

Scientific paper

# Optimization of the Sample Preparation Procedure for the Conversion of Enriched $^{28}\text{Si}$ Single Crystal to Enriched Gaseous $^{28}\text{SiF}_4$

Monika Inkret,<sup>a\*</sup> Staf Valkiers,<sup>a</sup> Michael Berglund,<sup>a</sup>  
Nineta Majcen,<sup>a</sup> Philip Taylor<sup>a</sup> and Jure Zupan<sup>b</sup>

<sup>a</sup>EC-JRC-Institute for Reference Materials and Measurements, Retieseweg 111, B-2440 Geel, Belgium

<sup>b</sup>National Institute of Chemistry, Laboratory for Chemometrics, Hajdrihova 19, SI-1001, Ljubljana, Slovenia

\* Corresponding author: E-mail: monika.inkret@ec.europa.eu

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## Abstract

This work is a detailed study of the investigation of the optimization of the procedure for the conversion of highly enriched  $^{28}\text{Si}$  single crystal into gaseous silicon tetrafluoride ( $^{28}\text{SiF}_4$ ) with the highest purity ever achieved. The gaseous  $^{28}\text{SiF}_4$  of highest possible purity is required for the determination of silicon molar mass via performing silicon isotope ratio measurements on highly enriched  $^{28}\text{Si}$  (> 99.99% of  $^{28}\text{Si}$ ) using electron impact gas mass spectrometry. The problem is in avoiding the contamination of enriched  $^{28}\text{Si}$  samples with silicon of natural isotopic composition. The maximal allowed contamination is in order of  $10^{-9}$  g of silicon of natural isotopic composition. The sample preparation of highly enriched  $^{28}\text{Si}$  samples is the largest contributor to the relative combined uncertainty of silicon isotope ratio measurements, which should not exceed  $1 \times 10^{-4}$ . Accordingly this contribution affects the relative combined uncertainty of silicon molar mass. The experiments necessary to achieve this uncertainty in the procedure were carefully designed to avoid superfluous work and to reduce the costs which might be high due to the required quantities of very expensive enriched  $^{28}\text{Si}$  samples. The optimal sample preparation conditions (and execution of these measurements) obtained within this work are part of the large-scale experiments designed for the calibration of Si isotope ratio measurements of highly enriched  $^{28}\text{Si}$ , needed for the final determination of Si molar mass as one of the input quantities needed for determination of the Avogadro constant.

**Keywords:** sample preparation, optimization, enriched  $^{28}\text{Si}$  single crystal, isotope ratio measurements

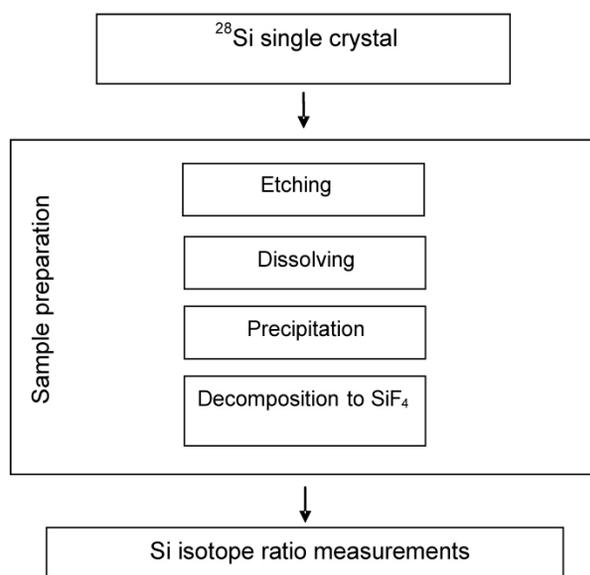
## 1. Introduction

Silicon is the second most abundant element in the earth's crust after oxygen. It never appears free in nature because of its high affinity especially to the oxygen. Silicon consists of three stable isotopes which abundances in naturally occurring silicon are 92.23% of  $^{28}\text{Si}$ , 4.67%  $^{29}\text{Si}$  and 3.10%  $^{30}\text{Si}$ . One of the most important applications of elemental silicon is in the semiconductor industry, while silicon compounds can be used as components in many materials such as cement, bricks, glass, rubber etc.<sup>1,2</sup> Silicon has also being chosen as a material to be investigated in the frame of the redetermination of the Avogadro constant ( $N_A$ ) using the X-Ray Crystal Density Molar Mass Method (XRCD method) as it is relatively easily available in large amounts.<sup>13</sup> The results of the presented experiments are part of this project.

In the previous phases of this project that dates back to

the 1980ies, measurements were always carried out on silicon of natural isotopic composition.<sup>3-9</sup> Relative combined uncertainty of  $N_A$  obtained using this material was only  $3.1 \times 10^{-7}$ , which was not good enough in order to realize the redefinition of the kilogram, which is the aim of the project for the redetermination of Avogadro constant.<sup>14</sup> In order to realize the redefinition of the kilogram, as one of the basic SI units, determination of silicon molar mass with relative combined uncertainty of  $1 \times 10^{-8}$  and accordingly determination of Avogadro constant with relative combined uncertainty of  $2 \times 10^{-8}$  have to be successful.<sup>15</sup> Therefore some improvements of XRCD method with further decreasing of relative combined uncertainty of  $N_A$  was started to be done with measurements to be performed on a single crystal produced from silicon that is isotopically highly enriched in  $^{28}\text{Si}$ . The reason of using highly enriched  $^{28}\text{Si}$  (> 99.99% of  $^{28}\text{Si}$ ) is almost perfect crystal structure with very low degree of impurities.

Silicon molar mass determination as one of the input quantities for the determination of Avogadro constant, are required involving determinations of the isotope abundances ( $f_i$ ) of the three silicon stable isotopes with atomic masses  $A_r(^i\text{Si})$ ,  $i = 28, 29, 30$ , which are done via isotope ratio measurements. These measurements are performed using an electron impact gas mass spectrometry which requires the conversion of enriched  $^{28}\text{Si}$  single crystal to the gaseous silicon tetrafluoride ( $^{28}\text{SiF}_4$ ) as shown in Fig. 1.<sup>5,16</sup>



**Figure 1:** Flowchart of the procedure for the conversion of highly enriched  $^{28}\text{Si}$  single crystal to gaseous silicon tetrafluoride.

As it is very well known, one of the most critical parts in any measurement procedure is the sample preparation and therefore it needs to be performed in a conscientious and controlled way. The study and the optimization of any method mean conducting a set of experiments which provide the data about one or more method performance characteristics under a variety of conditions. The experiments are designed to determine the relationship between the input variables affecting the process and the output of the process.

The conversion of highly enriched  $^{28}\text{Si}$  single crystal to the gaseous silicon tetrafluoride (Fig. 1) via dissolution of highly enriched  $^{28}\text{Si}$  in the mixture of conc. HF and conc.  $\text{HNO}_3$  was investigated and optimized as the novel sample preparation procedure for the conversion of highly enriched  $^{28}\text{Si}$  single crystal to the gaseous silicon tetrafluoride. Up to now, this conversion was done via a dissolution of silicon of natural isotopic composition in dil.  $\text{NaOH}$ .<sup>(5)</sup> Enriched  $^{28}\text{Si}$  single crystal can easily be contaminated during the chemical treatment with silicon of natural isotopic composition as silicon is the second most abundant element in the earth's crust and thus it can be present as an

impurity in any material, chemicals (conc. HF, conc.  $\text{HNO}_3$ ,  $\text{BaCl}_2$  etc.) and also in laboratory environment. Contamination is thus an important bias on silicon isotope ratio measurements and accordingly the silicon molar mass determination. If we want to fulfil the requirement in obtaining relative combined uncertainty of silicon molar mass of  $1 \times 10^{-8}$  needed for the determination of Avogadro constant with relative combined uncertainty of  $2 \times 10^{-8}$ , then relative standard uncertainty of measured silicon isotope ratios may not be higher than  $1 \times 10^{-4}$ . The major problem in fulfilling those requirements is the contamination of enriched  $^{28}\text{Si}$  with silicon of natural isotopic composition during the whole measurement procedure. As the simulations have shown, during the sample preparation of about 50 mg of enriched  $^{28}\text{Si}$  (> 99.99% of  $^{28}\text{Si}$ ) the contamination with only 0.5  $\mu\text{g}$  of silicon of natural isotopic composition with standard uncertainty of 1%, already effects the silicon molar mass for  $4 \times 10^{-8}$ .<sup>16–20</sup>

Therefore the purpose of the optimization is to minimize contamination with silicon of natural isotopic composition in order to obtain relative combined uncertainty of silicon molar mass of  $1 \times 10^{-8}$  and relative combined uncertainty of Avogadro constant of  $2 \times 10^{-8}$ . Due to that, all the research work presented here was done at the border of nowadays capabilities regarding the measurement uncertainty.

The optimization also gives an overview of effect of all input quantities on the measured isotope ratios and its measurement uncertainty. A very well described and evaluated measurement uncertainty is a precondition of each measurement result, also the isotope ratio measurements.

## 2. Experimental

All sample preparations were carried out in the ultra clean laboratory at the Institute for Reference Materials and Measurements. The Teflon labware was cleaned by leaching with supra pure  $\text{HNO}_3$  and subsequently rinsed with MQ water prior to use in the experiments.

### 2.1. Sample preparation procedure

There are several steps in the sample preparation procedure for the conversion of enriched  $^{28}\text{Si}$  single crystal to gaseous  $^{28}\text{SiF}_4$  but the main four are:

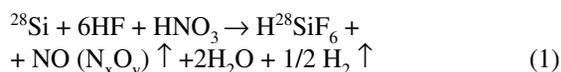
1. Etching of the  $^{28}\text{Si}$  sample
2. Dissolving/digestion of the  $^{28}\text{Si}$  sample
3. Precipitation to the  $\text{Ba}^{28}\text{SiF}_6$
4. Decomposition to the  $^{28}\text{SiF}_4$

All these steps may influence the measured responses which are the measured silicon isotope ratios.

The usual mass of the  $^{28}\text{Si}$  sample taken for the conversion of enriched  $^{28}\text{Si}$  single crystal to enriched  $^{28}\text{SiF}_4$  is about 50 mg and as the  $^{28}\text{Si}$  samples are available as slices they have to be cut into small pieces and weighed prior to start with the chemical treatment.

Due to cutting and polishing after the crystal growth and exposing of  $^{28}\text{Si}$  single crystal to the open air, a surface layer is formed. It can be described as a mixture of  $\text{SiO}_x$  with  $x$  from 1 to 2 with a major part of  $\text{SiO}_2$  with possible contamination by silicon of natural isotopic composition incorporated in this surface layer. Upon this, there is also a possibility that any other dust sticks to the surface. These possible contaminations give slightly higher measured Si isotope ratios and thus decrease the enrichment of the sample. A suitable method to remove the surface layer, dust and other particles from the  $^{28}\text{Si}$  surface is a wet etching process. A widely used isotropic Si etchant is a mixture of  $\text{HNO}_3$  (69%), HF (49%) and  $\text{CH}_3\text{COOH}$  (99%). A typical mixture composition is  $\text{HNO}_3$ :HF: $\text{CH}_3\text{COOH}$  with the mixing ratios 2:1:1 (v/v) and the etching rate about  $20 \mu\text{m min}^{-1}$ . All the acids used for preparation of etching mixture must be concentrated ultrapure acids to avoid possible contamination.  $^{28}\text{Si}$  sample is immersed in the etching solution as described above for 3 min and rinsed in MQ water immediately after etching.

Silicon in the crystalline form is relatively unreactive towards aqueous acids except the aggressive mixture HF/ $\text{HNO}_3$  and hot aqueous alkali solutions. Digestion (Eq. 1) of the enriched  $^{28}\text{Si}$  sample is performed in the 1.8 mL of conc. HF (49%) and 0.3 mL of conc.  $\text{HNO}_3$  (69%) mixture and in a preweighed and partially covered Teflon beaker to avoid possible losses of  $^{28}\text{Si}$  as a volatile  $^{28}\text{SiF}_4$  and to allow generated hydrogen to be evacuated.



It is known, that there is not only NO formed during the digestion of  $^{28}\text{Si}$  sample in HF/ $\text{HNO}_3$  mixture but different nitrogen oxides ( $\text{N}_x\text{O}_y$ ) can be formed. As generated NO was found to be one of the dominant N-oxides (see also Fig. 4), we balanced the Eq. 1 only for NO, but we have to be aware that there is also a possibility of other nitrogen oxides ( $\text{N}_x\text{O}_y$ ) to be formed.

Next step in the sample preparation procedure is a precipitation of  $^{28}\text{Si}$  to  $\text{Ba}^{28}\text{SiF}_6$  by adding a 0.1% solution of  $\text{BaCl}_2$  to  $\text{H}_2^{28}\text{SiF}_6$  in 2% excess (Eq. 2).



While adding of  $\text{BaCl}_2$ , the solution must be stirred in order to prevent conglomeration. As soon as the addition of  $\text{BaCl}_2$  is finished, the evaporation starts at  $100 \text{ }^\circ\text{C}$  to complete dryness of the precipitate which is used for the decomposition to the gaseous  $^{28}\text{SiF}_4$ .

Decomposition (Eq. 3) is done in the conversion unit (Fig. 2) under vacuum of  $10^{-4} \text{ Pa}$ .



The ampoule filled with about 100 mg of  $\text{Ba}^{28}\text{SiF}_6$  is dried in two steps; first at  $100 \text{ }^\circ\text{C}$  for 1 h and another at  $150 \text{ }^\circ\text{C}$  for 15 minutes. All more volatile compounds are pumped off to eliminate all traces of water and air and to reduce the  $\text{N}_x\text{O}_y$  coming from decomposition of the nitrate. After this drying process the conversion of  $\text{Ba}^{28}\text{SiF}_6$  is completed at  $540 \text{ }^\circ\text{C}$  in 30 minutes. The generated  $^{28}\text{SiF}_4$  gas stays condensed in the system while other less volatile gases are collected in the spiral trap cooled with a mixture of ethanol and dry ice ( $T = -80 \text{ }^\circ\text{C}$ ). After conversion, the  $^{28}\text{SiF}_4$  gas is collected in an ampoule and solidified in liquid nitrogen.  $^{28}\text{SiF}_4$  gas is then ready for silicon isotope ratio measurements.

Silicon isotope ratio measurements are performed using electron impact gas mass spectrometry. The ampoule with  $^{28}\text{SiF}_4$  gas is connected to the mass spectrometer and  $^{28}\text{SiF}_4$  gas is introduced into the inlet system of mass spectrometer. After conditioning the mass spectrometer, ion current measurements are performed at  $m/z = 85$  ( $^{28}\text{SiF}_3^+$ ), 86 ( $^{29}\text{SiF}_3^+$ ) and 87 ( $^{30}\text{SiF}_3^+$ ) and the ion current ratios  $I(^{29}\text{SiF}_3^+)/I(^{28}\text{SiF}_3^+)$  and  $I(^{30}\text{SiF}_3^+)/I(^{28}\text{SiF}_3^+)$  are calculated for each measurement time  $t$ . The silicon isotope ratios are afterwards determined by the extrapolating the ion current ratios to the time zero ( $t_0$ ).

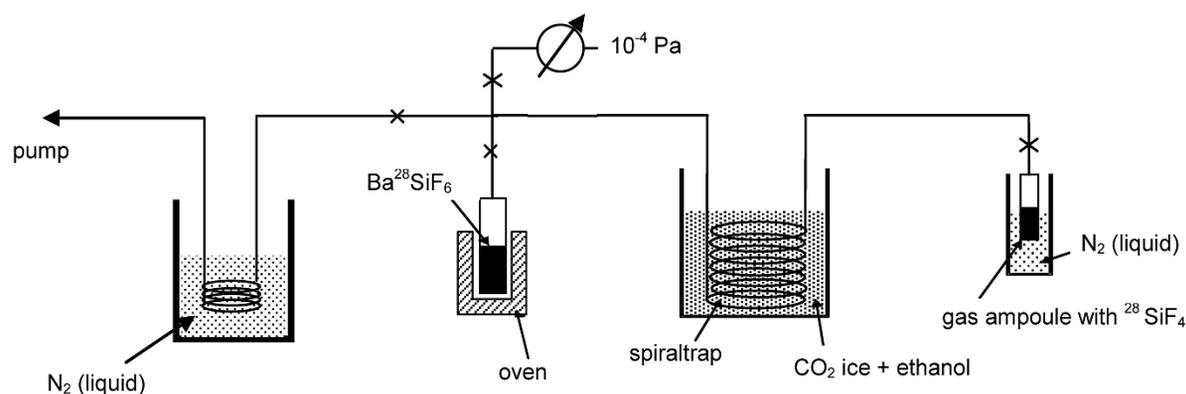


Figure 2. Conversion unit for the decomposition of  $\text{Ba}^{28}\text{SiF}_6$  to  $^{28}\text{SiF}_4$ .

## 2. 2. Optimization of the Sample Preparation Procedure

Optimization of the sample preparation procedure for the conversion of  $^{28}\text{Si}$  single crystal to the gaseous  $^{28}\text{SiF}_4$  was designed in such a way that within the four main steps in the sample preparation procedure seven variables were investigated (Table 1).

**Table 1:** Different variables studied during the optimization of the sample preparation procedure

| Variable                                    | Value                             |                                 |  |
|---|-----------------------------------|---------------------------------|--|
|   | low                               | medium                          | high   |
| Etching time                                | 0 min                             | 1 min                           | 3 min  |
| Volume of acids for digestion               | 1.8 mL HF + 0.3 mL $\text{HNO}_3$ | 3 mL HF + 0.5 mL $\text{HNO}_3$ | 6 mL HF + 1 mL $\text{HNO}_3$  |
| Excess of $\text{BaCl}_2$ for precipitation | 0%                                | 2%                              | 10%  |
| Drying step                                 | no drying                         | 1 drying at 100 °C              | 1 <sup>st</sup> drying at 100 °C +<br>2 <sup>nd</sup> drying at 150 °C |
| Drying time for first drying at 100 °C      | 15 min                            | 30 min                          | 60 min   |
| Drying time for second drying at 150 °C     | 10 min                            | 15 min                          | 30 min   |
| Conversion time at 540 °C                   | 15 min                            | 20 min                          | 30 min   |

All variables were investigated at three levels one after the other while during changing one variable the values of others were kept constant.

### 2. 2. 1. Etching

The etching time was the first variable to be studied within this optimization. A  $^{28}\text{Si}$  sample was cut into several pieces and three of them were taken for the investigation of the etching. Each  $^{28}\text{Si}$  enriched piece (sample) was weighed prior to immerse in the etching solution of conc.  $\text{HNO}_3$  (69%), conc. HF (49%) and conc.  $\text{CH}_3\text{COOH}$  (99%) with mixing ratios 2:1:1 (v/v). Three different etching times were chosen for the investigation (0, 1 min and 3 min). The  $^{28}\text{Si}$  samples were rinsed in MQ water immediately after etching. To investigate the effect of different etching times on the measured Si isotope ratios and the enrichment of  $^{28}\text{Si}$  samples, the samples were converted to the gaseous  $^{28}\text{SiF}_4$  using several sample preparation steps (paragraph 2.1) and the Si isotope ratios were measured.

### 2. 2. 2. Digestion

The volume of dissolving mixture was investigated as the second variable. The stoichiometric volumes of conc. HF (49%) and conc.  $\text{HNO}_3$  (69%) for the digestion of 50 mg of enriched  $^{28}\text{Si}$  are so small that they not even cover the whole piece of  $^{28}\text{Si}$  sample which can result in an ex-

ceedingly long time for complete dissolving of  $^{28}\text{Si}$ . To find the optimal volumes of conc. HF (49%) and conc.  $\text{HNO}_3$  (69%), meaning the smallest possible volumes of ultra pure conc. HF and conc.  $\text{HNO}_3$ , which would result in complete digestion of enriched  $^{28}\text{Si}$  samples in a reasonable short time, the experiments with three different volume ratios (Table 1) were performed.

### 2. 2. 3. Precipitation

Next step in the sample preparation procedure for the conversion of highly enriched  $^{28}\text{Si}$  single crystal to gaseous  $^{28}\text{SiF}_4$  is a precipitation of  $\text{Ba}^{28}\text{SiF}_6$  by adding a 0.1% solution of  $\text{BaCl}_2$  to  $\text{H}_2^{28}\text{SiF}_6$  (Eq. 2). To investigate the completeness of the precipitation and eliminate any loss of  $^{28}\text{Si}$ , the experiments with three different additions (Table 1) of  $\text{BaCl}_2$  (third variable) were performed and the yield of the precipitation was checked gravimetrically.

### 2. 2. 4. Decomposition

The last step in the sample preparation procedure is the decomposition of  $\text{Ba}^{28}\text{SiF}_6$  to  $^{28}\text{SiF}_4$  (Eq. 3). Within this step four variables (Table 1) were investigated and optimized. These variables are the number of drying steps, drying time for each particular drying step and the time of the conversion.

With the first three experiments only one drying step by using 3 different times (Table 1) was investigated. An ampoule with  $\text{Ba}^{28}\text{SiF}_6$  was dried at 100 °C first for 15 min, in the second experiment for 30 min and in the third experiment for 1 h. All the valves on the conversion unit (Fig. 2) stayed open in order to pump of all more volatile compounds. After that conversion was started at 540 °C for 30 minutes, the generated  $^{28}\text{SiF}_4$  gas was collected and introduced into the gas mass spectrometer for scanning of the first hundred masses.

To investigate the second drying step additional to the first drying step at 1 h, a second drying step at 150 °C was added and three different times (Table 1) were investigated. An ampoule with Ba<sup>28</sup>SiF<sub>6</sub> was dried at 100 °C for 1 h. All the valves on the conversion unit stayed open in order to pump of all more volatile compounds. After 1 h, the temperature was raised to 150 °C for 10 min in the first experiment, then for 15 min in the second experiment and for 30 min in the last experiment. After the second drying the conversion started at 540 °C for 30 minutes, the generated <sup>28</sup>SiF<sub>4</sub> gas was collected and afterwards introduced into the gas mass spectrometer for peak scanning.

The decomposition of Ba<sup>28</sup>SiF<sub>6</sub> to <sup>28</sup>SiF<sub>4</sub> needs to be complete therefore three different times (seventh variable in Table 1) of the decomposition at 540 °C were investigated and the yield of the decomposition was checked gravimetrically.

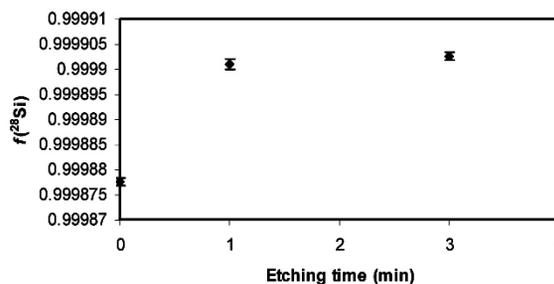
### 2. 2. 5. Investigation of the Effect of NO Gas on the Silicon Isotope Abundance Ratio Measurements

During the investigation and optimization of seven variables (Table 1) different nitrogen oxides (N<sub>x</sub>O<sub>y</sub>) were found to be cogenerated with the <sup>28</sup>SiF<sub>4</sub> gas during the decomposition step. The most abundant N<sub>x</sub>O<sub>y</sub> compound was found to be NO gas which is coming from the excess of HNO<sub>3</sub> needed for the digestion of <sup>28</sup>Si. N<sub>x</sub>O<sub>y</sub> compounds are also a potential danger for creating oxyfluorides (<sup>28</sup>SiOF<sub>2</sub>H<sup>+</sup>, <sup>28</sup>SiOF<sub>2</sub>H<sub>2</sub><sup>+</sup>, <sup>29</sup>SiOF<sub>2</sub>H<sup>+</sup>, <sup>29</sup>SiOF<sub>2</sub>H<sub>2</sub><sup>+</sup>, ...), if they react with <sup>28</sup>SiF<sub>4</sub>. And additionally, they can isobarically interfere silicon isotope ratio measurements. Therefore some investigations were done in order to find a way to eliminate the N<sub>x</sub>O<sub>y</sub> compounds. A cryogenic purification of <sup>28</sup>SiF<sub>4</sub> gas was done by freezing it in liquid nitrogen and pumping off all the remaining volatile compounds.

Furthermore, the effect of NO (as the most abundant N<sub>x</sub>O<sub>y</sub> compound) on Si isotope ratio measurements was studied by making a synthetic addition of different amounts of NO gas to the <sup>28</sup>SiF<sub>4</sub> gas. Five samples-gas mixtures were prepared, one with pure SiF<sub>4</sub> gas and the others with 0.8 vol. %, 2.8 vol. %, 6.0 vol. % and 7.7 vol. % addition of NO gas and the silicon isotope abundance ratios were measured.

## 3. Results and Discussion

As already described in paragraph 2.1, the <sup>28</sup>Si sample must be etched to remove the surface layer which otherwise contaminates the <sup>28</sup>Si sample during the chemical treatment within the sample preparation procedure. To investigate the effect of different etching times on Si isotope ratios and on the enrichment of the <sup>28</sup>Si samples, the Si isotope ratios were measured. The measurement results for all three different etching times are presented in the Table 2 and on the Fig. 3.



**Figure 3:** <sup>28</sup>Si isotope abundance fraction in the <sup>28</sup>Si sample depending on the etching time.

As already mentioned, dust and different surface layers on the surface of enriched <sup>28</sup>Si samples contribute to the higher measured Si isotope ratios and accordingly decreasing the enrichment of <sup>28</sup>Si sample. The lowest Si isotope ratios were measured after 3 min etching in the etching mixture HNO<sub>3</sub>:HF:CH<sub>3</sub>COOH with the mixing ratios 2:1:1 (v/v), which means that all the dust and the oxide layer composed from the Si of natural isotopic composition were removed. The <sup>28</sup>Si sample which was etched only for 1 min had a slightly lower enrichment. This could be explained by the fact that 1 min etching time was not sufficient to remove the oxide layer and thus it contributed to the higher measured Si isotope ratios and lower <sup>28</sup>Si enrichment. The non etched <sup>28</sup>Si sample had significantly higher isotope ratios and as a consequence of that a significantly lower enrichment. *T*-tests for comparing the mean values of the measured Si isotope ratios showed at 95% confidence level that there are differences in the mean values for the measured Si isotope ratios obtained after etc-

**Table 2:** Different etching times used in the wet etching procedure and their effect on the measured <sup>28</sup>Si isotope abundance fraction (the repeatabilities, which are equal to standard deviation *s*, are obtained experimentally by repeated measurements of 3 replicates and are given in the parentheses applying to the last two digits in the number on the left)

| Etching time (min) | Etching mixture                                 | <i>R</i> <sub>29/28</sub> | <i>R</i> <sub>30/28</sub> | <i>r</i> <sup>28</sup> |
|--------------------|---|---------------------------|---------------------------|------------------------|
| 0                  | HNO <sub>3</sub> :HF:CH <sub>3</sub> COOH=2:1:1 | 0.00009421 (43)           | 0.00002810 (67)           | 0.99987770 (80)        |
| 1                  | HNO <sub>3</sub> :HF:CH <sub>3</sub> COOH=2:1:1 | 0.00008449 (59)           | 0.00001450 (82)           | 0.99990102 (99)        |
| 3                  | HNO <sub>3</sub> :HF:CH <sub>3</sub> COOH=2:1:1 | 0.00008408 (52)           | 0.00001320 (61)           | 0.99990273 (80)        |

hing using different etching times. According to the investigations made, it is possible to conclude that the optimal etching time is 3 min, which is long enough to remove all the dust and the oxide layer, but sufficiently short to avoid excessive digestion of  $^{28}\text{Si}$  sample. Additionally, this conclusion was justified with the results of longer etching time (4 min) which showed no difference of measured silicon isotope ratios from that obtained after 3 min etching time.

Digestion of enriched  $^{28}\text{Si}$  sample in HF/HNO<sub>3</sub> mixture was found in our particular case the optimal choice as the time of digestion was short enough and it required only two more chemical steps for the conversion to the gaseous  $^{28}\text{SiF}_4$ . That was the reason why the investigations were not done via hot aqueous alkali solutions as from the theoretical point of view they would require more chemical steps for the conversion to the  $^{28}\text{SiF}_4$  gas and accordingly potential danger for higher natural Si contamination. Due to too small stoichiometric volumes of HF and HNO<sub>3</sub> an increase of the volumes of those acids is required to speed up a time of digestion. One of the possibilities would be a use of diluted acids which would increase the probability for the possible contamination with Si of natural isotopic composition. As a consequence of this, the volumes of ultra pure concentrated HF and HNO<sub>3</sub> acids were increased and the completeness and the time of digestion were monitored and also the presence of N<sub>x</sub>O<sub>y</sub> in the  $^{28}\text{SiF}_4$  gas was checked by mass scanning.

**Table 3:** Complete digestion of  $^{28}\text{Si}$  samples in the solution of different volumes of HF and HNO<sub>3</sub>

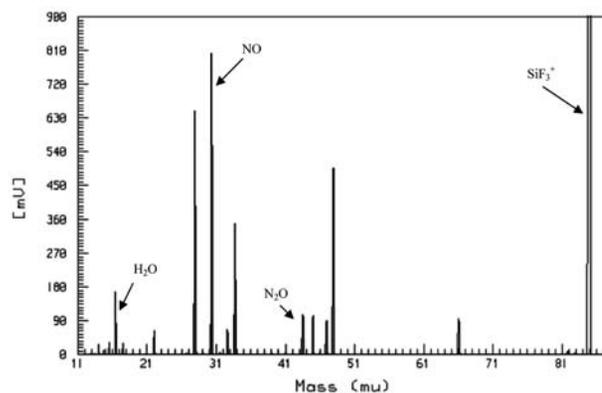
| Dissolving mixture (mL)       | $^{28}\text{Si}$ dissolves completely |
|-------------------------------|---------------------------------------|
| HF:HNO <sub>3</sub> = 6:1     | ✓                                     |
| HF:HNO <sub>3</sub> = 3:0.5   | ✓                                     |
| HF:HNO <sub>3</sub> = 1.8:0.3 | ✓                                     |

The results (Table 3) show that all three investigated volumes of dissolving mixture completely dissolve  $^{28}\text{Si}$  sample. Thus a mixture of 1.8 mL of conc. HF and 0.3 mL of conc. HNO<sub>3</sub> was found optimal as the volume of solution was the smallest but big enough to cover the  $^{28}\text{Si}$  sample completely and to entirely dissolve about 50 mg of the enriched  $^{28}\text{Si}$  sample in a reasonable short time.

A completeness of the precipitation of Ba $^{28}\text{SiF}_6$  by adding three different additions of 0.1% solution of BaCl<sub>2</sub> to the H<sub>2</sub> $^{28}\text{SiF}_6$  was investigated and it was found that only 2% of an excess of 0.1% of BaCl<sub>2</sub> gave 100% yield of the precipitation.

In absence of a drying before the decomposition of Ba $^{28}\text{SiF}_6$  to  $^{28}\text{SiF}_4$  gas, water and N<sub>x</sub>O<sub>y</sub> compounds with x,

y = 1 to 2 coming from the nitrates remained in Ba $^{28}\text{SiF}_6$  powder due to the nonstoichiometric amount of conc. HNO<sub>3</sub> in the digestion mixture. Thus above mentioned compounds are cogenerated with  $^{28}\text{SiF}_4$  gas. A mass scan of  $^{28}\text{SiF}_4$  gas which was generated by a decomposition of Ba $^{28}\text{SiF}_6$  without prior drying is presented on Fig. 4. It shows present impurities which can react  $^{28}\text{SiF}_4$  gas and produce oxyfluorides at  $m/z = 82\text{--}84$  which can interfere Si isotope ratio measurements. In order to decrease them, a drying prior to the decomposition needs to be performed.



**Figure 4.** Mass scan of the  $^{28}\text{SiF}_4$  gas sample introduced into the gas mass spectrometer.

First drying step at 100 °C for 1 h resulted in complete removal of water and only in a small reduction of N<sub>x</sub>O<sub>y</sub> compounds. In order to further remove the N<sub>x</sub>O<sub>y</sub> compounds, a second drying step at 150 °C was added. It was found, that N<sub>x</sub>O<sub>y</sub> compounds were additionally reduced with the second drying step for 15 minutes but not completely. These experiments also showed no significant difference in reduction of N<sub>x</sub>O<sub>y</sub> compounds between the second drying for 15 minutes and the one for 30 minutes. It was concluded that two drying steps needed to be done before starting the conversion at 540 °C for 30 minutes. The first drying step must be done at 100 °C for 1 h and the second drying step at 150 °C for 15 minutes. The optimal time for the decomposition at 540 °C was found to be 30 min as the yield of the decomposition was 100%.

The N<sub>x</sub>O<sub>y</sub> compounds remained in the  $^{28}\text{SiF}_4$  gas even though two drying steps were added and therefore several investigations to find the way to eliminate them were performed. A trial to eliminate the nitrates in the sample with rinsing Ba $^{28}\text{SiF}_6$  with MQ water, split the insoluble Ba $^{28}\text{SiF}_6$  from the liquid part with soluble nitrates using a centrifuge and drying Ba $^{28}\text{SiF}_6$  to complete dryness, prior to start the conversion to the gaseous  $^{28}\text{SiF}_4$ , showed that it is impossible to completely eliminate the nitrates. The scans of the  $^{28}\text{SiF}_4$  gas after the decomposition and prior performing the Si isotope ratio measurements showed that N<sub>x</sub>O<sub>y</sub> compounds with x, y = 1 or 2 were still present.

Apparently, it would not even be possible to comple-

tely remove the  $N_xO_y$  compounds from the sample with additional cryogenic purification and/or additional drying, as  $N_xO_y$  is continuously released with increased time and temperature due to nitrate bonded in  $BaSiF_6$ . As no other possibility to reduce nitrates and accordingly  $N_xO_y$  compounds was taken into considerations, we tried to evaluate the effect of  $N_xO_y$  on measured silicon isotope ratios.

NO gas was found to be the most abundant  $N_xO_y$  compound, therefore the effect of NO on Si isotope ratio measurements had been studied by making synthetic addition of different amounts of NO gas to the  $^{28}SiF_4$  gas. The results of *F*-tests showed at 95% confidence level no significant difference between the variances of the measured Si isotope ratios of the different gas mixtures containing different amounts of NO gas and also the *t*-tests showed at 95% confidence level that there is no significant difference between the mean values of the measured silicon isotope ratios for the samples containing less than 6 vol. % of NO. Upon those results we concluded that, if the gas sample contains 6 vol. % or more of NO gas than this not only contributes to the uncertainty of the measured isotope ratios but also significantly (> 5%) affects the values of the measured isotope ratios themselves.

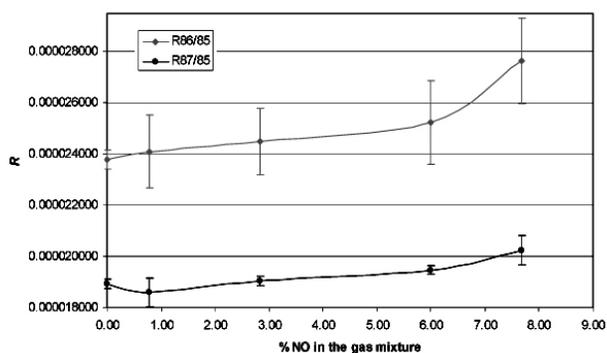


Figure 5: Measured Si isotope ratios depending on the addition of NO gas in the gas mixture.

## 4. Conclusion

The conversion of the highly enriched  $^{28}Si$  (> 99.99% of  $^{28}Si$ ) single crystal to gaseous  $^{28}SiF_4$  via a dissolution of  $^{28}Si$  in the mixture of conc. HF and conc.  $HNO_3$  as the novel sample preparation procedure for the conversion of enriched  $^{28}Si$  to  $^{28}SiF_4$  needed for determination of silicon molar mass, consists of several steps; etching the  $^{28}Si$  sample, dissolving/digestion of the  $^{28}Si$  sample, precipitation to  $Ba^{28}SiF_6$  and the decomposition to  $^{28}SiF_4$ . All these steps play an important role in the whole sample preparation procedure and as they can significantly influence the measured silicon isotope ratio measurements and silicon molar mass determination. The crucial problem of the whole measurement procedure, especially the sample pre-

paration procedure, is the contamination of enriched  $^{28}Si$  with silicon of natural isotopic composition due to its everywhere presence. Therefore the purpose of the investigation and optimization of sample preparation was to minimize possible contamination with silicon of natural isotopic composition in order to obtain relative combined uncertainty of silicon molar mass of  $1 \times 10^{-8}$  and relative combined uncertainty of Avogadro constant of  $2 \times 10^{-8}$ , which would lead to the possible replacement of the definition of the kilogram as one of the base SI unit. The experiments carried out during the investigation of the sample preparation procedure (Table 4) provided the optimal conditions for each sample preparation step in order to obtain optimal results of silicon isotope ratios measurements with relative standard uncertainty of about  $1 \times 10^{-4}$ , which is sufficient for obtaining relative combined uncertainty of silicon molar mass of  $1 \times 10^{-8}$  and relative combined uncertainty of Avogadro constant of  $2 \times 10^{-8}$ .

Table 4: Optimal results obtained for the sample preparation procedure

| Parameter                               | Optimal value                               |
|---|---|
| Etching time                            | 3 min                                       |
| Volume of acids for digestion           | 1.8 mL HF + 0.3 mL $HNO_3$                  |
| Excess of $BaCl_2$ for precipitation    | 2%  |
| Drying step                             | 1st drying at 100 °C + 2nd drying at 150 °C |
| Drying time for first drying at 100 °C  | 60 min                                      |
| Drying time for second drying at 150 °C | 15 min                                      |
| Conversion time at 540 °C               | 30 min                                      |

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## Povzetek

V tem članku je predstavljena podrobna študija optimizacije postopka za pretvorbo obogatene  $^{28}\text{Si}$  monokristala v plinasti silicijev tetrafluorid največje možne čistote dosežene do sedaj. Plinasti  $^{28}\text{SiF}_4$  z visoko stopnjo čistote se uporablja pri določitvi molske mase silicija z merjenjem izotopskega razmerja obogatene  $^{28}\text{Si}$  (> 99.99 %  $^{28}\text{Si}$ ), pri čemer se uporablja plinska masna spektrometrija s trki elektronov. Največjo težavo pri tem predstavlja kontaminacija obogatene  $^{28}\text{Si}$  s silicijem z naravno sestavo izotopov, pri čemer najvišja dovoljena masa silicija z naravno sestavo izotopov (kontaminacija) ne sme biti večja od  $10^{-9}$  g. Priprava obogatene  $^{28}\text{Si}$  predstavlja tako največji prispevek k relativni kombinirani merilni negotovosti izmerjenega izotopskega razmerja, ter posredno vpliva tudi na merilno negotovost molske mase silicija. Vsi eksperimenti za doseg ustreznosti merilne negotovosti so bili skrbno načrtovani in so tako omogočili znižanje stroškov zaradi zelo dragih vzorcev obogatene  $^{28}\text{Si}$ . Optimalni pogoji priprave vzorca so bili tako doseženi v okviru velikega števila eksperimentov, načrtovanih za kalibracijo, ki je pogoj za določitev molske mase silicija kot ene od vhodnih veličin za določitev Avogadrove konstante.