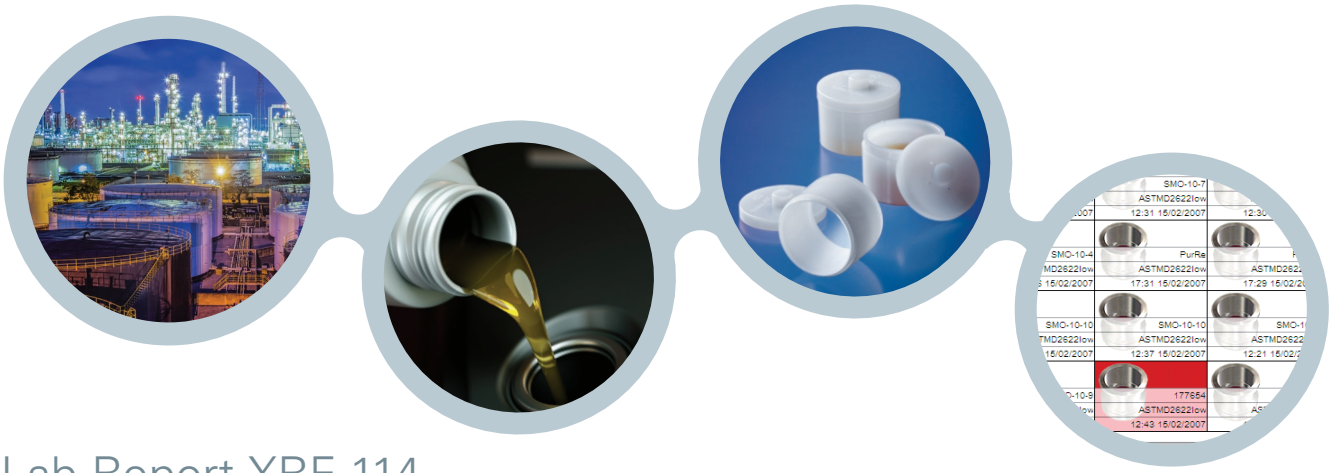

Lab Report XRF 114

S8 TIGER ECO "Petro"

ASTM D 6443 Standard Test Method for the Determination of Ca, Cl, Cu, Mg, P, S, and Zn in Unused Lubricating Oils

Introduction

Lubricating oils are formulated with additives which act as detergents, coolants, anti-oxidants and anti-wear agents in engines. These additives typically contain calcium, copper, magnesium, phosphorus, sulfur and zinc compounds. To ensure the functionality of the lubricant, these compounds must be controlled. The respective elements can be measured and used to monitor the final compound concentrations in the oil. In addition contaminants, such as chlorine, can influence the lubricant performance. A control of these elements is important to ensure a high product quality. The ASTM standard test method D 6443 describes how the added elements and chlorine are determined in lubrication products. This ASTM method is based on wavelength dispersive X-ray fluorescence (WDXRF) spectrometry.

The analysis of lubricating oils by WDXRF provides a non-destructive method that is easily incorporated into a production environment. The S8 TIGER ECO "Petro" brings additional advantages for the analysis of additives in lubricants. It performs the analysis compliant to ASTM D 6443 and is easily satisfying the requirements even for advanced technical lubricants. Additives are quickly analyzed with high accuracy and precision, therefore product grades are easily controlled. This allows meeting the product specifications without spending higher amounts of expensive additive compounds. The S8 TIGER ECO "Petro" has been optimized to combine low cost of

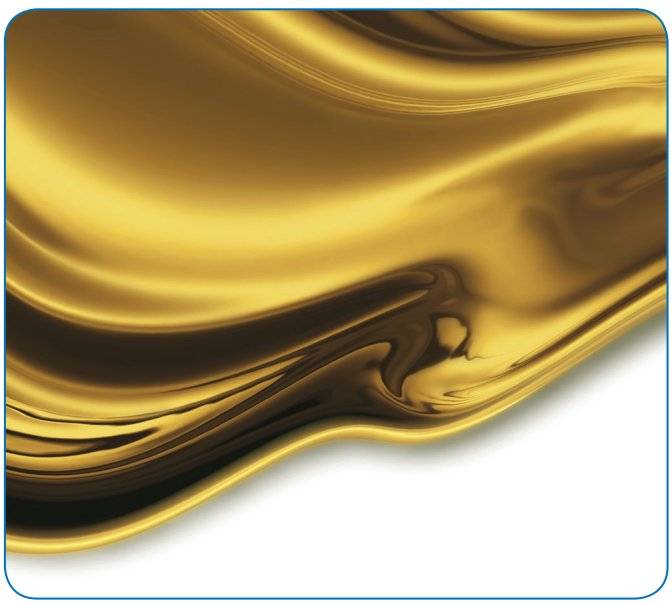

Figure 1: Lubricating oil with additives

ownership by reducing the energy and helium consumption with an optimal spectrometer configuration for dedicated performance.

This lab report shows the performance of the S8 TIGER ECO "Petro" for ASTM D 6443 including precision and lower limits of detection (LLD) and describes the specific benefits for this analytical task.

Instrument

The S8 TIGER ECO "Petro" for ASTM D 6443 is the optimal solution for performing the analysis of additives in lubricating products. Configured with one collimator for enhanced sensitivity, three analyzer crystals and the proportional flow counter it covers the entire element range for oil analysis. The measurement of peak and background positions in sequential mode ensures that for each matrix the accurate net intensity is determined. With the 1 kW X-ray tube optimized for prolonged tube life excellent long term stability is guaranteed. Light element lines, such as lines of Mg to Cl, are efficiently excited using 20 kV and 50 mA; for the analysis of heavy elements 50 kV and 20 mA are applied. The switch of the excitation conditions happens instantly without increasing the measurement time.

The S8 TIGER ECO "Petro" for ASTM D 6443 is optimized for highest instrument uptime, lowest cost of ownership and ultimate reliability. The unique vacuum seal of the S8 TIGER ECO "Petro" outperforms other conventional WDXRF devices due to its complete protection of the goniometer and its parts. It locks out fumes from oils products which otherwise will enter the spectrometer chamber damaging crystals, motors and detectors. In addition it significantly reduces the helium consumption and therefore the cost of operation, because helium flushing is only required for the small sample chamber, while the goniometer remains always in vacuum. Without the need for an additional external cooling device and no need of compressed air the installation and reliable operation is guaranteed for the S8 TIGER ECO "Petro".

Experimental

22 lubricating oil standards were used to set up the calibration. These standards had been prepared gravimetrically using reagents traceable to NIST certified reference materials. The concentration ranges for the calibration standards used are listed in Table 1, several samples with blank values for each element were available.

Table 1: Calibration ranges for additives in lubricating oils according to ASTM D6443.

	Min [ppm]	Max [ppm]
Mg	50	2000
P	2	1500
S	2000	7500
Cl	50	1500
Ca	100	5000
Cu	10	500
Zn	200	1500

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

Measurement

The intensities at the peak and off-peak background angles were measured from the liquid samples using optimized parameters. The measurement method is shown in Table 2, the standard collimator used has the opening angle of 0.46°.

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 the "Fundamental Parameters" program, but finally the Variable Alphas model was used to cover the wider concentration ranges. This function is a standard part of the SPECTRA*plus* software. The Variable Alphas model calculates the alpha coefficients individually from each sample 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, for Cu in Figure 3, and for Ca in Figure 4.

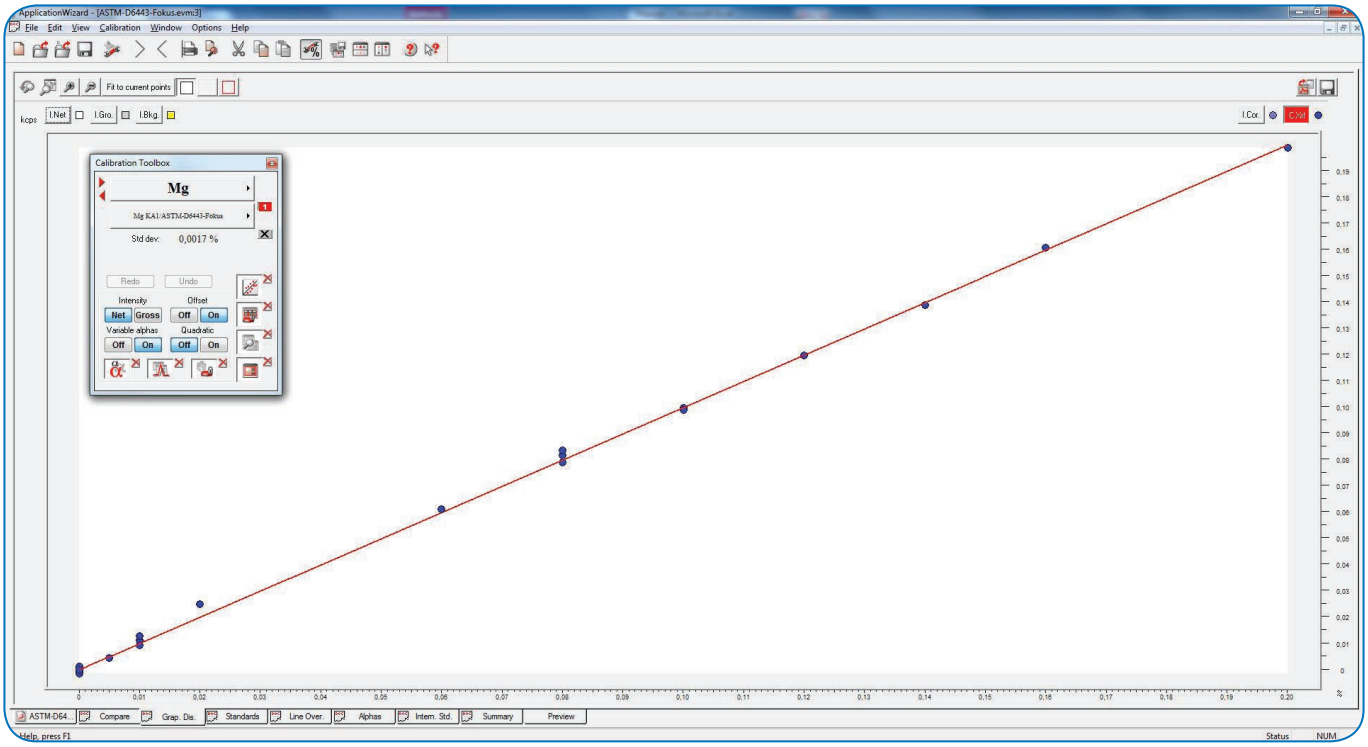

Figure 2: Calibration curve for Mg in lubricating oil

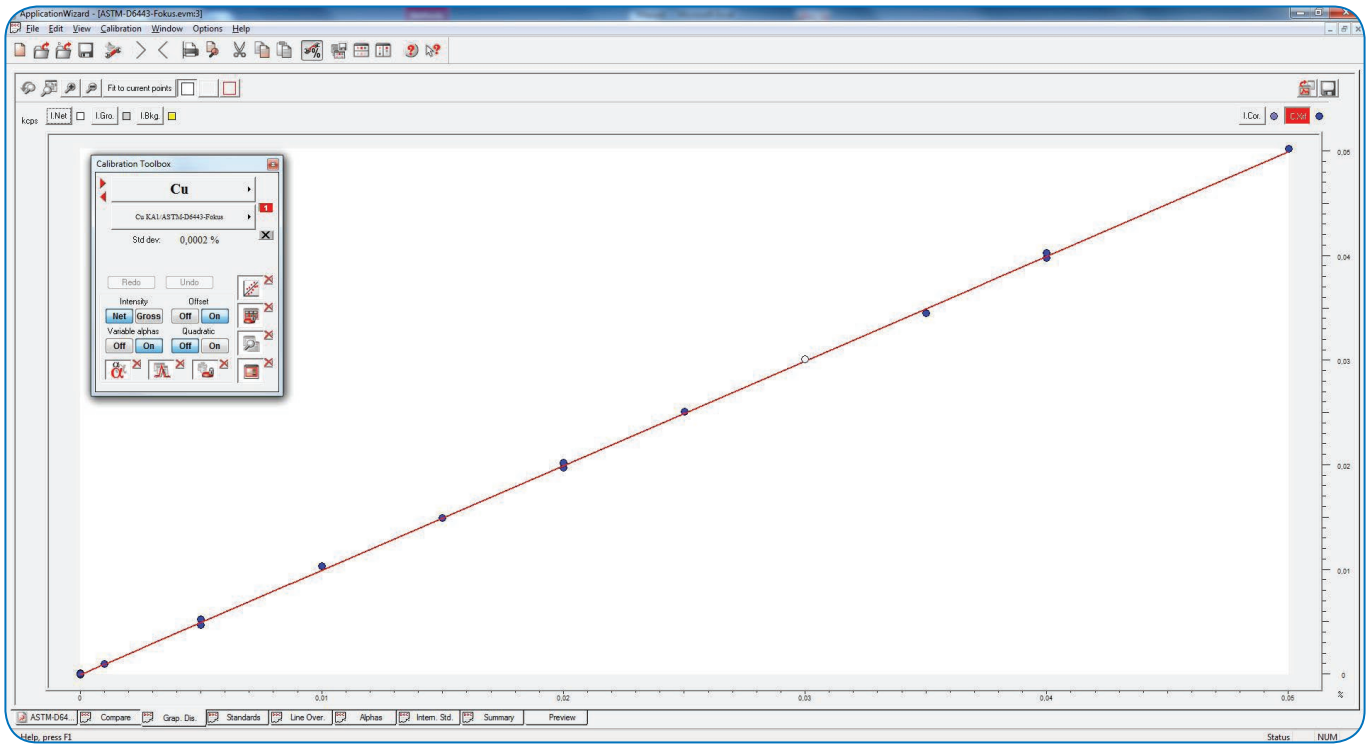

Figure 3: Calibration curve for Cu in lubricating oil

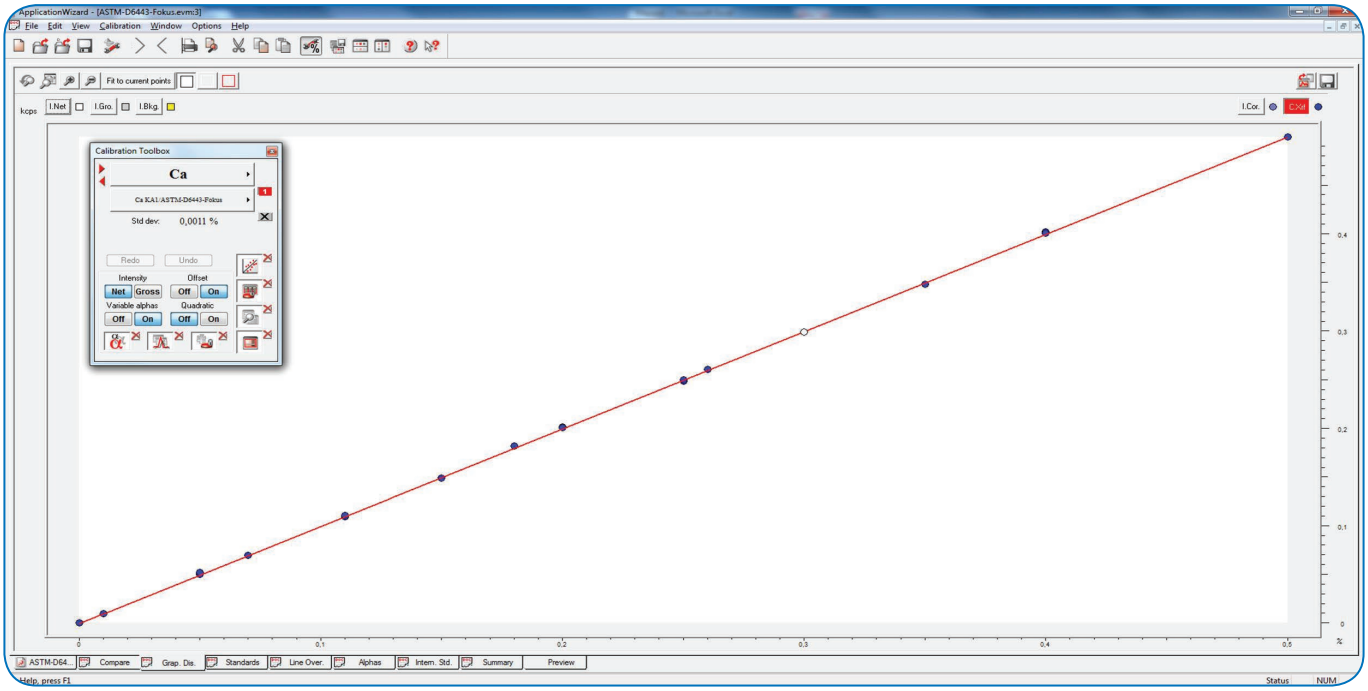

Figure 4: Calibration curve for Ca in lubricating oil

Table 2 lists the calculated calibration details as well as 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 accepted formula given beside, 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

Table 2: Optimized measurement method for additives in lubricating oils with the S8 TIGER ECO "Petro"

Element Line	Excitation Voltage	Excitation Current	Crystal	Peak Position [2θ°]	Bkg 1 Position [2θ°]	Bkg 2 Position [2θ°]	L.O.D [ppm]	Measure-ment Time [s]
Mg Kα	20 kV	50 mA	XS-55	20.747	19.752	21.742	2.3	64 s/32 s
P Kα	20 kV	50 mA	PET	89.427	86.540		2.1	24 s each
S Kα	20 kV	50 mA	PET	75.773	79.495		1.6	40 s each
Cl Kα	20 kV	50 mA	PET	65.423	67.415		3.0	32 s each
Ca Kα	50 kV	20 mA	LiF200	113.124	105.160	121.160	1.1	24 s/12 s
Cu Kα	50 kV	20 mA	LiF200	45.040	44.222	47.500	0.8	24 s/10 s
Zn Kα	50 kV	20 mA	LiF200	41.820	44.222	47.500	1.1	12 s/10 s

Results

The analytical performance of the S8 TIGER ECO "Petro" for lubricating oils was tested for short term precision by running one sample 11 times in 3.5 h (alternated with a second sample, that each time the sample was loaded and unloaded.). The measurements for long term precision were done in more than two weeks time. The results are shown in Table 3 and Table 4. The typical variation of the concentration range was in the lower ppm range of 10 ppm at 0.05 % for Zn or 20 ppm at 0.082 % for Mg. Even elements with higher volatility, such as Cl, are analyzed accurately and precisely with the S8 TIGER ECO "Petro". At 0.05 % Cl the maximum variation was only 4 ppm. With a limit of detection 3 ppm (32 s measurement time plus one background position) even very low traces of Cl can be determined efficiently.

Table 3: Short term repeatability test with the quality check sample for ASTM D 6443 covering typical concentrations in the medium range

Time	Mg (%)	P (%)	S (%)	Cl (%)	Ca (%)	Cu (%)	Zn (%)
09:47	0.082	0.049	0.277	0.050	0.200	0.0198	0.050
10:13	0.082	0.049	0.274	0.050	0.199	0.0197	0.049
10:33	0.082	0.049	0.275	0.050	0.199	0.0198	0.049
10:42	0.082	0.050	0.274	0.051	0.201	0.0197	0.049
11:39	0.082	0.050	0.274	0.050	0.200	0.0198	0.049
11:48	0.083	0.049	0.274	0.050	0.201	0.0198	0.050
11:56	0.083	0.049	0.276	0.050	0.200	0.0198	0.049
12:10	0.081	0.050	0.276	0.049	0.199	0.0199	0.049
12:30	0.083	0.049	0.275	0.050	0.200	0.0198	0.049
12:39	0.082	0.049	0.274	0.050	0.199	0.0198	0.049
13:10	0.083	0.049	0.275	0.050	0.199	0.0199	0.050
Average [%]	**0.0823**	**0.0493**	**0.2749**	**0.0500**	**0.1997**	**0.0198**	**0.0493**
Abs.Std.Dev. [%]	**0.0006**	**0.0005**	**0.0010**	**0.0004**	**0.0008**	**0.0001**	**0.0005**
Rel.Std.Dev.	**0.8%**	**0.9%**	**0.4%**	**0.9%**	**0.4%**	**0.3%**	**0.9%**
MIN [%]	**0.081**	**0.049**	**0.274**	**0.049**	**0.199**	**0.0197**	**0.049**
MAX [%]	**0.083**	**0.050**	**0.277**	**0.051**	**0.201**	**0.0199**	**0.050**
Range [%]	**0.002**	**0.001**	**0.003**	**0.002**	**0.002**	**0.0002**	**0.001**

Table 4: Long term repeatability test (18 days) with the quality check sample for ASTM D 6443 covering typical concentrations in the medium range

Date / Time	Mg (%)	P (%)	S (%)	Cl (%)	Ca (%)	Cu (%)	Zn (%)
21.06.2013 18:44	0.079	0.049	0.274	0.050	0.200	0.0197	0.049
24.06.2013 11:16	0.081	0.049	0.276	0.051	0.198	0.0199	0.049
24.06.2013 17:42	0.082	0.050	0.276	0.050	0.199	0.0198	0.049
25.06.2013 09:47	0.082	0.049	0.277	0.050	0.200	0.0198	0.050
26.06.2013 10:43	0.083	0.049	0.274	0.050	0.201	0.0198	0.049
27.06.2013 09:35	0.081	0.049	0.275	0.050	0.198	0.0191	0.049
28.06.2013 08:44	0.082	0.049	0.275	0.050	0.199	0.0193	0.049
01.07.2013 10:43	0.079	0.049	0.274	0.050	0.199	0.0192	0.049
02.07.2013 11:04	0.081	0.049	0.273	0.050	0.199	0.0194	0.049
03.07.2013 10:53	0.083	0.049	0.275	0.050	0.198	0.0194	0.049
04.07.2013 11:01	0.082	0.049	0.274	0.050	0.199	0.0193	0.049
05.07.2013 09:19	0.082	0.049	0.274	0.050	0.199	0.0194	0.049
09.07.2013 11:44	0.083	0.049	0.274	0.050	0.199	0.0195	0.049
Average [%]	**0.0815**	**0.0491**	**0.2747**	**0.0501**	**0.1991**	**0.0195**	**0.0491**
Abs.Std.Dev. [%]	**0.0013**	**0.0003**	**0.0011**	**0.0003**	**0.0009**	**0.0003**	**0.0003**
Rel.Std.Dev.	**1.6%**	**0.6%**	**0.4%**	**0.6%**	**0.4%**	**1.3%**	**0.6%**
MIN [%]	**0.079**	**0.049**	**0.273**	**0.050**	**0.198**	**0.0191**	**0.049**
MAX [%]	**0.083**	**0.050**	**0.277**	**0.051**	**0.201**	**0.0199**	**0.050**
Range [%]	**0.004**	**0.001**	**0.004**	**0.001**	**0.003**	**0.0008**	**0.001**

Conclusions

The results for the short term and long term precision achieved with the S8 TIGER ECO "Petro" are excellent. The typical relative standard deviation for the medium concentration ranges are below 1 %, the range of variation was typically below 40 ppm. This allows to closely monitor the product grades and to meet the specifications without spending higher amounts of additives. The measurement time with the S8 TIGER ECO "Petro" is typically 10 minutes only. By prolonging the measurement time per element, the range of variation can be decreased. This allows achieving a sample throughput of more than 140 samples per day at unique low cost of ownership.

With the reduced helium and electrical power consumption, the savings on cooling water and prolonged tube life the cost of ownership are uniquely low but come in handy with excellent analytical performance. With 5 years warranty on the X-ray tube peace of mind is guaranteed.

System Configuration

S8 TIGER ECO „Petro" for lubricating oils (ASTM D 6443)
Includes

- 1 kW Long Life Time X-ray tube with 5 years warranty pro rated
- Collimator: 0.46°
- Analyzer crystals: XS-55, PET, LiF 200
- EasyLoader for 75 positions (optional)
- Helium flushing and vacuum with vacuum seal
- SPECTRA plus Analytical Software V3
- Premium PC (Windows 7)

Recommended accessories

7KP19018FA	Liquid cups for S8 TIGER 35/40 mm inner/outer diameter, 500 off
7KP78048CB	Prolene foil, 4µm, 500 precut foils
862165	ASTM D6443 Additives in Lubricants Set of 22 calibration standards for Ca, Cl, Cu, Mg, P, S, Zn in 100 mL Quality Check sample 1000 mL Drift Correction sample, 200 mL

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