

Analysis of Oils

Thermo Scientific ARL PERFORM[®]X 4200 Advanced WDXRF Spectrometer

Key Words

- ARL PERFORM[®]X
- Analysis of oils
- XRF
- X-ray fluorescence



Introduction

Our company offers a range of X-ray fluorescence 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 Thermo Scientific 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 Thermo Scientific ARL PERFORM[®]X spectrometer for demanding applications in a central laboratory, we 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



Instrument

The ARL PERFORM[®]X spectrometer used in this analysis is a 4200 watt system. This system is configured as standard with 6 primary beam filters, 4 collimators, up to nine crystals, two detectors, and our 5 GN Rh X-ray tube for best performance from ultra light to heaviest elements.

Along with these standard features, the ARL PERFORM[®]X was equipped with helium flush capability for performing liquid analysis. The unique integrated

shutter provides a barrier between the primary analysis chamber and the spectral tank. This system offers not only a greater security for crystal and detector stability, but also reduces the amount of helium needed during analysis.



The ARL PERFORM[®]X can be equipped with a choice of tube protections. The first choice is an anti-drip filter fitted to the programmable beam filter mechanism. It is so transparent to X-rays that even light elements can be measured when it is engaged. The second choice is an X-ray tube shield protection that covers the entire end of the tube to ensure complete protection for liquid spills.

As a leader in innovation, the ARL PERFORM[®]X offers sample recognition technology to help protect your instrument from analyzing liquid samples under vacuum.

Analytical measurement

A series of samples were prepared from a Conostan standard containing 50 ppm of the elements listed in Table 1. Dilutions with base oil were used to produce standard samples containing concentrations up to 50 ppm. The standard oils were poured directly into liquid cells which were fitted with 6 micron thick polypropylene film. The base dilution oil was also used as a blank standard in the calibrations.

Typical performance

Table 1 gives a summary of analytical results obtained using a set of international standards. Limits of detection (LoD) were determined using 100 seconds per element counting times: $LoD = 3 \text{ square root (BEC/Qt)}$ where:

- BEC is background equivalent concentration in %
- Q is the sensitivity in counts per second per percent
- t is the counting time

Primary beam filters are used for several elements, namely Ni, Cu, Zn, Hg, Tl, As, Pb, Ag and Cd in order to improve the peak to background ratio or to suppress Rh lines due to the X-ray tube anode.

UniQuant standard-less analysis

As in many real life cases, obtaining any or enough standards to create a calibration is not always possible especially in case of oil mixtures, such as waste oils. In such situations, our company offers the most comprehensive standard-less package on the market: Thermo Scientific UniQuant program.

The UniQuant package is a factory calibration based on 64 pure element standards that allows for concentration determination of unknown samples in any matrix by using complex mathematical algorithms. These algorithms

Element/ Line	Crystal/ Detector	KV-mA	Number of Samples	SEE ppm	PBF	LoD (ppm)
Na K α	AX06/FPC	30/120	6	4.1		8.45
Mg K α	AX06/FPC	30/120	6	1.9		2.21
Al K α	PET/FPC	30/120	6	0.9		0.99
S K α	PET/FPC	30/120	6	0.8		0.58
Si K α	InSb/FPC	30/120	6	0.8		0.54
P K α	Ge111/FPC	30/120	6	0.53		0.33
Sn L α	LiF200/FPC	30/120	6	0.45		0.52
Ca K α	LiF200/FPC	30/120	6	0.6		0.14
Ba L α	LiF200/FPC	50/72	6	0.4		0.34
Ti K α	LiF200/FPC	50/72	6	0.45		0.11
V K α	LiF200/FPC	50/72	6	0.23		0.1
Cr K α	LiF200/FPC	50/72	6	0.41		0.1
Mn K α	LiF200/FPC	50/72	6	0.41		0.11
Fe K α	LiF200/FPC	50/72	6	0.26		0.12
Ni K α	LiF200/SC	50/72	6	0.45	Yes	0.07
Cu K α	LiF200/SC	50/72	6	0.34	Yes	0.07
Zn K α	LiF200/SC	50/72	6	0.44	Yes	0.07
Hg L α	LiF200/SC	50/72	2	N.A.	Yes	0.15
Tl L α	LiF200/SC	50/72	2	N.A.	Yes	0.11
As K β	LiF200/SC	50/72	6	1.7	Yes	0.58
Pb L β	LiF200/SC	50/72	6	0.56	Yes	0.3
Mo K α	LiF200/SC	60/60	6	0.48		0.22
Ag K α	LiF200/SC	60/60	6	1.1	Yes	0.88
Cd K α	LiF200/SC	60/60	6	0.54	Yes	0.94

Table 1: Limits of detection (LoD) in oils

PBF= Primary beam filter
N.A.= not applicable
FPC = Flow proportional counter
SC = Scintillation counter

correct for matrix effects as well as inter-elemental effects to provide highly accurate and precise results.

Conclusion

It is seen that analysis of oil can be performed with ease using the ARL PERFORM[®]X sequential XRF spectrometer. Most limits of detection are below 0.5 ppm except for lighter elements and the elements that are interfered by Rh lines from the X-ray tube. In the first case it is due to the X-ray fluorescence absorption by the polypropylene foil that retains the sample in the liquid cell. In the

latter case it is due to the use of the primary beam filter to remove the Rh lines from the spectrum.

Excellent stability and precision is achieved for all elements thanks to the integrated helium shutter. The counting time (analysis time) will be selected for each element depending on the performance (precision and limit of detection) and throughput required.

Furthermore, operation is made easy through the new state-of-the-art OXSAS software which is able to operate with the latest Microsoft Windows[®] 7 system.

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

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