

# Determination of Ethylene Glycol in Used Engine Oil by Headspace-Gas Chromatography

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## Introduction

The presence of ethylene glycol in used motor oil is an indication of antifreeze coolant leakage into the crankcase of an internal combustion engine, thus predicting engine-wear problems. Several options for the determination of glycols currently exist, including colorimetric tests which are easy to perform, but subjective in interpretation and not particularly sensitive, fast or cost effective. Gas chromatography (GC) can also be used for analysis, but the ethylene glycol is difficult to detect and quantify due to its low molecular weight, low volatility and high polarity. Ethylene glycol chromatographic peak shape is often difficult to control and carryover can be a problem.

Injecting used engine oil directly into a gas chromatograph for the determination of ethylene glycol introduces high-molecular-weight oil and non-volatile components into the injector and the column. Consequently, the chromatography is very long, the column lifetime is shortened and the sample throughput is low, since high boiling components from the oil matrix must elute before the next injection.

ASTM Method D4291-98 specifies diluting the oil sample with hexane, extracting the glycol into water and analysis by GC. This is a very labor intensive sample preparation procedure and an unforgiving chromatographic method, whereby water and the polar analyte are injected on-column.

An alternative to ASTM Method D4291-98 is investigated here, which involves a very simple in-situ derivatization technique that allows the glycols to be made more volatile and less polar. Headspace extraction is used to isolate the glycols from the complex sample matrix and inject into a gas chromatograph for rapid separation and quantification without the oil matrix. The result is a rapid, high-throughput method capable of analyzing hundreds of samples per day for ethylene glycol and propylene glycol in motor oil.

## Experimental

The system used for this work and the GC conditions are shown in Table 1.

### Standards calibration

Prepare glycol standards over the quantification range of 0.01% to 1.0% w/w in motor oil.

### Sample preparation

Add 100  $\mu$ L of the sample oil into a 22-mL headspace vial. Add 5 mg of derivatizing reagent (PerkinElmer Part Number N9301741). Seal the vial for headspace analysis. A positive displacement pipette is used to accurately dispense oil samples due to viscosity. Vials can be pre-inoculated with derivatizing reagent for faster sample preparation.

Table 1. GC System and Conditions.

Headspace Sampler:	PerkinElmer® TurboMatrix™ HS-40 or HS-110			
Temperatures (°C):	Sample oven: 120	Needle: 150	Transfer line: 160	
Timing (min):	Thermostat: 18 Period from injection to injection: 3	Inject: 0.01	Withdraw: 0.5	GC cycle time: 3
Pressure:	40 psig Helium	Pressurize: 1.0 min	Transfer line: 320 µm deactivated fused silica	
Vials:	22-mL headspace vials, PTFE-lined silicone septa			
Gas Chromatograph:	PerkinElmer Clarus® 500 GC			
Injector:	Split/Splitless with PPC		180 °C 25 psig	Split: 50 mL/min
Detector:	FID with PPC Air: 450 mL/min	Range: x1 H <sub>2</sub> : 45 mL/min	Attn: x32	Temperature: 250 °C
Column:	15 m x 0.32 mm ID x 0.25 µm Elite-5 Equilibration Time: 0		100 °C for 2 min (isothermal) PerkinElmer Part Number N9316073	

## Results

The derivatization goes to completion quickly and easily under the heated headspace conditions. The headspace extraction removes the volatile components from the sample matrix for a very clean injection into the chromatographic column. The high molecular weight motor oil, soot and other non-volatiles are never introduced into the column. Peak retention is optimized to resolve ethylene glycol from early eluting derivatization by-products. The isothermal GC method allows for a 3-minute time or less between injections. This is a 10-fold increase in throughput when compared with current ASTM methods. Excellent quantitative linearity (0.999), shown in Figure 2 and precision (3% RSD) were demonstrated over the range of 0.01% to 1.0% ethylene glycol.

System maintenance consists of headspace o-ring seal replacement after roughly 2000 injections.

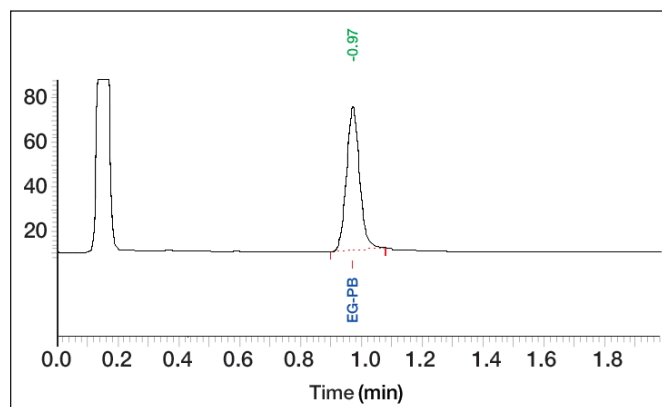


Figure 1. Chromatogram of glycol in used oil using derivatization and headspace extraction.

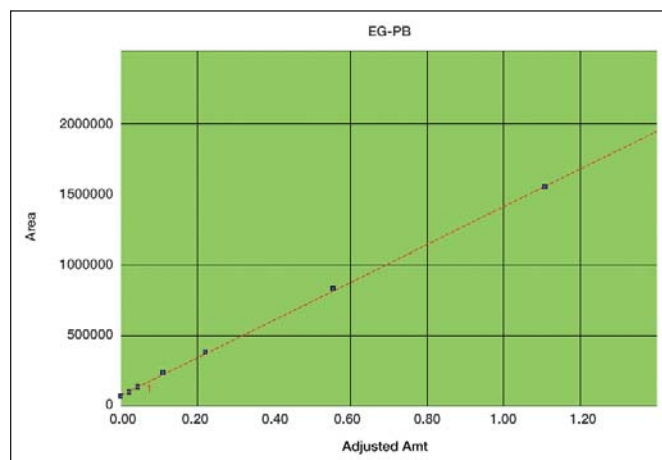


Figure 2. Calibration linearity of 0.999%.

## Conclusion

A practical method has been developed and tested which will allow for high throughput testing of ethylene glycol as a diluent in used motor oil. Up to 400 samples per day can be analyzed using this method, which provides results directly comparable to established methods.

The headspace injection of used motor oil means less sample preparation, high throughput and less human error. Cost analysis (without labor and initial startup costs) has been calculated to be less than \$0.70 US per sample.

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