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Characterization of Cr/Ni reference material

Abstract:

New Cr/Ni primary and secondary reference standards have been characterized with a direct relation to reference measurements using the ICP (Inductively Coupled Plasma) method.

Experimental details

Primary reference materials (Cr layer on Ni base) have been analyzed using data from XRF and the ICP method. XRF measurements have been carried out using a Fischerscope XDL-M at a measuring distance of 15.08 mm to increase the sensitivity at Cr thicknesses > 15 µm. The experimental parameters are summarized in Tables I and II. For the measurement of the primary standards almost the whole area of the circular samples (51.785 mm²) has been covered with 16 measurement spots arranged in two circles with different diameters. The diameter of the samples was 8.12 ± 0.01 mm. 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	MD = 15.08
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	51.78 mm²	2 circles w. 8 spots and diff. r
Anode current	460 mA	

Table I : experimental parameters for the XRF measurement of the Cr/Ni primary and secondary 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 2K13217.

Parameter	Value	Comments
Device	Fischerscope© XDL-M	MD = 15.08
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/Ni secondary reference standards to be calibrated.

Data analysis and results

Table III summarizes 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 (S.E.) is the absolute standard error of 16 individual measurements. The relative analysis uncertainty of ICP-OES values is 0.5 %.

		mass		mass per unit area				
ICP report sample code	sample	ICP-OES [mg]	area [mm²]	ICP-OES mg/cm²	XRF FP mean mg/cm²	σ mg/cm²	S.E. mg/cm²	Difference mg/cm²
2K13217-1	Cr 11	10,09	51,7847567	19,48	20,95	0,396	0,211	-1,46
2K13217-2	Cr 12	9,616	51,7847567	18,57	20,29	0,520	0,277	-1,73
2K13217-3	Cr 21	9,765	51,7847567	18,86	21,10	0,373	0,199	-2,24
2K13217-4	Cr 31	8,14	51,7847567	15,72	16,50	0,244	0,130	-0,78
2K13217-5	Cr 32	8,246	51,7847567	15,92	17,08	0,516	0,275	-1,16
2K13217-6	Cr 41	7,611	51,7847567	14,70	15,06	0,198	0,106	-0,36
2K13217-7	Cr 42	7,674	51,7847567	14,82	15,57	0,163	0,087	-0,75
2K13217-8	Cr 51	5,869	51,7847567	11,33	11,05	0,059	0,032	0,28
2K13217-9	Cr 61	5,884	51,7847567	11,36	11,13	0,056	0,030	0,23
2K13217-10	Cr 71	3,94	51,7847567	7,61	7,29	0,083	0,044	0,32
2K13217-11	Cr 72	3,825	51,7847567	7,39	7,10	0,015	0,008	0,29
2K13217-12	Cr 81	3,945	51,7847567	7,62	7,33	0,093	0,049	0,29
2K13217-13	Cr 91	1,945	51,7847567	3,76	3,57	0,010	0,005	0,19
2K13217-14	Cr 101	2,02	51,7847567	3,90	3,68	0,049	0,026	0,22
2K13217-15	Cr 111	0,944	51,7847567	1,82	1,70	0,004	0,002	0,12
2K13217-16	Cr 112	0,948	51,7847567	1,83	1,79	0,008	0,004	0,04
2K13217-17	Cr 121	0,932	51,7847567	1,80	1,68	0,005	0,003	0,12

Table III : Summary of experimental data from ICP-OES measurements from fem für Foschungsinstitut, Edelmetalle & Metallchemie, rep. no. 2K13217 and XRF measurements for the Cr/Ni primary reference standards. Experimental uncertainties are 0.5% for ICP values and the given standard errors for XRF measurements. (S.E. = standard error, difference refers to the difference between the absolute values of ICP and 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.
A weighted linear regression using a polynomial of 2rd order was chosen to describe the direct correlation between the difference (ICP-XRF) and XRF data. The appropriateness of this approach is demonstrated in Fig.2 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. The data from sample 2K13217-16 (Cr 112) were omitted since Fig. 2 suggests to treat this point (no. 16) as outlier. This correlation has been used to calibrate the XRF data of the secondary reference standards. A small difference in the absolute intensity of the measurements of primary and secondary reference standards is compensated using a proportional correction.
In order to obtain high-quality secondary standards 24 out of 431 samples have been selected representing samples with the smallest relative uncertainty. The calibration of the new reference materials is summarized in Table IV.

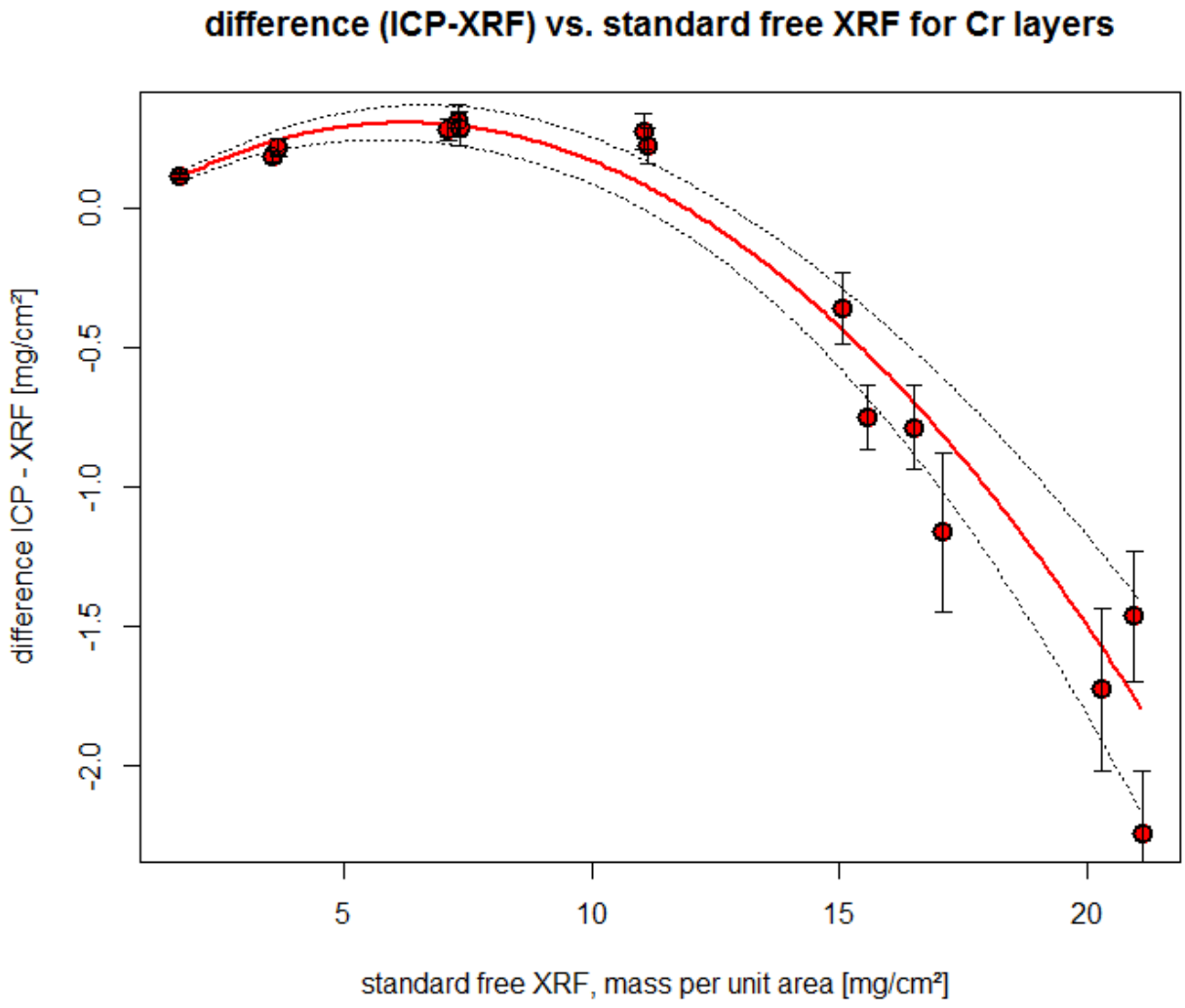

Fig 1 : Comparison of the absolute difference between ICP-OES and XRF data plotted vs. XRF. A weighted linear regression line represents the correlation between y and x-axis and is used as calibration for the standard free XRF values.[1]

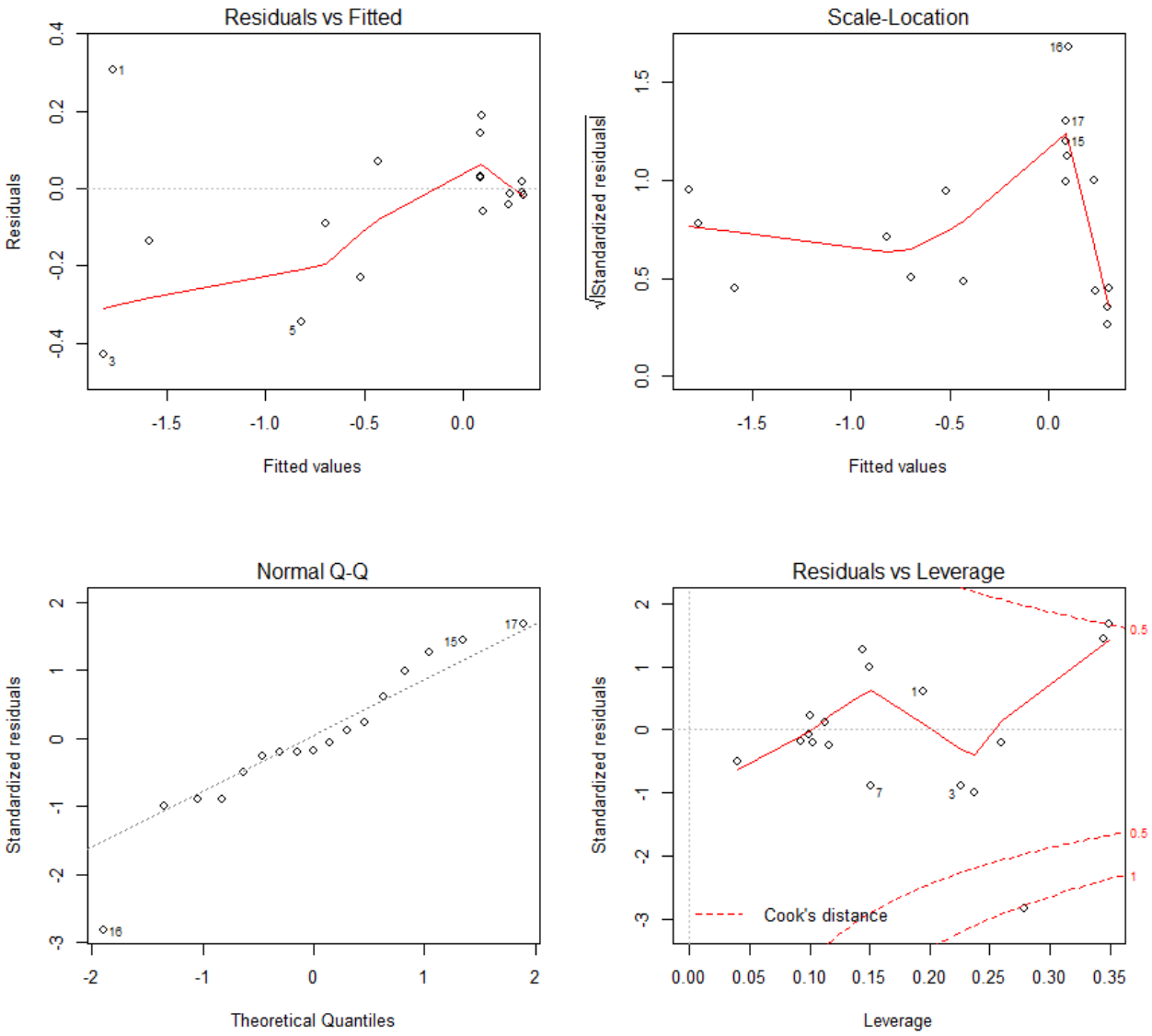

Fig 2 : Appropriateness of the fit for Cr/Ni primary reference standards. Data at point no 16 were treated as outliers.

[1] Fit and plots have been produced using the statistical programming language R

Table IV:

Calibrated results of the new Cr/Ni secondary reference standards

Sample	Code	standard free XRF			calibrated results				
		mass per unit area	S.E.	norm	mass per unit area	U(k=2)	thickness	U(k=2)	
		mg/cm²	mg/cm²	mg/cm²	mg/cm²	mg/cm²	µm	µm	%
CrNi2_11	ADZYM	19,63	0,047	19,67	18,41	0,36	25,60	0,50	2,0
CrNi2_07	ADZYN	20,09	0,059	20,12	18,76	0,39	26,09	0,54	2,1
CrNi2_26	ADZYO	19,91	0,065	19,94	18,62	0,39	25,90	0,54	2,1
CrNi4_08	ADZYP	15,21	0,025	15,23	14,79	0,21	20,57	0,29	1,4
CrNi4_10	ADZYQ	15,11	0,028	15,14	14,71	0,21	20,46	0,29	1,4
CrNi4_20	ADZYR	15,26	0,029	15,29	14,84	0,21	20,64	0,30	1,4
CrNi5_03	ADZYS	10,98	0,008	11,00	11,05	0,11	15,36	0,16	1,0
CrNi5_10	ADZYT	11,02	0,010	11,04	11,09	0,12	15,42	0,16	1,0
CrNi5_06	ADZYU	11,11	0,009	11,13	11,16	0,12	15,53	0,16	1,0
CrNi7_16	ADZYV	7,150	0,003	7,16	7,41	0,07	10,30	0,10	1,0
CrNi8_24	ADZYW	7,224	0,003	7,23	7,48	0,07	10,40	0,10	1,0
CrNi7_20	ADZYX	7,119	0,003	7,13	7,38	0,07	10,26	0,10	1,0
CrNi9_04	ADZYY	3,538	0,001	3,54	3,77	0,04	5,24	0,06	1,1
CrNi9_13	ADZYZ	3,590	0,002	3,59	3,82	0,04	5,31	0,06	1,1
CrNi9_23	ADZZA	3,544	0,001	3,55	3,77	0,04	5,25	0,06	1,1
CrNi2_04_2	ADZZB	1,732	0,001	1,73	1,87	0,02	2,60	0,03	1,2
CrNi1_05_2	ADZZC	1,713	0,001	1,71	1,85	0,02	2,57	0,03	1,2
CrNi2_02_2	ADZZD	1,753	0,002	1,75	1,89	0,02	2,63	0,03	1,2
CrNi4_02_2	ADZZE	0,679	0,001	0,679	0,737	0,009	1,024	0,013	1,2
CrNi4_04_2	ADZZF	0,675	0,001	0,675	0,732	0,009	1,018	0,013	1,2
CrNi4_01_2	ADZZG	0,678	0,001	0,677	0,735	0,009	1,023	0,013	1,2
CrNi5_03_2	ADZZH	0,348	0,000	0,347	0,378	0,006	0,525	0,008	1,5
CrNi5_04_2	ADZZI	0,344	0,000	0,343	0,373	0,006	0,519	0,008	1,5
CrNi5_02_2	ADZZJ	0,336	0,000	0,335	0,365	0,005	0,507	0,008	1,5

Table IV : Summary of XRF data using the standard free fundamental parameter method, normalized values and calibrated data for the Cr/Ni secondary reference materials (S.E. = standard error, "norm" refers to the normalized standard free values that are intensity compensated with respect to the data of the primary reference standards. The thickness has been calculated using a Cr density of 7.19 g/cm³.

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