

Article

Development of in-House Industrial Fluosilicic Acid Certified Reference Material: Certification of H_2SiF_6 Mass Fraction

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Abstract: Fluosilicic acid is a by-product of the chemical phosphate industry, mainly during the manufacture of phosphoric acid and triple super phosphate (TSP). To ensure the accurate measurement of the H_2SiF_6 mass fraction in this by-product, method validation is required, which needs a certified reference material (CRM) with its traceability to the International System of Units (SI). This work describes the development of a certified reference material of fluosilicic acid, which is commercially unavailable. Details of all steps, such as sample preparation, homogeneity and stability studies, value assignment, establishment of metrological traceability, and uncertainty estimation of the certified reference material, are fully described. The H_2SiF_6 mass fraction in the CRM was quantified by two analytical methods, i.e., UV-VIS as a primary method of analysis and flame mode atomic absorption spectroscopy (AAS) as a second method. It is worth noting that the results obtained from each method were in good agreement. The CRM certified value and corresponding expanded uncertainty, obtained from the combined standard uncertainty multiplied by the coverage factor ($k = 2$), for a confidence interval of 95%, was $(91.5 \pm 11.7) \text{ g} \cdot \text{kg}^{-1}$. The shelf life of the developed CRM is determined to be 1 year, provided that storage conditions are ensured. The developed CRM can be applied to validate analytical methods, improve the accuracy of measurement data as well as to establish the meteorological traceability of analytical results.

Keywords: certified reference material; hexafluorosilicic acid; UV-VIS; AAS; method validation



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1. Introduction

Fluosilicic acid is an undesirable by-product of the phosphate fertilizer industry. It is mainly produced during the production of phosphoric acid and triple superphosphate from fluoroapatite [1]. Indeed, a typical chemical reaction consists of a sedimentary phosphate rock attack by concentrated sulfuric acid at high temperature. This reaction is exothermic and leads to emanation of silicon tetrafluoride SiF_4 and hydrofluoric acid HF with the gas stream [2]. These fluoride gases are washed in scrubbers and are transformed into fluosilicic acid [3]. This research work is carried out in order to be in agreement with environmental regulations which continue to limit chemical processing emissions. For this reason, phosphate plant operators are required to neutralize fluoride gas [3]. It is more environmentally friendly to capture these fluorinated gases in the form of fluosilicic acid by water absorption in scrubbers [3]. Interestingly, H_2SiF_6 by-product is considered to be an important source of silica and fluorine, which have several uses in many chemical industries [4–6].

To optimize the control of the fluosilicic acid recovery process and to investigate the valorization pathways of this by-product, the H_2SiF_6 mass fraction must be determined

during all the scrubbing cycles. Therefore, the validation and quality assurance of H_2SiF_6 analysis are of great importance.

Certified reference materials (CRMs) are the key factor in the validation or verification of analytical methods as well as for ensuring the reliability of analytical results in testing laboratories by using them for quality control and accuracy improvement. CRMs are characterized by metrologically valid procedures for specified properties. They are applied for different purposes, including for laboratory quality control and accreditation, training practitioners, instrument calibration, proficiency testing, methods validation and verification as well as for assigning values to other materials and establishing metrological traceability, etc. [7,8].

Since there are currently no fluosilicic acid certified reference materials commercially available, the present work describes the development of a new CRM of this matrix. The preparation includes two steps: sampling operation and sample preparation procedures. Quantification of the H_2SiF_6 mass fraction was performed using two independent analytical methods based on UV-VIS and flame mode AAS. The results obtained by both methods were in good agreement by taking into account their uncertainties. The assessment of homogeneity testing and stability testing, the assignment of reference value and uncertainty evaluation were carried out in accordance with ISO 35 Guide requirements [9].

2. Materials and Methods

2.1. Sampling and Preparation of Candidate CRM Sample

To carry out this study, a five-liter HDPE (high-density polyethylene) container of a sample was collected from the fluosilicic acid recovery process line. After mechanical homogenization of the container, 100 pre-cleaned polyethylene bottles were filled (approximately 50 mL of fluosilicic acid in each bottle) and sealed. The bottles were then numbered randomly from one (1) to one hundred (100) and stored at stable room temperature (25 °C).

2.2. Analytical Methods Used for Characterization

As there are no standardized methods to determine the H_2SiF_6 mass fraction, two indirect analytical methods were used for the characterization of the candidate material, i.e., UV-VIS and flame AAS. They are based on the analysis of the silicon mass fraction, which is proportional to that of H_2SiF_6 .

2.2.1. Determination of the H_2SiF_6 Mass Fraction by UV-VIS

For reference value-assignment, homogeneity testing, and stability testing studies, we used UV-VIS as a primary method to determine the silicon mass fraction in the sample in accordance with the standard for the determination of soluble silicates by molecular absorption spectrophotometry at the wavelength of 650 nm [10]. Then, the silicon concentration obtained was converted to the H_2SiF_6 mass fraction.

The silicon analysis of the samples was conducted using a Shimadzu 2600 spectrophotometer. A test portion of approximately 200 mg of the sample, weighed by a precision balance, AT 261 Mettler-Toledo AG, was diluted to 500 mL in a volumetric flask with high purity water (conductivity < 0.05 $\mu\text{S cm}^{-1}$). After that, a 5 mL aliquot of the solution was diluted to 100 mL. The complexation of the silicon, reduction of the complex, and measurement were carried out in accordance with the NF T90-007 standard method [10]. The spectrophotometer calibration was carried out by diluting a 1 g·L⁻¹ silicon standard reference material (SRM) from the National Institute of Standards and Technology (NIST).

2.2.2. Determination of the H_2SiF_6 Mass Fraction by Flame AAS

A flame atomic absorption spectrometer (Perkin Elmer PinAAcle 900T, Waltham, MA, USA), equipped with a nebulizer and a HF resistant spray chamber, was used to determine the total silicon concentration in the fluosilicic acid samples. The mineralization of the samples was carried out in plastic flasks by mixing 1 mL of aqua regia (mixture of two volumes of hydrochloric acid (wt. 37%) with a volume of 65% nitric acid (wt. 65%)), and

then 5 mL of hydrofluoric acid (wt. 40%). The flasks were immediately closed and were left to stand overnight at room temperature and were then filled to the mark after adding 60 mL of 50 g·L⁻¹ boric acid. Calibration was performed by using mono-elemental silicon standards, prepared from a 1000 ppm Si standard reference material from the National Institute of Standards and Technology (NIST). The measurement was carried out in a reducing flame of nitrous oxide-acetylene. The operating parameters of the instrument are summarized in Table 1. The results of silicon analysis are then converted to (g·kg⁻¹) H₂SiF₆ mass fraction.

Table 1. Atomic absorption spectrometer measuring conditions.

Element	Si
Wavelength (nm)	251.61
Slit (nm)	0.2
Acetylene flow rate (L·min ⁻¹)	8.3
Nitrous oxide flow rate (L·min ⁻¹)	6.0
Lamp current (mA)	40
Background correction	Yes
Repetition times	3

2.3. Homogeneity Study

The number of units used for the homogeneity study is given by Equation (1), according to ISO 35 Guide [9].

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

where N_{\min} and N_{prod} indicate the minimum number of units used for the homogeneity study and the total number units of the candidate material (100 units), respectively.

By this method, ten units (Units No. 009, No. 013, No. 021, No. 040, No. 048, No. 056, No. 070, No. 076, No. 086, No. 095) were randomly selected from the batch using the random number tool in Microsoft Office Excel® (2016).

The H₂SiF₆ mass fraction of these ten stratified random samples was analyzed using the UV-VIS method. Homogeneity testing was evaluated using the analysis of variance (ANOVA) on triplicate results. Figure 1 summarizes the scheme of this study.

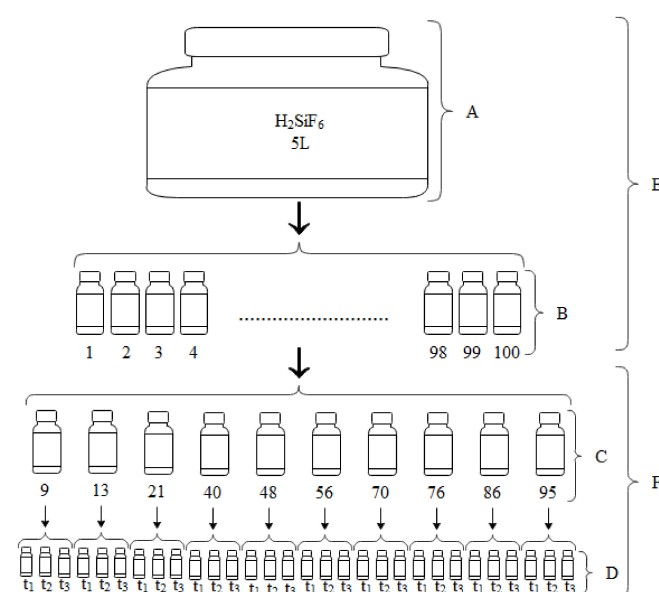


Figure 1. Scheme of the homogeneity study. (A) batch of fluosilicic acid; (B) sampling; (C) stratified samples contributing to the between-bottle variation; (D) aliquots contributing to within-bottle variation; (E) preparation; (F) measurement.

2.4. Stability Study

A stability study was performed by determining the H_2SiF_6 mass fraction in the samples using the UV-VIS method. In this work, the long-term stability was studied throughout one year at twelve different times. Each month, one bottle randomly chosen from the sampling batch stored at room temperature (about 25 °C) was analyzed on duplicate. The results were taken as the first point ($t = 0$ month) and were evaluated statistically using linear regression analysis.

The short-term stability of the candidate material was evaluated with and without heating the bottles at 35 °C for one week. Two randomly selected bottles stored in the laboratory (about 25 °C) were analyzed ($t = 0$ day) and then transferred to an oven set at 35 °C for a period of 7 days. For each bottle, two aliquots were taken and analyzed.

2.5. Confirmation of the Metrological Traceability

To obtain the comparability of measurement results to the International System of Units (SI), the metrological traceability of the reference value is a prerequisite [11]. For this, the metrological traceability of our material has been established according to the EURACHEM guide [12]. A calibrated precision balance (AT 261, Mettler-Toledo AG) was used for weighing the samples. The volumetric glassware used are class A and are checked regularly using the NF EN ISO 4787 standard method [13]. The spectrophotometer optical density was checked by using reference filters F2-666, F3-666, and F4-666, and wavelength accuracy was checked by using a holmium oxide reference filter. The spectrophotometer was calibrated by diluting a $1 \text{ g} \cdot \text{L}^{-1}$ silicon standard reference material (SRM) from the National Institute of Standards and Technology (NIST). The results obtained were compared with a second analytical method by flame AAS (Perkin Elmer Pin AAcle 900T).

2.6. Results Validation

The validation of the obtained results was carried out by analyzing an analytical grade fluosilicic acid 34% (w/w) in parallel with the candidate CRM sample, using a spectrophotometric method. The granted H_2SiF_6 mass fraction in analytical fluosilicic acid was in the range between 33.5% and 35% (w/w).

2.7. Assignment of Reference Value and Estimation of Uncertainty

The results from the homogeneity study of the candidate material were also used for the assignment of reference value. The mean value was assigned as the certified value of the H_2SiF_6 mass fraction.

The combined uncertainty of the certified value, including the uncertainties from characterization (u_{char}), homogeneity (u_{hom}), and stabilities (u_{Its} and u_{sts}), was calculated using Equation (2) according to the ISO 35 guide [9].

$$u_{\text{CRM}} = \sqrt{u_{\text{char}}^2 + u_{\text{hom}}^2 + u_{\text{Its}}^2 + u_{\text{sts}}^2} \quad (2)$$

The characterization uncertainty estimation was performed by using the law of propagation of uncertainties according to the ISO/IEC Guide 98-3 [14] and the Eurachem/Citac Guide [15].

Finally, the expanded uncertainty of the certified H_2SiF_6 mass fraction value (U_{CRM}) was calculated using a coverage factor $k = 2$ with 95% level of confidence.

3. Results and Discussion

3.1. Homogeneity Assessment of CRM

Homogeneity assessment of the candidate material was performed by analyzing ten randomly selected samples on triplicate as shown in Figure 2. The mean value for each sample was calculated. Thereafter, the data were initially assessed to determine the presence of outlier means by performing the Grubbs test with a 0.01 and 0.05 risk of error [16,17], and we verified that there were no outlying mean values (Table 2).

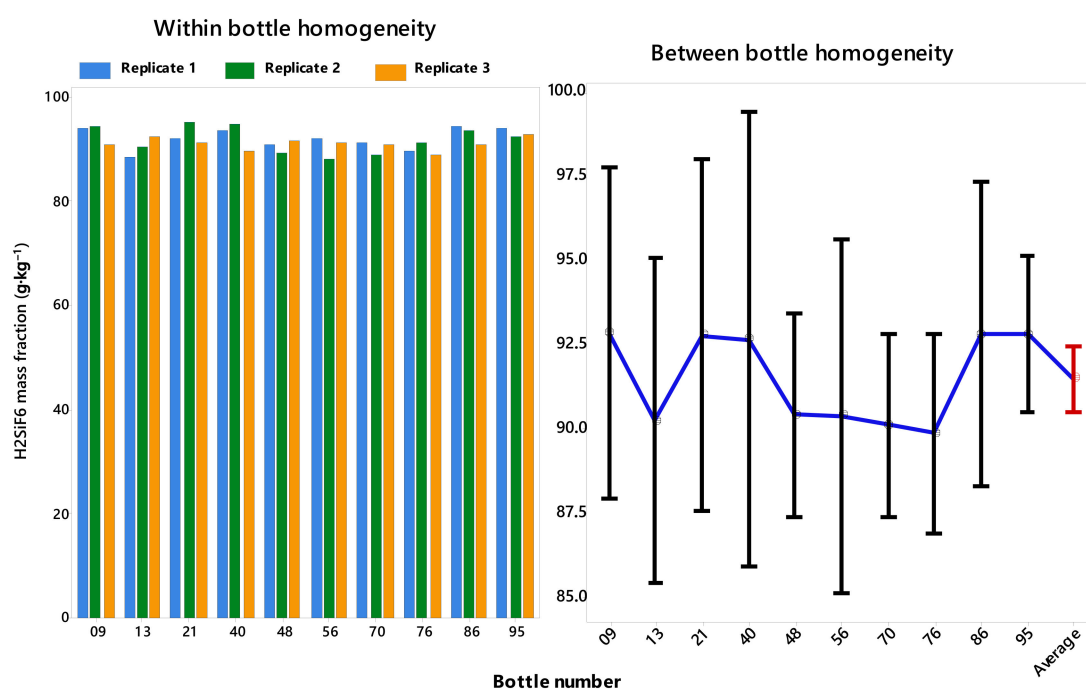


Figure 2. Within (wb) and between (bb) bottle homogeneity of the H₂SiF₆ mass fraction of the candidate CRM. Blue, green, and orange bars show the results of first, second, and third analysis of each sample, respectively.

Table 2. Means homogeneity by Grubbs test.

Criteria Observed for:	
The smallest average	1.195
The highest average	0.991
Limit for 1% risk	2.564
Limit for 5% risk	2.355

Figure 2 illustrates the within (wb) and between (bb) bottle homogeneity of the H₂SiF₆ mass fraction in the candidate certified reference material.

The within bottle homogeneity in the presented measurements series was determined for the 10 bottles (No. 09, 13, 21, 40, 48, 56, 70, 76, 86, 95). The blue, green, and orange bars in the diagram give the triplicate result for each sample.

The figure, which graphically shows the between bottle homogeneity, summarizes the average of the H₂SiF₆ mass fraction of aliquots taken from each sample together with the corresponding expanded uncertainty values, and the average value (red line) was determined as the average of the H₂SiF₆ mass fraction for all the analyzed units.

A first reading of the obtained graphs allows us to conclude that the individual results of the H₂SiF₆ mass fraction in the aliquots taken from the bottle are within the range given for the mean value of the analyzed package. The calculated intervals for the H₂SiF₆ mass fraction in the samples have a common part in the interval corresponding to the average value.

To statistically evaluate the homogeneity between different bottles and within the same bottle, a single-factor analysis of variance (ANOVA) at 95% confidence level [9] was used. The results of this test are presented in Table 3.

Table 3. One-way analysis of variance for the homogeneity study of the H₂SiF₆ mass fraction.

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square M	F-cal	p-Value	F-crit
Between bottles	50.89	9	5.65	1.74	0.14	2.39
Within bottles	64.87	20	3.24			
Total	115.76	29				

From the ANOVA analysis, it was observed that the F-calculated value was less than the F-critical value at 95% confidence level, demonstrating no significant difference between the between bottle (bb) and within bottle (wb) homogeneity criteria for the H₂SiF₆ mass fraction, which also indicates that the material was regarded to be sufficiently homogeneous.

It was also observed from the one-way ANOVA of the homogeneity testing results that the mean square between bottles (M_{between}) was higher than the mean square within bottles (M_{within}), which means that the method of measurement has good repeatability. In this case, the standard uncertainty associated with between bottle variance (u_{bb}) was calculated based on the ANOVA results by using Equations (3) and (4) (number of replicates $n_0 = 3$ and degrees of freedom of mean square within bottles $v_{M\text{within}} = 20$) [9]. However, the higher u_{bb} value (Equation (3)) was chosen for calculating the u_{CRM} [18].

$$u_{bb} = \sqrt{\frac{M_{\text{between}} - M_{\text{within}}}{n_0}} \quad (3)$$

$$u_{bb} = \sqrt{\frac{M_{\text{within}}}{n_0}} \cdot \sqrt[4]{\frac{2}{v_{M\text{within}}}} \quad (4)$$

The relative standard uncertainty due to between bottle inhomogeneity (u_{bb}) was 1.0% for the H₂SiF₆ mass fraction.

3.2. Stability Assessment of CRM

3.2.1. Long-Term Stability

The long-term stability of the H₂SiF₆ mass fraction in industrial CRM fluosilicic acid was assessed over a time interval of 12 months. Two subsamples of the material from one bottle, selected randomly, were analyzed at each time point (each month). The time at which the homogeneity was assessed was taken as day 0.

Figure 3 shows the change in the H₂SiF₆ mass fraction of the candidate material with the elapse of storage time at laboratory temperature (25 °C).

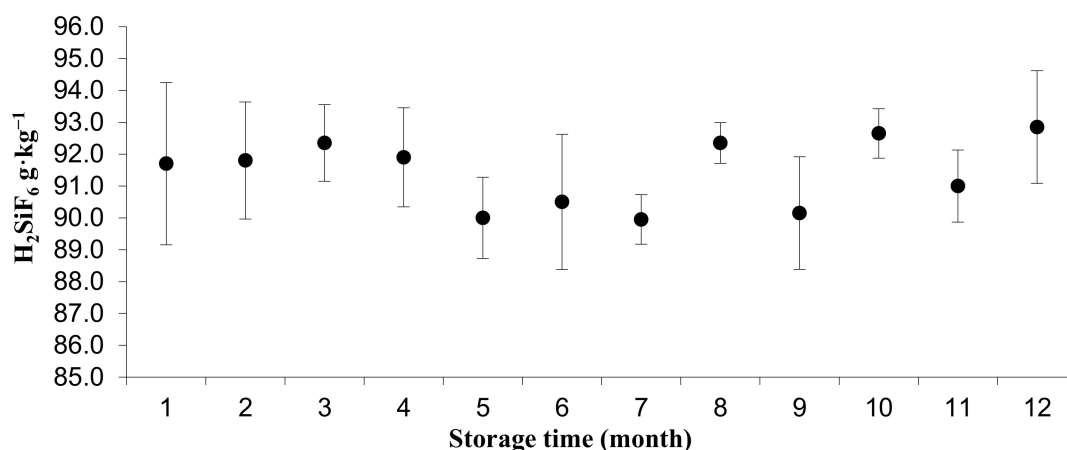


Figure 3. H₂SiF₆ mass fraction during the long-term stability test. Points and bars show the mean values and standard deviations, respectively.

As seen in Figure 3, the H_2SiF_6 mass fraction in industrial fluosilicic acid was shown to be stable over a period of at least one year.

Statistical evaluation of the study results was also performed using linear regression analysis aims to identify any instability in the analyte in accordance with the ISO Guide 35 [9]. When there is no model that realistically describes the degradation mechanism of a reference material, a linear model is usually used as an empirical model [19]. In this model, the intercept (b_0) is expected to be equal to the value obtained in the characterization, while the slope (b_1) should not be significantly different from zero [19]. Table 4 summarizes the analytical results of the long-term stability test.

Table 4. Linear regression analysis of the long-term stability.

	Slope (b_1)	Intercept (b_0)	Slope Standard Deviation (s_{b1})	p -Value (95%)	Student's t -Value	Student's t_{crit}
H_2SiF_6 ($\text{g}\cdot\text{kg}^{-1}$)	0.0185	91.3129	0.0935	0.8469	0.198	2.228

The statistical test used to demonstrate that the slope is not significantly different from zero was a Student's t -test for $n-2$ degrees of freedom at the 95% level of confidence [9]. Satisfactory results (Table 4) were obtained for this test ($t < t_{\text{crit}}$), in which the candidate CRM was analyzed each month throughout one year.

Additionally, to confirm the absence of significant instable trends during the time course, a Shapiro–Wilk test [20] was also introduced to assess the conformity of the distribution of residual regression line to normal distribution, and the results obtained from this test were satisfactory ($W > W_5\%$). Figure 4 shows the distribution of residuals of the regression line.

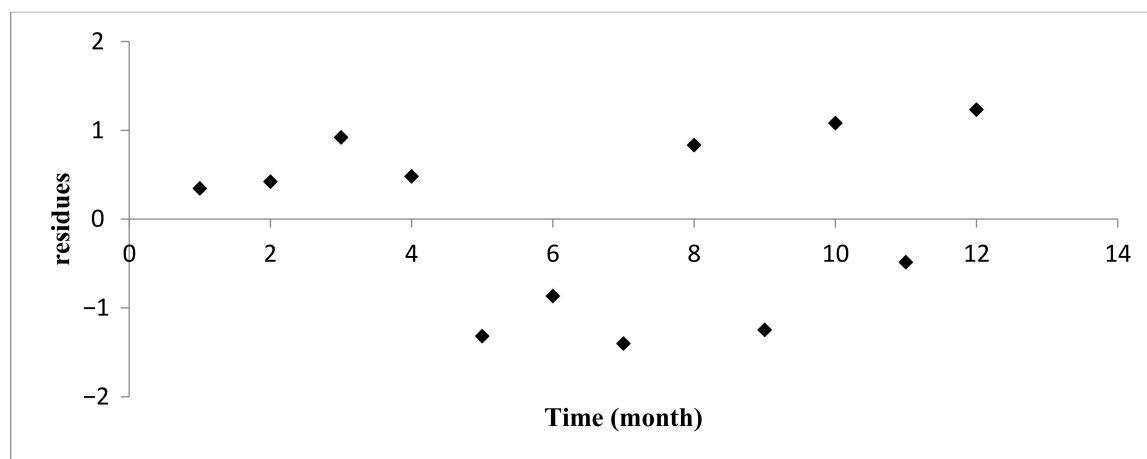


Figure 4. Residual regression line distribution of long-stability study results.

The standard uncertainty due to long-term stability of the material u_{Its} has been assessed in accordance with ISO Guide 35 [9]. u_{Its} was estimated based on the following Equation (5):

$$u_{\text{Its}} = t \times s(b_1) \quad (5)$$

where “ t ” represents the period of validity (12 months) and “ $s(b_1)$ ” represents the standard error of the slope. Thus, the “ u_{Its} ” value calculated for an expiry date of 12 months was used as the standard uncertainty due to the long-term instability during storage. The calculated value was $1.13 \text{ g}\cdot\text{kg}^{-1}$.

3.2.2. Short-Term Stability

In addition to the long-term stability, it is also important to consider the short-term stability of the CRM. Therefore, the short-term stability of the CRM was evaluated during

one week at two different temperatures; 35 °C and room temperature. Indeed, two bottles of samples were placed in each temperature point (in the oven at 35 °C and at room temperature), and then individually analyzed at the same time. The measured values of the H_2SiF_6 mass fraction in the material were $92.0 \text{ g}\cdot\text{kg}^{-1}$ ($s = 0.6 \text{ g}\cdot\text{kg}^{-1}$) and $91.3 \text{ g}\cdot\text{kg}^{-1}$ ($s = 0.8 \text{ g}\cdot\text{kg}^{-1}$) at 35 °C and room temperature, respectively.

These results indicate negligible differences in the H_2SiF_6 mass fraction at both storage temperatures, which proves that the material is stable and without significant changes in its chemical composition. Therefore, the uncertainty associated with the short-term stability (u_{sts}) was estimated as zero according to ISO Guide 35 [9].

3.3. Confirmation of Metrological Traceability

Metrological traceability is defined as a property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty [21]. The standards ISO/IEC 17025 and ISO 17034 require its demonstration [22,23].

The metrological traceability of the obtained results to the SI system was established by evaluating the measured variables included in the calculation according to the EU-RACHEM/CITAC Guide [12].

The H_2SiF_6 mass fraction, expressed in $\text{g}\cdot\text{kg}^{-1}$ and determined according to the Standard NF T90-007 [10], is calculated using the following Equation (6):

$$\text{H}_2\text{SiF}_6 (\text{g}\cdot\text{kg}^{-1}) = \frac{C}{m} \times V_t \times \frac{V}{v} \times \frac{M_{\text{H}_2\text{SiF}_6}}{M_{\text{SiO}_2}} \times 10^{-3} \quad (6)$$

where C is the concentration of SiO_2 , in milligrams per liter, in the test sample solution; V_t is the volume of the test sample in milliliters (500 mL); V is the volume of dilution (100 mL); v is the aliquot intake for dilution (5 mL); m is the mass of the sample in grams; and $M_{\text{H}_2\text{SiF}_6}$ and M_{SiO_2} are the molar masses of H_2SiF_6 and SiO_2 , respectively.

With:

$$C = \frac{A - B_0}{B_1} \quad (7)$$

where A is the absorption of the silicon complex in the sample solution; B_1 is the slope of the calibration curve; and B_0 is the intercept of the calibration curve.

It is worth noting that there are seven important parameters influencing the result in Equation (6): the concentration of SiO_2 in the test sample solution obtained from the calibration curve (C), the volume of the test sample (V_t), the volume of dilution (V), the volume of the aliquot (v), the mass of the sample (m), the molar mass of H_2SiF_6 , and the molar mass of SiO_2 . In order to establish the traceability of the result, it is necessary to establish the traceability of these influence parameters.

The absorbance (A), the intercept (B_0), and the slope (B_1) associate the concentration (C) of SiO_2 in the sample solution by Equation (7) to the concentration of the calibration solutions, establishing traceability to the values of the calibration solutions. These calibration solutions were obtained by diluting the reference solution of $(999.4 \pm 3.4) \text{ mg}\cdot\text{L}^{-1}$ of silicon (Si) in water. The concentration of the reference solution is traceable to a NIST SRM solution (NIST SRM No 3150) according to the manufacturer's certificate. The dilution steps were carried out using volumetric glassware, whose manufacturer specifies the value of the volume and its tolerance. The calibration solutions were measured using a molecular absorption spectrophotometer at $(650 \pm 10) \text{ nm}$, then the absorption values and the concentration of the calibration solution were used to calculate the intercept (B_0) and slope (B_1) of the calibration curve by least square linear regression. Photometric accuracy of the spectrophotometer was determined by comparing the difference between the measured absorbance of the reference standard materials and the established standard value [24]. Neutral density glass-filters F2-666, F3-666, and F4-666 certified by DKD (Germany) of various transmittance values at 440, 465, 546.1, 590, and 635 nm were used for this verification. The wavelength accuracy of the spectrophotometer was evaluated by measuring a known

wavelength of a holmium oxide filter standard reference [24], certified by DKD (Germany). The results of these two tests were satisfactory. These activities achieve traceability for the concentration of SiO_2 (C), which has the largest contribution to the overall uncertainty.

The various volumetric instruments used are class A. Because glassware can deform slightly over time and the glassware calibration is a dominant uncertainty source, the volume of the flask is checked regularly by weighing the given volume of water according to the laboratory glassware standard NF EN ISO 4787 [13]. The uncertainty of the glass expansion is taken into account in the uncertainty calculation.

The mass (m) needs to be traceable to measurement standards with sufficiently small uncertainty. This is provided regularly by normal calibration procedures for the balance with standard weights of class E2 traceable to the SI system by DKD (Germany). The associated calibration certificate is issued after each calibration. The linearity of the balance is checked regularly with internal standard weights.

The molecular weights of H_2SiF_6 and SiO_2 were calculated from the IUPAC atomic weights of the elements [25].

To strengthen this metrological traceability, the obtained results with the reference method [10] were compared to a second method of analysis by AAS. The obtained results are summarized in Table 5.

Table 5. Comparison of the H_2SiF_6 mass fraction obtained by UV-VIS and AAS.

No of Sample	H_2SiF_6 Mass Fraction ($\text{g}\cdot\text{kg}^{-1}$) Obtained by UV-VIS	H_2SiF_6 Mass Fraction ($\text{g}\cdot\text{kg}^{-1}$) Obtained by AAS	Relative Deviation
09	93.20	91.20	2.1%
13	90.43	90.09	0.4%
21	92.80	90.37	2.6%
40	92.67	90.54	2.3%
48	89.57	90.08	−0.6%
56	91.07	90.70	0.4%
70	89.80	91.70	−2.1%
76	89.53	92.97	−3.8%
86	92.83	90.60	2.4%
95	93.17	89.47	4.0%

Statistical evaluation of the difference between the analytical results obtained from both methods by an F-test to ensure that the variances from each method are statistically similar ($F < F_{\text{crit}} 5\%$) and a Student's *t*-Test for Equal Means from two samples ($t < t_{\text{crit}} 5\%$) [26] demonstrated that the differences were not significant. Therefore, the mass fractions determined using both protocols with very different principles were in good agreement. In addition, the relative deviation between the two methods is low compared to the uncertainty of the certified value (Section 3.5), which confirms the traceability of the certified value.

3.4. Accuracy of the Analytical Method Used for the Characterization

Accuracy study is the most important validation criteria and it is an indicator of the utility and applicability of a method with real samples [27]. It is also known that the result can be biased. Different components contribute to the persistent bias, such as laboratory bias, method bias, and the matrix-variation effect [27].

Since there are no certified fluosilicic acid solutions available commercially, and no laboratories willing to analyze these solutions independently could be found, method accuracy was therefore problematic. An indication of method trueness can be obtained by comparing the reference method with a second method [27], as reported in Section 3.3 (Table 5). The obtained results from the two methods are in good agreement. Another additional way to evaluate the accuracy of the analytical method used for the characterization of the CRM was by analyzing a pure fluosilicic acid at 34% (*w/w*), with a purity of 33.5%

to 35%, by molecular absorbance spectrophotometry [10], even if its concentration is not certified.

The value of pure fluosilicic acid was therefore in the range of 335 to 350 g·kg⁻¹, while the mean of the measured values under intermediate precision conditions [28] was 339 g·kg⁻¹ (s = 2.01 g·kg⁻¹), and it was in the range of the uncertainty of the assumed value. Therefore, no significant difference was observed between the measured and assumed values.

3.5. Assignment of Certified H₂SiF₆ Mass Fraction Value and Its Uncertainty

The certified value of the H₂SiF₆ mass fraction in industrial CRM fluosilicic acid is the mean of the analytical results obtained by molecular spectrophotometry [10] of the ten randomly selected samples analyzed on triplicate. The calculated value was found to be 91.5 g·kg⁻¹.

According to the ISO Guide 35 [9], the combined standard uncertainty for the certified H₂SiF₆ mass fraction (u_{CRM}) can be obtained following Equation (2) by combining u_{char} (the standard uncertainty due to characterization), u_{hom} (the standard uncertainty due to inhomogeneity), and u_{Its} and u_{sts} (the standard uncertainties due to long-term and short-term stabilities, respectively).

Table 6 summarizes the contribution of each factor to the overall combined uncertainty for the certified value.

To estimate standard uncertainty due to the characterization of the H₂SiF₆ mass fraction (u_{char}), the uncertainties from each component in Equation (6) were combined according to the ISO Guide 98-3 (law of propagation of uncertainties approach) [14] using the following Equation (8).

$$u(\text{char}) = \text{H}_2\text{SiF}_6 \left(\text{g} \cdot \text{kg}^{-1} \right) \times \sqrt{\frac{u^2(C)}{C^2} + \frac{u^2(m)}{m^2} + \frac{u^2(V_f)}{V_f^2} + \frac{u^2(V)}{V^2} + \frac{u^2(v)}{v^2} + \frac{u^2(M_{\text{H}_2\text{SiF}_6})}{M_{\text{H}_2\text{SiF}_6}^2} + \frac{u^2(M_{\text{SiO}_2})}{M_{\text{SiO}_2}^2}} \quad (8)$$

The uncertainty components for analyzing the H₂SiF₆ mass fraction are presented as a cause-and-effect diagram in Figure 5.

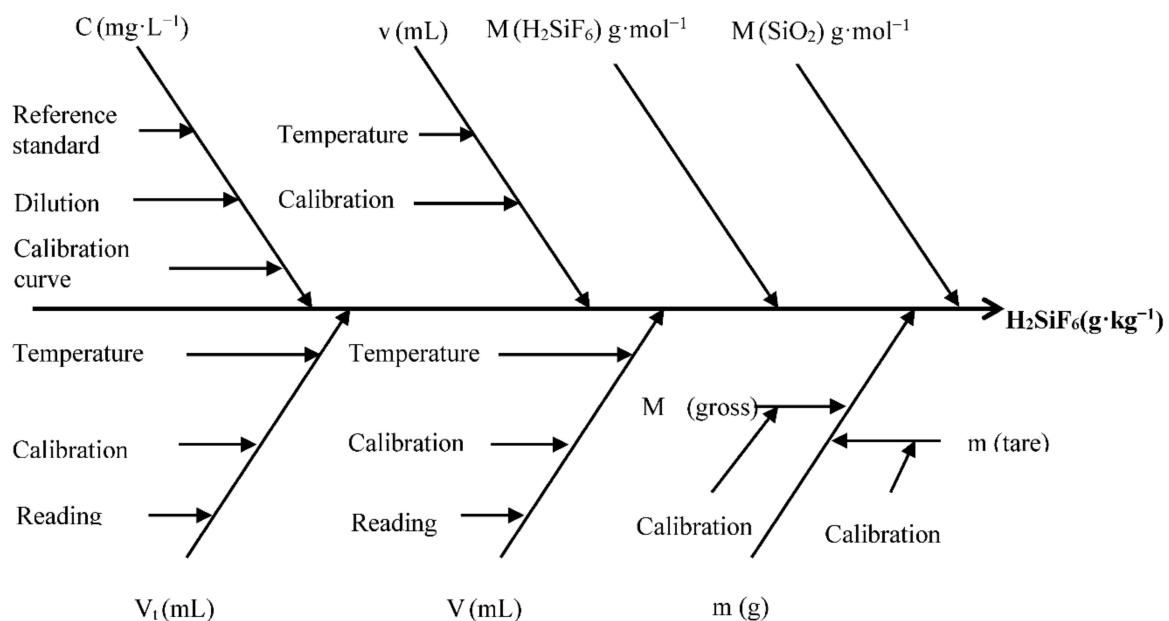


Figure 5. Cause and effect diagram with uncertainty sources of the H₂SiF₆ mass fraction characterization.

The concentration of SiO₂ (C in mg·L⁻¹) is calculated using a calibration curve. The linear least squares fitting procedure used assumes that the uncertainties of the values of the x-axis are considerably smaller than the uncertainty of the values of the y-axis [15].

Consequently, the usual uncertainty calculation procedures for C only reflect the uncertainty due to random variation in the absorbance and not the uncertainty of the calibration standards, nor the inevitable correlations induced by successive dilution from the same stock solution [15]; however, the uncertainty of the calibration standards is sufficiently small to be neglected. Thus, the estimated standard uncertainty of C is $0.044 \text{ mg}\cdot\text{L}^{-1}$ with an average of $0.763 \text{ mg}\cdot\text{L}^{-1}$. The uncertainty associated with the mass of the sample is estimated, using the data from the calibration certificate and the manufacturer's recommendations on uncertainty estimation, as being $U = (0.75 + 0.0034 \times m)$ in mg (coverage factor $k = 2$). This contribution has to be counted twice, once for the tare and once for the gross weight. This gives for the standard uncertainty of the masse ($u(m)$) a value of 0.00143 g .

The volumetric instruments used are influenced by three major sources of uncertainty: the uncertainty due to the calibrated internal volume of the instrument, the uncertainty due to the glass and solution temperatures differing from the temperature at which the volume was calibrated, and the uncertainty due to the variation in filling the instrument to the mark. The three contributions are combined to give the standard uncertainty of the volume. The typical uncertainties of the 500 mL flask, the 100 mL flask, and the 5 mL pipette are 0.33 mL, 0.07 mL, and 0.01 mL, respectively.

The standard uncertainties of the molar masses of H_2SiF_6 and SiO_2 have been calculated by combining the uncertainty of the atomic weights of their constituent elements published in the current IUPAC table [25]. The estimated standard uncertainties are $0.0006 \text{ g}\cdot\text{mol}^{-1}$ for the molar mass of H_2SiF_6 and $0.0007 \text{ g}\cdot\text{mol}^{-1}$ for the molar mass of SiO_2 .

By combining the uncertainties for each component as follows in Equation (8), the standard uncertainty of the analytical method (u_{char}) has been estimated at $5.32 \text{ g}\cdot\text{kg}^{-1}$.

The combined standard uncertainty of the certified value (u_{MRC}) was based on the combination of u_{char} , u_{hom} (Section 3.1), u_{ITS} (Section 3.2.1), and u_{STS} (Section 3.2.2), as follows in Equation (2), and was calculated to be $5.84 \text{ g}\cdot\text{kg}^{-1}$. As observed, the major contribution to the overall combined uncertainty (Table 6) came from the uncertainty of method characterization (u_{char}), while the contribution from the uncertainty of long-term stability (u_{ITS}) was less significant.

Table 6. Certified value uncertainty budget.

Source of Uncertainty	Symbol	Absolute Uncertainty ($\text{g}\cdot\text{kg}^{-1}$)	Relative Standard Uncertainty
Analytical method	u_{char}	5.3	5.8
Homogeneity	u_{hom}	2.1	2.3
Long-term stability	u_{ITS}	1.1	1.2

The expanded uncertainty (U_{MRC}) was calculated to be $11.7 \text{ g}\cdot\text{kg}^{-1}$ by multiplying the combined standard uncertainty (u_{MRC}) by the coverage factor k ($k = 2$).

4. Conclusions

A certified reference material of industrial fluosilicic acid was developed in this study, with homogeneity and stability testing studies, the establishment of metrological traceability, the assignment of reference value, as well as uncertainty evaluation. The H_2SiF_6 mass fraction of the developed CRM was determined by UV-VIS as a primary method of measurement. The accuracy of the results that were obtained by the primary analytical method (UV-VIS) was evaluated by comparing the results with those obtained with a second analytical method (AAS). As demonstrated, both results were in good agreement. In addition, a pure 34% (w/w) fluosilicic acid was analyzed with the first method and presented satisfactory results. The developed CRM showed good homogeneity and high stability for at least one year. The uncertainty of the certified value was estimated by combining the uncertainties due to the analytical method, homogeneity, and stability. The certified value of CRM developed in this study is traceable to the International System of

Units (SI). Since there is no available CRM fluosilicic acid in the market, this material will be useful for routine testing in the laboratory, especially for the validation and/or verification of internally developed analytical methods, for analytical instrument calibration, or for quality control.

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