
## Lab Report XRF 139

# S8 TIGER Series 2 for ASTM D 6443

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

### Introduction

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 ASTM Standard Test Method D 6443 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 lab report covers the performance of the S8 TIGER Series 2 for ASTM D 6443 including precision and Lower Limits of Detection (LLD).

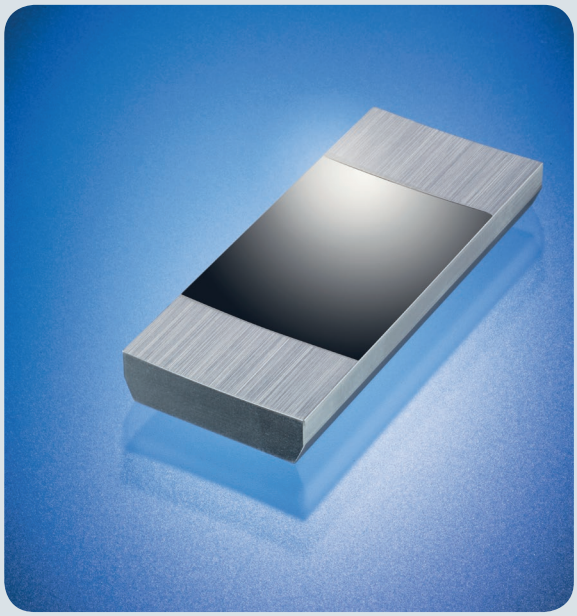

Figure 1: Curved germanium crystal XS-GE-C

The reliable and precise analysis of trace elements requires the highest sensitivity and best possible resolution. Laterally curved crystals are focussing the emitted fluorescence radiation towards the center of the detector. This arrangement achieves for elements with high reflection angles more intensities and an increased resolution in comparision to the flat crystal geometry. The analyzer crystal XS-GE-C is based on a curved Ge(111) crystal and offers the enhanced analytical perfomance for the elements P, S, Cl.

## Instrument Configuration

The S8 TIGER Series 2 is an ideal solution for analyzing 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 optimization of the voltage and current settings provides maximum sensitivity for all elements. The lower atomic number elements are typically analyzed using low kV and high mA settings, while the higher atomic number elements are analyzed with high kV and lower mA settings.

The S8 TIGER Series 2 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 analyzer 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 utilizes 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 minimizes the time required to switch between vacuum and helium mode 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. The automatic sample recognition of the EasyLoad magazine prevents that a liquid sample is analyzed while the spectrometer is in a vacuum mode. The software 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 at the same time 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 analyzed 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.

Figure 2: Prepared lubricating oil sample

## Experimental

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. Compositions for the calibration standards used are listed in Table 3.

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.


Figure 3: S8 TIGER Series 2 WDXRF spectrometer with safe sample handling for unrivalled instrument uptime and lowest running costs

The intensities at the peak and off-peak background angles were measured from the liquid 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 SPECTRA$^{plus}$ software has provisions for doing an optimized 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. Theoretical influence coefficients (alphas) were calculated using a "Fundamental Parameters" program and the Variable Alphas model that is a standard part of the SPECTRA$^{plus}$ software. The Variable Alphas model calculates the alpha coefficients individually from each standard composition instead of using an average composition. This gives more appropriate alpha factors and allows 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, for Cu 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 SPECTRA$^{plus}$ 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 excepted 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

| 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

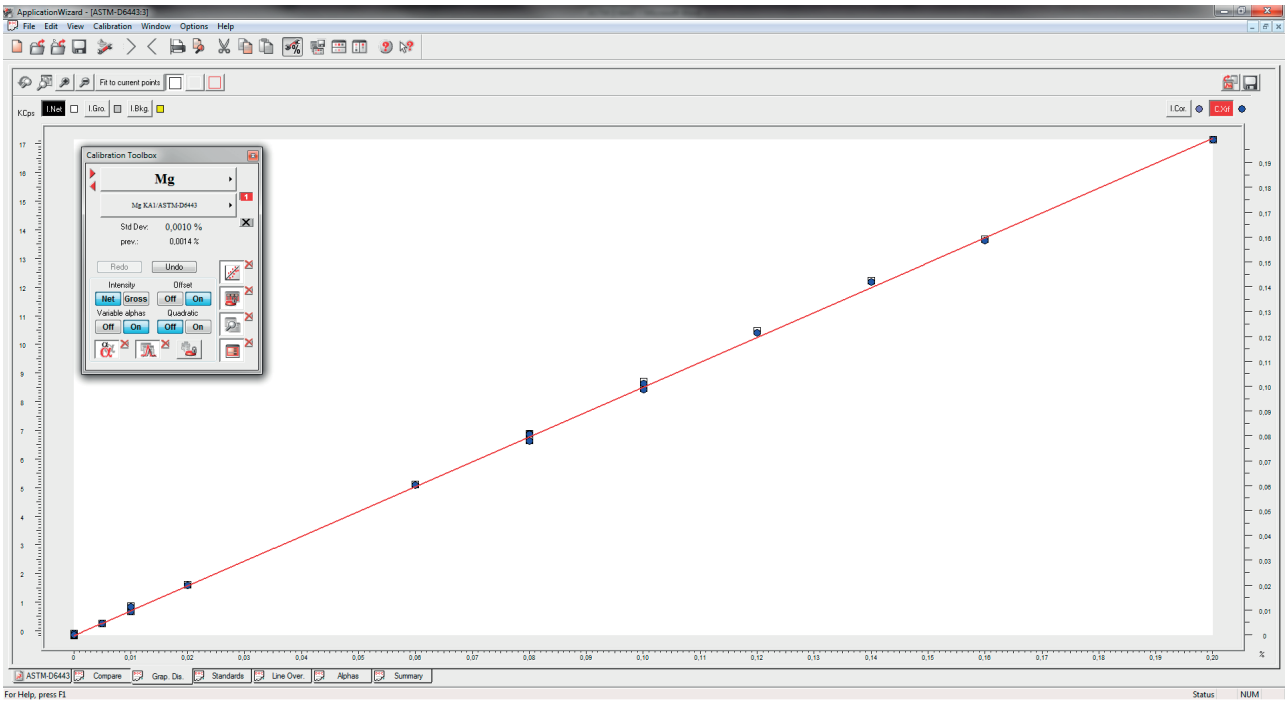


Figure 4: Calibration curve for Mg in lubricating oil

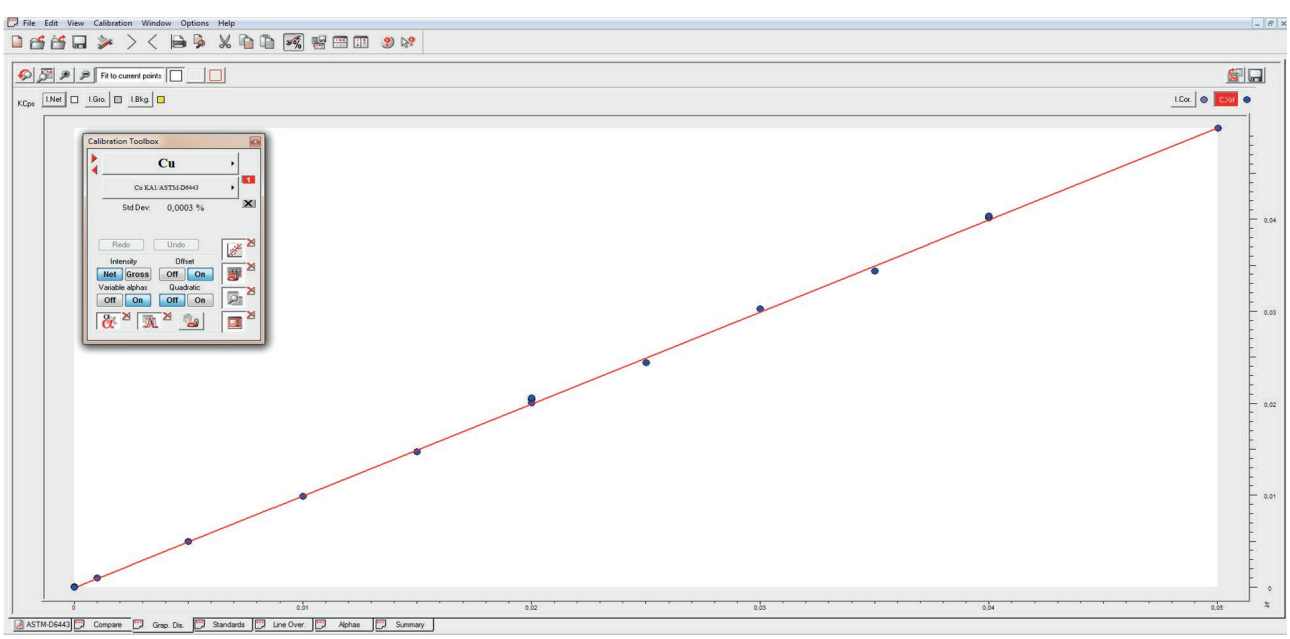


Figure 5: Calibration curve for Cu in lubricating oil

A precision test was performed on twenty individual sample preparations for one check sample with known concentrations. The results of this precision test and statistical evaluation of the data is summarized in Table 2. This table includes a comparison to the known chemical concentrations for each analyte in the sample. It 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 Series 2 were all within the prescribed limits.

| 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 Series 2 and the curved Ge analyzer crystal XS-GE-C.

Figure 5: Easy and quick analysis of oil samples with PETRO-QUANT and the S8 TIGER

The PETRO-QUANT basic universal calibration for petrochemicals is prepared using the powerful SPECTRA$^{plus}$ analytical software suite. Since matrix effects caused by the sample composition and the changing sample geometry influences the quality of the results the analytical software must cope with these effects. The unique variable alpha model for matrix correction is enabling wide concentration ranges and huge variations in sample composition, geometry and sample weight. No other fundamental parameter model can achieve a similar analytical flexibility. Typically each matrix type such as lube oils or fuels requires a different calibration. However, Bruker AXS PETRO-QUANT solutions don't: It enables a universal calibration for all kinds of hydrocarbons. PETRO-QUANT lets you analyze up to 30 elements with just one calibration. It covers all relevant trace elements, additives, and major elements saving you weeks of calibration work. All you need to do is: One click of a button and you can see the results of your analysis.

Bruker AXS also provides the fully calibrated S8 TIGER Series 2 spectrometers to match the needs of your laboratory. You select the norms and Bruker AXS sets up the analyzer in the factory, saving you a great deal of time and effort. After the on-site installation, the spectrometer can perform routine analysis on the spot with no need for highly trained personal, saving lots of time and money. Additionally to PETRO-QUANT you can order the ASTM D 6443 ready to analyze calibration based on the set of standards listed in table 3.

## 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 analysis are also summarized below:

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

**2)** The sample handling capabilities of the S8 TIGER Series 2 allows both liquid and solid samples to be analyzed simultaneously decreasing the overall analyzing 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 two known samples showed the repeatability of the S8 TIGER Series 2 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 Series 2 fully meets the requirements for the determination of calcium, chlorine, copper, magnesium, phosphorus, sulfur and zinc in unused lubricating oils and additives as outlined in ASTM D 6443. The S8 TIGER Series 2 is ideally suited for the wide range of process control applications found in the petroleum industry.

| | Mg (%) | P (%) | S (%) | Cl (%) | Ca (%) | Cu (%) | Zn (%) |
|---|---|---|---|---|---|---|---|
| ASTM-D6443_01 | 0.06 | 0.06 | 0.275 | 0.08 | 0.3 | 0.03 | 0.06 |
| ASTM-D6443_02 | 0.01 | 0.15 | 0 | 0.1 | 0.25 | 0 | 0.15 |
| ASTM-D6443_03 | 0.16 | 0.15 | 0 | 0 | 0.5 | 0.035 | 0.02 |
| ASTM-D6443_04 | 0.12 | 0.08 | 0.2 | 0.01 | 0.35 | 0 | 0 |
| ASTM-D6443_05 | 0.1 | 0.1 | 0.3 | 0 | 0.11 | 0.015 | 0.05 |
| ASTM-D6443_06 | 0.2 | 0.05 | 0.25 | 0.1 | 0.2 | 0 | 0.15 |
| ASTM-D6443_07 | 0 | 0 | 0.45 | 0.05 | 0 | 0.025 | 0.02 |
| ASTM-D6443_08 | 0.1 | 0.03 | 0.4 | 0.03 | 0.15 | 0 | 0.04 |
| ASTM-D6443_09 | 0.16 | 0 | 0.35 | 0.15 | 0.25 | 0.01 | 0.08 |
| ASTM-D6443_10 | 0.005 | 0.03 | 0.75 | 0.15 | 0.11 | 0.04 | 0.15 |
| ASTM-D6443_11 | 0 | 0 | 0.75 | 0.05 | 0.26 | 0 | 0 |
| ASTM-D6443_12 | 0.14 | 0.08 | 0.5 | 0 | 0.2 | 0.005 | 0.08 |
| ASTM-D6443_13 | 0.02 | 0.02 | 0.2 | 0 | 0 | 0.005 | 0.02 |
| ASTM-D6443_14 | 0.08 | 0.14 | 0.65 | 0.15 | 0.07 | 0.02 | 0.15 |
| ASTM-D6443_15 | 0 | 0.15 | 0 | 0 | 0.05 | 0 | 0 |
| ASTM-D6443_16 | 0.08 | 0 | 0.5 | 0 | 0.4 | 0.001 | 0.02 |
| ASTM-D6443_17 | 0 | 0.02 | 0.6 | 0.02 | 0.18 | 0.02 | 0.06 |
| ASTM-D6443_18 | 0.01 | 0.02 | 0 | 0.01 | 0.4 | 0.001 | 0 |
| ASTM-D6443_19 | 0.01 | 0.02 | 0.2 | 0.02 | 0.01 | 0.04 | 0.1 |
| ASTM-D6443_20 | 0 | 0.008 | 0 | 0.005 | 0.05 | 0.05 | 0.12 |
| ASTM-D6443_21 | 0.08 | 0.05 | 0.275 | 0.05 | 0.2 | 0.02 | 0.05 |
| ASTM-D6443_22 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

Table 3: Concentration list of the standards of PETRO QUANT ASTM D 6443 solution (Order No: PQ2-ASTMD6443-INST)

## Authors

Larry Arias, Kai Behrens, Arnd Bühler
Bruker AXS GmbH, Karlsruhe, Germany

**Links**

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**Bruker AXS GmbH**

info.baxs@bruker.com

**Worldwide offices**

bruker.com/baxs-offices

**Online information**

bruker.com/s8tiger

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