APPLICATION NOTE

No. AN41668

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

## Thermo Scientific ARL PERFORM'X Series Advanced X-Ray Fluorescence Spectrometers

**Key words**
ARL PERFORM'X 4200 W, 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

Thermo Scientific ARL PERFORM'X series spectrometer used in this analysis was a 4200 watt system. This system is configured with 6 primary beam filters, 4 collimators, up to nine crystals, two detectors, helium purge and our 5GN+ Rh X-ray tube for best performance from ultra-light to heaviest elements thanks to its 50 micron Be window. This new X-ray tube fitted with a low current filament ensures an unequalled analytical stability month after month.

The ARL PERFORM'X offers the ultimate in performance and sample analysis safety. Its unique LoadSafe design includes a series of features that prevent any trouble during sample flushing and loading. Liquid cassette recognition prevents any liquid sample to be exposed to vacuum by mistake. Over exposure safety automatically ejects a liquid sample if X-ray exposure time is too long.

The Secutainer system protects the primary chamber by vacuum collecting any loose powders in a specially designed container, easily removed and cleaned by any operator. For spectral chamber protection, the ARL PERFORM'X uses a helium shutter designed for absolute protection of your goniometer during liquid analysis under helium operation. In the "LoadSafe Ultra" optional configuration, a special X-ray tube shield provides total protection against sample breakage or liquid cell rupture.

### Sample preparation

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 | Collimater |
|---|---|---|
| **Mg** | AX06/FPC | 0.40° |
| **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 30 kV, 90 mA 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, 2 and 3 represent the calibration curves obtained for P, Ca and Ba and show the excellent accuracy obtained on a large range of concentrations.

| Element | Range | SEE |
|---|---|---|
| **Mg** | LoD -0.19% 1 | 2 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

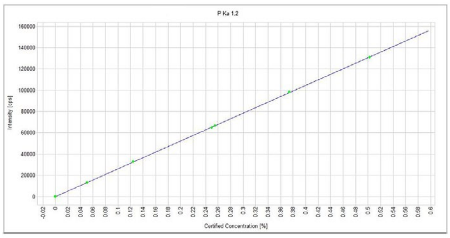

Figure 1: Calibration curve for P

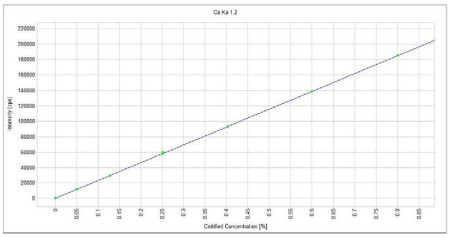

Figure 2: Calibration curve for Ca

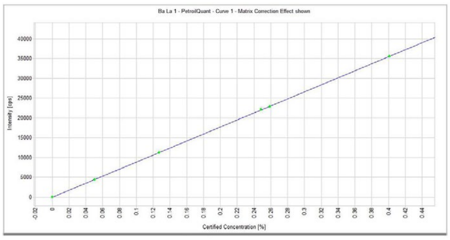

Figure 3: Calibration curve for Ba

## 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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