

## Determination of trace icing inhibitors (ether type) in free-floating fuels by gas chromatography-mass spectrometry

Ho-Sang Shin<sup>1,2</sup>, Hye-Sil Ahn<sup>3</sup> · Dong-Gyun Jung<sup>3</sup>

<sup>1</sup>RRC/NMR, <sup>2</sup>Abuse Drug Research Center, Kongju National University, Kongju, Korea

<sup>3</sup>Department of Environmental Science, Kongju National University, Kongju, 314-701, Korea

Hyesil@kongju.ac.kr

### Abstract

A gas chromatography/mass spectrometric assay method was developed for the simultaneous determination of ethylene glycol monomethyl ether (EGME) and diethylene glycol monomethyl ether (DEGME) in spilled aviation fuels. Ethylene glycol monobutyl ether (EGBE) and ethylene glycol monoethyl ether (EGEE) were used as internal standard and surrogate, respectively. The sample preparation consists of back-extraction with 7 mL of methylene chloride after extraction of 50 mL of fuel with 2 mL of water. The extract was concentrated to dryness and dissolved with 100L of methanol and analyzed by GC-MS (SIM). The peaks had good chromatographic properties by using semi-polar column and the extraction of these compounds from fuel also gave high recoveries of 75 and 85 % with small variations for EGME and DEGME, respectively. Method detection limits were 1.3 ng/mL for EGME and 1.0 ng/mL for DEGME in spilled fuel. The method may be useful for fuel-type differentiation between kerosene and JP-8, which may originate from the storage tank.

Keywords : JP-8, icing inhibitor, GC-MS, fuel-type differentiation

### 1. Introduction

Refined fuels used for automotive or aircraft propulsion contains a variety of additives such as lubricants, antioxidants, corrosion inhibitors and gum inhibitors. It is often believed that each manufacturer has a unique set of additives which can be used in tracing their source by identifying these additives in free floating products, soil or ground water.

The worldwide aviation fuel is consumed thousands barrels per day. Jet fuel formulations are kerosene-based mixtures of hydrocarbons. Military jet fuel (JP-8) contains mandatory performance additives that are not usually blended with commercial jet fuel (Jet-A), which is generally manufactured mainly from straight-run kerosene [1]. JP-8 can therefore be described as kerosene containing three performance additives; icing inhibitor, antioxidants and antistatic compounds [1]. Many of these additives are oxygen-containing compounds such as ethers or phenols, and useful for spilled fuel-type differentiation between kerosene and JP-8. Ethylene glycol monomethyl ether (2-methoxy ethanol, EGME) and diethylene glycol monomethyl ether [2-(methoxy, ethoxy) ethanol, DEGME] are representative icing inhibitor, which have low octanol-water partition coefficient. The change in composition of EGME and DEGME in fuel occurs due to the loss of water-soluble icing inhibitors to water phase after an aviation fuel is released into environment. Therefore, identification of these additives in environmental samples requires specialized analytical methods.

To date, several analytical methods for determination of EGME and DEGME in aviation fuels have been described [2,3]. Standard test method describes the detection with refractometer after extraction with water [2]. Bernabei [3] determine two anti-icing additives in jet fuel based on a gas-chromatographic technique using a mass spectrometer without sample pre-treatment. But these methods cannot be applicable to detection of trace EGME and DEGME in spilled aviation fuels. The quantitative methods of ethylene glycol in environment [4,5] or biological samples [6] for this research were referred.

Our aim was to develop analytical method, which allows the simultaneous quantification of trace EGME and DEGME in spilled aviation fuels at the low-ng/mL. We present an analytical method with GC-MS for the quantification of trace EGME and DEGME in spilled aviation fuels. The target compounds can be extracted with water and cleaned with hexane, and then back extracted with methylene chloride by salting-out with sodium sulfate.

## 2. Experimental

### 2.1. Chemicals and reagents

Ethylene glycol monomethyl ether (EGME), ethylene glycol monoethyl ether (EGEE), diethylene glycol monomethyl ether (DEGME) and ethylene glycol monobutyl ether (2-butoxy ethanol, EGBE) were purchased from Aldrich (USA). Neat kerosene samples were obtained from commercial oil tank and JP-8 from L-oil Company. Weathered jet fuels were collected from sampling wells as a neat oily phase found floating on top of the water. The sampling wells were located at American Army Base in Seoul, Korea. The fuel samples, after they arrived for the study, were analyzed immediately

### 2.2. Spiking

Spiked samples were prepared by kerosene(50mL) with 30-200uL of standard solutions at a concentration of 5.0~50 $\mu$ g/mL and with 100 uL of the solution containing internal standards at a concentration of 50  $\mu$ g/mL.

### 2.3. Extraction procedure

50 mL volume of fuel sample and 2 mL of milli-Q water were placed in a 150 mL separating funnel. 100uL of internal standard (50  $\mu$ g/mL in acetone) were added to the solution and shaken for 10 min. The aqueous extract was purified by extraction with 20 mL of n-hexane, and transferred to a 20 mL glass stoppered test tube. The aqueous solution was back-extracted with 7 mL of methylene chloride by adding large amount (above 5 g) of anhydrous sodium sulfate to dryness. The organic layer was evaporated to dryness with nitrogen stream and then dissolved with 100uL of methanol. The solution was transferred into a V-shape in auto vial. At appropriate times, a 2uL sample of the solution was injected in the GC system.

## 2.4. Gas chromatography-mass spectrometry

Table 1. GC-MS conditions for the determination of the target compounds

Parameter	Conditions			
Column	INNOWAX, 30m×0.25mmI.D.×0.25µm F.T.			
Carrier	He at 1.0mL/min			
Oven Temp.	10°C/min 40°C → 180°C post run 230°C (3min)			
Split Ratio	1 : 10			
Injector Temp.	260°C			
Transfer Temp.	280°C			
Selected Ion Mode	Group	Strat time(min)	Compound	Selected Ions, m/z
Group	1	4.0	EGME	45, 58, 76
	2	5.5	EGEE	31, 59, 72
	3	7.0	EGBE	45, 57, 87
	4	9.0	DEGME	45, 59, 90

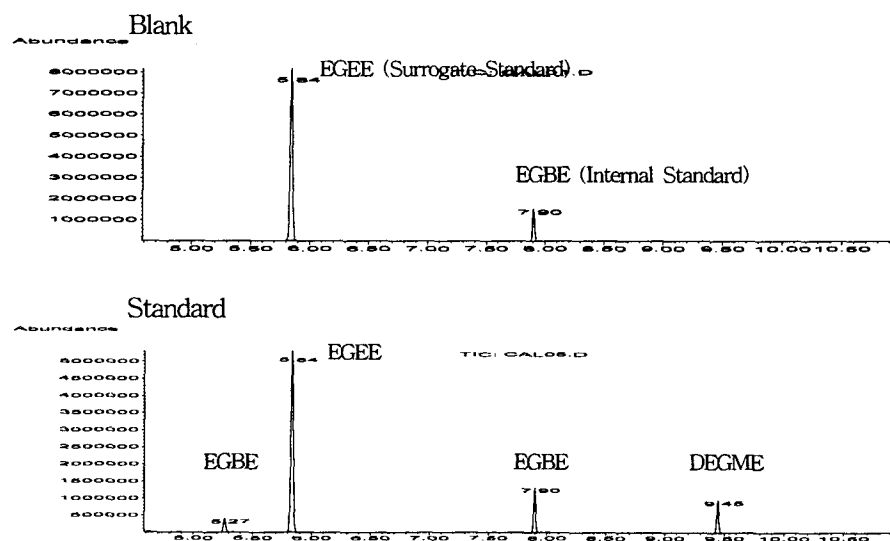
## 2.5. Calibration and quantification

Calibration curves for EGME and DEGME were established by extraction after adding 0.15, 0.3, 0.6, 1.25, 2.5, 5.0 and 10 µg of standards and 5.0 µg of internal standard in 50 mL of kerosene. The ratio of the peak area of standard to that of internal standard was used in the quantification of the compound.

## 3. Results and discussion

### 3.1. Chromatography

For the GC separation of EGME, EGEE, EGBE and DEGME, the use of the semi polar stationary phase was found to be efficient. Chromatograms are shown in Fig. 1. As can be seen from the figure, the peaks of EGME, EGEE, EGBE and DEGME are symmetrical and separation of the analytes from the background compounds in samples was very good.



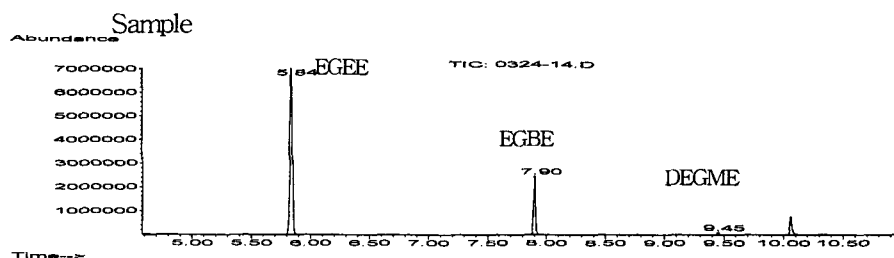


Fig. 1. Chromatograms of the extracts from kerosene (blank), kerosene spiked with 50 ng/mL of standards, and a free-floating product (sample).

### 3.3. Extraction and clean up

Test samples at 100 ng/mL were prepared and the relative recovery was calculated by percentage of the analytes recovered. The recoveries of the test compounds were more than 74 % as shown in Table 2.

Table 2. Recoveries of the target compounds from sample spiked in kerosene (n=5)

Compounds	Amount spiked (ng/mL)	Recovery(%) $\pm$ RSD(%)
EGME	100.0	74.9 $\pm$ 3.5
DEGME	100.0	85.2 $\pm$ 7.1

### 3.4. Linearity and detection limits

Table 3. Linearity and detection limits of the target compounds

Compounds	Detection Range(ng/mL)	No of points	Linear equation	Linearity	Method Detection Limit (ng/mL)
EGME	3.0~200	7	$Y=0.0057x+0.0020$	0.997	1.3
DEGME	3.0~200	7	$Y=0.0104x-0.0348$	0.998	1.0

### 3.5. Precision and accuracy

Table 4. Precision and accuracy of EGME and DEGME spiked in kerosene (n=5)

Compounds	Conc spiked (ng/mL)	Results	
		Calculated Conc.(ng/mL)	Mean $\pm$ SD (RSD%)
EGME	50	39.6, 41.9, 46.8, 48.2, 49.7	45.2 $\pm$ 4.3 (9.5%)
	200	198.9, 186.0, 189.4, 182.8, 181.1	187.6 $\pm$ 7.0 (3.7%)
DEGME	50	39.9, 42.5, 42.1, 46.5, 47.5	43.7 $\pm$ 3.2(7.3%)
	200	199.9, 188.5, 202.8, 201.4, 174.8	193.5 $\pm$ 11.9(6.1%)

## 4. Conclusions

The peaks have good chromatographic properties and offer very sensitive response for the EI-MS (SIM). Analytical procedure of target compounds with a range of method detection limits of 1.0-1.3 ng/mL was established. The detection limits from this study were lower than those obtained by

procedures described before [2,3].

Military jet fuel (JP-8) is kerosene containing icing inhibitor. It can be used in tracing its source by identifying the additive in free-floating products. Because icing inhibitors of ether type contain many oxygen atoms in their structure, they are water-soluble. Therefore, it becomes difficult to identify the intact additive in free-floating products and analysis method of the low-ng/mL is needed. The developed method may be very valuable in identifying the EGME or DEGME remaining in free floating products.

## 5. References

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