

S4 PIONEER

MAGNESIUM-ANALYSIS ACCORDING TO DIN 51431-2

Introduction

DIN 51431-2^[1] describes the determination of the magnesium content (mass fraction in g/100g, in the following wt%) in lubricants by wavelength dispersive X-ray fluorescence spectrometry (WD-XRF). The magnesium concentration range is 0.01 wt% up to 0.50 wt%.

As the composition of the respective samples varies significantly, the application of a matrix correction is mandatory. In DIN 51431-2 this correction is based on Br 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 stan-

dard 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 Br $L\alpha$.



Sample Preparation

Standard and analysis samples are prepared by weighing 10 portions of sample or standard sample and 2 portions of a 1% Br 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

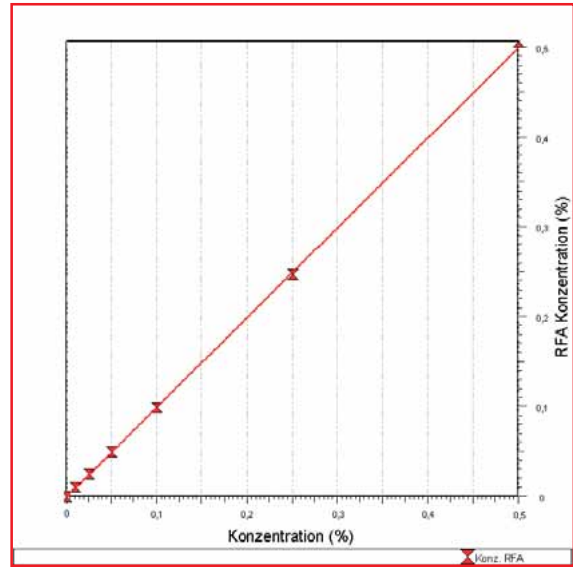
All data were obtained using the following measurement parameters:

Anode	Rhodium
Voltage	30 kV
Current	135 mA
Collimator	0.46°
Crystal	OVO-55 (Multilayer)
Mg Line Position	20.638°
Measuring Time	20 s
Background Position	18.802°
Measuring Time	20 s
Br Line Position	17.293°
Measuring Time	20 s
Detector	Flow counter with pulse height analysis
Discrimination Window	45 - 155%
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.

Calibration

A norm compliant calibration applies Br 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]
0.000	0.000	0.000	0.0001	27
0.010	0.011	0.001	0.0001	27
0.025	0.025	0.000	0.0002	27
0.050	0.050	0.000	0.0002	28
0.100	0.099	-0.001	0.0003	28
0.250	0.247	-0.003	0.0004	30
0.500	0.506	0.006	0.0005	32

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

Concentration Range	0.000 - 0.50
Number of Standards	7
Intensity Model	Net Intensities
Calibration Model	Internal Standard Br
Regression Minimizes	Relative Errors
Mean Regression Deviation	0.003
Counting Statistic Deviation	≤0.0005
Limit Of Detection (LOD) (3 σ, 20 s)	0.003

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

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/ $\sqrt{2}$ reproducibility ranges, are presented in the following table (concentrations in wt%):

Sample	Conc.	DIN R/ $\sqrt{2}$ range	
MO401	0.0260	0.0254 - 0.0310	✓
MO402	0.0293	0.0288 - 0.0352	✓
MO Engine Oil			

All results were found within the demanding round-robin DIN R/ $\sqrt{2}$ ranges.

Repeatability

In addition to the accuracy of the analysis method, the precision was tested analyzing the DIN round-robin MO402 base oil sample 20 times. According to DIN 51431-2, the difference between two consecutive results must not exceed 0.7 % relative i.e. 0.0021 wt% at a concentration of 0.0300 wt%. The respective measurements were carried out on test portions of a sufficient volume of MO402 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
23.07.2004 08:47	0.0300	
23.07.2004 08:50	0.0306	0.0006
23.07.2004 08:52	0.0307	0.0001
23.07.2004 08:54	0.0304	-0.0003
23.07.2004 08:57	0.0301	-0.0003
23.07.2004 08:59	0.0296	-0.0005
23.07.2004 09:01	0.0297	0.0001
23.07.2004 09:04	0.0302	0.0005
23.07.2004 09:06	0.0301	-0.0001
23.07.2004 09:09	0.0306	0.0005
23.07.2004 09:11	0.0299	-0.0007
23.07.2004 09:13	0.0300	0.0001
23.07.2004 09:16	0.0295	-0.0005
23.07.2004 09:18	0.0295	0.0000
23.07.2004 09:20	0.0293	-0.0002
23.07.2004 09:23	0.0301	0.0008
23.07.2004 09:25	0.0302	0.0001
23.07.2004 09:27	0.0296	-0.0006
23.07.2004 09:30	0.0301	0.0005
23.07.2004 09:32	0.0299	-0.0002
Average	0.0300	
Mean Abs. Std. Dev.	0.0004	
Minimum	0.0293	0.0000
Maximum	0.0307	0.0008
Range	0.0014	
Maximum Difference of the Norm		0.0021

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 PIONEER. To get additional data for a long-time stability, the same prepared sample MO402 was analyzed over a period of 53 days. The results are presented in the following table (n = 14; concentrations in wt%):

Date	Concentration	Difference
23.07.2004 08:47	0.0300	
26.07.2004 10:43	0.0291	-0.0009
27.07.2004 08:19	0.0296	0.0005
28.07.2004 09:22	0.0288	-0.0008
29.07.2004 08:21	0.0288	0.0000
30.07.2004 08:31	0.0295	0.0007
02.08.2004 08:26	0.0288	-0.0007
03.08.2004 08:16	0.0300	0.0012
04.08.2004 08:38	0.0295	-0.0005
05.08.2004 09:24	0.0299	0.0004
06.08.2004 08:20	0.0296	-0.0003
09.08.2004 10:39	0.0306	0.0010
27.08.2004 10:05	0.0300	-0.0006
15.09.2004 15:17	0.0297	-0.0003
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Average	0.0296	
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Mean Abs. Std. Dev.	0.0005	
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Minimum	0.0288	0.0000
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Maximum	0.0306	0.0012
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Range	0.0018	
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Maximum Difference of the Norm		0.0021

Even over a period of 53 days, the same parameters are reached compared to the short-time stability measurements. Range (0.0014 wt% resp. 0.0018 wt%) and mean absolute deviation (0.0004 wt% resp. 0.0005 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 PIONEER is, among other features, based on the unique 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, especially for the analysis of light elements like magnesium, are guaranteed from the very beginning of any measurement.

Conclusion

The S4 PIONEER is perfectly suited to run magnesium analyses according to DIN 51431-2 in the concentration range 0.010 - 0.50 wt%.

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/ $\sqrt{2}$ range.

The mean and the maximum difference of the short-time stability measurements (about 45 min) of the same sample were far below the maximum value specified in the norm. Even for long-time stability measurements (53 days), the same outstanding parameters were obtained.

Notes

- [1] DIN 51431-2 (1999-07) Testing of lubricants – Determination of magnesium content – Part 2: Analysis by wavelength dispersive X-ray spectrometry (XRS); Beuth Verlag GmbH, Berlin

The picture on page 1 was kindly provided by OMV AG.

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