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 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.

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

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.

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

<table>
<thead>
<tr>
<th>Element</th>
<th>22Ti</th>
<th>23V</th>
<th>24Cr</th>
<th>28Ni</th>
<th>29Cu</th>
<th>30Zn</th>
<th>47Ag</th>
<th>48Cd</th>
<th>50Sn</th>
<th>51Sb</th>
<th>56Ba</th>
<th>82Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLD (300 sec)</td>
<td>1.2</td>
<td>1.3</td>
<td>1.2</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3</td>
<td>0.7</td>
<td>0.9</td>
<td>1.9</td>
<td>2.8</td>
<td>9.9</td>
<td>0.3</td>
</tr>
<tr>
<td>LLD (100 sec)</td>
<td>2.2</td>
<td>2.2</td>
<td>2.1</td>
<td>0.7</td>
<td>0.6</td>
<td>0.5</td>
<td>1.3</td>
<td>1.5</td>
<td>3.2</td>
<td>4.9</td>
<td>17.2</td>
<td>0.5</td>
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</tbody>
</table>

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.

![Calibration Curves for Cr, Ni, Ag, Cd, Sb, Pb](image)

Table 2 Accuracy of Calibration Curves

<table>
<thead>
<tr>
<th>Element</th>
<th>22 Ti</th>
<th>23 V</th>
<th>24 Cr</th>
<th>28 Ni</th>
<th>29 Cu</th>
<th>30 Zn</th>
<th>47 Ag</th>
<th>48 Cd</th>
<th>50 Sn</th>
<th>51 Sb</th>
<th>56 Ba</th>
<th>82 Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accuracy (1σ)</td>
<td>1.5</td>
<td>1.0</td>
<td>3.3</td>
<td>2.2</td>
<td>1.7</td>
<td>1.6</td>
<td>1.3</td>
<td>1.4</td>
<td>1.3</td>
<td>2.1</td>
<td>3.9</td>
<td>1.6</td>
</tr>
</tbody>
</table>

■ 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

<table>
<thead>
<tr>
<th>Element</th>
<th>22 Ti</th>
<th>23 V</th>
<th>24 Cr</th>
<th>28 Ni</th>
<th>29 Cu</th>
<th>30 Zn</th>
<th>47 Ag</th>
<th>48 Cd</th>
<th>50 Sn</th>
<th>51 Sb</th>
<th>56 Ba</th>
<th>82 Pb</th>
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</thead>
<tbody>
<tr>
<td>Concentration</td>
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<td>1</td>
<td>300 298 295 305 300 299 301 304 303 304 312 295</td>
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<td>2</td>
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<td>4</td>
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<td>8</td>
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<td>10</td>
<td>306 299 298 301 301 300 305 303 303 299 320 299</td>
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<tr>
<td>Average</td>
<td>302 298 297 303 300 300 303 303 303 299 308 298</td>
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<tr>
<td>Standard Deviation</td>
<td>3.0 1.7 2.0 2.2 2.4 2.4 2.0 1.6 3.3 2.3 9.3 1.6</td>
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<tr>
<td>Coefficient of Variation [%]</td>
<td>1.0 0.6 0.7 0.7 0.8 0.8 0.7 0.5 1.1 0.8 3.0 0.6</td>
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</tbody>
</table>

Analytical Conditions

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

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