

S4 EXPLORER

PHOSPHOR-ANALYSIS ACCORDING TO DIN 51363-2

Introduction

DIN 51363-2^[1] describes the determination of the phosphorus content (mass fraction in g/100g, in the following wt%) of lubricating oils and additives by wavelength-dispersive X-ray fluorescence spectrometry (WD-XRF). The phosphorus concentration range is 0.001 wt% up to 1.0 wt%.

As the composition of the respective samples varies significantly, the application of a matrix correction is mandatory. In DIN 51363-2 this correction is based on Zr as internal standard. When applying an internal standard, the calibration relates an intensity ratio of analyte and internal standard to the analyte concentration. As (matrix) differences between standard samples and real samples as well as intensity drift of spectrometers will affect both measurements (analyte and internal standard) in equal measure, an intensity ratio is free of these interferences, depending on the analyte concentration only. The sample itself must not contain the internal standard element. For equal response on perturbances, the internal standard element must have a fluorescence line close to the analyte. Finally, the internal standard line must not be noticeably enhanced by the analyte line (thus attenuating the analyte intensity depending on the respective concentration ratio). All these requirements are fulfilled by Zr $L\alpha$.



Sample Preparation

Standard and analysis samples are prepared by weighing 10 portions of sample or standard sample and 2 portions of a 12 - 18% Zr solution and stirring thoroughly.

In each case, 5.0 ± 0.1 g of this solution were poured into liquid cups (inner diameter 3.5 cm), that were covered with a 4 μm Prolene[®] film. Each cup was placed on a printing or weighing paper for a 30 s tightness testing and the sample was subsequently measured.

Measurement Parameters

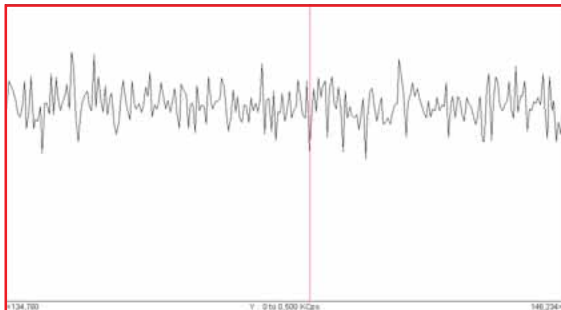
All data were obtained using the following measurement parameters:

Anode	Rhodium
Voltage	30 kV
Current	33 mA
Collimator	0.46°
Crystal	Germanium
P Line Position	140.963°
Measuring Time	60 s
Zr Line Position	136.748°
Measuring Time	20 s
Detector	Flow counter with pulse height analysis
Discrimination Window	40 - 165%
Optical Path	Helium (with vacuum seal)
Film	4 μm Prolene®

Because of the low volatility of fuel samples, the helium mode of reduced pressure is applied.

Check Of Cell Window (Film)

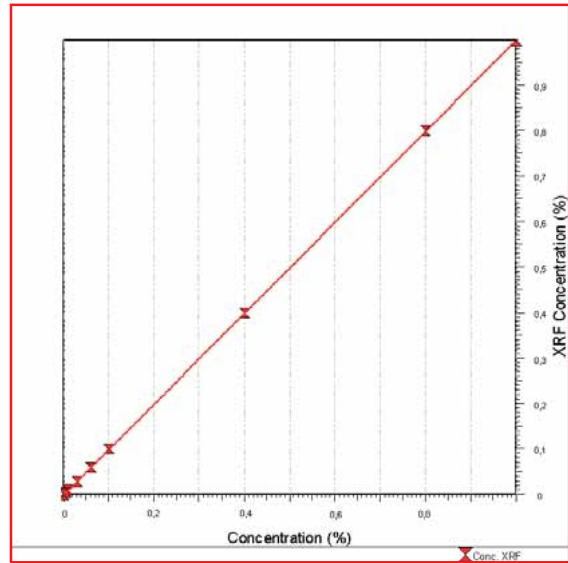
The recent version of DIN 51363-2 includes a check of the sample cell window. A scan in the region of the phosphorus line has to be performed on each new batch of film. A potential phosphorus peak must not exceed more than two times the noise level. The following graph shows the scan of a Paraffin (white oil) sample sealed with 4 μm Prolene® film:



Obviously there is no blank signal at all. So neither the film nor the white oil are contaminated with the analyte.

Calibration

A norm compliant calibration applies Zr as an internal standard. Therefore the following graph shows concentration obtained by XRF calibration "XRF Concentration" vs. concentration calculated according preparation "Concentration" (concentrations in wt%):



Conc.	Conc. XRF	Absolute Deviation	Count.Stat. Deviation	LOD [mg/kg]
0.0000	-0.0002	-0.0002	0.0000	3
0.0010	0.0009	-0.0001	0.0000	3
0.0050	0.0048	-0.0002	0.0000	3
0.0100	0.0100	0.0000	0.0001	3
0.0300	0.0303	0.0003	0.0001	3
0.0600	0.0606	0.0006	0.0001	3
0.1000	0.1003	0.0003	0.0001	3
0.4000	0.4001	0.0001	0.0003	3
0.8000	0.7995	-0.0005	0.0004	3
1.0000	0.9970	-0.0030	0.0004	3

The calibration can be summarized as follows (concentrations in wt%):

Concentration Range	0.0000 - 0.1000
Number of Standards	10
Intensity Model	Raw Intensities
Calibration Model	Internal Standard Zr
Regression Minimizes	Relative Errors
Mean Regression Deviation	0.0010
Counting Statistic Deviation	≤0.0004
Limit Of Detection (LOD) (3 σ, 60 s)	0.0003

$$LOD = \frac{3}{m} \cdot \sqrt{\frac{I_{Bgr}}{t_{Bgr}}}$$

- m Sensitivity of sulfur calibration [cps/(m/m)]
 I_{Bgr} Count rate at background position [cps]
 t_{Bgr} Counting time at background position [s]

Accuracy

As a first step, the accuracy of the calibration was checked by analysis of a few DIN round-robin samples. The results, including respective DIN R/√2 reproducibility ranges, are presented in the following table (concentrations in wt%):

Sample	Conc.	DIN R/√2 range	
MO401	0.1274	0.1192 - 0.1334	✓
MO402	0.1169	0.1111 - 0.1253	✓
MO Engine Oil			

All results were found within the demanding round-robin DIN R/√2 ranges.

Repeatability

In addition to the accuracy of the analysis method, the precision was tested analyzing the DIN round-robin MO401 base oil sample 20 times. According to DIN 51363-2, the difference between two consecutive results in the range of 0.12 wt% must not exceed 0.005 wt% in more than one out of 20 cases. The respective measurements were carried out on test portions of a sufficient volume of MO401 that was prepared at one time. Therefore, the results reflect the spectrometer stability excluding preparation effects by internal standard mixing. The results and differences of the respective measurements are given in the following table (n = 20; concentrations in wt%):

Date	Concentration	Difference
20.07.2004 16:25	0.1260	
20.07.2004 16:28	0.1262	0.0002
20.07.2004 16:30	0.1260	-0.0002
20.07.2004 16:33	0.1257	-0.0003
20.07.2004 16:36	0.1264	0.0007
20.07.2004 16:38	0.1263	-0.0001
20.07.2004 16:41	0.1260	-0.0003
20.07.2004 16:43	0.1260	0.0000
20.07.2004 16:46	0.1266	0.0006
20.07.2004 16:48	0.1265	-0.0001
20.07.2004 16:51	0.1260	-0.0005
20.07.2004 16:53	0.1264	0.0004
20.07.2004 16:56	0.1260	-0.0004
20.07.2004 16:58	0.1264	0.0004
20.07.2004 17:01	0.1263	-0.0001
20.07.2004 17:03	0.1264	0.0001
20.07.2004 17:06	0.1263	-0.0001
20.07.2004 17:09	0.1259	-0.0004
20.07.2004 17:11	0.1262	0.0003
20.07.2004 17:14	0.1264	0.0002
Average		0.1262
Mean Abs. Std. Dev.		0.0002
Minimum		0.1257 0.0000
Maximum		0.1266 0.0007
Range		0.0009
Maximum Difference of the Norm		0.0050

Mean deviation as well as maximum deviation of two consecutive measurements are far below the value specified in the norm.

These results demonstrate the outstanding short-time stability of the S4 EXPLORER. To get additional data for a long-time stability, the same prepared sample MO401 was analyzed over a period of 57 days. The results are presented in the following table (n = 14; concentrations in wt%):

Date	Concentration	Difference
20.07.2004 16:25	0.1260	
21.07.2004 11:05	0.1266	0.0006
22.07.2004 11:29	0.1263	-0.0003
23.07.2004 08:59	0.1261	-0.0002
26.07.2004 08:48	0.1264	0.0003
27.07.2004 10:17	0.1263	-0.0001
28.07.2004 07:59	0.1258	-0.0005
29.07.2004 08:59	0.1260	0.0002
30.07.2004 07:55	0.1256	-0.0004
02.08.2004 08:08	0.1257	0.0001
03.08.2004 08:03	0.1257	0.0000
04.08.2004 07:56	0.1260	0.0003
05.08.2004 09:04	0.1259	-0.0001
06.08.2004 08:01	0.1257	-0.0002
27.08.2004 08:24	0.1265	0.0008
15.09.2004 11:32	0.1260	-0.0005
<hr/>		
Average	0.1260	
<hr/>		
Mean Abs. Std. Dev.	0.0003	
<hr/>		
Minimum	0.1256	0.0000
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Maximum	0.1266	0.0008
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Range	0.0010	
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Maximum Difference of the Norm		0.0050

Even over a period of 57 days, the same parameters are reached compared to the short-time stability measurements. Range (0.0009 wt% resp. 0.0010 wt%) and mean absolute deviation (0.0002 wt% resp. 0.0003 wt%) are almost the same and far beyond the limit specified in the norm. So it is reasonable to assume that individually prepared samples match the norm requirements as well. These results also reflect the experience of recent years' round-robin tests.

The excellent stability of the S4 EXPLORER is, among other features, based on the unique

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vacuum seal separating sample and spectrometer chamber. This component allows a complete and fast exchange of mode air (sample change) and helium (measurement) in the small sealed volume of the sample chamber. Thus, highest stability conditions are guaranteed from the very beginning of any measurement.

Conclusion

The S4 EXPLORER with 1 kW maximum power ensures Phosphorus analyses according to DIN 51363-2 in a quality that one is used to getting from 4 kW instruments. This holds for the concentration range 0.010 - 0.50 wt%. Based on a power optimization to 1 kW and on the development of the sealed proportional counter Pro4, this quality can be achieved even in laboratory environments that provide neither cooling water nor detector gas.

The accuracy of the calibrations was verified by the analysis of DIN round-robin samples. All available samples were analyzed and all the results matched the demanding DIN R/√2 range.

The mean and the maximum difference of the short-time stability measurements (about 50 min) of the same sample were far below the maximum value specified in the norm. Even for long-time stability measurements (57 days), the same outstanding parameters were obtained.

Notes

[1] DIN 51363-2 (2003-02) Determining the phosphorus content of lubricating oils and additives by wavelength dispersive X-ray spectrometry (XRF); Beuth Verlag GmbH, Berlin

The picture of a cooling lubricant on page 1 was kindly provided by Aral AG.

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