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Development of New Series of Certified Reference Materials for Ferrosilicon Magnesium Alloys

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Abstract: This paper presents a practical approach to the production of certified reference materials (CRMs) for ferrosilicon magnesium alloys. These new CRMs are predicted to be used in fast X-ray fluorescence spectrometry (XRF) analysis, which does not require sample digestion and does not result in the production of acidic sewage and emissions, contrary to the classical and instrumental techniques currently used in laboratories. Four new certified reference materials (CRMs) were developed to fill the gap in the reference materials market and ensure fast and traceable analyses. The materials were produced with an industrial process and then homogenized and mixed to achieve the required compositions and level of homogeneity. The homogeneity was determined using specially developed analytical methods and confirmed statistically by ANOVA. Additionally, the results of the tests show the short- and long-term stabilities of the new materials. The certified values for specific element contents were determined in interlaboratory tests. All results were assessed statistically for outliers. The results from three or more independent and different analytical methods were used for the calculations. In parallel homogeneity, the stability, and characterization standard uncertainties were calculated and used in the estimation of the final expanded uncertainties of the certified values. Finally, four new CRMs were assisted with the proper certificates according to ISO standards.

Keywords: certified reference materials; silicon alloys; traceability

Citation: Kostrzewa, J.; Anyszkiewicz, J.; Gorewoda, T.; Jamroz, E.; Blandhol, K.; Guldhav, A.Y.; Knapik, M.; Charasińska, J.; Jakóbik-Kolon, A. Development of New Series of Certified Reference Materials for Ferrosilicon Magnesium Alloys. *Processes* **2024**, *12*, 1017. https://doi.org/10.3390/pr12051017

Academic Editor: Adina Musuc

Received: 22 April 2024
Revised: 9 May 2024
Accepted: 14 May 2024
Published: 17 May 2024

1. Introduction

Ferrosilicon magnesium (FSM) is a type of ferroalloy obtained from a combination of iron, silicon and magnesium [1]. Ferrosilicon alloys are commercially produced in an electric furnace, at 1700–1750 °C, using quartz as the silicon source [2]. The reactivity of the reducing materials is critical in ferrosilicon and silicon production. The selection of the most suitable quartzites for the production of ferrosilicon is made through time-consuming industrial trials or laboratory studies [3,4]. The main application of FSM is in the processing of spherical graphite for the production of cast iron, which increases its strength and supplies magnesium for cast-iron smelting. It can also be used as a deoxidizing and desulfurizing additive to steel, as well as a coating in electric welding [5,6]. The important industrial roles of FSM result in its relatively high market demand, which generates the need for fast and accurate analyses. The chemical composition of FSM alloy must be properly defined, as it significantly affects its properties and, similar to other industrial materials, is one of the indicators used in quality control. Various analytical techniques can be used for this purpose. Some techniques that are used during scientific studies are not suitable for daily industrial use. For example, the contents of two main phases, α-$FeSi_2$ and Mg_2Si, present in the FSM alloy are determined using electron microprobe analysis (EPMA) [7]. In other studies, electron microscope and X-ray fluorescence spectrometry (XRF) analyses have been used [8]. Al-Mg-Si alloys have also been tested by differential scanning calorimetry (DSC) and transmission electron microscopy (TEM) [9]. Other methods used to analyze the composition of ferrosilicon are instrumental neutron activation analysis (INAA), which allows for the precise and accurate determination of large numbers of elements [10], and XRF, which allows for multi-elemental analysis but requires special sample preparation by borate fusion [11–13]. However, in industrial and daily practices, the chemical compositions of FSM and similar materials, such as ferrotitanium, ferronickel, ferrochrome silicon, zirconium ferrosilicon, and manganese ferrosilicon, are determined using multi-elemental inductively coupled plasma optical emission spectrometry (ICP-OES). This technique allows for the determination of both impurities and alloying elements, but it requires dissolving the samples and the use of solution standards. In the case of trace elements at very low levels (ppb), another wet instrumental method, inductively coupled plasma mass spectrometry (ICP-MS), can be used [14]. Samples can be prepared in various ways, for example, in a closed microwave system or in open vessels via simple acidic digestion in the form of pellets or fusion beads [15–18].

Previously, there was one certified reference material (CRM) for FSM available on the market, SRM-347, by NIST [19]. This CRM does not contain all of the elements currently required for industrial quality control (i.e., Ba and Fe). Moreover, SRM-347 was developed, in 1990, without the ISO 17034 standard [20] of consistency, and it is not currently available. Presently, work is being carried out to produce CRMs for the silicon industry, but none of them correspond, in terms of the composition, to the CRM for FSM presented in this manuscript [21,22].

In general, all of these analytical techniques are comparable and require measurement traceability. This can be accomplished by using a laborious method that proves a chain connection to the International System of Units (SI) or, more efficiently, by using CRMs, for example, in the calibration of instruments or the validation of an analytical procedure. In modern quality-controlled laboratories, CRMs are, therefore, an important part of chemical composition analyses, confirming the maintenance of metrological traceability. Therefore, the presence of CRMs on the market is very important. The silicon industry is growing dynamically, with market forecasts clearly indicating further development of the silicon materials market; the value of this market is predicted to increase from USD 6520 million in 2017 to USD 9170 million in 2024 [23]. In cooperation with large silicon companies, we found a gap in the CRM market for FSM materials that may match the composition of currently produced materials and be manufactured in accordance with the ISO 17034 standard [20], regarding the competence of the reference material producers. As a result, in 2020, a Polish–Norwegian research project under the acronym SilRef was established. The aim of the project was to develop new required CRMs for three types of silicon materials, including three grades of FSM. The alloys designed for the CRMs were produced by the Elkem company, a Norwegian silicon materials producer. Then, they were processed at Łukasiewicz—IMN to obtain the required homogeneity. One of the materials was a mixture of two FSMs developed to obtain the required chemical composition. Further analytical steps, such as the determination of the homogeneity and the stability uncertainty, as well as the determination of certified values and their uncertainty, were carried out. To determine the values of its characteristics, a multilaboratory strategy was used. Finally, four new CRMs were prepared for introduction onto the market.

2. Experiment

2.1. General Process of Development

The general process scheme is presented in Figure 1. While the general approach was determined by ISO 17034 [20], the individual stages had experimental and research characteristics. Because the reference materials for the FSM alloy were produced for the first time, it was necessary to develop a methodology to obtain a homogeneous material with a specified elemental composition. Furthermore, in subsequent stages, it was necessary to develop analytical methods that meet specific criteria. The technical and statistical approach to the process was carried out in accordance with ISO Guide 35 [24], while the documentation formats were developed in compliance with ISO Guide 31 [25].

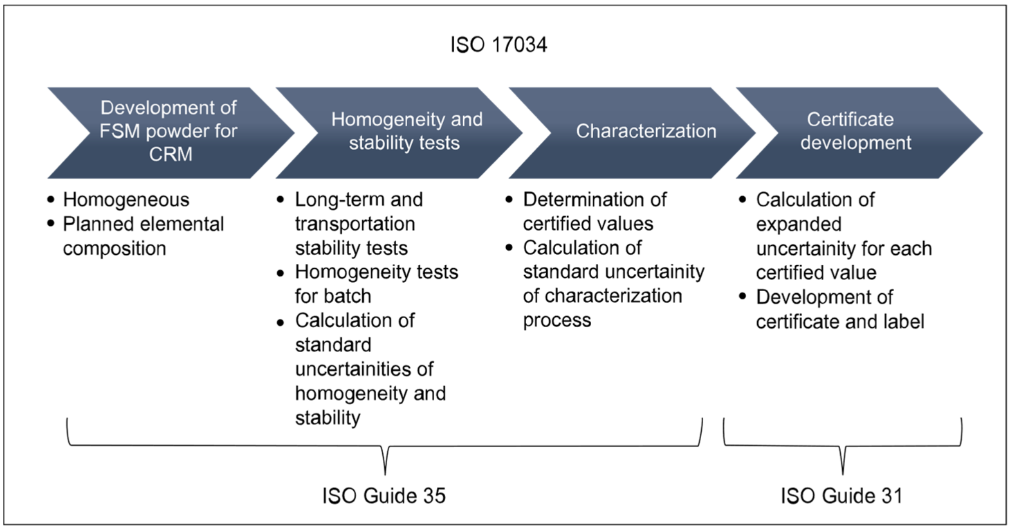

Figure 1. General scheme of development of the FSM CRMs [20,24,25].

2.2. Analytical Methods and Instrumentation

Several analytical methods were used in each stage of the CRMs' development.

2.2.1. Inductively Coupled Plasma Optical Emission Spectrometry

For the determination of Mg, Al, Ca, Ce, La, Ti, Cr, Mn, Ba, and P, an Ultima 2 ICP-OES spectrometer from Horiba Yobin-Yvon (Lyon, France) and a 5300 V ICP-OES spectrometer from Perkin Elmer (Cracow, Poland) were used. The difference between these two spectrometers is the manner of detection, as follows: the former is sequential, and the latter is simultaneous. Both spectrometers were calibrated based on synthetic standards.

First, 0.2 g of the sample was digested in a mixture of acids:HNO_3 and HF (VWR International Sp. z o.o., Gdańska, Poland) on a heating plate. The sample was evaporated to dryness, and the residue was dissolved in concentrated HCl (VWR International Sp. z o.o., Gdańska, Poland) with the addition of hydrogen peroxide (VWR International Sp. z o.o., Gdańska, Poland). Interference-free analytical lines were selected for the determination of the following individual elements: Mg—285.213 nm, Al—396.152 nm, Ca—422.673 nm, Ce—413.380 nm, La—333.749 nm, Ba—455.403 nm, Ti—336.121 nm, Cr—205.552 nm, Mn—257.610 nm, and P—178.229 nm (Supplementary Materials, File S1).

2.2.2. X-ray Fluorescence Spectrometry

For the determinations of Si, Fe, Mg, Ca, Ce, La, and Mn, an Axios Max WDXRF spectrometer equipped with a 4 kW rhodium anode tube, from Malvern Panalytical (Malvern, UK), was used. Samples were prepared in the forms of both pellets and borate beads.

To prepare samples as pellets, 4 g of the sample and 1 g of Licowax (i.e., binder; PD Instruments, Toszek, Poland) were weighed. The sample and binder were ground for 90 s in a grinder. Boric acid (VWR International Sp. z o.o., Gdańska, Poland) was prepared using a hydraulic press; then, the ground sample was placed in the press and pressed into a pellet.

The measurements were performed from a circular-shaped surface with a 20 mm diameter.

The spectrometer's operating parameters were as follows: analytical line (crystal, filter, detector type, tube parameters (kV/mA), and measurement time (s))—Fe Kα (LiF 200, Al 750 µm, scintillation, 60/66, and 20) and Si Kα (PE 002, none, flow, 25/160, and 20)

To prepare samples as borate beads, the following procedure was developed:

First, 2 g of sodium peroxide (VWR International Sp. z o.o., Gdańska, Poland), 1.5 g of sodium carbonate (VWR International Sp. z o.o., Gdańska, Poland), 0.2 g of sample, and 0.1 g of strontium carbonate (VWR International Sp. z o.o., Gdańska, Poland) were weighed and directly placed into a zirconium crucible. The crucible was put in the instrument (fusion machine, KATANAX X-300, Ms Spectrum, Warsaw, Poland), and ferroalloy pre-oxidation was started. After fusion and cooling, the crust of the Na_2O_2/Na_2CO_3/sample was broken in the zirconium crucible to reduce it to small pieces. Then, 4 g of flux (LiT/LiBr; PD Instruments, Toszek, Poland) was weighed in a platinum crucible, and 3 g of the Na_2O_2/Na_2CO_3/sample crust was added. The crust pieces were concentrated in the middle of the crucible. The rest of the flux (3 g) was weighted on the top to entirely cover the Na_2O_2/Na_2CO_3/sample crust. Finally, the crucible and mold were placed on the instrument, and the ferroalloy borate fusion method was started on the instrument.

The measurements were performed from a circular-shaped surface with a 27 mm diameter.

Spectrometer's operating parameters were as follows: analytical line (crystal, filter, detector type, tube parameters (kV/mA), and measurement time (s))—Fe Kα (LiF 200, none, scintillation, 60/66, and 12); Mg Kα (PX1, none, flow, 25/160, and 30); Ca Kα (LiF 200, none, flow, 30/133, and 30); Ce Lα (LiF 200, none, flow, 50/80, and 30); La Lα (LiF 200, none, flow, 50/80, and 30); Mn Kα (LiF 200, none, flow, 60/66, and 30); Sr Kα (LiF 200, Al 750 µm, scintillation, 60/66, and 12); and Sr Lα (PE 002, none, flow, 25/160, and 30) (Supplementary Materials, File S1).

2.2.3. Flame Atomic Absorption Spectrometry (FAAS)

For the determinations of Mg, Al, Ca, Cr, and Mn, a CE 3300 AAS-FAAS (Thermo Scientific, Dreieich, Germany) spectrometer was used. The samples were prepared in the same way as for the ICP-OES method (Supplementary Materials, File S1).

2.2.4. Gravimetric Method and Volumetric Method

The determinations of Si and Fe using classical methods were as follows:

The determination of silicon was performed using the gravimetric method, which included the following steps: melting 0.3 g of sample (in a nickel crucible) with an alkaline flux (a mixture of sodium–potassium carbonate and sodium tetraborate 10 hydrate; VWR International Sp. z o.o., Gdańska, Poland), adding sodium peroxide to the melted sample and melting it, leaching the cooled melt with water, precipitating the silicic acid (VWR International Sp. z o.o., Gdańska, Poland) with a solution of hydrochloric acid and gelatin, calcining the SiO_2 precipitate, and removing the silicon in the form of SiF_4. In the filtrate, after the separation of silicic acid, the iron was determined using the redoxometric titration method after two precipitations of iron(III) hydroxide, in HCl solution, reduction of Fe(III) to Fe(II) with $SnCl_2$, and titration with potassium dichromate solution with a concentration of $1/6\ K_2Cr_2O_7 = 0.1$ moL/L (0.1 N) until the color changed from green to purple, as indicated by the sodium salt of diphenylaminosulfonic acid (VWR International Sp. z o.o., Gdańska, Poland).

2.2.5. Prompt Gamma-Ray Activation Analysis (PGAA)

For the determinations of Si, Fe, Mg, Al, Ce, La, Cr, Mn, and Ti, the PGAA method was used. The samples were analyzed by detecting neutron-capture prompt gamma rays. The Budapest research reactor was a cold source of neutrons, which were guided by a neutron guide to the experimental positions. The samples were irradiated in a guided neutron beam, and the gamma rays from the radiative capture were detected. The main beam was divided into two beams using appropriate collimators; the upper beam served the PGAA facility. The beam can be collimated to a maximum cross-section of $2 \times 2\ cm^2$. Throughout the whole reactor campaign, the intensity of the incoming neutrons was monitored and recorded using an ORDELA Model 4511 N neutron detector (Ceric, Trieste, Italy). The chemical state of the material does not affect the energies and intensities of the peaks. All elements (except helium) can be analyzed without prior information about the analyte [26].

2.2.6. Neutron Activation Analysis (NAA)

For the determinations of Fe, Ce, La, Ba, and Cr, the NAA method was used. NAA is a method of quantitative analysis of the composition of chemical elements. During this type of analysis, stable nuclei of a sample are transformed into radioactive nuclei. The quantification of the reaction products is based on gamma radiation. NAA is characterized by favorable properties, such as a negligible matrix effect, excellent selectivity, and high sensitivity. Even small amounts (a few tens of mg) of (mostly solid) samples can be measured, in which about 35–75 elements in quantities of less than 0.01 µg can be determined with this method [27].

2.3. Standards and Materials

To ensure measurement consistency for the calibration of the spectral equipment and traceability of the results, the following standard was used: VWR International Sp. z o.o. (Gdańska, Poland) monoelement solution standard of Mg, Al, Ca, Ce, La, Ti, Cr, Mn, Ba, and P (1000 mg/L)

The calibrations of the XRF spectrometers were ensured using in-house materials produced by Elkem. The elemental contents of these materials were determined through interlaboratory comparisons. The measurement traceability of the XRF methodology was confirmed using a commercially available CRM, SRM-347, produced by the National Institute of Standards and Technology (Gaithersburg, MD, USA) [19].

2.4. Production and Postprocessing of Candidate CRM Materials

The planned compositions and forms of the 3 candidate materials were established in reference to the real market demand. The FSM materials were produced by Elkem Bjølvefossen in Norway (Si-FSM-1) and Elkem (Saguenay, Quebec, QC, Canada), with Si-FSM-2 and Si-FSM-3 as lumps of metal that required crushing before sieving. Because of the risk of explosion, the preparation company used an inert atmosphere in the crushing and milling process. The materials were sieved to obtain <100 µm fraction. Scanning electron microscope (SEM) pictures of the sample material are shown in Figure 2 (X-ray microanalyzer JXA 8230 from JEOL).

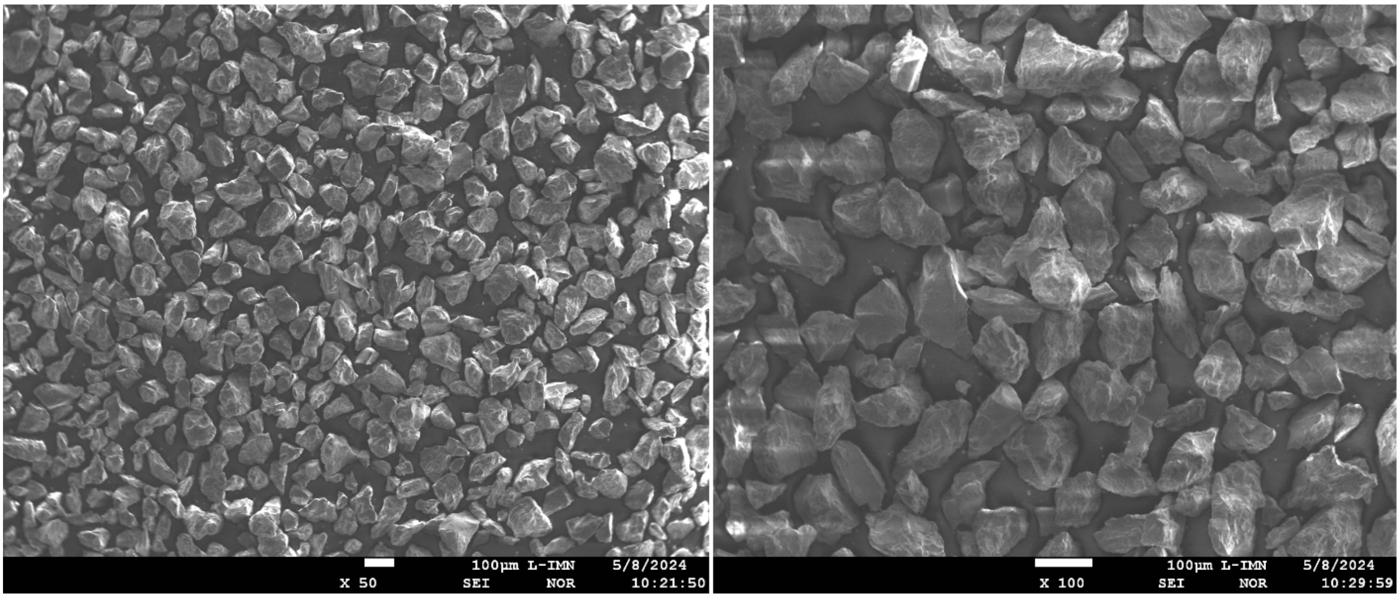

Figure 2. Morphology and topography of the Si-FSM-4 material: SEM SEIs (secondary electron images), with magnifications of 50× and 100×. White bar = 100 µm.

The initial homogeneity was routinely checked onsite before shipment due to unknown behavior during transport. Then, the preliminary compositions were determined using the

ICP-OES method (Mg, Al, Ca, Ce, La, Ti, Cr, Mn, Ba, and P) and the XRF method (Si and Fe) (Table 1).

Table 1. Results of the preliminary composition determinations (%).

	Si	Fe	Mg	Ce	La	Ca	Al	Ti	Mn	P	Ba	Cr
Si-FSM-1	48.0	45.3	3.4	0.47	0.24	0.94	0.41	0.39	0.48	0.011	0.14	0.081
Si-FSM-2	44.5	41.5	7.5	0.49	0.27	2.9	0.62	0.041	0.41	0.017	0.0051	0.029
Si-FSM-3	45.5	48.8	2.4	0.19	0.11	0.30	0.74	0.069	0.24	0.015	0.0035	0.070

The compositions of two of the three materials, Si-FSM-1 and Si-FSM-2, were acceptable, while the gap in the planned values was filled with the fourth material prepared as a mixture of two others, Si-FSM-2 and Si-FSM-3. In order to obtain a material with a satisfactory magnesium content, an attempt was made to mix the two types of FSM in the appropriate proportions. The first trial was carried out on a small scale, mixing 1 kg of each FSM with the highest and lowest Mg contents at a 1:1 ratio. The material was mixed for 1 h, after which 5 samples were taken from different points for testing to check the composition and homogeneity of the obtained material. The tests were carried out using the ICP-OES method (Mg, Al, Ca, Ce, La, Ti, Cr, Mn, Ba, and P) and the XRF method (Si and Fe). In order to obtain a satisfactory amount of material for the FSM type, a V-type mixer (EnviSense, Lublin, Poland) with a maximum load of 50 kg was used. Finally, the material was mixed at a 2:1 ratio, with 22 kg of FSM with the highest Mg content and 11 kg of FSM with the lowest Mg content introduced into the mixer. After 11 h of mixing (because of the heating of the mixing chamber, the process was divided into three stages: two for 4 h and one for 3 h), 3 samples were taken from 3 different places in the mixer (two parallel determinations were made from each sample), and chemical analyses were carried out using the methods of ICP-OES and XRF. Through this process, the material was found to be acceptable in terms of the magnesium content and homogeneity.

For the CRM candidate, research was conducted to determine its tendency to segregate. For this purpose, the sample was placed on a shaker, and the upper layer of the material was taken as a test sample after 2 h, 4 h, and 6 h of shaking. The analysis was performed using the ICP-OES and XRF (for Fe and Si) methods, and the results are presented in Table 2.

Table 2. Comparison of the composition of the FSM material before and after 2 h, 4 h, and 6 h of shaking (%).

	Si-FSM-4											
	Mg	Al	Ca	Ce	La	Ba	Ti	Cr	Mn	P	Fe	Si
2 h	5.63	0.61	1.99	0.38	0.22	0.0050	0.049	0.041	0.36	0.017	44.12	45.00
4 h	5.61	0.62	1.98	0.39	0.22	0.0049	0.049	0.040	0.36	0.017	44.00	44.91
6 h	5.63	0.61	1.99	0.40	0.22	0.0050	0.048	0.041	0.36	0.017	44.10	44.95

Finally, the 4 materials were split into final units (jars with 100 mL volume) using a plate divider. The planned and final compositions of the Si-FSM materials are shown in Table 3.

2.5. Homogeneity Tests

Homogeneity studies were conducted on batches of the materials after they were divided into target units. In accordance with the statistical rule (Equation (1)), 10 jars were randomly selected from which 3 independent samples of 0.2 g each were taken. The samples were analyzed, and the results and the methods are presented in Table 4.

Table 3. Planned and final compositions of the FSM materials for CRM (%).

		Si	Fe	Mg	Ce	La	Ca	Al	Ti	Mn	P	Ba	Cr
Si-FSM-1	Planned	48.0	45.3	3.4	0.47	0.24	0.94	0.41	0.39	0.48	0.011	0.14	0.081
	Final	48.34	45.21	3.41	0.484	0.2477	0.879	0.400	0.0380	0.488	0.0116	0.1401	0.0799
Si-FSM-2	Planned	44.5	41.5	7.5	0.49	0.27	2.9	0.62	0.041	0.41	0.017	0.0051	0.029
	Final	44.41	41.57	7.33	0.492	0.278	2.86	0.634	0.0449	0.440	0.0162	0.00553	0.0287
Si-FSM-3	Planned	45.5	48.8	2.4	0.19	0.11	0.30	0.74	0.069	0.24	0.015	0.0035	0.070
	Final	45.50	48.91	2.41	0.208	0.1082	0.293	0.713	0.0672	0.2509	0.0143	0.00332	0.0730
Si-FSM-4	Final	44.94	44.13	5.65	0.401	0.226	2.00	0.649	0.0512	0.375	0.0172	0.00494	0.0442

Table 4. Results of the homogeneity tests for the Si-FSM-4 material (%).

Unit No.	Si-FSM 4											
	Mg	Al	Ca	Ce	La	Ba	Ti	Cr	Mn	P	Si	Fe
11	4.984	0.616	1.927	0.331	0.208	0.0054	0.048	0.038	0.287	0.015	45.89	44.18
	4.931	0.608	1.940	0.325	0.208	0.0052	0.047	0.038	0.287	0.015	45.83	44.02
	4.881	0.623	1.867	0.335	0.206	0.0053	0.046	0.038	0.285	0.015	45.84	44.17
29	4.892	0.627	1.863	0.343	0.210	0.0053	0.046	0.038	0.290	0.015	45.91	44.28
	4.894	0.623	1.907	0.345	0.209	0.0052	0.047	0.038	0.290	0.015	45.91	44.41
	4.881	0.626	1.872	0.338	0.206	0.0052	0.047	0.038	0.294	0.015	45.78	44.09
58	4.794	0.626	1.886	0.342	0.207	0.0052	0.047	0.038	0.291	0.016	45.71	44.36
	4.928	0.649	1.907	0.343	0.211	0.0053	0.047	0.036	0.287	0.015	45.84	44.13
	5.020	0.678	1.957	0.352	0.211	0.0057	0.049	0.038	0.299	0.016	45.81	44.11
70	5.154	0.691	2.011	0.357	0.218	0.0059	0.049	0.038	0.294	0.015	45.89	44.15
	5.103	0.669	1.990	0.352	0.210	0.0055	0.050	0.038	0.289	0.016	45.81	44.51
	5.148	0.678	1.987	0.360	0.211	0.0058	0.048	0.037	0.289	0.015	45.89	44.16
117	4.991	0.637	1.835	0.331	0.203	0.0055	0.048	0.036	0.287	0.016	45.28	44.49
	4.877	0.635	1.836	0.325	0.198	0.0054	0.045	0.037	0.288	0.017	45.84	44.08
	4.803	0.607	1.887	0.328	0.200	0.0051	0.045	0.035	0.274	0.016	45.84	44.32
124	4.797	0.639	1.908	0.332	0.201	0.0053	0.048	0.036	0.291	0.016	45.83	44.50
	4.688	0.626	1.819	0.321	0.197	0.0051	0.048	0.036	0.293	0.017	45.69	44.28
	4.872	0.609	1.833	0.323	0.198	0.0053	0.046	0.037	0.299	0.018	45.85	44.17
125	4.989	0.630	1.908	0.329	0.201	0.0052	0.047	0.038	0.287	0.016	45.87	44.35
	4.981	0.630	1.831	0.341	0.194	0.0054	0.046	0.038	0.285	0.017	45.80	44.22
	4.964	0.610	1.851	0.327	0.197	0.0052	0.049	0.038	0.293	0.016	45.84	44.12
175	5.015	0.652	1.959	0.358	0.216	0.0057	0.049	0.038	0.299	0.016	45.80	44.10
	4.985	0.655	1.934	0.355	0.217	0.0056	0.049	0.038	0.294	0.016	45.83	44.15
	4.965	0.671	1.964	0.354	0.217	0.0057	0.050	0.038	0.294	0.015	45.87	44.02
190	4.963	0.643	1.879	0.326	0.194	0.0058	0.046	0.036	0.289	0.017	45.80	43.96
	4.987	0.613	1.830	0.336	0.196	0.0053	0.047	0.036	0.295	0.017	45.83	44.00
	4.961	0.627	1.829	0.337	0.204	0.0052	0.047	0.038	0.290	0.017	45.87	44.00
193	4.929	0.625	1.881	0.334	0.199	0.0054	0.046	0.038	0.296	0.016	45.70	44.24
	4.966	0.624	1.852	0.327	0.199	0.0052	0.048	0.036	0.293	0.016	45.93	44.18
	4.970	0.627	1.906	0.341	0.205	0.0056	0.049	0.037	0.291	0.016	45.66	44.00

The statistical rule for the minimum number of units for testing, as follows:

$$N_{min} = \max\left(10, \sqrt[3]{N_{prod}}\right) \quad (1)$$

where N_{min} is the minimum number of units for testing, and N_{prod} is the number of produced units.

The homogeneity test results were statistically evaluated using one-way analysis of variance (ANOVA). On the basis of this analysis, it was determined whether there were statistically significant differences between the elemental compositions of the individual samples, and the standard uncertainty of homogeneity was calculated according to the following equation:

Standard deviation between subjects:

$$s_{bb} = \sqrt{\max\left(\frac{MS_{among} - MS_{within}}{n}, 0\right)} \tag{2}$$

Standard uncertainty of within-subject standard deviation:

$$u'_{bb} = \sqrt{\frac{MS_{within}}{n}} \sqrt[4]{\frac{2}{N(n-1)}} \tag{3}$$

where MS_{among} is the variance between objects (between groups), MS_{within} is the variance within an object (within a group), n is the number of results for a single sample, and N is the number of samples selected for testing.

The larger of the determined values is the homogeneity uncertainty (u_h).

The final values of the homogeneity uncertainty are presented in Table 5. The acceptance criterion for homogeneity uncertainty in terms of its contribution to the uncertainty budget was also checked in reference to the relationship described by Equation (4).

Table 5. Statistical evaluation of the homogeneity uncertainty (u_h) of Si-FSM-4 (%).

(%)	Si	Fe	Mg	Al	Ca	Ce	La	Ba	Ti	Cr	Mn	P
s_{bb}	0.022	0.066	0.077	0.019	0.045	0.011	0.007	0.0001	0.0008	0.0006	0.005	0.002
u'_{bb}	0.034	0.046	0.027	0.004	0.010	0.002	0.002	0.0001	0.0004	0.0003	0.001	0.0003
u_h	0.034	0.066	0.077	0.019	0.045	0.011	0.007	0.0001	0.0008	0.0006	0.005	0.002

The homogeneity acceptance criterion in terms of its contribution to the uncertainty budget is:

$$\frac{s_r}{\sqrt{n}} \leq \frac{u_{targ}}{3} \tag{4}$$

where s_r is the standard deviation of repeatability, n is the number of results for a single sample, and u_{targ} is the assumed uncertainty of the property value.

2.6. Stability Tests

Stability tests were designed to demonstrate that the certified values did not change during the storage or transportation of the CRMs. In accordance with the guidelines of the PN-EN ISO 17034:2017-03 standard [20], both long-term and short-term stability tests were conducted. The long-term stability involved periodic testing of certified values to assess their stability. In the case of silicon materials, these tests were conducted twice a year (in January and June) until the completion of the production process. The samples for the stability studies were randomly taken from a selected jar. The short-term stability, which refers to the transport stability, was evaluated under conditions mimicking the transport of CRMs to customers. Three samples were taken from the selected unit, each stored at a different temperature, as follows: 40 °C, 5 °C, and −18 °C. The tests were repeated on days 2, 5, 8, and 10. The ICP-OES and XRF methods were used for the tests of the Si-FSM-4 material.

The uncertainty of the stability is part of the uncertainty budget. It is possible to declare the uncertainty of the stability irrelevant, in which case it will not be included in the uncertainty budget.

On the basis of the results of the short-term and long-term stability tests, statistical calculations were made to determine the uncertainty of stability.

2.7. Determination of Interlaboratory Reference Values: Characterization Process

The characterization (in this case, interlaboratory attestation) of materials for CRMs is a stage of production that involves external laboratories. The candidate material is distributed to evaluate the value of its properties. To ensure that the determined values are correct, it is preferable to involve as many laboratories as possible in this stage, and the analyses should be performed using various analytical techniques. The amount of sample needed to perform the analysis, the method of transport, and the time needed to perform the analysis were agreed among the laboratories.

2.8. Statistical Approach

On the basis of the results obtained from individual laboratories in the interlaboratory attestation, the following parameters were calculated as part of the assessment:

- Average of the results for each analyzed element for the set of results from each laboratory separately;
- Standard deviation for each analyzed element for the set of results from each laboratory separately;
- Average of the results for each analyzed element for the averages calculated for the results from the individual laboratories;
- Standard deviation for all results for each element analyzed.

For each element, a comparison was made among the results obtained with the different methods in the different laboratories. This comparison was graphically visualized in the form of a chart on which the median values for all results were plotted in a simple form, with a range separated by the value of two times the standard deviation for all results from the mean for all results, and the average results obtained in the laboratories with their standard deviations as error bars.

The Dixon Q test was used to compare, first, the results of each laboratory separately and then the averages among laboratories, showing that there were no statistically significant differences. On the basis of the approved results from the attestation process, a metrologist determined the certified values, understood as the arithmetic mean of the arithmetic averages of the partial results obtained in individual laboratories. Then, the uncertainty values of the attestation stage (u_{char}) were determined.

Uncertainty in the characterization process was calculated as:

$$u_{char} = \frac{s_{char}}{\sqrt{n}} \tag{5}$$

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

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

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

3. Results and Discussion

3.1. Method Validation

Before starting the research, an appropriate analytical method was selected and developed for each stage of CRM development. The XRF technique was selected to study the homogeneities and stabilities of Si and Fe, and the method was developed for the WDXRF Axios MAX spectrometer. For the remaining elements included in the CRMs (Mg, Al, Ca, Ce, La, Ba, Ti, Cr, Mn, and P), the ICP-OES technique was selected, and the analytical method was developed for the ICP-OES ULTIMA 2 spectrometer. In addition to XRF and ICP-OES, the following techniques were also involved in the characterization process: FAAS, gravimetric method, volumetric method, PGAA, and NAA. Each of the methods developed at the Center of Analytical Chemistry Łukasiewicz—IMN was validated. The method validation was carried out by performing four series of measurements (four repetitions in a series) of the SRM-347 purchased from the National Institute of Standards and Technology [19]. Validation parameters including intermediate precision, repeatability, and recovery were determined, and the uncertainty of the developed methods was estimated. Based on the obtained results, the usefulness and correctness of the methods developed for the intended purpose were confirmed.

3.2. Homogeneity and Stability Studies of Candidate CRM

Homogeneity tests were carried out using XRF and ICP-OES. The units for the study were selected randomly. Three independent samples (from different depths of the jar) were taken from each unit, obtaining a set of 30 results for each analyzed element. Statistical calculations were performed based on the obtained results. Table 5 presents the following determined parameters: s_{bb} and u'_{bb}.

Satisfactory homogeneity test results were obtained for each certified element. Each element met the homogeneity criterion.

The same analytical techniques were used for the short-term and long-term stability studies as those used for the homogeneity studies. The samples for the short-term stability studies were stored at different temperatures and collected for testing every 2 days, whereas the samples for the long-term stability studies were stored in storage conditions and collected for testing up to 6 months. The set of results allowed for a statistical evaluation according to the recommendations of the ISO Guide [24]. It was verified that the tested material met the stability condition for all reference components in both short- and long-term stabilities. Table 6 shows the results for Mg as an example.

$$A = |X_{CRM} - X_{moni}|$$

$$B = 2X\sqrt{u_{CRM}^2 + u_{moni}^2}$$

where u_{CRM} is the standard uncertainty of the certified value, and u_{moni} is the standard uncertainty of the analytical method used for the stability monitoring analysis

Table 6. Checking the stability of the magnesium ferrosilicon alloy (Si-FSM-4) at 40 °C; (%); ICP-OES method.

Day	Mg	u_{CRM}	u_{moni}	A	B	A < B
0	5.65	0.11	0.11 *	0	0.707	Yes
2	5.62	0.11	0.10	0.035	0.297	Yes
6	5.60	0.11	0.10	0.025	0.297	Yes
8	5.67	0.11	0.10	0.015	0.297	Yes
10	5.63	0.11	0.10	0.055	0.297	Yes

* As the primary result is the certified value obtained in the characterization process, the standard uncertainty of the analytical method used for the stability monitoring analysis was equal to the certified value.

The stability monitoring results show that there was no evidence of instability of the ferrosilicon magnesium alloy.

3.3. Participation in International Comparison

In order to correctly determine the certified values of all standard components, the material was sent to eleven different laboratories, at which determinations were made using various analytical methods.

Each laboratory provided six independent results or one result with uncertainty (for accredited methods). The obtained results were evaluated statistically.

A certified value was assigned, and the measurement of the uncertainty of the certified value of the candidate CRM material was evaluated.

The obtained results were evaluated statistically as follows:

1. For datasets from individual laboratories, the coefficient of variation was determined, which could not exceed 15% (for elements with <1%) or 5% (for elements with >1%).
2. The Q-Dixon test was performed, which allowed us to eliminate outliers within datasets obtained from a given laboratory and outliers from all obtained results.
3. The results were evaluated graphically. An exemplary graph of the results obtained for Mg is shown in Figure 3.

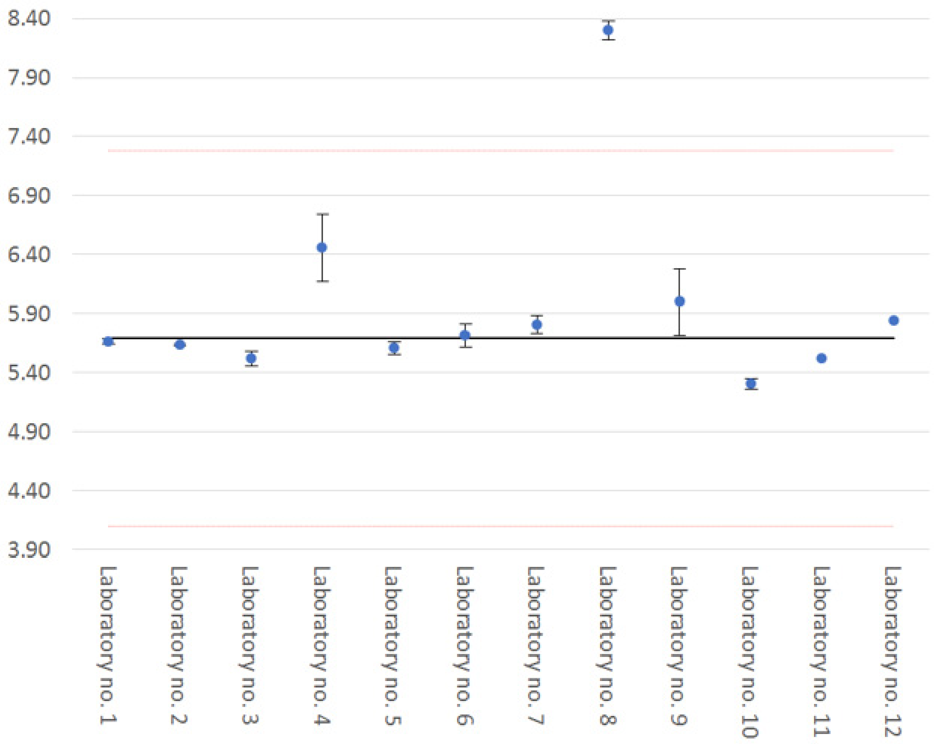

Figure 3. Graphical comparison of the results obtained for Mg. The blue points are laboratory results, with error bars corresponding to the laboratory standard deviation. The black line is the median of the results. The red lines indicate the limits for the 0.95 level of confidence.

On the basis of the accepted sets of results, certified values were determined, and their uncertainties were calculated. The chemical composition of the developed CRM is presented in Table 7.

Table 7. Chemical composition of the developed CRM Si-FSM-4: element concentration (C, mass %) and expanded uncertainty (U).

		Si (%)	Fe (%)	Mg (%)	Al (%)	Ca (%)	Ce (%)	La (%)	Ba (mg/kg)	Ti (%)	Cr (%)	Mn (%)	P (%)
Si-FSM-4	C	44.94	44.13	5.65	0.649	2.00	0.401	0.226	49.4	0.0512	0.0442	0.375	0.0172
	U	±0.99	±0.54	±0.22	±0.041	±0.12	±0.027	±0.017	±3.9	±0.0028	±0.0024	±0.017	±0.0039

The process of producing certified reference materials ended with the creation of appropriate documentation, such as a certificate and a label. These documents are consistent with the requirements of the ISO standard 17034 [20], as well as ISO Guide 31 [25]. The certificate contains all the necessary information, the most important of which include the designated certified values with expanded uncertainty, information on ensuring measurement traceability, analytical methods used in the interlaboratory attestation process and laboratories participating in it, information on intended use, and expiration date. Labels, on the other hand, enable direct identification of the CRM.

Taking into account the number of analytical methods used in the characterization (ICP-OES, FAAS, XRF, PGAA, NAA, gravimetric, and volumetric methods), the new CRMs may be used as a traceability factor for each of them. There are several differences among the analytical techniques, which may be considered in choosing the most suitable for the laboratory—uncertainty of the method, time and energy consumption, or access to specific analytical instruments. However, the most reasonable and environmentally friendly are methods which do not require dissolving and using other chemicals in the sample preparation, such as XRF. The new CRMs, as the first matrix reference materials for FSM, are essential for this method of solid-state sample analyses allowing for the obtainment of completely quantitative and traceable results. As the material's stability was proved, the CRMs could also be used in the periodical internal control of the quality and stability of the XRF spectrometer results.

4. Conclusions

New silicon matrix CRMs were developed in agreement with a scheme to produce four materials with the required elemental composition; verify their homogenization, investigate their stability, homogeneity, and compliance with segregation; determine the certified values using an interlaboratory test scheme; and perform a statistical evaluation of the results and calculation of the uncertainties. Three materials (Si-FSM-1 to 3) were produced, while the fourth (Si-FSM-4) was obtained by mixing two original ones to achieve the desired elemental composition. This allowed us to obtain a series with various concentrations of elements meeting the required concentration ranges. As the materials have a granulate form, a shaking test was carried out to test the compliance with the segregation. The method of preparing the materials for the CRM allowed us to achieve a material with a satisfactory low standard uncertainty of homogeneity for all elements. Long-term and short-term stability tests confirmed that the material properties did not change under the time and temperature conditions. The strategy for determining certified values assumed an analysis of elements among a network of eleven laboratories using available and suitable analytical methods. This approach, according to ISO Guide 35 [24], allowed us to decrease the impact of bias characteristic of each specific method. All analytical methods used in the process were validated, and the traceability was ensured mainly by using certified standard solutions. The results obtained in each stage were assessed statistically, and standard uncertainties resulting from homogeneity, stability, and characterization were calculated. Finally, four CRMs with certified values of Si, Fe, Mg, Al, Ca, Ce, La, Ba, Ti, Cr, Mn, and P and their accompanying expanded uncertainties (calculated with propagation of the standard uncertainty value) were obtained. The complete process was carried out in agreement with ISO standard 17034 [20] and ISO Guides [24,25]; thus, proper certificates were finally developed that meet the requirements of ISO Guide 31 [25]. Four matrix CRMs for ferrosilicon magnesium were prepared for introduction onto the international market.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr12051017/s1, File S1: The detailed information (analytical lines, measurement conditions) regarding the method of carrying out analyzes using the ICP-OES, XRF, FAAS methods developed by the Center of Analytical Chemistry Łukasiewicz—IMN.

Author Contributions: Conceptualization, J.K., J.A. and T.G.; methodology, J.K., J.A., K.B., A.Y.G., M.K. and J.C.; investigation, J.K. and E.J.; writing—original draft, J.K.; writing—review & editing, J.A., T.G. and A.J.-K.; supervision, T.G. and A.J.-K. All authors have read and agreed to the published version of the manuscript.

Funding: The research leading to these results has received funding from the Norway Grants 2014–2021 via the National Centre for Research and Development.

Data Availability Statement: Data are contained within the article and Supplementary Materials.

Conflicts of Interest: Authors Kjell Blandhol and Alf Yngve Guldhav were employed by the company Elkem ASA. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest. The Elkem ASA Company had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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