

GC Nexis™ GC-2030

## Determination of Trace Amount of Ethylene Glycol in Used Engine Oil by GC-FID based on ASTM D4291-04

Jessin Mathai , Shailesh Damale, Raj Makhamale and Kumar Raju.  
Shimadzu Middle East Africa FZE-Dubai.

### User Benefits

- ◆ This GC-FID method is used for the quantitative determination of trace levels of ethylene glycol in used engine oil.
- ◆ This method uses simple instrumentation with minimal chemicals to quantify trace levels of ethylene glycol from used engine oils as per ASTM D4291-04 guidelines with minor modifications.

### Introduction

**Overview:** Ethylene glycol or Ethane-1,2-diol in combination with water has been used widely as an anti-freezing agent and engine coolant in automobile engines. The reason for this is due to its typical colligative properties such as depression in freezing point and elevation of boiling point which plays an important role at extreme temperature conditions. However, due to engine overheating, the cylinder head gasket or cylinder head in the engine gets damaged resulting in the mix-up of coolant with the engine oil. This can lead to severe consequences in the performance of the engine. The leakage of aqueous coolant into the crankcase weakens the lubrication ability of the engine oil that can favor deposit formations and boost friction which ends up in further overheating of the engine. It causes severe damage to the engine parts if left unattended. The destructive potential of ethylene glycol can harm the health of automobile engines within no time.

Hence it is imperative to test the quality of used engine oil so often. Such periodic evaluations of the used engine oil open the possibility of recycling, thereby reducing the carbon footprint in the environment. ASTM has prescribed methods to quantitate ethylene glycol in used engine oils. Initially, ASTM D4291 put forward the use of GC-FID with an on-column injector and packed column for quantifying ethylene glycol from used engine oil. Later this was modified as ASTM D4291-04, which permits the use of capillary wax column for the same application. Both these methods recommend the use of liquid-liquid extraction as a sample preparation methodology.



Figure 1. Nexis™ GC-2030 + AOC™-30i

### System Configuration

The system configuration consists of Shimadzu Nexis™ GC-2030 FID with AOC™-30i autosampler (Figure 1) and an on-column injector (OCI-2030). The system configuration and the instrument parameters are given in Tables 1 & 2, respectively.

Table 1. System Configuration

Model	: Nexis™ GC-2030/AOC™-30i
Injection Port	: OCI-2030
Detector	: FID
GC Column	: Stabilwax (P/N 10667) (15m x 0.53mm ID, df: 2µm)

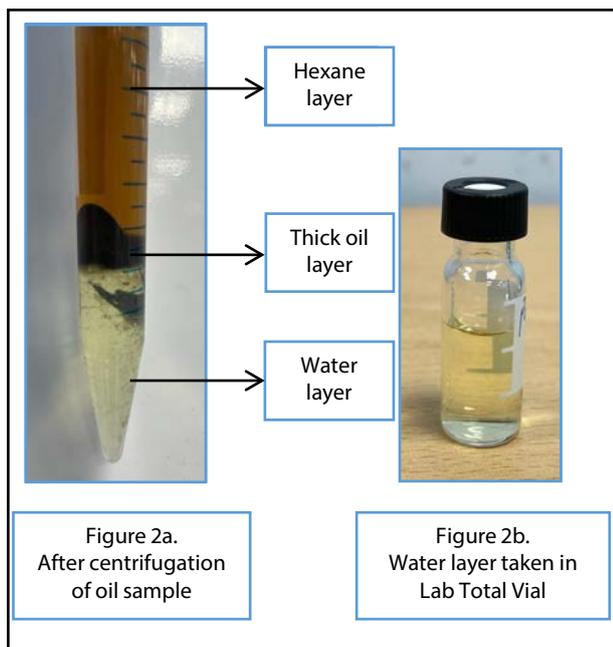
Table 2. Instrument Parameters

<u>GC Parameters</u>	
Injector temperature	: 225 °C
Carrier gas	: He
Flow mode	: Constant flow
Column flow	: 18 mL/min
Purge flow	: 3 mL/min
Injection volume	: 1.0 µL (Sample) + 0.5 µL (Methanol as co-injection)
Oven temperature program	: 70 °C (1min) – 12 °C /min – 200 °C (5 min)
Stop time	: 16.83 min
<u>FID Parameters</u>	
Detector temperature	: 300 °C
Makeup gas	: N <sub>2</sub>
Makeup gas flow	: 24 mL/min
H <sub>2</sub> gas flow	: 32 mL/min
Air flow	: 200 mL/min

### Experimental

This application note is a modification of the ASTM D4291-04 method. The quantification method followed was an external-standard method with calibration standards ranging from 5-200 ppm. The sample extraction procedure was adopted from the official ASTM method, with minor changes in the instrument operating conditions.

**Preparation of stock and calibration standards:** 5000 ppm w/w of ethylene glycol was prepared as stock solution using Milli-Q water as diluent. Approximately, 100 mg of ethylene glycol was weighed into a 20 mL standard flask. To this, 20 g of water was added.



The stock solution prepared was mixed thoroughly using a vortex mixer. From the above stock, 5, 50, 100, and 200 ppm (w/w) calibration standards were prepared with Milli-Q water.

**Sample preparations:** Sample preparations were made according to the ASTM procedure. Two used engine oil samples were taken for this experiment. The first sample was a pooled used engine oil whereas the second sample was collected from a single car during the first service.

In accordance with the ASTM procedure, 3 g of both samples were taken in separate 15 mL polypropylene tubes with screw caps. To each of this, 3 g of water was added followed by 5 mL of hexane. The mixture was vortexed for 1 min and centrifuged for 30 min at 7500 RPM. This results in the formation of three separate layers; a hexane layer at the top, a thick dark layer of oil at the middle, and a water layer at the bottom as shown in Figure 2a. The hexane layer at the top was then carefully discarded using a pasture pipette. To the remaining solution, 5 mL of hexane was again added and centrifuged. The hexane layer was again discarded. This process was repeated about three times until a clear water layer was obtained at the bottom of the centrifuge tube. The thick oil band formed on the top of the water layer was skimmed off carefully. Approximately 1 mL of the water layer was then carefully transferred to a Shimadzu Lab Total Vial as shown in Figure 2b. using a micropipette. The content in the vial was then analyzed using Gas Chromatograph.

**Recovery standard preparations:** Recovery standard was prepared using the second engine oil sample which did not contain ethylene glycol. Three different concentrations of spike standards were prepared following the same steps used for samples.

In the original ASTM method, the column oven was maintained at a constant temperature of 150 °C throughout. However, when ethylene glycol standard was injected using an OCI, the analyte peak splitting was observed. This was solved by co-injecting 0.5 µL of methanol along with 1 µL of sample/standard. However, it is observed that methanol peak masks the early eluting ethylene glycol peak. To counter this, a gradual oven temperature program was introduced. The temperature program was started at 70 °C and ramped to 200 °C at a rate of 12 °C /min. With this temperature program, ethylene glycol peak elutes approximately at 6.4 min whereas in the ASTM method it was at 1 min.

Besides this, ethylene glycol is a highly polar compound and is known to have residual carryover. It is observed that the carry over is mainly originated from the autosampler syringe. The carryover issue was minimized by performing syringe washings with ethyl acetate and water immediately after injection. Additionally, ASTM suggested to perform water injections multiple times after every injections of standard/sample until no peak is found at the ethylene glycol retention time. Hence as a procedure, every injection of standard or sample was followed with three injections of water. It was observed that after third injection, the presence of ethylene glycol become negligible in the chromatogram.

All the linearity standards were injected in duplicates. The summary of the linearity is shown in Table 3. and the calibration curves for both injections are shown in Figure 3. The regression ( $R^2$ ) obtained was greater than 0.99. An overlay of the chromatograms for the different standards are shown in Figure 4.

Table 3. Linearity results

Conc. (ppm)	Calculated conc. (ppm)		Ave. Accuracy (%)	Ave. Linearity ( $R^2$ )
	Rep 1.	Rep 2.		
4.8	5.9	5.0	113	0.9930
49	42.8	42.0	87	
99.5	95.9	91.5	94	
195	201.8	211.6	106	

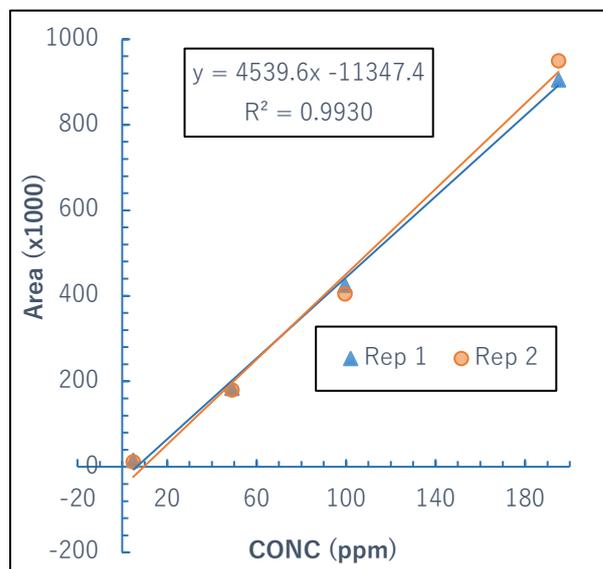


Figure 3. Calibration curves of ethylene glycol standards

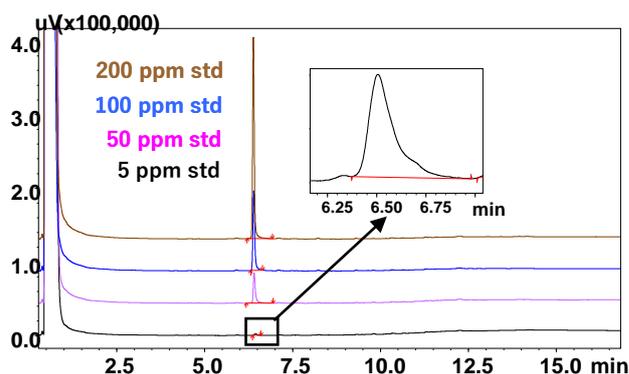


Figure 4. Overlaid chromatograms of calibration standards

Among the two samples, the pooled engine oil sample was found to have considerable amount of ethylene glycol (>100 ppm). The Chromatogram of this sample is shown in Figure 5. However, ethylene glycol was not detected in the second engine oil sample. Hence second sample was selected for performing recovery studies. As mentioned early, three different levels of recovery standards were prepared. Additionally, each vial was analyzed twice to evaluate the reproducibility of the analysis and the results are shown in Table 4. The recovery for the spike standards were found to be within the acceptable range of 80-120 %. An overlay of chromatograms of un-spiked sample along with the three spike samples are shown in Figure 6. The variation in injection to injection was evaluated. The % RSD was found to be less than or equal to 2 % for all the spike standards.

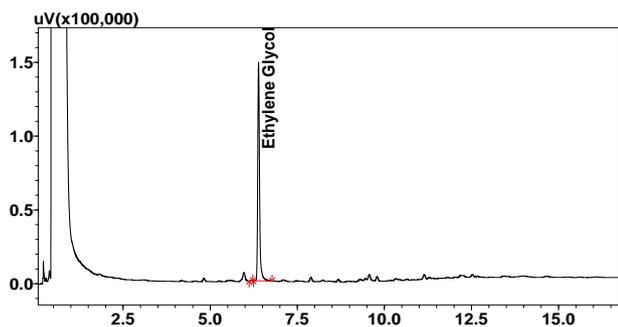


Figure 5. Chromatogram of a used engine oil sample having ethylene glycol

Table 4. Spike recovery results

Trial No.	Spiked conc. (ppm,w/w)	Observed conc. (ppm) Rep 1.	Observed conc. (ppm) Rep 2.	Ave. conc. (ppm)	RSD (%)	Recovery (%)
1	4.75	4.29	4.17	4.23	2.0	89
2	72.73	58.62	57.62	58.12	1.2	80
3	145.68	122.79	124.77	123.78	1.1	85

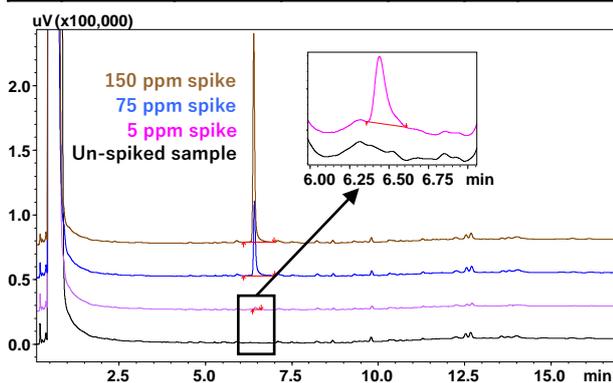


Figure 6. Overlaid chromatograms for un-spiked used engine oil, 5 ppm, 75 ppm and 150 ppm spiked used engine oil samples.

## Conclusion

This application note demonstrates the use of Shimadzu Nexis™GC-2030 with OCI-2030 for the estimation of ethylene glycol from used engine oils. The sample preparation was carried out following ASTM D4291-04 guideline which is based on liquid-liquid extraction. The advanced feature (sandwich injection protocol) of the new autosampler AOC™-30i was utilized for this analysis to improve the peak shape of ethylene glycol by co-injecting methanol with standards and samples.

The calibration curve for the analyte was found to be linear with regression ( $R^2$ ) greater than 0.99. Two used engine oil samples from different sources were tested. Out of these two samples, the analysis result shows that one sample have considerable amount of ethylene glycol (>100 ppm). The result of second sample found to have no ethylene glycol and this sample was taken from a single car during the first service at 10,000 km. The result of the second sample further tells that there is no leakage in the crank case of the engine compartment of this car. The results of the recovery studies were found to be within 80-120 % with precision  $\leq 2$  % in all three concentrations (5, 75 & 150 ppm).

This application note demonstrates the capability of Nexis™GC-2030 for the estimation of ethylene glycol in used engine oils accurately. The instrument is capable of analyzing ethylene glycol in sub ppm levels from the crude engine oils using ASTM recommended sample preparation protocol.

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