Additive in lube oil analysis made easy: How to win the SAPS challenge!

Executive Summary

New lube oil specification, especially the reduction in SAPS, requires complex new formulations. These new formulations require tighter control limits. Using XRF instead of ICP-AES and other techniques enables the analysis of lube oils with one instrument, while being ASTM norm compliant. Not only will switching to XRF enable more precise analysis at lower cost but it also enables testing right in production, saving time and avoiding any delays.

Cost reduction approaches, made necessary by the economic situation, require rugged instrumentation solutions enabling payback right from the start. XRF as a technique can deliver this, with the ease of use of an ATM.

New challenges, new limits

Emission regulations drive the change in engine oils and fuels. E.g. PC-10, the API specification CJ-4, was developed to comply with EPA emission limits for 2007. Part of the new specification was to reduce the content of both sulphur and phosphorus. Development of so called SAPS (new low/ no sulphated ash, phosphorus/sulphur) oils to comply with new emission requirements and engine emission management systems accounted for most of recent development work.

The PC10 specifications are forcing lube oil formulators and additive companies to accept chemical limits of sulphur (0.4% mass) and phosphorus (0.12 %mass).

In a global economy, with exports to Europe and the Pacific region, additional requirements for other elements as well as compliance to different specs must be established. How can compliance and product control be established while keeping costs down? How can blending operations be simplified and yet rigorously certified? Mix-ups are costly and can lead to an expensive recall situation and liability issues.

Additive content analysis

Elemental analysis must be performed by accepted methods from the ASTM D committee in the US and/or by ISO methods. The most common instrumental analysis methods are based on ICP (inductively coupled plasma spectrometry) and XRF (X-ray fluorescence spectrometry). ICP based Atomic Emission spectrometry (ICP-AES) has been used since the early 60's. However , recent developments in the x-ray instrumentation segment have greatly changed the pricing and performance landscape.

This paper will illustrate the difference between ICP and XRF, focused on the application on unused lubricating oils, their development and production as well as blending operations.

Spectroscopic analysis of lubrication oils

Elemental analysis is done by spectroscopic methods, whereas a measurable signal characteristic to the element is measured. The signal intensity is proportional to the concentration; since spectroscopic techniques are relative the proportionality has to be established by means of a calibration.

Atomic emission spectrometry

Inductively coupled plasma (ICP) Atomic Emission spectrometry (AES) is a multi-element analytical technique used to determine trace elements in a variety of liquid and solid sample materials. With ICP, the objective is to have the elements generate characteristic wavelength-specific light that can be measured. With these measurements, the elements in a particular sample can be analysed.
In ICP, the excitation energy comes from superheated plasma. Argon, an expensive noble gas, is used as the plasma, and also as a purge, coolant and carrier gas. A nebulizer sprays the sample into the plasma and detectors measure the light emitted by the sample atoms. The light originates from electronic transitions in the outer shells of the atoms, creating a "free" atom.
The sample must be atomised in the plasma, therefore usually no solid samples can be analysed. Samples with high solids content need to be digested to run. There are different type of detectors and set-ups determining the price and performance of ICP: Simultaneous ICP instruments can collect spectra from multiple elements at the same time, but often from a limited energy range. CCD detector chip technology advances were key in recent performance increase and price decrease. Sequential ICP instruments can collect data from the entire spectrum, but therefore take longer to analyse a sample. Sequential systems have nearly disappeared, displaced by the more affordable and "more" resolving CCD based ICP-AES systems. Robotic auto samplers can process a large number of samples unattended, with measurement time being around 200 seconds per sample on average (number of elements is not a factor).

Not every oil sample can be analysed directly, due to viscosity constraints of the auto sampler and nebulizer and therefore usually have to be diluted with a solvent. Dilution is usually 1:10 or higher using solvents like Kerosene. These steps can be fully automated increasing the complexity of the set-up considerably. If the oils (such as used oils) contain particles larger than 5 microns it is necessary to digest the sample in acid and under pressure to ensure homogeneity.
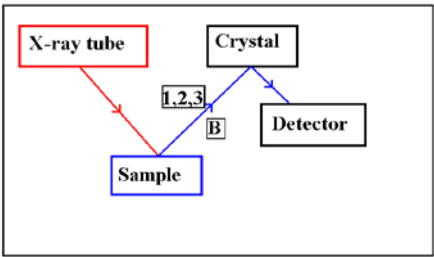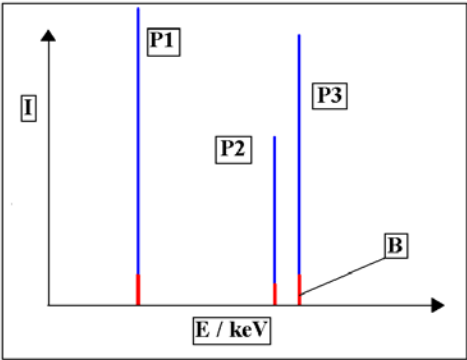Since the emission of light is best from metals the range of elements which can be analysed is "metal" oriented: Sulfur and Chlorine capabilities are rare options in an ICP-AES hampered by the available emission lines and artefacts from the Argon plasma. Usually XRF and UV systems are used for these elements, increasing the number of laboratory instruments.

Employing usually only 2-4 point calibrations the system needs to be calibrated daily and after every cleaning or change of injection cones. The number of consumables are many: high purity compressed Argon to create the plasma, chemicals for the sample preparation and dilution including the disposal of all remaining agents, glass and platinum parts of the injection system, as well as the cones used to inject the sample into the plasma. Maintenance, done via contract or in house is essential to ensure throughput. An attempt for cost comparison can be found in the article "Money to burn" by Robert J. Thomas (Today's Chemist at work,2000) illustrating a cost of $6,800 US in 2000. This does not count work time, maintenance and instrument write off!
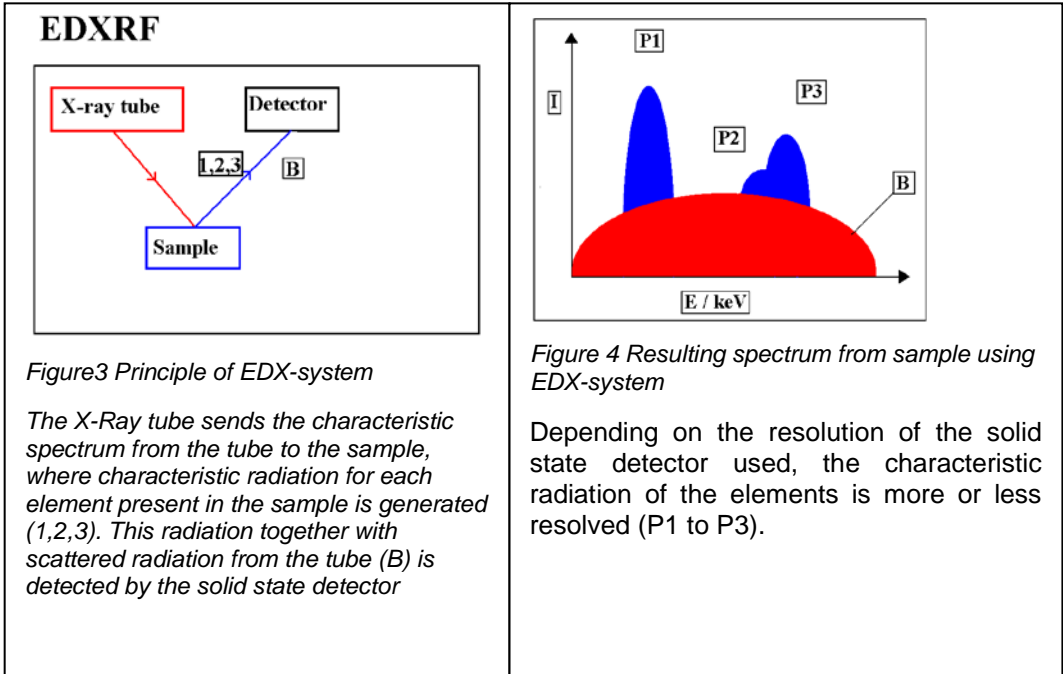
Direct analysis with X-ray spectrometry

X-ray spectrometry, in use since the early 50's for metals, is using an X-ray beam directed on the sample to excite characteristic X-rays of the elements in the sample. Solids and liquids can be analysed directly and the samples do not have to be atomised. X-ray spectrometers also can be separated into sequential high resolution, high performance wavelength dispersive systems(WD XRF) and simultaneous systems employing solid state detectors referred to as energy dispersive (ED XRF).

WD XRF is highly flexible instrumentation used in refinery process control or centralized laboratories. It is used when lowest the limits of detection (e.g. 0.2 ppm LLD for Sulfur) and highest sample throughput is needed for a large variety of material types.

Figure 1 Principle of WD-XRF system

White X-Ray Radiation from the tube is directed to the sample, where the elements are excited and their characteristic radiation is directed towards a selectable analyzer crystal. The analyzer crystal will only direct the radiation towards the detector which fulfills Bragg's Law. Therefore it is possible to separate the radiation from the sample.

Figure 2 Resulting spectrum from sample using WDX technique

Compared to Figure 2 the differences between the signals P1 to P3 can be seen. WD-XRF has better resolution and will yield higher achievable count rates and therefore better precision.

ED XRF is generally a bench top based system, although for PMI applications it is mainly used as hand held equipment. A new detector technology, available commercially since the early 2000's, revolutionized the ED XRF segment and increased performance to replace ICP AES and dedicated S and Cl analyzers with one system:

EDXRF

Figure3 Principle of EDX-system

The X-Ray tube sends the characteristic spectrum from the tube to the sample, where characteristic radiation for each element present in the sample is generated (1,2,3). This radiation together with scattered radiation from the tube (B) is detected by the solid state detector

Figure 4 Resulting spectrum from sample using EDX-system

Depending on the resolution of the solid state detector used, the characteristic radiation of the elements is more or less resolved (P1 to P3).

The best detector technology in the past was thick Si(Li) based solid state detectors, which required extensive cooling by liquid nitrogen or multistage electronics. These detectors were limited in count rate and tended to degrade easily when not used correctly. The new Silicon Drift detector (SDD) technology removes all these limitations, enabling use with simple cooling or at room temperature, much higher count rate capability as well as better operational stability. This enables these detectors to bring the high end EDX segment into the industrial process environment.

Figure 1 Schematics of ED XRF system

ED XRF has become much more integrated and today occupies space on the bench on the order of an ICP-AES. The number of multi element systems sold over the last few years has increased as ED XRF became more affordable and capable.

Figure 2 S2 RANGER Benchtop ED XRF with auto sampler

Why is XRF the method of choice for lubes?

Whereas for all AES based spectrometry systems a technician with chemical and instrumentation background is needed to operate the complex system, XRF is aimed at the operator level when fielded as an analyser. Bruker's pioneering work on human machine interface, TOUCHCONTROL™ , enables the user to control the XRF analysers just with his/her finger tips. Modelled after the use of an ATM, TOUCHCONTROL ™ can now be found on all Bruker XRF instruments and has been copied by others as well.

Figure 3 TOUCHCONTROL(TM) interface

XRF systems can analyse all the usual lube/additive elements from Na to U directly in undiluted liquids since the dynamic range of the emission of x-rays is linear from ppm to % weight range ! (mg/kg to kg/kg). Technical grade helium is used as purge gas for the light element analysis (Mg-Ca), with air enabling the analysis from Ca to U.
Establishing the calibrations is done once during commissioning and then they are adjusted for any degradation of the X-ray source, when needed, and checked by daily QC samples.

Cost of operation, environmental impact and waste as well as complexity are much lower using XRF than any other atomic spectroscopy method.

With the increased demands of lowering the SAPS content, analysis of Sulphur and Phosphorus in much lower levels in addition to Ca, Zn and other elements is very important.

Instead of upgrading and patching the array of three or more analysers used in some labs today it is possible with one system to perform all needed determinations on Magnesium, Phosphorus, Sulphur, Chlorine, Calcium, Barium, Copper and Zinc.

One XRF analyser can measure lube oils, metalworking fluids, food grade oil, hydraulic and small engine oils on the same calibration and set-up using the same sample preparation.
Make cup, pour oil and analyse!
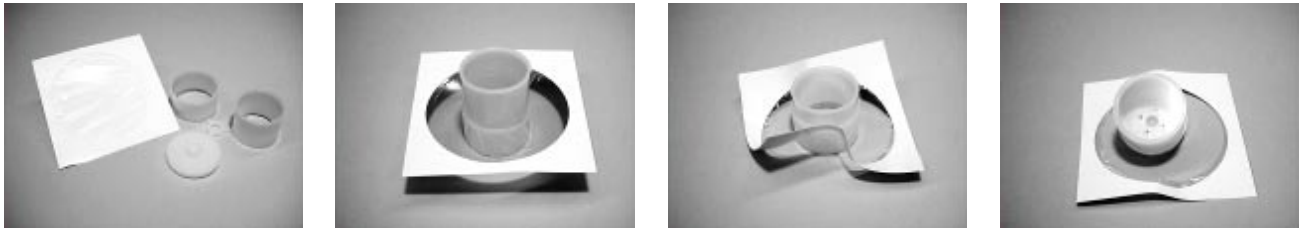
Since January 2009 a complete EDX turn key solution is available to cover this and other applications with unprecedented ease of use and ASTM compliant performance.

The S2 RANGER PETRO-QUANT turn key solution

The S2 RANGER is an all in one bench-top EDXRF system using Bruker's 4th generation Silicon Drift Detector technology (XFLASH ™). The high resolution and count rate capability allowed the pairing with a 50 Watt X-Ray source guaranteeing best precision in its class. The XFlash™ detector records the sample spectra in high resolution, neighbouring element lines are clearly separated, shown in fig. 3.
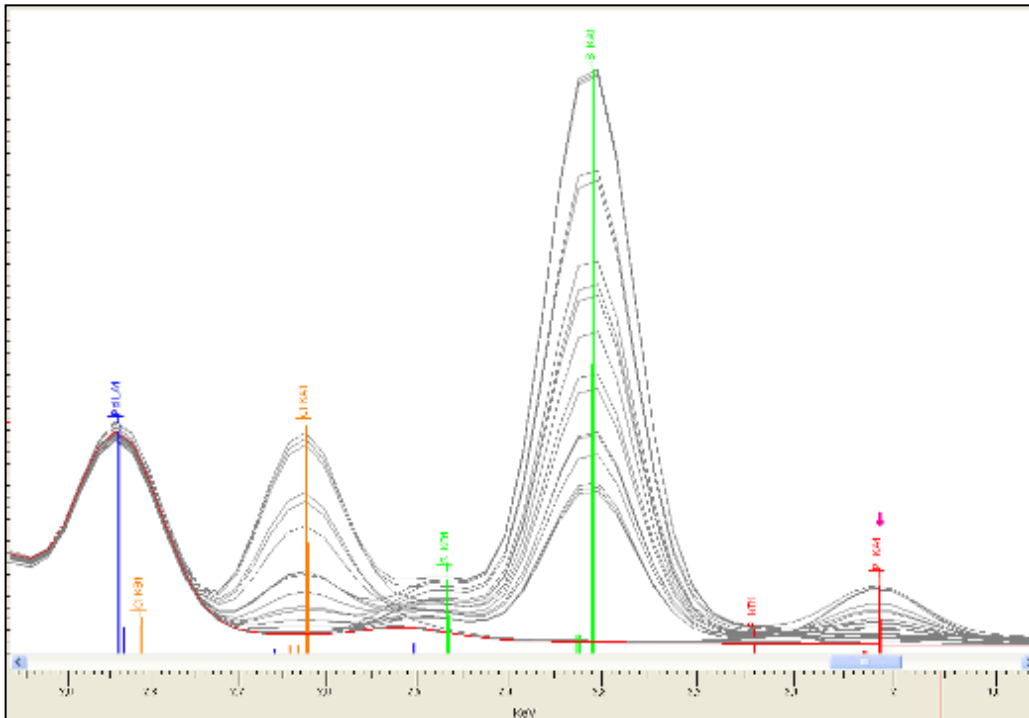
Figure 4 Spectra of the S2 RANGER recorded with the XFlash™ detector

Commonly used elements in additives for lube oils are Mg, P, S, Cl, Ca, Cu, Zn and Ba. Ranging from ppm to near % levels they can be determined simultaneously in less than 6 minutes.

The factory installed calibration is based on 23 NIST traceable high quality certified reference standards covering the 8 elements and concentration ranges.

The S2 RANGER with PETRO-QUANT features LUBE8, a 23, NIST traceable, (Analytical Services Inc.) lube oil standard based calibration.

The precision of the lube 8 method is illustrated by the data shown in table 1: 21 preparations of the same sample (which is used as the QC sample) measured under Helium atmosphere in less than 360 sec per sample.

Table 1 Summary of analytical results of additives in lube oil (Lube8 method)

LUBRICANT-8	Mg(%)	P(%)	S(%)	Cl(%)	Ca(%)	Cu(%)	Zn(%)	Ba(%)
Calibration Range [%]	0.2	0.15	0.755	0.15	0.505	0.05	0.15	0.2
Detection limits [ppm]	80	5.5	2.8	2.7	4.2	1.2	0.7	23
Precision Test								
Average [%]	0,0831	0,1407	0,6514	0,1524	0,0706	0,0202	0,152	0,0784
Abs.Std.Dev. [%]	0,0054	0,001	0,0039	0,0011	0,0005	0,0002	0,002	0,0011

Table 1: Summary of analytical results for additives in lube oils

As for ASTM 6481 compliance the S2 RANGER with PETRO-QUANT aces the test by a factor of 10.

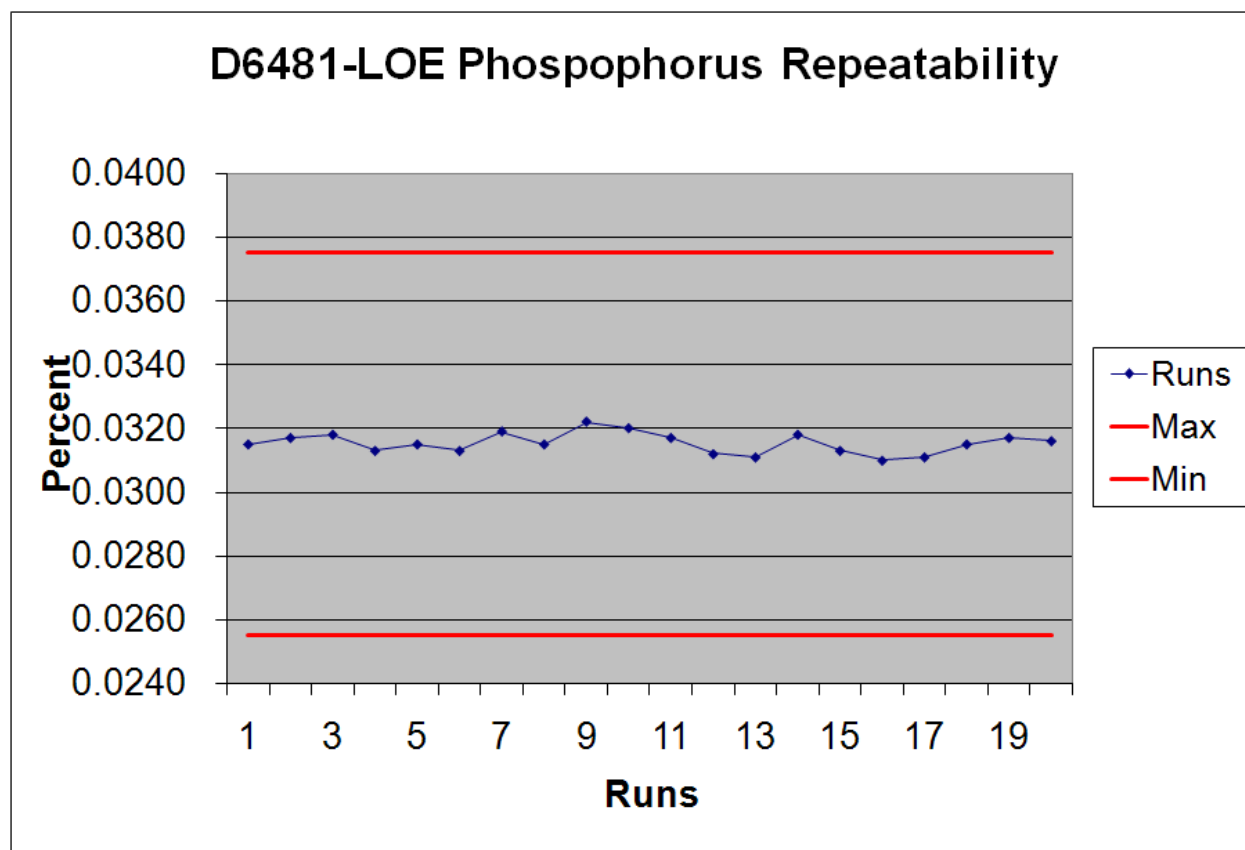| Sample	P (%)	S (%)	Ca (%)	Zn (%)
Average	0.0315	0.0294	0.0290	0.0296
Std.Dev.	0.0003	0.0003	0.0003	0.0003
ASTM 6481 Dev spec	< 0.0060	< 0.0020	< 0.0020	< 0.0010

Table 2: Summary of ASTM 6481 LOE compliance

Figure 5 Phosphorus repeatability for ASTM 6481

The LUBE 8 or ASTM 6481 calibration on the S2 RANGER with PETRO-QUANT are fulfilling all analytical requirements for the blending and QC approach.

The S2 RANGER fulfils not only the analytical requirements it also offers the intuitive TouchControl™ interface: Operation made simple with step by step workflows and a clear graphical user interface that is operated with a finger tip.

Samples can be added anytime in the random access sample changer, allowing full unattended operation with much less complexity than any auto sampler used in atomic spectroscopy. In the case of highest throughput and lower detection limits the WDXRF solution will be more than adequate, keeping the operation and consumable cost down.

Get started now by learning more about XRF and the S2 RANGER PETRO-QUANT solutions.

About Bruker AXS Inc.

Bruker AXS develops and manufactures advanced X-ray, OES and Combustion systems for elemental analysis, materials research, and crystallography. With a large global sales and service networks in more than 40 countries, Bruker AXS provides innovative solutions to scientists in a wide range of industries, including chemistry, pharmaceuticals, semiconductor, life science and nanotechnology. Our solutions drive technological advancements in materials research and process control and our instruments provide essential information about 3D molecular structures, chemical and physical properties, and elemental composition of solids and liquids.

If you need further information, please call 800-234-XRAY or email info@bruker-axs.com

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