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Development of New Certified Reference Materials for Silicon Metals

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ABSTRACT

Metalcasters rely on vendors to provide high quality, consistent products ensuring high-quality castings are manufactured. Metalcasters ensure their chemistry through standardizing their chemical analysis equipment through the use of Certified Reference Materials (CRM). But what if those standards did not exist? How could a foundry gage themselves against another? How could a customer ensure that the product from two different vendors would function the same? This was the case for the silicon metal industry. No common standards existed resulting in divergent readings of the same material from different analytical laboratories. Furthermore, differences in actual chemical analysis between vendors, supposedly produced to the same specification, are commonplace. This paper discusses the cooperative development and certification of nine new international CRM's for the silicon metal industry.

Keywords: certified reference materials, CRMs, silica, quality control, X-ray fluorescence spectrometry, XRF, traceability

INTRODUCTION

The unquestionable trend of the last two decades is the increased use of multi-element instrumental techniques with the greatest possible simplification and shortening of the sample preparation stage. This results directly from the need to obtain results in the shortest possible time and eliminates additional steps in the analytical method that may be a source of additional errors. The use of a fast, instrumental method, such as X-ray fluorescence spectrometry (XRF), requires calibration using certified reference materials with a matrix whose composition corresponds to the composition of the sample being analyzed.

Certified Reference Materials (CRM) are an integral part of chemical composition analysis in modern quality control of raw materials and products. According to the definition, these are reference materials, one or more properties of which have been characterized by a metrologically recognized procedure, accompanied by a certificate specifying the value of the specified properties, the related uncertainty and confirming the maintenance of metrological traceability.[1]

The silicon industry is one of the most important customers for the fast and accurate analytical methods for process control as well as quality assurance of silicon products. The silicon materials market is growing dynamically, with market forecasts clearly indicating further development of the market. The value of this market was predicted to increase from USD 6520 million in 2017 to USD 9170 million in 2024.[2] In cooperation with large silicon companies, a gap was found in the CRM market for silicon materials for representative samples of currently produced materials. Samples have been developed, but not in accordance with the ISO 17034 standard[1] regarding the competence of reference material producers.

As a result, in 2020 a joint research project called "SilRef" was established. The aim of the project was to develop new CRMs for three types of silicon materials, including four grades for magnesium ferrosilicon alloy (FSM), three grades for silica fume and 2 grades for silicon. Alloys designed for the CRMs were produced by a production facility that specializes in silicon materials. Then they were processed at Łukasiewicz-IMN to obtain the required homogeneity. Further analytical steps, such as determination of homogeneity, stability uncertainty and determination of certified values and their uncertainty were carried out. In order to determine the characteristic values, a multi-laboratory strategy was used.

Finally, nine new CRMs were prepared for market introduction. In this paper, the CRM development process is presented using the example of CRM for silicon with the symbol "Si-2." For the other materials, the general scheme was the same.

CONCEPT

While the general approach was determined by ISO 17034,[1] the individual stages had an experimental and research character. Because reference materials for silicon materials were produced for the first time, it was necessary to develop a methodology to obtain a homogeneous material with a specified elemental composition. In subsequent stages, it was necessary to develop analytical methods that met specific criteria. All developed analytical methods have been subjected to a validation process. The technical and statistical approach to the process was carried out in accordance with ISO Guide 35,[3] while the documentation formats were developed in compliance with ISO Guide 31.[4]

Homogeneity and stability are the basic features that CRM should have. Homogeneity is defined as the property of a material that determines its degree of compositional variability in relation to one or more properties. In the case of a silica CRM candidate, achieving the planned degree of homogeneity is a critical step in classifying it for further stages of production. An unsatisfactory level of homogeneity may result in it being returned to the manufacturing stage.

Stability, on the other hand, is a feature that determines the invariability of one or more properties in various conditions and over a long period of time. In the case of materials characterized by low durability (e.g., solution-based CRMs), this step is extremely important. Silica stability is usually a less important parameter than homogeneity, however stability testing and monitoring is required by ISO 17034.[1,5,6]

Equally important is the stage of the characterization process (otherwise known as interlaboratory attestation). This is the stage in which specialized external laboratories participate. In this stage, based on the average results obtained from individual laboratories, the certified value and the uncertainty of the characterization process are determined. Once the CRM development process is completed, appropriate documentation is issued. This includes a certificate and a label in accordance with the requirements of the ISO 17034 standard.[1] The following sections outline the procedure for assessing these production steps for CRM candidates for Si-2.

EXPERIMENTAL

HOMOGENEITY TESTS

Homogeneity tests were carried out in accordance with the ISO 17034 standard and ISO Guide 35.[1,4] Homogeneity must be demonstrated both within and between specimens. For statistical evaluation of homogeneity, samples were randomly selected. The number of specimens selected for testing was determined according to the formula as follows:[4]

$$N_{min} = \max\left(10, \sqrt[3]{N_{prod}}\right)$$

Where:
N_{min} = minimum number of specimens selected for testing;
N_{prod} = number of specimens produced.

Ten units were randomly selected for testing. From each unit three samples from three different depths were taken and dissolved in a mixture of acids. Quantitative analysis was carried out using optical emission spectrometry with inductively coupled plasma excitation (ICP-OES) using a sequential spectrometer Ultima 2 from Horiba Jobin-Yvon. The infrared sample combustion method was used to determine the C content using Elemental Analyzer Elementrac CS from ELTRA. The set of results obtained was used for statistical calculations, which were carried out based on one-way ANOVA. One-way ANOVA allows verification of the null hypothesis that the average results obtained for individual units do not differ in a statistically significant way.[7] On the basis of the calculations performed, the uncertainty characterizing the homogeneity was determined, which will constitute a component of the uncertainty budget of the expanded certified value. In order to determine the uncertainty of homogeneity, the following should be determined:

- standard deviation between objects
  $$s_{bb} = \sqrt{\max\left(\frac{MS_{among} - MS_{within}}{n}, 0\right)}$$
- standard uncertainty of the standard deviation within the object
  $$u'_{bb} = \sqrt{\frac{MS_{within}}{n}}\sqrt[4]{\frac{2}{N(n-1)}}$$

Where:
MS_{among} = variance between objects (between groups);
MS_{within} = variance within the object (within groups);
n = number of results for a single sample;
N = number of samples selected for testing.

The larger of the determined values is the homogeneity uncertainty (u_h), which is included in the budget of the extended uncertainty of the determined property value. An example of calculations for phosphorus (P) in Si-2 are shown in Table 1.

Table 1. Analysis of Variance: One-Way

Groups	Counter	Sum	Average	Variance
row 1	3	0.0127	0.0042	1.33E-08
row 2	3	0.0119	0.0040	3.33E-09
row 3	3	0.0126	0.0042	0
row 4	3	0.0114	0.0038	1.9E-07
row 5	3	0.0131	0.0044	4.33E-08
row 6	3	0.0121	0.0040	1.33E-08
row 7	3	0.0121	0.0040	3.33E-09
row 8	3	0.0118	0.0039	5.33E-08
row 9	3	0.0127	0.0042	5.33E-08
row 10	3	0.0126	0.0042	1E-08

VARIANCE ANALYSIS						
Source of variance	SS	df	MS	F	Value-p	Test F
Between groups	8.13 E-07	9	9.04 E-08	2.36	0.053	2.39
Within groups	7.67 E-07	20	3.83 E-08			
Sum	1.6 E-06	29				

s_{bb}	0.00013
u'_{bb}	0.00006
u_h	0.00013
$u_{h(rel)}$	3.21 %

The same calculation methodology was used for the remaining elements. Table 2 below summarizes the relative values of homogeneity uncertainty determined on the basis of the calculations performed. These values, in addition to the uncertainty related to characterization (attestation), constitute a component of the final uncertainty of the reference value.

Table 2. Relative Values of Homogeneity Uncertainty [%]

	Fe	Al	Ca	Ti	Cr	Ni	V	Mn	Cu	P	B	C
$u_{h(rel)}$	1.1	3.2	1.1	5.4	6.8	2.1	2.6	2.2	6.2	3.2	1.7	7.6

The values of the determined relative homogeneity uncertainties confirmed that the produced material was homogeneous for each reference element throughout the entire mass. This classified it for further stages of production.

STABILITY TESTS

CRM stability is understood as the invariability of the determined property values both over a long period of time and under various conditions (different temperatures). In accordance with the guidelines of the ISO 17034 standard and ISO Guide 35, long-term and short-term stability tests were carried out.[1,4] Long-term stability (u_{stab}) involves periodically performing property value tests to check their stability. From the moment the CRM material was developed until the project was completed, these tests were repeated approximately every six months, and then once every two years. Samples for stability tests were taken randomly. Short-term stability, understood as transportation stability (u_{trans}), is checked in the conditions in which the CRM can be shipped to the customer. For a given CRM, three samples were selected for testing, each stored at a different temperature. Test samples were stored at temperatures: 40C, 5C and -18C(104F, 41F,-0.4F). The tests were repeated on days 2, 6, 8 and 10.[8] To consider material stability for a certified value, the monitoring result must satisfy the equation:

$$|x_{CRM} - x_{mon}| \le 2 \cdot \sqrt{u_{CRM}^2 + u_{mon}^2}$$

Where: x_{CRM} = certified measurement value, x_{mon} = measurement value obtained in the monitoring analysis u_{CRM} = standard uncertainty of the certified measurement, value u_{mon} = standard uncertainty of the measurement value of the monitoring analysis.

An analysis of the linear trend over time was also performed (linear regression method) and the significance of the slope coefficient was tested (student's T test). The results obtained as part of the research allowed for statistical calculations, as a result of which the short-term uncertainty and the long-term stability uncertainty were determined. The same analytical methods were used for the tests as for homogeneity. The table below summarizes the relative uncertainty values of short-term and long-term stability determined on the basis of the calculations performed.

Table 3. Relative Values of Short- and Long-Term Stability Uncertainty [%]

	Fe	Al	Ca	Ti	Cr	Ni
$u_{trans(rel)}$	0.10	0.42	0.27	0.45	0.71	1.4
$u_{stab(rel)}$	0.05	0.10	0.08	0.13	0.25	0.64
	V	Mn	Cu	P	B	C
$u_{trans(rel)}$	1.2	0.31	1.6	2.2	0.45	1.1
$u_{stab(rel)}$	0.39	0.14	0.28	0.19	0.21	0.06

Based on the assessment of both short- and long-term stability, the material was determined to be stable. The determined values of short-term uncertainty and stability uncertainty for the analytical case were not included in the expanded uncertainty budget.

CHARACTERIZATION PROCESS

At this stage, the certified values were determined. Eight laboratories participated in the characterization process of the material with the symbol Si-2. The laboratories provided 6 independent results or one result with uncertainty. The obtained results were statistically evaluated using three criteria: (1) determination of the coefficients of variation for the results obtained from a given laboratory (requirement: <15%), (2) the Q-Dixon test performed for the results from a given laboratory and then for the average results from individual laboratories, (3) graphical evaluation - where the continuous line indicates the median of the obtained results, the red dashed lines are twice the value of the standard deviation of all results, and the results with standard deviations as error bars. Figure 1 shows an example graph for Fe in the Si-2 material.

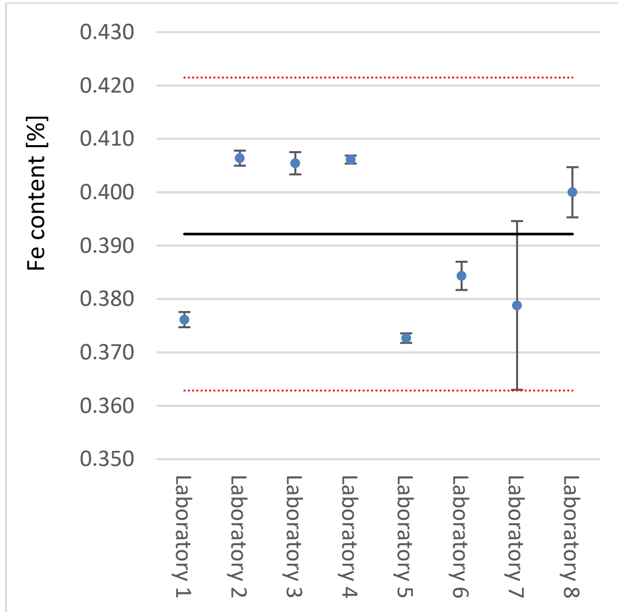

Figure 1. Graphical evaluation of the results obtained from individual laboratories for Fe in the Si-2 material.

Uncertainty in the characterization process was calculated as:

$$u_{char} = \frac{s_{char}}{\sqrt{n}}$$

Where:
s_{char} = standard deviation of a group of results (arithmetic means of partial results) obtained at individual laboratories, and n = the number of independent sets of these results (usually the number of laboratories or techniques).

The determined uncertainties of homogeneity and certification are components of the uncertainty of the determined certified value:

$$U = 2 \times \sqrt{u_{char}^2 + u_h^2}$$

Table 4 summarizes the determined certified values, components of the expanded uncertainty budget and its value for the elements in the Si-2 material.

Table 4. Determined Certified Values, Components of Expanded Uncertainty Budget and Expanded Uncertainty Value for Fe in Si-2 Material, [%]

	Fe
	[%]
X	**0.391**
u_{char}	0.0052
u_h	0.0042
$u_{h(rel.)}$	1.1%
U	**±0.014**

SUMMARY

As part of the SILREF project, nine new CRMs were developed and manufactured for three types of silicon materials: silicon, silica fume and magnesium ferrosilicon. This process was carried out in accordance with the requirements of the ISO 17034 standard, which enabled the inclusion of new CRMs in the scope of accreditation of the Polish Centre of Accreditation with number RM006. As a part of the work, homogeneity confirmation, short-term and long-term stability tests, as well as the process of characterizing materials on CRM were carried out.

The results obtained at each stage were statistically evaluated, and the standard uncertainties of each stage were determined. Finally, in silicon CRMS twelve elements: Fe, Al, Ca, Ti, Cr, Ni, V, Mn, Cu, P, B, C; in silica fume thirteen elements: Si, Fe, Al, Ca, Na, K, Mg, Cl, P, S, Zn, C, LOI; and in FSM twelve elements: Si, Fe, Mg, Al, Ca, Ce, La, Ba, Ti, Cr, Mn, P were certified. Based on the accepted results, certified values and the accompanying expanded uncertainty values were determined. Based on the information collected, a certificate and label were set for each new material.[9]

The developed CRMs were implemented in industrial laboratories as shown in Figures 2-4.

Figure 2. CRMs for silicon.

Figure 3. CRMs for magnesium ferrosilicon alloy (FSM).

Figure 4. CRMs for silica fume.

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