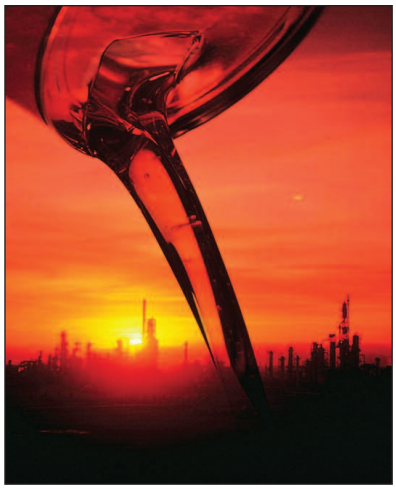
Application Note: 41908

Analysis of lubricant additive elements under ambient air using EDXRF

ARL QUANT'X Energy Dispersive X-Ray Fluorescence Spectrometer

Key Words

- ARL QUANT'X
- Blending control
- Lubricants
- Si(Li) Detector
- EDXRF



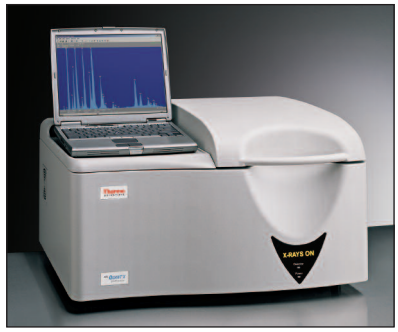
High quality lubricants are essential to reducing wear and heat between constantly moving and contacting surfaces within precision-engineered equipment. Formulated far beyond simple petroleum base oils through a complex variety of specialty organometallic additives, today's lubricants dramatically improve 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 concentration ranges and requiring virtually no sample preparation. This study focuses on analyzing common lubricant additive components phosphorous (P), calcium (Ca) and zinc (Zn).

Sample preparation and ambient air analysis

For this typical lubricant blending control application, six finished lubricant products were analyzed by EDXRF without any sample preparation. Liquid samples were poured into standard 32 mm plastic Chemplex cups to approximately 10 mm depth and sealed with 4 µm polypropylene support film (Prolene®). Whereas liquid samples in X-ray and other elemental analysis techniques (ICP, AA) are typically analyzed under a consumable inert gas atmosphere such as helium gas, analyses for this study were conducted under ambient air to provide a significant consumable gas lifetime cost savings.

Instrumentation



A Thermo Scientific ARL QUANT'X EDXRF spectrometer was configured with a 50 kV, 50 W Rhodium target X-ray tube and specialty Silicon Lithium (Si(Li)) electrically-cooled detector, providing a large active area for capturing low fluorescent yields, unsurpassed signal-to-noise with low background characteristics, and high X-ray capture and conversion across all elements.

The ARL QUANT'X employs primary filtered radiation to excite a sample and cause its constituent elements to fluoresce. With a set of eight filters specifically designed to optimize the peak-to-background for elements from Na to U, the ARL QUANT'X is a versatile research-grade instrument that can be easily adapted per application or element range. This study employed a custom 3-condition method for focus on three lubricant additive elements: phosphorous (P), calcium (Ca) and zinc (Zn) (Table 1).

Analyte	Filter	Voltage	Atmosphere	Live Time
P	None	5 kV	Air	30 sec.
Ca	Cellulose	10 kV	Air	15 sec.
Zn	Pd medium	20 kV	Air	15 sec.

Table 1. Filtered X-ray radiation excitation conditions.

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Calibration

In-house standards from a major lubricant manufacturer were used for instrument calibration, initially performed with relatively short 3-minute total measurement time per sample, i.e., one minute per element. To improve phosphorous results, a follow-up calibration was performed with P measurement extended to 5 minutes with Ca and Zn remaining 1 minute each, for a total analysis time of 7 minutes.

Table 2 shows calibration results in ppm with six standards analyzed as unknowns against the calibration with 3-minute and 7-minute total scanning times under air:

	Phosphorous					Calcium		
Standard	P given	1 min. result	% dev.	5 min. result	% dev.	Ca given	1 min. result	% dev.
1	710	756	+6.5 %	708	-0.3 %	2,150	2,162	+0.6 %
2	740	794	+7.3 %	796	+7.6 %	2,250	2,319	+3.1 %
3	770	707	-8.2 %	773	+0.4 %	2,340	2,267	-3.1 %
4	800	784	-2.0 %	802	+0.3 %	2,440	2,401	-1.6 %
5	840	844	+0.5 %	838	-0.2 %	2,530	2,530	0.0 %
6	870	854	-1.8 %	869	-0.1 %	2,630	2,658	+1.1 %

Table 2. Calibration results for P and Ca under air (in ppm)

Analytical precision

To confirm short-term analytical repeatability, ten replicate measurements were conducted on selected lubricant samples with two different analysis times (Table 3). Samples 1 and 5 were each analyzed for 2 total minutes per replicate, while Sample 4 employed 6 minutes per replicate for additional data capture on phosphorous.

	Sample 1			Sample 4			Sample 5		
Time (s)	p 60	Ca 30	Zn 30	P 300	Ca 30	Zn 30	P 60	Ca 30	Zn 30
Given	710	2150	n/a	800	2440	n/a	840	2530	n/a
Average	**716**	**2138**	**6000**	**808**	**2404**	**652**	**827**	**2525**	**694**
1-Sigma	36	15	5	12	16	6	52	11	6
% RSD	5.0	0.7	0.8	1.5	0.7	0.9	6.2	0.4	0.9
Replicates 1	696	2170	600	790	2392	654	822	2532	686
2	747	2137	605	790	2403	655	884	2531	692
3	722	2127	608	799	2393	658	814	2516	701
4	757	2141	593	814	2413	651	856	2523	687
5	732	2135	596	819	2406	644	820	2519	691
6	659	2112	605	819	2437	652	797	2506	697
7	750	2142	597	807	2402	651	909	2542	686
8	658	2144	601	803	2417	640	727	2538	697
9	730	2126	594	824	2379	657	788	2519	698
10	711	2145	603	810	2396	652	849	2525	703

Table 3. Analytical precision at various measuring times.

Conclusion

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

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