

## ASOMA PHOENIX II

### Analysis of P, S, Ca & Zn in Lube Oil



#### Summary

This report demonstrates the suitability of the PHOENIX II XRF analyzer for use in the quality control of lubricating oil blending. It will show that use of this instrument will deliver improvements in product quality by accurately and rapidly determining the important additive elements in lubricant oils, i.e. P, S, Ca and Zn.

It can also be seen that there is another advantage in easily and quickly measuring these elements during the blending process. Namely, by ensuring that additive package “overdosing” does not occur, significant reductions in operational costs can be achieved and high quality maintained.

The method described is fully compliant with EDXRF standard method ASTM D 6481-99.

#### Introduction

The PHOENIX II is an excellent benchtop XRF analyzer for at-line production QC analysis or the laboratory alike. The PHOENIX II offers a fast, precise, simple and non-destructive analysis technique well suited for the determination of sulfur, phosphorous, calcium and zinc in lubricating oils.

The PHOENIX II employs state-of-the-art optics. Polarization excitation offers unique benefits because it eliminates most of the background scatter emerging from the X-ray tube before it arrives at the sample. This results in a dramatic improvement in peak-to-background signal, especially in highly scattering materials such as petrochemical and oil products. This translates to vastly improved precision and lower detection limits than traditional direct excitation XRF systems can achieve.

The PHOENIX II uses an onboard PC computer with a simple touch screen interface. Thus, an external computer is not required. Data handling and results storage can be obtained on a thermal 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 a network 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. Performance is shown for using a total measurement time of 300 seconds (three 100 second conditions).

### Sample Preparation

Sample preparation is minimal. Solution samples are simply poured into a commercially available XRF sample cup. The instrument’s optical system is protected from inadvertent oil spillage by an easily changeable safety window.

### 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 different lube formulations) 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:** 48 kV 50 W Air-cooled X-ray Tube

**Detection:** Gas-filled Proportional Counter

**Analytes:** P, S, Ca & Zn

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

**Atmosphere:** Air

**Options:** HOPG Target, Secondary Target; Detector filters; Polypropylene 4 µm film

**Note: No helium purge is required.**

### XRF Sample Cup



### Easy assembly with film window

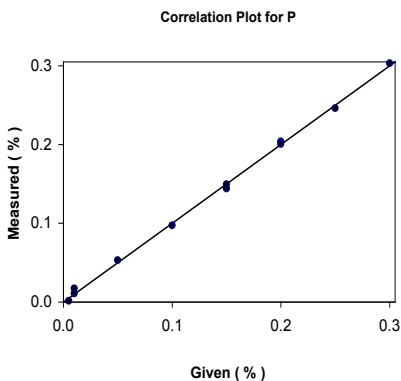


### Results for Lube Oils

**Note: All calibrations were built using commercially available lube oil standards.**

#### Calibration for Phosphorous

Element: Phosphorous		
Units: %      Std. Error of Estimate: 0.0035		
Sample	Given	Measured
1	0.005	0.001
2	0.000	-0.002
5	0.000	-0.001
6	0.250	0.246
7	0.150	0.144
8	0.200	0.204
9	0.010	0.017
10	0.150	0.150
11	0.200	0.201
13	0.100	0.097
14	0.010	0.011
15	0.300	0.303
16	0.050	0.053



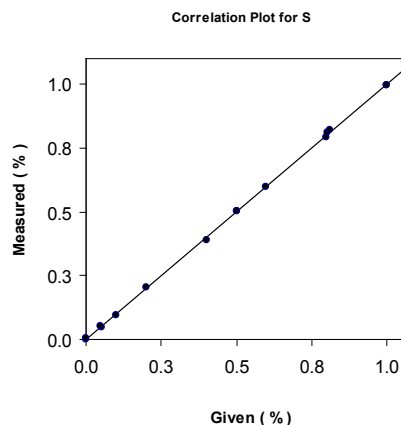
#### Precision for P in Lube Oil

**10 repeat analyses at 100 seconds per measurement**

Element: P				Units: %
Sample	Given	Mean	Std. Dev.	% Rel.
10	0.150	0.1505	0.0021	1.4
14	0.010	0.0093	0.0004	4.3
15	0.300	0.2983	0.0034	1.2

#### Calibration for Sulfur

Element: Sulfur		
Units: %      Std. Error of Estimate: 0.0064		
Sample	Given	Measured
1	0.051	0.046
2	0.000	0.001
3	0.000	-0.003
4	1.000	0.996
5	0.001	0.006
6	0.800	0.791
7	0.500	0.504
8	0.100	0.097
9	0.400	0.390
10	0.200	0.203
11	0.801	0.813
12	0.810	0.818
13	0.500	0.501
14	0.050	0.054
15	1.000	0.997
16	0.600	0.597



#### Precision for S in Lube Oil

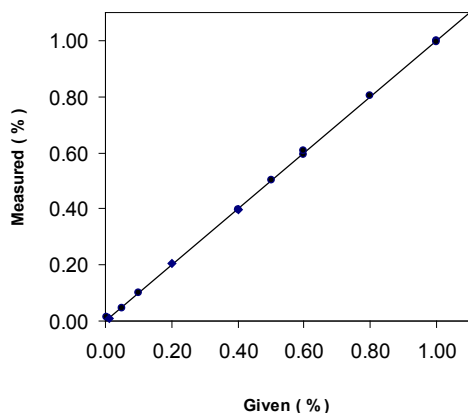
**10 repeat analyses at 100 seconds per measurement**

Element: S				Units: %
Sample	Given	Mean	Std. Dev.	% Rel.
7	0.500	0.4979	0.0034	0.7
14	0.050	0.0514	0.0024	4.7
15	1.000	0.9984	0.0047	0.5

**Calibration for Calcium**

Element: Calcium		
Units: %      Std. Error of Estimate: 0.0053		
Sample	Given	Measured
2	0.600	0.592
3	0.000	-0.003
4	1.000	1.001
5	0.000	-0.005
6	0.005	0.014
7	0.500	0.502
8	0.010	0.011
9	0.050	0.047
10	0.100	0.099
11	0.200	0.205
12	0.400	0.398
13	0.600	0.605
14	0.800	0.806
15	1.000	0.997
16	0.400	0.396

Correlation Plot for Ca

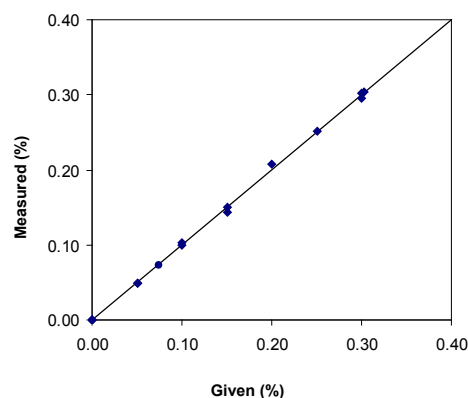


*Note: Results for Ba in lube oil are comparable to these Ca results over a similar concentration range.*

**Calibration for Zinc**

Element: Zinc		
Units: %      Std. Error of Estimate: 0.0032		
Sample	Given	Measured
1	0.050	0.048
2	0.000	-0.001
3	0.000	0.000
4	0.000	-0.001
5	0.300	0.296
6	0.303	0.303
7	0.150	0.150
9	0.075	0.073
10	0.200	0.207
11	0.100	0.099
12	0.300	0.302
13	0.050	0.049
14	0.100	0.103
15	0.150	0.143
16	0.250	0.252
17	0.000	0.000

Correlation Plot for Zn



**Precision for Ca in Lube Oil**

**10 repeat analyses at 100 seconds per measurement**

Element: Ca				Units: %
Sample	Given	Mean	Std. Dev.	% Rel.
7	0.500	0.4979	0.0034	0.7
14	0.050	0.0514	0.0024	4.7
15	1.000	0.9984	0.0047	0.5

**Precision for Zn in Lube Oil**

**10 repeat analyses at 100 seconds per measurement**

Element: Zn				Units: %
Sample	Given	Mean	Std. Dev.	% Rel.
13	0.050	0.0489	0.0006	1.2
7	0.150	0.1507	0.0006	0.4
12	0.300	0.2997	0.0008	0.3

## Minimum Detection Limits

The Minimum Detection Limit (MDL) for an element is determined as three times the standard deviation of ten analyses of the blank oil sample. The following MDLs were derived using this empirical method and apply to this lube oil matrix.

Element	Count Time	MDL
P	100 sec	12 ppm
S	100 sec	5 ppm
Ca	100 sec	25 ppm
Zn	100 sec	3 ppm

## Accuracy

In order to demonstrate the accuracy of the calibrations shown in this report, several ASTM round robin lube oil samples were analyzed, with the following results.

### ASTM Sample ID: LU0601

	ASTM Value (%)	ASTM Error (+/-)	SPECTRO Value (%)	Deviation SPECTRO - ASTM
P	0.141	*	0.1431	+0.0020
S	0.4497	0.1936	0.4567	+0.0070
Ca	0.3314	0.046	0.3372	+0.0058
Zn	0.1587	0.023	0.1629	+0.0042

\* not reported in the ASTM report

### ASTM Sample ID: LU0605

	ASTM Value (%)	ASTM Error (+/-)	SPECTRO Value (%)	Deviation SPECTRO - ASTM
P	0.0773	0.0199	0.0787	+0.0014
S	0.35	0.066	0.3515	+0.0015
Ca	0.2153	0.0258	0.2087	-0.0066
Zn	0.0888	0.0227	0.0884	-0.0004

### ASTM Sample ID: LU0609

	ASTM Value (%)	ASTM Error (+/-)	SPECTRO Value (%)	Deviation SPECTRO - ASTM
P	0.071	0.0222	0.0728	+0.0018
S	0.245	0.091	0.2413	-0.0037
Ca	0.1891	0.0136	0.1893	+0.0002
Zn	0.0803	0.0105	0.0807	+0.0004

### ASTM Sample ID: LU0701

	ASTM Value (%)	ASTM Error (+/-)	SPECTRO Value (%)	Deviation SPECTRO - ASTM
P	0.101	0.0144	0.1025	+0.0015
S	0.4092	0.09	0.4111	+0.0019
Ca	0.2636	0.0177	0.2715	+0.0078
Zn	0.1135	0.0114	0.1178	+0.0043

### ASTM Sample ID: LU0705

	ASTM Value (%)	ASTM Error (+/-)	SPECTRO Value (%)	Deviation SPECTRO - ASTM
P	0.0775	*	0.0762	-0.0013
S	0.247	*	0.2386	-0.0084
Ca	0.2104	*	0.2130	+0.0026
Zn	0.0916	*	0.0852	-0.0064

\* not reported in the ASTM report

These results show excellent accuracy, as the ASOMA values are very close to the ASTM results and well within the error in the ASTM values.

## Conclusion

As can be seen from the above data, the use of the PHOENIX II XRF system gives excellent performance when applied to the determination of P, S, Ca and Zn in lube oil. While Ba was not an element in the set of calibration used, if calibrated for Ba the results will be comparable to those of Ca. 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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