Fischer Traceability Report SD 2012 04

Primary reference standards for precious metal analysis (gold alloys)

Helmut Fischer GmbH applies primary reference standards to quantify "standard calibration set" products. This report describes the checking and recertification of different primary reference standards with Au, Ag, Cu, Ni, Zn, Pd and Cd for precious metal analysis.

The Au concentration of all primary reference standards is traceable to cupellation (fire assay) which was carried out by two different and independent laboratories. The concentrations of all other matrix elements are traceable to ICP measurements. Both methods are destructive analytical methods. Therefore, copies of each primary reference standard material were made by using the XRF as a comparative method. After that the copies are used for the destructive cupellation and ICP analysis. This procedure requires very homogenous materials, thus a lot of effort has to be made to obtain a suitable material for primary reference standard production and certification. For some alloys the material had to be melted several times and for the very inhomogeneous 9 ct alloy a special powder manufacturing process was applied to obtain a sufficient good homogenous material.

1. Experimental and spectrum evaluation (WinFTM *cf.* /1/)

Setup: Fischerscope© XDV-SDD, 50 kV, Al 500 primary filter, aperture 1 mm, AuAgCuZnNiPdCd application, ratio method.
All samples were measured with 16 measurements with 120 s uniformly distributed over the whole sample area.
The cupellation/ICP results (nominal values) have been used for a correction of the standard less XRF results which were obtained with the fundamental parameter based software package WinFTM /1/. The calibration routine of WinFTM takes into account matrix effects as well as the uncertainties of the calibration standards (in this case the uncertainties given by the cupellation/ICP method, the homogeneity of the material and the random precision of the XRF method itself). In this way new corrected values and uncertainties for the primary reference standards were obtained combining the results and information of all primary reference materials.
Figure 1 shows the difference between the nominal and the new corrected value for the Au concentration of all primary reference standards. Table 1 gives the respective measuring values and the calculated total uncertainties for Au. The results for all other elements present in the samples are listed in the appendix.

Table 1 *Nominal and corrected Au concentration for different precious metal alloys*

Code	Au in %			
	Nominal value	u ges	New (corrected) value	u ges
ABKLY	58,48	0,05	58,44	0,05
ABLCV	58,5	0,04	58,52	0,04
ABLIN	75,01	0,04	75,07	0,04
ADJYB	74,63	0,05	74,59	0,06
ADJCF	33,01	0,20	33,05	0,20
ABSAW	90,06	0,03	90,05	0,03
ABQKH	74,82	0,04	74,90	0,05
ABPJE	75,08	0,03	75,05	0,03
ABPPY	75,09	0,04	75,09	0,04
ABQAN	95,09	0,03	95,06	0,03
ABQHX	75,7	0,05	75,88	0,05
ABPNC	58,5	0,04	58,53	0,06
ABLHA	75,02	0,04	75,01	0,04
ABQGI	89,97	0,03	89,98	0,03
ABQBU	95,03	0,03	95,04	0,03
ABLDO	58,54	0,04	58,49	0,04
ABPJX	75,02	0,03	75,03	0,04
ABQGN	75,4	0,05	75,62	0,05
ABQJJ	74,57	0,04	74,78	0,04
ABPPR	75,03	0,04	74,98	0,04
ABPNR	58,09	0,04	58,25	0,05
ABPZM	94,95	0,02	95,00	0,03

ABQDP	89,8	0,02	89,86	0,03
ABKZT	58,56	0,04	58,55	0,04
ABLKH	75,01	0,05	74,92	0,05
ABLJG	75,01	0,04	75,08	0,04
ABPOD	58,27	0,04	58,31	0,05
ABSBH	90	0,03	89,99	0,03
ABKNK	58,35	0,05	58,41	0,05
ABPRT	75,1	0,04	75,04	0,04
ABQKB	74,85	0,04	74,94	0,05
CAIWN	74,67	0,05	74,61	0,05
CAIMC	75	0,04	74,89	0,04
ADJQL	58	0,05	57,96	0,06
ABLDA	58,53	0,04	58,48	0,04
CAGZJ	32,86	0,10	32,89	0,10
ADUNG	37,99	0,05	38,00	0,05
ADZNF	38,01	0,05	37,97	0,05
UPMR 30	41,79	0,03	41,79	0,03
UPMR 35	41,76	0,03	41,81	0,03
UPMR 36	41,97	0,07	41,89	0,07
UPMR 42	48,19	0,03	48,17	0,03
UPMR 45	58,47	0,06	58,41	0,06
UPMR 63	58,49	0,10	58,45	0,10
UPMR 65	58,21	0,03	58,25	0,04
UPMR 70	58,44	0,06	58,41	0,06
UPMR 80	58,52	0,03	58,46	0,04
UPMR 83	72,16	0,05	72,18	0,05

UPMR 85	75,04	0,04	74,91	0,04
UPMR 95	75,06	0,03	74,95	0,04
UPMR 100	75,02	0,05	74,98	0,05
UPMR 105	75,12	0,06	75,05	0,06
UPMR 106	75,08	0,09	74,88	0,09
UPMR 107	82,88	0,06	82,88	0,06

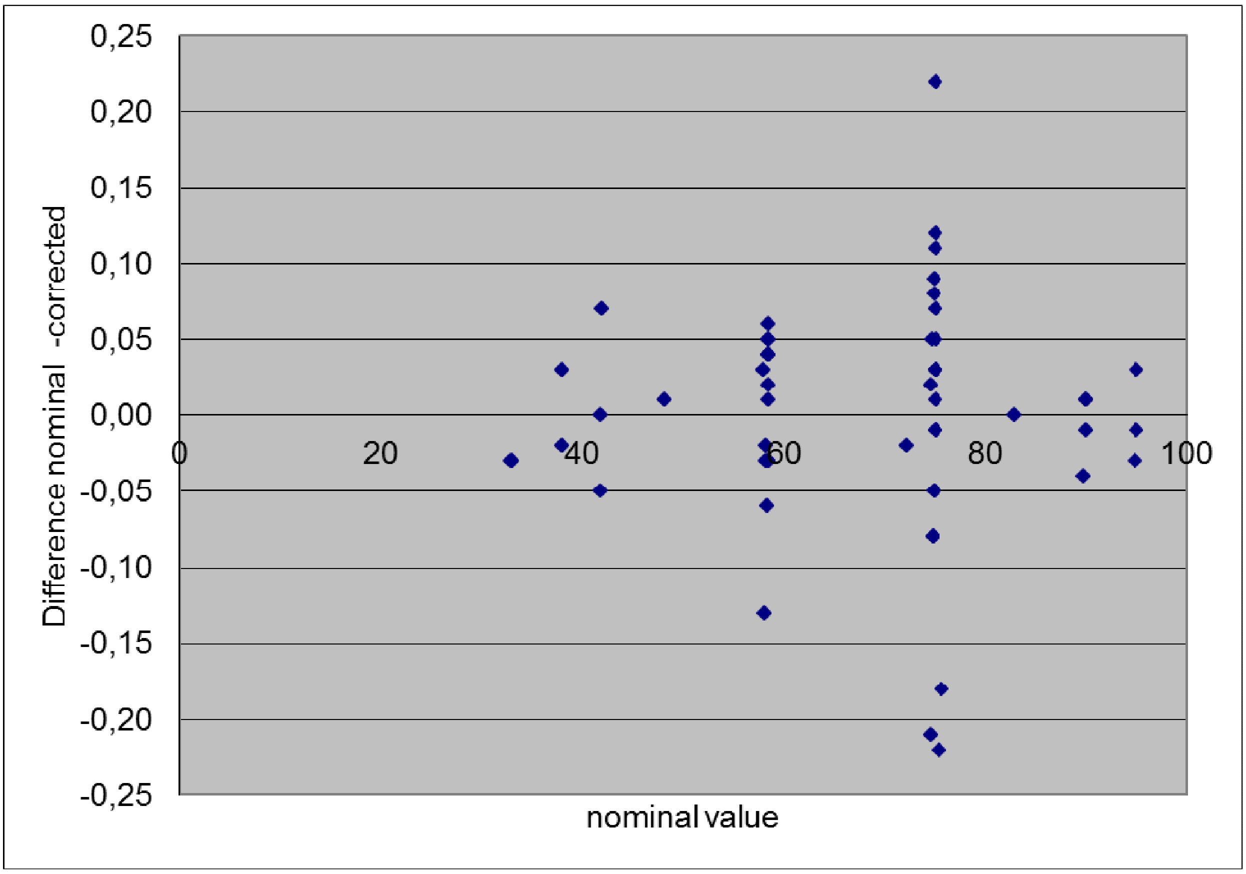

Figure 1 *Difference between the nominal (old value) and the new corrected Au value for the primary reference standards.*

2. Results and Discussion

The WinFTM calibration routine was used to calibrate the standard free XRF values using the cupellation/ICP results as nominal values (Table 1). In this way new recertified values were obtained for the primary reference standards. Figure 1 shows the difference between the nominal and the corrected value as a function of the nominal (cupellation) value. The new corrected results are in good agreement with the cupellation or ICP values. In most cases the differences (figure 1) are in the order of magnitude of the uncertainties given by the cupellation method and the inhomogeneity of the alloys.

Although the reasons for discrepancies cannot be explained in each case, the spatial inhomogeneity of the samples is probably the most important issue. Cupellation or fire assay is always a result for the mean composition of the whole sample where XRF has only an information depth a few µm (for Au approx. 7-8 µm). Therefore it is most important to use only very homogenous reference material for comparative measurements.

The WinFTM calibration with a very large number of independent reference standards can be interpreted as a smoothing of inhomogeneity effects by a physical theory.

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

3. References

/1/ V. Rößiger and B. Nensel, in “Handbook of practical X-Ray fluorescence analysis”, Springer 2006, p. 554.

4. <u>Appendix</u>

Compilation of the full composition of the primary reference samples

	Au [%]	u [%]	Ni [%]	u [%]	Cu [%]	u [%]	Zn [%]	u [%]	Pd [%]	u [%]	Ag [%]	u [%]	Cd [%]	u [%]
ABKLY	58,44	0,05			12,06	0,02					29,50	0,04		
ABLCV	58,52	0,04			36,97	0,03					4,51	0,04		
ABLIN	75,07	0,04			10,00	0,02	9,93	0,04			5,00	0,04		
ADJYB	74,59	0,06			20,43	0,03					4,98	0,04		
ADJCF	33,05	0,20			39,56	0,20	15,04	0,04			12,35	0,30		
ABSAW	90,05	0,03			4,94	0,01					5,01	0,03		
ABQKH	74,90	0,05			9,75	0,02					15,35	0,05		
ABPJE	75,05	0,03	6,88	0,11	8,06	0,11			10,01	0,12				
ABPPY	75,09	0,04			14,98	0,04					9,93	0,04		
ABQAN	95,06	0,03			2,46	0,02					2,49	0,03		
ABQHX	75,88	0,05			7,77	0,26					4,99	0,23	11,36	0,34
ABPNC	58,53	0,06							13,67	0,15	27,80	0,20		
ABLHA	75,01	0,04			10,02	0,04	9,99	0,04			4,98	0,04		
ABQGI	89,98	0,03			5,00	0,02					5,02	0,03		
ABQBU	95,04	0,03			2,48	0,02					2,48	0,03		
ABLDO	58,49	0,04			36,99	0,04					4,52	0,04		
ABPJX	75,03	0,04	6,91	0,11	8,09	0,11			9,97	0,12				
ABQGN	75,62	0,05			7,74	0,26					4,97	0,23	11,67	0,34
ABQJJ	74,78	0,04			9,87	0,04					15,35	0,05		
ABPPR	74,98	0,04			15,08	0,04					9,94	0,05		
ABPNR	58,25	0,05							13,97	0,14	27,78	0,20		
ABPZM	95,00	0,03									5,00	0,05		
ABQDP	89,86	0,03									10,14	0,09		
ABKZT	58,55	0,04			36,94	0,04					4,51	0,04		
ABLKH	74,92	0,05			20,04	0,04					5,04	0,04		
ABLJG	75,08	0,04			10,00	0,04	9,92	0,04			5,00	0,04		
ABPOD	58,31	0,05							14,01	0,14	27,68	0,20		
ABSBH	89,99	0,03			4,98	0,02					5,03	0,03		
ABKNK	58,41	0,05			12,10	0,04					29,49	0,05		
ABPRT	75,04	0,04			15,00	0,04					9,96	0,04		
ABQKB	74,94	0,05			9,73	0,04					15,33	0,05		
CAIWN	74,61	0,05			20,43	0,04					4,96	0,04		
CAIMC	74,89	0,04			9,92	0,04	10,19	0,04			5,00	0,04		
ADJQL	57,96	0,06			12,15	0,04					29,89	0,05		
ABLDA	58,48	0,04			37,00	0,04					4,52	0,04		
CAGZJ	32,89	0,10			39,68	0,20	15,13	0,20			12,30	0,15		
ADUNG	38,00	0,05			41,82	0,05					20,18	0,05		
ADZNF	37,97	0,05			41,91	0,05					20,12	0,05		
UPMR 30	41,79	0,03			40,03	0,15	7,98	0,05			10,20	0,10		
UPMR 35	41,81	0,03			40,72	0,08	5,97	0,03			11,50	0,10		
UPMR 36	41,89	0,07			41,10	0,14	5,84	0,06			11,17	0,06		
UPMR 42	48,17	0,03	0,45	0,005	35,96	0,10					15,42	0,07		
UPMR 45	58,41	0,06	8,56	0,03	25,31	0,12	7,72	0,06						
UPMR 63	58,45	0,10			24,47	0,07	4,22	0,01			12,86	0,08		
UPMR 65	58,25	0,04			30,46	0,08	6,30	0,08			4,99	0,09		
UPMR 70	58,41	0,06			29,18	0,10	4,75	0,15			7,66	0,10		
UPMR 80	58,46	0,04			30,02	0,09	6,80	0,02			4,72	0,07		
UPMR 83	72,18	0,05	1,22	0,02	15,27	0,07	0,54	0,02			10,79	0,12		
UPMR 85	74,91	0,04	5,61	0,02	14,26	0,05	5,22	0,02						
UPMR 95	74,95	0,04			10,32	0,03	0,08	0,03			14,65	0,06		
UPMR 100	74,98	0,05			12,51	0,04					12,51	0,09		
UPMR 105	75,05	0,06			9,57	0,09					15,38	0,15		
UPMR 106	74,88	0,09			9,88	0,05					15,24	0,12		
UPMR 107	82,88	0,06	0,30	0,004	12,69	0,08	0,33	0,01			3,80	0,05		