Early Warning of Engine Death – Powerful Wear Metal Analysis in Engine Oils and Analysis of Lubricating Oils by Modern WDXRF

Dr. Arnd Bühler, Dr. Kai Behrens, Bruker AXS
Oestliche Rheinbrueckenstrasse 49, 76187 Karlsruhe Germany

Lubricating oils are generally formulated with additives, which act as detergents, anti-oxidants, anti-wear agents, etc. These additives can contain calcium, copper, magnesium, phosphorus, sulfur, and zinc. Chlorine can also be present in these oils as a contaminant. The composition of the lubricating oil plays an important role in modern car engines. The ASTM Standard Test Method D6443 can be used to determine if the oils, additives, and additive packages meet specifications with respect to the added elements, and with respect to chlorine contamination. Modern fuel-saving engines contain more and more parts made out of light alloys. The high performance requires a strict focused development to make bearings and pistons last longer. Early warnings on engine break downs are based on the precise analysis of wear metals in the trace level. Therefore the analysis of metal alloys supports car manufacturers in engine development and helps to decrease the necessity of maintenance.

Fig.1: Prepared lubricating oil sample

Inductively coupled plasma techniques have been widely used for the analysis of wear metals in oils, but generally they tend to show lower concentrations due to particles which are filtered out before the analysis avoiding blockage of the spray chamber. In addition the operating costs for consumables and argon spent on ICP are high compared with X-ray fluorescence.

Typically each matrix type such as lube oils or fuels requires a different calibration. However, Bruker PETRO-QUANT solutions don't: they enable a universal calibration for all kinds of hydrocarbons. Whereas conventional spectrometers don't have the ability, Bruker's lets you analyse up to 30 elements with just one calibration. It covers all relevant trace elements, additives, and major elements saving you weeks of calibration work. This article will outline the analytical performance of modern wavelength dispersive X-ray fluorescence (WDXRF) spectrometers for this task and demonstrates also the capability to perform this analysis compliant to international standards such as DIN 51399 and ASTM D 6443.

Figure 2: WDXRF instrument S8 TIGER

The Instrument S8 TIGER WDXRF Spectrometer

The S8 TIGER has all of the features one expects for a complete WDXRF instrument in this class: a 10-position primary beam filter changer, up to 4 primary collimators, and up to 8 analyser crystals. It uses two detectors mounted side-by-side in the vacuum chamber. One is a scintillation detector, which is used to measure the higher energy lines, and the other is a gas flow proportional detector for measuring the lower energy lines.

Traditional liquid sample analysis requires the entire optical path in the X-ray spectrometer to be flushed with helium gas. Bruker has developed a unique vacuum seal that utilises a thin window between the spectrometer chamber and the sample chamber. This allows the spectrometer chamber to remain under vacuum at all times, and only the sample chamber needs to be flushed with helium when measuring liquids. This arrangement minimises the time required to switch between vacuum and helium modes of operation. The vacuum seal also provides a safety interlock between the sample and spectrometer chambers preventing liquids from contaminating the optical path in the event of sample cup leakage. This arrangement always keeps the flow detector in a vacuum atmosphere allowing ultra thin entrance windows to be used without the risk of them breaking. A software interlock is also provided to prevent a liquid sample from being analysed while the spectrometer is in a vacuum mode. The software will not allow the introduction of a sample identified as a liquid into a vacuum path, and can be set to require a password for all samples that will be measured in a vacuum path.

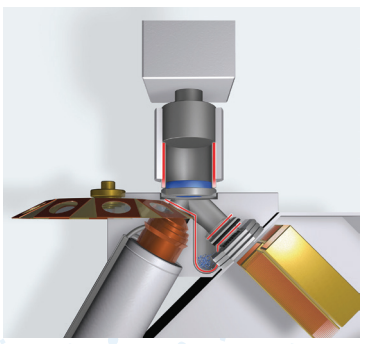

Figure 3: SampleCare protection of system components

Universal Analytical Solution for Petrochemicals PETRO-QUANT – the Easy Way to Good Results

Accurate quantitative elemental analysis via X-ray fluorescence requires conventional calibrations. When calibrating a spectrometer, a set of reference samples are analysed with an optimised set of measurement parameters. After the calibration is computed it is then used for the analysis of unknown samples. If an analyser for various sample matrices such as lube oils and fuels is calibrated, a highly trained specialist is required. The universal PETRO-QUANT calibration enables the analysis of petrochemical samples without the need for further sample matrix information. Time consuming calibrations for each application are not necessary. The universal calibration is prepared in the factory by experienced, highly trained scientists. This makes the start of routine analysis faster and safer than ever. This approach is possible due to the powerful 'variable alphas' correction model. It covers various sample types with just one calibration. This reduces the calibration effort to a minimum. PETRO-QUANT BASIC gives you an accurate and precise analysis of 30 elements in hydrocarbon samples with standard errors and 3 sigma detection limits in the lowest possible ppm-range. Sample preparation is easy and fast. The achievable detection limits are shown in table 1.

Norm Compliant Analysis of Additives in Lubricants

Even though that the universal approach of a universal solution for trace analysis has made its way to petrochemical labs, there are still places where the calibration must be done compliant to international standards, such as ASTM and DIN. For this case the WDXRF spectrometer S8 TIGER was calibrated to monitor the formulation of high performance engine oils.

Ten lubricating oil standards, which included a blank, were obtained from a

	Concentration-Range [mg/kg]	LoD (3s; 100s) [mg/kg]
Na	LoD – 500	2
Mg	LoD – 2000	1
Al	LoD – 500	0.5
Si	LoD – 500	0.4
P	LoD – 5000	0.2
S	LoD – 1000	0.2
S*	LoD – 5.50 %	
Cl	LoD – 1500	0.4
Cl*	LoD – 5,00 %	
K	LoD – 500	0.2
Ca	LoD – 5000	0.2
Ti	LoD – 500	0.2
V	LoD – 500	0.2
Cr	LoD – 500	0.2
Mn	LoD – 500	0.1
Fe	LoD – 500	0.2
Co	LoD – 500	0.1
Ni	LoD – 500	0.1
Cu	LoD – 500	0.1
Zn	LoD – 2500	0.1
As Kα As Kβ	LoD – 500	0.03 0.4
Br	LoD – 500	0.07
Zr	LoD – 500	0.4
Mo	LoD – 500	0.2
Ag	LoD – 500	1.4
Cd	LoD – 500	0.6
Sn	LoD – 500	0.7
Sb	LoD – 500	0.7
Ba	LoD – 2000	0.8
Tl Lα Tl Lβ	LoD – 500	0.1 0.2
Pb Lα Pb Lβ	LoD – 500	0.2 0.1
Bi Lα Bi Lβ	LoD – 500	0.2 0.1

Table 1: Detection limits for engine oil samples analyzed with PETRO-QUANT and the S8 TIGER 4 kW

commercial laboratory. These standards had been prepared gravimetrically using reagents traceable to NIST Standard Reference Materials.

Individual specimens were prepared by pipetting about 7 mL of each sample into a Bruker AXS 40 mm diameter liquid sample cell that was fitted with a 4µ Prolene® window. The sample cells used have vented caps to prevent the window from bulging during sample analysis. These liquid cells were then placed into sample cups fitted with stainless steel masks having openings of 34 mm in diameter.

Calibration coefficients were calculated using the 10 calibration standards by regressing the concentration data with the measured intensity data for each analyte.

A precision test was performed on twenty individual sample preparations for two Check Samples with known concentrations. The results of this precision test and statistical evaluation of the data is summarised in Table 2. These tables include a comparison to the known chemical concentrations for each analyte in the sample. The table also includes the ASTM expected repeatability limits along with those determined from the measured data. This repeatability is the difference between successive test results for the same sample obtained from a single operator using the same instrument. Over the long run 19 out of 20 values are expected to be within the prescribed limits. The results produced by the S8 TIGER were all within the prescribed limits.

	Mg	P	S	Cl	Ca	Cu	Zn
Calibration Range [ppm]	2000	1500	7500	1500	5000	500	1500
Detection Limit [ppm, 3σ, 100s]	1,7	0,7	6,6	1,9	1	0,5	0,3
Repeatability [21 times]							
Mean value [ppm]	740	500	2780	510	1960	199	500
Abs. Std. Dev. [ppm]	10	4	15	2	3	0,7	4,7
Precision [%]	1,42	0,51	0,52	0,32	0,17	0,36	0,3

Table 2: Precision test from twenty measurements of Lubricating Oil Check Sample 1 with the S8 TIGER and the curved Ge analyser crystal XS-GE-C.

Figure 4: Lubricating oil filled in a car engine

Analysis of Wear Metals in used Engine Oils to Detect Wear and Predict Engine Death

When analysing fresh lubricating oil the sample density and the composition of the base oil might be exactly known, but once the oils has been used in engines the matrix and density changes rapidly: Oxidation is taking place, water and fuel is collected and the long hydrocarbons chains will partly decay. This basically is influencing the analysis of all elements present in the sample.

Any change in the oxygen and nitrogen composition will strongly influence the result, but the S8 TIGER can adapt to keep on producing accurate results. The new feature of PETRO-QUANT is the Aut – O – matic functionality: The concentration of CH2 and an additional light element (which cannot be determined by XRF) is analysed using the Compton correction. The changes in the light matrix have a strong influence on the Compton signal. PETRO-QUANT is making use of it: All elements from Na upwards are measured directly; CH2 is calculated as balance to 100 %. Now based on the Compton signal the concentration of the oxygen is calculated, until a perfect fit is achieved. It is a clever way to determine even non-measurable elements.

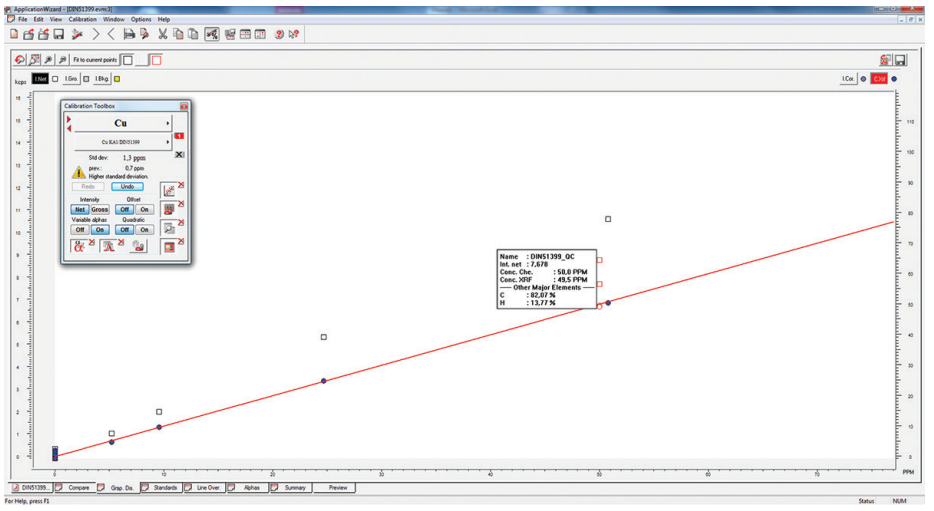

Figure 5: Matrix correction for wear metal Cu in oil

Matrix corrections (influence coefficients) were applied using a concentration based calibration model. Theoretical influence coefficients (alphas) were calculated using a "Fundamental Parameters" program and the Variable Alphas model that is a standard part of the SPECTRAplus software. The Variable Alphas model calculates the alpha coefficients individually from each samples composition instead of using an average composition.

This approach of PETRO-QUANT is now covered in the new german standard DIN 51399. When calibrated the WDXRF spectrometer S8 TIGER with fundamental parameters the quality of results is substantially enhanced correcting for changes due to matrix and density variation. The effect can be seen in figure 5: one quality check sample of Bruker DIN 51399 solution is evaluated with the FP approach, the result is perfectly calculated to 49.5 ppm for a 50 ppm Cu containing sample instead of 38 ppm (non – corrected result)

The accuracy and precision test for DIN 51399 was performed with running 17 measurements in 4 weeks analysing 18 elements (wear metals and additives) in used engine oils. The results are shown in table 3. The typical deviation compared to the reference value was in the lower ppm range, the relative standard deviation less than 2% for all the elements, which demonstrates the excellent performance of wavelength dispersive technology for this application and especially of the S8 TIGER analysing the oil samples in a safe and cost efficient way. The high analytical precision and the analysis of the total amount of wear metals (particles and dissolved elements) enables engineers in car development, racing teams and maintenance crews of big machines to monitor engine wear planning the next service or predicting engine death.

Summary

The optimum WDXRF system features used to efficiently measure additives in fresh lubricating oil and wear metals in used engine oils are listed below. The precision, Lower-Limit-of-Detection, and regression analysis are also summarised below:

1) The close coupled ultra-thin (75µ) end window X-ray tube operating at 4000 watts with up to 170 mA provides maximum intensity for the harder to analyse lighter elements found in these samples (Na, Mg, P, S).

2) The sample handling capabilities of the S8 TIGER allows both liquid and solid samples to be analysed simultaneously decreasing the overall analysing time. Random access of any position in the sample changer allows "rush" samples to be processed in a priority data collection mode.

3) A fail-safe vacuum interlock between the sample and the spectrometer chamber eliminates the risk of contaminating the optical path from accidental spills.

4) The repeatability test performed on various samples showed the repeatability of the S8 TIGER to be within the guide lines outlined in the ASTM Test Method D6443, DIN 51399, no matter if analysed calibrated according to international standards or using the factory calibration PETRO-QUANT.

5) The Lower-Limits-of-Detection (LLD) are excellent for the short given measurement time. High sample throughput, safe sample handling with high instrument uptime and excellent results with high precision are a given with the S8 TIGER.

The S8 TIGER fully meets the requirements for the determination of additives and wear metals in oils as outlined in ASTM D6443 and DIN 51399. The S8 TIGER is ideally suited for the wide range of process control applications found in the petroleum industry applying the fundamental parameter correction (variable alphas) and including the Aut – O – matic calculation.

Application	Mg (%)	P (%)	S (%)	Ca (%)	Zn (%)	Na (mg/kg)	Al (mg/kg)	Si (mg/kg)	Cl (mg/kg)	K (mg/kg)	Cr (mg/kg)	Fe (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Mo (mg/kg)	Sn (mg/kg)	Ba (mg/kg)	Pb (mg/kg)
Ref. Conc.	**0.0700**	**0.1248**	**1.4779**	**0.1249**	**0.1250**	**499.7**		**50.0**	**97.4**	**50.0**	**50.0**	**50.0**	**50.0**	**50.0**	**50.0**	**50.0**	**50.0**	**50.0**
Average	**0.0677**	**0.1213**	**1.4683**	**0.1245**	**0.1232**	**486.0**	**171.1**	**48.3**	**91.2**	**53.0**	**47.3**	**48.0**	**48.5**	**48.0**	**42.5**	**51.9**	**52.5**	**42.8**
Abs.Std.Dev.	**0.0006**	**0.0011**	**0.0136**	**0.0013**	**0.0008**	**11.9**	**21.5**	**1.7**	**1.3**	**1.0**	**1.0**	**0.5**	**0.4**	**0.4**	**3.8**	**0.8**	**1.8**	**3.2**
Rel.Std.Dev.	**0.9%**	**0.9%**	**0.9%**	**1.0%**	**0.6%**	**2.5%**	**12.6%**	**3.4%**	**1.4%**	**1.9%**	**2.1%**	**1.0%**	**0.9%**	**0.9%**	**9.0%**	**1.5%**	**3.4%**	**7.5%**

Table 3: DIN 51399 Precision and Accuracy test (17 measurements in 4 weeks)