Application Note: 41713

# Analysis of unused lubricating oils per ASTM D4927 and ASTM D6443

*ARL OPTIM'X Wavelength Dispersive X-Ray Fluorescence Spectrometer*


**Key Words**

- ARL OPTIM'X
- ASTM D 4927
- ASTM D 6443
- Lubricant additives
- Unused lubricating oils
- WDXRF


Properly formulated lubricants are critical to preventing premature engine and machinery failure through over-heating and excessive wear. To protect precision equipment operating under extreme temperatures and heavy loads, top quality lubricants depend on "performance packages" of specially formulated blends of organometallic additives. From high-end automotive engine and gear oils, to aviation and marine engine oils, to transmission and hydraulic fluids, finished lubricants must properly protect, seal, cool, and clean essential machinery moving parts.

| Additive package components | Common elements of interest |
|---|---|
| Detergents | Mg, Ca, Ba |
| Anti-wear & extreme-pressure (AW/EP) agents | P, S, Cl, Cu, Zn |
| Antioxidants | Ca, Cu, Ba, Mo |
| Rust & corrosion inhibitors | P, S, Zn |

Table 1. Important metals and other elements in lubricant additives.

Wavelength dispersive X-ray fluorescence (WDXRF) elemental analysis is an industry-preferred method to aid blending & quality control and new product development of lubricants and additives (Table 1) due to ease of sample preparation, fast multi-element analysis and precise results from low ppm to 5% or higher elemental concentrations. Two particular WDXRF test methods are accepted by petroleum industry as the leading quality standards for elemental determination of blended lubricants, additives and additive packages, ASTM D 4927 and ASTM D 6443 (Table 2). This study focuses on a cost-effective analysis solution for achieving these standards using a Thermo Scientific ARL OPTIM'X.

| | Mg | P | S | Cl | Ca | Zn | Cu | Ba |
|---|---|---|---|---|---|---|---|---|
| ASTM D 4927-05 | | 0.01-0.5 | 0.1-4.0 | | 0.01-0.8 | 0.01-0.5 | | 0.04-8.5 |
| ASTM D 6443-04 | 0.003-0.20 | 0.001-0.25 | 0.030-1.00 | 0.001-0.20 | 0.001-0.40 | 0.001-0.25 | 0.001–0.05 | |

Table 2. Comparison of elements and concentrations covered by ASTM methods (undiluted mass %)

## Instrumentation

The Thermo Scientific ARL OPTIM'X is a wavelength dispersive XRF instrument designed for ease of use with minimal running and maintenance costs. Its low power 50W Rhodium target X-ray tube provides equivalent sensitivity to conventional 200W instruments due to its unique Ultra Closely Coupled Optics. In addition, the patented miniaturized SmartGonio™ (Figure 1) provides spectral resolution 10 times better than high-end EDXRF instruments.

The SmartGonio's sequential analysis capabilities cover all lubricant elements of interest from Mg (Z=12) to Ba (Z=56) or heavier. For additional performance, two Multichromator™ fixed channels of specially curved and focused crystals can be fitted to reduce analysis time or improve sensitivity. As an added advantage, ARL OPTIM'X does not require the same auxiliary water cooling as higher-powered wavelength dispersive systems despite providing similar performance.

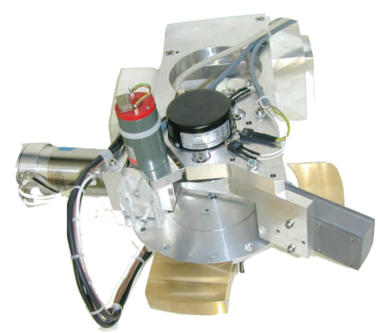

Figure 1. SmartGonio

## PetroilQuant™ pre-calibration

Instrument calibration for ASTM D 4927 and ASTM D 6443 consists of pre-analyzing calibration standard materials and applying subsequent mathematical corrections to compensate for interelement effects of X-ray excitation and fluorescence (D 4927 includes an alternative internal standard procedure requiring more prep time). Single element standards for Zn, P, S, Mg, Cl, Cu and Ca (from Conostan®, Champlain, New York) and a high-purity mineral oil dilution solvent were blended into multi-element calibration standards of varying concentrations from 0-1.5 mass % per each ASTM method.

Appropriate channel conditions were configured on the ARL OPTIM'X for intensity measurement of the K -spectral line for each analyte. The OXSAS software analysis package then calculated the interelement alpha correction factors and supplied a calibration curve for each element. Such calibrations need only be performed once and may be pre-installed on the ARL OPTIM'X using the PetroilQuant pre-calibration package. Due to its unique design, the ARL OPTIM'X once calibrated exhibits exceptional analytical stability over time (see long term stability results overleaf).

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## Sample preparation and analysis

Finished lubricant samples were analyzed directly without dilution or other sample preparation (more concentrated additive packages than per Table 2 may be diluted to suitable ranges). Lubricant samples were simply poured into Chemplex analysis cups to a standard depth of 10 mm fitted with 6  m polypropylene (Spectrolene) sealing film. Samples are analyzed under a helium environment to reduce ambient air interferences.

Sensitivities and limits of detection were calculated from the ASTM-derived calibration curves. In practice, the analysis time chosen for each element depends on the precision and throughput required. For this study 120 seconds counting time per element was used to calculate limits of detection in Table 3; shorter times are possible depending on specific application needs.

## Accuracy

The combinations of X-ray crystals and detectors used for analysis are shown in Table 3, along with Limits of Detection (LoD) achieved and accuracy measurements. The Standard Error of Estimate (SEE) measures the accuracy of the calibration curve regressions; the resulting data show the high accuracy of the calibration curves produced using ASTM guidelines.

| ELEMENT | SMARTGONIO CONFIGURATION | ASTM RANGES [mass %] | CALIBRATION RANGE LoD - ASTM max [mass %] | SEE [ppm] |
|---|---|---|---|---|
| Mg | AX06/FPC | 0.003 - 0.20 | 0.00080 - 0.20 | 9 |
| P | PET/FPC | 0.001 - 0.50 | 0.00020 - 0.50 | 7.9 |
| S | PET/FPC | 0.030 - 4.00 | 0.00017 - 4.00 | 3 |
| Cl | PET/FPC | 0.001 - 0.20 | 0.00100 - 0.20 | 19 |
| Ca | LIF200/FPC | 0.001 - 0.80 | 0.00015 - 0.80 | 9.5 |
| Cu | LIF200/SC | 0.001 - 0.05 | 0.00008 - 0.05 | 1.3 |
| Zn | LIF200/SC | 0.001 - 0.50 | 0.00006 - 0.50 | 5 |

Table 3. Instrument configuration and accuracy measurements

FPC: Flow proportional counter
SC: Scintillation counter
LoD: Limit of detection = $3\sqrt{(BEC/Qt)}$
SEE: Standard error of estimate reported at lower end of concentration range

## Analytical precision

Precision tests were performed for selected elements in order to verify compliance with ASTM stated limits. Results for a 1.00 mass % sulfur-containing additive (also containing appreciable Ca, Mg, P and Zn) per a typical marine lubricant are shown as an example in Figure 2. Seven different liquid cells of the same additive sample were prepared and analyzed. With an average sulfur concentration result of 1.002 % and relative standard deviation between measurements of only 0.49 %, the short term repeatability results obtained by the ARL OPTIM'X fell easily within the limits required by both ASTM methods.

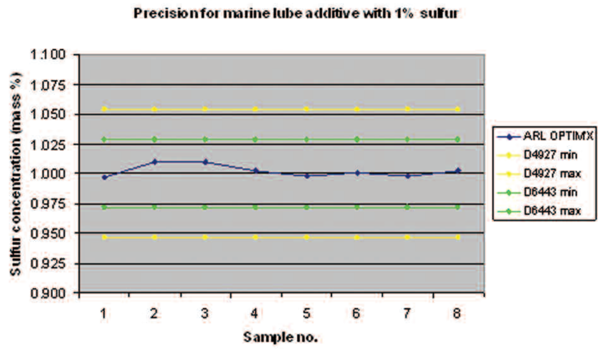


Figure 2. Precision for a lubricant additive

## Long term stability

Long term stability was evaluated over a two month span using the same marine additive diluted to 0.21 % sulfur. The standard deviation of measurements obtained was only 9.5 ppm (0.00095 %) at an average sulfur level of 2,102 ppm or relative 0.45 % deviation. These reproducibility values again lie well within the ASTM requirements. Once initially calibrated, the ARL OPTIM'X can perform such analyses for extended periods without requiring recalibration.

## Conclusion

Lubricant additives, performance packages and final blended lubricants require tight quality control to meet demanding specifications. Wavelength dispersive XRF due to its ease of sample prep, wide dynamic range and precision is the preferred analytical technique for measuring multiple elements in functional lubricant additives. The Thermo Scientific ARL OPTIM'X with PetroilQuant pre-calibration is a uniquely cost effective WDXRF instrument that well exceeds the precision and long-term stability requirements of the two main lubricant industry standard test methods ASTM D 4927 and ASTM D 6443.

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AN41713_E 12/09C