ASTM D 6443 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 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 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 article covers the performance of the Bruker AXS S8 TIGER for ASTM D6443, including precision and Lower-Limits-of-Detection (LLD).

Instrument Configuration

Fig.1: Prepared lubricating oil sample

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 optimization 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 gas. 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, 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.

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 controls 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 also is 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

Ten lubricating oil standards, which included a blank, were obtained from a commercial laboratory. These standards had been prepared gravimetrically using reagents traceable to NIST Standard Reference Materials. Compositions for the calibration standards used are listed in Table 1.

	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 1: Concentration list

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.

The intensities at the peak and off-peak background angles were measured from the liquid samples using the operating parameters listed in Table 2.

The counting time listed in this table was a maximum time to count each peak and off-peak background position. The SPECTRAplus software has provisions for doing an optimised counting time.

Spectrometer Mode	Helium with Seal
Sample Rotation	ON
Mask	34 mm

Element	Crystal	Colli.	Voltage	Current	Detector	Peak time	BKG time	Peak	BKG 1	BKG 2
Mg	XS-55	0.46°	30 kV	133 mA	Flow Counter	32 s	32 s	20,819	18,908	22,998
P	XS-GE-C	0.46°	30 kV	133 mA	Flow Counter	12 s	12 s	141,004	133,5	
S	XS-GE-C	0.46°	30 kV	133 mA	Flow Counter	20s	20 s	110,734	116,734	
Cl	XS-GE-C	0.46°	30 kV	133 mA	Flow Counter	16 s	16 s	92,789	94,789	
Ca	LiF 200	0.46°	50 kV	80 mA	Flow Counter	12 s	12 s	113,111	105,111	121,111
Cu	LiF 200	0.23°	60 kV	66 mA	Scintillation	20 s	20 s	45,032	44,245	47,032
Zn	LiF 200	0.46°	60 kV	66 mA	Scintillation	12 s	20 s	41.810	44,245	47,032

Table 2: Measurement parameters for ASTM D 6443 with the S8 TIGER WDXRF

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. A statistical error of 0.9% 3-sigma was used for all lines. This is equivalent to collecting 100,000 counts for each line measured.

Calibration coefficients were calculated using the 10 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 SPECTRAplus software. The Variable Alphas model calculates the alpha coefficients individually from each samples 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 2.
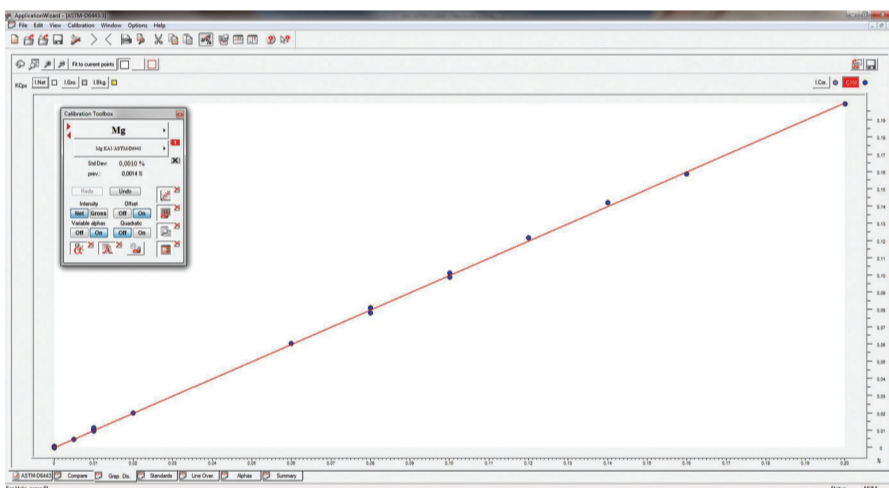

Fig 2: Calibration curve for Mg in lubricating oil

Table 3 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, and have also been expressed based on the given counting time. The SPECTRAplus software estimates the LLD for each of the calibration standards by calculating 3 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.

Element	LLD @ 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 3: Detection limits at given measurement time

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 summarized in Table 4. 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. Table 5 shows the software with automatic labeling of the limit check, green indicates within the limits, yellow would ~be near at limit and red would indicate out of range.

Table 4: Precision test from twenty measurements of Lubricating Oil Check Sample 1 with the S8 TIGER and the curved Ge analyser crystal XS-GE-C.

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 170 mA 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 two known samples 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.