A Novel Method for High-speed Determination of Fuel Diluents in Lubricating Oils

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Introduction

The performance of lubricating oil is significantly degraded by the presence of fuel contaminants such as gasoline and diesel. Recycled oil is particularly susceptible to this form of contamination. Consequently, producers and distributors of lubricating oil must go to great lengths to ensure the levels of fuel contamination are kept to a safe limit (typically 4 to 5%) in these products. Traditionally, this analysis is performed by flash point or by gas chromatography of the lubricating oil by direct injection into a gas chromatograph (GC) according to ASTM Methods D3524 and D3525. These methods are time consuming and will stress the instrumentation by the introduction of very heavy hydrocarbons and involatile material such as soot. Users may have hundreds of thousands of samples to run each year, so an alternative method that is fast and robust is desirable. This discussion outlines the principles and technology for such a method.

Experimental

The gas chromatograph used in this work was set up as described in Table 1 below.

Table 1. GC System and Conditions.

Gas Chromatograph:	PerkinElmer® Clarus® 500 with Autosampler				
Injector:	Programmable Split/Splitless (PSS) with PreVent™ Accessory				
Detector:	FID				
Pneumatics:	PPC Carrier for PSS (Helium), PPC FID Gases (Air & Hydrogen)				
Column:	15 m x 0.25 mm ID x 0.25 µm Elite-1, PerkinElmer Part Number N9316007				
Restrictor:	137 mm x 0.075 mm ID deactivated fused silica, PerkinElmer Part Number N6103081				
GC Oven:	225 ˚C for 2.25 minutes (isothermal)				
Equilibration Time:	0 minutes				
Carrier Pressure:	45 psig for 1.20 minutes, then 2.0 psig until end				
Carrier Split Flow:	100 mL/min				
PSS Temperature:	400 ˚C				
Auxiliary Pressure:	15 psig for 1.20 minutes, then 58 psig until end				
FID:	Range: x1	Attn: x4	Temp: 400	Air: 450 mL/min	H_2: 45 mL/min
Injection:	Syringe: 0.5 µL	Inj Volume: 0.1 µL	Speed: Fast	Viscosity: 0	
Wash Solvent:	Carbon Disulfide	Rinse: 2	Pump: 5	Wash: 2	

PerkinElmer® precisely.

Reagents: Blank base oil and diesel fuel for standards preparation, carbon disulfide for syringe wash.

Calibration: Add clean base oil to vial, spike with known amounts of fuel over the quantification range of 0.5 to 40% (v/v), then cap the vial.

Sample Preparation: Add about 1.5 mL of the sample oil into a standard 2-mL autosampler vial. Seal the vial and it is ready for analysis.

Typical oil sample.

Results

Peak separation is optimized to resolve fuel from the oil, but not resolve individual fuel components, as shown in Figure 1, thereby saving time. Overlap of diesel range organics with motor oil is defined at n-C_{20} alkane. Fuel is defined as the lump sum of any volatiles less than n-C_{20}. This will include gasoline and diesel range fuels. After n-C_{20} elutes, all higher boiling oil is backflushed rapidly off the head of the column to clean the column for the next injection without temperature programming. This is accomplished by the PreVent accessory by diverting the flow path out to vent. The isothermal GC method allows for a minimum time between injections of 3.5 minutes. This is a 10-fold increase in throughput from that shown in current ASTM methods.

Excellent quantitative linearity (0.999) is shown in Figure 2 over the range of 0.5 to 40% diesel fuel. Precision (3% RSD) is demonstrated in Figure 3 using a 5% diesel fuel standard. Each was demonstrated over the range of 0.5 to 40% diesel fuel. An option for an internal/check standard has also been developed, but has been found unnecessary at this time. Speciation between gasoline and diesel fuels can be accomplished by slower traditional GC methods, if the additional information is found to be necessary. System maintenance consists of daily septum change and injection-port liner replacement after roughly 2000 injections.

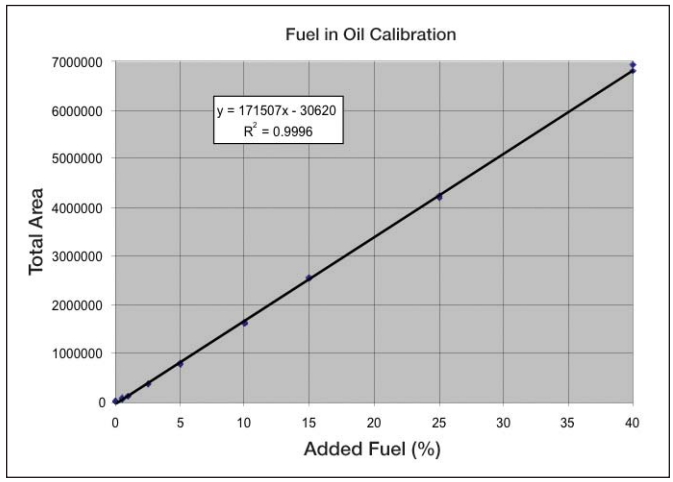

Figure 2. Calibration-curve linearity of 0.999%.

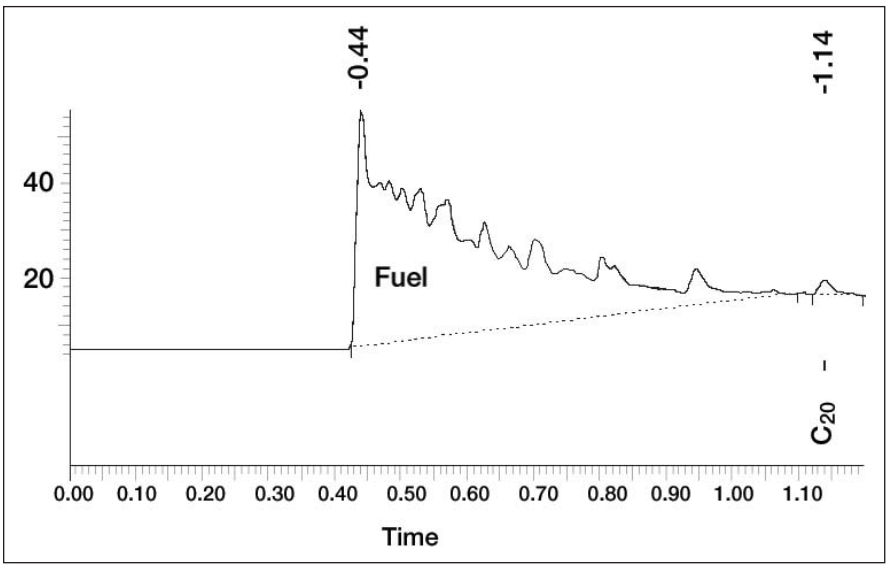

Figure 1. 5% diesel fuel in oil chromatogram.

Conclusion

A practical method has been developed and tested which will allow for high-throughput testing of fuel diluents in used motor oil for up to 400 samples per day. This method has withstood ruggedness testing in several laboratories and provides results directly comparable to established methods.

The direct injection of used motor oil means no sample preparation, high throughput and less human error. Cost analysis (less labor and initial startup costs) has been calculated to be less than $0.30 US per sample.

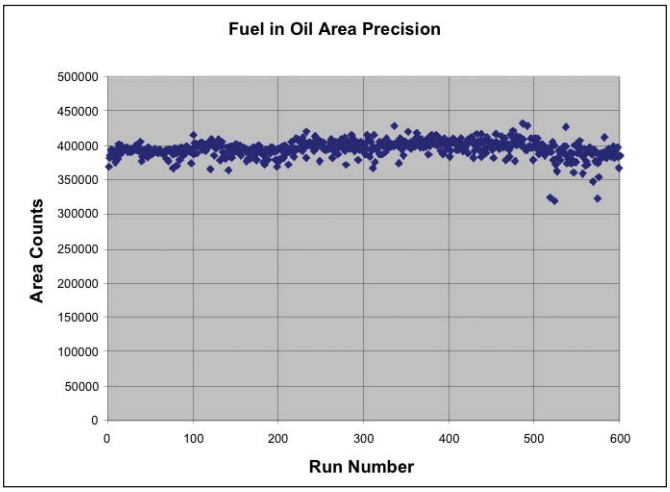

Figure 3. Precision of better than 3% RSD for more than 500 samples.

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