Rigaku

Application Note XRF 5003

Lubricating Oil Analysis by WDXRF According to ASTM D6443-04

Application

lubricating oil

Instrument

Wavelength dispersive X-ray fluorescence spectrometer
ZSX Primus

Keywords

lubricating oil
lube oil
lubricant
additives
oil
petroleum
ASTM

Introduction

Lubricating oil is given functional properties for specific purposes by mixing additives with base oil. Therefore, it is very important to control concentrations of additive elements in production plants of lubricating oil.

X-ray fluorescence (XRF) spectrometry has been used for quantitative analysis of additive elements such as Mg, P and Zn in lubricating oil owing to high precision and simple sample preparation of XRF analysis. In the XRF analysis of lubricating oil, a sample is simply poured into a liquid cell, and any complicated treatment such as chemical decomposition or dilution is not required.

This application note demonstrates quantitative analysis for lubricating oil according to ASTM D6443-04 on Rigaku ZSX Primus, a wavelength-dispersive XRF spectrometer.

Instrument

The ZSX Primus, a tube-below sequential wavelength dispersive X-ray fluorescence (WDXRF) spectrometer, is optimized for routine analyses that today's petroleum laboratories need to perform. The vacuum seal, programmably switchable, between the sample and optical chambers can keep the optical chamber under vacuum with the sample chamber under helium, and, therefore, minimizes helium gas consumption and time of atmosphere change in the sample chamber. The spectrometer is equipped with a 3 kW X-ray tube and the analyzing crystals, covering F to U. If higher sensitivity or precision is required, a 4 kW X-ray tube can be mounted.

The operation software is designed for ease of use in routine analyses. The Flowbar in quantitative analysis guides users in establishing calibration. The Sample ID Table and the Program Operation help operators carry out daily analysis.

Sample and sample preparation

Reference standard samples of lubricating oil provided by Analytical Services, Inc. were used for calibration.

Eight grams of each lubricating oil sample was poured into a liquid cell (Chemplex® 1095) with sample film of 3.6 µm Mylar® (Chemplex® 150).

Measurement and calibration

Measurements were performed on the ZSX Primus with a 3 kW Rh-target X-ray tube for Ca, Cl, Cu, Mg, P, S and Zn. A primary beam filter was inserted between the sample and the X-ray tube. The filter protects the X-ray tube window against damage from sample falling during measurement. In addition, the Al filter reduces the background to improve the ratio of peak intensity to background intensity. Measurement condition is shown in Table 1.

Table 1 Measurement condition

Path atmosphere		Helium/Vacuum					
Analysis area		30 mm in diameter					
Element	**Ca**	**Cl**	**Cu**	**Mg**	**P**	**S**	**Zn**
Line	Kα	Kα	Kα	Kα	Kα	Kα	Kα
kV-mA	40-60	30-80	50-48	30-80	30-80	30-80	50-48
Primary Filter	Be	Be	Al-2	Be	Be	Be	Al-2
Slit	S4	S2	S2	S4	S4	S4	S2
Crystal	LiF	Ge	LiF	RX25	Ge	Ge	LiF
Detector	PC	PC	SC	PC	PC	PC	SC
Time Peak(s)	16	40	10	40	40	10	10
BG(s)	8	20	4x2	10x2	20	4	4x2

Note) LiF: LiF(200), PC: F-PC

The calibration curves were generated with matrix correction applied for all the analytes but Mg, as indicated in ASTM D6443-04. The correction coefficients used were calculated theoretically by the fundamental parameter (FP) method. The calibration results are listed in Table 2 and the calibration curves are shown in Figure 1.

Table 2 Calibration results (unit: mass%)

Element	Calibration range	Accuracy
Ca	0 – 0.50	0.0053
Cl	0 – 0.15	0.0005
Cu	0 – 0.05	0.0003
Mg	0 – 0.20	0.0012
P	0 – 0.15	0.0009
S	0 – 0.75	0.0037
Zn	0 – 0.15	0.0008

The accuracy of calibration is 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.

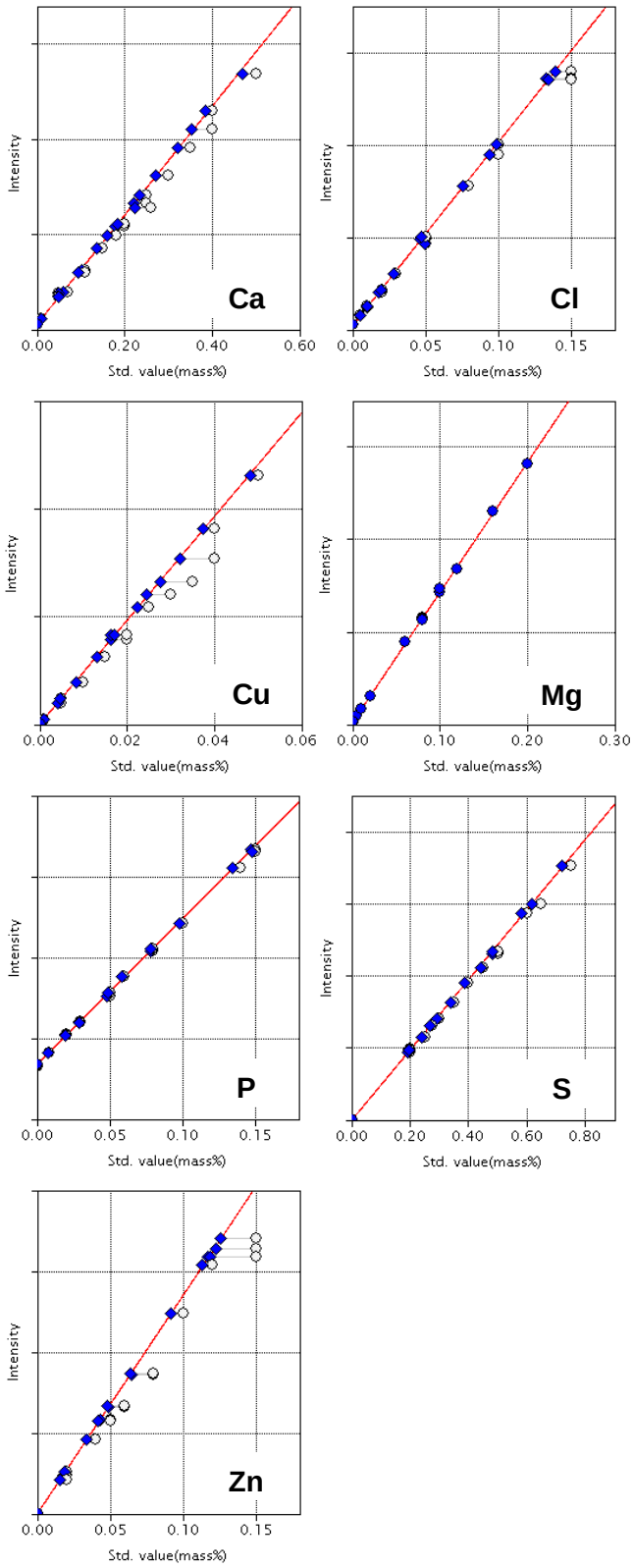

Figure 1 Calibration curve with matrix correction for lubricating oil

Circle (in blue or white): uncorrected point

Blue diamond: point with correction applied

Analysis results

Repeatability tests were carried out for two different samples. For the same sample, two aliquots were prepared and quantified with the calibration (Figure 1); this process was repeated twenty times. The test results are tabulated in Table 3, in which the average and the difference of two aliquots each are shown and "***r***" represents "repeatability" defined in ASTM D6443-04, which states that the difference between successive test results obtained by the same operator with the same apparatus under constant operation conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values in Table 4, which lists the repeatability (***r***) of each analyte, in only one case in twenty.

The test results shown in Table 3, where the difference of two aliquots does not exceed the repeatability (***r***) for each analyte, prove that the performance of the ZSX Primus meets the requirement of ASTM D6443-04.

Table 3 Repeatability test results (unit: mass%)

	Ca		Cl		Cu		Mg	
	Avg.	Diff.	Avg.	Diff.	Avg.	Diff.	Avg.	Diff.
1	0.1889	0.0002	0.0491	0.0001	0.0200	0.0001	0.0730	0.0014
2	0.1891	0.0005	0.0489	0.0002	0.0199	0.0002	0.0738	0.0029
3	0.1894	0.0001	0.0490	0.0003	0.0199	0.0002	0.0742	0.0021
4	0.1892	0.0004	0.0492	0.0001	0.0200	0.0000	0.0736	0.0009
5	0.1891	0.0002	0.0490	0.0004	0.0200	0.0001	0.0736	0.0009
6	0.1891	0.0002	0.0490	0.0003	0.0200	0.0001	0.0740	0.0018
7	0.1891	0.0002	0.0493	0.0004	0.0200	0.0001	0.0733	0.0032
8	0.1892	0.0000	0.0492	0.0006	0.0199	0.0001	0.0728	0.0022
9	0.1892	0.0001	0.0489	0.0001	0.0199	0.0001	0.0735	0.0009
10	0.1891	0.0000	0.0487	0.0002	0.0200	0.0001	0.0732	0.0003
11	0.1890	0.0003	0.0486	0.0000	0.0199	0.0002	0.0729	0.0008
12	0.1888	0.0000	0.0489	0.0006	0.0199	0.0001	0.0734	0.0018
13	0.1890	0.0003	0.0488	0.0008	0.0200	0.0001	0.0738	0.0011
14	0.1893	0.0003	0.0484	0.0000	0.0199	0.0002	0.0729	0.0007
15	0.1893	0.0003	0.0485	0.0002	0.0199	0.0001	0.0720	0.0010
16	0.1890	0.0003	0.0491	0.0010	0.0199	0.0000	0.0727	0.0023
17	0.1889	0.0001	0.0494	0.0005	0.0199	0.0001	0.0725	0.0027
18	0.1890	0.0002	0.0491	0.0001	0.0199	0.0002	0.0725	0.0028
19	0.1890	0.0002	0.0488	0.0004	0.0200	0.0001	0.0718	0.0042
20	0.1891	0.0004	0.0488	0.0003	0.0199	0.0000	0.0713	0.0031
Max		**0.0005**		**0.0010**		**0.0002**		**0.0042**
r		**0.0030**		**0.0020**		**0.0005**		**0.0068**

	P		S		Zn			
	Avg.	Diff.	Avg.	Avg.	Diff.	Avg.		
1	0.0502	0.0004	0.2793	0.0001	0.0489	0.0002		
2	0.0499	0.0003	0.2790	0.0007	0.0489	0.0002		
3	0.0497	0.0001	0.2788	0.0004	0.0489	0.0001		
4	0.0501	0.0010	0.2784	0.0012	0.0489	0.0000		
5	0.0503	0.0006	0.2781	0.0006	0.0488	0.0002		
6	0.0501	0.0001	0.2785	0.0001	0.0489	0.0003		
7	0.0500	0.0003	0.2784	0.0002	0.0489	0.0002		
8	0.0499	0.0002	0.2776	0.0014	0.0489	0.0001		
9	0.0499	0.0002	0.2770	0.0002	0.0489	0.0001		
10	0.0499	0.0002	0.2773	0.0003	0.0489	0.0002		
11	0.0498	0.0004	0.2774	0.0000	0.0490	0.0001		
12	0.0498	0.0004	0.2782	0.0015	0.0489	0.0001		
13	0.0500	0.0001	0.2783	0.0012	0.0488	0.0000		
14	0.0499	0.0001	0.2780	0.0006	0.0488	0.0000		
15	0.0499	0.0001	0.2778	0.0011	0.0489	0.0001		
16	0.0500	0.0001	0.2776	0.0008	0.0489	0.0001		
17	0.0499	0.0002	0.2781	0.0002	0.0488	0.0000		
18	0.0498	0.0000	0.2793	0.0021	0.0489	0.0002		
19	0.0498	0.0000	0.2784	0.0039	0.0489	0.0002		
20	0.0497	0.0002	0.2773	0.0017	0.0489	0.0001		
Max		**0.0010**		**0.0039**		**0.0003**		
r		**0.0026**		**0.0075**		**0.0015**		

Table 3 Repeatability test results (continued) (unit: mass%)

	Ca		P		S		Zn	
	Avg.	Avg.	Diff.	Avg.	Avg.	Diff.	Avg.	Diff.
1	0.0576	0.0000	0.0813	0.0008	0.2999	0.0016	0.1233	0.0005
2	0.0575	0.0002	0.0810	0.0001	0.2996	0.0009	0.1234	0.0003
3	0.0575	0.0001	0.0809	0.0003	0.2997	0.0007	0.1231	0.0002
4	0.0575	0.0000	0.0807	0.0000	0.2994	0.0001	0.1229	0.0002
5	0.0575	0.0001	0.0809	0.0003	0.2993	0.0002	0.1231	0.0006
6	0.0576	0.0003	0.0814	0.0007	0.3004	0.0023	0.1233	0.0002
7	0.0576	0.0002	0.0816	0.0003	0.3008	0.0015	0.1230	0.0005
8	0.0576	0.0001	0.0815	0.0001	0.3001	0.0002	0.1229	0.0004
9	0.0577	0.0001	0.0812	0.0007	0.3000	0.0004	0.1233	0.0004
10	0.0581	0.0008	0.0808	0.0000	0.2990	0.0016	0.1234	0.0002
11	0.0579	0.0012	0.0808	0.0000	0.2988	0.0012	0.1229	0.0009
12	0.0573	0.0001	0.0808	0.0000	0.2995	0.0002	0.1227	0.0006
13	0.0574	0.0003	0.0807	0.0003	0.2996	0.0000	0.1231	0.0001
14	0.0575	0.0001	0.0806	0.0001	0.2991	0.0011	0.1230	0.0002
15	0.0577	0.0005	0.0807	0.0002	0.2997	0.0023	0.1231	0.0003
16	0.0576	0.0007	0.0808	0.0000	0.3003	0.0011	0.1231	0.0002
17	0.0573	0.0002	0.0809	0.0001	0.2998	0.0001	0.1232	0.0003
18	0.0575	0.0002	0.0812	0.0006	0.3000	0.0004	0.1233	0.0000
19	0.0576	0.0000	0.0810	0.0010	0.3000	0.0005	0.1232	0.0002
20	0.0576	0.0000	0.0805	0.0000	0.2993	0.0008	0.1232	0.0002
Max		**0.0012**		**0.0010**		**0.0023**		**0.0009**
r		**0.0017**		**0.0036**		**0.0080**		**0.0028**

Table 4 Repeatability 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%

Conclusions

Lubricating oil can be routinely analyzed with high accuracy and precision on the ZSX Primus with a 3kW X-ray tube. This application note demonstrates that the performance of the ZSX Primus meets the requirement of ASTM D6443-04. In addition, the ZSX Primus also can be applied to the standard method of ASTM D4927-05, which covers higher concentration range of additive elements in lubricating oil.

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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