Evaluation of long-term stability of analysis of fuel dilution for engine oils using a backflush GC system

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Introduction

Fuel contamination such as gasoline/diesel in engine oil is known to decrease the viscosity of lubricating engine oil. This contamination also known as fuel dilution leads to a shortened lifetime of engine oil. For this reason, the extent to which a fuel is diluted (i.e. contaminated) is an important indicator of engine oil conditions.

Test methods used to measure the fuel dilution rate are standardized by U.S. ASTM D3524, D3525 and D7593. ASTM D7593 regulates gasoline, diesel oil and biodiesel. In this experiment, a long-term stability of Shimadzu GC was examined in the analysis of diesel fuel dilution in engine oil using a backflush system according to ASTM D7593.

Preparing Standard Samples

75 mm^2/s (cSt) base oil*1 was used to dilute diesel oil*2.

The diesel oil was distilled to remove 10 % of its light components before being diluted with the base oil. Four standards, including a blank base oil, were prepared with diesel oil dilution rates ranging from 0 to 10 %(w/w).

Retention time for 0.1 % n-C20*3 in the base oil was used as a guideline for the backflush start time (i.e. 1.8 minutes).

＊1 : CONOSTAN brand
＊2 : Kanto Chemical
＊3 : Tokyo Chemical Industry Co., Ltd., 99.5 % or higher

Methods（System Configuration and Analytical Conditions)

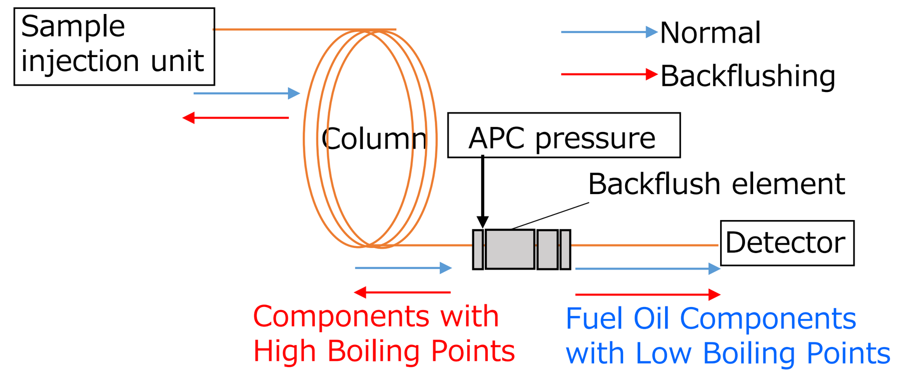

Fig. 1 Overview of Backflush System

The backflush system employs a device connected to the column outlet and APC (Shimadzu electronic pressure controller that regulates column outlet pressure). To backflush the column after target components have eluted, APC pressure is increased while GC inlet pressure is decreased to reverse a carrier gas flow and discharge unwanted high boiling components via the split vent in the injection port (Fig. 1).

Instruments

Fig.2 Nexis™ GC-2030 AF

Table 1 Analytical Conditions for Diesel

Mode :	Nexis™ GC-2030 AF/AOC-20i (Fig.2)
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 *4

*4: 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.

Result (Chromatogram and Linearity of Calibration Curve)

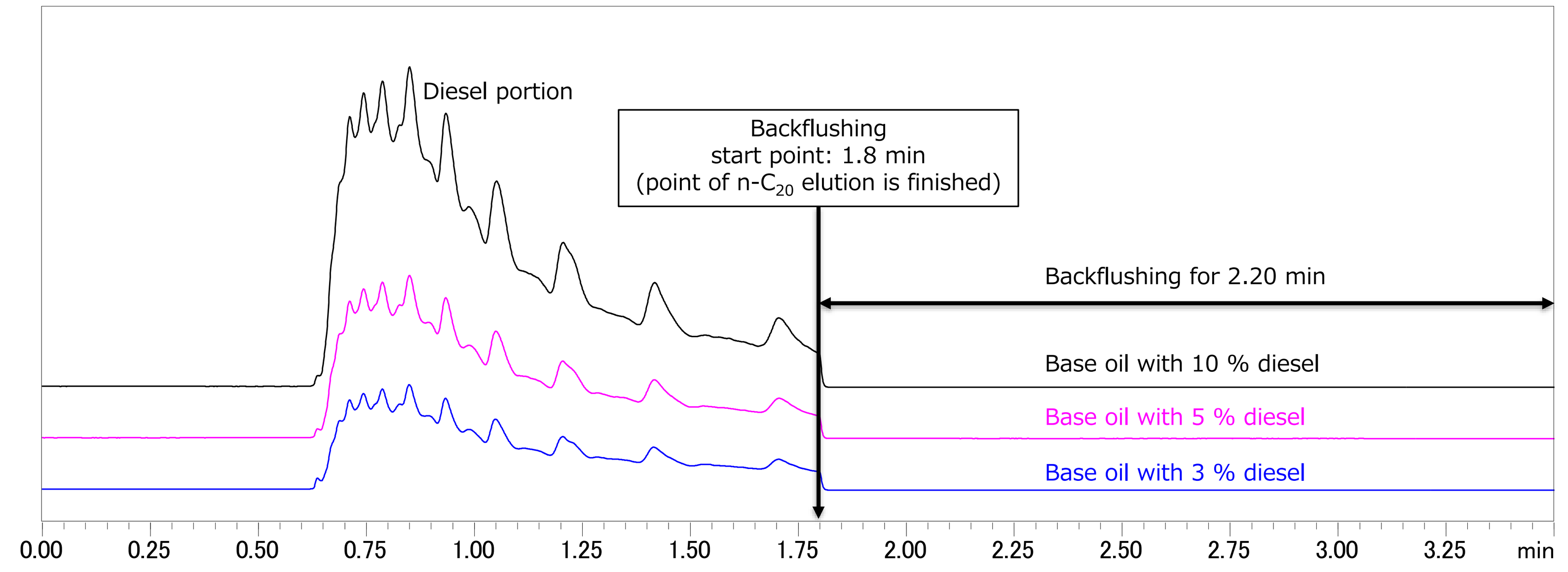

Fig.3 Chromatogram of Standard Samples

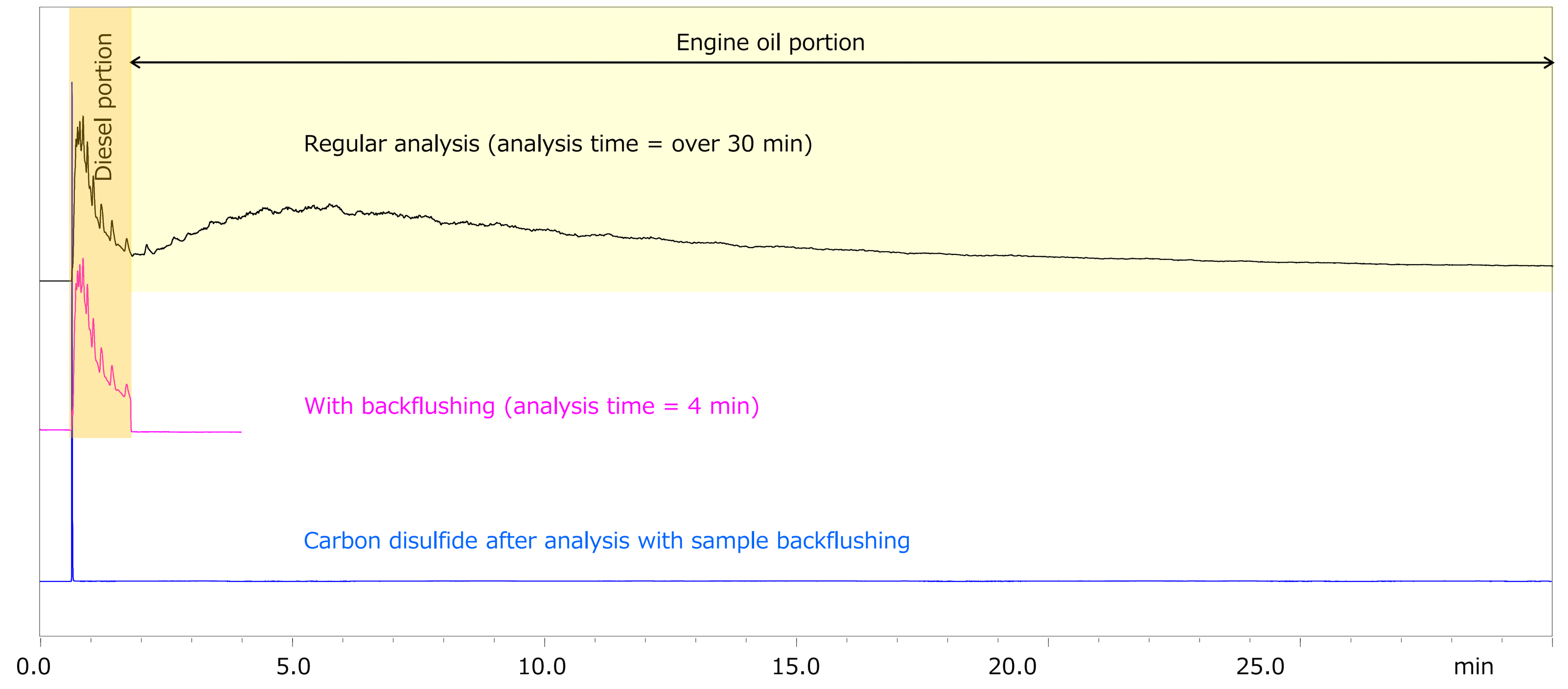

Fig. 4 Chromatogram of Engine Oil Containing Diesel

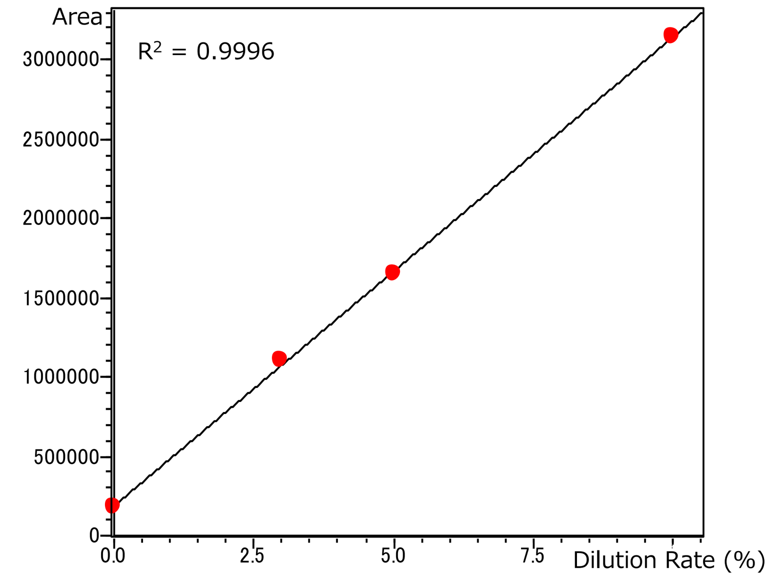

Fig.5 Calibration Curve Linearity

Fig.4 shows chromatograms measured from engine oil that contains diesel. Backflushing high boiling oil components enabled a significantly shorter analysis time (i.e. 4 minutes) compared to otherwise possible (i.e. > 30 minutes). No engine oil components from the previous backflush run were detected in a carbon disulfide (CS_2) blank sample. It confirms the backflushing was able to efficiently remove unwanted high boiling components. The calibration curve in Fig.5 was obtained based on the analytical conditions listed in Table 1. The linearity was acceptable with $R^2 \geq 0.999$ within the range of 0 to 10 %(w/w) diesel oil in the base oil.

Result (Long-Term Stability)

The long-term stability of the system was evaluated using 3 %(w/w) diesel standard and the following two tests were designed: one by analyzing a batch of 550 samples consecutively and repeating the batch 3 times (i.e. 550 x 3 samples in total) and the other by analyzing a batch of 200 samples consecutively and repeating the batch 3 times (i.e. 200 x 3 samples in total). Repeatability of both tests were calculated in %RSD and compared against one another.

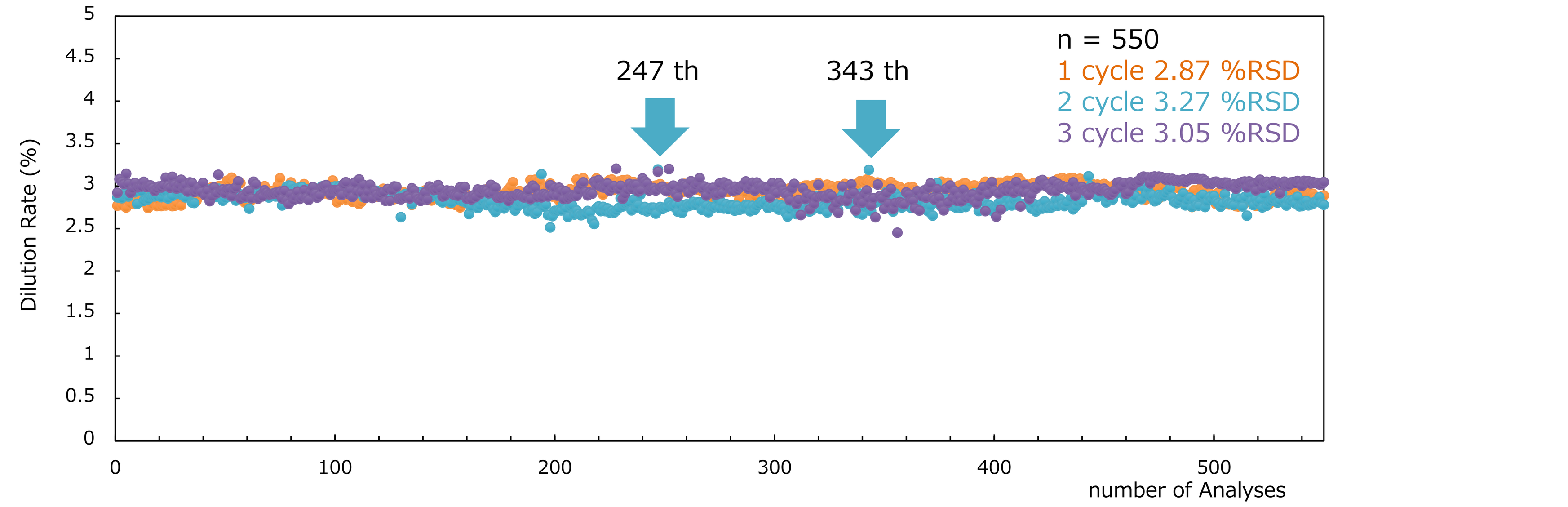

Fig.6 Long-Term Continuous Analysis of Base Oil with 3 % Diesel Content (n = 550)

In the 550 x 3 test, repeatability were 2.87 % in % RSD for the first cycle of 550 runs, 3.27 % for the second and 3.05 % for the third respectively (Fig.6). A closer look in Fig. 6 shows the 247th and 343rd points of the 2nd cycle failing the repeatability tolerance set by ASTM D7593. In other words, the system is capable of maintaining satisfactory repeatability at least up to 200 consecutive runs.

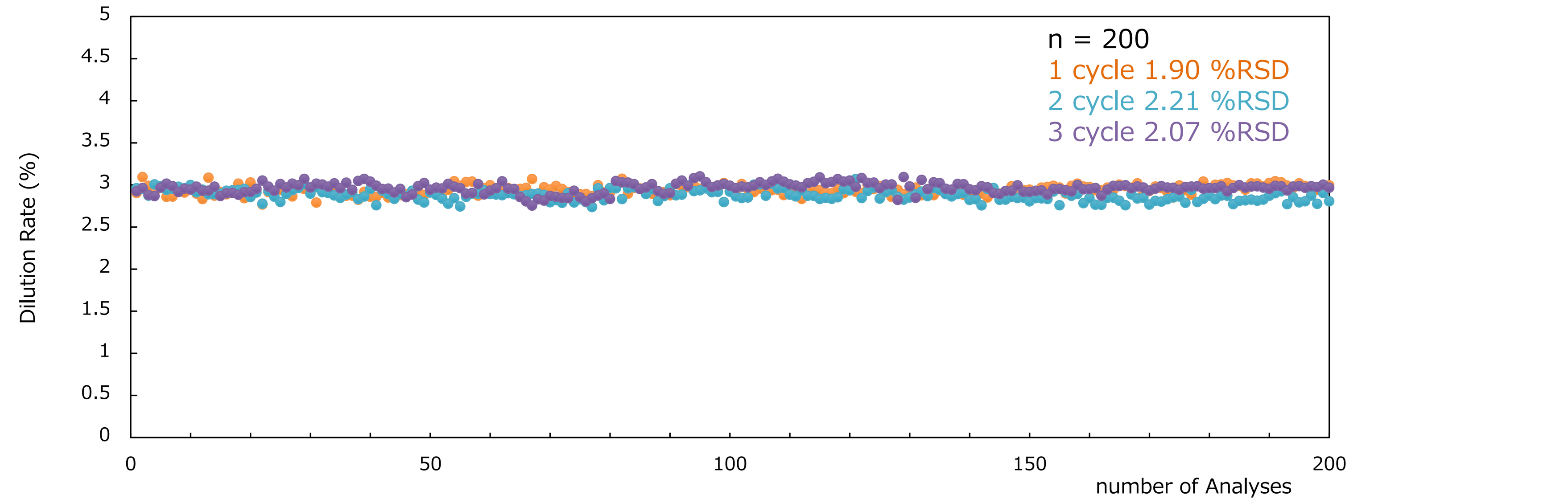

Fig.7 Long-Term Continuous Analysis of Base Oil with 3 % Diesel Content (n = 200)

In the 200 x 3 test, % RSD of fuel dilution was 1.90 % for the first cycle of 200 runs, 2.21 % for the second and 2.07 % for the third. All results in the three cycles met repeatability tolerance according to ASTM D7593.

The average % RSD (i.e. 2.06%) in the 200 x 3 test was approximately 1 %(absolute) lower than that of the 550 x 3 test (i.e. 3.06%).

Conclusion

Using the Shimadzu backflush system enabled a high-throughput analysis with cycle times of less than 5 minutes. Accuracy requirement set by standardized method ASTM D7593 was met with a nitrogen carrier gas using the analytical conditions listed in Table 1 and without much sample preparations (e.g. solvent dilution). Labor saved in forgoing sample pretreatments combined with a low cost of N_2 present more economical options for laboratories.

Last but not least, the two long-term stability tests proved this system is capable of providing excellent long-term stability without maintenance for approximately 200 consecutive analyses.

Reference Document : ASTM D7593-14