Low-Power WDXRF To Meet Changing Petroleum Demands

Robert Hergenrader, Thermo Fisher Scientific, Ecublens, Switzerland
Phone: +41 21 694 71 11 Email: analyze.ch@thermo.com

Wavelength dispersive X-ray fluorescence (WDXRF) analysis is a well-known laboratory technique for the measurement of a wide range of elements in petroleum industry products. Elements tested include contaminants such as sulfur and chlorine in fuels, additive elements such as zinc, phosphorous and calcium in lubricants, as well as poisons such as nickel and vanadium in used catalysts. For petroleum applications, WDXRF instruments are traditionally operated at high power, 3000 Watts or more, to achieve the highest levels of sensitivity down to sub-part-per-million (ppm) levels across the broadest sample range. For successful and efficient operation, high power instruments require external support, such as water cooling, power supply, X-ray tube replacement and operator training. Not surprisingly, the cost of ownership of such instruments is relatively high.

Recent technology advances in X-ray instrument design including key component miniaturisation allow new, lower power instruments to achieve impressively similar results to traditional high power systems with much less auxiliary support and significantly lower cost of ownership. Recently improved optical coupling and compact goniometer components have contributed to a substantial gain in sensitivities even at low power, permitting analysis of sulfur, for example, below 5ppm levels. Industry standard methodologies such as ASTM D 2622 for fuels and D 4951 for lubricants can also be satisfied by such instruments. This article reviews results obtained with a new low power 50 Watt XRF instrument.

Applications and Choice of Power

The traditional advantages of XRF analysis include ease of sample preparation for both liquids and solids, total element coverage in a single analysis and a wide dynamic range of measurement from low ppm to high percentage levels. These advantages position it as the method of choice for most of the common petroleum product measurements. Typical applications for XRF in a petro laboratory include:

- Sulfur (S) content in automotive fuels (two to ten ppm or less), also low chlorine (Cl) content
- Trace contamination in fuels, e.g., catalyst fines
- Residual heavy fuels analysis (six to eight important elements including high sulfur)
- Lubricant additive production (from six to twelve additive elements)
- Fuel and lubricant blending control
- Qualitative or semi-quantitative analysis of used cracking catalysts

To meet ever increasing application demands, a variety of X-ray technique solutions are available to the analyst in the petro industry today. They can be broadly classified as:

- High power systems for the most demanding applications, also requiring the most auxiliary support systems and highest cost per analysis, e.g., external water cooling, tube replacement frequency and cost
- Medium power instruments, sacrificing some sensitivity in the most demanding applications, but providing operating cost savings, for example, internal water cooling
- Low X-ray power systems (simultaneous and/or sequential analysis) for more routine analyses which require no water cooling at all with minimal running costs

Thus the choice of instrument is based not only on performance requirements, but also on the overall cost per analysis and throughput needed.

Shifting Analytical Demands

The need to analyse sulfur content in fuels and oils is increasing as worldwide environmental regulations tighten. The maximum permissible sulfur content for highway diesel fuel in the USA is currently 15 ppm (1) and gasoline sulfur levels were reduced in 2006 from 300 to 30 ppm (2). The European Union standardised motor fuels with sulfur levels less than 10 ppm as of this January (3). In order to ensure 10 ppm of sulfur at the gasoline/petrol station, gasoline must be produced with around 4 ppm of sulfur. Such regulations place increasing demands not only on fuel purification during production and reduction of contamination during transportation, but also on the ability of the corresponding analytical instruments to reach ever-lower limits of quantification.

This shift in fuel analysis demand is changing the traditional laboratory workload across various analytical techniques, including XRF. Specifically, demand is growing for new XRF instrumentation that focuses on a higher volume and somewhat narrower range of applications with a lower initial instrument cost, significantly lower cost of ownership, yet still meeting all applicable ASTM and ISO norms (Table 1).

Changing Demands for XRF Petro Analysis
Reduced operating costs (cost per analysis)
Increasing sample volume
Increased light fuels analysis
Lower limits of detection, i.e., S, Cl
Lower instrument replacement cost
Meet or exceed ASTM and ISO norms
Less downtime (increased reliability)

Table 1: Changing demands in XRF petro analysis

Lower Cost Analysis of Fuels

Shifting demands within the petro industry necessitate corresponding changes to WDXRF technology and design. Lower power systems address the critical needs for lower instrument and operating costs; the challenge has been to design such systems to meet the exacting standards required by ASTM/ISO norms and new lower regulatory standards.

A demonstration of the focused capabilities of new lower power systems was conducted on several petroleum products using a Thermo Scientific ARL OPTIM'X wavelength dispersive XRF system (Fig. 1) which, due to special coupling between the X-ray tube anode and the sample, performs analysis equivalent to conventional higher powered full-range WDXRF instruments. The instrument design uses an air-cooled Rhodium X-ray tube with thin Beryllium end-window (0.075 mm) combined with a maximum power of 50 Watts to achieve similar resolution and light elements detection capabilities of costlier instruments.

Figure 1: Thermo Scientific ARL OPTIM'X WDXRF spectrometer

The Thermo Scientific ARL OPTIM'X was calibrated for analysis of sulfur in petroleum products according to ASTM D 2622 and EN ISO 20884 norms; both methods require analysis of the sulfur k-alpha peak and a background position. A large variety of products can be analysed on the same sulfur calibration curve, some with very high viscosity requiring heating in order to flow into the liquid cell, e.g. heavy fuels and residues, while others may be quite volatile, e.g. gasoline. With a limit of detection of 1 ppm in 200 seconds counting time (or 1.4 ppm in 100 seconds) the ARL OPTIM'X monitors sulfur comfortably below today's most stringent standards. Precision tests were performed on three different samples in order to show the repeatability of analysis of the instrument. For each sample, seven different liquid cells were prepared and analysed. Table 2 summarises the results, averages and standard deviations obtained.

Run	Sample 1 (ppm)	Sample 2 (ppm)	Sample 3 (%)
Cell 1	25.4	100.6	0.997
Cell 2	25.7	100.7	1.010
Cell 3	26.4	101.8	1.010
Cell 4	26.0	102.3	1.002
Cell 5	25.0	98.4	0.998
Cell 6	25.9	100.5	1.001
Cell 7	26.7	101.5	0.998
Cell 8	25.9	100.8	1.002
St. Dev.	0.58 ppm	1.27 ppm	0.005 %

Table 2: Repeatability test on ARL OPTIM'X at various sulfur levels.

The accuracy of the ARL OPTIM'X even at low power was also verified through round robin testing of gasoline, diesel and used oil products (4). The results summarised in Table 3 show the high accuracy achieved for both high and low sulfur levels.

Sample	Number of participating laboratories	Average sulfur content	ARL OPTIM'X Result # 1	ARL OPTIM'X Result # 2
Gasoline Super Plus	32	7.65 ppm	7.5 ppm	8 ppm
Gasoline Super	31	5.68 ppm	5.5 ppm	5.5 ppm
Diesel - high S	35	342.4 ppm	339.4 ppm	340.1ppm
Diesel - low S	35	27.7 ppm	27.7 ppm	27.2 ppm
Used oil - high S	17	1.81%	1.824 %	1.833 %
Used oil - low S	17	0.562 %	0.563 %	0.562 %

Table 3: Round robin test results on sulfur analysis

The ARL OPTIM'X is not limited to analysis of sulfur but also satisfies other fuel applications, notably the analysis of silicon (Si) and chlorine, thus providing a useful complement to traditional inductively coupled plasma (ICP) analysis techniques.

Lower Cost Analysis of Lubricants

Low power instruments may also satisfy industry standard methods for lubricants such as ASTM D 4927 and D 6443 which include standard additive elements such as calcium, phosphorous, zinc, magnesium, chlorine, etc. In such a case, a series of CONOSTAN and Alpha Research standards were used to produce the calibration curves again on the ARL Optim'X instrument (ASTM D 4927 also recommends a list of additional standards). Chemplex 1440 type liquid cells were used employing a 4 micron polypropylene film to close the cell.

As net intensities are used for the analysis, background measurement is also required to be subtracted from the peak intensity. Consequently, the total analysis time increases by the time taken for each background measurement. As indicated in the ASTM method, only one background measurement per element was used in order to keep the total analysis time as short as possible. Ranges of analysis for the various elements are shown in Table 4 together with the Standard Error of Estimate calculated for each curve. This value represents the average accuracy of analysis for each element over the given concentration range and the table shows the excellent accuracy obtained on a large range of concentrations.

Conclusion

Although traditionally high-powered XRF systems analyse the widest range of petroleum products at the highest sensitivity, new trends in petroleum product analysis require corresponding changes to XRF designs. New low power XRF instruments with miniaturised components and optimised optical geometries satisfy increasingly stringent market demands for fuel and lubricant analysis, while providing a significantly lower cost of instrument ownership and less auxiliary support.

Element	Range	SEE
Mg	LoD - 0.19%	12 ppm
S	0.07% - 4.0%	0.02%
P	LoD - 0.5%	28 ppm
Ca	LoD - 0.5%	20 ppm
Cu	LoD - 0.06%	2.7 ppm
Zn	LoD - 0.17%	6.6 ppm
Ba	LoD - 1.0%	50 ppm

LoD = Limit of detection
SEE = Standard error of estimate, a measure of accuracy

Table 4: Accuracy across element ranges in lubricants

For more information about Thermo Scientific XRF solutions, please call: +1 800-532-4752,
email: analyze@thermo.com
or visit: www.thermo.com/xpetro

References:

1. Federal Register, 2000, 66 (12), 5064
2. Federal Register, 2000, 65 (28), 6754
3. Global Industrial Outlook 2009 North America & International Edition, Industrial Info Resources, Inc., 12/11/2008
4. FAM Ringversuch 642/1 and FAM Ringversuch 661/1, 2002-2003