EDXRF APPLICATION NOTE
ANALYSIS OF LUBE OILS
EMPIRICAL METHOD
#1003

SCOPE

This Application Note shows performance for the elemental analysis of P, S, Ca, Zn, Mg, Ba, Cu and Cl in a typical lubricating oil formulation using the empirical method. Calibration summary and typical detection limits are presented, and instrument repeatability is demonstrated.

BACKGROUND

Lubricating oils are used in on-road and off-road engines, as well as in the lubrication of mechanical machinery. The lube oils are formulated specifically for each type of use. Various additives are formulated in base lube oil to enhance lube oil performance and create the optimum lubricity properties desired for each situation.

Proper and safe operation of engines and machinery depends to a large degree on the quality and formulation of the lube oil. Therefore, quality control and quality assurance during the lube oil manufacturing process is essential. A fast, simple method of analyzing lube oils is important throughout the QC/QA process. The analytical technique must be simple enough for use by non-technical operators, yet powerful enough for expert use in the research & development of new lube oil formulations.

INSTRUMENTATION

Model:	Rigaku NEX CG
X-ray tube:	50 W Pd-anode
Detector:	SDD
Sample Type:	Liquid Lube Oil
Film:	Prolene
Analysis Time:	400 sec
Environment:	Helium Purge
Standard:	15-position Sample Tray (32mm)

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SAMPLE PREPARATION

Ensure each sample is homogeneous and stable. Simply fill an XRF sample cup with 5g of sample. Prolene (4um polypropylene) film was used to ensure optimal X-ray transmission.

CALIBRATION

Empirical calibrations were built using a suite of 23 certified calibration standards. The suite of calibration standards must be representative of the lube oil formulation to be analyzed. Use of empirical calibration ensures the particular lube oil formulation is exactly characterized and modeled, which yields optimum accuracy. Elements in the lube oil should vary evenly over each concentration range of interest, and the elements in the oil should vary independently of each other. Alpha corrections are then employed to automatically compensate for variations in X-ray absorption and enhancement effects within the sample due to the independent variations in element concentration. A summary of the empirical calibrations is shown here.

Element	Concentration Range	RMS Deviation	R^2 Confidence
P	0.020 – 0.150 %	0.003	0.9990
S	0.200 – 0.750 %	0.006	0.9998
Ca	0.050 – 0.500 %	0.004	0.9997
Zn	0.020 – 0.150 %	<0.001	0.9999
Mg	0.005 – 0.200 %	0.003	0.9987
Ba	0.010 – 0.200 %	0.001	0.9999
Cu	0.001 – 0.050 %	<0.001	0.9998
Cl	0.005 – 0.150 %	0.002	0.9995

DETECTION LIMITS

The empirical method was used to determine estimated detection limits. In the empirical method, ten repeat analyses of a blank lube oil (or mineral oil) sample are taken with the sample in static position and the standard deviation is determined. The Lower Limit of Detection (LLD) is then defined as three times the standard deviation. The following typical LLDs are reported here for the lube oil formulation shown above using a Count Time of 100 sec.

Element	LLD
P	< 3 ppm
S	< 3 ppm
Ca	3 ppm
Zn	< 3 ppm
Mg	45 ppm
Ba	3 ppm
Cu	<3 ppm
Cl	<3 ppm

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REPEATABILITY

Two representative samples from the calibration suite were chosen to demonstrate typical instrument repeatability (precision). Ten repeat analyses of the sample were performed with the sample in static position using a count time of 100 sec per analysis condition.

Sample: ASI 14 Units: %				
Element	**Standard Value**	**Average Value**	**Std Dev**	**% Relative**
P	0.140	0.139	0.001	0.7
S	0.650	0.659	0.004	0.6
Ca	0.070	0.069	<0.001	<1.4
Zn	0.150	0.149	<0.001	<0.7
Mg	0.080	0.084	0.009	11.3
Ba	0.080	0.080	<0.001	<1.3
Cu	0.020	0.020	<0.001	<5.0
Cl	0.150	0.147	0.002	1.3

Sample: ASI 21 Units: %				
Element	**Standard Value**	**Average Value**	**Std Dev**	**% Relative**
P	0.050	0.050	<0.001	<2.0
S	0.275	0.280	0.001	0.1
Ca	0.200	0.199	0.001	0.5
Zn	0.050	0.050	<0.001	2.0
Mg	0.080	0.077	0.007	8.8
Ba	0.100	0.096	<0.001	<1.0
Cu	0.021	0.020	<0.001	<4.8
Cl	0.050	0.051	<0.001	<2.0

CONCLUSION

The Rigaku NEX CG combines indirect excitation with secondary targets, polarization targets and a high performance SDD detector to yield the optimum performance for elemental analysis of lube oils. The results shown here indicate the NEX CG is an excellent tool for process and quality control in the manufacturing of lube oil formulations and blends.

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