

S-4 EXPLORER

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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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 D6443¹ 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 Wavelength Dispersive Spectroscopy (WDS) provides a non-destructive method that is easily incorporated into a production environment. Up until now the selection of a WDS system to perform this test was limited to high cost, high performance systems with 3kW to 4kW X-ray generators, or to low cost, low performance systems with 0.2kW to 0.4kW X-ray generators. This report discusses a low cost, high performance WDS system with an optimal configuration to analyze petroleum products. The level of precision and Lower-Limit-of-Detection (LLD) are also discussed.



Figure 1 - Bruker AXS S4 EXPLORER wavelength dispersive X-ray spectrometer.

Instrument Configuration

The Bruker AXS S4 EXPLORER is an ideal solution for analyzing petroleum products. This system is capable of matching the analytical performance of a high powered system at a fraction of the cost, and includes some unique features that make it better suited than most high powered systems for analyzing petroleum products. The S4 EXPLORER has a very small foot print and comes with casters. This allows the instrument to be placed into tight quarters and easily moved whenever service is required. The cost of operating the S4 EXPLORER has also been reduced because it does not require an external water supply, compressed air, or P10 gas for the detector. The only outside services required by the S4 EXPLORER are a power outlet and a helium supply for analyzing liquids.

The S4 EXPLORER uses a 1kW ceramic end-window X-ray tube with an ultra-thin 75 μ beryllium window that was designed by Bruker AXS specifically for this instrument. This X-ray tube is positioned below the sample to optimize liquid sample presentation to the X-ray beam. A closely coupled optical path helps provide high intensities and low detection limits for all elements. The lower operating power minimizes adverse effects from sample heating by the X-ray beam for example, degassing of the sample causing bubbles to form, deformation of the sample cell window, and evaporation. 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 milliampere settings provides maximum sensitivity for all elements. The light elements are typically analyzed using low kV and high mA settings (20kV/50mA), while the higher atomic number elements are analyzed with high kV and lower mA settings (50kV/20mA).

The S4 EXPLORER has the same features found in high cost systems: a 10-position primary beam filter changer, up to four primary collimators, and up to eight 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 newly developed "Pro4" sealed proportional detector for measuring the lower energy lines. This detector provides the same performance as a traditional gas flow detector, but without the added expense that goes along with a gas flow detector.

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 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 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. A software interlock is also provided to prevent a liquid sample from being analyzed while the spectrometer is in a vacuum mode. The software will not allow introduction of a sample identified as a liquid into a vacuum path.

The S4 EXPLORER's 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.

Operation and data reduction for the S4 EXPLORER are easily handled with the Bruker AXS SPECTRA^{plus} software package. This is a true 32-bit program designed for use on the Windows-NT platform for maximum stability. Its standard features include "standardless" analysis, sophisticated matrix corrections with integrated Fundamental Parameters, flexible data storage and retrieval, and full network capability.

Experimental

Twenty-two lubricating oil standards, which included a blank, were obtained from a commercial laboratory.² 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.

	Ca	Cl	Cu	Mg	P	S	Zn
LOE22-01	0.300	0.081	0.030	0.060	0.060	0.275	0.062
LOE22-02	0.250	0.100	0.000	0.010	0.150	0.000	0.150
LOE22-03	0.500	0.001	0.035	0.160	0.150	0.000	0.020
LOE22-04	0.350	0.011	0.000	0.120	0.080	0.200	0.000
LOE22-05	0.110	0.000	0.015	0.100	0.100	0.300	0.050
LOE22-06	0.200	0.100	0.000	0.200	0.050	0.251	0.154
LOE22-07	0.000	0.050	0.025	0.000	0.000	0.450	0.020
LOE22-08	0.150	0.030	0.000	0.100	0.030	0.400	0.040
LOE22-09	0.250	0.152	0.010	0.160	0.000	0.350	0.080
LOE22-10	0.110	0.150	0.040	0.005	0.030	0.750	0.151
LOE22-11	0.260	0.051	0.000	0.000	0.000	0.750	0.000
LOE22-12	0.200	0.000	0.005	0.140	0.080	0.501	0.080
LOE22-13	0.000	0.000	0.005	0.020	0.020	0.200	0.020
LOE22-14	0.070	0.150	0.020	0.080	0.140	0.650	0.150
LOE22-15	0.050	0.000	0.000	0.000	0.150	0.000	0.000
LOE22-16	0.400	0.001	0.001	0.080	0.000	0.501	0.020
LOE22-17	0.180	0.020	0.020	0.000	0.020	0.611	0.060
LOE22-18	0.400	0.011	0.001	0.010	0.020	0.000	0.000
LOE22-19	0.010	0.020	0.040	0.010	0.020	0.201	0.100
LOE22-20	0.050	0.005	0.050	0.000	0.008	0.000	0.121
LOE22-21	0.200	0.050	0.020	0.080	0.050	0.000	0.050
LOE22-22	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 1 - Calibration standard compositions in mass %.

Individual specimens were prepared by pouring each sample into a 40 mm diameter plastic cell that was fitted with a 4 μ Prolene[®] window(3). Each cell was vented 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 28mm 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 used at the peak angle, and at each of the background angles. The total time required to measure each sample was nine minutes, which includes sample introduction time.

El.	Analyzer Crystal	Peak Angle (deg. 2-q)	Bkgd. Angle (deg 2-q)	Collimator	Detector	Beam Filter	kV/mA	Count Time (sec)
Ca	LiF(200)	113.10	117.50	0.46°	Pro4	None	50/20	20
Cl	Ge(111)	92.74	94.10	0.23°	Pro4	None	20/50	60
Cu	LiF(200)	45.04	47.44	0.23°	SC	Al 500 um	50/20	10
Mg	OVO-55	21.07	23.70	0.46°	Pro4	None	20/50	60
P	Ge(111)	140.94	136.60	0.46°	Pro4	None	20/50	20
S	Ge(111)	110.69	114.80	0.46°	Pro4	None	20/50	30
Zn	LiF(200)	41.78	39.30, 43.60	0.23°	SC	None	50/20	10

Table 2 - Instrument operating parameters used to measure the lubricating oil samples

Calibration coefficients were calculated using 21 of the 22 standards by regressing the concentration data with the measured intensity data for each analyte. One of the calibration standards (LOE22-19) was held back for use as a control sample. Matrix corrections (influence coefficients) were applied using a concentration based calibration model with the form:

$$C_i = a_i + b_i I_i (1 + \sum \alpha_{ij} C_j)$$

Where:

- C_i = concentration of the analyte element i .
- a_i = intercept of the calibration line for analyte element i on the concentration axis.
- b_i = slope of the calibration line for analyte element i in %/kCPS

- I_i = net measured intensity for analyte element i in kCPS.
- α_{ij} = influence coefficient for the effect of an absorbing element j on the analyte element i .
- C_j = concentration of an interfering element j as a weight fraction.

Theoretical influence coefficients (alphas) were calculated using a "Fundamental Parameters" program which is a standard part of the SPECTRA^{plus} software. The results of the regression analysis using the 21 standards are shown in Figure 1 through Figure 7, and have been summarized in Table 3.

Analyte	Conc. Range (mass %)	Calibration Line Offset (mass %)	Calibration Line Slope (mass %/kCPS)	Standard Deviation (mass %)
Ca	0 - 0.500	-0.00238	0.07281	0.0028
Cl	0 - 0.152	-0.00213	0.23770	0.0011
Cu	0 - 0.050	-0.00206	0.09955	0.0005
Mg	0 - 0.200	-0.00393	0.07014	0.0013
P	0 - 0.150	-0.00014	0.04901	0.0010
S	0 - 0.750	-0.00021	0.07005	0.0043
Zn	0 - 0.154	-0.00046	0.02722	0.0015

Table 3 - Calibration summary for Unused Lubricating Oils and Additives

Table 4 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 a counting time of 100 seconds for comparison purposes. The SPECTRA^{plus} 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 accepted formula given below, except instead of using "m" to convert the intensity to a concentration the calibration coefficients are used.

$$LLD = (3/m) (I_b/T_b)^{1/2}$$

where:

- m = sensitivity of analyte in CPS/mass-%
- I_b = background intensity for analyte in CPS
- T_b = counting time in seconds at the background angle.

Analyte	Count Time (seconds)	LLD Actual Time (ppm)	LLD 100 Sec. (ppm)
Ca	20	2.3	1.0
Cl	60	2.3	1.8
Cu	10	2.0	0.6
Mg	60	3.0	2.3
P	20	1.3	0.6
S	30	1.2	0.7
Zn	10	0.9	0.3

Table 4 - Lower Limits of Detection for Unused Lubricating Oils

A precision test was performed on twenty individual sample preparations for one of the Lubricating Oil standards. This standard was not used to define the calibration curve. The results of this precision test, and statistical evaluation of the data is summarized in Table 5. This table includes a comparison to the known chemical concentrations for each analyte in the sample. The table also includes the ASTM prescribed repeatability limits along with those determined from the measured data. This repeatability is the difference between successive test results obtained from a single operator using the same instrument on one sample, and over the long run 1 out of 20 values would be within the prescribed limits. The results produced by the S4 EXPLORER were all within the prescribed limits.

Sample	Ca mass %	Cl mass %	Cu mass %	Mg mass %	P mass %	S mass %	Zn mass %
LOE22-19-A	0.0100	0.0200	0.0406	0.0093	0.0201	0.2022	0.1008
LOE22-19-B	0.0098	0.0201	0.0404	0.0091	0.0201	0.2011	0.1025
LOE22-19-C	0.0098	0.0199	0.0410	0.0094	0.0205	0.2027	0.1019
LOE22-19-D	0.0102	0.0206	0.0416	0.0095	0.0204	0.2046	0.1033
LOE22-19-E	0.0100	0.0201	0.0411	0.0092	0.0206	0.2035	0.1041
LOE22-19-F	0.0097	0.0201	0.0407	0.0093	0.0201	0.2036	0.1036
LOE22-19-G	0.0100	0.0197	0.0412	0.0093	0.0202	0.2027	0.1029
LOE22-19-H	0.0101	0.0199	0.0411	0.0092	0.0206	0.2027	0.1028
LOE22-19-I	0.0101	0.0197	0.0414	0.0096	0.0202	0.2024	0.1033
LOE22-19-J	0.0099	0.0193	0.0408	0.0097	0.0203	0.1987	0.1021
LOE22-19-K	0.0101	0.0200	0.0414	0.0095	0.0204	0.2039	0.1037
LOE22-19-L	0.0097	0.0198	0.0409	0.0092	0.0199	0.2005	0.1021
LOE22-19-M	0.0100	0.0199	0.0408	0.0090	0.0201	0.1976	0.1018
LOE22-19-N	0.0098	0.0198	0.0402	0.0091	0.0200	0.1997	0.1007
LOE22-19-O	0.0101	0.0199	0.0407	0.0090	0.0200	0.1997	0.1015
LOE22-19-P	0.0099	0.0194	0.0413	0.0095	0.0204	0.2013	0.1027
LOE22-19-Q	0.0101	0.0203	0.0410	0.0094	0.0205	0.2020	0.1034
LOE22-19-R	0.0102	0.0201	0.0410	0.0091	0.0202	0.2004	0.1024
LOE22-19-S	0.0102	0.0199	0.0408	0.0092	0.0207	0.2013	0.1039
LOE22-19-T	0.0099	0.0198	0.0410	0.0094	0.0207	0.2009	0.1022
Number of Tests	20	20	20	20	20	20	20
Maximum	0.0102	0.0206	0.0416	0.0097	0.0207	0.2046	0.1041
Minimum	0.0097	0.0193	0.0402	0.0090	0.0199	0.1976	0.1007
Range	0.0005	0.0013	0.0014	0.0007	0.0008	0.0070	0.0034
Average	0.0100	0.0199	0.0410	0.0093	0.0203	0.2016	0.1026
Abs. Std. Dev. (1σ)	0.0002	0.0003	0.0003	0.0002	0.0002	0.0018	0.0010
Rel. Std. Dev. (1σ)	1.6	1.5	0.8	2.1	1.2	0.9	0.9
True Concentration	0.0100	0.0200	0.0400	0.0100	0.0200	0.2000	0.1000
Abs. Difference	0.0000	-0.0001	0.0009	-0.0007	0.0003	0.0016	0.0026
Rel. Difference	-0.3	-0.4	2.4	-7.1	1.5	0.8	2.6
ASTM Repeatability	0.0007	0.0010	0.0006	0.0036	0.0014	0.0056	0.0024
Actual Repeatability	0.0004	0.0009	0.0006	0.0004	0.0005	0.0051	0.0017
Summary							

Table 5 - Precision test from twenty measurements of Lubricating Oil standard LOE22-19 with the S4 EXPLORER

The Optimum WDS 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 ultra-thin (75 μ) end window X-ray tube operating at 1000 watts provides more intensity when compared to other low cost systems which typically operate at only 200 to 400 watts.
- 2) Maximizing the sample handling capabilities allows both liquid and solid samples to be analyzed simultaneously decreasing the overall analyzing time. Random accessing 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 standard deviation of the calibration curves were as follows: Ca 0.0028% (28 ppm), Cl 0.0011% (11 ppm), Cu 0.0005% (5 ppm), Mg 0.0013% (13 ppm), P 0.0010% (10 ppm), S 0.0043% (43 ppm), and Zn 0.0015% (15 ppm). This is an indication of the accuracy of the method since it includes all errors associated with the measurement process (errors in the known concentration values of the standards, errors from preparing the specimens and errors in the measurements).
- 5) A precision and repeatability test showed repeatability to be within the guide lines prescribed by the ASTM Test Method D6443. The absolute standard deviations from 20 replicate measurements of one sample were as follows: Ca 0.0002% at the 0.0100% level, Cl 0.0003% at the 0.0200% level, Cu 0.0003% at the 0.0400% level, Mg 0.0002% at the 0.0100% level, P 0.0002% at the 0.0200% level, S 0.0018% at the 0.2000% level, and Zn 0.0010% at the 0.1000% level.
- 6) The Lower-Limits-of-Detection (LLD) based on 100 seconds of counting time were calculated to be 0.00010% (1.0 ppm) for Ca, 0.00018% (1.8 ppm) for Cl, 0.00006% (0.6 ppm) for Cu, 0.00023% (2.3 ppm) for Mg, 0.00006% (0.6 ppm) for P, 0.00007% (0.7 ppm) for S, and 0.00003% (0.3 ppm) for Zn.

The S4 EXPLORER fully met the requirements for the

determination of calcium, chlorine, copper, magnesium, phosphorus, sulfur, and zinc in unused lubricating oils and additives as outlined in ASTM D6443. The S4 EXPLORER is ideally suited for the wide range of process control applications found in the petroleum industry.

References

- [1] D6443-99 Standard Test Method for Determination of Calcium, Chlorine, Copper, Magnesium, Phosphorus, Sulfur, and Zinc in Unused Lubricating Oils and Additives by Wavelength Dispersive X-ray Fluorescence Spectrometry (Mathematical Correction Procedure), American Society for Testing and Materials, West Conshohocken, PA, Copyright 1999.
- [2] Analytical Services, Inc, Woodlands, Texas 77387, (409) 273-1780
- [3] ®Prolene is a registered trademark of Chemplex Industries, Inc., Stuart, Florida 34997, (561) 283-2700

Figure 1 - Calibration data for Magnesium in unused

lubricating oils and additives using the S4 EXPLORER.

Abridged calibration data for line Mg KA1

21 standards from 0.000 to 0.200 %

Standard Deviation: 0.0013 % (13 ppm)

Intensity model: Net Intensity

Absorption correction: Fixed alphas (theoretical values for average standard)

Slope: 0.07014 %/KCps / Sensitivity: 14.26 KCps/% (Adjustable by regression)

Intensity offset: 0.05606 KCps (Adjustable by regression) or -39.3 ppm

Standard	Peak Int. kCPS	Bkgd. Int. kCPS	Net Int. kCPS	Chem. Conc. mass %	XRF Conc. mass %	Abs. Dev. mass %	Rel. Dev. % rel.
LOE22-01	1.147	0.134	1.013	0.060	0.062	0.002	2.9
LOE22-02	0.333	0.128	0.204	0.010	0.009	-0.001	-6.5
LOE22-03	2.602	0.127	2.475	0.160	0.156	-0.004	-2.3
LOE22-04	2.061	0.130	1.931	0.120	0.120	0.000	0.3
LOE22-05	1.764	0.137	1.628	0.100	0.101	0.001	1.0
LOE22-06	3.270	0.150	3.120	0.200	0.199	-0.001	-0.5
LOE22-07	0.183	0.126	0.057	0.000	0.000	0.000	
LOE22-08	1.747	0.134	1.613	0.100	0.100	0.000	0.0
LOE22-09	2.684	0.146	2.537	0.160	0.161	0.001	0.4
LOE22-10	0.297	0.159	0.138	0.005	0.005	0.000	1.3
LOE22-11	0.220	0.138	0.082	0.000	0.001	0.001	
LOE22-12	2.371	0.142	2.229	0.140	0.141	0.001	0.3
LOE22-13	0.488	0.121	0.367	0.020	0.020	0.000	-2.1
LOE22-14	1.466	0.159	1.306	0.080	0.081	0.001	1.6
LOE22-15	0.152	0.109	0.044	0.000	-0.001	-0.001	
LOE22-16	1.463	0.137	1.326	0.080	0.082	0.002	2.2
LOE22-17	0.206	0.141	0.065	0.000	0.000	0.000	
LOE22-18	0.324	0.115	0.210	0.010	0.010	0.000	-4.5
LOE22-20	0.162	0.122	0.039	0.000	-0.001	-0.001	
LOE22-21	1.443	0.123	1.320	0.080	0.081	0.001	1.4
LOE22-22	0.150	0.108	0.041	0.000	-0.001	-0.001	

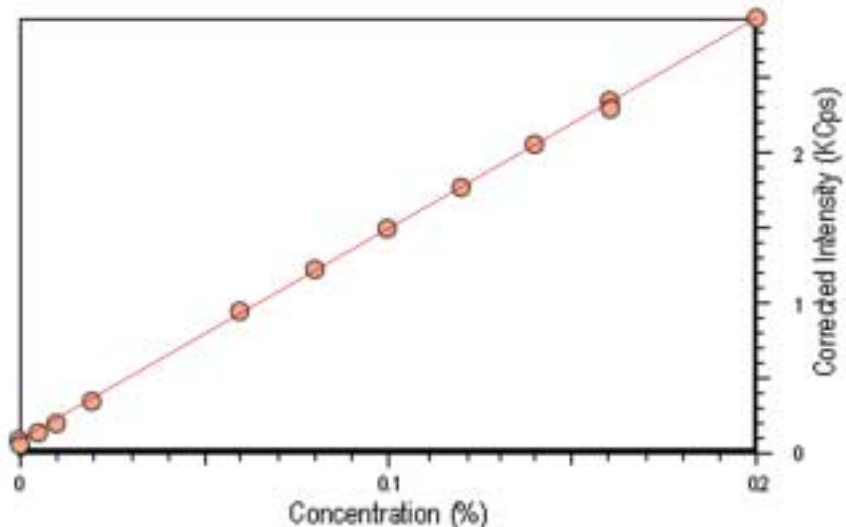


Figure 2 - Calibration data for Phosphorus in unused lubricating oils and additives using the S4 EXPLORER.

Abridged calibration data for line P KA1

21 standards from 0.000 to 0.150 %

Standard Deviation: 0.0010 % (10 ppm)

Intensity model: Net Intensity

Absorption correction: Fixed alphas (theoretical values for average standard)

Slope: 0.04901 %/KCps / Sensitivity: 20.41 KCps/% (Adjustable by regression)

Intensity offset: 0.00286 KCps (Adjustable by regression) or -1.4 ppm

Standard	Peak Int. kCPS	Bkgd. Int. kCPS	Net Int. kCPS	Chem. Conc. mass %	XRF Conc. mass %	Abs. Dev. mass %	Rel. Dev. % rel.
LOE22-01	4.696	0.177	4.519	0.060	0.060	0.000	-0.2
LOE22-02	11.535	0.177	11.358	0.150	0.150	0.000	0.1
LOE22-03	11.199	0.171	11.028	0.150	0.147	-0.004	-2.4
LOE22-04	6.224	0.174	6.050	0.080	0.080	0.000	-0.3
LOE22-05	7.778	0.185	7.593	0.100	0.100	0.000	0.3
LOE22-06	3.856	0.170	3.687	0.050	0.049	-0.001	-1.2
LOE22-07	0.171	0.165	0.006	0.000	0.000	0.000	
LOE22-08	2.457	0.169	2.289	0.030	0.030	0.000	0.5
LOE22-09	0.170	0.167	0.002	0.000	0.000	0.000	
LOE22-10	2.487	0.194	2.294	0.030	0.031	0.001	2.4
LOE22-11	0.182	0.181	0.001	0.000	0.000	0.000	
LOE22-12	6.140	0.190	5.950	0.080	0.079	-0.001	-0.7
LOE22-13	1.720	0.166	1.555	0.020	0.020	0.000	0.6
LOE22-14	10.669	0.199	10.470	0.140	0.141	0.001	0.8
LOE22-15	11.915	0.184	11.731	0.150	0.152	0.002	1.4
LOE22-16	0.170	0.172	-0.002	0.000	0.000	0.000	
LOE22-17	1.689	0.175	1.514	0.020	0.020	0.000	-0.3
LOE22-18	1.697	0.157	1.540	0.020	0.020	0.000	-0.3
LOE22-20	0.793	0.158	0.635	0.008	0.008	0.000	2.3
LOE22-21	4.048	0.165	3.883	0.050	0.051	0.001	1.8
LOE22-22	0.155	0.158	-0.004	0.000	0.000	0.000	

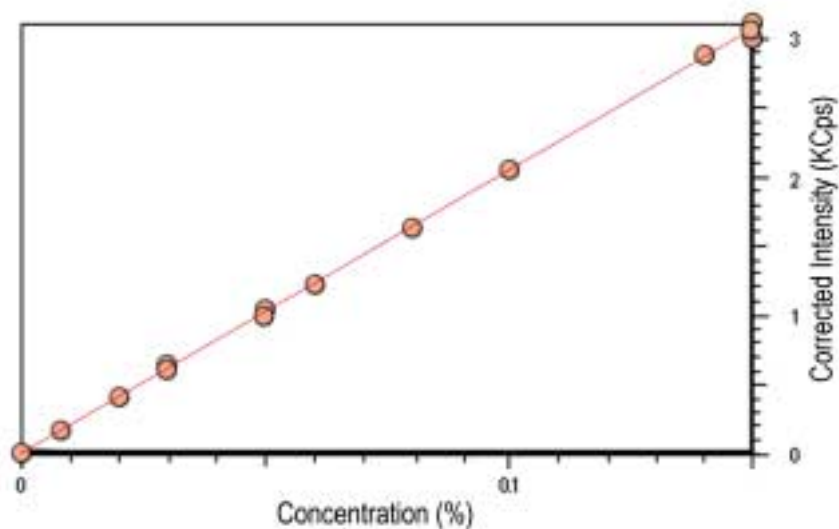


Figure 3 – Calibration data for Sulfur in unused lubricating oils and additives using the S4 EXPLORER.

Abridged calibration data for line S KA1

21 standards from 0.000 to 0.750 %

Standard Deviation: 0.0043 % (43 ppm)

Intensity model: Net Intensity

Absorption correction: Fixed alphas (theoretical values for average standard)

Slope: 0.07005 %/KCps / Sensitivity: 14.28 KCps/% (Adjustable by regression)

Intensity offset: 0.00294 KCps (Adjustable by regression) or -2.1 ppm

Standard	Peak Int. kCPS	Bkgd. Int. kCPS	Net Int. kCPS	Chem. Conc. mass %	XRF Conc. mass %	Abs. Dev. mass %	Rel. Dev. % rel.
LOE22-01	20.814	0.189	20.625	0.275	0.276	0.001	0.3
LOE22-02	0.246	0.165	0.081	0.000	0.001	0.001	
LOE22-03	0.206	0.162	0.044	0.000	0.000	0.000	
LOE22-04	15.037	0.179	14.858	0.200	0.198	-0.002	-1.2
LOE22-05	22.781	0.191	22.590	0.300	0.302	0.002	0.7
LOE22-06	18.274	0.187	18.088	0.251	0.245	-0.007	-2.6
LOE22-07	34.494	0.209	34.285	0.450	0.451	0.001	0.3
LOE22-08	29.964	0.198	29.766	0.400	0.396	-0.004	-0.9
LOE22-09	26.082	0.201	25.882	0.350	0.347	-0.003	-0.8
LOE22-10	55.969	0.236	55.733	0.750	0.760	0.010	1.3
LOE22-11	56.611	0.230	56.381	0.750	0.754	0.004	0.5
LOE22-12	36.681	0.204	36.478	0.501	0.494	-0.007	-1.4
LOE22-13	15.804	0.188	15.616	0.200	0.204	0.004	1.7
LOE22-14	47.539	0.224	47.315	0.650	0.652	0.002	0.4
LOE22-15	0.209	0.172	0.037	0.000	0.000	0.000	
LOE22-16	37.368	0.206	37.161	0.501	0.496	-0.005	-1.0
LOE22-17	45.431	0.220	45.211	0.611	0.605	-0.006	-1.0
LOE22-18	0.209	0.171	0.038	0.000	0.000	0.000	
LOE22-20	0.248	0.170	0.078	0.000	0.001	0.001	
LOE22-21	0.702	0.168	0.535	0.000	0.007	0.007	
LOE22-22	0.207	0.168	0.039	0.000	0.000	0.000	

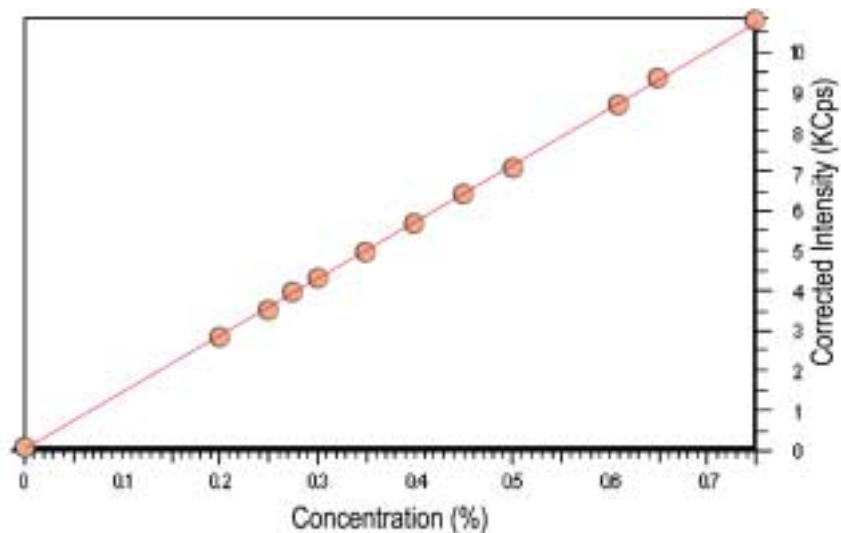


Figure 4. Calibration data for Chlorine in unused lubricating oils and additives using the S4 EXPLORER.

Abridged calibration data for line Cl KA

21 standards from 0.000 to 0.152 %

Standard Deviation: 0.0011 % (11 ppm)

Intensity model: Net Intensity

Absorption correction: Fixed alphas (theoretical values for average standard)

Slope: 0.2377 %/KCps/Sensitivity: 4.207 KCps/% (Adjustable by regression)

Intensity offset: 0.00897 KCps (Adjustable by regression) or -21.3 ppm

Standard	Peak Int. kCPS	Bkgd. Int. kCPS	Net Int. kCPS	Chem. Conc. mass %	XRF Conc. mass %	Abs. Dev. mass %	Rel. Dev. % rel.
LOE22-01	2.289	0.096	2.193	0.081	0.081	-0.001	-0.6
LOE22-02	2.851	0.094	2.758	0.100	0.099	-0.001	-1.1
LOE22-03	0.181	0.086	0.095	0.001	0.001	0.000	
LOE22-04	0.432	0.087	0.344	0.011	0.011	0.000	-3.2
LOE22-05	0.154	0.090	0.064	0.000	0.000	0.000	
LOE22-06	2.711	0.096	2.615	0.100	0.097	-0.003	-2.8
LOE22-07	1.473	0.094	1.379	0.050	0.050	0.000	-0.3
LOE22-08	0.930	0.094	0.837	0.030	0.030	0.000	-1.3
LOE22-09	4.096	0.101	3.995	0.152	0.150	-0.002	-1.1
LOE22-10	3.936	0.101	3.835	0.150	0.153	0.003	1.8
LOE22-11	1.450	0.092	1.358	0.051	0.052	0.001	1.1
LOE22-12	0.157	0.086	0.071	0.000	0.001	0.001	
LOE22-13	0.153	0.090	0.062	0.000	0.000	0.000	
LOE22-14	3.903	0.098	3.804	0.150	0.152	0.002	1.1
LOE22-15	0.158	0.092	0.066	0.000	0.000	0.000	
LOE22-16	0.169	0.087	0.082	0.001	0.001	0.000	
LOE22-17	0.668	0.089	0.579	0.020	0.020	0.000	2.0
LOE22-18	0.451	0.091	0.361	0.011	0.011	0.000	-3.1
LOE22-20	0.293	0.093	0.200	0.005	0.005	0.000	-0.6
LOE22-21	1.556	0.096	1.460	0.050	0.050	0.000	0.6
LOE22-22	0.160	0.093	0.067	0.000	0.000	0.000	

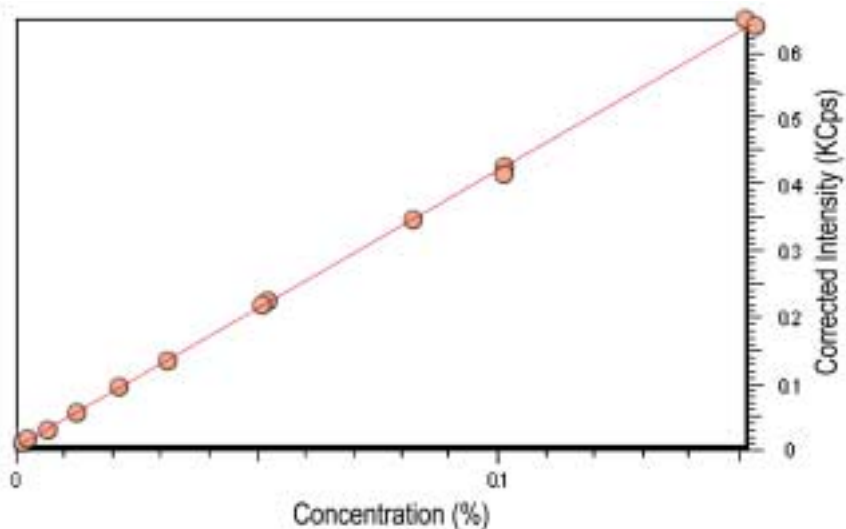


Figure 5 - Calibration data for Calcium in unused lubricating oils and additives using the Bruker AXS S4 EXPLORER.

Abridged calibration data for line Ca KA1

21 standards from 0.000 to 0.500 %

Standard Deviation: 0.0028 % (28 ppm)

Intensity model: Net Intensity

Absorption correction: Fixed alphas (theoretical values for average standard)

Slope: 0.07281 %/KCps / Sensitivity: 13.73 KCps/% (Adjustable by regression)

Intensity offset: 0.03265 KCps (Adjustable by regression) or -23.8 ppm

Standard	Peak Int. kCPS	Bkgd. Int. kCPS	Net Int. kCPS	Chem. Conc. mass %	XRF Conc. mass %	Abs. Dev. mass %	Rel. Dev. % rel.
LOE22-01	31.369	0.436	30.933	0.300	0.302	0.002	0.5
LOE22-02	27.036	0.447	26.589	0.250	0.251	0.001	0.3
LOE22-03	52.462	0.468	51.993	0.500	0.493	-0.008	-1.5
LOE22-04	37.167	0.468	36.700	0.350	0.350	0.000	-0.1
LOE22-05	12.092	0.445	11.646	0.110	0.110	0.000	0.0
LOE22-06	20.667	0.435	20.232	0.200	0.198	-0.002	-1.1
LOE22-07	0.482	0.418	0.064	0.000	-0.002	-0.002	
LOE22-08	16.121	0.428	15.693	0.150	0.151	0.001	0.7
LOE22-09	25.507	0.446	25.062	0.250	0.249	-0.001	-0.3
LOE22-10	11.241	0.434	10.807	0.110	0.112	0.002	2.1
LOE22-11	26.619	0.433	26.186	0.260	0.268	0.008	3.0
LOE22-12	20.426	0.429	19.997	0.200	0.199	-0.001	-0.7
LOE22-13	0.514	0.447	0.067	0.000	-0.002	-0.002	
LOE22-14	7.216	0.422	6.794	0.070	0.070	0.000	-0.4
LOE22-15	6.074	0.461	5.613	0.050	0.049	-0.002	-3.0
LOE22-16	40.714	0.457	40.257	0.400	0.399	-0.001	-0.2
LOE22-17	18.730	0.432	18.298	0.180	0.182	0.002	1.1
LOE22-18	44.823	0.477	44.346	0.400	0.403	0.003	0.7
LOE22-20	6.242	0.469	5.772	0.050	0.050	0.000	-0.5
LOE22-21	22.579	0.457	22.123	0.200	0.202	0.002	1.0
LOE22-22	0.511	0.463	0.049	0.000	-0.002	-0.002	

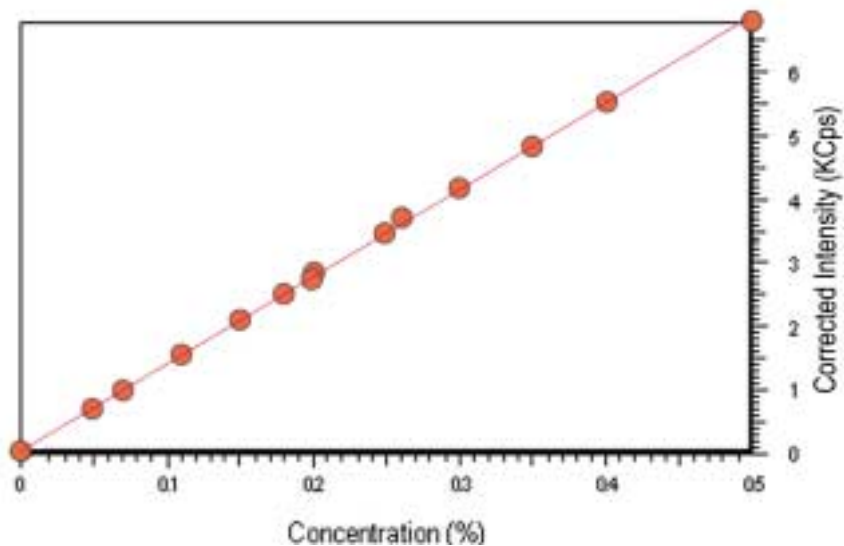


Figure 6 - Calibration data for Copper in unused lubricating oils and additives using the Bruker AXS S4 EXPLORER.

Abridged calibration data for line Cu KA1

21 standards from 0.000 to 0.050 %

Standard Deviation: 0.0005 % (5 ppm)

Intensity model: Net Intensity

Absorption correction: Fixed alphas (theoretical values for average standard)

Slope: 0.09955 %/KCps / Sensitivity: 10.04 KCps/% (Adjustable by regression)

Intensity offset: 0.02072 KCps (Adjustable by regression) or -20.6 ppm

Standard	Peak Int. kCPS	Bkgd. Int. kCPS	Net Int. kCPS	Chem. Conc. mass %	XRF Conc. mass %	Abs. Dev. mass %	Rel. Dev. % rel.
LOE22-01	6.326	0.158	6.167	0.030	0.029	-0.001	-4.2
LOE22-02	0.566	0.153	0.413	0.000	0.000	0.000	
LOE22-03	7.374	0.176	7.198	0.035	0.034	-0.001	-1.6
LOE22-04	0.585	0.169	0.416	0.000	0.000	0.000	
LOE22-05	3.827	0.179	3.648	0.015	0.015	0.000	-1.7
LOE22-06	0.578	0.157	0.421	0.000	0.000	0.000	
LOE22-07	6.359	0.168	6.191	0.025	0.026	0.001	2.7
LOE22-08	0.581	0.164	0.418	0.000	0.000	0.000	
LOE22-09	2.582	0.156	2.426	0.010	0.010	0.000	1.8
LOE22-10	9.942	0.190	9.752	0.040	0.040	0.000	0.4
LOE22-11	0.584	0.165	0.419	0.000	0.000	0.000	
LOE22-12	1.587	0.168	1.418	0.005	0.005	0.000	0.0
LOE22-13	1.801	0.182	1.620	0.005	0.005	0.000	-5.6
LOE22-14	4.684	0.169	4.516	0.020	0.021	0.001	6.2
LOE22-15	0.619	0.178	0.441	0.000	0.000	0.000	
LOE22-16	0.760	0.158	0.602	0.001	0.001	0.000	
LOE22-17	4.769	0.174	4.595	0.020	0.021	0.001	3.7
LOE22-18	0.844	0.172	0.672	0.001	0.001	0.000	
LOE22-20	12.529	0.193	12.336	0.050	0.050	0.000	-0.3
LOE22-21	5.089	0.176	4.914	0.020	0.020	0.000	0.2
LOE22-22	0.614	0.183	0.431	0.000	0.000	0.000	

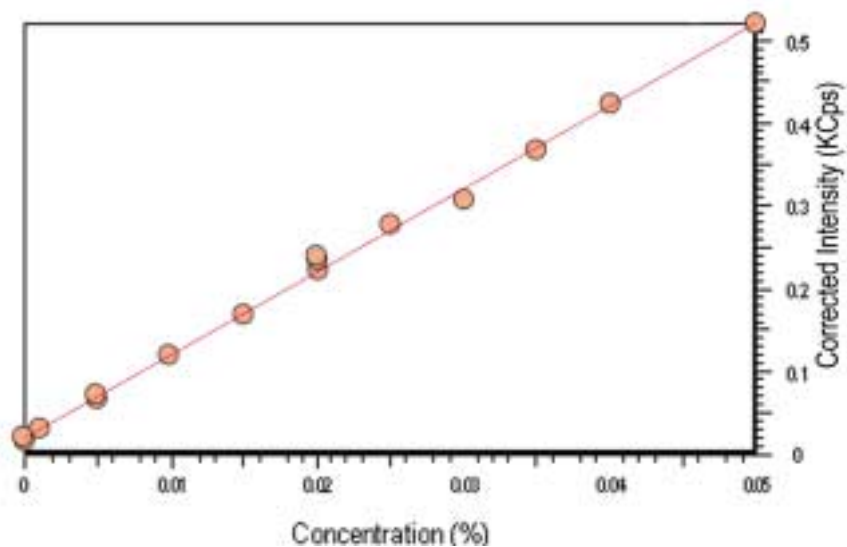


Figure 7 - Calibration data for Zinc in unused lubricating oils and additives using the S4 EXPLORER.

Abridged calibration data for line Zn KA1

21 standards from 0.000 to 0.154 %

Standard Deviation: 0.0015 % (15 ppm)

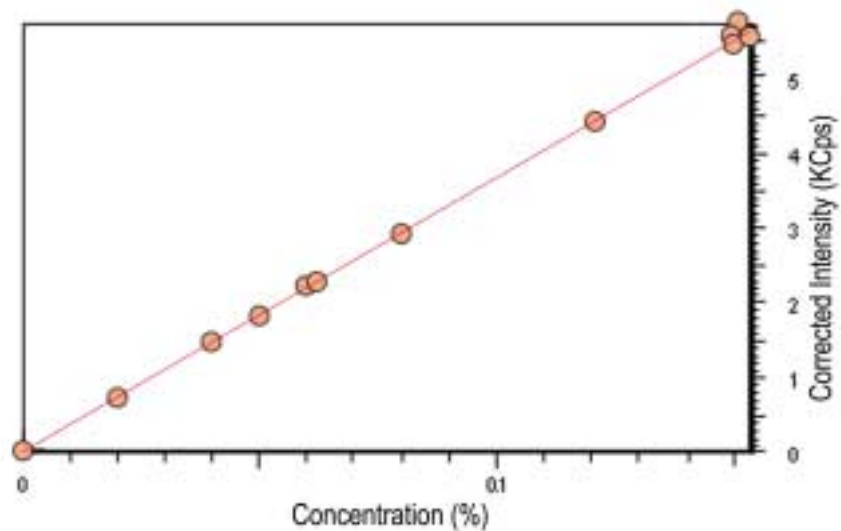
Intensity model: Net Intensity

Absorption correction: Fixed alphas (theoretical values for average standard)

Slope: 0.02722 %/KCps / Sensitivity: 36.73 KCps/% (Adjustable by regression)

Intensity offset: 0.0169 KCps (Adjustable by regression) or -4.6 ppm

Standard	Peak Int. kCPS	Bkgd. Int. kCPS	Net Int. kCPS	Chem. Conc. mass %	XRF Conc. mass %	Abs. Dev. mass %	Rel. Dev. % rel.
LOE22-01	68.800	4.230	64.570	0.062	0.062	0.000	-0.3
LOE22-02	165.610	4.696	160.910	0.150	0.149	-0.001	-0.9
LOE22-03	25.020	3.993	21.030	0.020	0.020	0.000	0.4
LOE22-04	4.880	4.078	0.800	0.000	0.000	0.000	
LOE22-05	60.720	4.514	56.210	0.050	0.049	-0.001	-1.2
LOE22-06	162.330	4.554	157.780	0.154	0.150	-0.004	-2.4
LOE22-07	28.640	4.551	24.090	0.020	0.020	0.000	1.2
LOE22-08	49.010	4.396	44.610	0.040	0.040	0.000	0.3
LOE22-09	85.910	4.243	81.670	0.080	0.079	-0.001	-1.0
LOE22-10	157.830	4.388	153.440	0.151	0.156	0.005	3.2
LOE22-11	4.710	3.989	0.720	0.000	0.000	0.000	
LOE22-12	87.400	4.274	83.120	0.080	0.080	-0.001	-0.7
LOE22-13	30.470	4.826	25.640	0.020	0.020	0.000	0.5
LOE22-14	155.880	4.407	151.470	0.150	0.152	0.002	1.1
LOE22-15	5.590	4.778	0.810	0.000	0.000	0.000	
LOE22-16	24.540	3.992	20.550	0.020	0.020	0.000	0.2
LOE22-17	67.600	4.263	63.340	0.060	0.060	0.000	0.3
LOE22-18	5.010	4.264	0.750	0.000	0.000	0.000	
LOE22-20	152.570	5.261	147.310	0.121	0.120	-0.001	-0.8
LOE22-21	62.560	4.629	57.930	0.050	0.050	0.000	-0.5
LOE22-22	5.820	5.004	0.820	0.000	0.000	0.000	



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