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Application News

Inductively Coupled Plasma Mass Spectrometer

Determination of Elemental Impurities in Petroleum Distillates Using ICP-MS ~ASTM D8110-17~

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User Benefits

- Enables the analysis of elemental impurities in various kinds of petroleum distillates (light and middle distillates) with the sample preparation method that involves only dilution with organic solvents.
- Metal elements in petroleum distillates (light and middle distillates) can be accurately analyzed over a long period of time.
- 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

The concentration of metal elements in petroleum products needs to be controlled due to concerns that they can act as catalyst poisons and affect product quality. Additionally, it is important to measure the concentration of heavy metals to reduce environmental impact during emissions. Traditionally, analytical methods using ICP Optical Emission Spectrometry (ICP-OES), such as ASTM D7111-16[1], have been employed to determine metal elements in petroleum products. However, in recent years, there has been a demand for more sensitive analytical methods using ICP mass spectrometry (ICP-MS), such as ASTM D8110-17[2], to detect trace amounts of metal elements.

ASTM D8110-17 is the test method for the analysis of elements in petroleum distillates (light and middle distillates) using ICP-MS. Since this method involves diluting the sample with organic solvents, it is necessary to introduce organic solvent samples into the ICP-MS.

In this Application News, various light and middle distillates were diluted with organic solvents in accordance with ASTM D8110-17 and trace elements were analyzed using the ICPMS-2050 (Fig. 1). The validity of the analytical results was confirmed through spike recovery tests and the analysis of reference material for residual fuel oil. Additionally, the stability of the analysis over long periods of time was evaluated.

Fig. 1 ICPMS-2050 and AS-20

■ Samples and Reagents

- Samples

Commercially available diesel oil, petroleum benzine (light distillate with a boiling point range of 50 to 80 °C), petroleum ether (light distillate with a boiling point range of 30 to 60 °C), and the Reference Material of Nickel and Vanadium in Residual Fuel Oil (the Japan Petroleum Institute) were used.

- Diluent

PremiSolv (CONOSTAN) was used as the diluent.

- Reagents for preparing standards

The oil-based mixed standard solution S-21 and the oil-based single-element standard solutions for Li, P, K, Co, As, Se, 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

Diesel oil, petroleum benzine, and petroleum ether were diluted 10 times (w/w) with PremiSolv to prepare the analytical samples. Additionally, samples with spiked standard solutions were prepared in the same way for spike recovery tests.

Furthermore, after warming and stirring the reference material for residual fuel oil, it was diluted 1000 times (w/w) with PremiSolv to prepare the analytical sample of reference material for residual fuel oil.

- Calibration standards

S-21 and single-element standard solutions (Li, P, K, Co, As, Se, Sb and S) 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.

- Check Standard

To confirm the continuous validity of calibration curves, Check Standard was prepared to have the same concentration as STD2. A different concentration level of S-21 was used than that used in the preparation of calibration standards. Elements not contained in S-21 were prepared from the same standard solution used for the calibration standards.

- 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 250 ng/g, while the concentrations of Y and In are 25 ng/g, and Bi is 5 ng/g.

Table 1 Concentrations of Analytes in Calibration Standards

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

■ Configurations and Analytical Conditions

Table 2 shows the configuration of the ICP-MS. The "Organic Solvent Injection System" was used as the introduction system. By utilizing 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. The analytical conditions used for petroleum distillates can be easily set from the preset methods registered in LabSolutions™ ICPMS (Version 2.10 and later), thus eliminating the need for complex condition testing.

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	: 0.60 L/min				
Dilution Gas Flowrate	: 0 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	9.0
Cell Voltage (V)	:	-	-35	-30	-55
Energy Filter (V)	:	-	7.0	7.0	7.0

■ Removal of Interference and Detection Limit

To analyze metal elements with high sensitivity in organic solvents, it is important to eliminate interference caused by carbon from the organic solvent. For example, there are carbon-derived polyatomic ion interferences such as $^{12}C^{12}C^+$ for ^{24}Mg, $^{12}C^{16}O^+$ for ^{28}Si, and $^{40}Ar^{12}C^+$ for ^{52}Cr. By using collision mode with helium gas or reaction mode with hydrogen gas, these interferences can be eliminated, enabling sensitive analysis. As an example, Fig. 2 shows the calibration curve for Mg under each condition. In the No Gas mode, the influence of $^{12}C^{12}C^+$ results in a high background equivalent concentration (BEC), making it challenging to analyze trace amounts of ^{24}Mg. However, in collision mode, the interference from $^{12}C^{12}C^+$ was reduced, and BEC of 80 ng/g was obtained. Furthermore, in reaction mode, the interference from $^{12}C^{12}C^+$ was significantly reduced, and BEC of 0.8 ng/g was obtained, which enables trace amounts of ^{24}Mg analysis.

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

Table 4 Detection Limits (DLs)

Elements	Cell Condition	Internal Standard	IDL (ng/g)
^{7}Li	No Gas	^{9}Be	0.08
^{23}Na	No Gas	^{9}Be	0.3
^{24}Mg	H_2-B	^{45}Sc	0.2
^{27}Al	He	^{45}Sc	0.3
^{28}Si	H_2-A	^{45}Sc	2
^{31}P	He	^{45}Sc	20
^{34}S	H_2-A	^{45}Sc	500
^{39}K	H_2-A	^{45}Sc	0.7
^{40}Ca*	H_2-A	^{45}Sc	0.3
^{47}Ti	He	^{45}Sc	0.8
^{51}V	H_2-A	^{45}Sc	0.02
^{52}Cr	H_2-A	^{45}Sc	0.02
^{55}Mn	H_2-A	^{45}Sc	0.03
^{56}Fe	H_2-A	^{45}Sc	0.06
^{59}Co	He	^{45}Sc	0.009
^{60}Ni	He	^{45}Sc	0.1
^{63}Cu	He	^{45}Sc	0.07
^{66}Zn	He	^{45}Sc	0.1
^{75}As	He	^{89}Y	0.02
^{78}Se	H_2-A	^{89}Y	0.03
^{95}Mo	He	^{89}Y	0.004
^{111}Cd	H_2-A	^{115}In	0.02
^{118}Sn	He	^{115}In	0.02
^{121}Sb	He	^{115}In	0.02
^{138}Ba	He	^{115}In	0.008
^{208}Pb	He	^{209}Bi	0.01

IDL (Instrument Detection Limit):
3σ (standard deviation of STD0) × slope of calibration curve
*: Analysis of Ca with a mass number of 40 is permitted exclusively in LabSolutions ICPMS Ver2.10 and later.

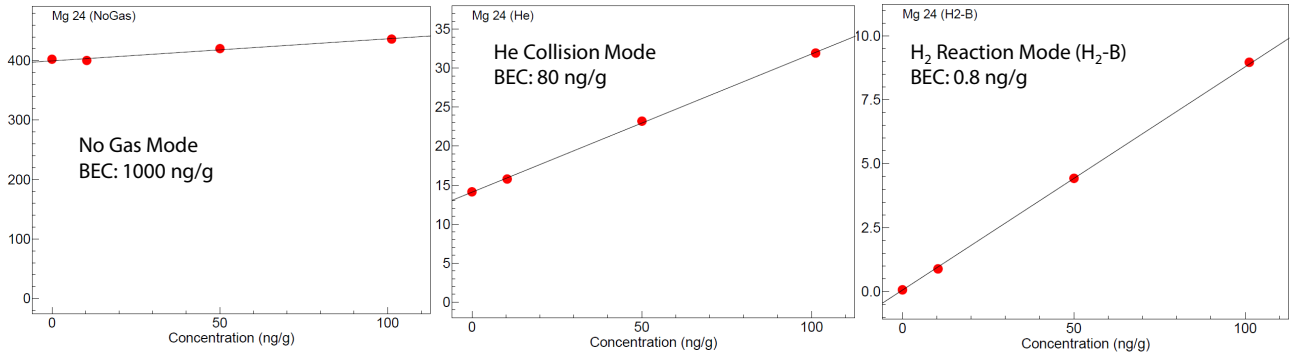

Fig. 2 Calibration Curve of Mg under Each Cell Condition (vertical axis: intensity ratio, horizontal axis: concentration)

■ Analysis of Reference Material for Residual Fuel Oil

Ni, V, and S in the reference material for residual fuel oil was measured using the calibration standards shown in Table 1. The results are presented in Table 5. The analytical results were sufficiently close to the certified values (reference value for S), confirming the accuracy of the ICPMS-2050 analysis.

Table 5 Analytical Results of RM of Residual Fuel Oil

Element	Certified Value (Reference Value for S)	Quantitative Result	Recovery
Ni	22 ± 1 ppm (w/w)	22 ppm (w/w)	100 %
V	53 ± 1 ppm (w/w)	52 ppm (w/w)	98 %
S	3.39 % (w/w)	3.45 % (w/w)	102 %

■ Spike Recoveries

Trace elements in light and middle distillates were quantitatively analyzed using the calibration standards shown in Table 1. To confirm the validity of the analytical results, the spike recoveries were evaluated. The results of the quantitative analysis and the spiking recoveries are shown in Table 6.

Good recoveries from 82 to 115 % were obtained, demonstrating that trace metal elements in various light and middle distillates can be accurately analyzed using only dilution with organic solvents.

■ Long Term Stability

To evaluate the long-term stability of organic solvent analysis using the ICPMS-2050, light and middle distillates were analyzed over approximately 6 hours.

To confirm the variability of the quantitative results, Check Standards were analyzed before sample analysis, every 10 samples, and at the end of the analysis. The results are shown in Fig. 3. All quantitative results of the Check Standard fell within the range of 90 to 110 % based on the prepared concentrations, which meets the validation requirements of ASTM D8110-17 (red dashed line).

Additionally, the change in the intensity of the internal standard elements over approximately 6 hours are shown in Fig. 4. The change in intensity of the internal standard elements were within 90 to 120 %, which also falls within the validation requirements of 50 to 150 % as specified in ASTM D8110-17 (red dashed line).

These results indicate that the ICPMS-2050 has sufficient long term stability for the analysis of organic solvent samples.

Table 6 Quantitative Results and Spike Recoveries

Elements	IDLs (ng/g)	Spike Conc. (ng/g)	Diesel Oil			Petroleum Benzine			Petroleum Ether		
			Unspiked Sample (ng/g)	Spiked Sample (ng/g)	Spike Recoveries (%)	Unspiked Sample (ng/g)	Spiked Sample (ng/g)	Recoveries (%)	Unspiked Sample (ng/g)	Spiked Sample (ng/g)	Spike Recoveries (%)
^{7}Li	0.08	50	0.27	49.4	98	0.17	53.3	106	0.10	56.3	112
^{23}Na	0.3	50	0.6	48.2	99	N.D.	53.6	107	N.D.	54.1	108
^{24}Mg	0.2	50	0.2	48.3	96	0.3	50.0	99	0.5	52.4	104
^{27}Al	0.3	50	N.D.	47.2	94	N.D.	49.1	98	N.D.	52.9	106
^{28}Si	2	50	N.D.	52	104	9	64	110	18	72	108
^{31}P	20	5,000	N.D.	5,040	101	N.D.	4,100	82	N.D.	4,150	83
^{34}S*1	500	-	700	-	-	N.D.	-	-	N.D.	-	-
^{39}K	0.7	50	N.D.	48.0	96	N.D.	52.4	105	N.D.	53.6	107
^{40}Ca*2	0.3	50	N.D.	48.3	97	N.D.	49.8	100	N.D.	51.1	102
^{47}Ti	0.8	50	N.D.	47.8	96	N.D.	48.2	96	N.D.	50.5	101
^{51}V	0.02	50	N.D.	49.0	98	0.24	51.8	103	0.10	54.0	108
^{52}Cr	0.02	50	N.D.	47.8	96	N.D.	51.8	104	N.D.	53.9	108
^{55}Mn	0.03	50	N.D.	47.4	95	N.D.	50.8	102	N.D.	52.5	105
^{56}Fe	0.06	50	N.D.	47.9	96	N.D.	49.3	99	N.D.	50.5	101
^{59}Co	0.009	50	0.015	46.7	93	0.021	48.1	96	0.010	50.3	101
^{60}Ni	0.1	50	0.2	46.9	93	N.D.	47.1	94	N.D.	48.9	98
^{63}Cu	0.07	50	N.D.	45.9	92	N.D.	45.8	92	N.D.	47.7	95
^{66}Zn	0.1	50	N.D.	44.0	88	0.2	43.6	87	N.D.	44.9	90
^{75}As	0.02	50	0.03	51.1	102	0.04	46.7	93	N.D.	46.9	94
^{78}Se	0.03	50	0.04	51.4	103	0.04	44.9	90	N.D.	46	92
^{95}Mo	0.004	50	N.D.	48.3	97	0.007	50.0	100	0.005	52	104
^{111}Cd	0.02	50	N.D.	50.4	101	0.04	48.2	96	N.D.	50.2	100
^{118}Sn	0.02	50	N.D.	48.8	98	0.03	47.9	96	0.02	50.0	100
^{121}Sb	0.02	50	N.D.	51.8	104	0.02	50.1	100	0.02	52.6	105
^{138}Ba	0.008	50	0.013	52.6	105	0.140	53.8	107	0.099	57.8	115
^{208}Pb	0.01	50	N.D.	52.1	104	0.08	53.4	107	0.07	56.5	113

N.D.: Not Detected (lower than detection limit)
Spike Recovery (%): (spiked sample – unspiked sample) / spike conc. ×100
*1: Spike recovery test for S was not performed.
*2: Analysis of Ca with a mass number of 40 is permitted exclusively in LabSolutions ICPMS Ver2.10 and later.

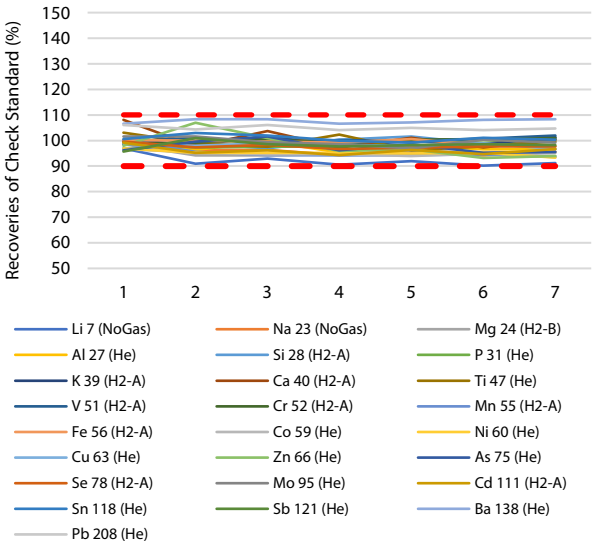

Fig. 3 Recoveries of Check Standard

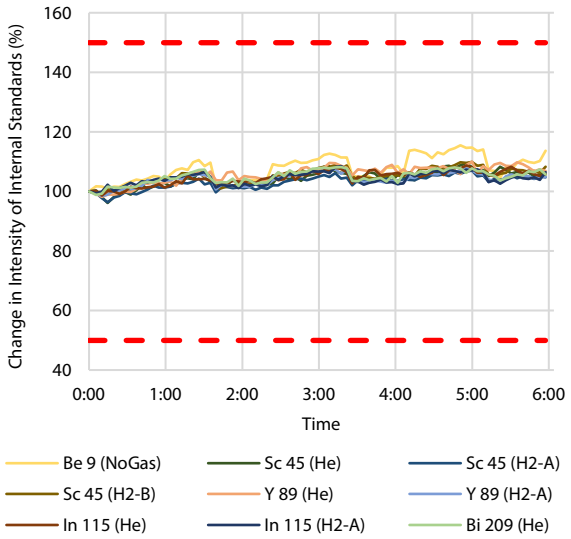

Fig. 4 Change in Intensity of Internal Standard Elements

■ Conclusion

In this Application News, the analysis of metal elements in light and middle distillates was performed using the ICPMS-2050 and the organic solvent introduction system. Good results were obtained from spiking recovery tests and the analysis of reference material for residual fuel oil, demonstrating that trace metal elements in light and middle distillates can be accurately quantified with a simple sample preparation method that involves only dilution with organic solvents. Furthermore, the recoveries of the Check Standards and the change in intensity of the internal standard elements also satisfied the validation requirements of ASTM D8110-17, confirming stable analysis over long periods of time.

Since it is possible to analyze without the complex procedures required for acid decomposition, the risk of volatilization or contamination of the target elements 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.

<References>

1) ASTM D7111-16 Standard Test Method for Determination of Trace Elements in Middle Distillate Fuels by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)
2) ASTM D8110-17 Standard Test Method for Elemental Analysis of Distillate Products by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

<Related Applications>

1. Determination of Additive Elements and Trace Elements in Lubricating Oil Using ICP-MS Application News No. 01-00921A
2. Analysis of Additive 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

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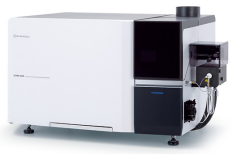

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