Application Note: 41637

Analysis of Lubricant Additive Elements per ASTM D 4927 by X-Ray Fluorescence

ARL ADVANT'X Series with IntelliPower™ Sequential X-Ray Fluorescence Spectrometer

Key Words

- ARL ADVANT'X – 3600W
- Oil
- X-Ray Fluorescence
- XRF

Introduction

Wavelength Dispersive X-ray fluorescence (WDXRF) can be used to analyze various elements in oils in the range of a few parts per million to percent levels. This report presents results achieved for various additive elements in oils, namely Ba, Ca, Cu, Mg, P, S and Zn. The analytical results reported here have been obtained following the ASTM D 4927 method.

Instrument

The powerful and stable Thermo Scientific ARL ADVANT'X WDXRF instrument was used for this study.

The instrument geometry is optimized to provide the highest sensitivity including configuration with a Rh anode X-ray tube, type 4 GN. Ease of operation is obtained through the state-of-the-art OXSAS software.

Sample preparation

Analysis of liquids or oils by WDXRF requires special liquid cassettes or cups and a helium environment in the primary chamber.

A series of CONOSTAN standards and Alpha Research standards were used to produce the calibration curves. The ASTM D 4927 method also recommends a list of additional standards.

Chemplex 1440 type liquid cells have been used employing a 4 micron polypropylene (PP) film to close the cell.

A fixed mass of sample was taken rather than a fixed volume as it is very simple and convenient: 20 grams of oil is poured directly into the liquid cell which is placed on a balance.

Each sample should be prepared in triplicate to average out the errors arising from sample preparation, the errors being attributable to differences in the weighing, PP film thickness and the possibility of sample inhomogeneity.

Background and matrix corrections

The background levels of different samples are not constant. This is due to varying concentration ranges for the various elements and particularly the heavy elements, e.g. Ba from 0 to 1%. Hence there is the need for background subtraction in order to obtain net intensities.

An important correction factor is the absorption of the element by itself. This absorption coefficient can be calculated either empirically or by using fundamental parameter algorithms. Empirical methods require a large number of standard samples which is often neither practical, nor possible. On the other hand, oils represent a case study in the use of fundamental parameters in the determination of theoretical alpha correction factors. These will be used in the regression calculation in order to derive calibration curves and help improve the accuracy of analysis.

Theoretical alpha factors are generated for a specific matrix, e.g. mineral oil, for the various elements present in the sample and the instrumental parameters such as anode type, voltage applied, incident and emergent angles.

ELEMENT	CRYSTAL/DETECTOR	COLLIMATOR
Mg	AX06/FPC	0.6°
S	Ge111/FPC	0.15°
P	Ge111/FPC	0.15°
Ca	LiF200/FPC	0.15°
Cu	LiF200/FPC	0.15°
Zn	LiF200/FPC	0.15°
Ba	LiF200/FPC	0.15°

Table 1: Choice of crystal, detector and collimator

Measurement conditions and results

The Rh target X-ray tube conditions are 30kV, 90mA for all elements. Analysis time is typically 30 s per element except for Mg where 60 s was used. However in view of the improved sensitivity of today's WD-XRF instruments 10 to 20 s counting time per element would be sufficient. Other measurement conditions are listed in Table 1. As net intensities are used for the analysis, background measurement is also required to be subtracted from the peak intensity. Consequently, the total analysis time increases by the time taken for each background measurement. As indicated in the ASTM method, only one background measurement per element was used so as to keep the total analysis time as short as possible.

Ranges of analysis for the various elements are shown in Table 2 together with the Standard Error of Estimate calculated for each curve. This value represents the average accuracy of analysis for each element over the given concentration range. Figures 1 and 2 represent the calibration curves obtained for S and Ba and show the excellent accuracy obtained on a large range of concentrations.

ELEMENT	RANGE	SEE
Mg	LoD -0.19 %	12 ppm
S	0.07 % - 4 %	0.02 %
P	LoD -0.5 %	28 ppm
Ca	LoD -0.5 %	20 ppm
Cu	LoD -0.06 %	2.7 ppm
Zn	LoD -0.17 %	6.6 ppm
Ba	LoD -1 %	50 ppm

Table 2: Range of calibration and standard error of estimate achieved

LOD = Limit of detection
SEE = Standard error of estimate: a measure of accuracy

Conclusion

Quantitative analysis of oils can be achieved successfully by WDXRF with very good accuracy providing an adequate set of calibration samples is used. Several factors such as matrix, background and overlap corrections influence the quality of the regressions and the final results.

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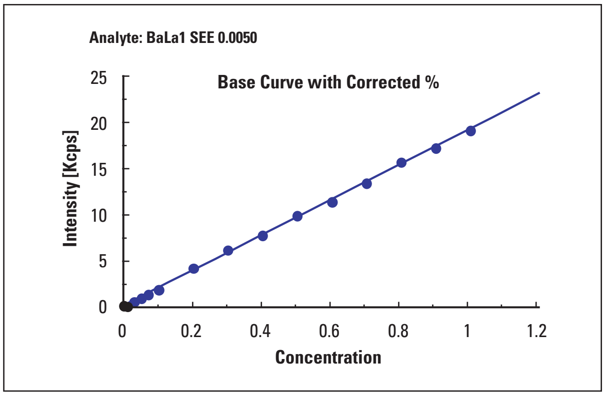

Figure 1: Calibration curve for Ba

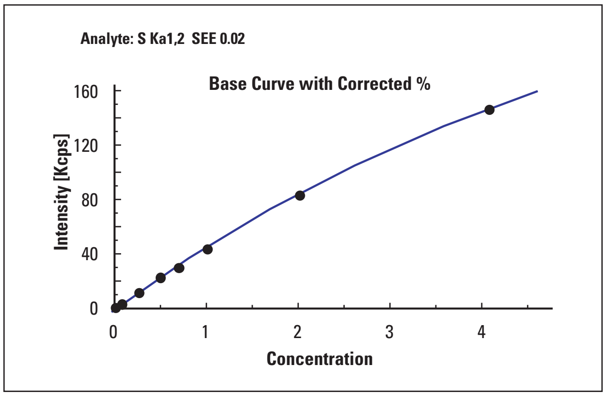

Figure 2: Calibration curve for S

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