Specialized, versatile, compact WDXRF spectrometer

Supermini200 (RX9)

Ultra low P, S, and Cl. Analyze elements from O to U. All on a single benchtop system

1. Introduction

The benchtop wavelength dispersive X-ray fluorescent spectrometer Supermini200 and its predecessors have been on the market since 2000 and are being used on every continent in the world for research and industrial applications. Since its inception, demands for controlling lower levels of phosphorous (P), sulfur (S) and chlorine (Cl) have been on the rise. To meet these challenges, the Supermini200 is now available with the highly sensitive analyzing crystal RX9 realizing 0.1 ppm lower limit of detections (LLD) for P, S and Cl in hydrocarbon-based samples.

2. Demand for lower LLDs

The negative impact of chlorine and corrosion have been known for a long time[1], but the estimated figures from a comprehensive study mandated by the U.S. Congress in 1999 and a subsequent report by the National Association of Corrosion Engineers (NACE) in 2016 are staggering. According to the 2016 NACE report, the global cost of corrosion was estimated to be US$2.5 trillion, equivalent to 3.4% of the global GDP in 2013[2]. Production and manufacturing sectors of chemicals, petroleum refining and exploration, food processing, pulp and paper are amongst the most severely impacted[3]. Demand by such industries to reduce chlorine in products for the protection of assets such as pipelines is increasing and will continue for the foreseeable future.

Ever more stringent regulations imposed on the petroleum industry to decrease S content in fuels has increased the demand to test petroleum products quickly and reliably. There are several well established standardized test methods to meet this purpose. For example ASTM D2622, approved for use by the U.S. Department of Defense[4] and the Environmental Protection Agency for the Tier 3 rule[5], can be applied for various petroleum products such as diesel, gasoline, jet fuels, kerosene and many more.

It is known that P is poisonous to automotive catalytic converters[6] and therefore its content in fuels such as gasoline need to be low[7]. One of the costliest environmental problems in the United States known as “nutrient pollution” can be caused by excess amounts of P in wastewater and therefore also needs to be kept low. Tightening of P content for various lubricating oil

specifications to impede gear wear and failure is another application example.

3. Supermini200 (RX9) performance

To meet the widespread need to determine lower P, S and Cl levels, the Supermini200 is now available with the highly sensitive analyzing crystal RX9 for the analysis of P, S and Cl. Figure 1 showing Cl-Kα spectra visualizes that samples with Cl 0, 0.5, 1 and 5 mg/kg in oil can be differentiated. Note that the Cl-Kα measurement line does not suffer from large spectral interference by Rh-L line as is the case for floor-standing high-powered spectrometers equipped with rhodium anode X-ray tubes. Supermini200 (RX9) being equipped with a palladium anode X-ray tube in combination with the RX9 analyzing crystal excels especially for the analysis of Cl realizing analysis at a detection level of 0.1 ppm. Detection levels for P and S are 0.1 ppm as well.

Instrument performance of P, S and Cl analysis detailed in Rigaku Application Note XRF1072 are summarized below. Table 1 shows concentration ranges, accuracies and lower limit of detections (LLD) for P, S and Cl calibrations set up using NIST traceable oil standards on Supermini200 (RX9). Measurement conditions are shown in Table 2, calibrations in Fig. 2.

Three mixtures, each containing P, S and Cl at same concentration levels were prepared at 0.5, 1 and 5 mg/kg to test the short and long term stability performance of the instrument. For the short term test, 20 consecutive measurements were carried out using a newly prepared aliquot each time. Long term stability data was collected over 12 days with two non-measurement days after five test days to mimic the operational practice of for example a laboratory providing testing services. On each of the ten test days, a fresh aliquot was analyzed in the morning and evening, a total of 20 measurements over the test period. The instrument was shut down for seven days between the short and long term tests.

Summary statistics of the analysis results are shown

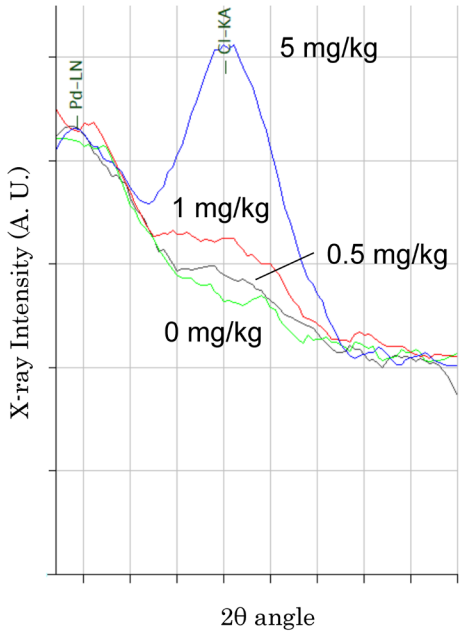

Fig. 1. Spectra of Cl 0, 0.5, 1 and 5 mg/kg in oil.

Table 1. Calibration results.

Unit: mg/kg

Element	P	S	Cl
Calibration range	0–75	0–12	0–11
Calibration Accuracy	0.1	0.1	0.1
LLD (300 sec.)	0.1	0.1	0.1

Table 2. Measurement conditions.

Element	P	S	Cl
Element Line	P-Kα	S-Kα	Cl-Kα
X-ray tube	Pd anode, 50 kV–4.0 mA		
Crystal	RX9		
Detector	F-PC		
Path atmosphere	Helium		
Counting Time	Peak 150 sec, Background 150 sec		
Sample film	Prolene® 4.0 μm		
Sample amount	~4 grams		

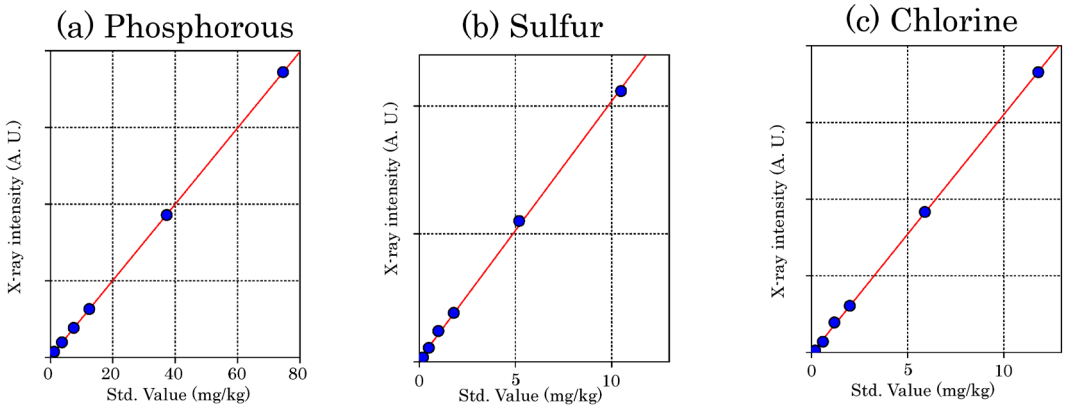

Fig. 2. (a) Phosphorous, (b) sulfur and (c) chlorine calibrations.

Table 3. Short and long term results for (a) 0.5 mg/kg, (b) 1.0 mg/kg and (c) 5.0 mg/kg test samples.

unit: mg/kg

Short Term	(a) 0.5 mg/kg			(b) 1.0 mg/kg			(c) 5.0 mg/kg		
	P	S	Cl	P	S	Cl	P	S	Cl
Average	0.5	0.6	0.4	1.1	1.1	0.9	5.0	5.1	5.1
Std. Dev.	0.10	0.11	0.10	0.12	0.10	0.11	0.20	0.17	0.13
Max	0.6	0.8	0.6	1.2	1.3	1.1	5.4	5.4	5.4
Min.	0.3	0.5	0.3	0.8	0.9	0.8	4.6	4.8	4.8
Range	0.3	0.3	0.3	0.4	0.4	0.3	0.8	0.6	0.6

unit: mg/kg

Long Term	(a) 0.5 mg/kg			(b) 1.0 mg/kg			(c) 5.0 mg/kg		
	P	S	Cl	P	S	Cl	P	S	Cl
Average	0.5	0.5	0.4	1.1	1.0	1.0	4.9	5.0	5.1
Std. Dev.	0.11	0.10	0.10	0.14	0.10	0.09	0.21	0.19	0.12
Max	0.6	0.7	0.6	1.4	1.2	1.2	5.4	5.3	5.3
Min.	0.3	0.4	0.3	0.9	0.8	0.8	4.5	4.6	4.9
Range	0.3	0.3	0.3	0.5	0.4	0.4	0.9	0.7	0.4

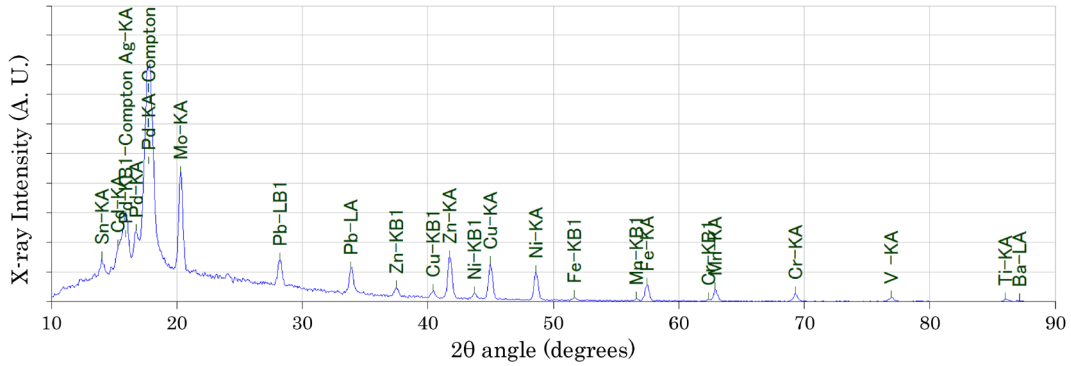

Fig. 3. Spectrum of multi-element oil standard for heavy element (Ti~) range.

in Table 3. The data confirms what is easily visible in Fig. 1−the 0.5 and 1 mg/kg test samples can be differentiated. Further examination of the statistics show that the analysis result ranges of the 0.5 and 1 mg/kg test samples do not overlap, both in case of short and long term tests.

In addition to function as a dedicated machine for routine measurements, it can also serve as a general purpose instrument for non-routine samples. An analyst at a central laboratory of a large facility is usually susceptible to receive requests to analyze various unknown samples, typically from other departments unaware of the challenges involved in the process. Determining the material of a piece of unwanted metal found in the production line to identify the source, checking the presence of certain elements in accumulated sludge scraped off the bottom of a boiler, amount of wear metals in lube oil collected from somewhere in the plant to assess the need for an oil change, elemental characterization of a faulty product−the list goes on. Running such samples on the Supermini200 (RX9) is fast, easy and can also be performed without standard samples using the semi-quantitative analysis function based on the fundamental parameter (FP) method.

Figure 3 shows the spectrum of a commercially available multi-element oil standard for elements Ti and higher atomic number. Element concentrations are 500 ppm. Peaks of common analytes such as Fe, V and Ni (heavy fuels), Cu and Ni (wear metals), Pb (gasoline), Ba, Mo and Zn (lubricating oils) can be seen. The instrument is able to measure elements from O to U. Semi-quantitative analysis result of the multi-element oil is shown in Table 4. The results obtained in less than ten minutes without setting up calibrations are in good agreement with the standard values.

Table 4. Semi-quantitative analysis result of a multi-element oil standard sample (500 ppm).

Standard values: 500 ppm unit: ppm

Mg	Al	Si	P	Ca	Ti	V	Cr	Mn	Fe
475	536	538	516	537	514	465	552	561	549
Ni	Cu	Zn	Mo	Ag	Cd	Sn	Ba	Pb	CH_2
559	535	525	463	527	477	531	465	471	Balance

4. Summary

The Supermini200 equipped with the sensitive analyzing crystal RX9 realizes analysis with LLD 0.1 ppm for P, S and Cl. It can not only serve as an instrument for routine analysis of these elements, but also as a general purpose elemental analyzer of non-routine unknown samples from O to U. Its compact footprint and hassle-free installation have also contributed to the Supermini200 (RX9) currently operating in various industries such as petroleum refining, chemical manufacturing and testing laboratories.

References

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