SHIMADZU

Detailed analysis of lubricant deterioration using multiple analyzers

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1. Introduction

Engine lubricants play an important role in lubrication, cooling, cleaning, and rust prevention for vehicles, construction machinery, ships, airplanes, and other equipment with internal combustion or turbine engines. As the lubricant deteriorates through use, its performance will decline and the inside of the engine can wear, leading to a decrease in service life and potential malfunction. Lubricants deteriorate due to decomposition and chemical changes of oil components and additives caused by physical and thermal stresses, as well as contamination by metal wear particles and incorporated fuel. Therefore, it is recommended to analyze the lubricant throughout its lifespan to assess its quality, utility, and remaining service life. These analyses can be accomplished with a number of instruments, including FTIR, GC, and ICP-AES.

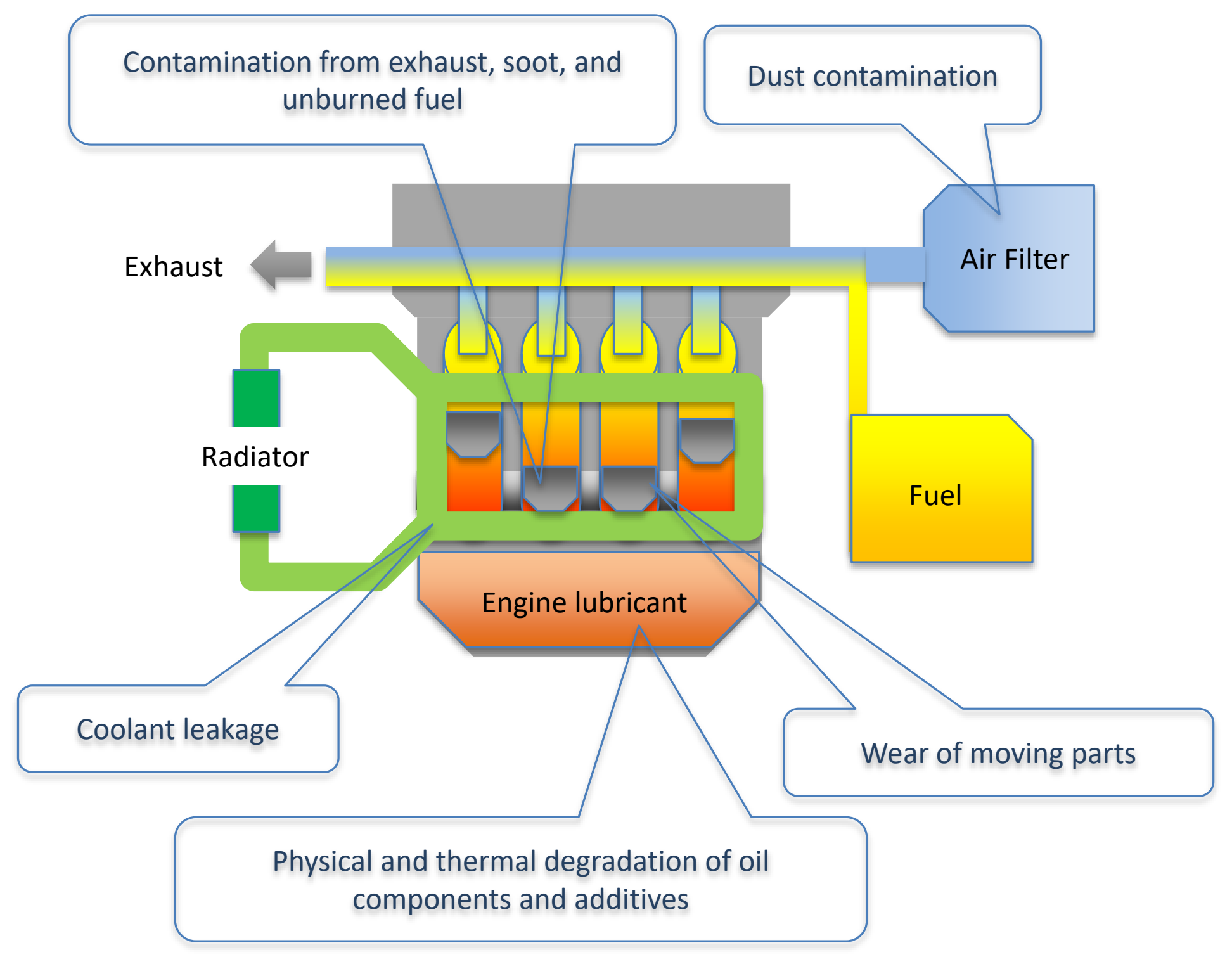

Figure 1: Typical causes of engine lubricant deterioration

Condition Assessment		Instrument	Standard(s)
Deterioration	Oxidation	FT-IR	ASTM E2412
	Nitration		
	Sulfate by-products		
Contamination	Water	FT-IR	ASTM E2412
	Soot		
	Gasoline	GC	ASTM D3525 ASTM D7593
		FT-IR	ASTM E2412
	Diesel	GC	ASTM D3524 ASTM D7593
		FT-IR	ASTM E2412
	Coolant (B, Na, K)	ICP-AES	ASTM D5185
		FT-IR	ASTM E2412
	Antifreeze (Na)	ICP-AES	ASTM D5185
	Dust (Si)		
	Seal materials (Si)		
Wear	Metals (Al, Fe, Cu, Cr, Ni, Zn, etc.)	ICP-AES	ASTM D5185
Additives	Anti-oxidant (Zn, Cu, B)	ICP-AES	ASTM D4951
		FT-IR	ASTM E2412
	Anti-wear agents (B, Cu, K, S, Zn, etc.)	ICP-AES	ASTM D4951
		FT-IR	ASTM E2412
	Detergent inhibitors (Ba, Mg, Ca, etc.)	ICP-AES	ASTM D4951
	Corrosion inhibitors (Ba, Zn)		
	Anti-rusting agents (K, Ba)		
	Friction modifier additives (Mo)		

Table 1: Examples of ASTM lubricant analysis methods

ASTM specifies methods for evaluating the deterioration of lubricants. Here, we demonstrate the analysis and evaluation of lubricant deterioration, contamination, wear, and additives by an analysis method based on ASTM standards using a Fourier transform infrared spectrometer (FT-IR), gas chromatograph (GC), and inductively coupled plasma atomic emission spectrometer (ICP-AES).

2. Lubricant deterioration analysis using compact FT-IR

Infrared spectroscopy provides spectral data that reflect the molecular structure of a substance. FT-IR analysis demonstrate deterioration due to compositional changes such as sulfation, nitration, and increase in carbonyl groups due to oxidation. It also provides information about contamination by soot and other particulates as well as increases in hydroxyl groups due to moisture contamination. In addition, in the case of lubricants containing anti-oxidants or anti-wear components, it is possible to determine the degradation of additives by assessing the spectral peak generated by those components. In this study, we evaluated lubricant deterioration using a compact and high-performance FT-IR and an easy-to-use liquid analysis cell.

IRSpirit offers the highest S/N ratio in its class and high reliability using the technology inherited from the high-end model. The dedicated IR Pilot program simplifies routine analyses for all users. The combination of Pearl Liquid Analyzer and IRSpirit makes it possible to analyze lubricating oil with ease.

- Space-efficient with high expandability
- Easier to disassemble and clean than traditional liquid cells
- Accurate transmission pathlength

Figure 2: Combination of IRSpirit and Pearl Liquid Analyzer

2-1 Method

Used oil and new oil of Sample A and Sample B were analyzed by the combination system of IRSpirit and Pearl with 0.1 mm optical pathlength cell. Details of Sample A and Sample B are as follows.

Table 2: Sample Details

Sample A	Sample B
10W-60 gasoline engine lubricant Travel distance 3000 km Period of use: 3 months Used at high RPM range	0W-20 gasoline engine lubricant Travel distance 5000 km Period of use: 1 year Used at low RPM range

2-2 Results

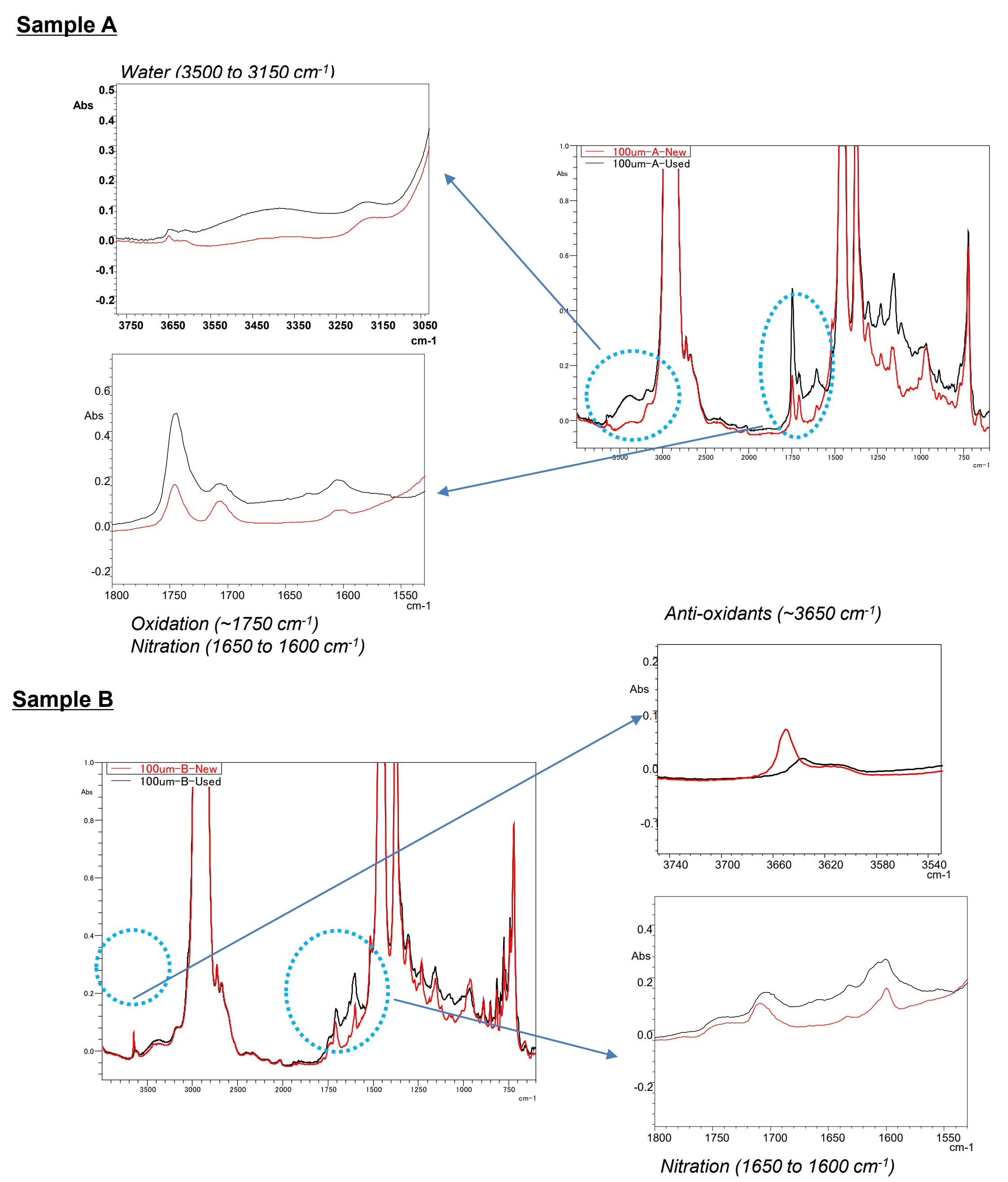

Figure 3: Spectra of Sample A and Sample B

As a result of FT-IR analysis, water contamination and deterioration due to oxidation and nitration were confirmed in Sample A. In Sample B, the amount of the anti-oxidant decreased, and no change in the spectrum indicating oxidation deterioration was observed. Presumably, oxidation of the oil was prevented by the anti-oxidant.

The analysis of lubricants by FT-IR does not require sample pretreatment, and the Pearl Liquid Analyzer makes it easy and quick to clean the cells for each analysis. In addition, data conforming to ASTM E2412 can be acquired with high reproducibility by the precisely maintained optical pathlength. However, it is difficult to identify certain contaminants, such as fuel and coolant, at low concentrations because the FT-IR method is not as highly sensitive as other techniques. The GC and ICP-AES methods are applicable to these detailed analyses.

3. Rapid analysis of fuel dilution of lubricants by GC

If fuel such as gasoline or diesel is mixed in the engine lubricant, the viscosity decreases and the performance of the lubricant deteriorates. Therefore, fuel dilution is regarded as an indicator of the need for changing the lubricant. To accurately measure fuel dilution of engine lubricants, a GC with flame ionization detection (GC-FID) is used. However, when samples containing high boiling point compounds are analyzed, analysis requires more time, which reduces productivity. ASTM D7593 employs GC-FID and backflush methods to enable rapid analysis of fuel dilution. This system can be applied to dilution by gasoline, diesel, and biodiesel, and rapid analysis is possible by backflushing heavy components off of the column.
In this study, gasoline or diesel dilution of engine lubricants was analyzed using a GC backflush system and nitrogen carrier gas for cost-effective analysis.

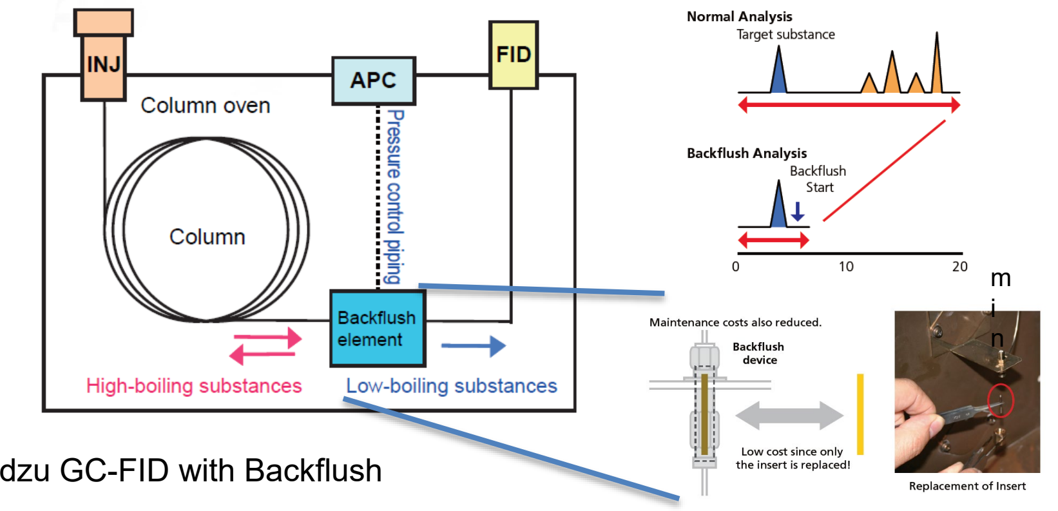

Figure 4: Shimadzu GC-FID with Backflush

3-1 Method

Fuel dilution of engine lubricants was analyzed by GC-2030 Gas Chromatograph with backflush system. Backflush timing was set based on the retention time of n-C12 for gasoline and n-C20 for diesel.

Table 3: Analytical conditions

Instrument:	Nexis™ GC-2030 AF/AOC-20i
Column:	SH-Rxi™-1ms (15 m× 0.25 mm I.D., df = 0.25 µm)
	Restrictor (500 mm× 0.15 mm I.D.)
Column Temp.:	225 ℃ (For gasoline 2 min, For diesel 4 min)
Injection Temp.:	350 ℃
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 (For gasoline 0.74 min, For diesel 1.8 min) – 20.0 kPa
APC Pressure:	210.0 kPa (For gasoline 0.74 min, For diesel 1.8 min) – 250.0 kPa
Detector:	FID Detector Temp.: 350 ℃
Injection Volume:	0.1 µL

3-2 Results

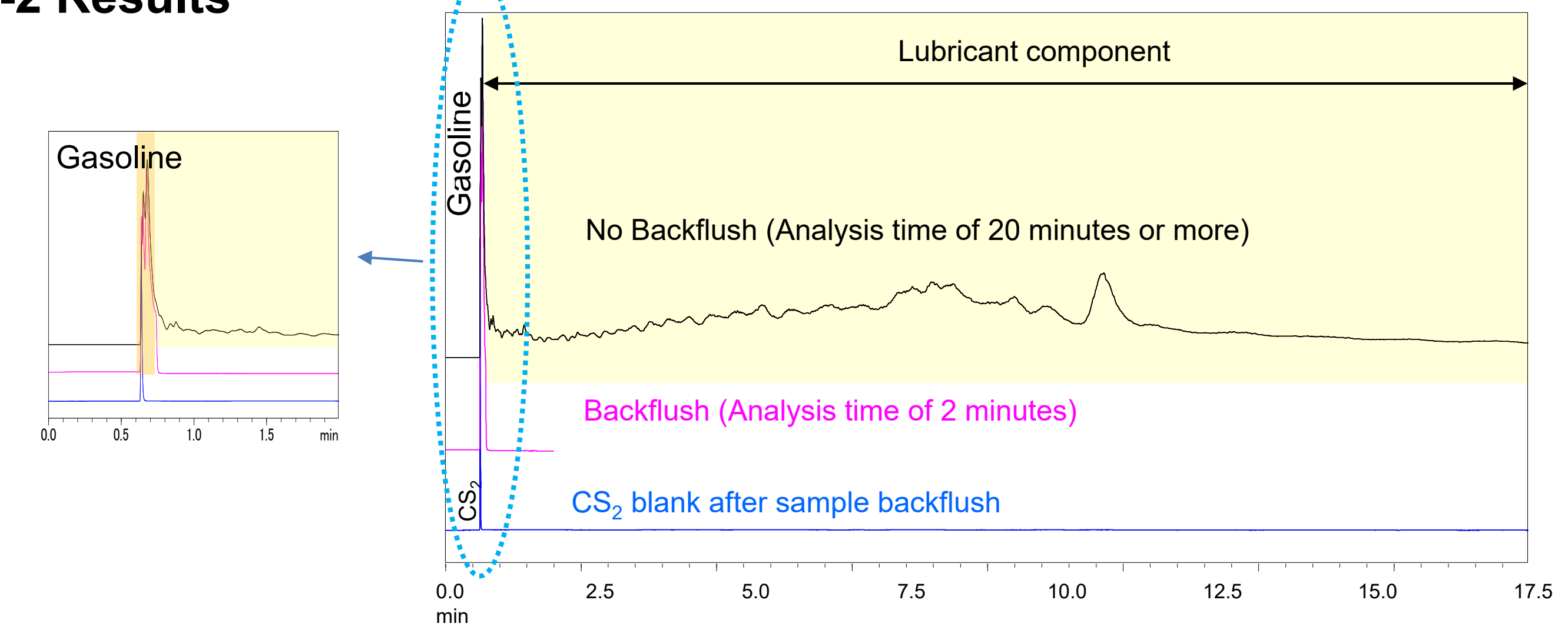

Figure 5: Chromatograms of gasoline dilution of lubricants

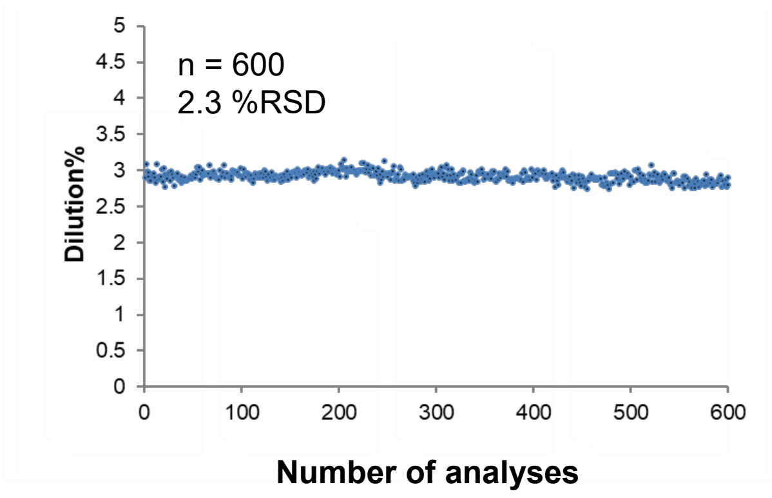

Figure 6: Long-term continuous analysis of base oil containing diesel

The backflush system can analyze gasoline dilution in 2 min and diesel dilution in 4 min. The sample is analyzed by placing it in a vial without pretreatment, such as dilution with a solvent. Productivity can be doubled by using a dual line backflush analysis line.
This system has good reproducibility satisfying the ASTM D7593 with inexpensive nitrogen carrier gas. The reproducibility %RSD of the dilution rate was 2.3% in the 600 analysis with the maintenance of consumables such as septum in every 200 analyses, showing excellent long-term stability. Especially in a quality control department, low cost and rapid analysis are required for routine analyses to process a great number of samples. In this work, we demonstrate cost-effective, rapid analysis methods for the fuel dilution of engine lubricants using Shimadzu's GC-2030 and backflush system.

Table 4: Repeatability of gasoline dilution (%, n = 10)

	Sample1	Sample2	Sample3	Sample4	Sample5
1	2.58	2.97	4.95	1.14	4.08
2	2.52	3.01	4.97	1.16	4.10
3	2.50	3.01	5.11	1.16	4.11
4	2.54	2.97	4.98	1.15	4.13
5	2.51	2.98	5.01	1.13	4.18
6	2.52	2.94	4.99	1.17	4.04
7	2.55	2.97	4.97	1.14	4.08
8	2.53	2.95	4.94	1.12	4.16
9	2.49	3.01	4.98	1.14	4.11
10	2.57	2.92	4.92	1.12	4.07
Avg	2.53	2.97	4.98	1.14	4.11
%RSD	1.15	1.04	1.04	1.49	1.03

Table 5: Repeatability of diesel dilution (%, n = 10)

	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
Avg	2.97	4.85	7.06	8.95	10.08
%RSD	0.84	1.35	1.15	0.98	1.02

4. Analysis of Additive Elements, Wear Metals, and Contaminants in Used Lubricants using ICP-AES

The analysis of wear and additive metals in lubricants is useful information for estimating the deterioration of lubricating oil and the state of the engine. As an oil is used, it entrains particles of metal from the engine. Also, numerous organometallic additives are added to lubricants to enhance performance. It is important to assess the concentration of various elements to assess engine wear and performance of additives. According to ASTM D5185 and D4951, ICP-AES with organic solvent dilution is specified for measurement of additive elements, wear metals, and contaminants present in used lubricants.

Here, using the Shimadzu ICPE-9820 simultaneous ICP atomic emission spectrometer, we conducted analysis of 22 elements specified according to ASTM D5185, including the 9 elements described in ASTM D4951, in used and unused lubricants diluted in organic solvent. The ICPE-9820 provides stable analytical results for organic solvent samples without requiring the flow of oxygen through the system.

4-1 Method

Measurement was conducted using the Shimadzu ICPE-9820 ICP-AES. The measurement conditions are shown in Table 6. When conducting analysis of organic solvent samples with most conventional ICP instruments, oxygen must typically be introduced into the plasma torch to prevent carbon deposition on the torch. With the Shimadzu ICPE-9820, however, the adoption of a plasma torch that suppresses carbon deposition has nearly completely eliminated the deposition of carbon originating from the sample and organic solvent. Therefore, even in analysis of organic solvent samples such as kerosene, xylene, and MIBK, the ICPE-9820 eliminates the need to introduce oxygen to suppress the precipitation of carbon. Also, since the Shimadzu ICPE-9820 uses a vacuum spectrometer, elements such as S with a wavelength in the vacuum ultraviolet region can be analyzed at a low running cost without the need for costly high-purity gas, typically required with a purge-type spectrometer.

Table 6: Analytical conditions

Instrument:	ICPE-9820
Radio Frequency Power:	1.40 kW
Plasma Gas Flowrate:	16.0 L/min
Auxiliary Gas Flowrate:	1.40 L/min
Carrier Gas Flowrate:	0.70 L/min
Sample Introduction:	Nebulizer, 10UES
Spray Chamber:	Organic solvent chamber
Plasma Torch:	Torch
Observation:	Radial

Used automotive lubricants (Used for approximately 4000 km) and new lubricants were used for analysis samples. To prepare the sample, approximately 10 g of each sample was weighed and then diluted with 100 mL of kerosene. The standard solutions were prepared by appropriately diluting the SPEX oil-based 21-element mixed standard solution (500 µg/g) and SPEX oil-based single-element standard solution (5000 µg/g), and heavy oil sulfur content standard sample (1.05 % by weight) into kerosene.

In addition, an oil-based Y (yttrium) single-element standard solution (5000 µg/g) was diluted with kerosene and added to all the samples as the internal standard element so at a fixed concentration in all the samples and standards.

For validation of the measurement values, the above standard solution was added to the used lubricating oil to prepare a 5 mg/L solution to serve as a low-concentration element spike-and-recovery test sample. In addition, for high-concentration elements, the used lubricant was diluted 50-fold with kerosene to prepare a diluted test sample.

4-2 Results

Table 7 shows the analytical results. Recoveries near 100% were obtained in the dilution test for the high-concentration elements and the spike-and-recovery test for the low-concentration elements. The analytical results obtained in analysis of the unused lubricants are also listed for reference. Using the ICPE-9820, dissolved elements in used lubricants can be analyzed precisely without the introduction of oxygen.

Table 7: Analytical results of lubricants

Element	Used lube (µg/g)	Used lubricant spike recovery (%)	Used lube dilution test (%)	Unused lube (µg/g)	Detection limit (µg/g)
Ag	<	100	-	<	0.02
Al	10	101	-	6.51	0.3
B	65.9	-	98	121	-
Ba	0.123	101	-	<	0.02
Ca	3970	-	98	2250	-
Cr	1.03	101	-	<	0.01
Cu	0.65	100	-	<	0.02
Fe	10.8	101	-	0.43	0.01
K	22.1	99	-	<	0.6
Mg	10.4	100	-	5.48	0.02
Mn	0.618	101	-	0.139	0.002
Mo	184	-	98	183	-
Na	2.5	100	-	<	0.4
Ni	<	102	-	<	0.05
P	756	-	99	731	-
Pb	<	100	-	<	0.5
S	3980	-	100	3810	-
Si	8.96	103	-	5.07	0.03
Sn	<	100	-	<	0.5
Ti	<	100	-	<	0.01
V	<	103	-	<	0.02
Zn	872	-	97	882	-

Spike recovery rate (%) = (C1-C2)/B× 100 (C1: Spiked sample quantitative value; C2: Non-spiked sample quantitative value; B: Spike concentration)
Dilution test (%) = I/S × 100 (I: Quantitative value of sample before dilution; S: Quantitative value of 5-fold diluted sample × 5)
Detection limit: DL = 3× σBL× κ (σBL: Standard deviation of background intensity;κ: Concentration/intensity) <: Less than the detection limit

5. Conclusions

- Useful information for the analysis of lubricant deterioration can be obtained by using FT-IR, GC and ICP-AES.
- Data conforming to ASTM E2412 can be easily obtained by combining compact IRSpirit and Pearl.
- Cost-effective analysis of fuel dilution of lubricants is possible by using GC -2030 backflush system in compliance with ASTM D7593.
- Using the ICPE-9820, dissolved elements in lubricants can be analyzed without the introduction of oxygen to generate results for ASTM D4951 and D5185.

6. References

ASTM E2412-10, ASTM D7593-14, ASTM D5185-18, ASTM D4951-14