

ASOMA® PHOENIX II

Determination of S, V, Fe & Ni in Residual Oil Using Direct Excitation

Summary

This report demonstrates the suitability of the ASOMA® PHOENIX II Benchtop XRF analyzer with direct excitation optics for measuring sulfur, vanadium, iron and nickel in residual oil. The performance is suitable for measuring these elements in other heavy hydrocarbon oils, such as crude and bunker fuel.

The PHOENIX II quickly and precisely gives results for these elements in heavy hydrocarbon oils at-line during monitoring and quality control of the oil.

In addition to ensuring the quality of the oil, the XRF measurement requires little if any sample preparation. These benefits work together to maximize quality and reduce operational costs.

Introduction

The PHOENIX II is an excellent QC benchtop analyzer that offers a fast, precise, simple and non-destructive analysis technique well suited for the analysis of sulfur, vanadium, iron and nickel in residual oil and other heavy hydrocarbon oils.

The PHOENIX II is a powerful tool for monitoring these elements in hydrocarbon oils. The analyzer uses a rugged, time-proven proportional counter as its detection system and a direct excitation X-ray tube. This combination of ruggedness, power and simplicity using a small benchtop analyzer enables fast and precise results.

Data handling and results storage can be obtained on a paper print out and are also stored in the hard drive of the PHOENIX II. The data can be readily transferred to a USB thumb-drive or accessed via an Ethernet connection.

Calibrations are readily carried out using assayed standards. This ensures easy traceability of results for quality purposes. This initial calibration process is a “once only” procedure. Subsequently, the curve can be restandardized, if required, by the touch of a button on the main analysis screen.

The PHOENIX II offers power, versatility and performance all in a small, compact, easy-to-use design.

Experimental Portion

Equipment

All measurements were conducted using a PHOENIX II XRF analyzer using direct excitation optics. Performance is shown for a measurement time of 100 sec for S, and a total of 200 sec for the measurement of V, Fe & Ni.

Sample Preparation

No sample preparation is required. Each sample cup was placed in the sample chamber for analysis.

Measurement Parameters

All measurement parameters are easily controlled through the touch screen on the display panel. Operators simply choose the correct method from the analysis screen (there may be more than one method stored, e.g. to



deal with residual oil or crude, etc.) and then press the green ANALYZE button.

The results can be reported using a variety of different options: results are reported on the display screen; on a thermal paper printout; on an optional external printer; and in the database history within the analyzer.

Instrument Configuration

ASOMA® PHOENIX II

Excitation: Direct excitation 30 kV 9 W Air-cooled X-ray Tube

Detection: Gas-filled Proportional Counter

Analyte Optimization: X-ray voltage, current and X-ray filters

Atmosphere: Air

Options: Tube filter; Sample spinner

Note: No consumable gases required.

XRF Sample Cup



Easy assembly with film window



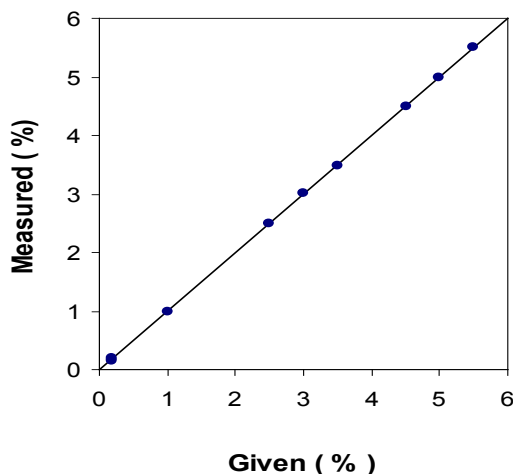
The following results section show performance using commercially available calibration standards for residual oil.

Results - Sulfur

Calibration for Sulfur

Element: S	Std. Error of Estimate: 0.016	
Units: %	RMS: 0.004	
Sample	Given	Measured
Std. 1	0.175	0.152
Std. 2	0.500	0.489
Std. 3	1.00	0.986
Std. 4	0.175	0.179
Std. 5	2.00	2.019
Std. 6	2.50	2.496
Std. 7	3.00	3.012
Std. 8	3.50	3.479
Std. 9	0.18	0.207
Std. 10	4.50	4.504
Std. 11	5.00	4.998
Std. 12	5.50	5.503

Correlation Plot for S



Precision for Sulfur

10 repeat analyses at 100 seconds per measurement

Element: S	Units: %			
Sample	Given	Mean	Std. Dev.	% Rel.
Std. 2	0.500	0.497	0.005	1.0
Std. 5	2.00	2.007	0.009	0.4
Std. 10	4.50	4.590	0.008	0.2

Minimum Detection Limit - Sulfur

The Minimum Detection Limit (MDL) for an element is determined as three times the standard deviation of ten analyses of the blank oil sample containing no S. The following MDL was derived using this empirical method and applies to this matrix and concentration range.

Element	Count Time	MDL
S	100 sec	0.0015%

Minimum Detection Limit - Vanadium

The Minimum Detection Limit (MDL) for an element is determined as three times the standard deviation of ten analyses of the blank oil sample containing no V. The following MDL was derived using this empirical method and applies to this matrix and concentration range.

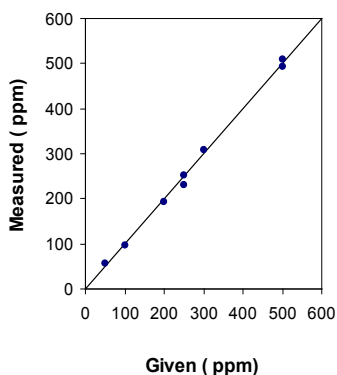
Element	Count Time	MDL
V	200 sec	9 ppm

Results for Vanadium

Calibration for Vanadium

Element: V		Std. Error of Estimate: 9.8	
Units: ppm		RMS: 2.4	
Sample	Given	Measured	
Std. 2	500	507.7	
Std. 3	25	30.3	
Std. 4	250	232	
Std. 5	100	97.3	
Std. 6	400	405	
Std. 7	300	309	
Std. 8	200	194	
Std. 10	250	252	
Std. 11	500	492	
Std. 12	50	56.2	

Correlation Plot for V



Precision for Vanadium

10 repeat analyses at 200 seconds per measurement

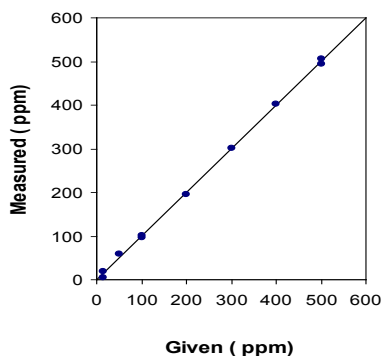
Element: V		Units: ppm		
Sample	Given	Mean	Std. Dev.	% Rel.
Std. 5	100	96	4	4.2
Std. 7	300	307	4	1.3
Std. 2	500	497	4	0.8

Results for Iron

Calibration for Iron

Element: Fe		Std. Error of Estimate: 6.5	
Units: ppm		RMS: 1.6	
Sample	Given	Measured	
Std. 1	14	5.4	
Std. 2	300	291	
Std. 3	500	507	
Std. 4	100	97	
Std. 5	200	204	
Std. 6	400	402	
Std. 7	14	18.5	
Std. 8	500	495	
Std. 9	100	101	
Std. 10	300	301	
Std. 11	200	196	
Std. 12	50	59.4	

Correlation Plot for Fe



Precision for Iron

10 repeat analyses at 200 seconds per measurement

Element: Fe		Units: ppm		
Sample	Given	Mean	Std. Dev.	% Rel.
Std. 7	14	16	2	13
Std. 5	200	203	2	1.0
Std. 10	300	304	3	1.0

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Minimum Detection Limit - Iron

The Minimum Detection Limit (MDL) for an element is determined as three times the standard deviation of ten analyses of the blank oil sample containing no Fe. The following MDL was derived using this empirical method and applies to this matrix and concentration range.

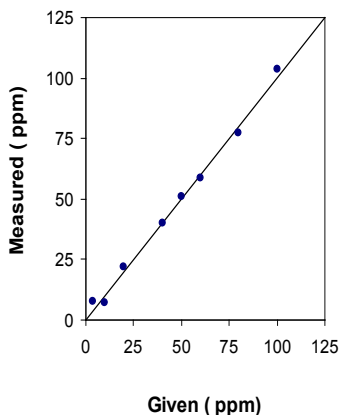
Element	Count Time	MDL
Fe	200 sec	3 ppm

Results for Nickel

Calibration for Nickel

Element: Ni	Std. Error of Estimate: 2.8	
Units: ppm	RMS: 0.75	
Sample	Given	Measured
Std. 2	10	7.4
Std. 3	100	98.1
Std. 4	80	77.1
Std. 5	40	39.8
Std. 6	5	3.5
Std. 7	60	58.5
Std. 8	4	7.6
Std. 9	100	103.8
Std. 10	50	51.2
Std. 11	20	22.0

Correlation Plot for Ni



Precision for Nickel

10 repeat analyses at 200 seconds per measurement

Element: Ni		Units: ppm		
Sample	Given	Mean	Std. Dev.	% Rel.
Std. 2	10	8.0	0.4	5.0
Std. 5	40	40.9	0.6	1.4
Std. 7	60	60.1	0.6	1.0

Minimum Detection Limit - Nickel

The Minimum Detection Limit (MDL) for an element is determined as three times the standard deviation of ten analyses of the blank oil sample containing no Ni. The following MDL was derived using this empirical method and applies to this matrix and concentration range.

Element	Count Time	MDL
Ni	200 sec	1.5 ppm

Conclusion

As can be seen from the above data, the use of the PHOENIX II XRF system using direct excitation gives excellent performance when applied to the determination of S, V, Fe & Ni in Residual Oil. Results are rapid, precise and analysis is easily carried out, even by non-laboratory personnel. Because no consumable chemicals are used, the relative "cost of ownership" is much lower than other analytical techniques.



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