Fischer Traceability Report JL-2014-12-Au-foils Sindelfingen, 12/19/2014

Characterization of self-supporting Au foils and Au layers on mylar

Abstract:

New Au primary reference material made of self-supporting Au foils has been produced and used for the calibration of secondary reference standards. These secondary standards consist either of recalibrated older CRM or new material.

Experimental details

New primary reference material made of self-supporting Au foils has been produced using the accredited mass-per-unit-area-approach of the Fischer calibration laboratory. On the basis of these new foils the existing secondary Au standards (Au on Mylar and self-supporting Au foils) have been re-evaluated. They will serve as accurate, precise and traceable reference standards for the production of Au reference material.

For the raw material consisting of 4 self-supporting Au foils mass and area have been measured. The resulting quantity mass per unit area is used to calibrate reference free XRF measurements. Finally a XRF device in combination with the reference free fundamental parameter method is used as a comparator for the calibration of the existing secondary reference material. XRF measurements have been carried out using the Fischerscope XUV from the DAkkS laboratory and Software Version WinFTM 6.32x (24.10.2014). The experimental parameters are summarized in Tables I and II. For the measurement of the primary standards BBN, BBP, BBQ almost the whole area of the foil samples has been mapped with 525 measurement spots arranged in a 25x25 matrix. The dimension of the samples was approx. 50 x 50 mm. The fourth sample, BBR, was only about 30x20 mm and was mapped with 300 spots arranged in a 20x15 matrix. The data of each of the secondary standards to be characterized were obtained as mean value of 16 individual measurements distributed over a 4x4 matrix in a central area of 2mm x 2 mm.

Parameter	Value	Comments
Device	Fischerscope© XUV	
Voltage, Filter	50keV, Al 1000 µm primary filter	
Aperture collimator	0.6 mm	
Software version	6.32x	
Spots per sample	525 (300)	25x25 (20x15) matrix
Duration per spot	120 s	
Measured area	148.4 mm² (active size) (84.8 mm²)	
Anode current	1000 mA	

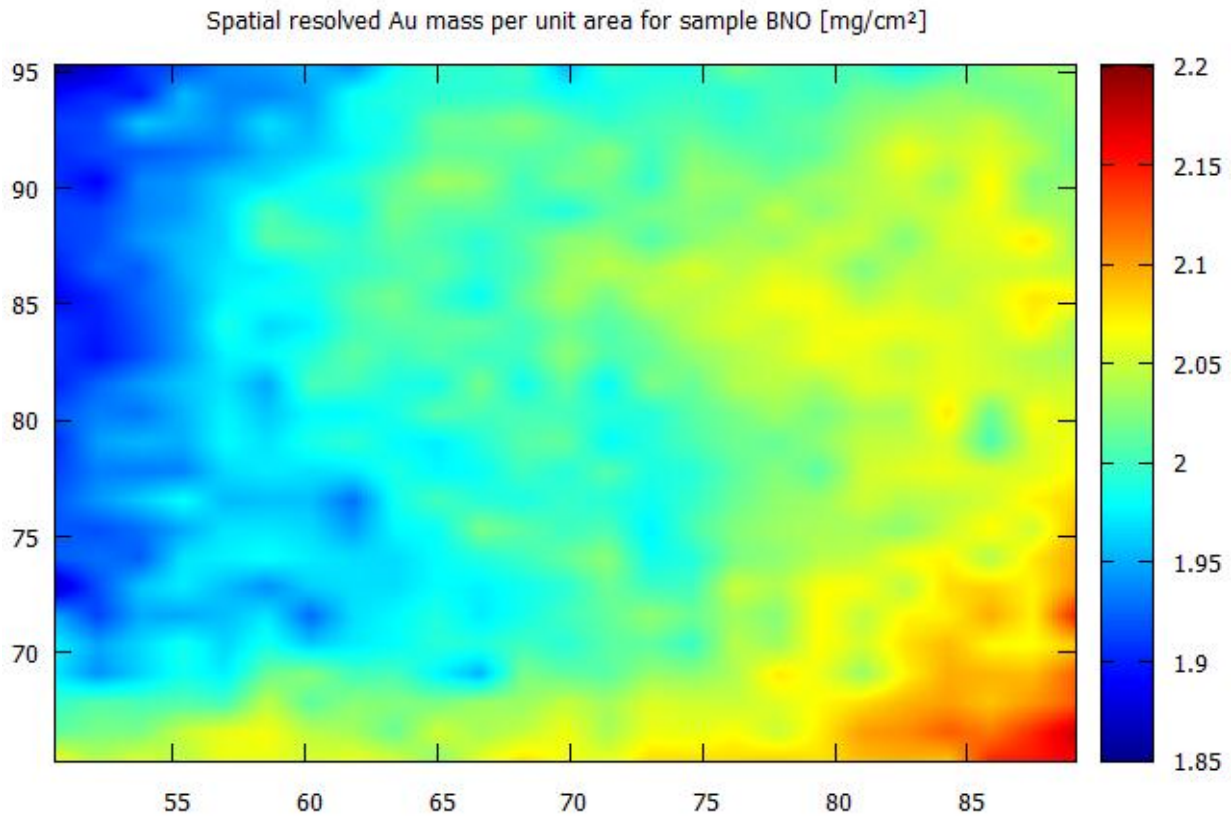
Table I : experimental parameters for the XRF measurement of the Au primary standards.

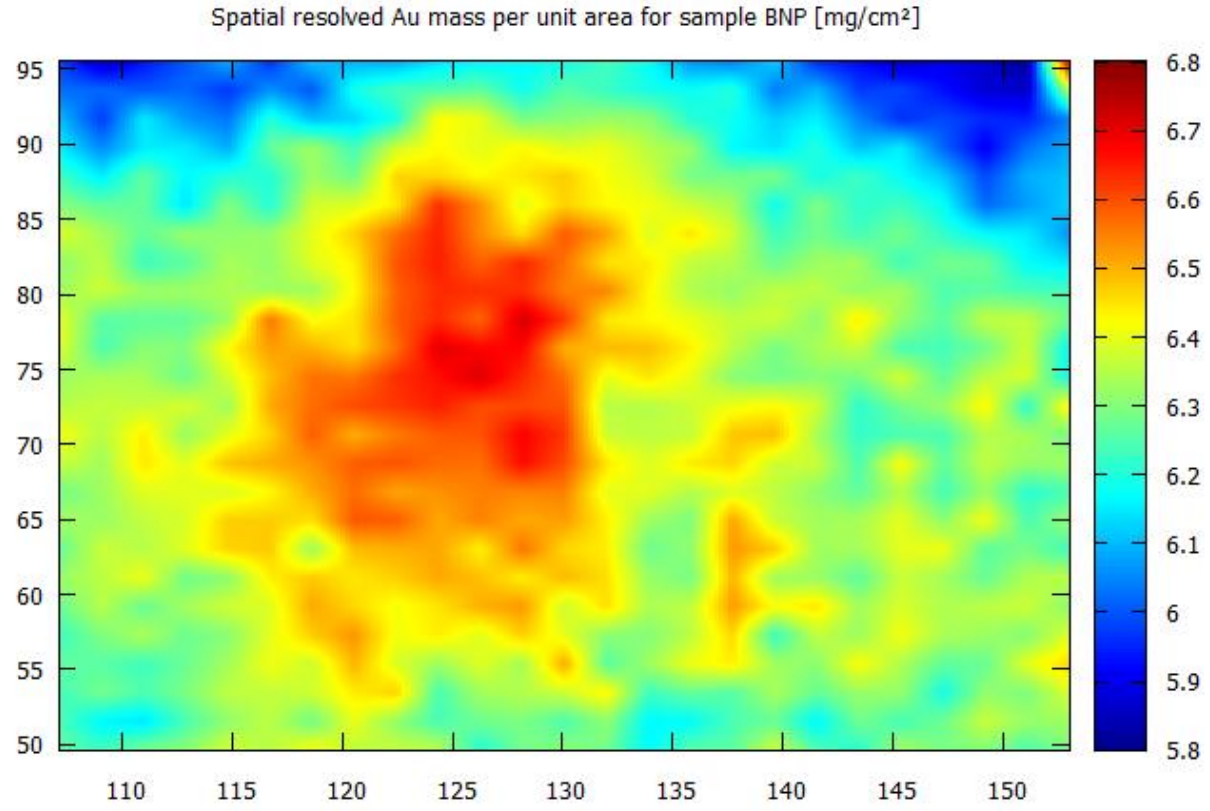
The mean value of the 525 (300) individual XRF measurements per sample is representative for the mean value of the foil as a whole and can be correlated to the result from the gravimetric approach.

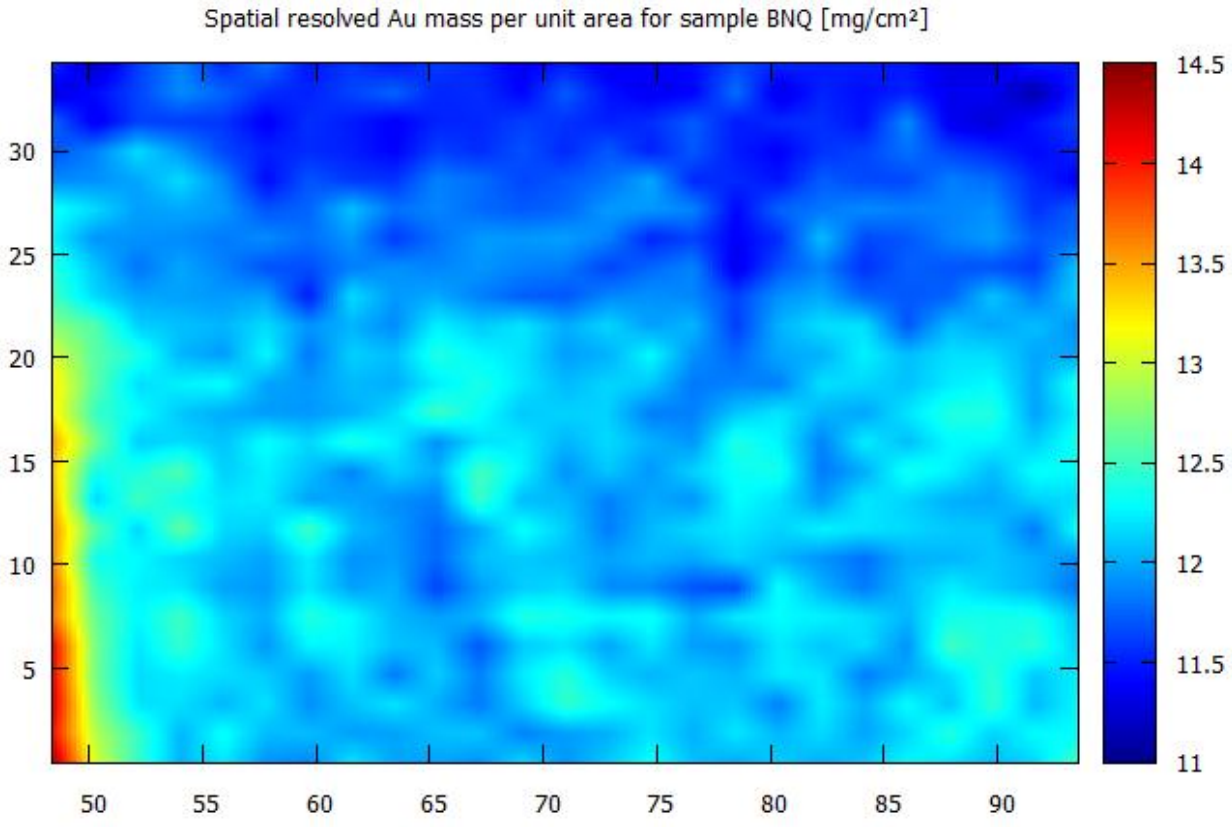
Parameter	Value	Comments
Device	Fischerscope© XUV	
Voltage, Filter	50keV, Al 1000 µm primary filter	
Aperture collimator	0.6 mm	
Software version	6.32x	
Spots per sample	16	
Duration per spot	120 s	
Measured area	4.5 mm² (active size)	4x4 Matrix with intermediate spots
Anode current	1000 mA	

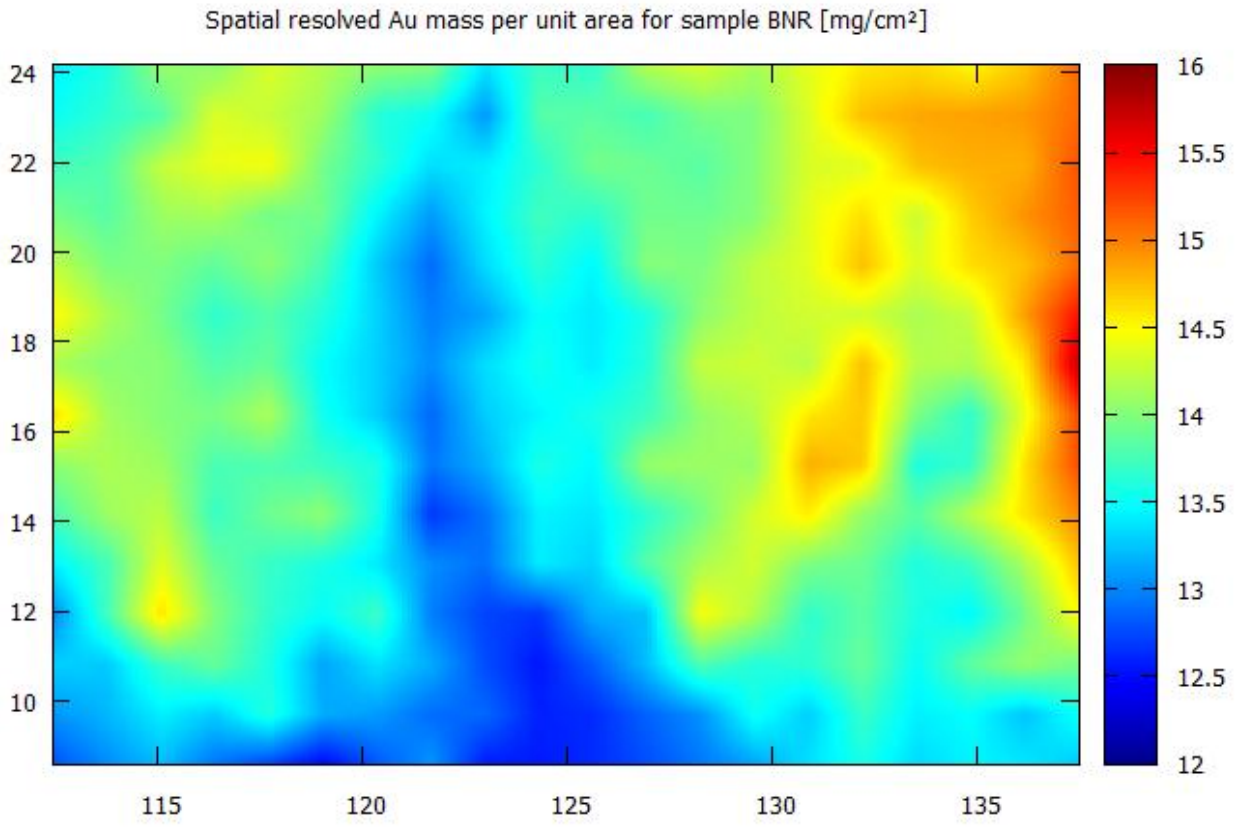
Table II : experimental parameters for the XRF measurement of the Au secondary reference standards to be re-evaluated

The spatial resolved XRF results for the primary reference standards are displayed using heat maps in the next four pictures. It is noteworthy that all foils exhibit rather large inhomogeneities in their thickness.




Spatial resolved Au mass per unit area for sample BNP [mg/cm²]
95
90
85
80
75
70
65
60
55
50
110
115
120
125
130
135
140
145
150
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6
5.9
5.8


Spatial resolved Au mass per unit area for sample BNQ [mg/cm²]
30
25
20
15
10
5
50
55
60
65
70
75
80
85
90
14.5
14
13.5
13
12.5
12
11.5
11



Data analysis and results

Table III displays a summary of reference free XRF measurement of the 4 foils and a zero probe together with results from gravimetry (mass per unit area). The deviations from reference free XRF measurements to the gravimetric reference values are in the order of 2-3% only and displayed as well.

		XRF FP			Gravimetry			
Block no	Code	FM mg/cm²	St.Dev. mg/cm²	S.E.	FM mg/cm²	u(k=1) mg/cm²	Diff XRF-G mg/cm²	u mg/cm²
29	ZERO	0,001	0,001	0,001	0	0	0,001	0,00025
6	BBP	2,0082	0,0499	0,0020	1,9451	0,0009	0,0631	0,0022
7	BBN	6,3292	0,1573	0,0063	6,1136	0,0028	0,2156	0,0069
8	BBQ	12,0033	0,4026	0,0161	11,5711	0,0047	0,4322	0,0168
9	BBR	13,8024	0,6029	0,0348	13,3609	0,0060	0,4415	0,0353

Table III : XRF analysis of primary reference material

Using the statistical programming language R a linear regression (polynomial 1st order) was performed to correlate reference values and the difference (XRF – G), i.e. the difference between the reference free EDXRF values and the mass per unit area values from the gravimetric approach. Data and fit are shown in Fig. 5 together with the corresponding confidence bands (95%). The fit parameters and uncertainties are summarized below.

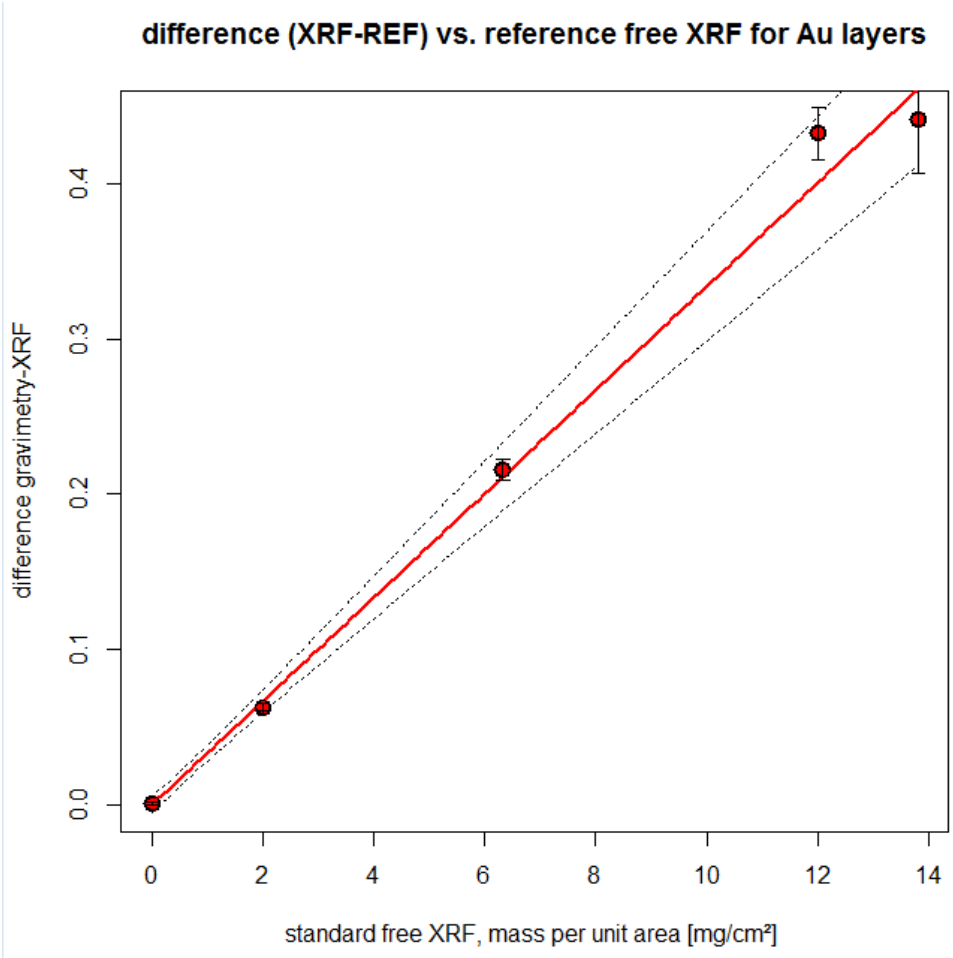


Fig. 5 Linear regression between the difference (gravimetry - standard free XRF) vs. standard free XRF using a linear correlation. The area between the dotted lines represents the confidence band. Fit and graphics have been produced using the statistical programming language R.

Weighted Residuals:

1	2	3	4	5
0.1786	-2.0221	0.6820	1.9634	-0.4938

Coefficients:

Estimate	Std. Error	t value	Pr(>|t|)	
(Intercept)	0.0009222	0.0004244	2.173	0.118
XRF	0.0331832	0.0011173	29.700	8.38e-05 ***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 1.701 on 3 degrees of freedom

Multiple R-squared: 0.9966, Adjusted R-squared: 0.9955

F-statistic: 882.1 on 1 and 3 DF, p-value: 8.383e-05

The coefficients were finally used for the production / calibration of new or existing secondary reference materials by using the predicted differences (interpolated data) for the corresponding XRF data. Uncertainties are calculated using the Gaussian error propagation where the uncertainty of the mean of the XRF value is given as

$$u = \frac{\sigma}{\sqrt{N}}$$

with N is either 525 or 300 for the primary reference material and 16 for the secondary reference material. Results are summarized in table IV.

	Code	FM mg/cm²	St.Dev. mg/cm²	S.E. mg/cm²	Pred DIFF mg/cm²	u mg/cm²	cal FM mg/cm²	U(k=2) mg/cm²	thickness µm	U(k=2) µm	thickness µ''	U(k=2) µ''
	ADKET	0,1041	0,0013	0,0003	0,0044	0,0022	**0,0997**	**0,0044**	0,0517	0,0023	2,0337	0,0896
	ADKEU	0,2090	0,0019	0,0005	0,0079	0,0030	**0,2011**	**0,0061**	0,1042	0,0031	4,1021	0,1240
	ADKEV	0,5039	0,0027	0,0007	0,0176	0,0043	**0,486**	**0,009**	0,2519	0,0045	9,9192	0,1768
	ADKEW	1,016	0,006	0,001	0,035	0,009	**0,98**	**0,02**	0,508	0,009	20,01	0,36
	ADKEX	1,976	0,008	0,002	0,066	0,013	**1,91**	**0,03**	0,989	0,014	38,96	0,55
	ABVAZ	2,957	0,019	0,005	0,099	0,028	**2,86**	**0,06**	1,481	0,029	58,30	1,16
	ABVBQ	4,548	0,022	0,006	0,152	0,034	**4,40**	**0,07**	2,278	0,036	89,68	1,41
	ABVGH	8,467	0,060	0,015	0,282	0,087	**8,19**	**0,18**	4,241	0,091	166,97	3,59
	ACLUT	12,42	0,13	0,03	0,41	0,19	**12,01**	**0,38**	6,22	0,20	244,9	7,8
New CRM												
AECNK	50	0,1026	0,0010	0,0002	0,0043	0,0019	**0,098**	**0,004**	0,0509	0,0020	2,0043	0,0783
AECNL	100	0,4080	0,0030	0,0007	0,0145	0,0044	**0,394**	**0,009**	0,2039	0,0046	8,0270	0,1826
AECNM	250	0,4708	0,0033	0,0008	0,0165	0,0049	**0,454**	**0,010**	0,2354	0,0052	9,2669	0,2048
AECNN	500	0,9379	0,0049	0,0012	0,0320	0,0075	**0,906**	**0,015**	0,4694	0,0078	18,4789	0,3085
AECNO	1000	1,867	0,009	0,002	0,063	0,014	**1,804**	**0,028**	0,935	0,014	36,80	0,57
AECNP	1300	2,671	0,018	0,004	0,090	0,026	**2,582**	**0,052**	1,338	0,027	52,67	1,07
AECNQ	2300	4,543	0,013	0,003	0,152	0,023	**4,39**	**0,05**	2,275	0,024	89,58	0,96
AECNR	3000	5,903	0,027	0,007	0,197	0,042	**5,71**	**0,09**	2,956	0,044	116,39	1,75
AECNS	4000	5,48	0,09	0,02	0,18	0,12	**5,29**	**0,24**	2,74	0,12	108,0	4,9
AECNT	7000	14,10	0,19	0,05	0,47	0,26	**13,63**	**0,53**	7,06	0,28	278,1	10,8

Table IV: Results of the calibration using coefficients from the linear regression to the primary reference standards (see above). The upper part of this table summarizes the results (re-evaluation) for existing reference foils, the lower part refers to new CRM.

ADEKT-ACLUT refer to existing CRM whereas AECNK-AECNT are new secondary reference standards. The agreement between the new values and the nominal values from the last calibration for samples ADEKT-ACLUT is good (see table V). The statistical uncertainties could be reduced by 20-30%.

	Old Thickness µm	U(k=2) µm	New Thickness µm	U(k=2) µm
ADKET	**0,053**	0,003	**0,052**	0,002
ADKEU	**0,107**	0,004	**0,104**	0,003
ADKEV	**0,260**	0,006	**0,252**	0,004
ADKEW	**0,520**	0,012	**0,508**	0,009
ADKEX	**1,014**	0,024	**0,989**	0,014
ABVAZ	**1,50**	0,04	**1,48**	0,03
ABVBQ	**2,287**	0,042	**2,278**	0,036
ABVGH	**4,236**	0,04	**4,241**	0,091
ACLUT	**6,289**	0,24	**6,22**	0,20

Table V: Comparison between the results from the calibration in this report and the last calibration. Due to the new primary reference material the statistical uncertainty could be reduced compared to the older ones.

Sindelfingen, 12/19/2014

Dr. Jörg Leske