

Ultra Low P, S, Cl Analysis in Liquids with a Benchtop WDXRF Spectrometer

Application

Petroleum products
Organic Solvents



Instrument

Benchtop wavelength dispersive
X-ray fluorescence spectrometer
Supermini200



Keywords

Petroleum products
Phosphorous
Sulfur
Chlorine
ASTM D2622
ISO20884
JPI-5S-73
benchtop

Introduction

Phosphorous, sulfur and chlorine are commonly analyzed elements in liquids such as petroleum products and organic solvents. For example, phosphorous is added to lubricating oils to prevent wear of gears under high pressure. Sulfur content in automotive fuel oils are regulated by the US environmental protection agency (EPA) and directives such as EURO VI to minimize air pollution due to automotive vehicles. Chlorine, contained for example in crude oil, is an unwanted element known for corroding oil processing installations and liquid transmission pipelines.

To better meet demands of such applications, the benchtop wavelength dispersive X-ray fluorescent (WDXRF) spectrometer Supermini200's analyzing crystal set has been newly reconfigured to optimize performance for trace level analysis of P, S and Cl.

XRF analysis allows rapid and precise elemental characterization of such samples with minimum sample preparation. Laborious sample treatment such as acid digestion or serial dilution are not required. Liquid samples are simply poured into a plastic cup covered with film for measurement and results can be obtained in minutes.

This application note demonstrates Supermini200's performance for low level P, S, Cl in oil samples for both short and long durations.

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 and large floor space.

Equipped with a unique air cooled 200 watt X-ray tube, two detectors and three analyzing crystals, the Supermini200 is capable of measuring elements from oxygen to uranium. Analysis of P, S and Cl is optimized with the analyzing crystal RX9 newly available on the Supermini200. Standardless semi-quantitative analysis is also available allowing quick and simple characterization of non-routine samples.

Software running the Supermini200 "ZSX Guidance" shares the same platform as the high-power WDXRF spectrometer ZSX PrimusIV. This means that the same advanced algorithms, multiple language modes and intuitive user-friendly interface are available on a compact benchtop system.

Calibration and measurement

P, S, and Cl calibrations were setup on a Supermini200 with analyzing crystal RX9. Six calibration samples were prepared by diluting a NIST traceable lubricating oil standard obtained from AccuStandard® (P, S, Cl in white mineral oil, ASTM-P-0121-13). Calibration range, accuracy and lower limit of detection (LLD) are shown in Table 1, measurement condition in Table 2 and

calibrations in Figures 1, 2 and 3.

Test samples with P, S, Cl at 0.5, 1 and 5 mg/kg were prepared by mixing and diluting 3 single element standards obtained from ASI Standards (PMO1C-1000, S(PS)MO1C-1000, CIMO1C-1000). Short term reproducibility test was performed by consecutively running 20 aliquots. Long term reproducibility test was performed by running 2 aliquots per day (morning and afternoon) over 10 days. Instrument was shut down for one week between short and long terms tests.

Table 1 Calibration results unit: mg/kg

Element	P	S	Cl
Calibration range	0 - 75	0 - 12	0 - 11
Calibration Accuracy	0.1		
LLD	0.1		

Calibration accuracy is calculated as follows.

$$Accuracy = \sqrt{\frac{\sum_i^n (C_i^{Calc.} - C_i^{Std.})^2}{n - m}}$$

$C_i^{Calc.}$ Calculated value of calibration sample

$C_i^{Std.}$ Standard value of calibration sample

n Number of calibration samples

m Degrees of freedom (2 for linear)

LLD is calculated as follows.

$$LLD = 3 \times \frac{1}{S} \times \sqrt{\frac{I_B}{1000 \times t}} = \frac{3\sigma_B}{S}$$

S Calibration sensitivity $kcps/(mg/kg)$

I_B Blank sample intensity $kcps$

σ_B Standard deviation of I_B $kcps$

t Counting time 300 sec

Table 2 Measurement condition

Element	P	S	Cl
Measurement Line	P-K α	S-K α	Cl-K α
X-ray tube	Pd anode, 50 kV - 4.0 mA		
Crystal	RX9		
Detector	F-PC		
Path	Helium		
Counting Time	Peak 150 sec., Background 150 sec.		

Sample preparation

About 4 grams of sample was poured into a liquid cell (Chemplex® 2140). Prolene® film (Chemplex® 416) with 4 μ m thickness was used as sample film.

To minimize potential analysis errors due to contamination, precautionary measures such as wiping cells with ethanol prior to measurement were taken.

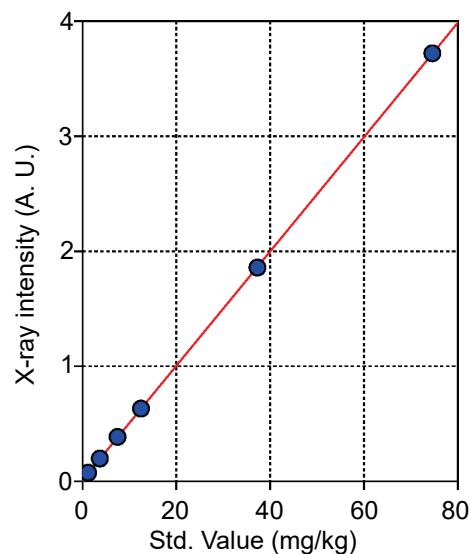


Figure 1 Phosphorous calibration curve

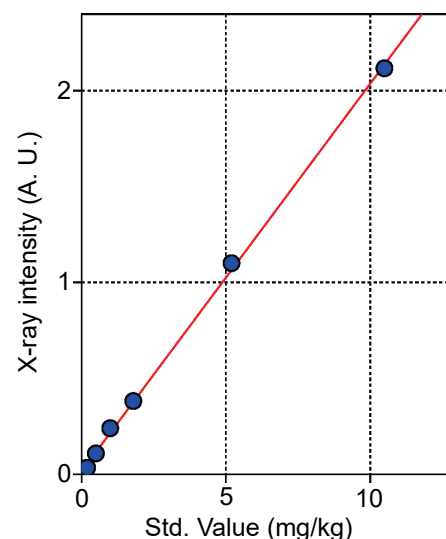


Figure 2 Sulfur calibration curve

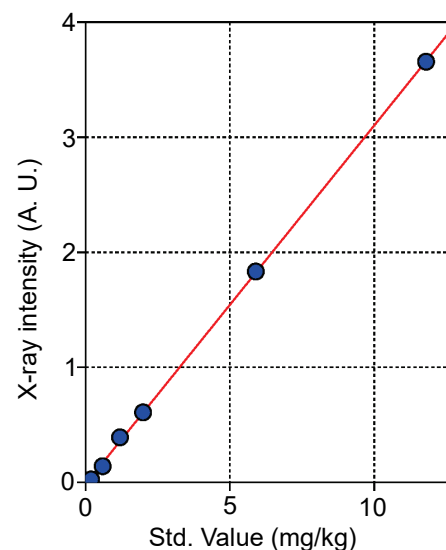


Figure 3 Chlorine calibration curve

Table 3 0.5 mg/kg result Summary unit mg/kg

0.5 mg/kg	Short Term			Long Term		
Run	P	S	Cl	P	S	Cl
1	0.4	0.8	0.5	0.5	0.7	0.5
2	0.3	0.6	0.5	0.4	0.4	0.4
3	0.6	0.7	0.3	0.6	0.6	0.6
4	0.5	0.6	0.3	0.4	0.5	0.5
5	0.4	0.5	0.4	0.3	0.5	0.3
6	0.5	0.7	0.5	0.5	0.4	0.4
7	0.5	0.5	0.3	0.6	0.6	0.6
8	0.5	0.8	0.4	0.6	0.5	0.5
9	0.3	0.5	0.4	0.5	0.4	0.3
10	0.6	0.6	0.5	0.3	0.5	0.4
11	0.5	0.5	0.4	0.4	0.4	0.6
12	0.6	0.6	0.6	0.5	0.5	0.3
13	0.5	0.7	0.3	0.5	0.6	0.5
14	0.4	0.8	0.3	0.6	0.7	0.3
15	0.6	0.5	0.3	0.4	0.6	0.4
16	0.5	0.7	0.3	0.3	0.5	0.4
17	0.3	0.8	0.5	0.4	0.6	0.5
18	0.6	0.7	0.5	0.5	0.5	0.5
19	0.5	0.8	0.6	0.3	0.6	0.4
20	0.5	0.7	0.5	0.5	0.4	0.5
Average	0.5	0.6	0.4	0.5	0.5	0.4
Std. Dev.	0.10	0.11	0.10	0.11	0.10	0.10
Max	0.6	0.8	0.6	0.6	0.7	0.6
Min.	0.3	0.5	0.3	0.3	0.4	0.3
Range	0.3	0.3	0.3	0.3	0.3	0.3

Table 5 5 mg/kg result Summary unit mg/kg

5 mg/kg	Short Term			Long Term		
Run	P	S	Cl	P	S	Cl
1	5.0	5.0	5.1	5.2	5.0	5.3
2	5.0	4.9	5.0	4.6	4.8	5.1
3	5.1	5.0	5.1	5.0	5.2	4.9
4	5.1	5.1	5.3	4.8	5.1	4.9
5	5.0	4.9	5.1	5.0	4.8	5.3
6	4.9	4.8	5.2	4.8	4.6	5.0
7	4.9	5.0	5.4	5.1	4.9	5.2
8	5.1	4.9	5.0	5.1	5.3	5.3
9	4.9	5.1	5.2	4.7	5.1	5.0
10	5.1	5.1	5.1	4.8	5.3	5.2
11	4.6	4.8	5.0	4.8	5.1	5.2
12	5.0	5.2	5.1	5.0	4.9	5.1
13	5.3	5.2	5.3	4.9	4.9	5.2
14	5.3	5.0	4.8	5.0	5.0	5.1
15	5.1	5.2	5.2	5.0	4.8	5.1
16	5.4	5.2	5.0	4.5	5.0	5.0
17	5.1	5.3	5.2	4.7	5.2	5.0
18	4.8	5.4	5.1	5.2	4.8	5.1
19	4.8	5.1	5.2	5.4	4.9	5.0
20	4.6	5.2	5.0	5.0	4.9	5.1
Average	5.0	5.1	5.1	4.9	5.0	5.1
Std. Dev.	0.20	0.17	0.13	0.21	0.19	0.12
Max	5.4	5.4	5.4	5.4	5.3	5.3
Min.	4.6	4.8	4.8	4.5	4.6	4.9
Range	0.8	0.6	0.6	0.9	0.7	0.4

Table 4 1 mg/kg result Summary unit mg/kg

1 mg/kg	Short Term			Long Term		
Run	P	S	Cl	P	S	Cl
1	1.1	1.0	0.9	1.0	0.9	0.9
2	1.2	1.1	1.0	1.3	0.9	1.1
3	1.2	1.1	0.9	1.2	0.8	1.0
4	0.9	1.1	1.0	1.4	1.1	0.9
5	1.2	1.1	0.9	1.0	1.2	1.0
6	1.0	1.0	0.9	1.0	1.0	1.1
7	0.8	1.1	0.8	1.0	1.0	0.9
8	1.2	1.0	0.9	1.0	0.9	1.0
9	1.0	1.0	0.8	1.3	1.0	1.0
10	1.1	1.2	0.8	1.0	1.2	0.9
11	0.9	1.0	0.9	1.0	1.0	1.1
12	1.1	1.2	0.8	1.1	1.1	1.0
13	1.1	1.2	1.1	1.0	1.0	0.8
14	1.2	1.3	1.1	1.3	1.0	1.2
15	1.2	1.0	0.9	0.9	0.9	1.1
16	1.0	0.9	0.8	1.1	1.0	1.2
17	1.2	1.2	0.8	1.3	1.0	1.0
18	1.1	1.0	1.1	1.2	1.1	1.0
19	1.0	1.1	1.0	1.0	0.9	1.0
20	0.9	0.9	0.9	1.2	1.1	1.0
Average	1.1	1.1	0.9	1.1	1.0	1.0
Std. Dev.	0.12	0.10	0.11	0.14	0.10	0.09
Max	1.2	1.3	1.1	1.4	1.2	1.2
Min.	0.8	0.9	0.8	0.9	0.8	0.8
Range	0.4	0.4	0.3	0.5	0.4	0.4

Analysis result and discussion

Short and long term analysis results for P, S, Cl test samples at 0.5, 1 and 5 mg/kg are shown in Tables 3, 4 and 5 respectively. The data shows Supermini200's capability to perform high precision analysis with high accuracy over both short and long term durations. Drift correction over the course of the data collection period was not performed.

The largest S result difference between two consecutive short term measurements of the 5 mg/kg sample is 0.4 mg/kg, between run 11 and 12. ASTM D2622-16 prescribes that difference between successive results for a 5 mg/kg sample may exceed 0.5 mg/kg only in one case in twenty. For ISO 20884:2011, the criterion is 1.8 mg/kg. Results show that instrument meets precision requirement of both test methods. Sulfur levels 0.5 and 1 mg/kg are below the lower range covered by either test method.

Chlorine standard test method JPI-5S-73-2014 issued by the Japanese Petroleum Institute requires that analysis result difference of Cl between successive results is less than 1.3 ppm with 95% probability. This criterion is met as well. Chlorine levels 0.5 and 1 mg/kg are below the lower range covered by the test method.

Conclusion

This application note demonstrates that Supermini200 is able to analyze low level P, S and Cl in liquids in a single run with high precision and accuracy. Instrument meets precision required by test methods such as ASTM D2622-16, ISO 20884:2011 and JPI-5S-73-2014. Measurement result can be obtained in minutes with quick and easy sample preparation allowing processing of large quantities of samples. Minimal installation prerequisites, not requiring expensive consumables and dangerous acids contributes to safe and low cost of ownership.

Being able to analyze elements from oxygen to uranium, the Supermini200 equipped with analyzing crystal RX9 is both a versatile and specialized instrument. A broad array of application demands of various sample types and multiple elements are met with a single compact instrument.

References

ASTM D2622 (2016), Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry
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