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Recertification of Zn and Zn/Fe secondary ("master") reference standards

The Helmut Fischer GmbH applies primary reference standards to quantify "standard calibration set" products. This report describes the check or recertification of Zn and Zn/Fe primary reference standards.

All primary reference standards were checked together with an ensemble of traceable and carefully examined self-supporting Zn foils (table 1) quantified according to a gravimetric procedure accredited by either DKD or DAkkS /1/.

Gravimetric primary reference standards (foils)
All primary standard foils of Tab. 1 have been used to calibrate the standardless XRF technique. The respective XRF results do not meet the gravimetric values completely. The differences have the order of magnitude of the measuring uncertainties itself.

Table 1 *Zn thickness of primary reference foils used for the recertification. Thickness values (given in µm) were converted from mass per unit area data assuming a density of 7.14 g/cm^3.*

Code	Zn in µm			
	gravimetric value	u (k=2)	XRF value	u (k=2)
BAA Zn 2,5 µm 260312	2,4735	0,0015	2,47	0,02
BAB Zn 5 µm 260312	4,7551	0,0015	4,75	0,05
BAC Zn 15 µm 260312	15,2521	0,0039	15,10	0,15
BAD Zn 20 µm 260312	19,7225	0,0550	19,81	0,20
BAE 3 Zn 25 µm 020512	22,9469	0,0069	22,70	0,23
BAF 2 Zn 35 µm 180412	34,1186	0,0175	34,05	0,34

Experimental and Spectrum evaluation (DefMA, *cf.* /2/)

Fischerscope© XDAL, 50 kV, Ni primary filter, aperture Ø 0.6 mm; all samples were measured with a Zn/Fe application. The self-supporting Zn foils were therefore put on a Fe plate. The Zn thickness or the Zn mass per unit area is determined only from the Zn-K characteristic radiation. Enhancement from the base material (Fe) does not occur.
All samples except of the gravimetric primary reference standard foils were measured with 9 measurements with 45 s uniformly distributed over an area of 2 mm x 2 mm (with

scan mode). The gravimetric primary reference standard foils were measured with 400 measurements with 45 s (with the scan mode) uniformly distributed over an area of 5 cm *5 cm. Since the measuring distance affects the geometry factor, it must be fixed within a small tolerance. The Fischerscope X-Ray system's autofocus tool achieves an acceptable range of about 20-50 µm.
The measurements were repeated several times to ensure consistency. Over the time period of the experiment (3 days) no drift was detected.

Results of recalibration

The standardfree XRF method calibrated with 6 primary foil standards (Tab. 1) together with the existing secondary reference standards itself has been applied for the recertification of secondary standards (masters) of table 2 and 3. Figure 1 shows the rel. difference as a function of the standard free XRF value. The values for the primary foil standards are plotted in red and the secondary standards in blue. All samples are taken into account for the calculation of the best-fit line. The estimated weighed of the primary ref. standards is three times higher than for the secondary standards.

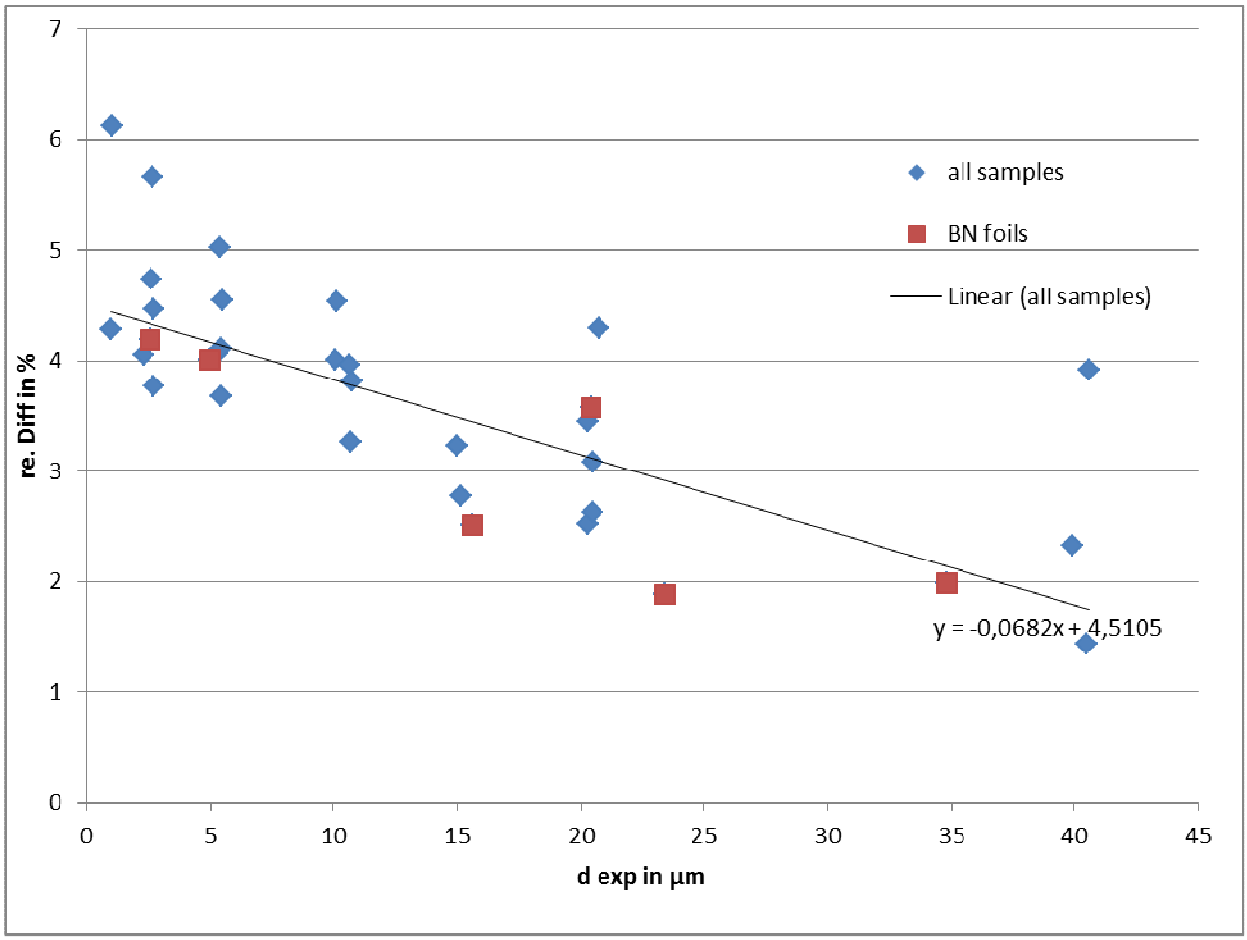

***Figure 1**: Rel. difference between the nominal and standard free value as a function of the standard free XRF value. The results for the primary foil standards are plotted in red ("BN foils") and the secondary standards in blue.*

All values for Zn are converted from the mass per unit area data with the density of Zn = 7,14 g/cm^3. The given uncertainties are standard measuring uncertainties for a confidence level 95 % (k = 2)

Table 2 *Self-supporting Zn foils*

Code	Zn in µm			
	old value	u (k=2)	new value	u (k=2)
Set 18707				
ACXVF	0,96	0,01	0,96	0,01
ACXVI	2,5	0,03	2,54	0,03
ACXVK	5,1	0,05	5,15	0,05
ACXVQ	19,6	0,20	19,66	0,20
ACXVM	9,68	0,10	9,75	0,10
ACXVO	14,75	0,15	14,64	0,15
Set 15849				
ABHAA	2,61	0,03	2,61	0,03
ABAKS	5,25	0,05	5,27	0,05
ABBBD	10,36	0,10	10,36	0,10
ABAYT	19,85	0,20	20,09	0,20
ABAZD	39,02	0,4	39,22	1

Table 3 *Zn/Fe standards*

Code	Zn in µm			
	old value	u (k=2)	new value	u(k=2)
Set 18706				
ACXVG	0,95	0,02	0,97	0,02
ACXVH	2,48	0,02	2,49	0,02
ACXVJ	5,07	0,03	5,07	0,05
ACXVL	9,7	0,04	9,72	0,10
ACXVN	14,5	0,08	14,46	0,15
ACXVP	19,75	0,08	19,62	0,20

Set 15846				
ABGZW	2,235	0,008	2,23	0,02
ABAKP	5,203	0,013	5,20	0,05
ABBAU	10,21	0,029	10,23	0,10
ABAYP	19,955	0,028	19,85	0,20
ABAYV	39,92	0,05	39,80	1

Discussion

As shown in the tables above, in most cases the recertified values are very close to the old ones. The differences are usually in the same order of magnitude as the measuring uncertainties. Although the reasons for these discrepancies cannot be explained in each case, the spatial inhomogeneity is probably an important issue which has not previously been accounted for. Consequently, the recalibrated results are mean values valid for the very restricted area of just 2 mm x 2 mm.

Further basic reference material will be produced in future to achieve improved data with smaller measuring uncertainties.

References

/1/ Reg. No. D-K-15076-01-00.

/2/ V. Rößiger and B. Nensel, in “Handbook of practical X-Ray fluorescence analysis”, Springer 2006, p. 554.