# OIL-MULTI-PAK

## for multi-elements analysis of oils using pre-calibration package


### 1. Introduction

X-ray fluorescence (XRF) spectrometry allows both simple sample preparation and high precision analysis. The method is highly popular among various fields, including quality control and research & development. Recent advanced data processing techniques and higher instrument sensitivities have improved analytical accuracies in "standardless FP analysis" using Fundamental Parameter (FP) method which does not require standard samples. However, standard samples which are similar sample type to analysis samples are still required to create calibration curves in order to obtain high accuracy analysis results.

There are wide variety of analyzing elements and concentration ranges to analyze common oil types such as fuel oils of gasoline and heavy oil, lubricating oil, and waste oil. It requires high level knowledge of X-ray fluorescence analysis in order to purchase suitable commercial reference materials and create all calibration curves after setting proper measuring parameters. Furthermore, it requires high cost and time. Therefore, there has been high demands of simple analysis startup method for accurate analysis of various types of oils.

The new analysis package for oil analysis is designed for beginners of X-ray analysis to setup quantitative analysis of oils easily and quickly by supplying a package of data media consisting of intensities of standard samples, analytical parameters and drift correction samples.

Oil analysis is carried out by measuring oil sample using liquid cell directly filled with oil sample, which is covered by sample film. However, since the sample film mainly consists of light elements such as carbon and hydrogen, the film causes negative impacts to the sample analysis as follows:

- Since main components of oils are hydrocarbons added with oxygen, it is required to correct for the influence of composition variation of carbon, hydrogen, and oxygen.
- For analysis of heavy elements in light matrix samples, incident X-rays penetrates into sample deeply and fluorescent X-rays generated in deep area can transmit sample area and detected. However, there are areas where generated fluorescence are not detected in deep area inside sample and the undetected area depends on X-ray optics of the spectrometer. This phenomenon is called geometry effect.

Moreover, there is a wide variety of sample films and selection depends on analysis type and purpose such as sensitivities, impurities, and durability against chemical characteristics of liquid and X-ray damage.

OIL-MULTI-PAK, application package for multi-element analysis in oils provides solutions to solve the problems above allowing accurate analysis for wider range of oils, including used lubricating oil, lubricating oils with various types of base oils, and fuel oils such as heavy oil, diesel oil, and gasoline.

### 2. Specification and Features of Pre-calibration Package OIL-MULTI-PAK

OIL-MULTI-PAK is a dedicated analysis package for ZSX Primus IVi for analyzing 27 elements in oils by liquid method. The package consists of sensitivity coefficients obtained by measuring 120 standard samples of mineral oil standard materials with optimum measuring conditions and correction methods. By using the attached software media, in which analysis conditions and various parameters are stored, install the data to ZSX Guidance software of ZSX Primus IVi. Then, simply measure the drift correction samples attached to complete startup of the package.

The ZSX Guidance software installed with the oil analysis package allows oil analysis with the corrections

of the influences of hydrocarbon-oxygen and geometry effect using the FP method. Furthermore, it is possible to preset sample film information of a commercial sample film from local supplier selected for an analyzing oil type.

### 2.1. Analysis elements and concentration ranges

The Table 1 shows analysis elements and the concentration ranges of the package. The concentration ranges are wide to cover various types of oils such as lubricating oils.

The analysis range of sulfur is up to 4.5 mass% for sulfur in fuel oils such as heavy oil and it can also be used for the analysis of many trace heavy elements.

**Table 1.** Elements and concentration ranges.

| Element | Conc. range (ppm) | Element | Conc. range (ppm) |
|---|---|---|---|
| Na | (9)–5000 | Co | (0.4)–600 |
| Mg | (2.5)–4000 | Ni | (0.4)–600 |
| Al | (1.6)–1250 | Cu | (0.4)–1250 |
| Si | (1.8)–2000 | Zn | (0.4)–5000 |
| P | (0.9)–5000 | Br | (0.3)–2000 |
| S | (1.0)–4.5 mass% | Mo | (1.5)–2000 |
| Cl | (4.6)–2.0 mass% | Ag | (3.3)–500 |
| K | (1.0)–2000 | Cd | (3.3)–500 |
| Ca | (0.8)–3.0 mass% | Sn | (3.3)–600 |
| Ti | (1.0)–600 | Sb | (3.3)–600 |
| V | (1.0)–600 | Ba | (2.9)–8000 |
| Cr | (0.7)–600 | Pb | (1.0) 1250 |
| Mn | (0.7)–600 | Bi | (1.0) 600 |
| Fe | (0.4)–2000 | | |

The values of lower limit of detection (LLD) are indicated in parentheses. The LLD depends on the measurement time, the sample film, and the composition of the analysis sample.

### 2.2. Correction for the influence of hydrocarbon and oxygen

Since XRF analysis is a relative quantification method, quantitative analysis requires standard samples to be used as a reference sample. However, the standard samples should be a similar sample type to analysis samples in order to reduce the influence of the difference of sample matrices.

Oils are mainly composed of hydrocarbons, and also oxygen depending on oil types. Oxygen in oils affects the analysis result of measuring elements. Lubricant oils have a wide ranges of compositions, including additives and hydraulic oil is constantly oxidized and the composition change process is complicated. If the proportion of these hydrocarbons and oxygen is known, it is possible to correct for the influence of oxygen. However, preparing matrix matched standards for each sample type and sample cannot be effective in many cases. Since carbon is a main element in any types of sample films, carbon in liquid samples cannot be measured to determine carbon content.

It does not require the information of hydrocarbon and oxygen content for the oil analysis in using OIL-MULTI-PAK, since the software automatically corrects for the influence of the components by using scattered X-ray intensity.

In order to verify the correction, a commercial multi-element lubricant oil standard was diluted with a solvent containing oxygen to verify the correction for hydrocarbons and oxygen and the results are listed in Table 2. A standard sample containing 900 ppm each of 23 elements of "Wear metals in oil calibration standard" supplied from ASI was diluted with 2-ethylhexanoic acid ($C_8H_{16}O_2$) to be 20 mass% oxygen in the mixed sample.

Without the correction, the analysis results are lower than the standard values, indicating the influence of the absorption of coexisting oxygen. The correction is applied to the matrix effects of hydrocarbons and oxygen and to the inorganic elements in the sample. With the corrections, Table 2 shows good agreement between the analysis result values and standard values.

**Table 2.** Analyzed results with and without correction of hydrocarbons and oxygen.

| | Element (ppm) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Correction | Na | Mg | Al | Si | P | K | Ca | Ti | V | Cr | Mn |
| With | 80 | 84 | 72 | 82 | 96 | 99 | 85 | 84 | 87 | 82 | 88 |
| Without | 64 | 66 | 56 | 63 | 73 | 74 | 64 | 63 | 65 | 61 | 65 |
| Std. value | 88 | 88 | 88 | 88 | 88 | 88 | 88 | 88 | 88 | 88 | 88 |

| | Element (ppm) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Correction | Fe | Ni | Cu | Zn | Mo | Ag | Cd | Sn | Sb | Sb | Pb |
| With | 84 | 92 | 85 | 88 | 93 | 93 | 96 | 84 | 87 | 87 | 89 |
| Without | 62 | 69 | 65 | 68 | 89 | 91 | 94 | 63 | 65 | 65 | 79 |
| Std. value | 88 | 88 | 88 | 88 | 88 | 88 | 88 | 88 | 88 | 88 | 88 |

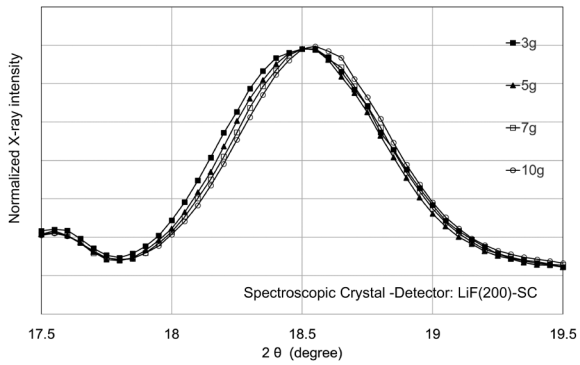


**Fig. 1.** Rh K$\alpha$ Compton Spectra obtained by samples filled 3, 5, 7, and 10 g of liquid paraffin.

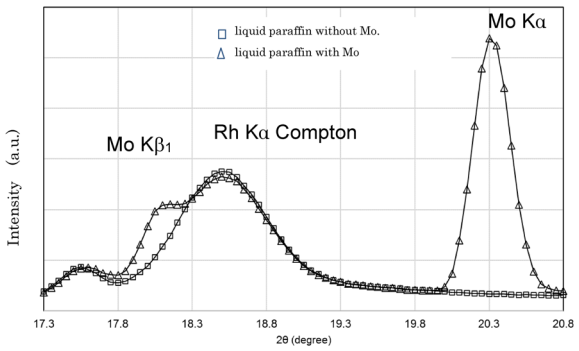


**Fig. 2.** Rh K$\alpha$ Compton Spectra of liquid paraffin with and without Mo.

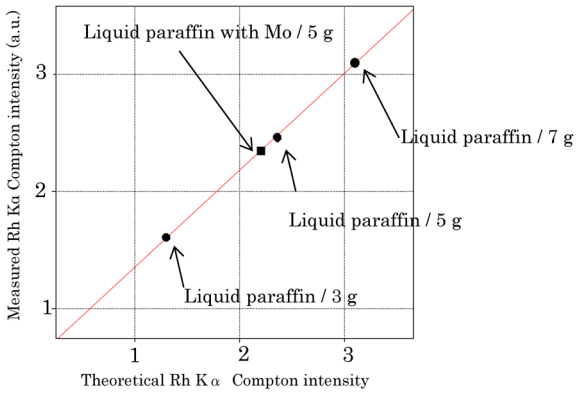


**Fig. 3.** FP sensitivity calibration curve by Rh K$\alpha$ Compton of liquid paraffin with and without Mo.

The correction for the influence of hydrocarbons and oxygen uses Rh K$\alpha$ Compton scattering X-ray intensity. Since the scattering intensities vary with concentrations of hydrocarbons and oxygen which are the main components of the oils, the ratios of hydrocarbons and oxygen can be determined using the scattering intensity in the FP method. However, the peak profile of Rh K$\alpha$ Compton scattering varies with the amount of liquid sample to be filled. Figure 1 shows the spectra of Rh K$\alpha$ Compton obtained by measuring 3 g, 5 g, 7 g, and 10 g of liquid paraffin in a sample cells covered with sample films. The profiles are normalized with the intensities at 18.50°. As shown in Fig. 1, the Rh K$\alpha$ Compton peaks shifts to the right side in larger sample volumes. When Rh K$\alpha$Compton peak intensity by using fixed angle method is measured as in the conventional analysis, this intensity change of the Rh K$\alpha$ Compton caused by peak shift gives impact to the analysis result. In order to eliminate the influence of the intensity change due to the peak shift, we have developed an algorithm for determining the net intensity as for Rh K$\alpha$ Compton integral intensity by 2$\theta$ angle scan measurement. The development provides accurate net intensity for various sample volumes. In addition, accurate net intensities of Rh K$\alpha$ Compton by using integrated intensities can be obtained since peak profiles of Rh K$\alpha$ Compton can vary with oil types.

In addition, when Mo is contained in an oil sample, the Rh K$\alpha$ Compton peak is overlapped with Mo K$\beta$1 (Fig. 2). Since the net Rh K$\alpha$ Compton intensities are calculated by profile processing of the above mentioned Rh K$\alpha$Compton spectrum after removal of Mo K$\beta$1 line overlap, even if Mo is contained in the samples, the accurate net intensity can be obtained. Figure 3 shows the sensitivity calibration curves (correlation between theoretical and measured intensities) for Rh K$\alpha$ Compton using 3 g, 5 g and 7 g of liquid paraffin and 5 g of liquid paraffin containing Mo (Mo: 2000 ppm). The calculated Rh K$\alpha$ Compton intensities are plotted on the sensitivity curve of the liquid paraffin samples, the graph indicates that the influence of Mo has been correctly removed.

## 2.3. New correction by Sample film

Materials of sample films to cover sample cells are roughly classified by polypropylene, polyester, and polyimide. Polyester film is generally used for oil analysis since it does not generally swell easily during oil analysis. However, polyester films contain more impurities than polypropylene films. There are cases where polypropylene films are suitable for the analysis of trace levels of Na, Mg, Si, Ca, and P. Various types of sample films for X-ray fluorescence analysis with different materials and thicknesses are commercially available. If sample film with different material and thickness is used, the absorptions of incident X-rays to sample and fluorescent X-rays from sample by the film change resulting in different measured fluorescent X-ray intensities.

In the conventional approach, sample film type for an analysis has to be decided beforehand. All standard samples have to be measured using same type of sample film to create calibration for quantitative analysis. One has to use a specific sample film for any application. Accordingly, sample film type cannot be changed in each application.

In the new film correction approach, the function incorporates information of film material, thickness, and impurity for theoretical intensity calculations, allowing to use a single sensitivity constant for each element without regard to film type and impurity. By using this

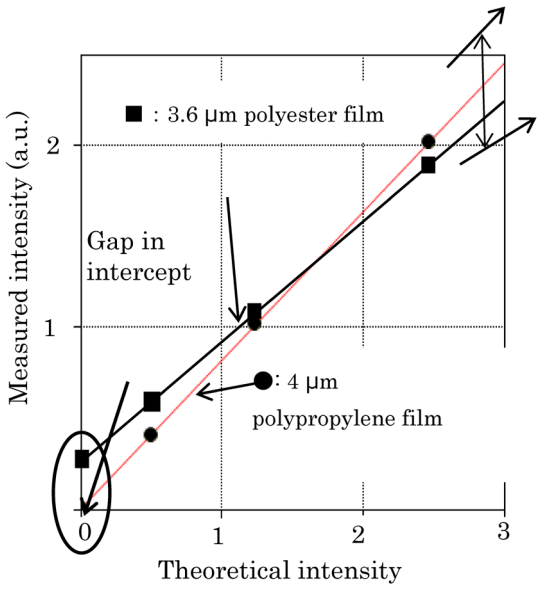


**Fig. 4.** Conventional method.

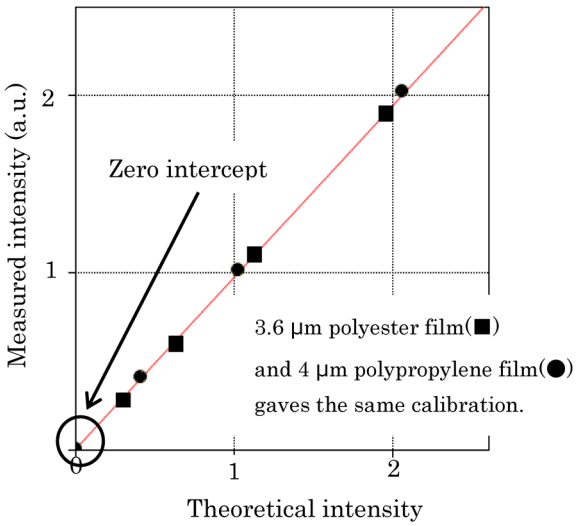


**Fig. 5.** New film correction.

function, analysis can be performed even with different film types using the film correction.

For phosphorous analysis in lubricant oils, sensitivity calibration curves of FP method for P K$\alpha$ line by both conventional method and the new film correction are shown comparing 3.6 $\mu$m polyester and 4 $\mu$m polypropylene sample films. In calibration by the conventional method shown in Fig. 4, the amounts of phosphorous impurity vary with film types, and the intercepts of calibrations are different. Also, since the absorption of X-rays by sample films varies depending on its thickness, the resulting calibration slopes are different due to different sensitivities.

On the other hand, the calibration slope is same even for different film types in the new film correction method as shown in Fig. 5. Since the theoretical intensity calculation for sensitivity calibration curve includes calculation of fluorescent X-ray absorption caused by the sample film and fluorescent X-ray from impurities in the film itself. The package of OIL-MULTI-PAK can be used with the new film correction method to analyze with common sensitivity calibration curves without regard to film types. This function allows selecting a suitable sample film for actual oil samples considering sample characteristics and analysis objectives.

## 2.4. Geometry correction

When liquid sample is poured into a sample cell, actual measuring area inside the sample, where generated fluorescent X-rays are detected is limited and the area varies with the depth from the analyzing surface level of sample. This area depends on optical geometry of the incident X-ray side (X-ray tube) and detection side of fluorescent X-rays.

The general sample model for theoretical intensity calculation (Fig. 6b) assumes that all generated fluorescent X-rays are detected in all depth from analyzing surface and detection areas are not limited. However, for high energy X-ray measurements in light element matrix samples like oils, the proportion of detectable area depends on the depth from the analyzing

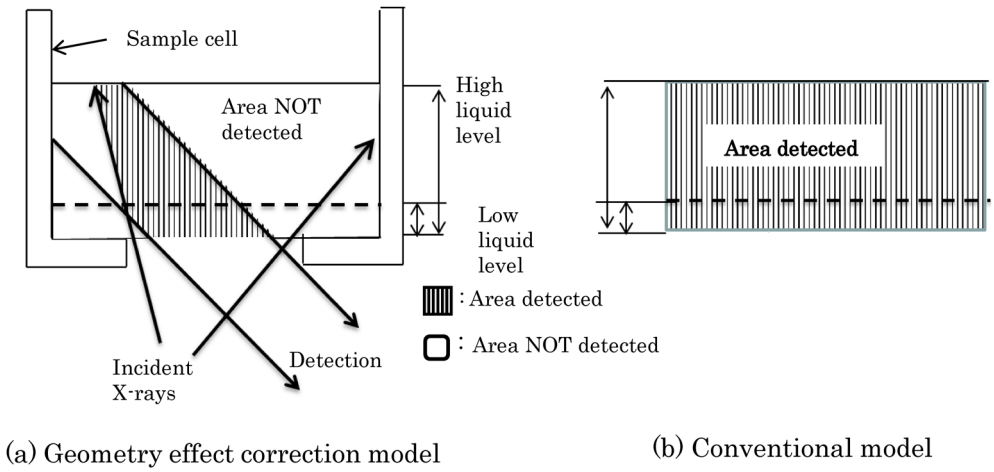


**Fig. 6.** Theoretical intensity calculation model for geometry effect correction in liquid sample.

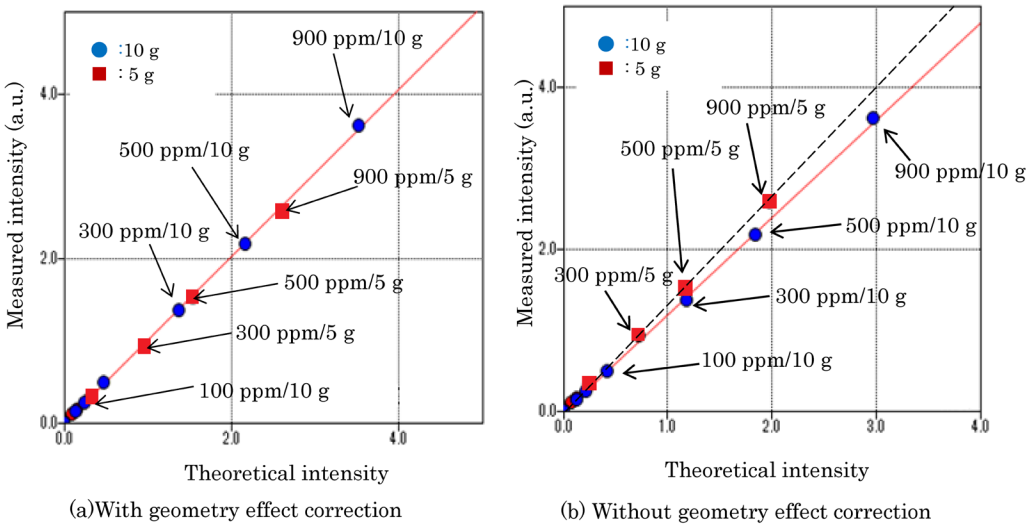


**Fig. 7.** Sensitivity calibrations of Cd K$\alpha$ line with geometry effect correction.

surface of sample. The geometry effect is significant particularly for high energy X-ray measurement of heavy elements at deeper regions of the sample as shown in Fig. 6a.

The influence of geometry effect is corrected in the theoretical intensity calculation of FP method in the package of OIL-MULTI-PAK.

In order to verify the geometry effect correction, an example of measurement for Cd in oil (analysis line: Cd K$\alpha$) is introduced. Samples of four concentration levels 100, 300, 500, and 900 ppm of Cd were prepared. The two sample masses poured into sample cells were 5 g and 10 g, respectively. The sensitivity calibration curves of FP method with and without geometry effect correction are shown in Fig. 7. In both cases, sample thicknesses obtained from sample masses were used in the theoretical intensity calculation for geometry effect correction. Sensitivity calibration curves without geometry effect correction are split into two separated lines of the 5 g and 10 g samples and the influence of sample thickness (height of liquid level) is significant. On the other hand, an unified single sensitivity calibration curve was obtained for samples of both sample thicknesses in the graph with geometry effect correction demonstrating that theoretical intensity calculation with geometry effect correction are accurately performed. Accordingly, it is not required to keep using constant sample masses for all samples which makes this oil package more flexible.

As an example of the quantitative analysis of Cd in oils, a reference sample 10 g was prepared, and the unknown sample 5 g was analyzed as shown in Table 3. The correct quantification value is obtained by applying the geometry effect correction.

In order to use geometry effect correction, the information of liquid sample thickness is required. However, it is not easy to accurately measure the height of the liquid level in a sample cell in practice. Therefore, a tool is included in the package that allows calculation of the sample thickness from the sample mass and density.

**Table 3.** Analyzed result of Cd with and without geometry effect correction.

| Cd Standard value (ppm) | Geometry effect correction | |
|---|---|---|
| | Applied | Not applied |
| 900 | 905 | 1013 |
| 500 | 484 | 540 |
| 300 | 280 | 320 |

## 3. Applications of OIL-MULTI-PAK (sulfur analysis for heavy oil, diesel oil, and gasoline)

It is easy to select specific analyzing elements from the original OIL-MULTI-PAK application and create a new customized application with the original sensitivity coefficients and application parameters depending on the oil to be measured. Measurements of standard samples are not required. By using the customized application, high throughput analysis is possible by measuring only the minimum number of elements required.

Sulfur analyses was performed on heavy oils with high sulfur concentrations and diesel and gasoline with low sulfur concentrations by using customized applications from the package.

The results are listed in Table 4.1 and Table 4.2. Sulfur analysis results of the samples with the high and low sulfur concentrations are in good agreement with the standard values. The sample film used was polyester film which has strong resistance to fuel oil samples.

## 4. Details of the Package of OIL-MULTI-PAK in Details

### 4.1. Contents of package including accessories

The analysis package consists of the followings:

– Data media: Analytical parameters such as application conditions, elements to analyze and sensitivity calibration coefficients
– Drift correction samples to adjust stored sensitivity coefficients
– Blank samples: liquid paraffin

**Table 4.1.** Sulfur analysis result of heavy oils (unit: mass%).

| Type of oil | Sample name | Supplier | Standard value | Analyzed value |
|---|---|---|---|---|
| Heavy oil | Heavy oil sulfur standard | JPI* | 0.11 | 0.11[1] |
| | Heavy oil sulfur standard | JPI* | 0.21 | 0.21[3] |
| | Heavy oil sulfur standard | JPI* | 0.53 | 0.53[3] |
| | Heavy oil sulfur standard | JPI* | 1.98 | 1.96 |
| | Heavy oil sulfur standard | JPI* | 3.04 | 3.18 |
| | Heavy oil sulfur standard | JPI* | 4.26 | 4.34 |

**Table 4.2.** Sulfur analysis result of diesel oils and gasoline (unit: ppm).

| Type of oil | Sample name | Supplier | Standard value | Analyzed value |
|---|---|---|---|---|
| Diesel oil | SRM 2723a Sulfur in diesel fuel oil | NIST** | 10.90 | 9.7 |
| | SRM 2724b Sulfur in diesel fuel oil | NIST** | 426.5 | 419 |
| | Diesel oil sulfur standard | JPI* | 9.7 | 10.4 |
| | Diesel oil sulfur standard | JPI* | 49.8 | 50.0 |
| | Diesel oil sulfur standard | JPI* | 103 | 105 |
| | Diesel oil sulfur standard | JPI* | 201 | 203 |
| | Diesel oil sulfur standard | JPI* | 479 | 491 |
| Gasoline | SRM 2298 Sulfur in gasoline (high octane) | NIST** | 4.7 | 5.4 |
| | SRM 2299 Sulfur in gasoline (reformulated) | NIST*** | 13.6 | 11.5 |
| | SRM 2296 Reformulated gasoline (ETBT 13%) | NIST*** | 40 | 38.2 |

*: JPI: The Japan Petroleum Institute

**: NIST: National Institute of Standards and Technology

– Validation sample: multi-element lubricating oil
– Density cup for 10 mL
– Portable scale
– Sample cells, disposable syringes
– Sample films (two types: polyester and polypropylene films)
– Tool for liquid cell assembly

The application is easy to setup for lubricating oil analysis by simply installing the application parameters from the data media into the ZSX Guidance software on the ZSX Primus IVi data processing PC.

After measuring the drift correction samples, the spectrometer is ready to confirm analysis values by analyzing the validation sample.

## 4.2. Measuring time

Table 5 shows default counting times of peak and background for 27 elements and total measuring time is about 12 minutes. When possible, background angles are shared by two elements in order to reduce total measurement time.

## 4.3. Lower limit of Detection (LLD)

Lower limit of detection is defined as the concentration corresponding to three times the statistical variation of the background intensity.

The LLDs for oil analysis are listed in Table 6. Statistical variation of net intensity includes the statistical variation of the background intensity. The count times used are default settings in the application package as shown in Table 5.

**Table 5.** Default counting times in the package.

| Element | Na | Mg | Al | Si | P | S | Cl | K | Ca | Ti |
|---|---|---|---|---|---|---|---|---|---|---|
| Peak(s) | 40 | 40 | 10 | 10 | 10 | 10 | 10 | 6 | 6 | 8 |
| Background(s) | 40 | 40 | 10 | 10 | 10 | 10 | 10 | 6 | 12 | 8 |

| Element | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Br | Mo |
|---|---|---|---|---|---|---|---|---|---|---|
| Peak(s) | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
| Background(s) | 8 | 8 | 8 | 24 | 24 | 24 | 24 | 24 | 16 | 8 |

| Element | Ag | Cd | Sn | Sb | Ba | Pb | Bi |
|---|---|---|---|---|---|---|---|
| Peak(s) | 8 | 8 | 6 | 6 | 8 | 8 | 8 |
| Background(s) | 8 | 8 | 6 | 12 | 8 | 16 | 16 |

LLDs can vary with sample volume, sample composition, sample film type, and amount of impurities contained in sample film. Therefore, LLDs in the table are for reference.

## 4.4. Analyzing precision

Reproducibility results of 20 different aliquots of a commercial lubricant sample is shown in Table 7. The

**Table 6.** Lower limits of detection for oil analysis (for reference).

| Element | Na | Mg | Al | Si | P | S | Cl | K | Ca | Ti |
|---|---|---|---|---|---|---|---|---|---|---|
| LLD (ppm) | 9.5 | 2.5 | 1.6 | 1.8 | 0.9 | 1.0 | 4.6 | 1.0 | 0.8 | 1.0 |

| Element | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Br | Mo |
|---|---|---|---|---|---|---|---|---|---|---|
| LLD (ppm) | 1.0 | 0.7 | 0.7 | 0.4 | 0.3 | 0.4 | 0.4 | 0.4 | 0.3 | 1.5 |

| Element | Ag | Cd | Sn | Sb | Ba | Pb | Bi |
|---|---|---|---|---|---|---|---|
| LLD (ppm) | 3.3 | 3.3 | 3.3 | 3.3 | 2.9 | 1.0 | 1.0 |

When sample film of Prolene®4.0 $\mu$m is used (Prolene is a registered trademark of Chemplex Industries, Inc).

count times used are default count times of the package shown in Table 5. Good precisions could be obtained, and the values of relative standard deviations (RSD) are less than 1% for elements in the concentration range from 100 to 2000 ppm.

**Table 7.** Repeatability test result (20 times analyses).

| Element | Ca | Zn | P | S | Mo | Mg |
|---|---|---|---|---|---|---|
| Average (ppm) | 1902 | 795 | 763 | 2205 | 80.1 | 361 |
| Std. dev. (ppm) | 8.4 | 3.0 | 3.9 | 10.2 | 0.5 | 3.6 |
| RSD (%) | 0.44 | 0.38 | 0.51 | 0.46 | 0.56 | 0.99 |

## 5. Summary

The combination of ZSX Primus IVi and OIL-MULTI-PAK allows accurate analysis for a wide variety of oil types, including trace elements in lubricating oil, waste oil, and fuel oils such as heavy oil, diesel, gasoline, and bio-fuels.

OIL-MULTI-PAK employs new advanced correction functions. Accurate correction for influence of hydrocarbon and oxygen can be applied even for oils with unknown and different base oil types are different or not known. Geometry correction eliminates requirement of precise volume sampling allowing accurate analysis. Furthermore, the new sample film correction increases the flexibility to choose sample film. These new features of OIL-MULTI-PAK improve versatility of the package for oil analysis and make oil analysis easier with quick setup.