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PREPARATION AND CERTIFICATION OF LOW ALLOY STEEL REFERENCE MATERIALS FOR SPECTROMETRIC ANALYSIS

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Abstract –Matrix certified reference materials are versatile tools to support quality, correctness and credibility of measurement results. CRMs are used to provide the traceability of the measurement results to the SI unit. Seven low alloy steel certified reference materials were developed by the national institute of standards (NIS), Egypt. Homogeneity and stability were studied by x-ray fluorescence spectrometer. The characterization of RMs was performed using independent chemical methods as gravimetric methods, x-ray fluorescence spectrometry, optical emission spectrometer and atomic absorption spectrometer. Both the assigned values and their associated uncertainty were calculated by weighted mean approach after the statistical analysis of measurements results for the homogeneity of variances, equality of means, normality of data and outliers.

Keywords: Low alloy steel, Homogeneity, Reference materials, Traceability

1. Introduction

The quantities of steel products used for different industrial activities are enormous. The determination of chemical compositions of steel products are important not only for the users but also for the manufacturing as well. The assessment of compliance of iron and steel products with their technical specifications is the main tool to judge their quality and to decide their industrial application. This assessment is done by measurements using different techniques as X-ray fluorescence spectrometry, optical emission spectrometry, Atomic Absorption Spectrometry, and Inductivity coupled plasma techniques [1]. Laboratories are required to use standard methods or validated methods if possible. Certified reference materials are versatile tools for internal validation studies.They play important role in the verification of the accuracy of analytical measurement results. Certified reference materials are used to 1) assure the quality of the measurement results; 2) to establish the traceability of internationally agreed standards to SI units, 3) calibration of measuring instrument to establish the reliability of its reading and 4) to estimate the uncertainty of the measurement process enabling the measurement results to be compared with other results, references, specifications or standards [2-3]. In the present work, seven compositions of low alloy steel were prepared. The process of certification and characterization is described. These reference materials were certified for mass fraction of carbon, silicon, phosphorus, sulphur, manganese, chromium, nickel, tin, molybdenum, copper, cobalt, aluminum, titanium and vanadium using independent analytical methods [4]. Both the assigned values and their associated uncertainty were calculated by weighted mean approach according to Paule and mandel [5-6] after the statistical evaluation of measurements results for the homogeneity of variances, equality of means, normality of data and outliers [7-8].

2. Materials and methods

2.1. Raw materials and steel production

Low carbon steel (carbon ≤ 0.1 %), ferrosilicon alloy (silicon content, 75%), low carbon ferromanganese alloy (carbon ≤ 0.1 % and manganese content 80%), pure metallic copper 99.50%, pure nickel, 99.5%, low carbon ferrochromium (carbon ≤ 0.1 % and chromium content 70%) and Ferrovanadium alloy (vanadium content 70 %) were used for the manufacture of low alloy steel. Production technology was developed to guarantee the maximum homogeneity of readability of the chemical composition values. Melting was conducted in a medium frequency electric induction furnace with 100 kg capacity at Central Metallurgical Research and Development Institute (CMRDI) experimental foundry.

2.2. Chemicals and reagents for sample digestion

Nitric acid, 69% was purchased from Analar, England. Hydrochloric acid, 37% and hydrofluoric acid, 40% were obtained from Merck, Germany. Lanthanum Chloride, 99.99% and cesium chloride, 99.9% were obtained from Alfa Aesar, Germany. Hydrogen peroxide 30% and ammonium persulphate were purchased from Elnasr Co, Egypt.

2.3. Analytical instruments

X-ray fluorescence spectrometer, Axios, Panalytical, Elmelo, the Netherlands, with Rhodium target, V=60 kV and A=160 mA was used for quantitative analysis and homogeneity study. The atomic absorption spectrometer (ZEEnit 700, Analytik Jena, Germany) used for quantitative analysis was equipped with a hollow cathode of the element operated at a current recommended by the lamp and instrument manufacturer. An automatic deuterium background-correction was used for flame atomizer measurement. Microwave digestion instrument, TOPwave Analytic Jena, Germany was used for sample preparation. Optical Emission Spectrometer, Analytical Instrument, Thermo Electron, USA, was used for quantitative analysis as well. Combustion cell, Leco, U.S.A. was used for direct analysis of carbon in oxygen atmosphere.

2.4. Sample preparation for atomic absorption spectrometer

2.4.1. Wet preparation

Half gram of sample was weighed and transferred into 100 mL volumetric flask. 25 mL of 3N sulphuric acid was added and then heated until sample was completely dissolved then10 mL of 12 % ammonium persulfate solution was added. The sample was boiled vigorously until a clear solution was obtained. It was left to cool then diluted to the specified volume with deionized water [9].

2.4.2. Microwave digestion preparation

Two hundred mg of the sample was weighed into the digestion vessel. 3 mL of HNO_3, 3 mL of HCl and 3 mL of HF were added. The mixture was stirred carefully and the sample was left for 10 minutes before closing the microwave vessel. Parallel with the sample preparation, the same procedure was used to prepare a blank sample using the same quantities of all the reagents. Also two NIST SRMs were used to check the recovery of the measurements [10].

2.5. Homogeneity study

The produced steel samples were divided into equal-sized groups. Each group was identified prior to analyses. Stratified random samples were selected from all groups to ensure good sample representation. The selected samples were polished and quantitatively measured by X-ray fluorescence spectrometer (XRF) to check the homogeneity of the prepared samples. Every sample was measured three times in order to check the within and between sample variability. The calibration of x-ray fluorescence spectrometer (XRF) was performed using NIST SRMs1765, 1766, 1767, 1761a, 1762a, 1261a and 1263a which were certified for Carbon, Aluminum, Silicon, Phosphorus, Sulfur, Titanium, Vanadium, Chromium, Manganese, Cobalt, Nickel, Cupper, Arsenic, Molybdenum and Tin. Two control samples were used to check the drift of XRF during measurements. One way-Analysis of Variance (ANOVA) was used to judge the homogeneity of the samples.

3. Results and discussion

Seven sets of low alloy steel were produced and quantitatively analyzed. They were identified in alphabetical order (A, B, C, D, F, K & S). The chemical compositions of the produced alloys are shown in Table 1.

Table 1. Chemical compositions of the produced alloys

Batch	A	B	C	D	F	K	S
C	0.366	0.566	0.382	0.563	0.46	0.185	0.455
Si	0.361	0.851	1.00	0.295	0.191	0.292	0.27
P	0.015	0.020	0.010	0.010	0.0162	0.011	0.020
S	0.0035	0.002	0.020	0.009	0.003	0.0028	0.030
Mn	1.61	0.273	0.459	0.900	0.650	1.190	0.800
Cr	1.85	1.020	4.900	1.070	0.170	1.050	1.100
Ni	0.904	0.113	0.170	1.51	0.0501	0.067	0.200
Cu	0.135	0.130	0.090	0.140	0.020	0.060	0.016
Mo	0.150	0.090	1.200	0.454	0.005	0.0190	0.198
Sn	0.010	0.012	0.007	0.010	0.008	0.0055	-
V	0.005	0.150	0.900	0.066	-	0.0050	-
Ti	0.001	0.002	0.0015	-	0.035	0.0030	-
Al	0.0313	0.0255	0.0202	0.013	0.035	0.0341	0.0287
W	-	1.800	-	-	-	-	-
Co	0.001	0.015	0.006	-	0.010	-	-

3.1. Traceability of measurements

The traceability was achieved by using NIST SRMs for XRF, OES and AAS calibrations which are1765, 1766, 1767, 1761a, 1762a, 1261a, 361, 363,1261a, 1262a and 1263a.

3.2. Homogeneity study

The homogeneity study was designed so that the between sample variability and within sample variability can be studied [11]. The results obtained from the homogeneity study were analyzed by ANOVA (one-way layout). From this data, $F_{cal}\backslash F_{tab}$ for α =5% was small which means that the result of the homogeneity is insignificant. Thus, it can be concluded that the samples were homogenous. The uncertainty of the material homogeneity σ_h^2 was also calculated from the ANOVA using "(1)" [12].

$$\sigma_h^2 = \frac{MS_{Between} - MS_{Within}}{n} \qquad (1)$$

Where $MS_{between}$ is the mean square for the between sample variability, MS_{within} is mean square for the within sample variability and n is the three measurements taken for each of the 6 samples. Values of P-values, F_{cal}, F_{Crit} and σ_h^2 for batch D as an example are shown in Table 2.

Table 2: homogeneity data of batch D

Element		D1-1	D1-2	D1-3	D1-4	D1-5	D1-6	*F*	*P-value*	*F crit*	σ_h^2
C	R1	0.5350	0.5400	0.5500	0.5430	0.5480	0.5455	0.1697	0.9689	3.1059	0.0000117
	R2	0.5560	0.5410	0.5380	0.5500	0.5410	0.5380				
	R3	0.5390	0.5460	0.5470	0.5470	0.5440	0.5529				
Si	R1	0.2880	0.2990	0.2920	0.2816	0.2830	0.2909	0.4247	0.8229	3.1059	0.000005
	R2	0.2970	0.2890	0.2900	0.2952	0.2890	0.2909				
	R3	0.2810	0.2900	0.2950	0.2899	0.2920	0.2909				
P	R1	0.0094	0.0098	0.0095	0.0086	0.0103	0.0092	1.8435	0.1787	3.1059	0.0000001
	R2	0.0106	0.0096	0.0105	0.0099	0.0115	0.0095				
	R3	0.0103	0.0100	0.0107	0.0095	0.0109	0.0110				
S	R1	0.0030	0.0041	0.0038	0.0033	0.0049	0.0020	0.272727	0.770255	5.143253	0.00000006
	R2	0.0042	0.0035	0.0031	0.0030	0.0048	0.0020				
	R3	0.0043	0.0036	0.0037	0.0030	0.0049	0.0020				
Mn	R1	0.9100	0.8880	0.8980	0.9000	0.8940	0.8806	2.2756	0.1129	3.1059	0.00001
	R2	0.8806	0.8770	0.8572	0.8970	0.9180	0.9010				
	R3	0.8696	0.8880	0.8572	0.9030	0.9140	0.9090				
Cr	R1	1.0700	1.1000	1.1100	1.0600	1.0797	1.0950	1.8121	0.1849	3.1059	0.000005
	R2	1.1000	1.0900	1.0700	1.0700	1.1070	1.0940				
	R3	1.1000	1.1100	1.0800	1.0600	1.0934	1.0540				
Ti	R1	0.0011	0.0015	0.0011	0.0012	0.0012		3.1427	0.0646	3.4780	0.000000009
	R2	0.0012	0.0012	0.0014	0.0012	0.0012					
	R3	0.0010	0.0015	0.0012	0.0012	0.0012					
Ni	R1	1.4600	1.4500	1.4900	1.5100	1.5015	1.5012	2.3130	0.1087	3.1059	0.000021
	R2	1.4700	1.4800	1.4900	1.5200	1.5036	1.5012				
	R3	1.4900	1.4300	1.5100	1.4400	1.5026	1.5012				
Mo	R1	0.4630	0.4780	0.4610	0.4848	0.4730	0.4770	2.5843	0.0826	3.1059	0.000056
	R2	0.4610	0.4750	0.4540	0.4528	0.4520	0.4830				
	R3	0.4560	0.4560	0.4540	0.4554	0.4620	0.4900				
Sn	R1	0.0100	0.0090	0.0094	0.0081	0.0090		3.0332	0.0704	3.4780	0.00000015
	R2	0.0096	0.0100	0.0089	0.0095	0.0090					
	R3	0.0105	0.0098	0.0095	0.0090	0.0090					

Cu	R1	0.1410	0.1490	0.1390	0.1430	0.1420	0.1410	1.7054	0.2078	3.1059	0.0000017
	R2	0.1420	0.1400	0.1400	0.1440	0.1420	0.1400				
	R3	0.1390	0.1460	0.1390	0.1430	0.1420	0.1480				
Co	R1	0.0152	0.0186	0.0168	0.0150	0.0148	0.0162	3.0830	0.0511	3.1059	0.00000059
	R2	0.0172	0.0161	0.0178	0.0151	0.0150	0.0161				
	R3	0.0164	0.0157	0.0168	0.0150	0.0149	0.0142				
V	R1	0.0665	0.0691	0.0688	0.0603	0.0660	0.0672	2.9123	0.0600	3.1059	0.0000006
	R2	0.0679	0.0682	0.0649	0.0660	0.0640	0.0717				
	R3	0.0676	0.0688	0.0651	0.0670	0.0650	0.0694				
Al	R1	0.0134	0.0143	0.1300	0.0130	0.0130	0.0152	0.9898	0.4635	3.1059	0.0000026
	R2	0.0152	0.0137	0.0139	0.0137	0.0130	0.0152				
	R3	0.0134	0.0139	0.0135	0.0129	0.0130	0.0165				

3.3. Statistical treatment of the measurement results

The results obtained were tested for normality using Kolmogorov-smirov test, outliers using Dioxan Q-test, equality of Means, and homogeneity of variances at 95% confidence level using Bartlett's test and Levene's test. The statistical packages used are: Minitab 16 (Minitab Inc. Brandon Court, Progress Way, Coventry, UK), Costat statistical Software (CoHort Software, Pacific Grove, CA, U.S.A.), and XLSTAT 7.5.2 (Addinsoft, New York, U.S.A.). The results indicates that the data were normal after removing the outliers and the method variances were homogeneous except for sulfur in batches B & F, P in batch B, Cu in batch S, Mo in batch F, Sn in batch S, V in batches A, C, F, K &S, Ti in batches A, C, D, F, K & S , Al in batches A, K &S, Co in batches C, F &S. these elements were calculated as information values [7-8].

3.4. Assignment of reference value and its uncertainty

Several methods in different laboratories were used for characterization of the elements in low alloy steel RMs. The average mass fraction of each element obtained by the methods was calculated. The steps involved in combining the available data to form a certified value and an uncertainty are: Estimate the uncertainty of the method mean for each method used; Estimate the between-method variance component and compute weights; Compute the weighted mean and its variance; Estimate and incorporate material variability; Estimate the effective degrees of freedom for the combined variance; estimation of the bias allowance [5-6] .

Uncertainty of measurements of the mean of each method

Since more than one analytical method is compared determine the certified value, it is important that the variability of the mean for each method is estimated correctly. In order to estimate the standard uncertainty of the mean, two- way fully nested ANOVA was used to determine which design factors have significant effect on the measurements. To calculate the type A uncertainty of each of the method means, use "(2)".

$$Var(\overline{y}) = \frac{MS_{Sample}+MS_{run}-MS_{error}}{Total\ Number\ of\ measurements} \qquad (2)$$

Between method variance and method weights

The measured values produced by each method are modeled as the sum of the true value, method bias and random error using "(3)".

$$m + b_i + e_{ij} \qquad (3)$$

Method weights are derived by assuming that the random errors (e_{ij}) are independent, have mean 0, and have different variance of each method (σ_i^2). The variance σ_b^2 may be estimated from the between method difference. According to this model, the variance of the average of n_i measurements from the i_{th} method is:

$$\frac{\sigma_i^2}{n_i} + \sigma_b^2 \qquad (4)$$

To combine the averages of the analytical methods for each element, a weighted average of the method means was calculated according to the weighting algorithm of Paule and Mandel which is implemented for multi- method CRMs certification [5-6, 13-14]. The weight for each method, W_i is inversely proportional to the sum of the combined standard uncertainty of the mean, S^2_i and the between- method variance, σ_b^2 . The method weights are defined implicitly as follows:

$$W_i = \frac{1}{S_i^2+\sigma_b^2} \qquad (5)$$

The weighing factor is

$$w_i = \frac{W_i}{\sum_1^M W_j} \qquad (6)$$

And $\tilde{X}$ the weighted average of the $\overline{X}$s

$$\tilde{X} = \sum_1^M w_i \overline{X_i} \qquad (7)$$

Using the above equations, the method weights, the weighted means and the average weighted mean of the different methods for each element have been calculated and the results are given in Table 3.

Combining the uncertainties

The combined standard uncertainty of the weighted mean is the weighted root sum of squares of the combined standard uncertainties for the methods according to:

$$S^2 = \sum_1^M \omega_i^2 \ S_i^2 \qquad (8)$$

This variance estimate does not include the between method variance. The variance of the mean summarizes random errors in the mean. It seems more realistic to include an allowance for bias or systematic error due to the difference in methods. It is taken as the maximum absolute deviation of any method mean from the weighted mean:

$$Bias\ allowance = max\left|\widetilde{X}_\imath - \overline{X}\right| \qquad (9)$$

In order to estimate an appropriate interval for the certified value, the effective degree of freedom of the total variance is estimated according to SATTERTHWATTE formula [5] which is:

$$df(effective) = \frac{\left(\sum_1^M \omega_i^2\, S_i^2 + \sigma_h^2\right)}{\left(\sum_1^M \frac{\left(\omega_i^2 S_i^2\right)^2}{n_i - 1} + \frac{\sigma_h^4}{df_h}\right)} \qquad (10)$$

Where df_h is the number of samples measured induplicate for material variability estimation minus one.

The total expanded uncertainty associated with the certified values was according to:

$$\mathrm{U} = t_{1-\alpha/2}\sqrt{\left(S^2\left(\tilde{X}\right) + \sigma_h^2\right)} + Bias\ allowance \qquad (11)$$

Where $S^2\left(\tilde{X}\right)$ is the weighted combined standard uncertainty and σ_h^2 is the uncertainty of the material heterogeneity.

The certified values and their associated expanded uncertainties were shown in Table 3

Table 3: The certified values and their associated expanded uncertainties for seven low alloy steel batches

Batch		A	B	C	D	F	K	S
C	Certified Value, (%)	0.5508	0.5708	0.3919	0.5508	0.4430	0.1858	0.4309
	Uexp (%)	0.0352	0.0443	0.0200	0.0352	0.0329	0.0136	0.0270
Si	Certified Value, (%)	0.3546	0.8315	1.0072	0.2940	0.1893	-	0.2734
	Uexp, (%)	0.0291	0.0353	0.0324	0.0115	0.0119	-	0.0187
P	Certified Value, (%)	0.0158	-	0.0106	0.0101	0.0126	0.0114	0.0184
	Uexp (%)	0.0027	-	0.0022	0.0020	0.0028	0.0025	0.0022
S	Certified Value, (%)	0.0035	-		0.0027	-	0.0034	0.0324
	Uexp (%)	0.0004	-		0.0010	-	0.0010	0.0075
Mn	Certified Value, (%)	1.6156	0.2768	0.4735	0.8572	0.6148	1.2115	0.8282
	Uexp (%)	0.0282	0.0203	0.0205	0.0334	0.0396	0.0604	0.0239
Cr	Certified Value, (%)	1.8975	1.0381	4.8832	1.0681	0.1744	1.0744	1.0931
	Uexp (%)	0.0313	0.0211	0.0580	0.0326	0.0181	0.0374	0.0682
Ni	Certified Value, (%)	0.9512	0.1148	0.1640	1.5107	0.0514	0.0672	0.2150
	Uexp (%)	0.0181	0.0114	0.0033	0.0515	0.0044	0.0038	0.0114
Cu	Certified Value, (%)	0.1348	0.1287	0.0843	0.1430	0.0218	0.0603	-
	Uexp (%)	0.0136	0.0074	0.0062	0.0074	0.0048	0.0040	-
Mo	Certified Value, (%)	0.1449	0.0903	1.2085	0.4786	-	0.0197	0.2131
	Uexp (%)	0.0091	0.0055	0.0329	0.0428	-	0.0015	0.0099
Sn	Certified Value, (%)	0.0106	0.0123	0.0070	0.0094	0.0070	0.0106	-
	Uexp (%)	0.0029	0.0033	0.0019	0.0026	0.0019	0.0029	-
V	Certified Value, (%)	-	0.1534	-	0.0671	-	-	-

	Uexp (%)	-	0.0039	-	0.0064	-	-	-
Ti	Certified Value, (%)	-	0.0017	-	-	-	-	-
	Uexp (%)	-	0.0009	-	-	-	-	-
Al	Certified Value, (%)	-	0.0136	0.0198	0.0142	0.0349	-	-
	Uexp (%)	-	0.0007	0.0028	0.0022	0.0021	-	-
Co	Certified Value, (%)	0.01225	0.01608	-	0.0155	-	0.0122	-
	Uexp (%)	0.0025	0.0004	-	0.0037	-	0.0025	-
W	Reference Vaue, (%)	-	1.8428	-	-	-	-	-
	Uexp (%)	-	0.097	-	-	-	-	-

*Empty values were reported as information value

4. Conclusion

Low alloy steel batches are matrix certified reference materials that have been certified for the content of Carbon, Silicon, Manganese, Phosphorus, Sulfur, Chromium, Nickel, Copper, Molybdenum, Vanadium, Tungsten, Aluminum, Cobalt and Niobium using six independent analytical methods in different laboratories. Certification was carried out in full compliance with ISO Guide 30-35 and measurement results were statistically treated for normality, outliers, equality of means and variances. The produced certified reference materials provide a basis for further improvement in quality of alloys analysis and production.

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