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Application News

No.X253

X-ray Analysis

Quantitative Analysis of Waste Oil by EDX-7000

In recent years, elemental analysis by EDX has been increasing due to the heightened concern for the environment. Even waste oil can quickly and easily be analyzed by EDX by merely pouring it as is into a container.
We evaluated the repeatability and limit of detection in analysis using new, unused commercially available general oil that is similar waste oil using the EDX-7000. The results demonstrated an improvement in sensitivity that was 1.5 to 4 times that obtained with the conventional model[*1], while achieving a shorter measurement time for each sample.
*1: Shimadzu Application News No.X242

Sample

Wear Metals in 75 cSt Hydrocarbon Oil
A23-10, 30, 50, 100, 300, 500
(each 10, 30, 50, 100, 300, 500 ppm)
Conostan Base Oil (0 ppm)

Elements

$_{22}$Ti, $_{23}$V, $_{24}$Cr, $_{28}$Ni, $_{29}$Cu, $_{30}$Zn, $_{47}$Ag, $_{48}$Cd, $_{50}$Sn, $_{51}$Sb, $_{56}$Ba, $_{82}$Pb

Sample Preparation

Approximately 8 mL of sample was placed as is in a container covered with 5-µm thick polypropylene film. Analysis was then conducted.
A photograph of the sample is shown in Fig. 1.

Fig. 1 Sample Preparation

Qualitative Analysis, Lower Limits of Detection (L.L.D.)

The spectral profiles for the elements of interest are shown in Fig. 2. The following expression was used to calculate the theoretical lower limits of detection from the spectral intensities (NET, BG) of A23 – 50. The results are shown in Table 1.
In addition, intensity overlap correction was applied when there was overlapping with coexisting elements such as Ti, V, Cr, etc.

$$L.L.D. = 3 \cdot \frac{C}{NET}\sqrt{\frac{BG}{T \cdot A}}$$

Intensity [cps/µA]
C : Concentration in oil [ppm]
T : Integration time [sec]
A : Current value [µA]

Table 1 Theoretical Lower Limits of Detection

[ppm]

Element	$_{22}$Ti	$_{23}$V	$_{24}$Cr	$_{28}$Ni	$_{29}$Cu	$_{30}$Zn	$_{47}$Ag	$_{48}$Cd	$_{50}$Sn	$_{51}$Sb	$_{56}$Ba	$_{82}$Pb
L.L.D. (300 sec)	1.2	1.3	1.2	0.4	0.3	0.3	0.7	0.9	1.9	2.8	9.9	0.3
L.L.D. (100 sec)	2.2	2.2	2.1	0.7	0.6	0.5	1.3	1.5	3.2	4.9	17.2	0.5

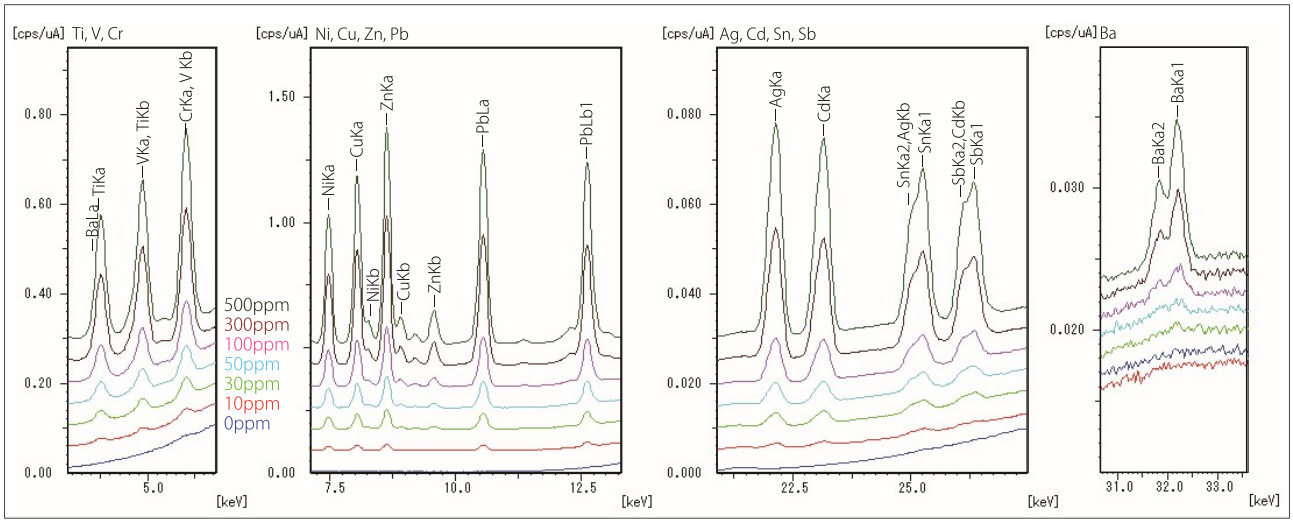

Fig. 2 X-Ray Fluorescence Spectra of Measured Elements

Calibration Curves

The calibration curves for Cr, Ni, Ag, Cd, Sb and Pb are shown in Fig. 3, and the accuracy (1σ) of the respective calibration curves are shown in Table 2. To obtain linearity of the calibration curves, internal standard scattered radiation correction was conducted for Ti, V, Cr, Ni, Cu, Zn and Pb.

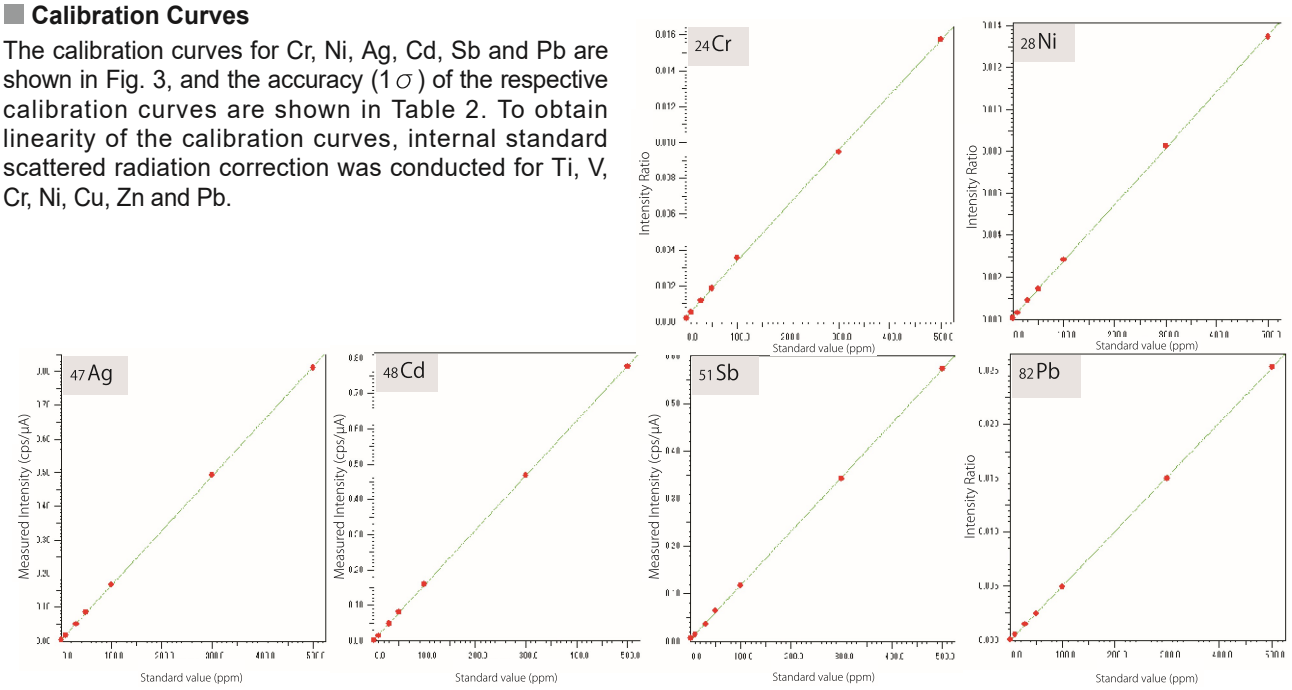

Fig. 3 Calibration Curves for Cr, Ni, Ag, Cd, Sb, Pb

Table 2 Accuracy of Calibration Curves

[ppm]

Element	$_{22}$Ti	$_{23}$V	$_{24}$Cr	$_{28}$Ni	$_{29}$Cu	$_{30}$Zn	$_{47}$Ag	$_{48}$Cd	$_{50}$Sn	$_{51}$Sb	$_{56}$Ba	$_{82}$Pb
Accuracy (1σ)	1.5	1.0	3.3	2.2	1.7	1.6	1.3	1.4	1.3	2.1	3.9	1.6

Repeatability

Using the above calibration curve method, the repeatability test results for A23 – 300 shown Table 3 were obtained by simply conducting 10 repeat measurements. An integration time of 100 seconds was used for each element.

Table 3 Repeatability for A23 – 300

[ppm]

Element	$_{22}$Ti	$_{23}$V	$_{24}$Cr	$_{28}$Ni	$_{29}$Cu	$_{30}$Zn	$_{47}$Ag	$_{48}$Cd	$_{50}$Sn	$_{51}$Sb	$_{56}$Ba	$_{82}$Pb
Concentration	300	300	300	300	300	300	300	300	300	300	300	300
1	300	298	295	305	300	299	301	304	303	304	312	295
2	297	295	297	300	299	295	302	304	296	299	303	298
3	303	298	301	300	298	302	303	302	306	298	301	298
4	299	294	297	306	298	303	302	303	304	299	310	299
5	302	299	297	303	302	298	306	303	300	301	303	300
6	305	299	296	302	303	299	302	303	306	297	316	295
7	300	298	295	306	305	298	304	304	301	297	321	299
8	306	298	297	302	302	299	300	301	301	302	298	299
9	299	298	300	303	297	304	304	305	306	298	295	297
10	306	299	298	301	301	300	305	300	303	299	320	299
Average	302	298	297	303	300	300	303	303	303	299	308	298
Standard Deviation	3.0	1.7	2.0	2.2	2.4	2.4	2.0	1.6	3.3	2.3	9.3	1.6
Coefficient of Variation [%]	1.0	0.6	0.7	0.7	0.8	0.8	0.7	0.5	1.1	0.8	3.0	0.6

Analytical Conditions

Instrument	:EDX-7000	Collimator[mmϕ]	:10
Elements	:Ti, V, Cr, Ni, Cu, Zn, Ag, Cd, Sn, Sb, Ba, Pb	Primary Filter	:#1, #2, #4
Analytical Group	:Working Curve	Atmosphere	:Air
X-ray Tube	:Rh target	Detector	:SDD
Tube Voltage [kV]	:15, 50	Integration Time[sec]	:100, 300
Current [μA]	:Auto	Dead time [%]	:Max. 30

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