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Application News

Inductively Coupled Plasma Mass Spectrometer

Determination of Additive and Trace Elements in Lubricating Oil Using ICP-MS

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User Benefits

- Metal elements in lubricating oil can be accurately analyzed by dilution with organic solvents.
- Solvent-resistant peristaltic pump tubing enables the addition of internal standard elements in-line, even for organic solvent analysis, thereby eliminating the need for manual addition.

■ Introduction

Organic metal compounds are added to lubricating oil to provide various functional properties. Therefore, monitoring the concentrations of these additives is important for ensuring quality control. In addition, the analysis of wear metals and contaminant metals in lubricating oils (engine oils) used in automobiles and ships is a crucial method for assessing the condition of the engine. Traditionally, these analyses have utilized ICP Optical Emission Spectrometry (ICP-OES) as outlined in ASTM D4951-14[1)] and ASTM D5185-18[2)]. However, for the analysis of trace metal elements that are difficult to detect with ICP-OES, the more sensitive ICP mass spectrometry (ICP-MS) is more suitable.

In this Application News, lubricating oil was diluted with organic solvents, and the additives and trace elements in the oil were analyzed using the ICP-MS 2050. To verify the accuracy of the analytical results, spike recoveries were also evaluated.

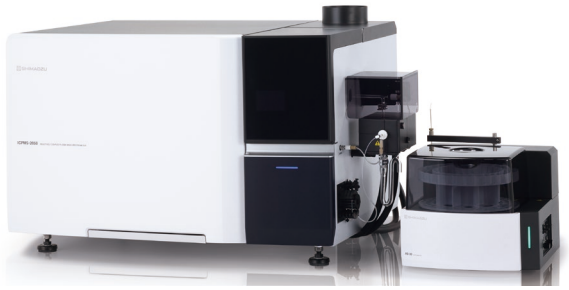

Fig. 1 ICPMS-2050 and AS-20

■ Samples and Reagents

- Samples

Commercially available automotive engine oil (mineral oil) was used.

- Diluent

PremiSolv (CONOSTAN) was used.

- Reagents for standards

The oil-based mixed standard solution S-21 and the oil-based single-element standard solutions for Li, P, K, Co, Sb, Be, Y, In, and Bi (CONOSTAN), and the oil-based single-element standard solution for S, Sc (LGC Standards) were used.

■ Preparation of Samples and Standards

- Sample Preparation (for Trace Element Analysis)

Samples were diluted 50-fold (w/w) with PremiSolv to prepare them for analysis of trace elements. Spiked samples were prepared similarly, with one solution containing trace elements excluding sulfur (S), and another solution containing only S.

- Sample Preparation (for Additive Element Analysis)

The sample was diluted 5000-fold (w/w) with PremiSolv to prepare a sample solution for analysis of the additive elements.

- Calibration standards

S-21 and single-element standard solutions were mixed and diluted with PremiSolv to prepare the calibration standards. The concentrations of each element in the calibration standards are shown in Table 1.

- Internal standard solution

Oil-based single-element standard solutions of Be, Sc, Y, In, and Bi were mixed and diluted with PremiSolv. The concentrations of Be and Sc in the internal standard solution are 1000 µg/kg, while the concentrations of Y and In are 100 µg/kg, and Bi is 20 µg/kg.

■ Configurations and Analytical Conditions

Table 2 shows the configuration of the ICP-MS. The "Organic Solvent Injection System" was used as the sample introduction system. By using a platinum sampling cone, damage to the cone from prolonged exposure to organic solvents can be minimized. Additionally, the use of solvent-resistant peristaltic pump tubing enables the in-line addition of internal standard elements, thereby streamlining the sample preparation process.

Table 3 shows the analytical conditions. To prevent the precipitation of carbon from the organic solvent in the interface, a mixed gas of argon (70 %) and oxygen (30 %) was introduced into the quadrupole structure organic solvent torch. To reduce the effects of non-spectral interferences, such as ionization interference from highly concentrated additive elements in lubricating oil, dilution gas was introduced. The analytical conditions used for lubricating oils can be easily registered from the preset methods of LabSolutions™ ICPMS (Version 2.10 and later), eliminating the need for complex condition testing.

Table 1 Concentrations of Analytes in Calibration Standards

Elements	Calibration Standards (µg/kg)						
	STD0	STD1	STD2	STD3	STD4	STD5	STD6
Li, Na, Al, K, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Cd, Sn, Sb, Pb	0	10	50	200			
B, Mg, Si, Ca, Zn, Mo	0		50	200			
P	0	1,000	5,000	20,000			
S	0				10,000	50,000	100,000

Table 2 ICP-MS System Configuration

Instrument	:	ICPMS-2050
Nebulizer	:	Nebulizer DC04
Chamber	:	Cyclone Chamber
Torch	:	Organic Solvent Torch
Sampling Cone	:	Platinum
Skimmer Cone	:	Nickel
Auto Sampler	:	AS-20 (Rinse station for organic solvents)
Peristaltic Pump Tubing	:	I.D. 0.76 mm for sample*1 I.D. 0.38 mm for internal standards*2 (materials: Solva PVC)
Internal Standard Elements	:	Online Internal Standard Kit (for Organic Solvents)*3 (sample: internal standard = about 4:1)

I.D.: Internal Diameter
*1: P/N: S018-31558-61
*2: P/N: S018-31558-62
*3: P/N: S211-95010-42

Table 3 Analytical Conditions

RF Power	: 1.60 kW				
Sampling Depth	: 8.0 mm				
Plasma Gas Flowrate	: 20.0 L/min				
Auxiliary Gas Flowrate	: 0.50 L/min				
Carrier Gas Flowrate	: 0.40 L/min				
Dilution Gas Flowrate	: 0.20 L/min				
Ar-O_2 Mixed Gas Flowrate	: 0.35 L/min				
Chamber Temperature	: -5 °C				
Pump Rotation Speed	: 15 r.p.m. (Low) / 45 r.p.m. (High)				
Cell Condition	:	No Gas	He	H_2-A	H_2-B
Cell Gas	:	-	He	H_2	H_2
Cell Gas Flowrate (mL/min)	:	-	6.0	7.0	7.0
Cell Voltage (V)	:	-	-35	-30	-20
Energy Filter (V)	:	-	7.0	7.0	7.0

■ Detection Limit

The instrument detection limits (IDLs) are shown in Table 4. The IDLs were calculated as the concentration that gives a signal equivalent to three times the standard deviation (σ) of the calibration blank sample (STD0).

■ Quantitative Analysis and Spike Recoveries

The trace metal elements in engine oil were quantitatively analyzed using the calibration standards shown in Table 1. The quantitative results were converted to the concentrations in engine oil by multiplying the dilution factors (trace elements: 49.89 times, additive elements: 4960 times). Additionally, to confirm the accuracy of the measurement, spike recoveries were evaluated. Table 5 shows the results of the quantitative analysis and the spike recoveries.

Good recoveries, ranging from 88 % to 116 %, were obtained, confirming that the influence of the inorganic matrix derived from the additive elements was sufficiently minimized. These results indicate that trace metal elements in engine oil can be accurately analyzed using only dilution with organic solvents.

■ Conclusion

In this Application News, the analysis of metal elements in lubricating oil was performed using the ICPMS-2050 with the organic solvent injection system. Good spike recoveries were achieved, confirming that trace metal elements in lubricating oil can be accurately quantified with a simple sample preparation involving only dilution with organic solvents. Since it is possible to analyze without the complex procedures required for acid decomposition, the risk of volatilization or contamination of the analytes during the sample preparation process is reduced. Additionally, the use of solvent-resistant peristaltic pump tubing enables the in-line addition of internal standard elements, further reducing the time required for sample preparation.

The analytical conditions can be easily registered from preset methods, allowing for analysis without the need to consider complex analytical conditions for organic solvents.

Table 4 Detection Limits (DLs)

Elements	Cell Condition	Internal Standards	IDLs (µg/kg)
^{7}Li	No Gas	^{9}Be	0.1
^{10}B	No Gas	^{9}Be	0.4
^{23}Na	No Gas	^{45}Sc	0.7
^{24}Mg	H_2-A	^{45}Sc	1
^{27}Al	He	^{45}Sc	0.6
^{28}Si	H_2-A	^{45}Sc	4
^{31}P	He	^{45}Sc	40
^{34}S	H_2-B	^{45}Sc	1,000
^{39}K	H_2-A	^{45}Sc	0.8
^{44}Ca	H_2-A	^{45}Sc	2
^{49}Ti	He	^{45}Sc	0.9
^{51}V	H_2-A	^{45}Sc	0.03
^{52}Cr	H_2-A	^{45}Sc	0.03
^{55}Mn	H_2-A	^{45}Sc	0.04
^{56}Fe	H_2-A	^{45}Sc	0.2
^{59}Co	He	^{45}Sc	0.03
^{60}Ni	He	^{45}Sc	0.3
^{63}Cu*	He	^{45}Sc	0.2
^{66}Zn	He	^{45}Sc	0.7
^{95}Mo	He	^{89}Y	0.03
^{111}Cd	H_2-B	^{115}In	0.05
^{118}Sn	He	^{115}In	0.06
^{121}Sb	He	^{115}In	0.02
^{138}Ba	He	^{115}In	0.03
^{208}Pb	He	^{209}Bi	0.05

IDL (Instrument Detection Limit): 3σ (standard deviation of STD0) × slope of calibration curve
*: In case that a large amount of Zn is contained, Cu may be affected by the peak tailing from Zn. To avoid peak tailing, Cu is measured in high resolution mode with double the standard resolution.

<References>

1) ASTM D4951-14 Standard Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry
2) ASTM D5185-18 Standard Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

<Related Applications>

1. Determination of Elemental Impurities in Petroleum Distillates using ICP-MS ~ASTM D8110-17~ Application News No.01-00922A
2. Analysis of Additive Elements in Lubricating Oil According to ASTM D4951: ICPE-9820 Application News No.J111A
3. Analysis of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oil According to ASTM D5185: ICPE-9820 Application News No.J114A

Table 5 Quantitative Results in Lubricating Oil and Spike Recoveries

	Elements	IDLs (µg/kg)	Spike Conc. (µg/kg)	Unspiked Sample (µg/kg)	Spiked Sample (µg/kg)	Spike Recoveries (%)	Results in Engine Oil (mg/kg)
Trace Elements + P, S (Analyzed in a 50-fold diluted sample)	^{7}Li	0.1	50	1.3	55.8	109	0.65
	^{23}Na	0.7	50	23.8	71.7	96	1.19
	^{27}Al	0.6	50	12.7	64.3	103	0.634
	^{28}Si	4	50	110	168	116	5.49
	^{31}P	40	5,000	3,770	9,480	114	188
	^{34}S	1,000	50,000	53,800	106,000	104	2,680
	^{39}K	0.8	50	10.2	62.6	105	0.509
	^{49}Ti	0.9	50	N.D.	50.6	101	N.D.
	^{51}V	0.03	50	0.60	47.0	93	0.030
	^{52}Cr	0.03	50	0.33	44.3	88	0.017
	^{55}Mn	0.04	50	5.15	56.6	103	0.257
	^{56}Fe	0.2	50	22.0	71.4	99	1.10
	^{59}Co	0.03	50	0.05	49.0	98	0.003
	^{60}Ni	0.3	50	1.5	51.6	100	0.075
	^{63}Cu	0.2	50	0.3	47.9	95	0.02
	^{111}Cd	0.05	50	0.09	53.9	108	0.005
	^{118}Sn	0.06	50	0.24	52.6	105	0.012
	^{121}Sb	0.02	50	0.27	53.5	106	0.014
	^{138}Ba	0.03	50	0.24	50.5	101	0.012
	^{208}Pb	0.05	50	0.59	50.8	100	0.029
Concentrated Elements (Analyzed in a 5000-fold diluted sample)	^{10}B	0.4		38.9			193
	^{24}Mg	1		68.5			340
	^{44}Ca	2		199			987
	^{66}Zn	0.7		144			714
	^{95}Mo	0.03		43.5			216

N.D.: Not Detected
Spike Recovery (%): (spiked sample – unspiked sample) / spike concentration ×100

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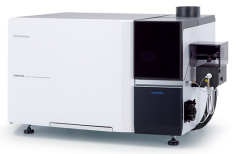

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