Fischer Traceability Report JL-2012-11-Cr/Cu-Cr/Fe Sindelfingen, 11/28/2012

Characterization of Cr/Cu, Cr/CuSn and Cr/Fe reference materials

Abstract:

New Cr/Cu, Cr/CuSn and Cr/Fe secondary reference standards have been characterized with a direct relation to reference measurements using the ICP (Inductively Coupled Plasma) method from 2 independent laboratories.

Experimental details

Primary reference materials (Cr layer on Cu, CuSn or Fe base) have been analyzed using data from XRF and the ICP method. XRF measurements have been carried out using a Fischerscope XDL-M. The experimental 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 4x4 matrix of 16 equidistant measurement spots covering an area of 6mm x 6mm in the central region of the primary standards was defined. The total size of all reference materials, primary and secondary, is 8mm x 8mm. 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© XDL-M	
Voltage, Filter	50keV, Ni 10 µm primary filter	
Aperture collimator	0.2 mm	
Software version	6.28 LabDB	
Spots per sample	16	
Duration per spot	120 s	
Measured area	6 x 6 mm	4x4 Matrix
Anode current	460 mA	

Table I : experimental parameters for the XRF measurement of the Cr/Cu and Cr/Fe primary standards.

ICP-OES measurements serving as reference for calibration of the primary standards were carried out by fem Foschungsinstitut für Edelmetalle & Metallchemie, Katharinenstr. 17, D-73525 Schwäbisch Gmünd, report 2K12541 and ThyssenKrupp Steel Europe, FuE-C-A-L, report 12-36696.

Parameter	Value	Comments
Device	Fischerscope© XDL-M	
Voltage, Filter	50keV, Ni 10 µm primary filter	
Aperture collimator	0.2 mm	
Software version	6.28 LabDB	
Spots per sample	16	
Duration per spot	120 s	
Measured area	2 x 2 mm	4x4 Matrix
Anode current	460 mA	

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

Data analysis and results

Tables III and IV summarize the results of ICP-OES measurements of the primary reference standards and compare them to values obtained from the universal standard free XRF fundamental parameter method. The XRF uncertainty given (σ-XRF) is the absolute standard error of 16 individual measurements.

ICP report Code	Sample	ICP mass [mg]	area [mm^2]	**mass per unit area ($mg{\cdot}cm^{-2}$)**		σ -XRF
				ICP	XRF	
2k12541-1	Cr/Cu 2a01	0,913	63,883	1,4292	1,302	0,001
2k12541-2	Cr/Cu 2a02	0,921	63,850	1,4424	1,311	0,002
2k12541-3	Cr/Cu 4a01	1,798	60,878	2,9534	2,738	0,004
2k12541-4	Cr/Cu 4a02	1,888	64,727	2,9169	2,713	0,003
2k12541-5	Cr/CuSn 8a01*	3,635	62,158	5,8480	5,51	0,004
2k12541-6	Cr/CuSn 8a02*	3,741	63,928	5,8519	5,49	0,004
2k12541-7	Cr/CuSn 12a01*	5,718	64,752	8,8306	8,28	0,04
2k12541-8	Cr/CuSn 12a02*	5,504	63,744	8,6345	8,15	0,03
2k12541-9	Cr/Cu 16a01	7,522	64,125	11,7302	10,96	0,007
2k12541-10	Cr/Cu 16a02	7,602	64,776	11,7358	10,93	0,01
2k12541-11	Cr/Cu 20a01	6,503	64,540	10,0759	9,37	0,01
2k12541-12	Cr/Cu 20a02	6,558	64,537	10,1616	9,45	0,01
2k12541-13	Cr/Cu 24a01	11,226	62,556	17,9455	17,84	0,09
2k12541-14	Cr/Cu 24a02	11,579	63,890	18,1233	17,94	0,12
2k12541-15	Cr/Fe 2a01	0,933	64,248	1,452	1,350	0,003
2k12541-16	Cr/Fe 2a02	0,948	64,476	1,470	1,349	0,003
2k12541-17	Cr/Fe 4a01	1,846	64,134	2,878	2,603	0,005
2k12541-18	Cr/Fe 4a02	1,844	64,726	2,849	2,572	0,004
2k12541-19	Cr/Fe 8a01	3,884	63,564	6,110	5,446	0,008
2k12541-20	Cr/Fe 8a02	3,941	63,989	6,159	5,473	0,009
2k12541-21	Cr/Fe 12a01	5,897	64,072	9,204	7,902	0,008
2k12541-22	Cr/Fe 12a02	5,865	64,753	9,057	8,208	0,034

2k12541-23	Cr/Fe 16a01	7,896	63,796	12,377	11,01	0,039
2k12541-24	Cr/Fe 16a02	7,749	64,465	12,020	11,13	0,038
2k12541-25	Cr/Fe 20a01	6,656	65,121	10,221	9,59	0,05
2k12541-26	Cr/Fe 20a02	6,751	64,393	10,484	9,52	0,03
2k12541-27	Cr/Fe 24a01	11,803	65,109	18,128	17,35	0,10
2k12541-28	Cr/Fe 24a02	11,704	64,729	18,082	17,13	0,13

Table III : Summary of experimental data from ICP-OES measurements from fem für Foschungsinstitut, Edelmetalle & Metallchemie, rep. no. 2K12541 and XRF measurements for the Cr/Cu, Cr/CuSn and Cr/Fe primary reference standards. Experimental uncertainties are 0.5% for ICP values and the given standard errors for XRF measurements. The star (*) marks samples with CuSn base material.

ICP report Code	Sample	ICP mass [mg]	area [mm^2]	mass per unit area ($mg \cdot cm^{-2}$)		σ -XRF
				ICP	XRF	
12-36696-001	Cr/CuSn 8a03*	3,93	63,96	6,14	5,676	0,020
12-36696-002	Cr/CuSn 8a04*	3,91	63,944	6,11	5,664	0,013
12-36696-003	Cr/Cu 20a03	6,93	64,354	10,77	9,715	0,057
12-36696-004	Cr/Cu 20a04	6,60	64,113	10,29	9,288	0,004
12-36696-005	Cr/Cu 24a03	11,64	64,947	17,92	17,5	0,07
12-36696-006	Cr/Cu 24a04	11,50	64,829	17,74	17,18	0,05
12-36696-007	Cr/Fe 12a03	5,78	64,638	8,94	8,19	0,10
12-36696-008	Cr/Fe 12a04	5,73	64,324	8,91	8,01	0,07
12-36696-009	Cr/Fe 20a03	6,56	64,444	10,18	9,23	0,08
12-36696-010	Cr/Fe 20a04	6,22	64,693	9,61	9,12	0,09

Table IV : Summary of experimental data from ICP measurements from ThyssenKrupp Steel Europe, rep. no. 12-36696 and XRF measurements for the Cr/Cu, Cr/CuSn and Cr/Fe primary reference standards. Experimental uncertainties are 0.9% for ICP values and the given standard errors for XRF measurements.

A graphical representation of the data is shown in Fig.1 where the absolute difference of XRF data to the ICP data is plotted against the XRF data. The data from the two ICP analyses are in good agreement for a given combination of materials, i.e. Cr/Cu, Cr/CuSn or Cr/Fe, but the calculated differences do not exhibit the same behavior for the two combinations of materials. This experimental finding can be attributed to the different influence of secondary excitation from the base materials (Cu or Fe) on Cr. To account for this effect two calibration curves to the XRF data have been used.

A weighted linear regression using a polynomial of 3rd order was chosen to describe the direct correlation between ICP and XRF data. The appropriateness of this approach is demonstrated in Figs.2 and 3 for Cr/Cu and Cr/CuSn displaying the residual errors plotted versus their fitted values (left) and the standard Q-Q plot to check whether the residual errors are normally distributed.

For Cr/Fe, the data from sample 20a04 were omitted since Fig. 4 suggests treating this point (no. 16) as outlier. In addition, the fit range was limited to the interval [0:10.5] since only two data points at much larger values were available making interpolation more uncertain. In order to circumvent this limitation a local calibration was performed for samples between [16:19] using a correction factor which was calculated from the ratio of the weighted means of the XRF and ICP values from the samples 24a03 and 24a04.

The calibration of the new reference materials is summarized in Table V for Cr/Cu and Cr/CuSn standards and Table VI for Cr/Fe standards, respectively.

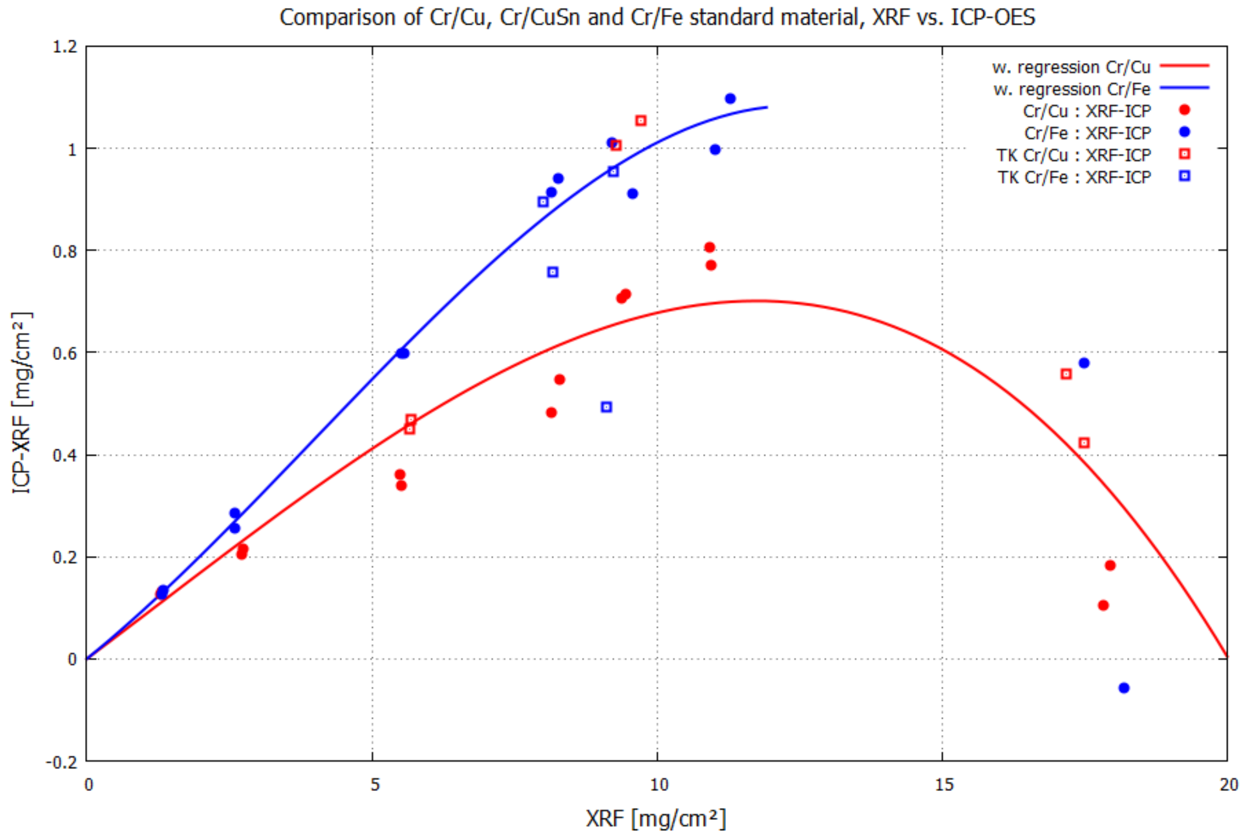
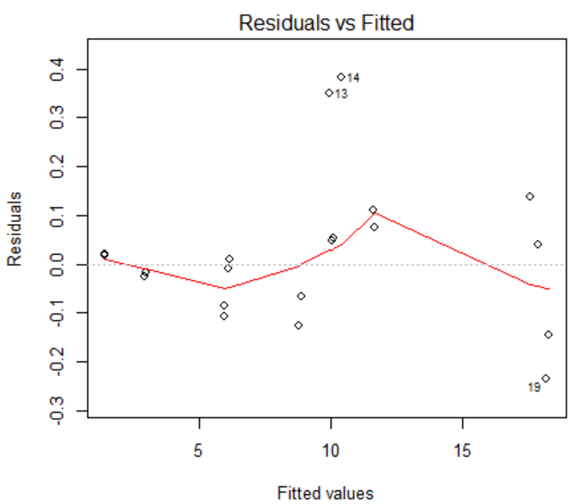


Fig 1 : Comparison of the absolute difference between ICP-OES and XRF data plotted vs. XRF. The red circles (squares) refer to data from fem (ThyssenKrupp) for Cr/Cu and Cr/CuSn. Blue symbols are for Cr/Fe. Weighted linear regression lines are drawn for the two combinations of materials to demonstrate the different behaviour of the respective data.



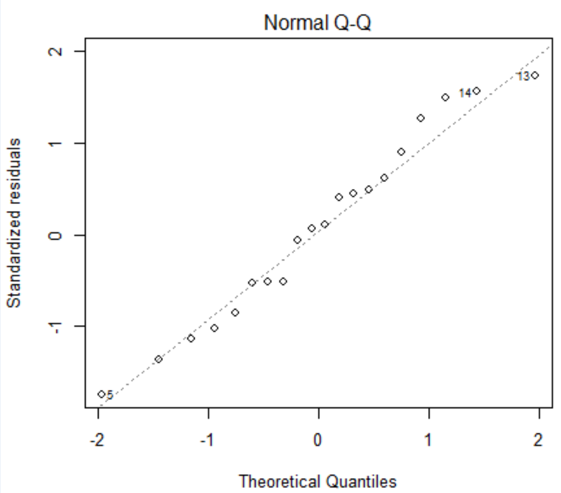


Fig 2 (left) : Appropriateness of fit for Cr/Cu and Cr/CuSn: residual errors vs. fitted values representing a residual error of approx. zero[1].

Fig 3 (right): Same fit as in Fig 2. Standard Q-Q-plot demonstrating that residual errors are normally distributed.

[1] plots produced with R version 2.15.2, http://www.r-project.org

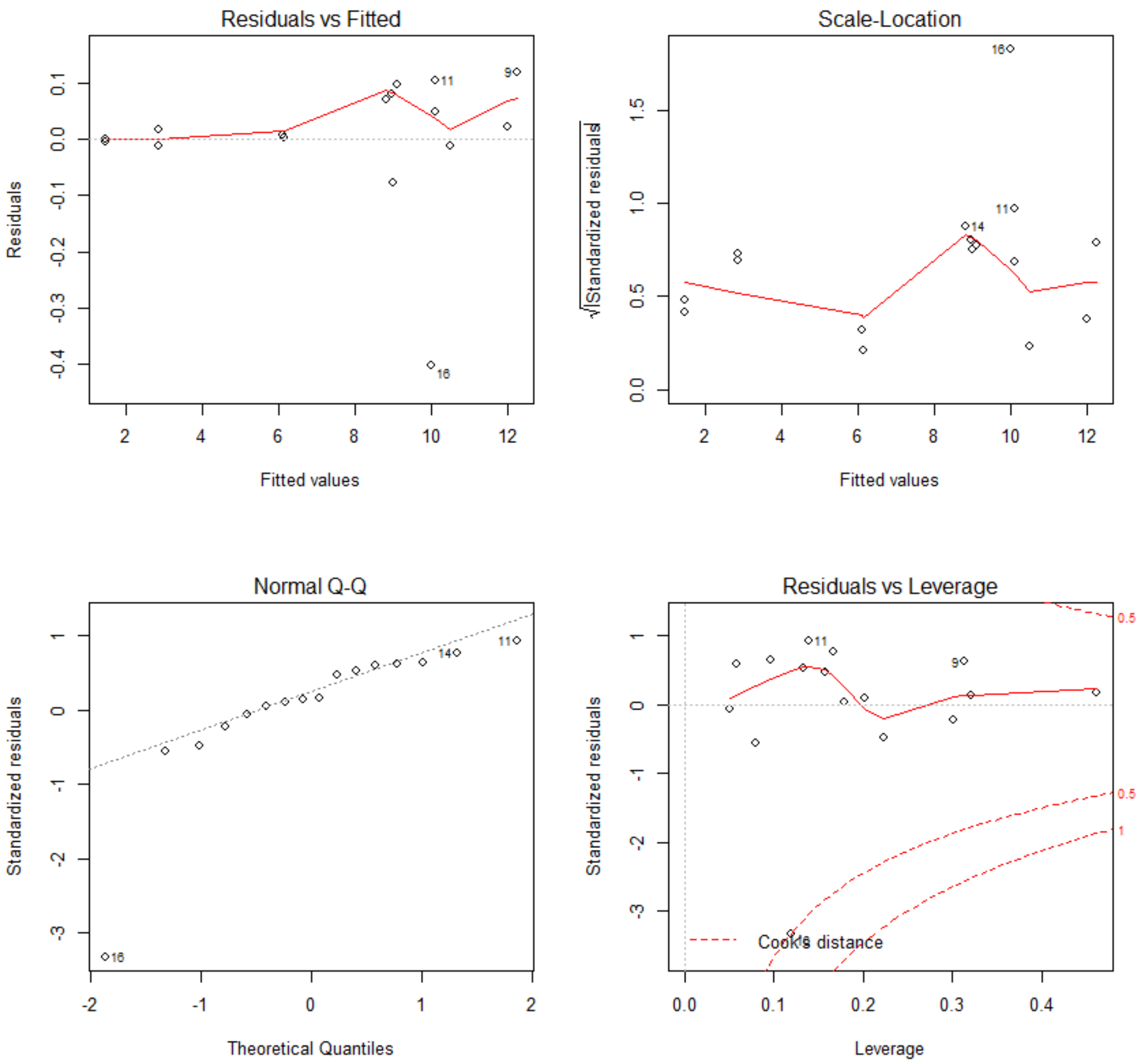


Fig 4 : Appropriateness of fit for Cr/Fe: Data at point no 16 (sample 20a04) were treated as outliers.

Table V:

Calibrated results of the new Cr/Cu reference standards.

Sample	Code	XRF [mg/cm²]	σ [mg/cm²]	calibrated [mg/cm²]	U(K=2) [mg/cm²]	U(%)
2a03	ADXZC	1,288	0,001	**1,40**	**0,02**	1,4
2a04	ADXZD	1,299	0,002	**1,41**	**0,02**	1,4
2a05	ADXZE	1,309	0,002	**1,42**	**0,02**	1,5
2a06	ADXZF	1,3	0,001	**1,41**	**0,02**	1,4
2a07	ADXZG	1,286	0,001	**1,39**	**0,02**	1,4
2a08	ADXZH	1,307	0,002	**1,42**	**0,02**	1,5
2a09	ADXZI	1,31	0,002	**1,42**	**0,02**	1,5
2a10	ADXZJ	1,289	0,001	**1,40**	**0,02**	1,4
4a03	ADXZM	2,664	0,005	**2,89**	**0,04**	1,2

4a04	ADXZN	2,628	0,004	**2,85**	**0,03**	1,2
4a05	ADXZO	2,673	0,002	**2,90**	**0,03**	1,0
4a06	ADXZP	2,703	0,004	**2,93**	**0,03**	1,2
4a07	ADXZQ	2,683	0,002	**2,91**	**0,03**	1,0
4a08	ADXZR	2,621	0,005	**2,84**	**0,04**	1,3
4a09	ADXZS	2,715	0,005	**2,94**	**0,04**	1,2
4a10	ADXZT	2,649	0,004	**2,87**	**0,03**	1,2
8a05*	ADXZY	5,498	0,004	**5,95**	**0,05**	0,8
8a06*	ADXZZ	5,613	0,014	**6,07**	**0,08**	1,3
8a07*	ADYAA	5,605	0,088	**6,06**	**0,42**	6,9
8a08*	ADYAB	5,578	0,012	**6,03**	**0,07**	1,2
8a09*	ADYAC	5,667	0,021	**6,13**	**0,11**	1,8
8a10*	ADYAD	5,433	0,002	**5,88**	**0,05**	0,8
12a03*	ADYAG	8,111	0,018	**8,72**	**0,11**	1,3
12a04*	ADYAH	8,434	0,030	**9,06**	**0,16**	1,8
12a05*	ADYAI	8,42	0,041	**9,04**	**0,21**	2,3
12a06*	ADYAJ	8,272	0,018	**8,89**	**0,11**	1,3
12a07*	ADYAK	8,11	0,005	**8,72**	**0,08**	0,9
12a08*	ADYAL	8,284	0,018	**8,90**	**0,12**	1,3
12a09*	ADYAM	8,49	0,033	**9,11**	**0,18**	1,9
12a10*	ADYAN	8,125	0,006	**8,73**	**0,08**	0,9
16a03	ADYAQ	10,97	0,012	**11,67**	**0,12**	1,1
16a04	ADYAR	10,94	0,009	**11,64**	**0,12**	1,0
16a05	ADYAS	11,16	0,025	**11,86**	**0,16**	1,4
16a06	ADYAT	10,9	0,008	**11,60**	**0,11**	1,0
16a07	ADYAU	11,09	0,020	**11,79**	**0,14**	1,2
16a08	ADYAV	10,97	0,009	**11,67**	**0,12**	1,0
16a09	ADYAW	11,13	0,030	**11,83**	**0,18**	1,5
16a10	ADYAX	11,36	0,054	**12,06**	**0,28**	2,3
20a05	ADYBC	9,313	0,006	**9,97**	**0,09**	0,9
20a06	ADYBD	9,607	0,024	**10,27**	**0,15**	1,4
20a07	ADYBE	9,701	0,032	**10,37**	**0,18**	1,7
20a08	ADYBF	9,494	0,017	**10,16**	**0,12**	1,2
20a09	ADYBG	9,64	0,037	**10,31**	**0,20**	1,9
20a10	ADYBH	9,362	0,011	**10,02**	**0,10**	1,0
24a05	ADYBM	17,44	0,076	**17,83**	**0,49**	2,7
24a06	ADYBN	18,21	0,161	**18,50**	**0,85**	4,6
24a07	ADYBO	18,66	0,178	**18,89**	**0,94**	5,0
24a08	ADYBP	17,74	0,087	**18,09**	**0,54**	3,0
24a10	ADYBR	17,78	0,126	**18,13**	**0,69**	3,8

(*) marks samples with CuSn base material

Table VI:

Calibrated results of the new Cr/Fe reference standards.

Sample	Code	XRF [mg/cm²]	σ [mg/cm²]	calibrated [mg/cm²]	U(K=2) [mg/cm²]	U(%)
2a03	ADYBU	1,350	0,003	1,48	0,02	1,1
2a04	ADYBV	1,349	0,003	1,48	0,02	1,1
2a05	ADYBW	1,334	0,001	1,46	0,01	0,6
2a06	ADYBX	1,325	0,002	1,45	0,01	0,8
2a07	ADYBY	1,317	0,003	1,45	0,02	1,1
2a08	ADYBZ	1,321	0,002	1,45	0,01	0,8
2a09	ADYCA	1,356	0,002	1,49	0,01	0,8
2a10	ADYCB	1,347	0,002	1,48	0,01	0,8
4a03	ADYCE	2,603	0,005	2,87	0,03	0,9
4a04	ADYCF	2,572	0,004	2,84	0,02	0,8
4a05	ADYCG	2,630	0,004	2,90	0,02	0,8
4a06	ADYCH	2,633	0,005	2,91	0,03	0,9
4a07	ADYCI	2,608	0,005	2,88	0,03	0,9
4a08	ADYCJ	2,678	0,010	2,96	0,05	1,7
4a09	ADYCK	2,661	0,005	2,94	0,03	0,9
4a10	ADYCL	2,617	0,004	2,89	0,02	0,8
8a03	ADYCO	5,446	0,008	6,04	0,05	0,8
8a04	ADYCP	5,473	0,009	6,07	0,05	0,9
8a05	ADYCQ	5,389	0,006	5,98	0,04	0,7
8a06	ADYCR	5,561	0,014	6,17	0,07	1,2
8a07	ADYCS	5,413	0,007	6,01	0,05	0,8
8a08	ADYCT	5,481	0,010	6,08	0,06	0,9
8a09	ADYCU	5,371	0,005	5,96	0,04	0,7
8a10	ADYCV	5,437	0,007	6,03	0,05	0,8
12a05	ADYDA	7,902	0,008	8,75	0,05	0,6
12a06	ADYDB	8,208	0,034	9,09	0,17	1,8
12a07	ADYDC	8,178	0,034	9,06	0,17	1,8
12a08	ADYDD	7,973	0,018	8,83	0,09	1,1
12a09	ADYDE	8,014	0,020	8,88	0,10	1,2
12a10	ADYDF	8,115	0,023	8,99	0,12	1,3
16a03	ADYDI	11,01	0,039	12,07	0,21	1,7
16a04	ADYDJ	11,13	0,038	12,19	0,21	1,7
16a05	ADYDK	11,31	0,049	12,38	0,26	2,1
16a06	ADYDL	11,00	0,032	12,06	0,18	1,5
16a07	ADYDM	11,02	0,024	12,08	0,15	1,3
16a08	ADYDN	11,28	0,044	12,35	0,24	1,9
16a09	ADYDO	10,61	0,054	11,65	0,27	2,3
16a10	ADYDP	11,10	0,057	12,16	0,29	2,4
20a05	ADYDU	9,59	0,045	10,58	0,22	2,1

20a06	ADYDV	9,52	0,029	10,50	0,15	1,4
20a07	ADYDW	9,41	0,034	10,38	0,17	1,6
20a08	ADYDX	9,14	0,034	10,09	0,17	1,7
20a09	ADYDY	8,93	0,016	9,87	0,09	0,9
20a10	ADYDZ	8,97	0,022	9,91	0,11	1,1
24a03	ADYEC	17,35	0,100	17,61	0,33	1,9
24a04	ADYED	17,13	0,132	17,38	0,31	1,8
24a05	ADYEE	17,56	0,120	17,82	0,25	1,4
24a06	ADYEF	17,05	0,071	17,30	0,38	2,2
24a07	ADYEG	17,27	0,163	17,52	0,28	1,6
24a08	ADYEH	16,76	0,096	17,00	0,35	2,1
24a09	ADYEI	17,24	0,147	17,50	0,41	2,4
24a10	ADYEJ	16,93	0,179	17,18	0,19	1,1

Sindelfingen, 11/28/2012

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