On the same wavelength

Didier Bonvin, Thermo Scientific, Switzerland and Colin Thurston, Thermo Fisher Scientific, UK, examine the latest advances in wavelength dispersive x-ray fluorescence alongside the growing demand for high performance fuels and lubricants.

The demand for high performance fuels and lubricants will rise rapidly through 2018, predicts a Frost and Sullivan market research report.[1] Its analysts believe that more manufacturers will see these specialised, additive infused fuels as a means to reduce engine emissions and comply with more stringent emissions standards.

The analysis expects demand for specialised fuels and lubricants to drive market earned revenues of US$ 18.8 billion in 2012 to a new high of US$ 23 billion in 2018, the result of functional fluids producers complying with new European pollution regulations.

Using x-ray fluorescence

To effectively minimise vehicle emissions through improved lubricant performance, the production of high performance petroleum products must be optimised. This challenge is felt worldwide, including in the important North American fuels market, where the biggest petroleum extraction and refining companies are growing their capacities to produce synthetic and high performance products. In fact, one of the largest petroleum companies recently announced a US$ 200 million investment to expand its capabilities for synthetic lubricant base stocks manufacturing and lubricants blending, packaging and storage.

In these new, state of the art facilities, the petroleum industry relies heavily on wavelength dispersive XRF spectrometers (WDXRF), a sophisticated analytical method used to determine the elemental composition of minerals and chemicals such as cement, metal, food, glass and, of course, petroleum and polymers. WDXRF instruments are particularly well suited for the analysis of sulfur in lubricants and fuels,[2] not to mention vital in R&D and QA/QC to verify proper chemical composition, notably in specially formulated liquids (Table 1).

During an analysis, these spectrometers simultaneously excite the elements of a petroleum sample, so radiation from the sample is diffracted through a crystal into a detector, which, when placed at a specific angle, can measure the intensity of an element wavelength (Figure 1). The petroleum industry adopted two particular WDXRF test methods as leading quality standards for elemental determination of blended lubricants, additives and additive packages: ASTM D4927 and ASTM D6443. Both methods can assist WDXRF users who need to perform a proper analysis of lubricant blends (Table 2).

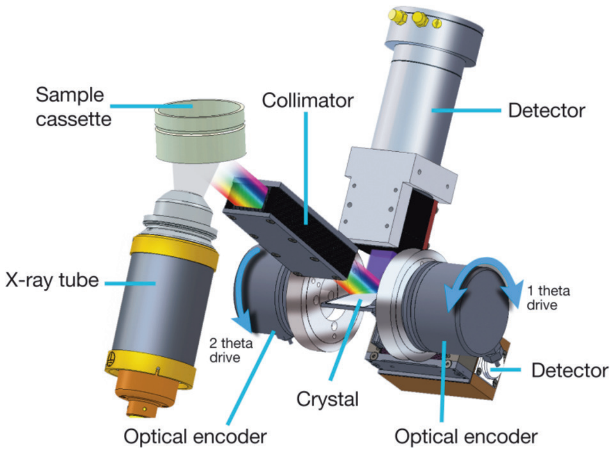

Figure 1. The heart of the Thermo Scientific ARL OPTIM'X WDXRF spectrometer.

Table 1. Important metals and other elements in lubricant additives

Additive package components	Common elements of interest
Detergents	Mg, Ca, Ba
Antiwear and extreme pressure (AW/EP) agents	P, S, Cl, Cu, Zn
Antioxidants	Ca, Cu, Ba, Mo
Rust and corrosion inhibitors	P, S, Zn

Table 2. Comparison of elements and concentrations covered by ASTM methods (undiluted mass %)

	Mg, %	P, %	S, %	Cl, %	Ca, %	Zn, %	Cu, %	Ba, %
ASTM D 4927-05	0.01 – 0.5		0.1 – 4.0		0.1 – 1.0	0.01 – 0.6		0.04 – 8.5
ASTM D 6443-04	0.003 – 0.21	0.001 – 0.25	0.030 – 1.00	0.001 – 0.20	0.001 – 0.40	0.001 – 0.25	0.001 – 0.05	

Advantages to WDXRF technology

To a great extent, the petroleum industry recognises wavelength dispersive XRF analysis as a preferred method for measuring multiple elements in functional lubricant additives because of its sensitivity and reliability.[3] The benefits are compounded by developments in WDXRF technology that have helped to improve the simplicity, affordability, reliability and flexibility of WDXRF analysis in the laboratory, improving the speed and accuracy of this analysis technique. Additionally, these instruments provide superior spectral resolution from low Z elements to heavy elements compared to energy dispersive XRF (EDXRF) systems.

WDXRF is also accompanied by proven, respected analytical methods that make these spectrometers an established option to perform qualitative and quantitative characterisation of lubricants, petrochemical liquids and catalysts. The newest WDXRF instruments boast innovative optics, a small footprint, and ease of operation and maintenance. Furthermore, they operate at lower power with greater efficiency allowing users to perform fast and accurate analyses with limited running and maintenance costs. Compared to traditional wet chemical and other spectroscopic methods like AA and ICP, the cost per analysis becomes very advantageous.

Advances in WDXRF technology

Depending on their configuration, WDXRF instruments provide a complete range of elemental analysis, from sodium to transuranics in liquids and from boron to transuranics in solids, more than satisfying the demands of a petroleum industry user. These instruments can also be calibrated to fit an end user's need, whether for versatile or routine XRF analysis.

Members of the latest generation of WDXRF instruments, such as the new 200 W version of the Thermo Scientific ARL OPTIM'X, offer the precise analysis capabilities needed for R&D and QA/QC in lubrication development (Table 3). ASTM methods like D4927 and D6443 can obviously be applied, and if needed, they can be extended with additional elements to suit the latest formulation of high performance lubricants.[4] Futhermore, analysis programs like UniQuant extend the ARL OPTIM'X analysis capabilities to all types of unknown samples, whether solids, liquids, pastes or emulsions, bringing much needed flexibility to the laboratory.

Improved laboratory integration

The precision required in testing high performance lubricants, coupled with the enormity of many petroleum production operations, means that laboratories have become increasingly complex. Massive amounts of information from laboratory instruments, including WDXRF, EDXRF, AA, ICP, GC, GC-MS, LC and LC-MS to name a few, must be integrated, organised and analysed for relevant insights. To maintain compliance with international regulations and industry standards such as ISO 17025, strict guidelines for instrument calibration and user training must be established and followed. In order to maintain the highest standards of safety, regulatory compliance and environmental commitment without sacrificing financial performance, many producers of high performance lubricants turn to a laboratory information management system (LIMS).

LIMS such as Thermo Scientific SampleManager, an industry standard for state of the art petroleum laboratories, can integrate instruments and technician workflows to create a paperless environment. In a paperless lab, errors inherent in a manual, paper based system are eliminated because instruments automatically transmit data to the LIMS as soon as final results are produced. A LIMS can then aggregate this data and compare it with information collected from online sampling systems, and even technicians in the field, enabling relevant information to be presented in a logical format to managers, which makes for fast, effective decision making.

Table 3. Concentration ranges and accuracy measurements

Element	ASTM Ranges (mass, %)	SEE (ppm)
Mg	0.003 – 0.20	9
P	0.001 – 0.50	7.9
S	0.030 – 4.00	3
Cl	0.001 – 0.20	19
Ca	0.001 – 0.80	9.5
Cu	0.001 – 0.05	1.3
Zn	0.001 – 0.50	5

**SEE: Standard error of estimate is a measure of the accuracy of the calibration curve*

Conclusion

Demand for high performance lubricants is set to rise dramatically over the next five years, and as producers scramble to meet the needs of their customers, they will make significant investments in their laboratories. Regulations and industry standards remain strict for leading petroleum companies around the world, so these new labs must increase throughput without sacrificing compliance, product quality or financial performance.

Two ways the petroleum industry will navigate these challenges are improved instruments and increased use of software. WDXRF spectrometers, which provide a more accurate picture of the chemical composition of lubricants while reducing costs, will help laboratories improve the quality of their products even as production increases and diversifies. Working in parallel, the adoption of fully integrated, paperless labs run through LIMS will feed managers more accurate, timely data from WDXRF and other instruments. Challenges in petroleum laboratories are being met with new technologies that produce higher efficiency and more accurate analysis.

References

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