

Elemental analysis

Thermo Scientific PetroilQuant for ARL PERFORM'X XRF spectrometer

X-Ray Fluorescence Analytical Package

As quality and environmental demands on the petroleum industry become stricter, key elemental contaminants require ever-lower levels of quantification, for example, stricter regulations on sulfur (S) in vehicle fuels, reduced trace metals that poison catalysts and induce corrosion such as nickel (Ni) and vanadium (V), and reduced catalyst fines of aluminum (Al) and silicon (Si). The proven ability of Wavelength Dispersive X-ray Fluorescence (WDXRF) to produce highly reliable and repeatable results is increasingly solicited for such analyses in the petroleum industry. Its main advantages for such analyses are:

- 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 (samples can be directly measured without dilution)
- Multi-element and multi-matrix capability

Numerous ASTM, ISO, IP and other international standard test methods have been developed for the petroleum industry using WDXRF. Our company offers a range of X-ray instruments and solutions depending on the elements needed, their concentration ranges, the variety of samples (liquids and solids) and the throughput requirements. The advanced Thermo Scientific™ ARL™ PERFORM'X spectrometer (Figure 2) provides full capabilities for demanding applications such as trace contaminant quantification in heavy fuels, wear metals in used lubricants, and fresh and spent catalyst characterization. The instrument is noted for high sensitivity and stability across a wide range of petroleum applications.



Figure 1. Loading of liquid cell



Figure 2. ARL PERFORM'X WDXRF spectrometer.

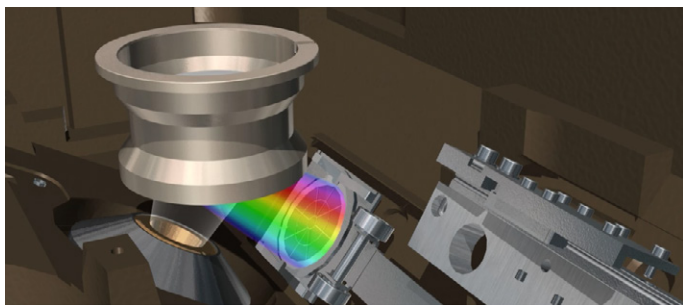


Figure 3. Cassette for liquids in analysis position over the X-ray tube with helium shutter in position.

Liquids analysis is performed rapidly as a quick change-over to helium environment can be done thanks to the helium shutter of the ARL PERFORM'X spectrometer. This state-of-art shutter allows to keep the goniometer under vacuum at all times, thus ensuring a high stability of results for liquids. The use of the optional shutter located between the spectrometer tank and the primary chamber provides the following advantages:

- Lowest Helium consumption
- Prevention of chemical attack on goniometer crystals due to volatile organic molecules in the spectrometer.
- Stable and repeatable measurements for both solids and liquids.

This shutter is part of the LoadSafe concept of the ARL PERFORM'X that includes in addition a safety against loading liquids in vacuum and an automatic unloading in case of over-exposure of the liquid cell to X-rays.

To provide faster solutions and meet tougher requirements in the evolving industry, we developed PetroilQuant, a unique pre-calibration program with petroleum analysts in mind. PetroilQuant is designed for use in conjunction with the ARL PERFORM'X X-ray spectrometer and is capable of quantifying up to 30 elements in a variety of light and heavy fuels, lubricants, crude oil and other petroleum process streams both quickly and cost-effectively.

With PetroilQuant, Thermo Scientific X-ray spectrometers are calibrated for a series of elements in a wide dynamic range covering multiple petroleum matrices. PetroilQuant requires no analytical expertise and provides a "ready to run" analytical package for beginners as well as advanced users of our XRF instruments. Further refinement or fine tuning for specific elements can always be achieved either in the factory prior to shipment or after installation using the customer's own set of standards.

In addition to Sulfur (S) in light and heavy fuels, PetroilQuant covers typical elements needed for blending control of fresh lubricants such as Zinc (Zn), Phosphorus (P), Chlorine (Cl), Calcium (Ca), Magnesium (Mg), Molybdenum (Mo), Silicon (Si), Barium (Ba). Additional elements are available on option. They are listed in the appended table.



Figure 4. PetroilQuant calibration maintenance kit.

The salient features of this unique package are:

- The pre-calibration program facilitates quantitative analysis for a number of elements in automotive fuels, lubricants, heavy residual oils and wear metals in lubricants
- PetroilQuant is developed with built-in knowledge and expertise in order to help the analyst deal with a variety of petroleum samples in wide concentration ranges
- PetroilQuant provides a "ready to run" analytical package for beginners as well as advanced users of our XRF instruments
- PetroilQuant saves time and money as it offers a global calibration program which otherwise would require many standards, analytical expertise, and instrument time
- In conjunction with ARL PERFORM'X Series, it offers the most cost-effective solution for any laboratory dealing with petroleum products

PetroilQuant can be installed on ARL PERFORM'X Series for an extended range of elements, lower concentration limits, higher throughput, and faster speed of analysis.

Specifications

A series of reference materials are used to derive calibration working curves for analysis of additives in a petroleum base. This factory pre-calibration can be optimized on-site using customer's own standard samples.

The standard PetroilQuant package for ARL PERFORM'X spectrometer includes up to 30 elements in petroleum products.

Analysis times typically range from 8 to 38 seconds depending on the element, the precision required and the power level. Table below shows typical limits of detection which are 3 sigma values from running a repeatability test on a blank oil sample.

A working curve is established for each element using the Multi-Variable-Regression incorporated in the instrument software package. This pre-calibration includes a set of setting-up samples for maintenance of the calibration curves over time. No standard samples are delivered with this pre-calibration.

Pre-calibrated elements

The 9 elements in bold are included in the basic package. The other elements are optional.

Element	Line	Analytical Range (%)	Typical LoD (ppm) 100s 4200W	Typical LoD (ppm) 100s 2500W	Typical LoD (ppm) 100s 1500W
Ag	K α	LoQ-0.06	2.01	2.4	3.12
Al	K α	LoQ-0.06	1.9	2.25	2.9
As	K β	LoQ-0.06	0.94	1.1	1.45
Ba	L α	LoQ-0.8	0.42	0.52	0.65
Bi	L α	LoQ-0.12	0.37	0.45	0.57
Br	K α	LoQ-0.12	0.2	0.24	0.31
Ca	K α	LoQ-3.0	0.2	0.24	0.31
Cd	K α	LoQ-0.06	2.5	3	3.88
Cl	K α	LoQ-2.0	0.91	1.1	1.39
Co	K α	LoQ-0.06	0.17	0.21	0.26
Cr	K α	LoQ-0.06	0.14	0.17	0.22
Cu	K α	LoQ-0.12	0.11	0.14	0.17
Fe	K α	LoQ-0.12	0.23	0.28	0.35
Hg	L α	LoQ-0.06	0.4	0.48	0.61
K	K α	LoQ-0.8	0.42	0.52	0.65
Mg	K α	LoQ-0.4	5.2	6.22	8
Mn	K α	LoQ-0.06	0.17	0.21	0.26
Mo	K α	LoQ-0.4	0.42	0.52	0.65
Na	K α	LoQ-0.4	36.5	44	56.6
Ni	K α	LoQ-0.06	0.14	0.17	0.22
P	K α	LoQ-0.5	0.45	0.54	0.7
Pb	L β	LoQ-0.12	0.37	0.45	0.57
S	K α	LoQ-5.0	0.41	0.49	0.64
Sb	L α	LoQ-0.06	0.62	0.74	1
Si	K α	LoQ-0.4	0.9	1.1	1.4
Sn	L α	LoQ-0.06	0.52	0.62	0.8
Ti	K α	LoQ-0.06	0.17	0.21	0.26
Tl	L α	LoQ-0.06	0.34	0.42	0.52
V	K α	LoQ-0.06	0.14	0.17	0.22
Zn	K α	LoQ-0.5	0.14	0.17	0.22

LoQ = 3 x LoD = Limit of Quantification

LoD = Limit of Detection

Table 1. Limits of detection at various power levels (100s counting time)

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