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Gas Chromatographic Analysis of Diesel Fuel Dilution for In-Service Motor Oil Using ASTM Method D7593

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Abstract

An Agilent 7890 Series gas chromatograph was used to measure the percentage of diesel fuel dilution for in-service motor oils. The GC was configured with a post column backflush Capillary Flow Technologies (CFT) device to remove the residual oil matrix from the column between each sample analysis. Calibration met or exceeded ASTM requirements using commercially prepared standards. The backflush technique provided analysis times of four minutes and excellent system robustness by completely removing the oil matrix. Precision of <2 % RSD was demonstrated for over 500 runs.

Introduction

Diesel fuel contamination in lubricating oils is an important indicator of impending engine failure or required maintenance. Diesel engine manufacturers and service facilities optimize their maintenance schedules by routinely monitoring the diesel content of in-service motor oils. To avoid catastrophic engine failure, they need a fast and robust analytical method for this measurement. ASTM method D7593 uses capillary gas chromatography (GC) to quickly quantify diesel fuel found in these oils. This method does not require any sample preparation, and can provide results within four minutes.

Instrument configuration and operating conditions

A 7890 Series gas chromatograph was configured to run ASTM D7593. Table 1 gives the details.

The Agilent 7650 ALS was fitted with wash vials containing carbon disulfide as the syringe wash. The Capillary Flow Technology (CFT) 2-way splitter with make-up gas was used as the backflush device for this analysis. An auxiliary Electronic Pressure Control (EPC) module provided a midpoint pressure source for control of the backflush operation.

Table 2 gives the operating conditions for analyzing diesel in oil samples.

The D7593 method improves analysis speed by quickly removing the heavy oil from the analytical column after the lighter fuel components have been detected. This technique is called backflushing. This configuration used a high column inlet pressure (45 psig) and lower Aux EPC pressure (27 psig) to maintain a forward column flow of 3.5 mL/min to separate diesel from motor oil. After the diesel fuel components have eluted, the column inlet pressure was automatically lowered to 2 psig while the Aux EPC pressure was

Table 1. GC Configured for ASTM D7593.

Parameter	Value
Automatic liquid sampler	Agilent 7650 ALS
Syringe	Autosampler syringe 0.5 µL (p/n G4513-80229)
Inlet	Split/splitless
Inlet liner	Low pressure drop, Ultra Inert with glass wool (p/n 5190-2295)
Analytical column	DB-1, 15 m × 0.25 mm, 0.25 µm (p/n 122-1012)
Backflush device	2-Way splitter with make-up (p/n G3180B)
Restrictor	Deactivated fused silica, 0.43 m × 0.1 mm id (p/n 160-2635-5)
Detector	Flame ionization (FID)

Table 2. Operating Conditions for ASTM D7593.

ALS Set points	
Sample injection volume	0.1 µL
Pre-injection solvent washes	5 × 0.25 µL carbon disulfide
Pre-injection sample washes	none
Sample pumps	5
Post injection solvent washes	5 × 0.25 µL carbon disulfide
Inlet set points	
Mode	split, 100 mL/min. split flow
Temperature	350 °C
Analytical column set points	
Carrier gas	helium
Initial pressure (flow)	45 psig (3.5 mL/min)
Backflush time	1.45 minutes
Backflush pressure (flow)	2 psig (−17 mL/min)
Backflush set points	
Aux EPC carrier gas	helium
Initial aux EPC pressure	27 psig
Backflush time	1.45 minutes
Backflush pressure	80 psig
Column oven set points	
Temperature	225 °C
Hold time	3.5 minutes
FID Set points	
Temperature	350 °C
Hydrogen flow	30 mL/min
Air flow	400 mL/min
Make-up flow	N_2 at 30 mL/min

simultaneously raised to 80 psig. This reversed the column flow and removed the heavy oil components through the split inlet vent. Figure 1 shows this process.

Backflush timing was determined experimentally. A carbon disulfide standard containing 10 mg/L each of dodecane (C_{12}) and eicosane (C_{20}) was prepared as a backflush timing standard. This solution was injected into the GC system under the operating conditions shown in Table 2, while keeping the inlet and aux EPC pressures constant at 45 psig and 27 psig respectively throughout the run with no backflush. The near complete elution of the eicosane peak marked the retention time boundary between the diesel components and the motor oil in the samples. Figure 2 shows that, in this case, the backflush time was determined to be 1.45 minutes. Backflush timing must be determined for every system due to small variations in column and flowpath dimensions. Additionally, the timing should be regularly checked as a part of the laboratory QA/QC program.
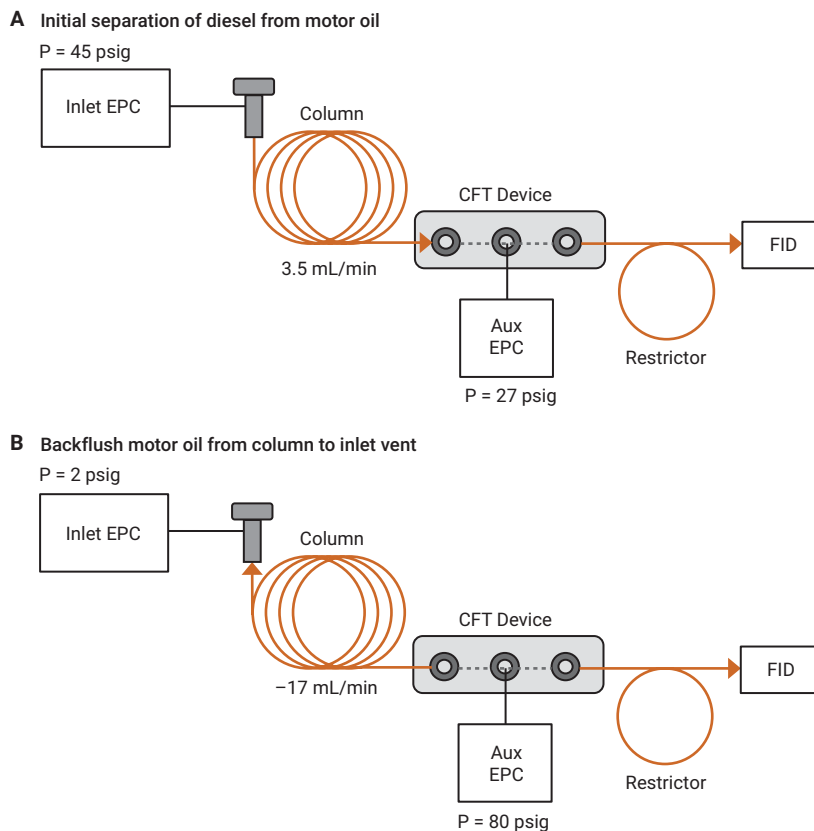
A Initial separation of diesel from motor oil
P = 45 psig

B Backflush motor oil from column to inlet vent
P = 2 psig

Figure 1. Capillary Flow Technologies (CFT) configuration used for post column backflushing.
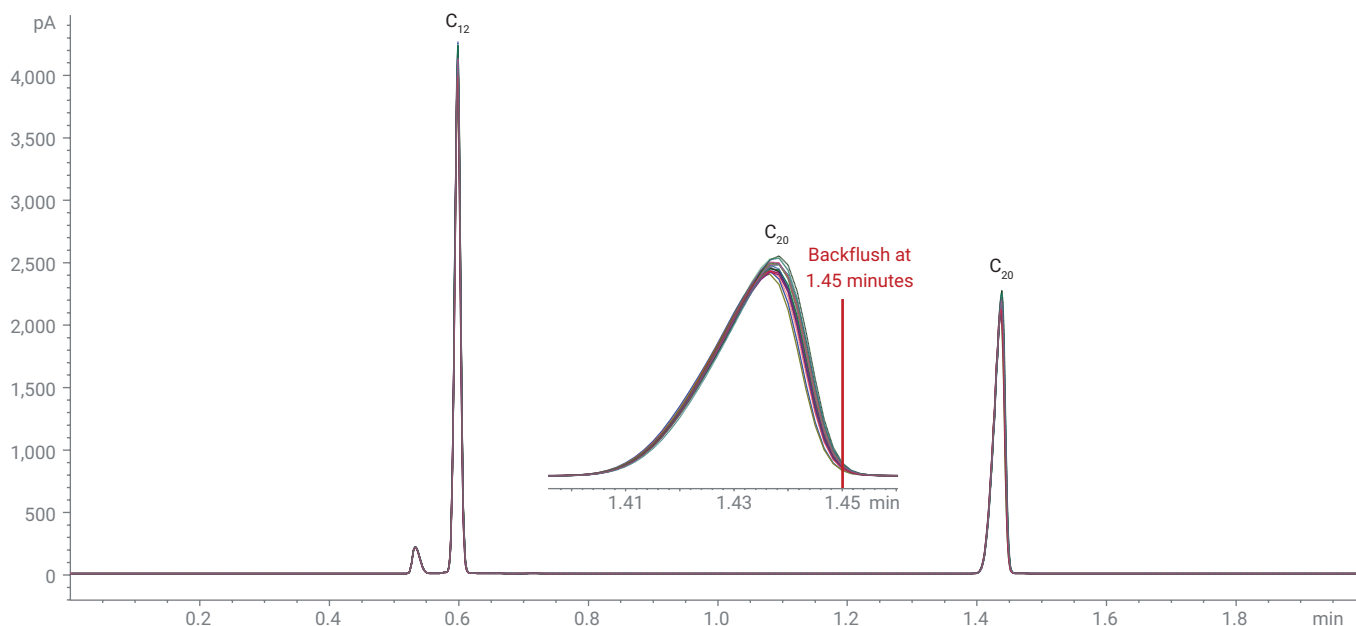
Figure 2. Ten injections of the backflush timing mix. Near complete elution of C_{20} at 1.45 minutes was used as the backflush time.

3

Instrument calibration

Calibration standards were purchased from LGC, LGC Standards USA, 276 Abby Road, Manchester, NH 03103, USA. Three standard mixtures contained 2 % (w/w), 5 % (w/w), and 10 % (w/w) aged diesel fuel in a 75 centistokes (cSt) base oil. Additionally, a base oil sample containing no diesel was used as a 0 % standard blank. All four standards were run in duplicate on the 7890 GC system using the operating parameters from Table 2.

Sample analysis

Five in-service motor oil samples were obtained from a diesel engine service facility. Each sample was known to contain different amounts of diesel fuel contamination. The samples were each analyzed 10 times to determine the average percent diesel content as well as an estimate of repeatability. Instrument blanks were implemented before and after the combined calibration and sample runs to evaluate backflush effectiveness. These blanks were run using the same GC conditions from Table 2, however instead of backflushing

the column, the oven temperature was programmed to 350 °C for several minutes to observe the elution of any residual high boiling matrix components.

Results and discussion

Figure 3 shows the chromatograms obtained with the four calibration standards. The diesel fuel response

was obtained by summing the peak area from the start of the FID response at 0.5 minutes to the backflush time at 1.45 minutes. Using these peak responses from each standard, a linear calibration curve was created, as shown in Figure 4.
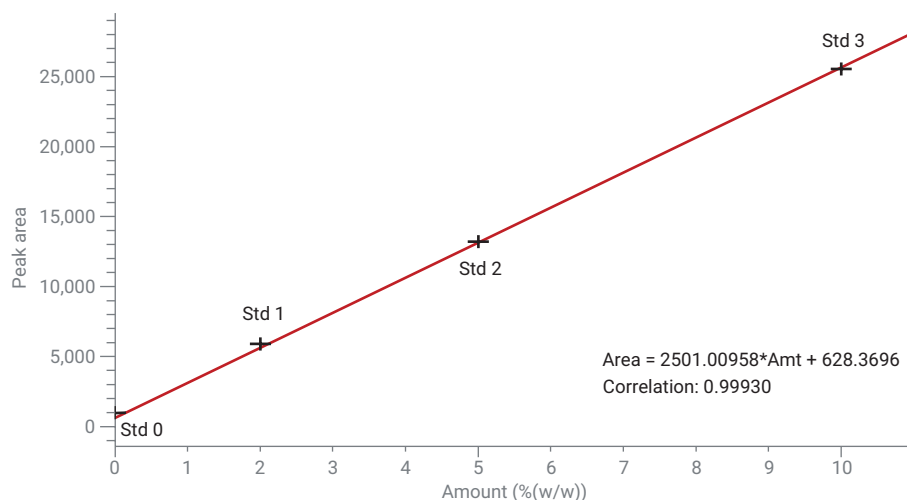

Area = 2501.00958*Amt + 628.3696
Correlation: 0.99930

Figure 4. Linear regression calibration curve for diesel fuel found in motor oil from 0 % (w/w) to 10 % (w/w).
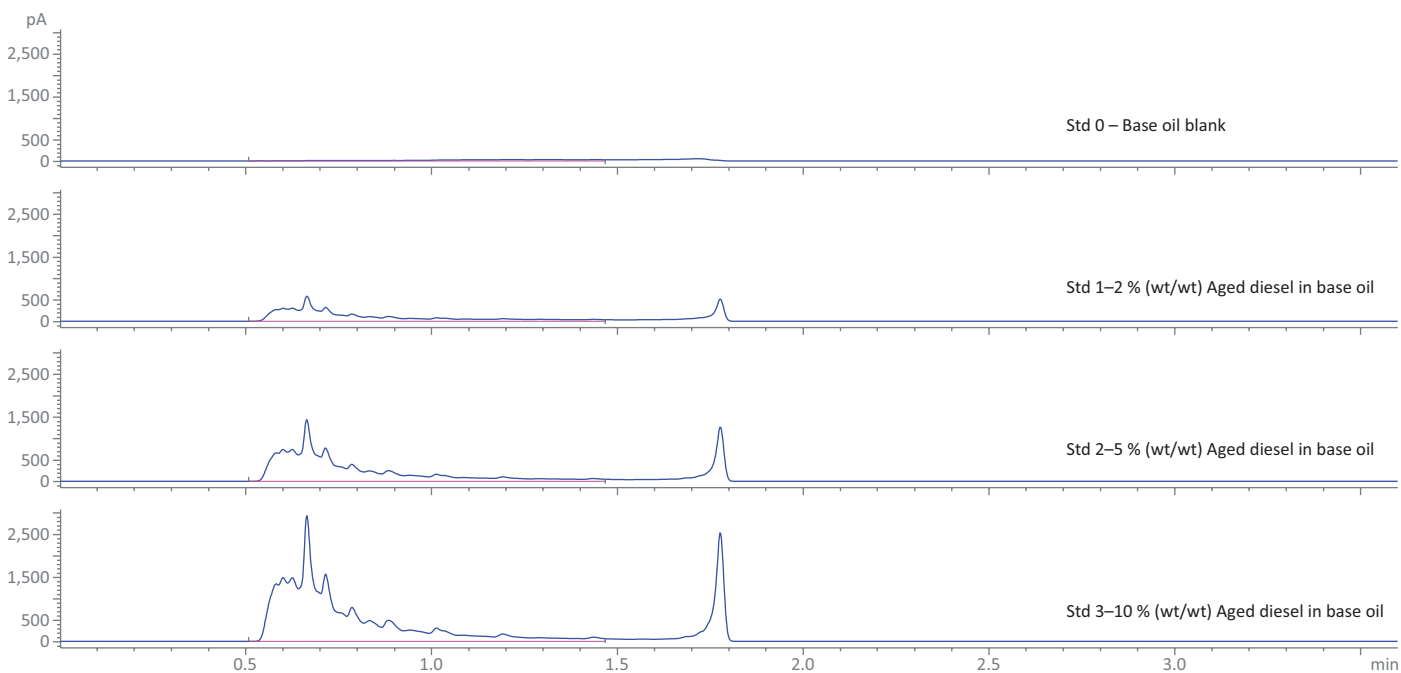

Figure 3. Chromatograms obtained from the four calibration standards prepared in 75 cSt base oil. Standard 0 is an oil blank containing no aged diesel fuel.

Figure 5 shows the chromatograms obtained from the analysis of the five in-service oil samples. Diesel fuel response for each sample run was measured in the same way as the calibration standards. Diesel fuel contents were then calculated using the linear regression curve. Table 3 shows the results obtained for the 10 analyses of each sample. High precision was calculated for each sample set with an overall average RSD of 1.09 %.

Longer term precision and system robustness was evaluated by performing 500 analyses of the 2 % (w/w) calibration sample over 10 days. Figure 6 shows the calculated diesel content for all 500 runs. The average recovery was 1.99 % (w/w) of diesel, and the RSD was 1.35 %.

Figure 7 shows the effectiveness of the backflushing technique for removing residual oil matrix from the analytical column. The prerun chromatographic baseline was nearly identical to the post run baseline obtained after 50 injections of in-service motor oil and 500 injections of the 2 % (w/w) calibration standard. This result indicated the complete removal of oil from the GC column.
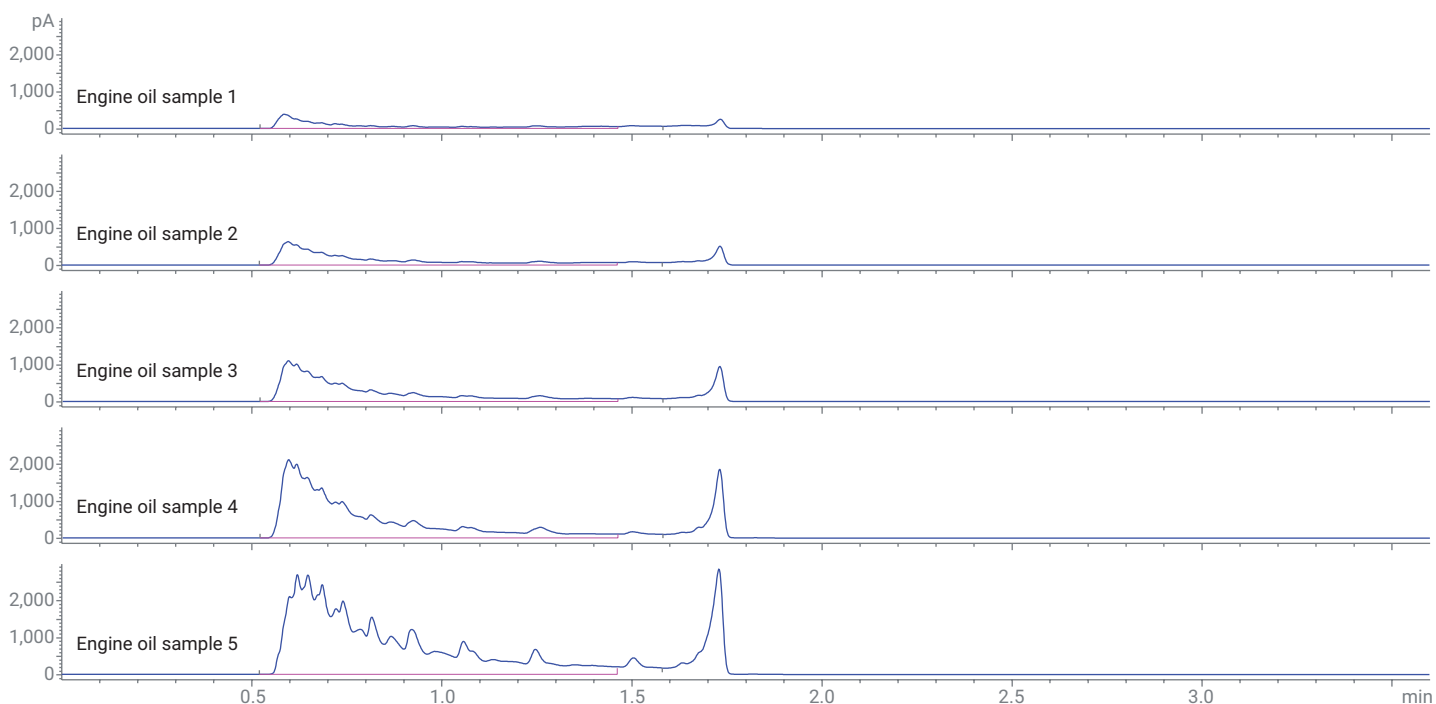

Figure 5. Analysis of diesel content for five in-service motor oil samples. For each sample, the diesel fuel hydrocarbons elute from 0.5 minutes to 1.45 minutes.

Table 3. Diesel fuel content (% w/w) found for in-service motor oils.

Run	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
1	3.1	5.7	10.1	18.9	33.7
2	3.1	5.6	10.1	18.7	34.0
3	3.2	5.8	10.2	18.9	33.7
4	3.2	5.7	10.2	19.0	33.6
5	3.1	5.8	10.1	18.8	33.5
6	3.1	5.8	10.1	18.9	34.5
7	3.2	5.8	10.2	19.2	34.5
8	3.2	5.7	10.2	18.9	34.4
9	3.2	5.7	10.1	19.3	34.2
10	3.1	5.6	10.0	19.1	33.8
Avg	3.1	5.7	10.1	19.0	34.0
Std dev.	0.046	0.075	0.065	0.180	0.377
RSD	1.45 %	1.32 %	0.64 %	0.95 %	1.11 %

Conclusions

- The 7890 Series gas chromatograph was shown to be an effective and reliable platform when measuring diesel fuel contamination for in-service motor oils according to ASTM method D7593. The GC was equipped with a CFT backflush device to easily and reliably remove the heavy oil components from the analytical column between each sample run.

- Calibration of the instrument was done using four commercially prepared standards containing aged diesel fuel in a base oil matrix. The resulting linear regression had a correlation (R^2) of 0.999, which exceeds the ASTM D7593 requirement of 0.993.

- Five in-service oil samples were each analyzed 10 times. These samples were found to contain diesel contamination from 3.1 % (w/w) to 34.0 % (w/w). The results showed exceptionally good precision for each sample, with RSDs between 0.64 % and 1.34 %. The overall average precision was 1.09 % RSD.

- Excellent long-term precision and system robustness was demonstrated by performing 500 injections of the 2 % (w/w) calibration standard over 10 days. The overall average recovery of diesel fuel was 1.99 % (w/w) with a precision of 1.35 % RSD.
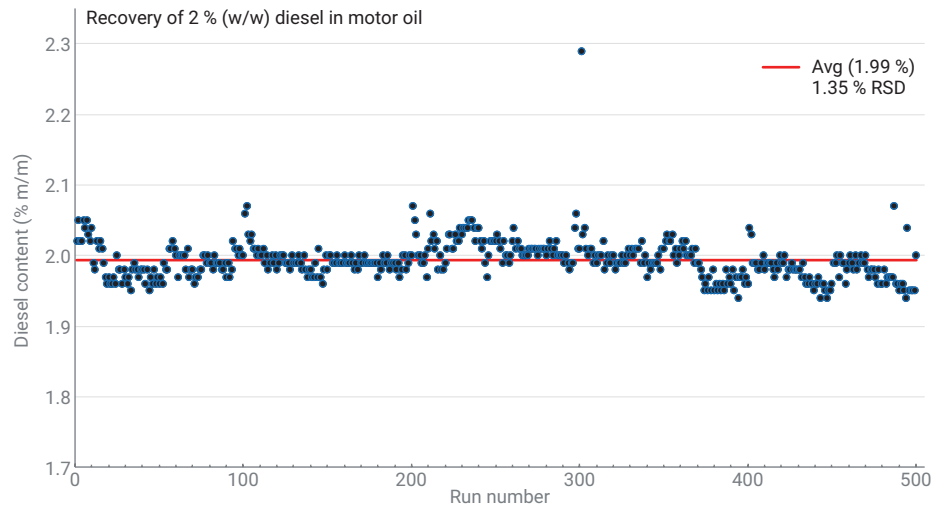

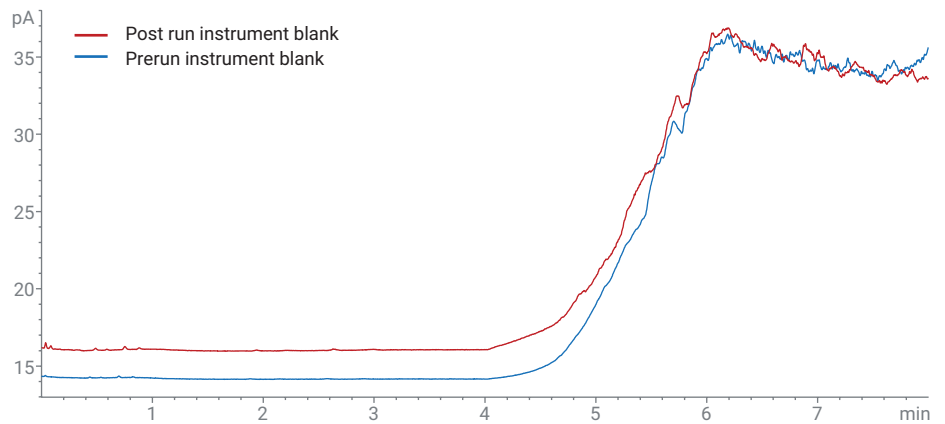**Figure 6.** Five hundred runs of the 2 % (w/w) diesel standard.

Figure 7. A comparison of the chromatographic baselines before (blue trace) and after (red trace) the analysis of 50 in-service motor oils. This shows the effectiveness of backflushing to remove any residual oil matrix from the analytical column.

- The effectiveness of the backflush procedure was demonstrated by comparing instrument blank baselines before and after the analysis of standards and samples. These baselines were nearly identical, indicating complete removal of all heavy oil components after each analysis.

Reference

1. ASTM D7593-14, Standard Test Method for Determination of Fuel Dilution for In-Service Engine Oils by Gas Chromatography, *ASTM International*, West Conshohocken, PA, **2014**, www.astm.org

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