APPLICATION NOTE

Gas Chromatography

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

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.

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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 (HS) 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 chromatographic conditions are shown in Table 1.

Standards Calibration

Prepare glycol standards over the quantification range of 0.01% to 0.2% w/w in motor oil.

Sample Preparation

Add 100 µL 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 preinoculated with the derivatizing reagent for faster sample preparation.

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 three minute time or less between injections as shown in Figure 1. This is a 10-fold increase in throughput when compared with current ASTM methods.

Excellent quantitative linearity (0.997), shown in Figure 2 and precision (3% RSD) were demonstrated over the range of 0.01% to 0.2% ethylene glycol. System maintenance consists of headspace o-ring seal replacement after roughly 2000 injections.

Table 1. Experimental conditions using Clarus® 580 GC and TurboMatrix™ HS driven by Waters® Empower® 3 Chromatography Data Software (CDS).

Headspace Sampler	**PerkinElmer TurboMatrix™ HS-40 or HS-110**		
Temperatures (°C)	Sample oven: 120	Needle: 150	Transfer line: 160
Timing (min)	Thermostat: 18	Inject: 0.01	Withdraw: 0.5
	GC cycle time: 3	Period from injection to injection: 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® 580 GC		
Injector	Split/Splitless with PPC	180 °C 25 psig	Split: 50 mL/min
Detector	FID with PPC	Range: x1 Attn: x32	Temperature: 250 °C
	Air: 450 mL/min	H2: 45 mL/min	
Column	15 m x 0.32 mm ID x 0.25 µm Elite-5	100 °C for 2 min (isothermal)	Equilibration Time: 0 min
Software	Empower® 3 CDS		

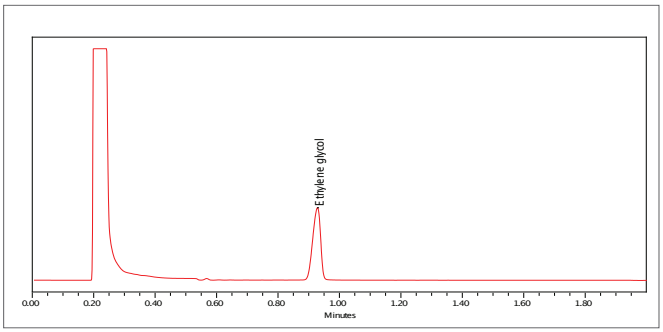

Figure 1. Chromatogram shows elution of ethylene glycol.

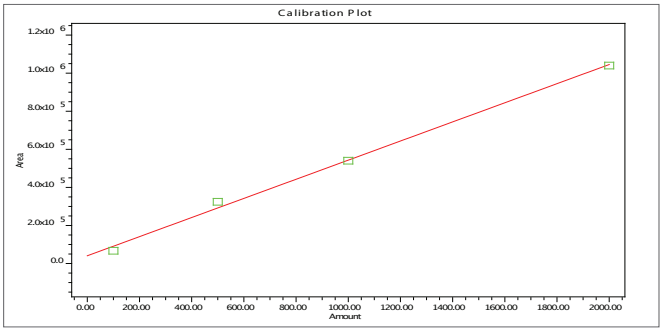

Figure 2. Calibration curve of ethylene glycol.

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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