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Application News

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Inductively Coupled Plasma Atomic Emission Spectrometry

Analysis of Additive Elements in Lubricating Oil According to ASTM D4951: ICPE-9820

Introduction

Numerous additives consisting of various types of organometallic substances are added to lubricating oils to enhance performance. It is important to manage the concentrations of these additives for the quality control of lubricating oils. Table 1 shows the main types of additives that contain organometallic compounds, and their functions.

Both ASTM D4951 of the ASTM International standards and JPI-5S-38-2003 of the Japan Petroleum Institute standards (Lubricating Oils - Determination of Additive Elements) specify the use of ICP atomic emission spectrometry with organic solvent dilution as the test measurement method for elements in additives.

We performed elemental analysis of the additives in commercially available engine oil, automatic transmission fluid (ATF), and gear oil, using the Shimadzu ICPE-9820 multi-type ICP atomic emission spectrometer, after diluting the samples with an organic solvent. The adoption of a vertically-oriented plasma torch in the ICPE-9820 reduces the possibility of carbon precipitation, while providing stable analytical results without requiring the flow of oxygen through the system.

Table 1 Function of Main Additive Agent That Contains Organometallic Compounds

Type	Function	Additive Elements
Cleaner	Prevents and suppresses deposition of degradation byproducts generated due to high temperature operation of machines such as engines.	Ba, Ca, Mg, etc.
Antioxidant	Reacts with radicals and peroxide to suppress formation of varnish and sludge, which form due to oxidation of oil.	Zn, etc.
Anti-corrosion additive	Neutralizes corrosive oxidation products resulting from the breakdown of lubricating oil.	P, Zn, etc.
Solid lubricant	Used as thin film or powder to reduce friction and wear.	Mo, B, etc.

Samples

- Engine oil (2 types)
- ATF (1 type)
- Gear oil (1 type)

Sample Preparation

Approximately 1 g of each sample was weighed, diluted with 100 mL of xylene, and then measured. For the dilution test sample, a 5-fold dilution of the engine oil (Sample 1) described above was used.

Additionally, a 5000 µg/g Y-in-oil standard (Conostan®) was diluted with xylene and added to each sample at a concentration of 1 mg/L, for use as an internal standard.

The standard samples were prepared by diluting the SPEX® multi-element oil standard (21 elements; 900 µg/g / 500 µg/g) and the Conostan® single element oil standards (5000 µg/g) with xylene. As with the measurement samples, each was spiked with Y at a concentration of 1 mg/L, for use as an internal standard.

Instrument and Analytical Conditions

The Shimadzu ICPE-9820 multi-type ICP atomic emission spectrometer was used to measure the samples. The measurement conditions are shown in Table 2.

When conducting analysis of organic solvent samples with conventional ICP instruments, it is typically required to introduce oxygen into the plasma to suppress the deposition of carbon at the tip of the torch. With the Shimadzu ICPE-9820, however, the vertical orientation of the plasma torch greatly reduces the likelihood that carbon from the sample will precipitate at the tip of the torch. Therefore, even for the analysis of samples in organic solvents such as xylene, kerosene, and MIBK, the ICPE-9820 eliminates the need to introduce oxygen to suppress the precipitation of carbon.

Table 2 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 UES10
Misting Chamber	: Chamber drain straight
Plasma Torch	: Torch
Observation	: Radial (RD)

Analysis

The calibration curve-internal standard method was used to conduct analysis for six types of additive elements used in lubricating oil (B, Ca, Mg, Mo, P, Zn).

[References]

1) ASTM International ASTM D4951
Standard Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry
2) Japan Petroleum Institute Standard JPI-5S-38-2003
Lubricating Oils - Determination of Additive Elements - Inductively Coupled Plasma Atomic Emission Spectrometry

Analytical Results

Table 3 shows the quantitative analysis results. The dilution test values using engine oil (Sample 1) showed excellent results at nearly 100 % recovery. Fig. 1 shows the spectral profiles of Ca and Mo, and Fig. 2 shows calibration curves for Ca, Mo, and Zn.

Conclusion

Use of the ICPE-9820 to perform elemental analysis of additives in lubricating oil permits stable analysis without the need to introduce oxygen.

Table 3 Analytical Results of Lubricating Oil (µg/g)

	Engine Oil			ATF Oil	Gear Oil
Element	Sample 1	Sample 1 Dilution test (%)	Sample 2	Sample 3	Sample 4
B	113	103	80	68	---
Ca	1100	100	2940	156	64
Mg	754	101	21	1.0	0.7
Mo	87	100	96	---	---
P	637	100	733	262	1010
Zn	736	103	848	20	7.6

Dilution test value (%) = I / S × 100
(I: quantitation value prior to sample dilution, S: Quantitation value of 5-fold diluted sample × 5)

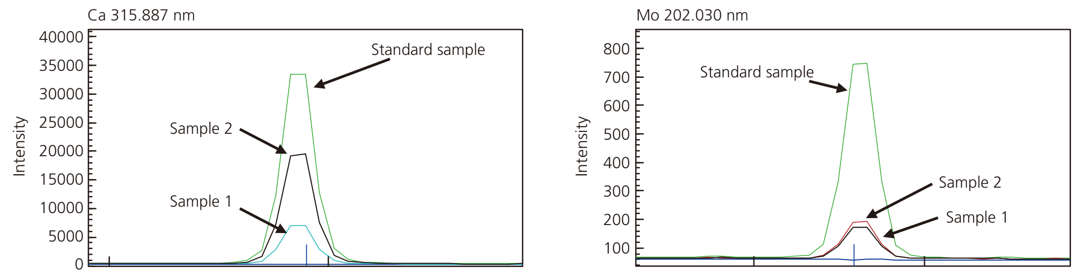

Fig. 1 Spectral Profiles of Ca and Mo

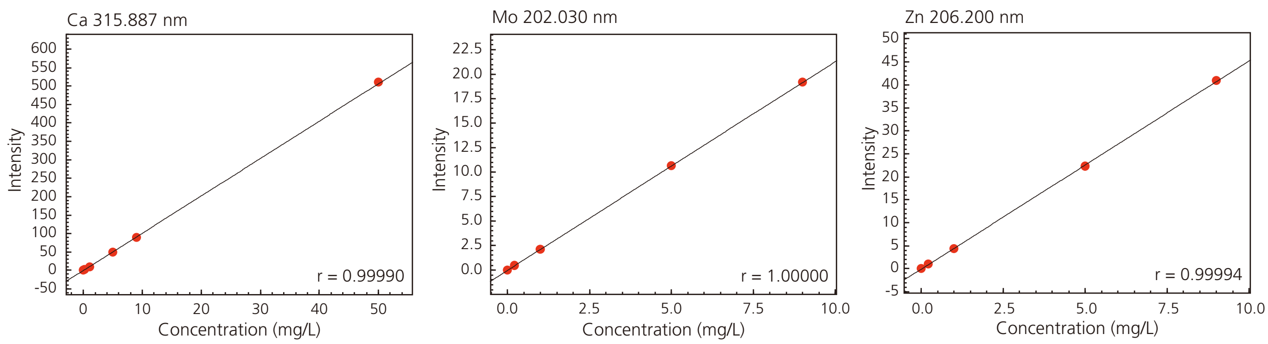

Fig. 2 Calibration Curves for Ca, Mo and Zn

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