



S8 TIGER

ASTM D6443 Standard Test Method for Determination of Ca, Cl, Cu, Mg, P, S and Zn in Unused Lubricating Oils and Additives

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Lubricating oils are generally formulated with additives which have varying modes of action including as detergents, anti-oxidants and anti-wear agents. These additives can contain calcium, copper, magnesium, phosphorus, sulphur and zinc. Chlorine can also be present in these oils as a contaminant. 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.

The analysis of lubricating oils by WDXRF provides a non-destructive method that is easily incorporated into a production environment. This report covers the performance of the S8 TIGER for ASTM D6443 including precision and Lower Limits of Detection (LLD).

Instrument Configuration



Figure 1: Curved germanium crystal XS-GE-C

The S8 TIGER is an ideal solution for analysing petroleum products. It uses a 4kW end-window X-ray tube with an ultra-thin 75µm beryllium window. A closely coupled optical path helps provide high intensities and low detection limits for all elements. Automatic computer control of the X-ray generator allows the kV and mA settings to be adjusted automatically for each element. This optimisation of the voltage and current settings provides maximum sensitivity for all elements. The lower atomic number elements are typically analysed using low kV and high mA settings, while the higher atomic number elements are analysed with high kV and lower mA settings.

The S8 TIGER has all of the features one expects for a complete Bruker AXS 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. Bruker AXS 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, with only the sample chamber needing to be flushed with helium when measuring liquids. This arrangement minimises the time required to switch between vacuum and helium mode of operation.



Figure 2: Prepared lubricating oil sample

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 feature always keeps the flow detector in a vacuum atmosphere allowing ultra thin entrance windows to be used without the risk of them breaking. The automatic sample recognition of the



Figure 3: S8 TIGER WDXRF spectrometer with safe sample handling for unrivalled instrument uptime and lowest running costs

EasyLoad magazine prevents a liquid sample being analysed while the spectrometer is in a vacuum mode. The software itself, will not allow the introduction of a sample identified as a liquid into the vacuum path.

The automatic sample loader is designed to handle both liquid and solid samples simultaneously with random access capabilities. Priority levels can be set for individual samples, which control the measurement sequence of these samples. This allows samples, which have just been loaded to become the very next samples to be measured without interruption of the current running sample. An immediate mode is also available, which allows rush samples to be analysed immediately by interrupting the current measurement without loss of data collected up to the point of interruption. These features allow a wide variety of samples to be handled routinely without any modifications to the system.

Experimental Applications

22 lubricating oil standards of the PETRO-QUANT ASTM D6433 solution, which included a blank, were used. These standards had been prepared gravimetrically using reagents traceable to NIST standard reference materials.

Individual specimens were prepared by dripping about 7ml of each sample into a Bruker AXS 40µm diameter liquid sample cell that was fitted with a 4µm 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 34mm in diameter.

The intensities at the peak and off-peak background angles were measured from the liquid

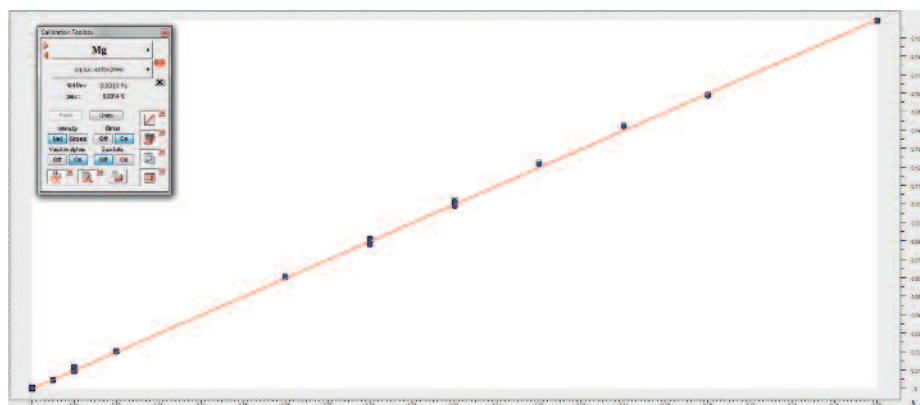


Figure 4: Calibration curve for Mg in lubricating oil

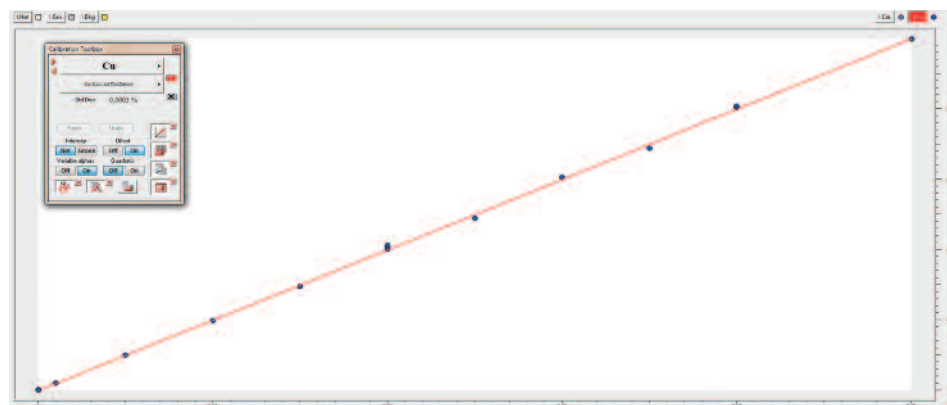


Figure 5: Calibration curve for Cu in lubricating oil

samples using the operating parameters of PETRO-QUANT. The counting time listed in table 1 was a maximum time to count each peak and off-peak background position. The SPECTRAplus software has provisions for doing an optimised counting time. In this mode the user enters a target statistical error and a maximum counting time. Each intensity is then measured to the desired statistical error or the maximum counting time, whichever is shorter. Calibration coefficients were calculated using the 22 calibration standards by regressing the concentration data with the measured intensity data for each analyte.

Matrix corrections (influence coefficients) were applied using a concentration based calibration model, whilst theoretical influence coefficients (alphas) were calculated using a "Fundamental Parameters" program; the Variable Alphas model that is a standard part of the SPECTRAplus software. The Variable Alphas model calculates the alpha coefficients individually from each standard composition instead of using an average composition, giving more appropriate alpha factors and allowing for accurate calibrations over wide concentration ranges. The calibration curve for Mg with excellent linear regression function and standard deviation covering a broad concentration range is shown in figure 4, Cu calibration curve is shown in figure 5.

Table 1 lists the estimated Lower-Limit-of-Detection (LLD) for each of the analyte elements. These LLD's were calculated based on the actual counting times used. The SPECTRAplus software estimates the LLD for each of the calibration standards by calculating 3 times standard deviations of the background intensity and converting this to a concentration. This is consistent with the generally accepted formula given below, except instead of using "m" to convert the intensity to a concentration the calibration coefficients are used. The detection limit is calculated according to

$$LLD = \frac{3}{m} \sqrt{\frac{I_b}{T_b}}$$

m = sensitivity of analyte in kcps/mass%

I_b = background intensity for analyte in kcps

T_b = counting time in seconds at the background angle

Summary

The optimum WDXRF system features used to efficiently measure unused lubricating oil and additive products are listed below. The precision, Lower Limit of Detection and regression parameters are also summarised below:

- 1) The close coupled ultra-thin (75µm) end window X-ray tube operating at 4000 watts with up to 170mA provides maximum intensity for the harder to analyse lighter elements found in these samples (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) A repeatability test performed on one known sample showed the repeatability of the S8 TIGER to be within the guide lines outlined in the ASTM Test Method D6443.
- 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 calcium, chlorine, copper, magnesium, phosphorus, sulphur and zinc in unused lubricating oils and additives as outlined in ASTM D6443. The S8 TIGER is ideally suited for the wide range of process control applications found in the petroleum industry.

Element	LOD@time	Peak time	Bkg time
Mg	1.7 ppm	32 s	32 s
P	0.7 ppm	12 s	12 s
S	6.6 ppm	20 s	20 s
Cl	1.9 ppm	16 s	16 s
Ca	1.0 ppm	12 s	12 s
Cu	0.4 ppm	20 s	20 s
Zn	0.3 ppm	12 s	20 s

Table 1: Detection limits at given measurement time

Sample	Mg (%)	P (%)	S (%)	Cl (%)	Ca (%)	Cu (%)	Zn (%)
1	0.0740	0.0490	0.2780	0.0510	0.1960	0.0199	0.0500
2	0.0740	0.0500	0.2800	0.0510	0.1960	0.0199	0.0490
3	0.0750	0.0500	0.2770	0.0510	0.1960	0.0200	0.0500
4	0.0730	0.0500	0.2780	0.0510	0.1960	0.0199	0.0500
5	0.0720	0.0490	0.2760	0.0500	0.1960	0.0199	0.0500
6	0.0740	0.0500	0.2760	0.0510	0.1960	0.0199	0.0490
7	0.0760	0.0500	0.2790	0.0510	0.1960	0.0200	0.0500
8	0.0760	0.0500	0.2790	0.0510	0.1960	0.0199	0.0500
9	0.0740	0.0500	0.2760	0.0510	0.1960	0.0199	0.0500
10	0.0730	0.0500	0.2790	0.0510	0.1960	0.0200	0.0500
11	0.0740	0.0500	0.2790	0.0510	0.1960	0.0199	0.0490
12	0.0750	0.0500	0.2790	0.0510	0.1960	0.0199	0.0500
13	0.0730	0.0500	0.2790	0.0510	0.1970	0.0201	0.0500
14	0.0740	0.0490	0.2780	0.0510	0.1960	0.0200	0.0500
15	0.0730	0.0500	0.2790	0.0510	0.1970	0.0200	0.0500
16	0.0730	0.0490	0.2760	0.0510	0.1960	0.0198	0.0490
17	0.0730	0.0500	0.2770	0.0510	0.1960	0.0199	0.0490
18	0.0730	0.0490	0.2750	0.0510	0.1960	0.0199	0.0490
19	0.0730	0.0500	0.2780	0.0510	0.1960	0.0199	0.0490
20	0.0750	0.0500	0.2810	0.0510	0.1970	0.0200	0.0500
21	0.0730	0.0500	0.2770	0.0500	0.1960	0.0198	0.0500
Average	0.0738	0.0498	0.2779	0.0510	0.1961	0.0199	0.0497
abs. SD	0.0011	0.0004	0.0015	0.0002	0.0004	0.0001	0.0005
rel. SD	1.46	0.88	0.56	0.43	0.18	0.36	0.97

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