



specs

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discuss analysis of
oil industry
products with
X-ray fluorescence
spectrometers.***

Standards such as ASTM, ISO, IP and other regulations and methods used in the petrochemical industry have been developed using wavelength dispersive X-ray fluorescence (WDXRF). They include ASTM D2622, ASTM D4927, ASTM D6443, ASTM D5059, IP433, ISO 20884 and others. Petrochemical regulations are becoming stricter demanding lower levels of quantification for key elements such as sulfur (S), nickel (Ni), vanadium (V), lead (Pb), etc. WDXRF is increasingly solicited for these analyses in the petroleum industry because the technique has several advantages over other methods, such as a high dynamic range (from sub ppm to 100%), and a high degree of flexibility in terms of measurement of analytical lines, background positions and internal references. Moreover, little or no sample preparation is needed in most cases (oils can be directly measured without dilution).

The latest X-ray instruments and solutions for the petrochemical industry can be selected depending on the number of analytes, throughput requirements, element coverage, concentration range and the variety of samples (solids and liquids). Starting from the more cost effective Thermo Scientific ARL OPTIM'X instrument (Figure 1) for simple and dedicated applications (sulfur in oils, lead in oils or a few elements-few

Figure 1. ARL OPTIM'X.



sample scenarios) to the most advanced Thermo Scientific ARL ADVANT'X Series IntelliPower™ (Figure 2) for demanding applications in a central laboratory, the most suitable solution for every area in petrochemical industry can be selected. The ARL ADVANT'X Series integrates an innovative shutter separating the primary chamber from the goniometer chamber. When liquid samples are analysed, helium gas is introduced only in the primary chamber keeping the goniometer under vacuum. This allows a rapid changeover from a vacuum to a helium environment (typically one minute and a half) 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.

Taking advantage of the proven instrumentation, a comprehensive analytical package called PetroilQuant™ from Thermo Fisher Scientific has been developed which covers the widest range of elements and concentrations in a variety of oils. In conjunction with the ARL OPTIM'X or ARL ADVANT'X Series it offers a cost effective solution for laboratories dealing with petrochemical products. It is a pre-calibration program that facilitates quantitative analysis for a number of elements in automotive fuels, lubricants, heavy residual oils and wear metals in oils. PetroilQuant is developed with built-in knowledge and expertise in order to help petrochemical analysts to deal with a variety of oil samples with wide elemental concentration ranges. Compared with individual or specific matrix based calibration programs, which are expensive and demand analytical expertise, PetroilQuant provides a 'ready to run' analytical package for



Figure 2. ARL ADVANT'X Series.



Figure 3. Plastic cups for liquids with plastic film.

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

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 100 s counting (Universal Gonio)	Typical LOD on ARL ADVANT'X Intellipower 1200 (3 sigma) [ppm] in 100 s counting (Universal Gonio)
Mg	LoQ - 0.4	9	8 ppm in 20 s	3.7	5.7
P	LoQ - 0.5	7.9	1 ppm in 12 s	0.33	0.5
S low %	LoQ - 0.1	3	1 ppm in 12 a	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 10 s	0.77	1.2
Ca	LoQ - 0.8	9.5	0.9 ppm in 8 s	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 8 s	0.63	1.0
Na	LoQ - 0.4	23	27 ppm in 20 s	11.8	18.5
Al	LoQ - 0.06	3.4	2.6 ppm in 16 s	1.1	1.7
Si	LoQ - 0.4	8	1.9 ppm in 14 s	0.7	1.1
K	LoQ - 0.8	8	1.1 ppm in 8 s	0.31	0.5
Ti	LoQ - 0.06	0.7	0.55 ppm in 8 s	0.15	0.2
V	LoQ - 0.06	0.6	0.55 ppm in 8 s	0.15	0.2
Cr	LoQ - 0.06	0.8	0.66 ppm in 8 s	0.19	0.3
Mn	LoQ - 0.06	0.1	0.55 ppm in 8 s	0.15	0.2
Fe	LoQ - 0.12	0.3	0.55 ppm in 8 s	0.15	0.2
Ni	LoQ - 0.06	0.1	0.44 ppm in 8 s	0.12	0.2
Br	LoQ - 0.06	0.5	0.55 ppm in 8 s	0.15	0.2
Mo	LoQ - 0.4	5.8	0.44 ppm in 8 s	0.12	0.2
Cd [‡]	LoQ - 0.06	0.8	4 ppm in 12 s	1.43	2.3
Sn	LoQ - 0.06	2.9	2.1 ppm in 12 s	0.73	1.1
Sb	LoQ - 0.06	0.6	2.3 ppm in 12 s	0.8	1.3
Pb	LoQ - 0.12	0.6	1.54 ppm in 8 s	0.44	0.7

Notes: *SEE: Standard error of estimate is a measure of accuracy. [†]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.

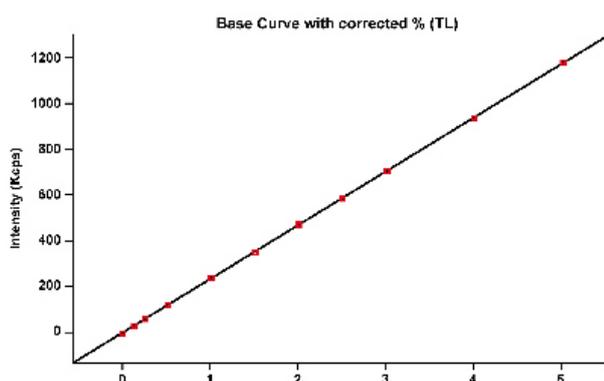


Figure 4. Wide range calibration curve for S in used oils.

beginners as well as advanced users of XRF instruments. This software saves an enormous amount of time and money for any petrochemical company knowing that it offers a global calibration program which otherwise would require many standards samples, analytical expertise and instrument time.

Installed on the ARL OPTIM'X equipped with the SmartGonio, it is best suited for key elements such as S and Pb in automotive fuels and other elements in lubricants when the sample throughput is reasonable. For a more

extended range of elements including residual oils and more demanding concentration limits, PetroilQuant can be installed on the ARL ADVANT'X Series (at 1.2 kW, 2.5 kW or 3.6 kW) with SmartGonio or Universal Goniometer. The highest power of 4.2 kW is not recommended in case of analysis of liquids because the higher heating effect generates a sagging of the film that retains the liquid sample.

Sample preparation

Various preparation parameters of liquid samples influence the results of analysis. These include:

- The inner diameter of the cup, which should be constant.
- The film material, the selection of which depends on the chemical resistance to the sample material.
- The filling height and sample mass.

The theoretically analysable layer thickness of hydrocarbons reaches the centimetre range, which is why the deviation from the 'infinitely' thick layer must be considered. This influence factor has been taken into account in the development of PetroilQuant.

Analytical conditions

On the ARL ADVANT'X fitted with the universal gearless goniometer, the crystals used are LiF200, LiF220, Ge111,

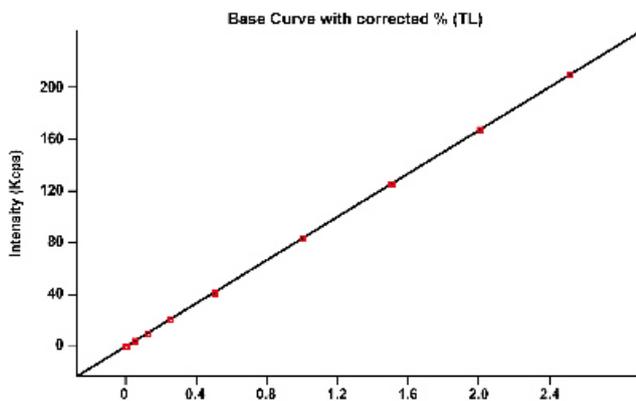


Figure 5. Calibration curve for Cl from ppm levels to 2.4%.

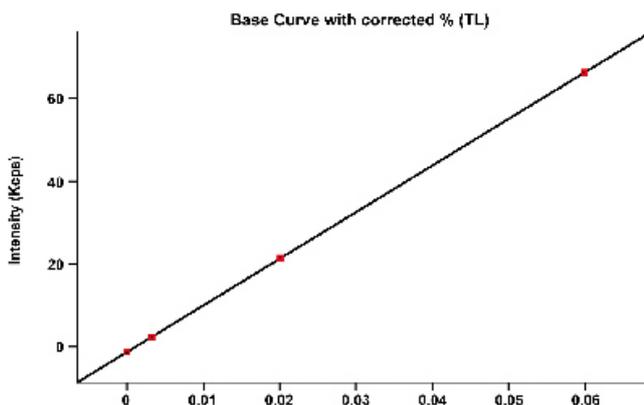


Figure 6. Calibration curve for Fe from ppm levels to 0.06%.

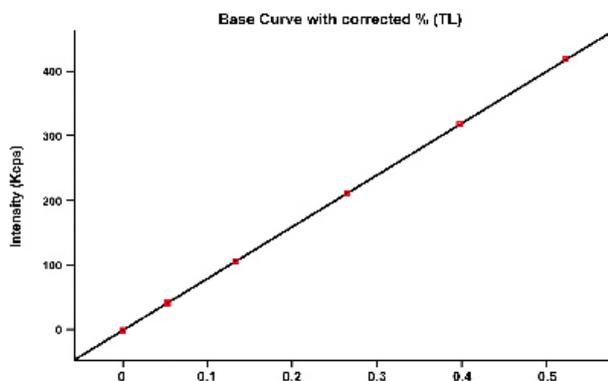


Figure 7. Calibration curve for Zn from ppm levels to 0.5%.

PET and AX06 multilayer synthetic crystal. When working with the 2500 W version instrument, the Rh target X-ray tube conditions are usually 60 kV/40 mA for heavy elements and 30 kV/80 mA for light elements. This mid power instrument has an advantage over a higher power system as it can be operated without an external water chiller for cooling.

The more critical factor is the total analysis time. Typical analysis time is 8 - 20 seconds per element/line with high power instruments. The limit of detection can be improved by increasing the analysis time. However, due to the local heating and radiation effects, the polypropylene film gets slowly deformed, which obviously affect the reproducibility of the measurement. In addition, prolonged analysis times can also create fluctuations in the liquid sample (density, bubbles, precipitation etc.)

Net intensities are used for the analysis which needs background measurement as well in addition to the peak intensity. This means that the total analysis time can increase every time background is included into the program. Only one background measurement was used per element to keep the total analysis time within limits.

On the ARL OPTIM'X the SmartGonio is used with crystals LiF200, PET and AX06. Its Rh target X-ray tube is powered up at 50 W. The lower power of this instrument allows use of a much longer counting time without any deformation of the plastic film used to retain the liquid in the cup. The machine also operates without any external water cooler.

Calibration range and results

A series of reference materials are used to derive calibration working curves. 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 information about the average accuracy that can be reached.

Matrix correction factors (fundamental parameters)

The quantitative analysis of oil industry products using XRF presents some particular problems with respect to the matrix effects and in some cases, line overlap effects. Matrix effects are generally classified as absorption and enhancement effects between different elements. However in the case of liquid, self-absorption, i.e. absorption of analyte intensity by itself, is very important and it should be included in the calibration method. This absorption coefficient can be calculated either empirically or by using fundamental parameter algorithms. The empirical methods require a large number of standard samples which is not always possible. On the other hand, the liquids or oils represent the best case to include fundamental parameters.

Calibration results

Typical examples of the MVR calibration curves obtained with the multi-variable regression module of the analytical software can be seen in Figures 4 - 7 for S, Cl, Fe and Zn.

Conclusion

The latest generation of WDXRF spectrometers can operate at low or mid power levels (50 W or 1200 - 2500 W) without requiring external water cooling. Therefore neither tap water, nor a water chiller is required for operation.

From simple automotive fuels to more complex residual oils, these X-ray fluorescence instruments can handle multi-element, multi-matrix situations, and the analysis of several elements can be performed in various types of oils. New calibration packages such as PetroilQuant™, designed specifically for the petrochemical industry, provide cost effective and easy to use analytical packages. With built-in expertise and databases, these analytical programs allow the laboratory chemist to refine and obtain accurate analysis for specific elements.

Such analytical programs are truly complementary to the ASTM, ISO and other regulatory requirements in a central analytical laboratory. 