

S4 PIONEER

CALCIUM AND ZINC ANALYSIS ACCORDING TO DIN 51391-2

Introduction

DIN 51391-2^[1] describes the determination of the additive elements (Ba, Ca, Cu and Zn) content (mass fraction in g/100g, in the following wt%) of lubricants by wavelength-dispersive X-ray fluorescence spectrometry (WD-XRF). The following discussions, as well as the recent years' round-robin test comparison data, focus on calcium and zinc since copper and barium lost their relevancy as additive elements.

As the composition of the respective samples varies significantly, the application of a matrix correction is mandatory. According to DIN 51391-2, this correction is based on an 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). An optimum matrix correction for the calcium determination is based on Sn $L\alpha$. The norm compliant zinc determination allows the application of two different internal standard elements. Copper is proposed in case the sample itself does not contain any copper. As copper may come in as an additive or wear metal, an alternative internal standard element cobalt was defined.



Sample Preparation - Calcium Determination

Standard and analysis samples are prepared by weighing 20.00 ± 0.01 g of sample or standard sample and 2.00 ± 0.01 g of a 11.7% Sn 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 μ m 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 Parameter - Calcium Determination

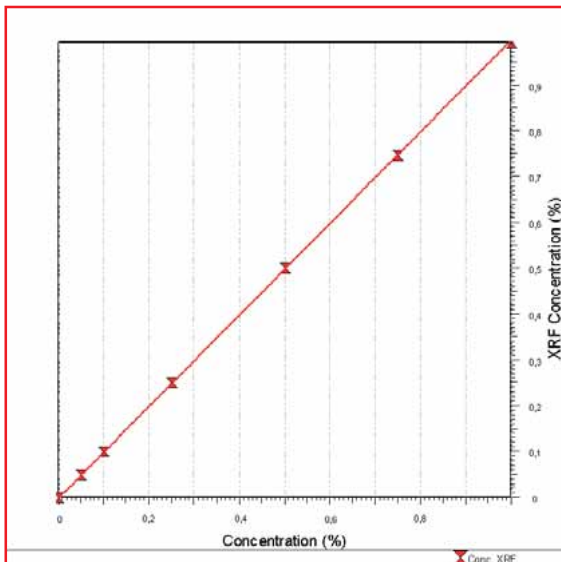
All data were obtained using the following measurement parameters:

Anode	Rhodium
Voltage	50 kV
Current	50 mA
Collimator	0.23°
Crystal	LIF200
Ca Line Position	113.122°
Measuring Time	16 s
Sn Line Position	126.777°
Measuring Time	16 s
Detector	Flow counter with pulse height analysis
Discrimination Window	50 - 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 - Calcium Determination

A norm compliant calibration applies Sn 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	-0.001	-0.001	0.0000	6
0.050	0.051	0.001	0.0001	6
0.100	0.101	0.002	0.0002	6
0.250	0.251	0.001	0.0003	6
0.500	0.499	-0.001	0.0004	6
0.749	0.753	0.005	0.0006	6
1.000	0.988	-0.013	0.0007	6

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

Concentration Range	0.000 - 1.000
Number of Standards	7
Intensity Model	Raw Intensities
Calibration Model	Internal Standard Sn
Regression Minimizes	Relative Errors
Mean Regression Deviation	0.0036
Counting Statistic Deviation	≤0.0007
Limit Of Detection (LOD) (3 σ, 16 s)	0.0006

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

- 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 - Calcium Determination

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	
MO381	0.401	0.386 - 0.414	✓
MO382	0.140	0.126 - 0.154	✓
MO401	0.231	0.218 - 0.247	✓
MO402	0.287	0.275 - 0.303	✓
MO Engine Oil			

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

Repeatability - Calcium Determination

In addition to the accuracy of the analysis method, the precision was tested analyzing the DIN round-robin MO381 engine oil sample 20 times. According to DIN 51391-2, the difference between two consecutive results in the range of 0.400 wt% must not exceed 0.01 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 has been 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 11:36	0.4033	
23.07.2004 11:38	0.4023	-0.0010
23.07.2004 11:40	0.4031	0.0008
23.07.2004 11:43	0.4017	-0.0014
23.07.2004 11:45	0.4010	-0.0007
23.07.2004 11:47	0.4032	0.0022
23.07.2004 11:49	0.4019	-0.0013
23.07.2004 11:51	0.4025	0.0006
23.07.2004 11:54	0.4025	0.0000
23.07.2004 11:56	0.4020	-0.0005
23.07.2004 11:58	0.4017	-0.0003
23.07.2004 12:00	0.4016	-0.0001
23.07.2004 12:02	0.4014	-0.0002
23.07.2004 12:04	0.4012	-0.0002
23.07.2004 12:07	0.4033	0.0021
23.07.2004 12:09	0.4029	-0.0004
23.07.2004 12:11	0.4030	0.0001
23.07.2004 12:13	0.4023	-0.0007
23.07.2004 12:15	0.4038	0.0015
23.07.2004 12:17	0.4020	-0.0018
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Average	0.4023	
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Mean Abs. Std. Dev.	0.0008	
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Minimum	0.4010	0.0000
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Maximum	0.4038	0.0022
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Range	0.0028	
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Maximum Difference of the Norm		0.0100

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 MO381 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 11:36	0.4033	
26.07.2004 10:36	0.4027	-0.0006
27.07.2004 08:14	0.4058	0.0031
28.07.2004 09:16	0.4026	-0.0032
29.07.2004 08:14	0.4022	-0.0004
30.07.2004 08:24	0.4029	0.0007
02.08.2004 08:18	0.4014	-0.0015
03.08.2004 08:11	0.4027	0.0013
04.08.2004 08:27	0.4032	0.0005
05.08.2004 09:17	0.4026	-0.0006
06.08.2004 08:13	0.4023	-0.0003
09.08.2004 10:31	0.4038	0.0015
27.08.2004 09:59	0.4033	-0.0005
15.09.2004 15:13	0.4021	-0.0012
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Average	0.4029	
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Mean Abs. Std. Dev.	0.0010	
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Minimum	0.4014	0.0003
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Maximum	0.4058	0.0032
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Range	0.0044	
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Maximum Difference of the Norm		0.0100

Even over a period of 53 days, the same parameters are reached compared to the short-time stability measurements. Range (0.0028 wt% resp. 0.0044 wt%) and mean absolute deviation (0.0008 wt% resp. 0.0010 wt%) are almost the same and far below 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 are guaranteed from the very beginning of any measurement.

Sample Preparation - Zinc Determination

Standard and analysis samples are prepared by weighing 20.00 ± 0.01 g of sample or standard sample and 2.00 ± 0.01 g of a 11.7% Sn 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 Parameter - Zinc Determination

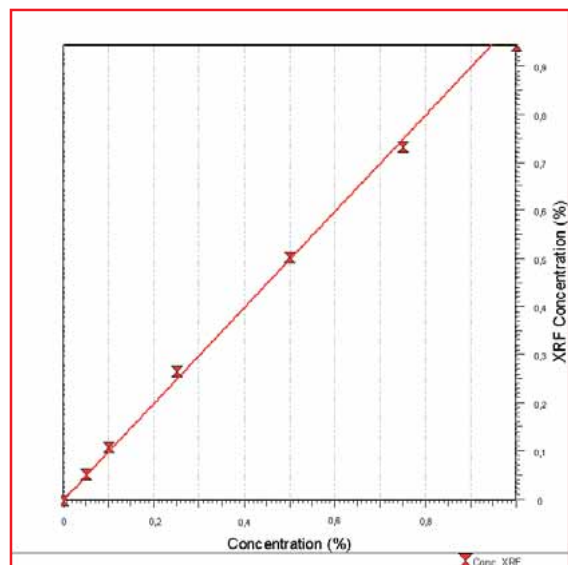
All data were obtained using the following measurement parameters:

Anode	Rhodium
Voltage	50 kV
Current	15 mA
Primary Beam Filter	800 μm Al
Collimator	0.23°
Crystal	LIF200
Zn Line Position	41.812°
Measuring Time	20 s
Background Position	46.500°
Measuring Time	20 s
Co Line Position	52.818°
Measuring Time	20 s
Cu Line Position	45.044°
Measuring time	20 s
Detector	Scintillation counter with pulse height analysis
Discrimination Window	30 - 170%
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 - Zinc Determination

In practice, cobalt is used as internal standard element for the zinc determination more often than copper. The latter is feared to be in the sample as wear metal in used oils or as additive element itself. As intensity ratioing to the internal standard element is restricted to the case that the respective element is not present in the sample, cobalt is preferred in practice. 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	-0.003	-0.003	0.0000	3
0.050	0.052	0.002	0.0001	3
0.100	0.107	0.007	0.0002	3
0.250	0.265	0.015	0.0003	3
0.500	0.504	0.004	0.0005	3
0.750	0.732	-0.018	0.0005	3
1.000	0.942	-0.058	0.0006	3

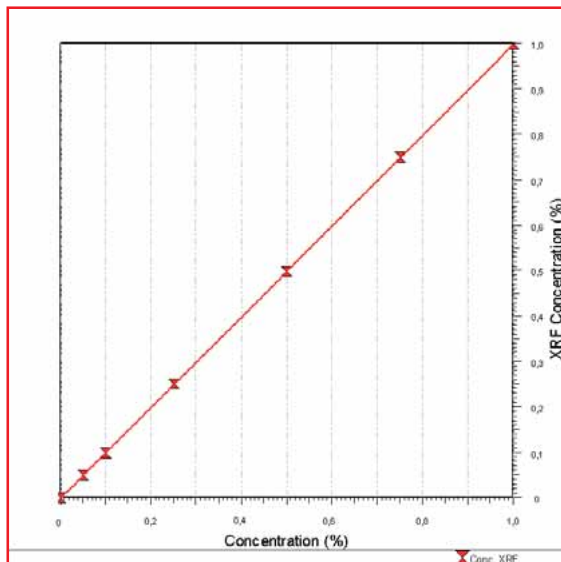
The calibration can be summarized as follows (concentrations in wt%):

Concentration Range	0.000 - 1.000
Number of Standards	7
Intensity Model	Net Intensities
Calibration Model	Internal Standard Co
Regression Minimizes	Relative Errors
Mean Regression Deviation	0.0026
Counting Statistic Deviation	≤ 0.0006
Limit Of Detection (3σ , 20 s)	0.0003

These data show clearly that when using cobalt as internal standard for the zinc determination it is

impossible to obtain a straight calibration curve. A calibration curve without internal standard is even more curved as the zinc fluorescence radiation is more absorbed inside the sample the higher the zinc content is (and so the heaviest matrix element). But contrary to other norms, it is not sufficient to relate the analyte intensity to a similarly behaving element line in case of cobalt. The calibration function is still slightly curved. This is reflected by a mean regression deviation of 0.026 wt% which is much too much for the given concentration range and repeatability.

Changing the linear internal standard calibration model to a quadratic one definitely improves the linearity of the calibration:



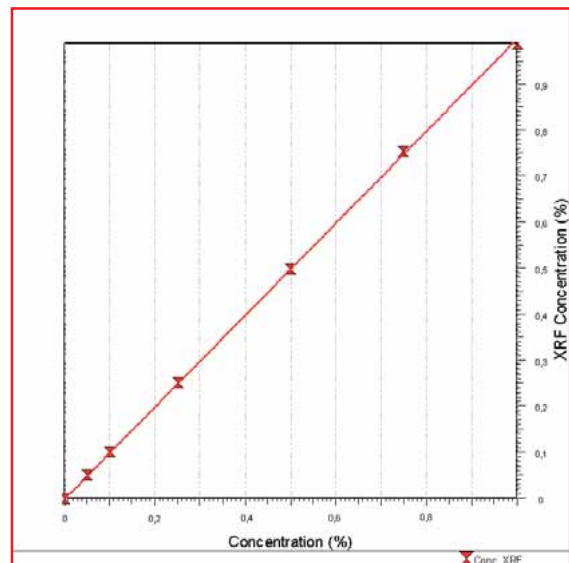
Conc.	Conc. XRF	Absolute Deviation	Count.Stat. Deviation	LOD [mg/kg]
0.000	0.000	0.000	0.0000	2
0.050	0.050	0.000	0.0001	2
0.100	0.100	0.000	0.0002	2
0.250	0.251	0.001	0.0003	2
0.500	0.498	-0.002	0.0004	2
0.750	0.751	0.001	0.0006	2
1.000	1.000	0.000	0.0007	2

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

Concentration range	0.000 - 1.000
Number of Standards	7
Intensity Model	Raw Intensities
Calibration Model	Internal Standard Co, quadratic
Regression Minimizes	Relative Errors
Mean Regression Deviation	0.001
Counting Statistic Deviation	≤0.0007
Limit Of Detection (3 σ, 20 s)	0.0002

The imperfect matrix correction by a cobalt based linear calibration is caused by the fact that one of the preconditions is breached. Indeed there is no cobalt present in the sample and the cobalt fluorescence line is close to the zinc one, but the analyte line significantly enhances the fluorescence of the internal standard in case of cobalt. Therefore the zinc intensity is attenuated and the cobalt intensity (secondary) enhanced. Considering, that the cobalt concentration is constant whereas the zinc concentration of the standard samples is increasing, leads to the fact, that the calibration curve differs (more to smaller values compared to straight line) the higher the zinc content is. As this curved deviation depends upon the analyte concentration, a quadratic application of the internal standard calibration model compensates this effect.

Copper instead of cobalt as internal standard should not show this effect at all or at this extent, as it's fluorescence line is enhanced by zinc less effectively than the cobalt line. The respective calibration is shown by the following graph and table:



Conc.	Conc. XRF	Absolute Deviation	Count.Stat. Deviation	LOD [mg/kg]
0.000	-0.001	-0.001	0.0000	6
0.050	0.051	0.001	0.0001	6
0.100	0.101	0.002	0.0002	6
0.250	0.251	0.001	0.0003	6
0.500	0.499	-0.001	0.0004	6
0.749	0.753	0.005	0.0006	6
1.000	0.988	-0.013	0.0007	6

Matrix correction, and so linearity of the calibration function, is much better using copper as internal standard compared to cobalt. There is just one sample with the highest zinc content showing a slight negative deviation. The calibration can be summarized as follows (concentrations in wt%):

Concentration Range	0.000 - 1.000
Number of Standards	7
Intensity Model	Net Intensities
Calibration Model	Internal Standard Cu
Regression Minimizes	Relative Errors
Mean Regression Deviation	0.006
Counting Statistic Deviation	≤ 0.0007
Limit Of Detection (3 σ , 20 s)	0.0006

In theory, the application of copper as internal standard for the zinc determination is preferred to the use of cobalt as the secondary enhancement of the cobalt line is more serious. In practice, the risk of a potential copper content of the samples is estimated more seriously so that in many cases a quadratic calibration of internal standard cobalt is used. Therefore the following determinations of accuracy and repeatability of the zinc content were based on this model.

Accuracy - Zinc Determination

As a next 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	
MO381	0.126	0.117 - 0.131	✓
MO382	0.139	0.131 - 0.145	✓
MO401	0.143	0.130 - 0.151	✓
MO402	0.134	0.121 - 0.138	✓
MO Engine Oil			

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

Repeatability - Zinc Determination

In addition to the accuracy of the analysis method, the precision was tested analyzing the DIN round-robin MO382 base oil sample 20 times. According to DIN 51391-2, the difference between two consecutive results in the range of 0.139 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 MO382 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 13:04	0.1390	
23.07.2004 13:07	0.1389	-0.0001
23.07.2004 13:10	0.1382	-0.0007
23.07.2004 13:12	0.1388	0.0006
23.07.2004 13:17	0.1396	0.0008
23.07.2004 13:19	0.1383	-0.0013
23.07.2004 13:22	0.1387	0.0004
23.07.2004 13:24	0.1379	-0.0008
23.07.2004 13:27	0.1399	0.0020
23.07.2004 13:30	0.1384	-0.0015
23.07.2004 13:33	0.1388	0.0004
23.07.2004 13:35	0.1390	0.0002
23.07.2004 13:38	0.1397	0.0007
23.07.2004 13:41	0.1393	-0.0004
23.07.2004 13:43	0.1391	-0.0002
23.07.2004 13:46	0.1385	-0.0006
23.07.2004 13:49	0.1386	0.0001
23.07.2004 13:52	0.1396	0.0010
23.07.2004 13:55	0.1386	-0.0010
23.07.2004 13:57	0.1383	-0.0003
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Average	0.1389	
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Mean Abs. Std. Dev.	0.0005	
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Minimum	0.1379	0.0001
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Maximum	0.1399	0.0020
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Range	0.0020	
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Maximum Difference of the Norm		0.0050

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

To get additional data for a long-time stability, the same prepared sample MO382 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 13:04	0.1390	
26.07.2004 10:38	0.1376	-0.0014
27.07.2004 08:17	0.1393	0.0017
28.07.2004 09:19	0.1398	0.0005
29.07.2004 08:18	0.1390	-0.0008
30.07.2004 08:28	0.1389	-0.0001
02.08.2004 08:23	0.1387	-0.0002
03.08.2004 08:14	0.1394	0.0007
04.08.2004 08:30	0.1401	0.0007
05.08.2004 09:21	0.1395	-0.0006
06.08.2004 08:17	0.1391	-0.0004
09.08.2004 10:35	0.1389	-0.0002
27.08.2004 10:04	0.1390	0.0001
15.09.2004 15:15	0.1400	0.0010
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Average	0.1392	
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Mean Abs. Std. Dev.	0.0006	
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Minimum	0.1376	0.0001
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Maximum	0.1401	0.0017
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Range	0.0025	
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Maximum Difference of the Norm		0.0050

Even over a period of 53 days, the same parameters are reached for the zinc determination compared to the short-time stability measurements. Range (0.0020 wt% resp. 0.0025 wt%) and mean absolute deviation (0.0005 wt% resp. 0.0006 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.

Conclusion

The S4 PIONEER is perfectly suited to run calcium and zinc analyses according to DIN 51391-2 in the concentration range 0.050 - 1.00 wt%.

The accuracy of the Ca and Zn 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 50 min) of the same sample were far below the maximum value specified in the norm for Ca and Zn. Even for long-time stability measurements (53 days), the same outstanding parameters were obtained for both elements.

In case of the zinc determination the application of internal standard elements copper and cobalt was compared. Copper was found to have the better matrix correction properties. In practice, it is feared to be present in the sample as additive or wear metal so that its use as an internal standard would fail. Contrary to this, cobalt is not expected to be in typical samples and this leads to its preferred application. Nevertheless the cobalt line is (secondarily) enhanced by the zinc fluorescence radiation. Therefore, the internal standard calibration has to use a quadratic model.

Notes

[1] DIN 51391 Part 2 (1994-03) Determination of additive elements content of lubricants by wavelength-dispersive X-ray fluorescence; Beuth Verlag GmbH, Berlin

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

Prolene® ist ein eingetragenes Warenzeichen der Firma Chemplex Industries Inc.

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