Fischer Traceability Report JL-2013-08-Cu Sindelfingen, 08/07/2013

Characterization of Cu primary and secondary reference materials

Abstract:

Four new Cu primary reference standards (Cu foils) have been produced and used for the calibration of existing Cu secondary reference standards.

Experimental details

Primary reference material (self-supporting Cu foils) has been produced on the basis of gravimetric measurements and data from the universal standard free XRF fundamental parameter method. XRF measurements have been carried out using a Fischerscope XUV. The experimental XRF parameters are summarized in Tables I and II, for the measurement of the primary reference materials and the secondary reference standards, respectively. For the measurement of the primary standards a 25x25 matrix of 625 equidistant measurement spots covering an area of approx. 50mm x 50mm (BBD,BBE, BBH) and 50mmx25mm (BBF)were chosen to cover the whole surface of the Cu foils. In addition the WinFTM scan mode was used to further increase the measured area. 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	6.28 LabDB	
Spots per sample	625 (375 for BBH)	Scan mode
Duration per spot	30 s	
Measured area	50 x 50 mm (BBD,BBE,BBF) 50 x 35 mm (BBH)	25x25 Matrix 25x15 Matrix
Anode current	300 mA	

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

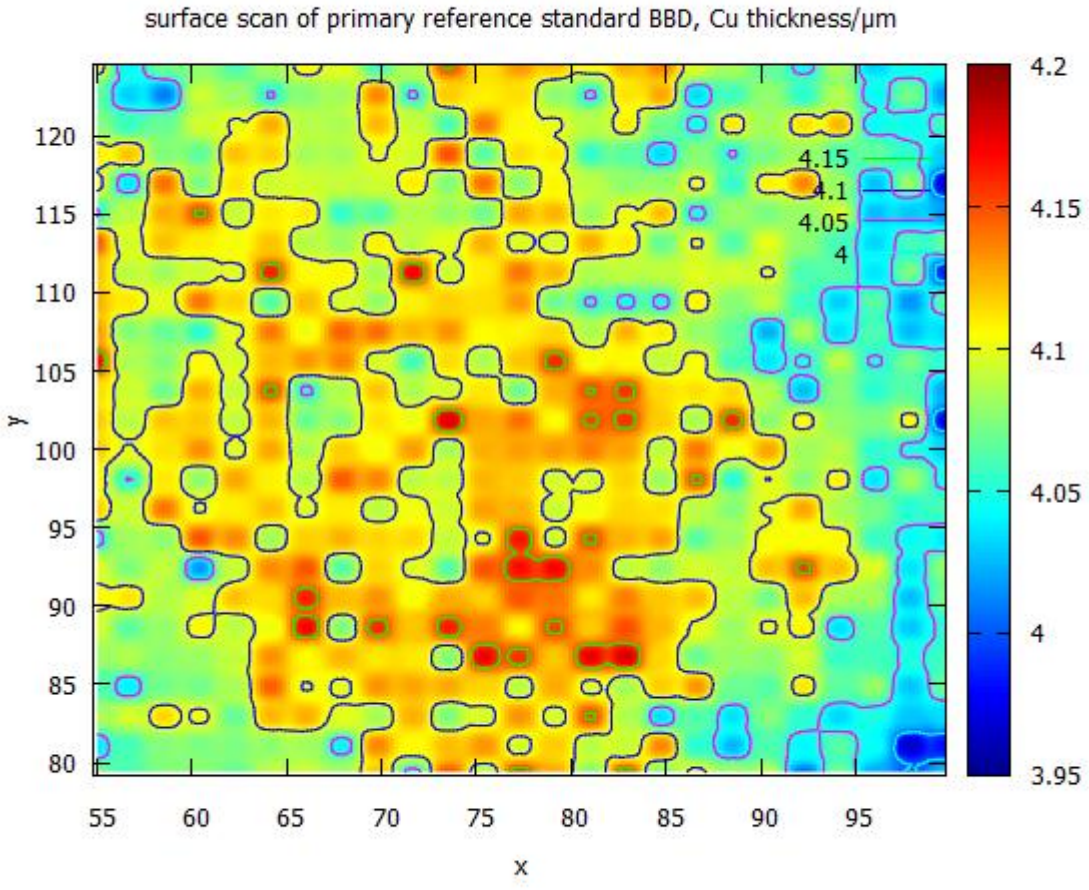
In addition weight and area of the four Cu foils for the production of primary reference standards have been measured following the standards of the DAkkS accreditation D-K-15076-01-00. The obtained mass per unit area is used as reference for the calibration of the standards free XRF values.

Parameter	Value	Comments
Device	Fischerscope© XUV	
Voltage, Filter	50keV, Al 1000 µm primary filter	
Aperture collimator	0.6 mm	
Software version	6.28 LabDB	
Spots per sample	16	
Duration per spot	30 s	
Measured area	2 x 2 mm	4x4 Matrix
Anode current	300 mA	

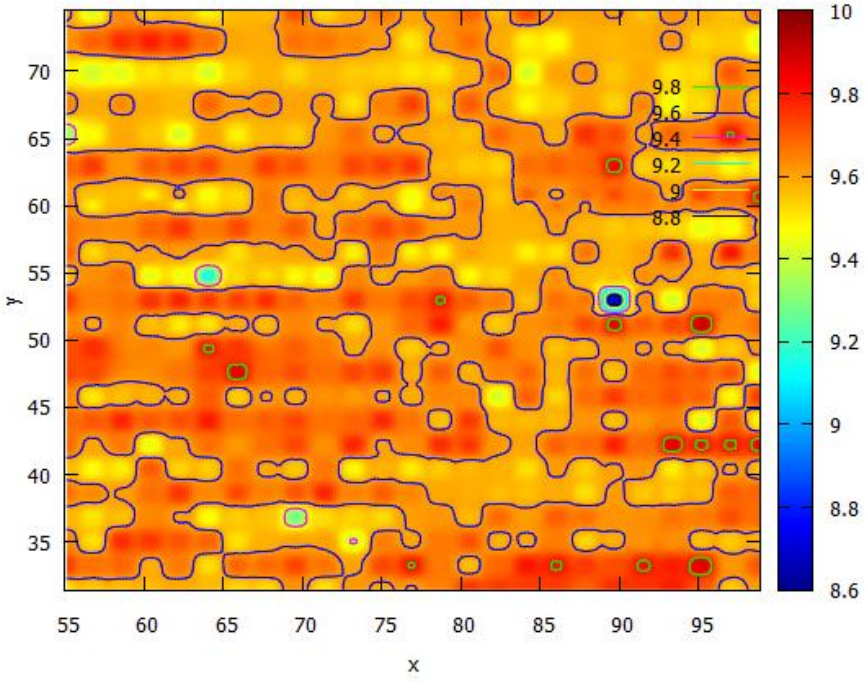
Table II : experimental parameters for the XRF measurement of the Cu secondary reference standards to be calibrated.

Data analysis and results

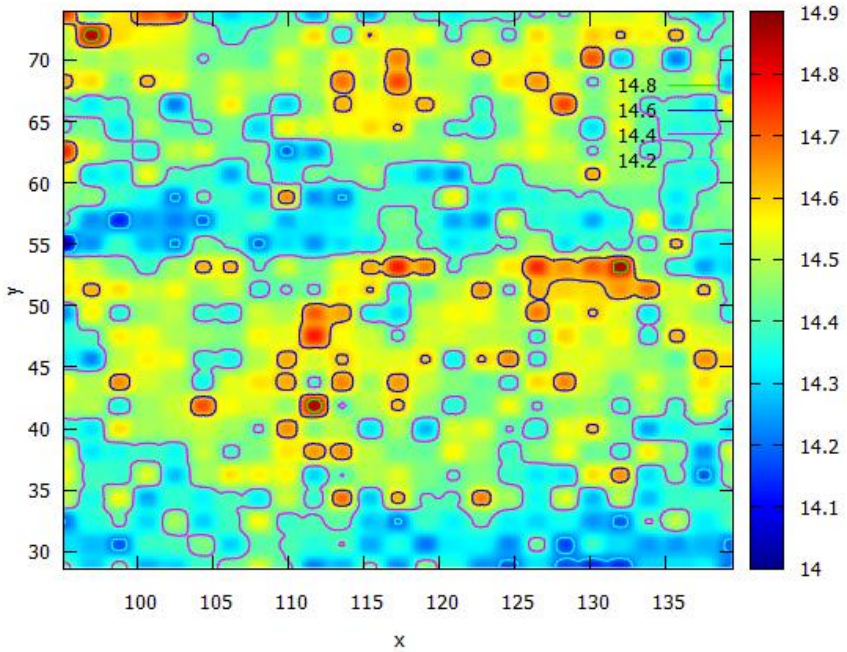
The following four figures represent heatmaps of Cu thickness values for the four primary reference standards BBD, BBE, BBF and BBH. It is noteworthy that all samples exhibit either thickness gradients or inhomogeneous thickness distribution in the order of 10%.

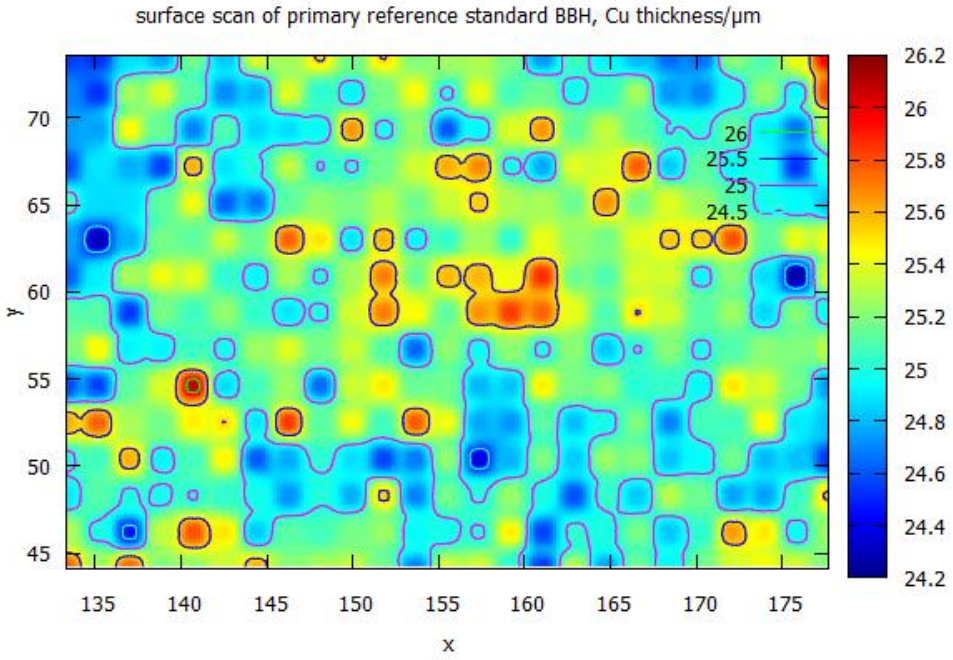


surface scan of primary reference standard BBE, Cu thickness/µm

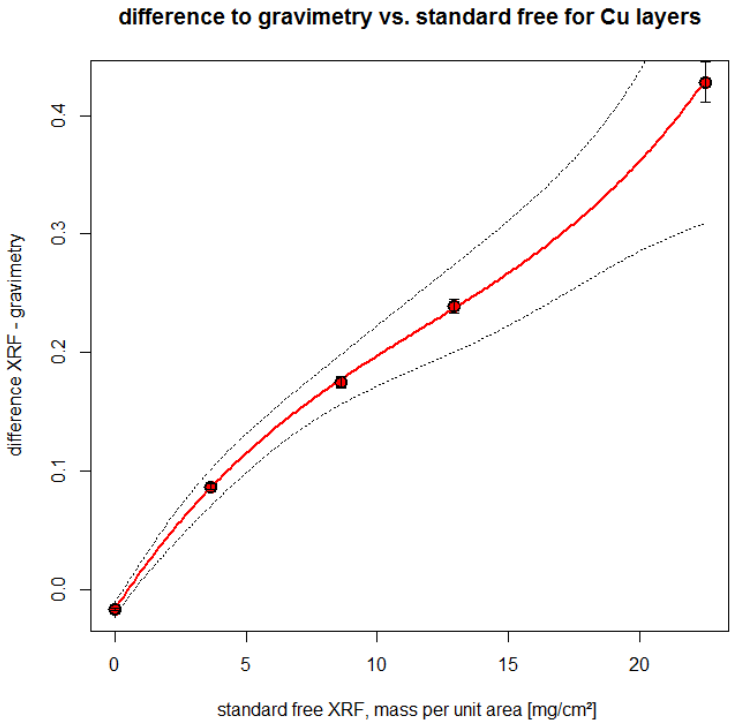


surface scan of primary reference standard BBF, Cu thickness/µm





The statistical programming language R has been used to express the correlation of the difference between gravimetric and XRF measurements and the XRF measurements in terms of a linear regression.



Linear regression between the difference (standard free XRF - gravimetric) vs. standard free XRF using a polynomial of 3rd order. The area between the dotted lines represents the confidence band. Fit and graphics have been produced using the statistical programming language R.

The results are summarized in table III.

Sample	Gravimetry thickness mg/cm²	σ mg/cm²	XRF thickness µm	SE µm	thickness mg/cm²	SE mg/cm²	Diff mg/cm²	σ mg/cm²
Zero	0,00	0,000	-0,02	0,001	-0,02	0,001	-0,017	0,001
BBD	3,58	0,002	4,09	0,001	3,67	0,001	0,087	0,002
BBE	8,44	0,003	9,61	0,004	8,61	0,004	0,175	0,005
BBF	12,70	0,003	14,44	0,005	12,94	0,005	0,239	0,006
BBH	22,07	0,004	25,11	0,016	22,50	0,015	0,428	0,017

Table III : Summary of experimental data from gravimetric measurements and XRF data using the standard free XRF fundamental parameter method for the primary reference standards. Experimental uncertainties are given as standard deviation σ and standard error of the mean (SE).

The correlation obtained from the regression was used to calibrate the standard free XRF values for the secondary standards. Results are summarized in Table IV. The overall agreement with former investigations (denoted as nominal or stated values) is excellent.

	nominal values		XRF FP method			calibrated values			
	stated mg/cm²	U(k=2) mg/cm²	mean mg/cm²	SD mg/cm²	SE mg/cm²	pred mg/cm²	U(k=2) mg/cm²	pred µm	U(k=2) µm
Set 16686									
ADLMP	1,999	0,06	2,001	0,012	0,003	1,96	0,06	2,18	0,06
ADZQS	3,593	0,11	3,670	0,017	0,004	3,58	0,08	4,00	0,08
ADLMR	8,34	0,25	8,46	0,053	0,013	8,28	0,20	9,25	0,22
ADLMS	13,37	0,4	13,62	0,149	0,037	13,37	0,54	14,92	0,62
ADLMT	16,19	0,48	16,44	0,106	0,027	16,15	0,40	18,02	0,44
ADLMU	22,16	0,66	22,93	0,279	0,070	22,48	0,52	25,09	0,58
D-K-15076-01-00									
ADLMZ	1,977	0,06	1,956	0,014	0,003	1,91	0,06	2,13	0,06
ADLNA	3,65	0,11	3,616	0,019	0,005	3,53	0,08	3,94	0,08
ADLNB	8,66	0,26	8,55	0,050	0,012	8,37	0,18	9,34	0,20
ADLNC	21,76	0,64	22,26	0,186	0,046	21,84	0,72	24,38	0,80

Table IV : Summary of experimental data from XRF measurements for the secondary Cu reference standards. Calibrated values have been calculated using the correlation between XRF and gravimetric measurements for the primary reference standards (see Table III).

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