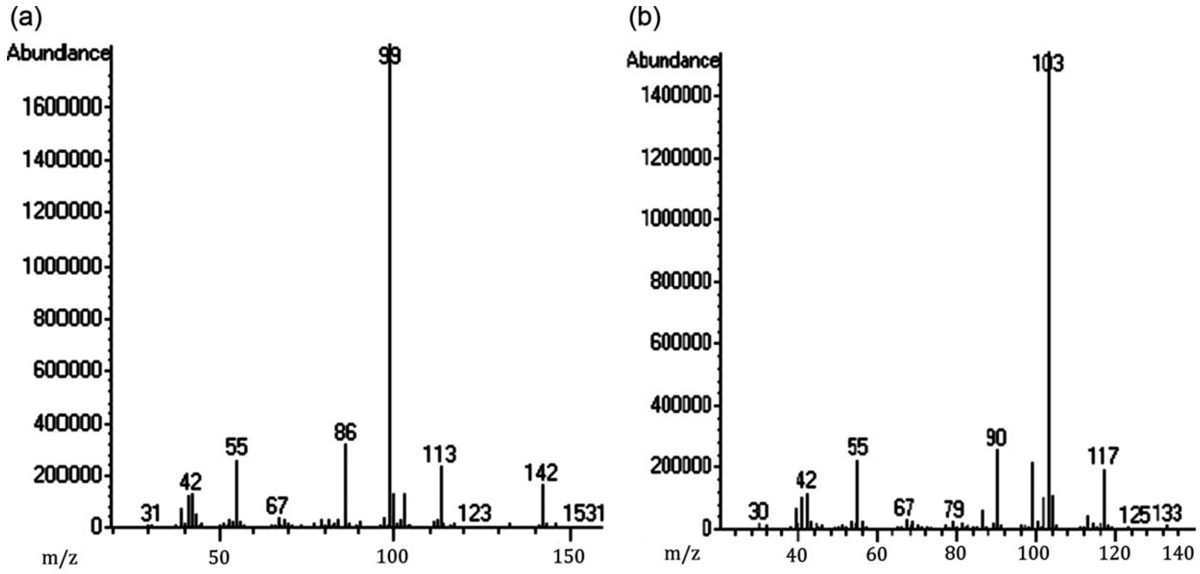

Figure 2. Mass spectra of (a) derivatized EG and (b) derivatized IS obtained from SPME-GC/MS.

Table 1. SPME fibers used.

Fiber coating type	Polarity	Hub color	Maximum temperature (°C)	Fiber conditioning
PEG, 60 μm	Polar	Purple	250	240 °C (0.5 h)
CAR/PDMS, 75 μm	Bipolar	Black	310	300 °C (1 h)
PDMS, 100 μm	Nonpolar	Red	280	250 °C (0.5 h)
PA, 85 μm	Polar	White	300	280 °C (1 h)
DVB/CAR/PDMS, 50 μm	Bipolar	Gray	270	270 °C (1 h)

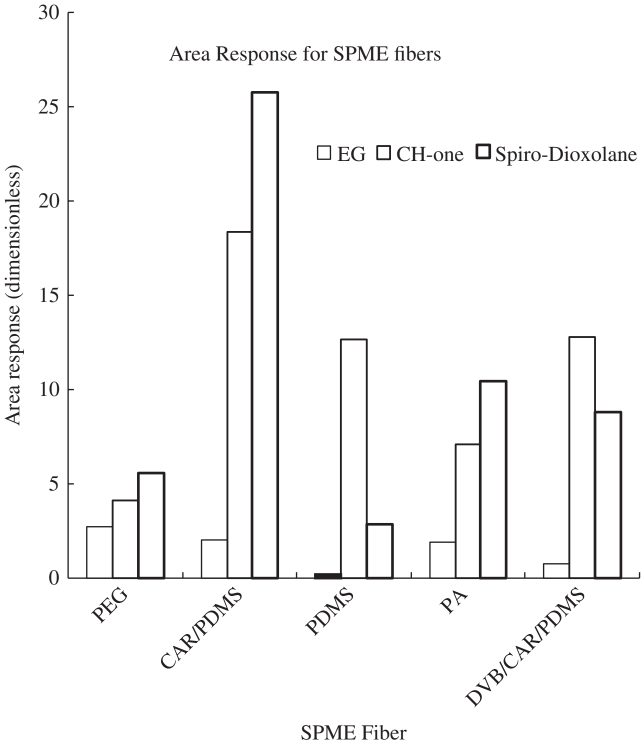

Figure 3. Area response for the base ions of ethylene glycol (EG), cyclohexanone (CH-one), and ketalized EG in the oil sample (1000 μg/g).

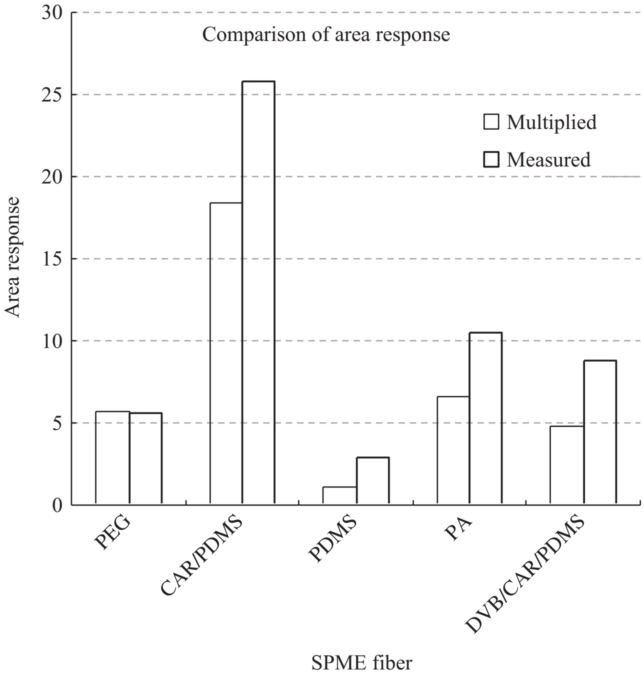

Figure 4. Comparison of the area response between the *m/z* 99 ions of ketalized EG and the multiplied area response with the *m/z* 31 ions of EG and the *m/z* 55 ions of CH-one.

limited number of adsorption sites; thus, increasing the spiro-dioxolane concentration resulted in a plateau at higher concentration.

The EG calibration curve in the standard lubricating oil samples is shown in Figure 6. The ratio of the area for the *m/z* 99 ions of 1,4-dioxaspiro[4.5]decane from EG at 7.96 min and the area for the *m/z* 103 ions in d_4-1,4-dioxaspiro[4.5]decane from the IS at 7.93 min was plotted against EG concentration. The EG calibration curve with CH-one exhibited a 0.9926 r^2 value and showed good linearity. The detection limit for the analysis was < 0.1 μg/g in the oil.

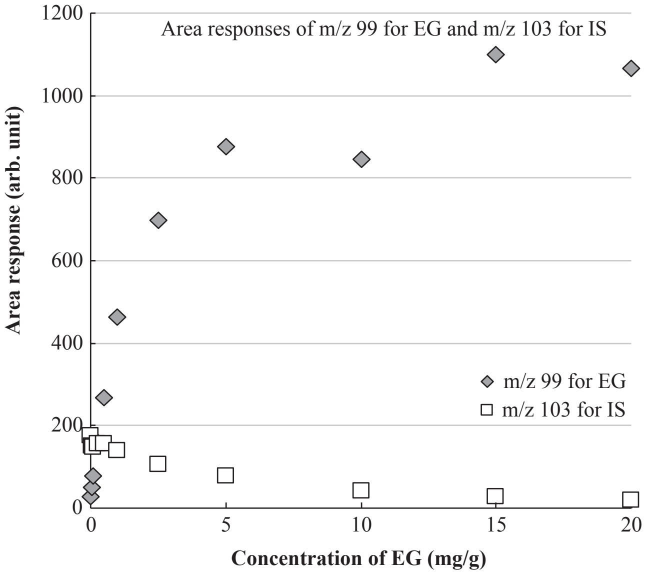

Figure 5. The area response of derivatized ethylene glycol (EG) (*m/z* 99) and derivatized internal standard (IS) (*m/z* 103) with CAR/PDMS fibers at 250 μg/g IS in the oil sample.

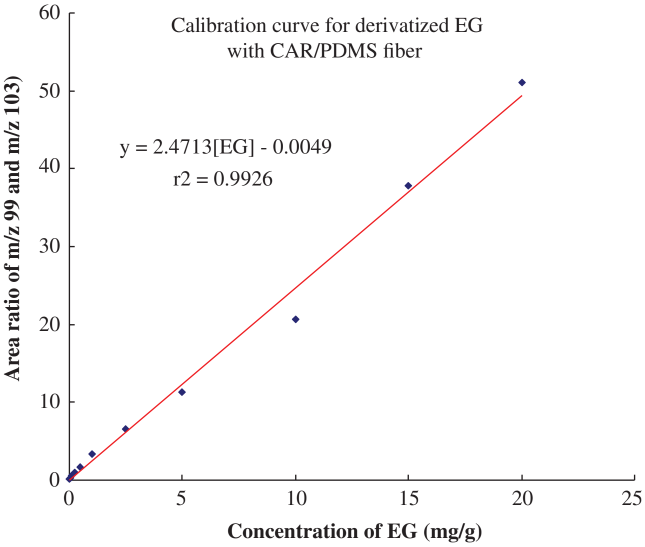

Figure 6. Ethylene glycol (EG) and CH-one calibration curve with CAR/PDMS fibers.

Table 2. Gerstel MPS2 A/S conditions.

Autosampler (A/S)		Condition
Agitator	Incubation temperature	40 °C
	Incubation time	10.00 min
	Speed	250 rpm
Fiber	Pre-bakeout time	10.00 min
	Derivatization mode	Post-extraction
	Derivatization time	0.20 min
Sample	Extraction time	5.00 min
	Desorption time	3.00 min

Table 3. GC/MS condition.

Instrument	Condition	
GC/MS	Injector temperature	250 °C
	Split ratio	40:1
	Transfer line temperature	280 °C
	Carrier gas	He 1.0 mL/min
	Oven temperature	60 °C (3 min) → (10 °C/min) → 130 °C → (25 °C/min) → 250°C (10.2 min)
	Column	DB-5MS (0.25 mm × 0.25 μm × 30 m)
	Ion source temperature	230 °C

And, this method is successfully applied to real samples with good accuracy and precision.

In this study, we examined EG in polluted oil using GC/MS analysis and a combined SPME fiber extraction and derivatization with CH-one. This method proved to be solvent free, easy, and fast.

Among the five kinds of SPME fibers, CAR/PDMS fiber showed better performance than that of the others. A saturation effect was observed at higher concentrations. The detection limit was < 0.1 mg/g, and the r^2 value of the calibration curve was 0.9926.

Experimental

EG, d_4-EG, CH-one, and trimethylchlorosilane (TMCS) were purchased from Sigma-Aldrich (St. Louis, U.S.A.). The SD5000 GOLD diesel engine oil was obtained from SK Lubricants (Seoul, Korea). The SPME fibers of PEG, CAR/PDMS, PDMS, PA, and DVB/CAR/PDMS were obtained from Supelco (St. Louis, U.S.A.). The GC/MS system was a 6890N GC and a 5973 MSD (Agilent Technologies (Munich, Germany)) with a Gerstel MPS2 autosampler (A/S). The analytical performance of the five kinds of SPME fibers was compared for EG and derivatized EG at the same concentrations (1000 μg/g of EG) as the oil sample. All experiments were performed at 40°C in an agitator of the MPS2 A/S under the conditions described in Table 2. In addition, the area responses of each fiber to CH-one with 10% TMCS were compared by extraction for 12 s at 40°C. The GC/MS condition was shown at Table 3. A comparison was made between the area response for each EG base ion (*m*/*z* 31), CH-one (*m*/*z* 55), and spirodioxolane (*m*/*z* 99). All SPME fibers were conditioned in the GC injector prior to use under the conditions described in Table 1.

EG was extracted in the head space of the heated (40°C) sample for 5 min under agitation (250 rpm), with the Gerstel MPS2 A/S under the conditions shown in Table 2. The sample vial of 10 mL was incubated for 10 min in the A/S agitator before extraction. The derivatization was conducted in a post-extraction mode by exposing the extracted EG on the SPME fiber to CH-one vapor containing 10% TMCS for 12 s.

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