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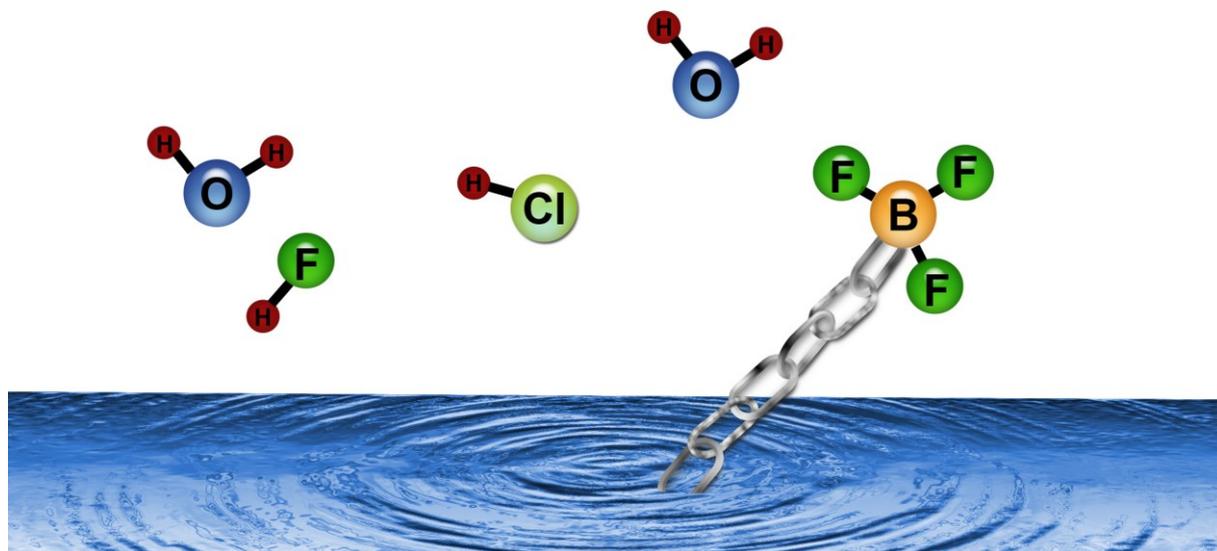
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Retention of boron in acidic solutions without addition of organic complexing agents.



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ARTICLE TYPE

## Determination of Boron in Silicon without use of additional complexing agents

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Methods for the determination of boron in various matrices described in the literature usually employ complexing agents like mannitol to retain the volatile boron species during matrix evaporation steps. However, also relatively high boron recoveries from silicon containing samples have been reported when no complexing agents were added to the digestion acids. The mechanism behind this matrix-dependant recovery has been investigated by studying the boron recovery in the analysis of solar grade silicon. It was found that the  $\text{NH}_4^+$  ion formed by the reduction of nitric acid during sample digestion is responsible for the higher recovery of boron, which leads to a possible analysis method without the use of complexing agents if the sample preparation procedure is carefully optimized.

### Introduction

Boron is an important analyte in various matrices and reagents linked with geosciences, nuclear reactor materials and photovoltaics. In many applications, not only the total content of boron is of interest for material characterization, but also the isotopic ratio of the two isotopes  $^{10}\text{B}$  and  $^{11}\text{B}$  is often determined by isotope ratio mass spectrometry to access the identification possibilities behind the isotopic signature, which for example allows to ascertain the provenance of samples and better understand geological processes<sup>1,2</sup>. For nuclear reactor materials like graphite, the knowledge of the boron content and, due to its high neutron cross-section, especially  $^{10}\text{B}$  is of utmost importance. In photovoltaics, boron is used as doping element in silicon solar cells. Its content must be therefore well known in raw and doping materials as well as the reagents used in the production process to precisely adjust the electronic properties of the solar cells.

The remarkable importance of boron as analyte in various matrices is reflected in the history of analytical chemistry by a vast spectrum of detection methods focusing on this element. Detection methods include the Hall effect<sup>3</sup>, spectrophotometry with various complexing agents<sup>4-8</sup> providing competitive detection limits down to the  $\text{ng mL}^{-1}$  range in liquids, infrared spectrometry<sup>9</sup> and many more<sup>10</sup>. Today, mainly mass spectrometric methods, sometimes in combination with isotope dilution<sup>11</sup> are used, since this techniques offer very high precision, low limits of determination and additional isotopic information.

The most prominent challenge faced in boron determination is the volatility of the boron species under the conditions used for sample preparation. Boron loss occurs particularly in combination with hydrohalogenic acids, especially when higher temperatures are applied for digestion of solid materials, or when matrix

evaporation of acids and water for the sake of analyte enrichment is applied. For silicon or silicon containing samples such as natural rocks, the use of hydrofluoric acid is necessary to achieve complete digestion, resulting in the *in-situ* formation of  $\text{BF}_3$  with a boiling point of  $-100.4^\circ\text{C}$ . The chlorine analog  $\text{BCl}_3$  is also very volatile with a boiling point of  $12.6^\circ\text{C}$ .

The most prevalent method to avoid volatilization of boron is the use of reagents which form non-volatile complexes with boron, notably 1,2-diols such as ethylene glycol, sorbitol, mannitol and other carbohydrates<sup>12-14</sup>, mannitol being used most frequently in the literature even for solid sampling purposes<sup>7, 8, 15-22</sup>. The molar boron mannitol ratios, the stability of the mannitol-boron complex and the optimal conditions for total recovery after matrix evaporation were subjects of several studies. A mannitol excess up to thousandfold was described<sup>18</sup>, but a smaller amount of reagents is generally preferable in order to reduce procedure blanks and consequently limits of determination.

As boron and mannitol form a stoichiometric 1:1 complex<sup>13, 23</sup>, Ishikawa et al.<sup>24</sup> found a recovery of about 100% from evaporated, pure hydrofluoric and hydrochloric acids already for a 1:1 molar ratio. This was even true if the acids were evaporated to dryness, as long as the additional heating ( $70^\circ\text{C}$ ) after dryness was reached did not take longer than 30 minutes. Xiao<sup>25</sup> found that addition of mannitol is strongly necessary for evaporation of water, but not diluted (0.1 M) HCl, even if performed to dryness. The results of Feldman<sup>26</sup> however suggested a strong concentration dependence of boron volatility for HCl, as the recoveries for concentrated HCl were poor even without evaporation to dryness. Moreover, a degradation of mannitol in nitric acid was observed, resulting in higher molar ratios necessary for total recovery. Generally, a tenfold excess of mannitol was considered practical and sufficient, a ratio which was also used by other authors<sup>20, 22</sup>.

The findings described above were mainly found for matrix-

**Table 1** ICP-MS operating parameters

Plasma Conditions	
RF-power / W	1350
Coolant gas flow / L min <sup>-1</sup>	15
Sample gas flow / L min <sup>-1</sup>	1
Auxiliary gas flow / L min <sup>-1</sup>	0.95
Additional gas flow / L min <sup>-1</sup>	0.06
Data acquisition	
Dwell time / ms	100
No. of scans	5
No. of replicates	4
Measurement time per sample / min	2.3

free liquids. Interestingly, Makishima et al.<sup>27</sup> found evidence for a matrix effect when analyzing silicate rocks. After dissolution with hydrofluoric acid and evaporation at 70 °C, the boron recoveries for matrix samples were around 80 %, but only 9 % for the matrix-free blanks. The reason for the enhanced boron retention was not investigated though, as the reproducibility for the somewhat lower boron recovery was poor and the addition of mannitol deemed to be necessary. Similar results were found by Mills et al.<sup>28</sup> for ashes and silicates. Evaporation (130 °C) to a residual volume of 0.5 mL without addition of mannitol led to a full recovery of boron, but at the same time 99.9 % of the silicon matrix was removed. Additional heating to dryness led to a loss of up to 15 % of boron. For the final procedure, the addition of mannitol was omitted. Instead, the evaporation process was monitored carefully and interrupted after only 1 mL of liquid was left.

The exact reason for the matrix effect was not further investigated in these papers, and its possibilities for mannitol-free determination of boron in silicate materials, as described by Mills, remain limited by the susceptible process control.

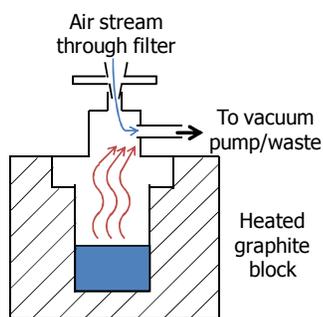
In our contribution, we study the boron retention mechanism and, using the example of solar grade silicon, demonstrate the applicability of adapted matrix evaporation procedures to achieve better recoveries of boron in the analysis of solid samples without addition of mannitol or other complexing agents.

## Experimental

### ICP-MS Instrumentation and conditions

An ICP-SFMS (inductively coupled plasma sector field mass spectrometer) of type Thermo Electron Element XR (Thermo Fisher Scientific, Dreieich, Germany), equipped with hydrofluoric acid-resistant 100 µL self-aspiratory PFA (perfluoroalkoxy copolymer) micro-concentric nebulizer (ESI, Omaha, NE, USA), PFA spray chamber and sapphire injector was used. Typical operating parameters are given in Table 1. The instrument was tuned daily for maximum sensitivity and signal stability of <sup>115</sup>In isotope as well as for maximum resolution. The isotopes monitored were <sup>9</sup>Be and <sup>11</sup>B in low resolution ( $m/\Delta m \approx 300$ ); <sup>9</sup>Be, <sup>10</sup>B and <sup>11</sup>B in medium resolution ( $m/\Delta m \approx 4\,000$ ).

The isotope <sup>9</sup>Be was used as internal standard and added to every sample and solution in an amount that the same final concentration (8 µg L<sup>-1</sup>) in the measurement solutions was obtained. The element was chosen because it could not be found at notable concentrations in solar grade silicon samples, it formed

**Fig. 1** Schematic illustration of the matrix evaporation in a PFA beaker.

no volatile fluorides, it showed good sensitivity and has a mass similar to boron, ensuring a comprehensive compensation of instrument drift during measurement.

### X-ray diffraction

An X-ray diffractometer Bruker D8 Discover (Bruker AXS GmbH, Karlsruhe, Germany) was used. The samples were measured over the range of  $2\theta = 8-90^\circ$  (2 kW, Cu-K $\alpha$ , 1.54106 Å, interval of 0.009°, integration time per measurement point 0.5 s).

### Reagents and materials

High-purity water with an electrical resistivity of 18.2 MΩ cm (Milli-Q, Millipore, Bedford, MA, USA) was used throughout for preparing all solutions. The Milli-Q system was equipped with an additional boron specific filter for lowest background concentrations. Nitric acid (65 % p.a.) and hydrofluoric acid (40 % p.a.) were purchased from Merck, Darmstadt, Germany and further purified in-house by subboiling distillation. Boron, mannitol and ammonium nitrate stock solutions were prepared in quartz flasks by dissolution of the solid powders in water. Boron standards were prepared from pharmaceutical grade boric acid (DAB 7, Laborchemie Apolda, Apolda, Germany). Mannitol “for the determination of boric acid”, ammonium nitrate p.a. and Silicon Certipur® standard solution [1000 mg L<sup>-1</sup> Si as (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> in H<sub>2</sub>O] were obtained from Merck.

Different silicon samples, including high-purity Czochralski silicon crystal samples and feedstock silicon samples with high boron content were provided by German photovoltaic companies.

Ultrapure water and acids were stored in PFA flasks and beakers from Savillex (Minnetonka, USA). Measurements were performed out of 15 mL polypropylene (PP) autosampler tubes (Greiner Bio-One, Kremsmünster, Austria) which were cleaned by a procedure based on the work of Rodushkin and coworkers<sup>29</sup>. The tubes were rinsed thoroughly with ultrapure water, filled with 5 %/5 % v/v subboiling HNO<sub>3</sub>/HF (referred to the commercially available concentrated, respective 65 % and 40 % acids) for storage and finally rinsed again with Milli-Q prior to use.

### Sample preparation

The samples for experiments with pure acids were prepared by adding hydrofluoric and/or nitric acid, boron and mannitol standard solutions and the internal standard in 30 mL PFA

**Table 2** Recovery of 20 µg boron from 4 mL HF and 2 mL HNO<sub>3</sub> standing for 72 h and evaporated to dryness at 150 °C (*n* = 2).

Molar ratio mannitol:boron	Recovery / %		
0:1	0	±	0
0.5:1	43	±	7
1:1	59	±	12
2:1	63	±	1
10:1	90	±	5

beakers. The amount of boron and mannitol solutions was adjusted according to the experiment as described in the next section. The stock standard solutions were prepared in concentrations that allowed all additions to be in the volume range of 50–200 µL, so that the acids were not substantially diluted. The acids were used in volumetric ratios close to those used to dissolve silicon, *i.e.* HF:HNO<sub>3</sub> = 2:1. Usually 4 mL HF and 2 mL HNO<sub>3</sub> were used.

Samples for experiments with real, solid silicon matrix were prepared either by dissolving large amounts of silicon in HF and HNO<sub>3</sub>, homogenizing the solution and aliquoting this solution into individual PFA beakers, or by dissolving smaller amounts of silicon directly in the 30 mL PFA beakers. The experimental details are later described for each individual experiment. Each sample was prepared at least in duplicate.

The matrix and acids were then evaporated in a matrix evaporation system described in detail earlier<sup>30</sup>. The system consists of a heated graphite block with bore holes congenial for the PFA beakers. Up to twelve samples could be evaporated at the same time. To ensure a maximum intra-experimental comparability between samples, the individual experiments were designed in a way that they preferably consisted of at most twelve samples.

For evaporation, only the caps of the sample beakers have to be changed into ones with two 1/4" fittings, allowing the connection of a vacuum pump and an aspiration port. Over a syringe filter (PTFE membrane, 0.2 µm pore size, 25 mm diameter, NeoLab, Heidelberg, Germany), air is aspirated by a PTFE membrane pump (KNF Neuberger, Freiburg, Germany) into the beakers and further transported together with evaporated matrix into waste vessels (Fig. 1). The graphite heating block was placed inside a class 100 laminar flow box to minimize the risk of contamination. Evaporation temperatures were 100–150 °C and the evaporation was always carried out to dryness.

The residue in the beaker was dissolved and diluted using 1%/0.5% *v/v* HNO<sub>3</sub>/HF and transferred into 15 mL PP (polypropylene) tubes. External calibration was performed in the experiments without Si matrix by measuring solutions prepared directly from the boric acid stock solution. Calibration by standard addition was used for experiments with silicon samples.

## Results and discussion

First, we wanted to verify if we encounter the same general results of boron loss and consequently also need to use mannitol with our evaporation system, as described in literature.

**Table 3** Recovery of 20 µg boron from 4 mL HF and 3 mL HNO<sub>3</sub>, 2:1 molar excess of mannitol, evaporated to dryness and heated at 100 °C for different times (*n* = 2).

Heating time / h	Recovery / %		
15	91.0	±	0.9
17.5	86.0	±	1.9
20	86.0	±	1.4
22.5	85.0	±	2.8

### Recovery without matrix

Different amounts of mannitol were added to 20 µg Boron in a mixture of 4 mL HF and 2 mL HNO<sub>3</sub>. The solutions were allowed to stand for 72 h to account for possible delays between sample dissolution and evaporation, as often encountered in routine silicon analysis in our lab. The results after evaporation to dryness at 150 °C are shown in Table 2. No boron could be recovered without addition of mannitol. Even with a tenfold molar excess of mannitol, the boron recovery was only 90%. This is consistent with the findings in the literature.

### Thermal stability of the boron-mannitol complex with time

Because the evaporation between different beakers was not absolutely uniform in time and individual beakers could not be immediately removed upon dryness from the hot graphite block because of their thermal expansion, it was important to investigate the thermal stability of the boron-mannitol complex with time. For this, 20 µg boron was added with a twofold molar excess of mannitol to 4 mL HF, 3 mL HNO<sub>3</sub> and evaporated at 100 °C, the highest temperature feasible for removing the PFA beakers from the graphite block during the evaporation process. The samples were taken out after 15–22.5 h, whereas dryness was already achieved after 12 h.

The recoveries (Table 3) are much better to the previous experiment with the same mannitol:boron ratio, owing to the lower temperature and possibly the direct evaporation after sample preparation, without the 72 h waiting time. The recovery decreases only slightly for 7.5 additional hours of heating. The results of this experiment, carried out at 100 °C, are not directly transferable to the routine silicon analysis procedure with an evaporation temperature of 150 °C, but can be extrapolated. The additional heating time applied here after dryness was up to 12.5 hours, whereas in the routine method, the time between sample dryness and the removal of the beaker after cooling down of the graphite block is less than 60 minutes. The short additional heating should have no dominating effect on the recovery.

### Behavior with low silicon matrix load

The first experiments with silicon matrix were carried out with low matrix load. Silicon was added as (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> in a Si:B molar ratio up to 25:1 with and without additional mannitol (molar ratio mannitol:boron 1:1). The samples were prepared in 4 mL HF and 2 mL HNO<sub>3</sub> and immediately evaporated at 150 °C. The results (Table 4) show that the recovery of boron is indeed very comparable whether silicon as (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> or mannitol is added to the solution. This would suggest a direct role of silicon in the retention of boron, which seemed unlikely. Further experiments were conducted to clarify the mechanism.

**Table 4** Recovery of 20 µg boron from 4 mL HF and 2 mL HNO<sub>3</sub> with addition of silicon standard solution as (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> with and without mannitol. Evaporation to dryness at 150 °C (*n* = 2).

Mannitol:B molar ratio	Si:B molar ratio	Recovery / %		
0	0	15	±	0.5
0	5	84	±	0.1
0	10	93	±	15
1	5	89	±	3
1	10	91	±	2
1	25	92	±	2

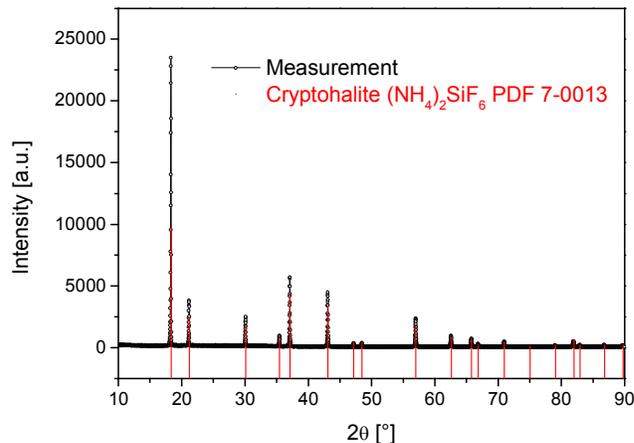
**Table 5** Recovery of 2.5 µg boron from 6 mL Si solution (0.5 g Si absolute) and boron blanks (no spike of boron) from 4 mL HF and 2 mL HNO<sub>3</sub> ("acid blanks", *n* = 5) with addition of different amounts of mannitol. Evaporation to dryness at 150 °C. *n* = 3 / *n* = 6 for acid blanks.

Matrix	Mannitol:B molar ratio	Recovery / %		
Si	0	99	±	7
Si	1	100	±	5
Si	2	101	±	4
Si	10	98.3	±	0.9
Si	50	98.3	±	0.4
Acid blank	0–50	1.7	±	0.4

#### 10 Boron in real silicon samples

For the first experiment with silicon matrix in form of real, solid samples, 20 g of pure Czochralski silicon were dissolved in 170 mL HF and 90 mL HNO<sub>3</sub> in a large PFA beaker. The solution was homogenized and 6 mL of this solution, containing 0.5 g of silicon (upon dissolution of silicon, reduction of the volume occurs) was transferred into PFA beakers for further addition of standard solutions. The native boron content of the silicon material used was 30 ng g<sup>-1</sup>, which is negligible compared to the standard addition of boron for this experiment, 2.5 µg absolute, corresponding to 5 µg g<sup>-1</sup> boron in solid silicon. Matrix-free control samples were prepared by mixing 4 mL HF and 2 mL HNO<sub>3</sub>. An up to 50-fold molar excess of mannitol was used. Independent of the addition of mannitol, all recoveries (Table 5) were about 100 %. While there was no difference in the values for recovery, the precision of mannitol-assisted boron determination was better than without mannitol.

As described earlier<sup>30</sup>, the evaporation of silicon with the procedure and apparatus used here is not complete. Usually, the dissolution and evaporation of 1 g silicon led to a total residue of about 5 mg. The amount of residue depends on the amount of acids used for the dissolution of silicon. In particular, the solution reacted very sensitive to an excess of HF. If 10 mL instead of 8.5 mL (the usual amount used for routine silicon analysis) of 40 % HF were used, the residue after evaporation would reach a mass of 40 mg and more. A slight excess of acids over the theoretical minimum however improved the reaction speed and the small amount of the residue of 5 mg was tolerable in ICP-MS measurements. The residue has been identified by x-ray diffraction as ammonium hexafluorosilicate (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> (Fig. 2). The ammonium ions found were reported to originate from the reduction of nitric acid during the dissolution of silicon<sup>31</sup>. One can assume that the boron retention is done in the same way as the silicon retention, by formation of non-volatile (NH<sub>4</sub>)BF<sub>4</sub>.



**Fig. 2** X-ray diffractogram of the silicon matrix evaporation residue.

**Table 6** Boron content of boron-rich silicon with and without the addition of mannitol and an artificial boron spike after dissolution of the matrix (*n* = 3).

Sample	Content rel. to solid sample / ng g <sup>-1</sup>	
Si	4572	± 90
Si + Mannitol	4509	± 55
Si + Mannitol + Boron	8346	± 154
Spike observed	3837	± 164
Spike added	3990	± 85

#### 50 Comparison between native and spiked boron content for real silicon matrix

To confirm that there is no difference in behavior between the native boron present in the silicon, which is the actual measurand for routine analysis, and the artificially added boron spike after the dissolution of silicon, multiple subsamples of 1 g of a boron-rich silicon material with a content of ca. 4.5 µg g<sup>-1</sup> were individually dissolved in 8.5 mL HF and 4.5 mL HNO<sub>3</sub> a) without addition of mannitol b) addition of mannitol with a ca. five-fold molar excess over boron and c) with addition of mannitol and an addition of the boron standard solution subsequent to the dissolution of silicon. The artificial boron spike, calculated gravimetrically with respect to the exact weighted sample, could be recovered to 96 ± 4 % (Table 6). Again, there was no significant difference between the recovery with and without mannitol.

#### Species of boron after evaporation of silicon samples

To confirm the chemical form of boron in the residue, 8 g of silicon were dissolved in an acid mixture corresponding to 9.15 mL HF and 4.85 mL HNO<sub>3</sub> per gram Si. The volume of the solution was aliquoted into eight 30 mL PFA beakers and 22, 110, 220 and 440 mg of boric acid (corresponding to 1, 5, 10 and 20 % of the molar amount of silicon) added in duplicate to the aliquots. The solution was evaporated at 150 °C and the residue analyzed with x-ray diffraction. The mass of the residue was ca. 40 mg for all samples. Likewise independently of the initial boron content, only (NH<sub>4</sub>)BF<sub>4</sub> could be detected in the residue, the limit of detection of the diffractometry being roughly 2 mass-percent. The equal recovery of boron, independent of the initial amount of boron, clearly demonstrates that the ammonium ions formed during the silicon digestion are the limiting factor in the

**Table 7** Recovery of 20 µg boron from 4 mL HF and 2 mL HNO<sub>3</sub> with addition of ammonium nitrate, standing for 72 h. Evaporated to dryness at 150 °C (*n* = 3).

Molar ratio ammonium:boron	Recovery /%		
0:1	7.6	±	0.4
5:1	79	±	4
20:1	78	±	1

recovery of both boron and silicon. When both boron and silicon are present, the ammonium tetrafluoroborate (decomposition temperature 316 °C<sup>32</sup>) is retained to a much higher degree than the silicon analog (decomposition at 100 °C), thus supporting the matrix separation in silicon analysis.

#### 10 Recovery of boron from acid solutions with addition of ammonium

To demonstrate the role of ammonium for the recovery of boron, the first experiment with pure acids has been repeated with the addition of ammonium instead of mannitol. An absolute amount of 20 µg boron was added to 4 mL HF and 2 mL HNO<sub>3</sub>. To these solutions, 50 or 200 µL of ammonium nitrate solution (15.4 g L<sup>-1</sup>), representing a *ca.* 5-/20-fold molar excess of ammonia over boron, was added. The solutions were allowed to stand for 72 h. The results, shown in Table 7, clearly demonstrate the retaining effect of ammonium, although the molar ratios studied seemed still to be too low for total recovery of boron.

#### Conclusions and outlook

In this work, we could show that the fairly high boron recovery observed by other authors in the analysis of silicon-rich samples even without addition of complexing agents such as mannitol can be related to the formation of ammonium ions. Those are formed by reduction of nitric acid during the sample dissolution. The ammonium cation forms a stable salt with the boron tetrafluoride anion (decomposition temperature 316 °C) but a far less stable salt with the silicon matrix analog [decomposition temperature of (NH<sub>4</sub>)SiF<sub>6</sub>: 100 °C]. This opens the way for selective evaporation of the matrix with full retention of the analyte. Examples of an exploitation of this effect can be found in the literature, where the difference in sublimation temperatures was used to separate boron and silicon in a technical process<sup>33</sup>.

This boron retention effect has proven useful for the analysis of silicon samples, for example for the photovoltaic industry, and should be applicable in various ways for other matrices. In this work and with the matrix evaporation system developed<sup>30</sup>, the recovery of boron reached up to 100 % without addition of any complexing agents, since the ammonium ion is formed *in situ* during the silicon dissolution process. A careful optimization of the sample preparation and matrix evaporation procedure is necessary but can render the addition of complexing agents obsolete. This simplifies the sample preparation and reduces cross-contamination, especially in cases where the boron content in silicon is very high and considerable amounts of complexing agent had to be added, or, on the other hand, where the rough boron content is unknown but low and the necessary amount of complexing agent could be considerably overestimated. For other matrices, ammonium nitrate or other ammonium sources can be added as alternative complexing agents, since both NH<sub>3</sub> and

HNO<sub>3</sub> can be produced in very high purity by subboiling distillation.

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