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Application News

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Inductively Coupled Plasma Atomic Emission Spectrometry

Analysis of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oil According to ASTM D5185: ICPE-9820

Introduction

Analysis of lubricants added to engine oils such as those used in automobiles and ships is an effective as well as important way to diagnose the state of the engine and other equipment.
According to ASTM International Standard D5185 [1], inductively coupled plasma (ICP) atomic emission spectrometry with organic solvent dilution is specified for measurement of additive elements, wear metals and contaminants present in used lubricants. Also, the Japan Petroleum Institute standard JPI-5S-44-2011 stipulates the use of ICP atomic emission spectrometry in Japan for analysis of Fe, Cu, Al, Pb, Cr and Sn in used lubricating oil.[2]
Here, using the Shimadzu ICPE-9820 multi-type ICP atomic emission spectrometer, we conducted analysis of 22 elements specified according to ASTM D5185 in samples consisting of a used lubricant (commercially available automotive lubricating oil) and, as a reference, the same, but unused lubricating oil, both of which were diluted with organic solvent. The ICPE-9820, which adopts a vertically-oriented plasma torch which reduces the possibility of carbon precipitation, provides stable analytical results for organic solvent samples without requiring the flow of oxygen through the system.

Samples

- Used lubricating oil (commercially available automotive lubricant, used for approximately 4000 km)
- Same lubricating oil as above, but in unused state

Sample Preparation

Approximately 10 g of each sample was weighed and then diluted with 100 mL of kerosene. The standard solutions were prepared by appropriately diluting with kerosene the SPEX oil-based 21-element mixed standard solution (500 µg/g), the Conostan® and SPEX oil-based single-element standard solution (5000 µg/g), and the Tokyo Kasei Kogyo Co., Ltd. heavy oil sulfur content standard sample (1.05 % by weight).
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.
Finally, the Conostan® 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 as to occupy a fixed concentration in all the samples.

Instrument and Analytical Condition

Measurement was conducted using the Shimadzu ICPE-9820 multi-type ICP atomic emission spectrometer. The measurement conditions are shown in Table 1.
When conducting analysis of organic solvent samples with most conventional ICP instruments, oxygen must typically be introduced into the plasma torch to suppress carbon deposition at the tip of the torch. With the Shimadzu ICPE-9820, however, the vertical orientation of the plasma torch and adoption of a plasma torch that suppresses carbon deposition has nearly completely eliminated the deposition of carbon originating from the sample. 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 adopts 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 1 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
Misting Chamber	: Organic solvent chamber
Plasma Torch	: Torch
Observation	: Radial (RD)

Analysis

The calibration curve method – internal standard method was used to conduct analysis of 22 elements (Al, Ba, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Mo, Ni, P, K, Si, Ag, Na, S, Sn, Ti, V, Zn) specified according to the ASTM standard.

Analytical Results

Table 2 shows the analytical results. Excellent results near 100 % were obtained in the dilution test for the high-concentration elements and the spike-and-recovery test for the low-concentration elements, both with respect to the used lubricating oil. In addition, the analytical results obtained in analysis of the unused lubricating oil are also listed for reference.
The spectral line profiles for Fe and P are shown in Fig. 1. The calibration curves for Fe, Mg and S are shown in Fig. 2.

Conclusion

Using the ICPE-9820, dissolved elements in used lubricating oil can be analyzed stably without the introduction of oxygen.

References

1) ASTM International Standard D5185
Standard Test Method for Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

2) The Japan Petroleum Institute Standard JPI-5S-44-2011
Method for Analyzing Fe, Cu, Al, Pb, Cr and Sn Contents in Used Lubricating Oil Using Solvent Dilution - Inductively Coupled Plasma Atomic Emission Spectrometry

Table 2 Analytical Results of Lubricating Oil

Element	Used lubricant (µg/g)	Used lubricant spike recovery rate (%)	Used lubricant dilution test (%)	Unused lubricant (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×σ_{BL}× κ (σ_{BL}: Standard deviation of background intensity; κ: Concentration/intensity)
<: Less than the detection limit

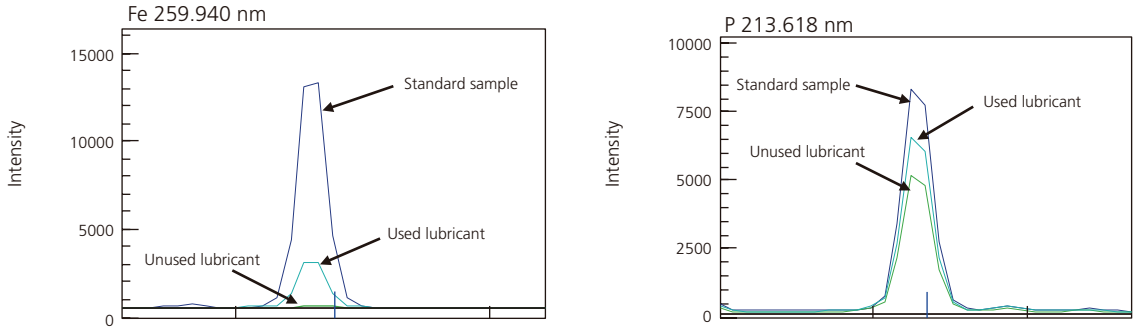

Fig. 1 Spectral Profiles of Fe and P

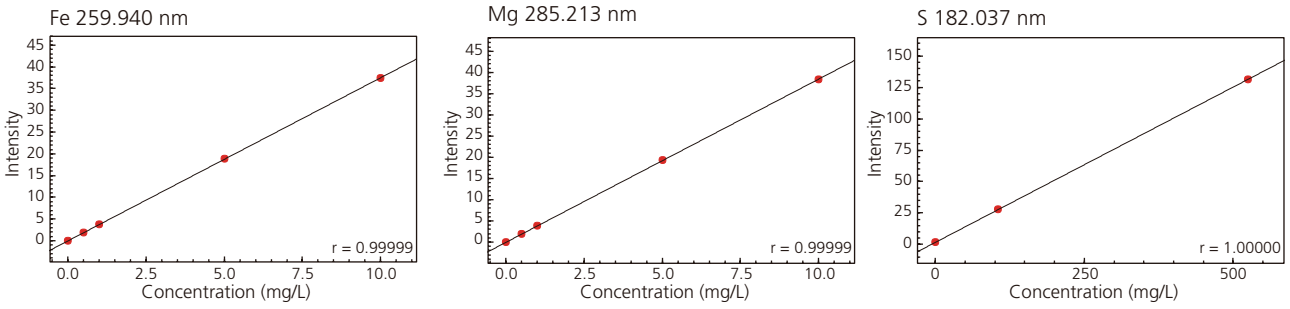

Fig. 2 Calibration Curves of Fe, Mg and S

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