Rigaku

Application Note XRF 5039

Lubricating Oil Analysis by Benchtop WDXRF According to ASTM D6443-04

Application

lubricating oil

Instrument

Benchtop wavelength dispersive X-ray fluorescence spectrometer
Supermini200

Keywords

lubricating oil
lube oil
lubricant
lubricant additives
oil
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benchtop

Introduction

Lubricating oils are given specific functional properties by mixing additives with base oil. In order to assure consistent and desirable performance, it is very important to control the concentrations of the additives during the lubricant manufacturing process.

X-ray fluorescence (XRF) spectrometry has become increasingly popular for quantitative elemental analysis of base oils as well as additives and lubricant products thanks to its high precision and simple sample preparation. With liquids, sample preparation for XRF typically means pouring the sample into a plastic cup equipped with a transparent film. Unlike traditional techniques, such as Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES), XRF does not require chemical decomposition, digestion or serial dilution. ASTM D6443-04 specifies the use of the wavelength-dispersive (WD) XRF technique, because it offers sufficiently high precision, resolution and light-element sensitivity to meet the industry's needs.

Traditionally, WDXRF spectrometers have been large, floor-standing models with substantial installation requirements and high cost of component replacement. In its search for greater cost-efficiency, the lubricant industry is turning to tools that not only do the job, but are also easier and less expensive to acquire, install and maintain.

This application note demonstrates the capability of a low-cost, compact benchtop WDXRF spectrometer for quantitative elemental analysis of Ca, Cl, Cu, Mg, P, S and Zn in base oils, lubricating oils and additives.

Instrument

The Supermini200 is a benchtop sequential WDXRF spectrometer designed specifically to deliver excellent performance while eliminating typical installation requirements, such as cooling water, special power supply, large floor space, etc. Featuring a unique air-cooled 200W X-ray tube, two detectors, programmable environment of vacuum or helium, and three analyzing crystals, the Supermini200 can analyze all relevant elements in just a few minutes with full spectral separation of all peaks and excellent sensitivity for light elements such as Mg, P and Cl.

The Windows-based software is shared with Rigaku's popular Primus family of higher-power WDXRF systems, which means that it has the same advanced algorithms, multiple language support and an intuitive interface that have made Rigaku the world's leader in X-ray instrumentation and industrial applications.

Standards and sample preparation

Organometallic reference standard samples for lubricating oil provided by AccuStandard®, Inc. were used for calibration.

Six grams of each sample was poured into a standard liquid cell (Chemplex® 1540) equipped with 4.0 µm Prolene® (Chemplex® 416). The cups are disposable and inexpensive.

Measurement conditions

All elements were measured in a helium atmosphere, using standard crystals, with the X-ray tube operating at 50 kV and 4.0 mA. Peak and background intensities were counted for each element line, and the total counting time was less than nine minutes.

Calibration

In accordance with ASTM D6443-04, empirical matrix corrections were applied for all analytes, except Mg. The calibration results are listed in Table 1, with the corresponding calibration curves shown in Figure 1.

Table 1 Calibration results for all elements

Element	Calibration Range (mass%)	Accuracy (mass%)	LLD (ppm)
Ca	0 – 0.50	0.0021	1.9
Cl	0 – 0.15	0.0005	0.8
Cu	0 – 0.05	0.0006	1.1
Mg	0 – 0.20	0.0044	20
P	0 – 0.15	0.0004	1.0
S	0 – 0.75	0.0032	0.9
Zn	0 – 0.15	0.0020	1.0

The accuracy of calibration was calculated by the following formula,

$$\text{Accuracy} = \sqrt{\frac{\sum_i \left(C_i - \hat{C}_i\right)^2}{n-2}}$$

C_i : calculated value of standard sample
$\hat{C}_i$: reference value of standard sample
n : number of standard samples.

The lower limit of detection (LLD) was calculated as

$$LLD = 3 \cdot {}^{1}\!/_{m} \cdot \sigma_B = {}^{3}\!/_{m} \cdot \sqrt{\frac{I_B}{1000 \times t}}$$

m : sensitivity of calibration (kcps/ppm)
σ_B : standard deviation of blank intensity (kcps)
I_B : blank intensity (kcps)
t : counting time (s).

Analysis results

In order to assess the repeatability of the method, two aliquots of a representative sample were prepared and quantified with the calibration; this process was repeated twenty times.
The test data were compiled in Table 2, which shows the average and the difference of the results for each two-aliquot measurement. ASTM D6443-04 specifies that “the difference between successive test results obtained by the same operator with the same apparatus under constant operation conditions on identical test material...in the long run” must not exceed the values in Table 3, which shows the formula for the

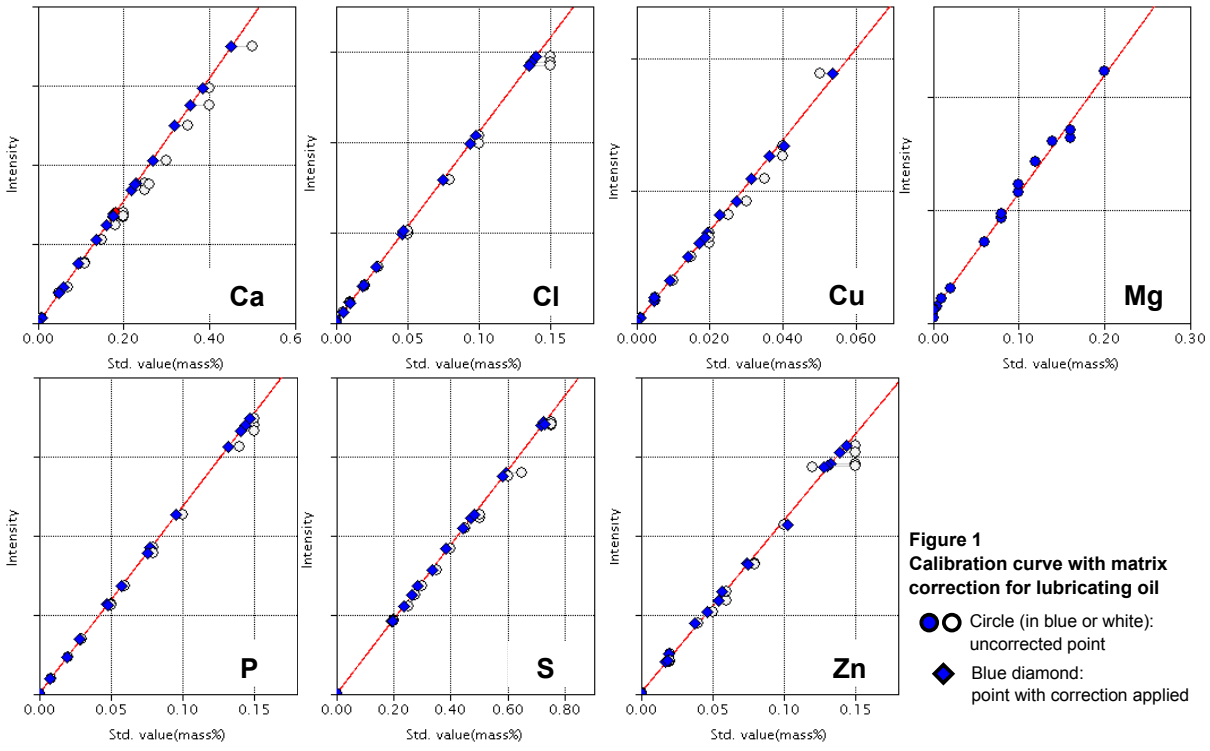

Figure 1
Calibration curve with matrix correction for lubricating oil

Circle (in blue or white): uncorrected point
Blue diamond: point with correction applied

maximum allowed repeatability (***r***) of each analyte. Please note that all units in Table 3 are in terms of mass%, including the standard's concentration X.

The maximum actual difference between successive results in Table 2 is labeled "Max", while "***r***" represents the maximum permissible difference as prescribed by the ASTM method (see Table 3). Since "Max" never exceeds "***r***", the repeatability of the Supermini200 easily satisfies the requirements of ASTM D6443-04.

Table 3 Repeatability as defined in ASTM D6443-04 (unit: mass%)

Element	Concentration range	Repeatability [*r*]
Ca	0.001 – 0.200	$0.006914\ (X+0.0007)^{0.5}$
Cl	0.001 – 0.030	$0.0356\ (X+0.0086)$
Cu	0.001 – 0.030	$0.002267\ (X+0.0013)^{0.4}$
Mg	0.003 – 0.200	$0.01611\ (X+0.0008)^{0.333}$
P	0.001 – 0.200	$0.02114\ X^{0.7}$
S	0.030 – 0.800	$0.02371\ X^{0.9}$
Zn	0.001 – 0.200	$0.01225\ X^{0.7}$

Note) X: concentration in mass%

Table 2 Repeatability test results (unit: mass%)

	Ca		Cl		Cu		Mg	
	Avg.	Diff.	Avg.	Diff.	Avg.	Diff.	Avg.	Diff.
1	0.0102	0.0001	0.0107	0.0000	0.0118	0.0002	0.0332	0.0020
2	0.0102	0.0001	0.0106	0.0002	0.0118	0.0001	0.0324	0.0004
3	0.0102	0.0000	0.0106	0.0001	0.0119	0.0001	0.0326	0.0000
4	0.0103	0.0001	0.0106	0.0000	0.0118	0.0002	0.0340	0.0027
5	0.0103	0.0001	0.0105	0.0002	0.0117	0.0000	0.0351	0.0005
6	0.0102	0.0000	0.0105	0.0002	0.0118	0.0002	0.0332	0.0033
7	0.0103	0.0002	0.0107	0.0001	0.0120	0.0001	0.0337	0.0044
8	0.0104	0.0001	0.0107	0.0000	0.0118	0.0004	0.0340	0.0039
9	0.0103	0.0001	0.0107	0.0000	0.0117	0.0001	0.0342	0.0043
10	0.0102	0.0001	0.0107	0.0001	0.0118	0.0001	0.0338	0.0050
11	0.0103	0.0003	0.0106	0.0001	0.0119	0.0002	0.0331	0.0035
12	0.0105	0.0001	0.0106	0.0001	0.0120	0.0000	0.0353	0.0009
13	0.0104	0.0002	0.0106	0.0001	0.0119	0.0002	0.0341	0.0032
14	0.0102	0.0003	0.0106	0.0001	0.0118	0.0001	0.0338	0.0025
15	0.0102	0.0003	0.0106	0.0001	0.0117	0.0000	0.0342	0.0016
16	0.0103	0.0000	0.0105	0.0000	0.0118	0.0001	0.0338	0.0008
17	0.0104	0.0002	0.0106	0.0001	0.0118	0.0000	0.0340	0.0005
18	0.0104	0.0002	0.0105	0.0003	0.0118	0.0001	0.0333	0.0009
19	0.0102	0.0002	0.0104	0.0001	0.0118	0.0002	0.0338	0.0019
20	0.0100	0.0003	0.0105	0.0001	0.0118	0.0002	0.0339	0.0016
Max		**0.0003**		**0.0003**		**0.0004**		**0.0050**
r		**0.0007**		**0.0007**		**0.0004**		**0.0053**

	P		S		Zn			
	Avg.	Diff.	Avg.	Diff.	Avg.	Diff.		
1	0.0100	0.0001	0.0474	0.0003	0.0113	0.0000		
2	0.0100	0.0001	0.0476	0.0001	0.0114	0.0001		
3	0.0100	0.0001	0.0477	0.0002	0.0115	0.0001		
4	0.0100	0.0000	0.0476	0.0005	0.0114	0.0002		
5	0.0101	0.0001	0.0474	0.0002	0.0113	0.0001		
6	0.0100	0.0003	0.0477	0.0003	0.0114	0.0003		
7	0.0098	0.0000	0.0478	0.0000	0.0115	0.0001		
8	0.0100	0.0003	0.0476	0.0005	0.0114	0.0001		
9	0.0102	0.0002	0.0477	0.0007	0.0113	0.0000		
10	0.0102	0.0003	0.0479	0.0002	0.0113	0.0000		
11	0.0101	0.0001	0.0479	0.0001	0.0114	0.0002		
12	0.0102	0.0001	0.0478	0.0002	0.0115	0.0000		
13	0.0101	0.0002	0.0477	0.0001	0.0115	0.0000		
14	0.0100	0.0000	0.0478	0.0003	0.0115	0.0000		
15	0.0099	0.0002	0.0477	0.0004	0.0116	0.0001		
16	0.0099	0.0002	0.0474	0.0003	0.0115	0.0002		
17	0.0100	0.0001	0.0474	0.0003	0.0114	0.0001		
18	0.0101	0.0003	0.0474	0.0002	0.0114	0.0001		
19	0.0100	0.0004	0.0474	0.0002	0.0114	0.0000		
20	0.0098	0.0000	0.0474	0.0002	0.0114	0.0000		
Max		**0.0004**		**0.0007**		**0.0003**		
r		**0.0008**		**0.0015**		**0.0005**		

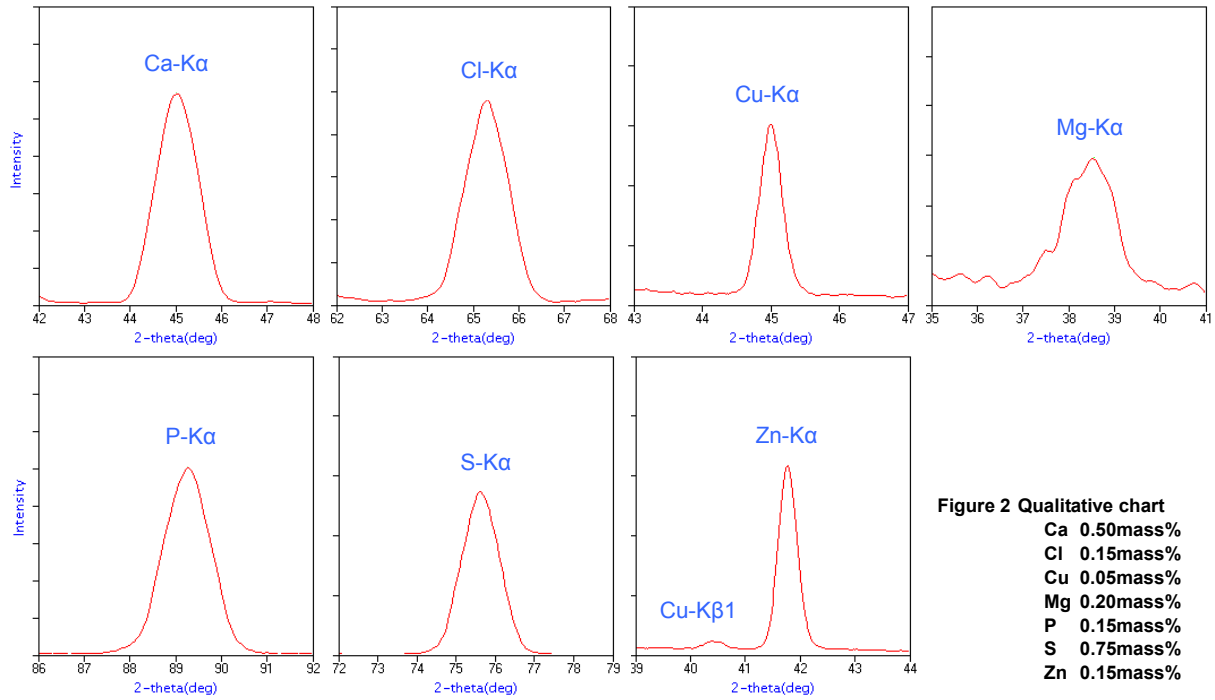

Figure 2 Qualitative chart
Ca 0.50mass%
Cl 0.15mass%
Cu 0.05mass%
Mg 0.20mass%
P 0.15mass%
S 0.75mass%
Zn 0.15mass%

Qualitative scans of each analyte element are shown in Figure 2 and demonstrate the excellent signal-to-noise and spectral resolution of the wavelength-dispersive technology in the Rigaku Supermini200.

Conclusions

This application note demonstrates that lubricating oils and additives can be routinely analyzed with excellent accuracy, sensitivity and repeatability using a benchtop WDXRF spectrometer with minimal site requirements. In particular, the Rigaku Supermini200 sequential WDXRF system meets the specifications of ASTM D6443-04, as well as those of ASTM D4927-05, which applies to higher concentrations of additive elements.

Reference

ASTM D6443-04 (2010) 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)

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