

S4 EXPLORER

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 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 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

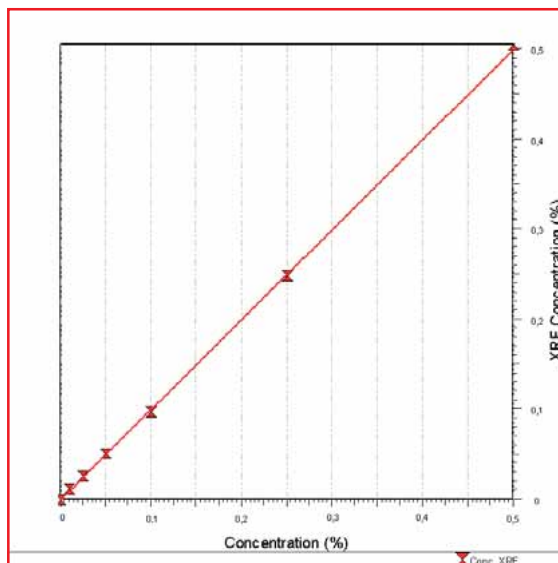
All data were obtained using the following measurement parameters:

Anode	Rhodium
Voltage	30 kV
Current	33 mA
Collimator	0.46°
Crystal	OVO-55 (Multilayer)
Mg Line Position	20.736°
Measuring Time	60 s
Background Position	18.860°
Measuring Time	60 s
Br Line Position	17.362°
Measuring Time	60 s
Detector	Proportional 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.

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]
0.0000	-0.0007	-0.0007	0.0002	12
0.0100	0.0109	0.0009	0.0002	12
0.0250	0.0257	0.0007	0.0002	12
0.0500	0.0504	0.0004	0.0002	12
0.1000	0.0972	-0.0028	0.0003	12
0.2500	0.2487	-0.0013	0.0004	13
0.5000	0.5046	0.0046	0.0006	13

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	0.002
Counting Statistic Deviation	≤0.0006
Limit Of Detection (LOD) (3 σ, 60 s)	0.001

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

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	0.0275	0.0254 - 0.0310	✓
MO402	0.0312	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. 0.0022 wt% at a concentration of 0.0320 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 12:52	0.0322	
23.07.2004 12:56	0.0318	-0.0004
23.07.2004 13:00	0.0318	0.0000
23.07.2004 13:04	0.0321	0.0003
23.07.2004 13:09	0.0315	-0.0006
23.07.2004 13:13	0.0325	0.0010
23.07.2004 13:17	0.0314	-0.0011
23.07.2004 13:21	0.0322	0.0008
23.07.2004 13:26	0.0323	0.0001
23.07.2004 13:30	0.0323	0.0000
23.07.2004 13:35	0.0319	-0.0004
23.07.2004 13:39	0.0321	0.0002
23.07.2004 13:43	0.0315	-0.0006
23.07.2004 13:47	0.0323	0.0008
23.07.2004 13:51	0.0325	0.0002
23.07.2004 13:56	0.0313	-0.0012
23.07.2004 14:00	0.0323	0.0010
23.07.2004 14:04	0.0319	-0.0004
23.07.2004 14:08	0.0323	0.0004
23.07.2004 14:13	0.0320	-0.0003
Average	0.0320	
Mean Abs. Std. Dev.	0.0004	
Minimum	0.0313	0.0000
Maximum	0.0325	0.0012
Range	0.0012	
Maximum Difference of the Norm		0.0022

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 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 12:52	0.0322	
26.07.2004 10:45	0.0317	-0.0005
27.07.2004 08:22	0.0312	-0.0005
28.07.2004 09:24	0.0313	0.0001
29.07.2004 08:24	0.0314	0.0001
30.07.2004 08:33	0.0309	-0.0005
02.08.2004 08:28	0.0320	0.0011
03.08.2004 08:20	0.0320	0.0000
04.08.2004 08:43	0.0320	0.0000
05.08.2004 09:27	0.0313	-0.0007
06.08.2004 08:23	0.0317	0.0004
09.08.2004 10:45	0.0317	0.0000
27.08.2004 08:50	0.0320	0.0003
15.09.2004 11:41	0.0323	0.0003
<hr/>		
Average	0.0317	
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Mean Abs. Std. Dev.	0.0004	
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Minimum	0.0309	0.0000
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Maximum	0.0323	0.0011
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Range	0.0014	
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Maximum Difference of the Norm		0.0022

Even over a period of 53 days, the same parameters are reached compared to the short-time stability measurements. Range (0.0012 wt% resp. 0.0014 wt%) and mean absolute deviation (0.0004 wt% in both cases) 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 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 EXPLORER with 1 kW maximum power ensures even magnesium analyses according to DIN 51431-2 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/ $\sqrt{2}$ range.

The mean and the maximum difference of the short-time stability measurements (about 80 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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Autor:
Arnd Bühler, Bruker AXS GmbH, Karlsruhe, Germany

BRUKER AXS GMBH
OESTLICHE RHEINBRUECKENSTR. 49
D-76187 KARLSRUHE
GERMANY
TEL. (+49) (721) 595-2888
FAX (+49) (721) 595-4587
EMAIL info@bruker-axs.de
www.bruker-axs.de

BRUKER AXS, INC.
5465 EAST CHERYL PARKWAY
MADISON, WI 53711-5373
USA
TEL. (+1) (800) 234-XRAY
TEL. (+1) (608) 276-3000
FAX (+1) (608) 276-3006
EMAIL info@bruker-axs.com
www.bruker-axs.com