Application Note: 41623

Analysis of oil industry products with PetroilQuant™

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

Key Words

- ARL ADVANT'X
- IntelliPower™
- Oil
- PetroilQuant™
- X-Ray Fluorescence
- XRF

Introduction

Thermo Scientific offers a range of X-ray instruments and solutions for the petrochemical industry depending on the elements needed, their concentration ranges, the variety of samples (solids and liquids) and the throughput requirements. From the cost effective ARL OPTIM'X instrument for simple and dedicated applications (sulphur in oils, Pb in gasoline or a few elements-few samples scenario) to the most advanced ARL ADVANT'X Series for demanding applications in a central laboratory, Thermo Scientific can provide the most suitable solution for every area in the petrol industry. Our XRF spectrometers have been shown to be compliant with various norms such as ASTM D2622, ASTM D4927, ISO 20884, etc. thanks to their high sensitivity and stability.

Petrochemical regulations are becoming stricter demanding lower levels of quantification for key elements such as sulfur (S), nickel (Ni), vanadium (V), lead (Pb), etc. Wavelength Dispersive X-ray Fluorescence (WDXRF) is increasingly solicited for these analyses in the petrol industry as it has several advantages over other methods:

- Excellent repeatability
- Excellent resolution, especially for light elements (Na to Ca)
- High dynamic range (sub-ppm to 100%)
- Flexibility in terms of measurement of analytical lines, background positions and internal references
- Little or no sample preparation in most cases (oils can be directly measured without dilution)
- Multi-element and multi-matrix capability

Instrumentation and calibration

The ARL ADVANT'X IntelliPower series can be fitted with SmartGonio™ or with Universal Goniometer for a more extended range of elements, lower concentration limits, higher throughput and faster speed of analysis.

With a clever management of power, the ARL ADVANT'X IntelliPower spectrometers can operate at 1200W and even 2500W without requiring external water cooling.

The analysis of liquids can be performed with ease and minimum sample preparation in XRF. The ARL ADVANT'X series integrates an innovative shutter separating the primary chamber from the goniometer chamber. When liquid samples are analyzed, helium gas is introduced only in the primary chamber keeping the goniometer under vacuum. This allows a rapid change-over from a vacuum to a helium environment (less than 2 min.) and permits the measurement of solids and liquids in the same batch without compromising the stability of analysis. In addition, it protects the goniometer from any liquid spillage. Helium consumption is also kept to a minimum.

ARL ADVANT'X IntelliPower 1200 and 2500 XRF spectrometers have been calibrated with Petroil Quant™, a unique pre-calibration program to help analysts in the petrol industry. PetroilQuant™ is designed for fast quantification of up to 24 elements in fuels, lubricants and heavy residual oils. In addition to sulfur in automotive fuels, analysis of other elements generally needed for blending control of fresh lubricants such as Sodium (Na), Magnesium (Mg), Silicon (Si), Phosphorus (P), Chlorine (Cl), Potassium (K), Calcium (Ca), Zinc (Zn), Molybdenum (Mo), Bromine (Br) and Barium (Ba) can be addressed with this analytical package. Further improvements on accuracy for specific elements can be obtained by fine tuning the basic calibration.

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Sample preparation and results

A series of reference materials are used to derive calibration working curves for analysis of additives in lube oils. Liquid cells are filled with constant volume of the various calibration standards.

The analysis time can range from 8 to 20 seconds depending on the element and the precision required.

A working curve is established for each element using the Multi-Variable-Regression incorporated in the new state-of-the-art OXSAS software package. Limits of detection for the various elements were calculated from these curves and are listed in Table 1. The values of Standard Error of Estimate (SEE) provide an information about the average accuracy that can be reached.

Element	Range [%]	Typical SEE [ppm]	Typical LOD on ARL ADVANT'X IntelliPower 2500 (3 sigma) [ppm] counting time shown	Typical LOD on ARL ADVANT'X IntelliPower 2500 (3 sigma) [ppm] in 100s counting Universal Gonio	Typical LOD on ARL ADVANT'X IntelliPower 1200 (3 sigma) [ppm] in 100s counting Universal Gonio
Mg	LoQ - 0.4	9	8 ppm in 20s	3.7	5.7
P	LoQ - 0.5	7.9	1 ppm in 12s	0.33	0.5
S low %	LoQ - 0.1	3	1 ppm in 12s	0.33	0.5
S high %	0.05 - 5	100	n.a.	n.a.	n.a.
Cl	LoQ - 2.5	19	2.4 ppm in 10s	0.77	1.2
Ca	LoQ - 0.8	9.5	0.9 ppm in 8s	0.25	0.4
Cu	LoQ - 0.12	1.3	0.45 ppm in 8s	0.12	0.2
Zn	LoQ - 0.5	5	0.55 ppm in 8s	0.15	0.2
Ba	LoQ - 0.4	2.2	2.2 ppm in 8s	0.63	1.0
Na	LoQ - 0.4	23	27 ppm in 20s	11.8	18.5
Al	LoQ - 0.06	3.4	2.6 ppm in 16s	1.1	1.7
Si	LoQ - 0.4	8	1.9 ppm in 14s	0.7	1.1
K	LoQ - 0.8	8	1.1 ppm in 8s	0.31	0.5
Ti	LoQ - 0.06	0.7	0.55 ppm in 8s	0.15	0.2
V	LoQ - 0.06	0.6	0.55 ppm in 8s	0.15	0.2
Cr	LoQ - 0.06	0.8	0.66 ppm in 8s	0.19	0.3
Mn	LoQ - 0.06	0.1	0.55 ppm in 8s	0.15	0.2
Fe	LoQ - 0.12	0.3	0.55 ppm in 8s	0.15	0.2
Ni	LoQ - 0.06	0.1	0.44 ppm in 8s	0.12	0.2
Br	LoQ - 0.06	0.5	0.55 ppm in 8s	0.15	0.2
Mo	LoQ - 0.4	5.8	0.44 ppm in 8s	0.12	0.2
Cd*	LoQ - 0.06	0.8	4 ppm in 12s	1.43	2.3
Sn	LoQ - 0.06	2.9	2.1 ppm in 12s	0.73	1.1
Sb	LoQ - 0.06	0.6	2.3 ppm in 12s	0.8	1.3
Pb	LoQ - 0.12	0.6	1.54 ppm in 8s	0.44	0.7

Table 1: Analytical results with various counting time for 1200W and 2500W configurations

- SEE : Standard Error of Estimate is a measure of accuracy
- n.a. = not applicable
- LOD : Limit Of Detection
- The Limit of quantification can be estimated from the LoD: LoQ = 3 x LoD
- *Cd requires the use of a primary beam filter to suppress overlapping lines due to the rhodium anode of the X-ray tube

Conclusion

Many different elements in various types of oil industry products can be analyzed with good accuracy and precision thanks to the PetroilQuant program coupled to ARL ADVANT'X IntelliPower XRF spectrometers. This represents a very cost effective analytical solution for any laboratory dealing with petrochemical products. The ARL ADVANT'X IntelliPower spectrometers can operate at 1200W and even 2500W without requiring external water cooling. Therefore neither tap water, nor a water cooler is required.

Furthermore the new state-of-the-art OXSAS analytical software under Windows® XP Professional provides comprehensive analytical functions and ease of use.

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

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