APPLICATION NOTE

Analysis of lubricant additive elements under ambient air using EDXRF

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Background

High quality lubricants are essential to reduce wear and heat between constantly moving and contacting surfaces within precision-engineered equipment. Formulated far beyond simple petroleum base oils through a complex variety of specialty organometallic additives, today's lubricants dramatically improve equipment performance and lifespan by also reducing oxidation, preventing rust, and sealing moving parts against contaminants such as dust, dirt and water.

Controlling the quality and blending operations of high-performance lubricants requires fast, accurate and repeatable measurement of additive metallic and other elemental constituents from parts-per-million to percentage levels. High-end energy dispersive X-ray Fluorescence (EDXRF) analysis is an established, cost effective and easy-to-run technique for lubricant quality control applications, delivering simultaneous analysis of multiple elements ranging from low to high concentrations and requiring virtually no sample preparation. This study focuses on analyzing common lubricant additive components phosphorous (P), calcium (Ca), zinc (Zn) and barium (Ba) in an air atmosphere. In particular, we report about the attainable detection limits.

Instrument

The ARL QUANT'X EDXRF spectrometer used for this application is equipped with a 50 kV, 50 W silver target X-ray tube and a silicon drift detector (SDD) of the latest generation. The ARL QUANT'X employs primary filtered radiation to excite the sample. A set of nine filters specifically designed to optimize the peak-to-background for elements from F to Am ensures that the ARL QUANT'X is easily adaptable per application or element range.

Sample preparation

The lubricant is measured as such by transferring 3 grams of product into a sample cup of 32 mm outer diameter, sealed with a 4 micron polypropylene film.

Excitation conditions

Table 1 shows the excitation condition used to perform the analysis. Four different filters have been used to generate the most optimal condition for each element. A live time of 100s is used for every condition.

Figure 1 shows a typical spectrum obtained using condition Mid Zc of a lubricant sample containing the elements of interest (P, Ca, Zn and Ba) at 90ppm. Condition Mid Zc is optimized to excite zinc.

Calibration

Linear calibration curves relating net intensities to concentrations are set up using standards prepared using a Conostan AM 900ppm standard, diluted using 75 cSt blank oil (also from Conostan). Three concentration levels; 23 ppm, 45 ppm, 90 ppm and a blank were prepared to set up the curves and to determine the detection limit. Figures 2a and 2b show the calibration curves obtained for phosphorous (P) and zinc (Zn). Root mean square errors (RMSE) of 1.2 ppm (P) and 0.27 ppm (Zn) are obtained. Table 2 also shows the RMSE values obtained for the other elements of interest.

Validation and repeatability

Five additional XRF cups were filled with 3 grams of the 23 ppm standard and measured to obtain a repeatability value at this concentraton (23 ppm). Results are shown in Table 3. Besides phosphorous (P) for which a concentration of 23 ppm is close to the limit of determination, the relative error is well below 5%.

Limit of detection

To determine the limit of detection (LoD), 10 XRF cups were filed with 3 grams of the blank oil. The LoD is calculated to be three times the standard deviation as derived for each element. Table 2 shows the results.

Conclusion

The unique capabilities of the ARL QUANT'X EDXRF spectrometer provide fast, accurate and repeatable control of finished lubricant product quality. Particularly valuable and convenient is the instrument's ability to measure lubricant samples under ambient air offering savings on costly helium gas consumption.

Table 1: Excitation condition used for additive elements in lubricants

Condition	Voltage (kV)	Current (mA)	Atmosphere	Live Time (s)	Analytes
Low Za ii	10	Auto	Air	100	P
Low Zb	10	Auto	Air	100	Ca
Mid Za	18	Auto	Air	100	Ba
Mid Zc	30	Auto	Air	100	Zn

Table 2: Concentration range, RMSE and LoD values for additive elements in lubricants

	P	Ca	Zn	Ba
Line	Kα	Kα	Kα	Lα
Concentration range [ppm]	0 - 90	0 - 90	0 - 90	0 - 90
RMSE [ppm]	1.2	0.14	0.27	1.3
LoD, 100s live time [ppm]	11	0.9	0.2	3

Figure 1: Typical spectrum for Zn at 90 ppm in lubricant oil using condition Mid Zc in an air atmosphere

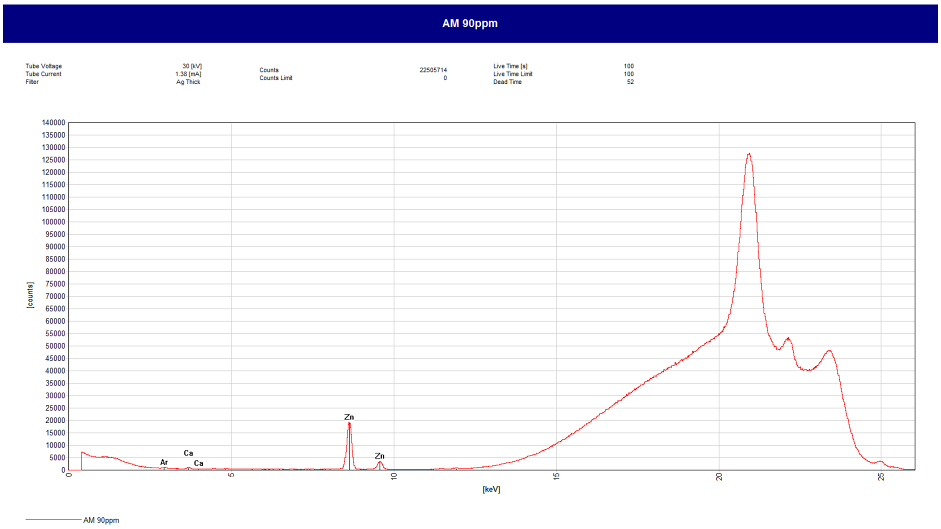


Table 3: Repeatability values for additive elements in lubricants

	P ppm	Ca ppm	Zn ppm	Ba ppm
AM 23 ppm R 1	17.0	24.0	22.5	26.1
AM 23 ppm R 2	20.0	24.0	22.9	26.3
AM 23 ppm R 3	17.5	24.0	22.9	27.5
AM 23 ppm R 4	18.7	23.5	22.8	25.2
AM 23 ppm R 5	17.2	23.4	22.6	25.1
Average	18.1	23.8	22.7	26.0
Std. Dev.	1.2	0.3	0.2	1.0
Rel. Error (%)	6.9	1.3	0.8	3.7

Figure 2a : Calculated versus given concentrations in the case of phosphorous (P)

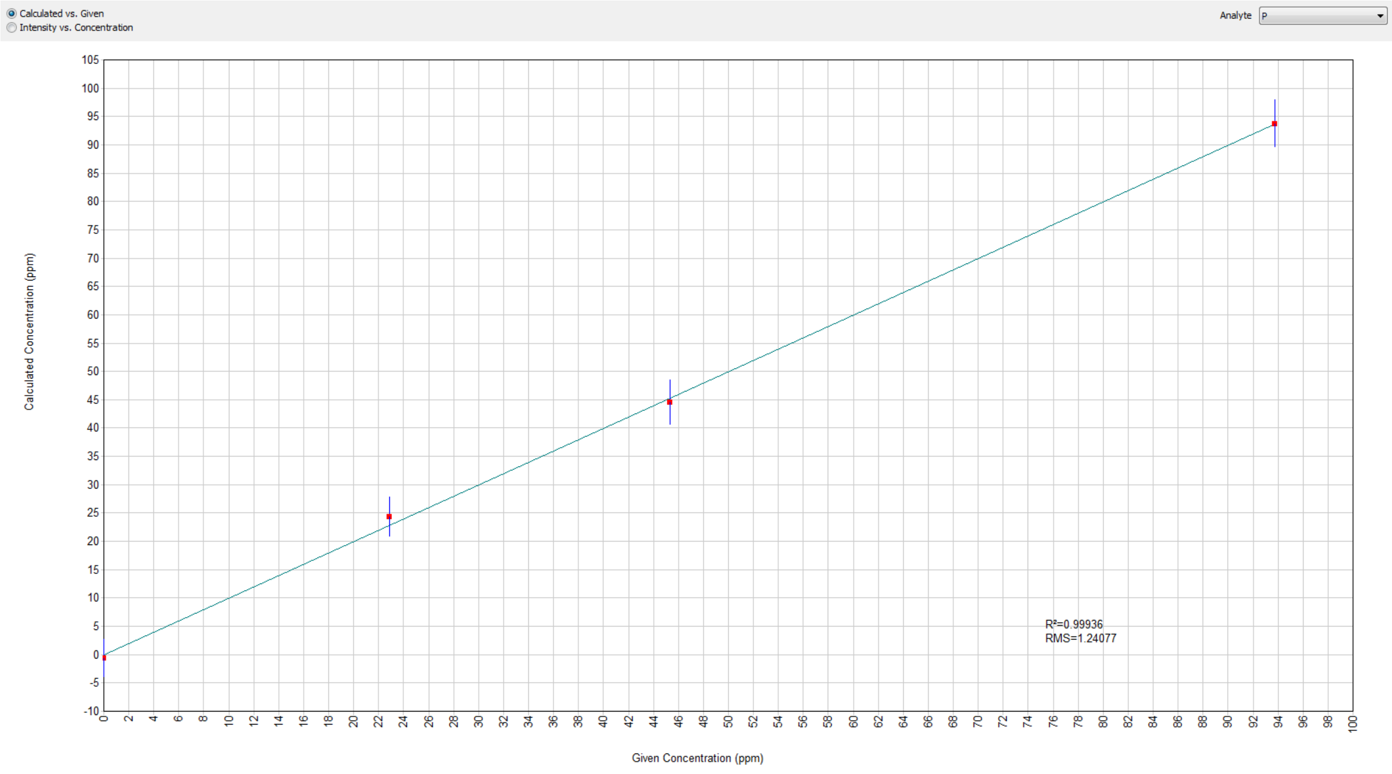
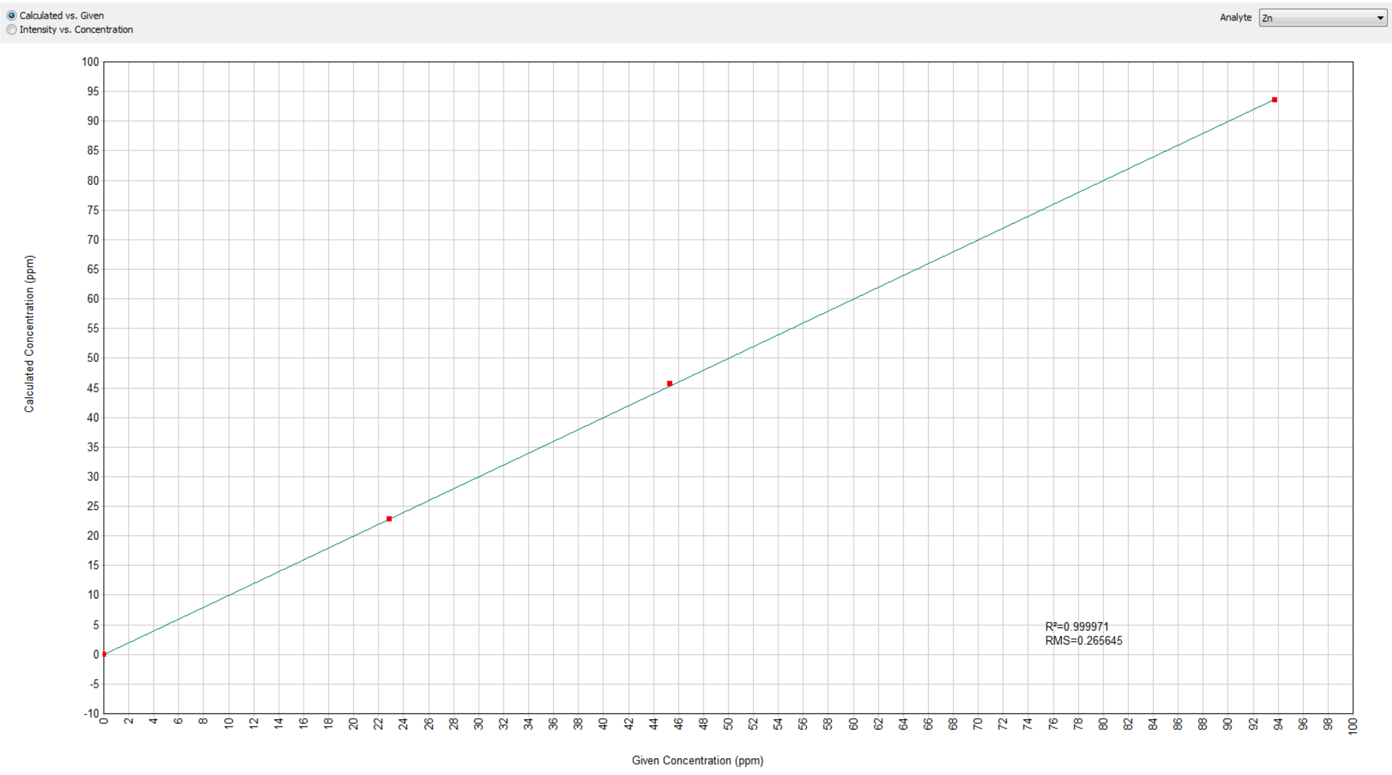


Figure 2b : Calculated versus given concentrations in the case of zinc (Zn)



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