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Application News

No. G314

Gas Chromatography

Testing the Dilution Rate of Diesel in Engine Oil in Accordance with ASTM D7593

If gasoline or diesel mixes into the engine oil, it decreases the oil viscosity and prevents achieving the proper performance as a lubricating oil. Measuring the fuel dilution rate serves as a key indicator during oil replacement, because it can determine the degradation status of engine oil.
The test methods used to measure the fuel dilution rate are specified in standards such as U.S. ASTM standards D3524, D3525, and D7593. ASTM D7593 governs gasoline, diesel, and biodiesel. This article describes an example of using an ASTM D7593-compliant backflush system to quickly analyze the dilution rate of diesel in engine oil.

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Preparing Standard Samples

Standard samples were prepared using a 75 mm^2/s (cSt)*1 base oil as the diluting solvent.
Diesel*2 was prepared by distilling to remove 10 % of the light components. Four standard samples were prepared, including a blank base oil sample, with diesel dilution rates ranging from zero to 10 %.
As a general guideline for the backflush start time, the elution time for n-C_{12}*3 was specified for gasoline, the n-C_{20} elution time*4 for diesel, and the n-C_{21} elution time*5 for biodiesel. To confirm elution times, a 0.1 % n-C_{20} sample was analyzed, which was prepared by dilution with 75 cSt base oil. Based on the elution times determined from that analysis, the backflush time was set to 1.8 minutes. Analytical conditions are indicated in Table 1.

*1: CONOSTAN brand
*2: Kanto Chemical Co.,Inc.
*3: FUJIFILM Wako Pure Chemical Corporation, Wako special grade
*4: Tokyo Chemical Industry Co., Ltd., 99.5 % or higher
*5: Tokyo Chemical Industry Co., Ltd., 99.0 % or higher

System Configuration and Analytical Conditions

The backflush system includes a specialized element connected to the column outlet and an APC electronic flow controller that controls the column outlet pressure. To backflush the column after target components are detected, the APC pressure is increased and the injection port pressure is simultaneously decreased to reverse the carrier gas flow and discharge unwanted high boiling point components out via the split vent at the injection port (Fig. 1).

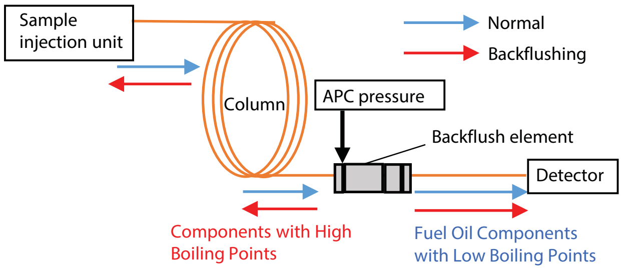

Fig. 1 Overview of Backflush System

Table 1 Analytical Conditions for Diesel

Mode :	Nexis™ GC-2030 AF/AOC-20i
Column :	SH-Rxi™-1ms (15 m × 0.25 mm I.D., df = 0.25 µm) Flow Restrictor (500 mm × 0.15 mm I.D)
Column Temp. :	225 °C (4 min)
Injection Temp. :	350 °C
Carrier Gas :	N_2, 2.3 mL/min
Total Flow :	105.3 mL/min
Purge Flow :	3 mL/min
Injection Method :	Split -1.0 (Split Flow 100 mL/min)
Carrier Gas Controller :	Constant pressure mode
Injection Pressure :	285.7 kPa (1.8 min) – 20.0 kPa
APC Pressure :	210.0 kPa (1.8 min) – 250.0 kPa
Detector :	FID
Detector Temp. :	350 °C
Injection Volume :	0.1 µL *6

*6: Syringes for OCI (P/N 227-35002-01) were used.
CS_2 was used as a rinsing solvent, rather than using samples for rinsing.
Plunger aspiration speed was slow.
Pumping was performed zero times.
The insert wool was positioned 18 mm from the top.

Chromatogram of Standard Samples

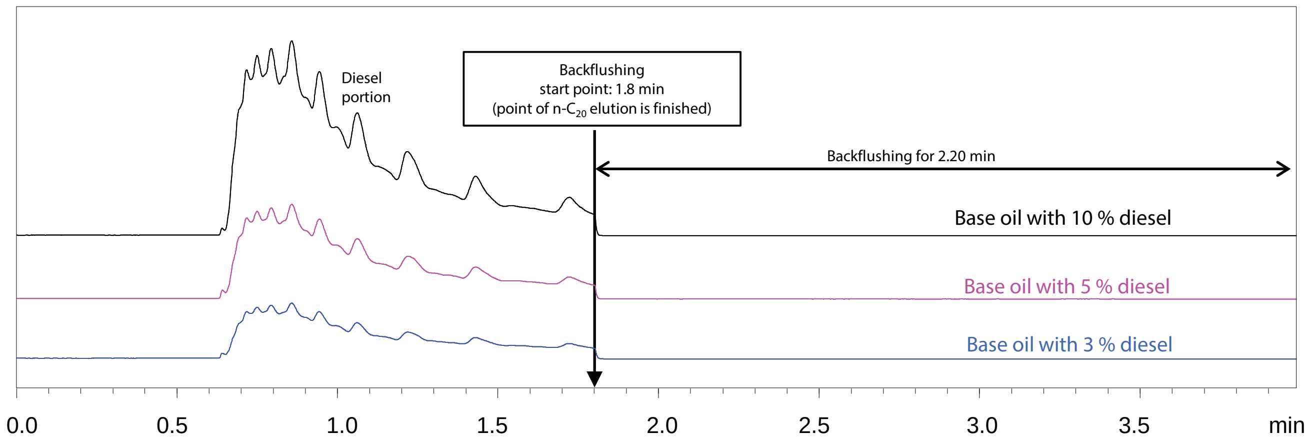

Fig. 2 Chromatogram of Standard Samples

Chromatogram of Engine Oil Containing Diesel

Fig. 3 shows a chromatogram measured from engine oil that contains diesel. Backflushing high boiling point oil components enabled a significantly shorter analysis time of four minutes. No engine oil peaks were detected in results from analyzing a carbon disulfide (CS_2) blank sample after backflushing. It confirms that backflushing was able to efficiently remove unwanted high boiling point components.

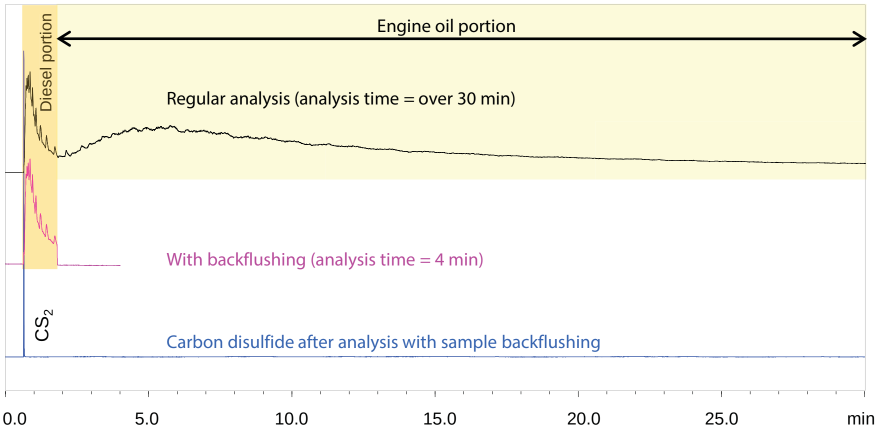

Fig. 3 Chromatogram of Engine Oil Containing Diesel

Linearity of Calibration Curve

The calibration curve in Fig. 4 was prepared based on results from using the analytical conditions in Table 1 to analyze standard samples.
The calibration curve was prepared for the zero to 10 % diesel range. The results indicated good linearity, with a contribution rate R^2 0.999 or higher.

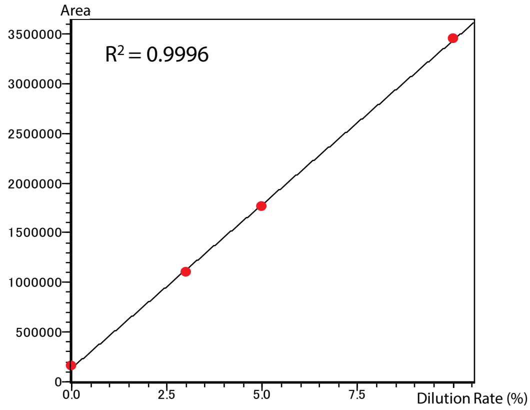

Fig. 4 Calibration Curve Linearity

Repeatability of Dilution Rates

The repeatability of diesel dilution rates in engine oil calculated from the calibration curve in Fig. 4 are shown in Table 2. Excellent repeatability %RSD (n = 10) results were obtained. The results also confirm that all within-laboratory accuracy values satisfy tolerances required by standards.

Table 2 Repeatability %RSD (n = 10) of Diesel Dilution Rates (%)

	Sample1	Sample2	Sample3	Sample4	Sample5
1	2.94	4.86	7.07	8.93	10.26
2	2.98	4.95	7.12	8.92	10.03
3	2.96	4.80	7.17	8.90	10.11
4	2.94	4.85	7.08	8.89	10.17
5	3.00	4.94	7.19	8.91	10.06
6	2.97	4.81	7.07	9.06	10.15
7	3.00	4.75	7.00	8.98	10.13
8	3.00	4.78	7.03	8.96	9.95
9	2.97	4.85	6.95	8.83	9.95
10	2.94	4.89	6.96	9.13	9.98
Average	2.97	4.85	7.06	8.95	10.08
%RSD	0.84	1.35	1.15	0.98	1.02

Long-Term Stability

Results from continuous analysis are shown in Fig. 5. The long-term system stability was evaluated by analyzing a 3 % dilution standard sample 600 times. Maintenance for septa and other consumables was performed after every 200 analyses. The %RSD repeatability of dilution rates after 600 analyses was 2.3 %, which indicates excellent long-term stability.

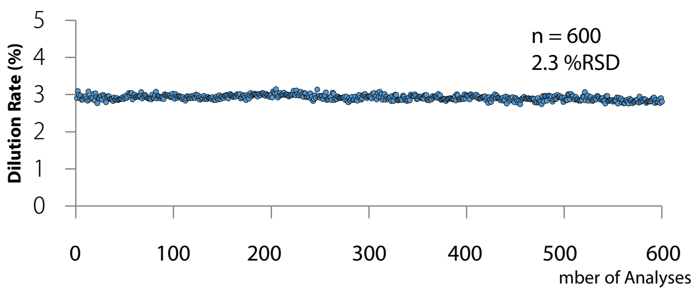

Fig. 5 Long-Term Continuous Analysis of Base Oil with 3 % Diesel Content

Summary

Using the backflushing method enabled high-throughput analysis with cycle times of 5 minutes or less. With the Nexis GC-2030, two analysis lines with backflushing can be installed, so that each GC unit can process twice as many samples.
Furthermore, accuracy levels required by applicable standards were achieved using the indicated analytical conditions and a nitrogen carrier gas, without involving dilution with solvents or other pretreatment steps. The labor savings and lower cost carrier gas help reduce laboratory costs as well.
Application News bulletins related to fuel dilution rates are indicated in the table of references below.

Reference Document
ASTM D7593-14

List of References

Standard	Item Analyzed	Application News No.
D3524	Diesel	G310
JPI-5S-23	Diesel	G311
D3525	Gasoline	G312
JPI-5S-24	Gasoline	G312
D7593	Gasoline	G313
	Diesel and biodiesel	G314

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