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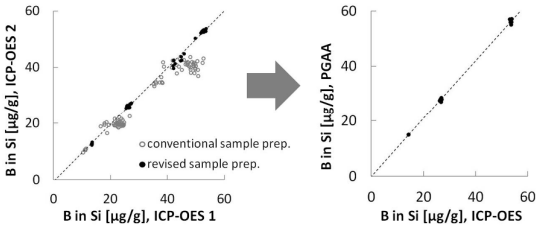

Textual abstract for the table of contents entry

A sample preparation protocol for accurate B quantification in metallurgical grade Si by ICP-OES is described and validated against PGAA.

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ARTICLE

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Boron speciation in acid digests of metallurgical grade silicon reveals problem for accurate boron quantification by inductively coupled plasma – optical emission spectroscopy

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The boron (B) content is a major parameter rigorously monitored during production of silicon (Si) for different industrial applications, since it is crucial for defining the electronic properties of the final product. During the validation of a newly acquired inductively coupled plasma-optical emission spectrometer (ICP-OES) in an industrial analytical laboratory a significant bias between results of the established and the new instrument was observed. During investigation of the reasons for the observed bias it was found that B in acidic Si digests, prepared using HNO_3 and HF, is present as at least two different molecular species. One of them is easily hydrolyzed during acid digestion and was identified as boric acid ($B(OH)_3$) by HPLC-inductively coupled plasma-mass spectrometry (HPLC-ICP-MS). The other B species -referred to as unknown B species- is stable under strongly acidic conditions, sensitive to oxidation by H_2O_2 and cannot be generated during sample digestion from isotopically labelled $^{10}B(OH)_3$. Indications for the unknown B species were found in all investigated metallurgical grade Si samples and identified as the source of significant measurement error in solution nebulisation ICP-OES based B quantifications. Oxidation of the unknown B species with a B/Si stoichiometry of approximately 1/10 with H_2O_2 significantly increased the B concentrations determined by ICP-OES and results agreed well with prompt gamma activation analysis (PGAA) measurements.

Introduction

Metallurgical grade silicon (MG-Si) is an important feed stock for the production of solar grade silicon (SoG-Si), highlighted by recent efforts regarding energy efficient production of SoG-Si from MG-Si via a metallurgical process route.[1, 2, 3] Since boron (B) is one of the key dopants defining the electronic properties of SoG-Si used for solar cell production, accurate knowledge of the B concentration of feed stock materials is imperative.[4, 5] Measurement of the B concentration in Si can either be performed directly using solid state analytical techniques or after sample dissolution, for example using a blend of HF and HNO_3.[5, 6] Solid-state analytical methods for B quantification in MG-Si are sensitive enough for measurements down to the ng/g range but are hampered by a lack of widely accessible, matrix matched calibration standards, do often not yield real bulk concentrations or suffer from comparably low sample throughput.[7, 8, 9] Solution based methods using HF offer the possibility to evaporate the Si matrix as SiF_4, reducing the matrix load for the measurement equipment.[10] To avoid the loss of volatile BF_3 during evaporation the use of mannitol has been suggested, but reports in literature regarding the efficiency of this method are not entirely consistent.[6, 11, 12] Other strategies to avoid the loss of volatile B species during wet chemical sample preparation include for example digestion with NaOH, use of ortho-phosphoric acid instead of mannitol, temperature control during evaporation or closed vessel digestion.[12, 13] Dissolved samples are often measured by inductively coupled plasma (ICP) methods. These are widely believed to give analyte response independent of the actual chemical species introduced into the instrument. ICP methods do however suffer from matrix effects and analyte memory. For B memory different remedies such as sample dilution, selective choice of rinsing solutions, increased rinse times, direct injection nebulisation and ammonia gas injection into the spray chamber have been reported in literature.[13, 14, 15, 16]

Analytical chemistry in an industrial environment is characterized by a need for short response times and a desire for sample preparation procedures of low sophistication. While B quantification in high purity SoG-Si is typically performed using mass spectrometric techniques for reasons of instrumental sensitivity, the higher B concentrations of MG-Si can usually be measured via inductively coupled plasma-optical emission spectroscopy (ICP-OES).[6, 17] Hence open vessel digestion of

MG-Si with HF and HNO_3, followed by direct analysis of dilute digests with ICP-OES is a viable route for routine B quantification and frequently used for this kind of analysis in industrial settings.

During the validation of a new ICP-OES, acquired to supersede an older instrument, it was noticed that the data obtained with the new ICP-OES was significantly above results obtained using the old ICP-OES. This observation prompted investigations aimed at identifying the reasons for this data distribution.

Experimental part

Materials, reagents and samples

Investigated MG-Si materials were obtained from four different main sources and include commercial samples as well as in-house control materials *Elkem1* and *Elkem 2* (Elkem AS, Kristiansand, Norway), commercial samples from Bluestar (Bluestar Silicones Co., Yong Deng, China), standard reference material NIST 57b (National Institute of Standards and Technology, Gaithersburg, MD, USA) and standard reference material IPT 134 (Instituto de Pesquisas Tecnológicas, São Paulo, Brazil). The B concentration for NIST 57b is only given as a reference value in the certificate and two different B concentrations are available in literature.[18] IPT 134 is not certified for its B content, does however contain a significant amount of B measurable by ICP-OES. Whenever samples were not obtained as granulates or powders, they were crushed to a particle size of 1 mm at Elkem's central laboratory with a jaw crusher equipped with zircon oxide jaws (model BB 51, Retsch, Haan, Germany). 48% HF, 65% HNO_3, 37% HCl and 30% H_2O_2 (analytical grade, Sigma Aldrich, Norway) were used for sample digestion and preparation of rinse solutions. Samples were diluted to volume using purified water of 15MΩ*cm resistivity (model Purelab Option, Elga, Oslo, Norway). Water of 18 MΩ*cm resistivity (Millipore, Watford, United Kingdom) and formic acid (LC/MS grade, Fisher Scientific, Loughborough, United Kingdom) were used for preparation of HPLC eluents. Matrix matched ICP-OES calibration standards were purchased from Holger Teknologi (Langhus, Norway). For ICP-MS measurements calibration standards were diluted from stock solutions of 1000 mg/L B and 10 000 mg/L Si in water (CPI International, Santa Rosa, CA, USA). Boric acid ($B(OH)_3$) of 99.97% purity (Sigma-Aldrich) was used for preparation of B stock solutions used in spike recovery experiments by ICP-OES. A $^{10}B(OH)_3$ spike (^{10}B 98% enriched, Cambridge Isotope Laboratories Inc. through Goss Scientific Instruments Ltd., Cheshire, United Kingdom) was used to investigate B conversion during sample digestion. Electronic grade Si (EG-Si) used for matrix matching in some experiments was purchased from Tokuyama (Tokyo, Japan). Laboratory grade Triton X-100 (TX-100) and 99.0% mannitol were purchased from Sigma-Aldrich (Norway). The standard reference material NIST 951a $B(OH)_3$ (National Institute of Standards and Technology) was used for mass bias correction in some isotope ratio measurements. All plastic ware used was made of polypropylene (PP).

Instrumentation

An Arcos (Spectro, Kleve, Germany) and Liberty (Varian, Melbourne, Australia) ICP-OES were used for B quantification of prepared sample digests. The Arcos ICP-OES was used for the measurement of transient B signal stabilities of sample digests and B wash-out behaviour. For all ICP-OES measurements B emission spectra at 208.959 nm were checked for spectral interferences. An Element 2 high resolution (HR)-ICP-MS (Thermo Scientific, Bremen, Germany) was used in combination with an Accela HPLC system for B speciation using a Hypercarb column (4.6 x 100 mm, Thermo Scientific). Typical chromatographic and ICP instrumental parameters are summarized in table 1.

Table 1 ICP-OES and HPLC-HR-ICP-MS parameters

ICP-OES parameters		
	Instrument 1	Instrument 2
Instrument brand and name	Spectro Arcos ICP-OES	Varian Liberty ICP-OES
Rf power [W]	1500	1000
Nebulizer gas flow or back pressure	0.65 L/min	160 kPa
Auxiliary gas flow [L/min]	1.4	1.5
Cool gas flow [L/min]	14	15
Nebulizer and spray chamber type	Cross flow and PFA Scott type	V-groove and Sturman Masters
Sample delivery to ICP-OES	peristaltic pumping	peristaltic pumping
Ar humidifier in use	no	yes
B detection wavelength [nm]	208.959	208.959
Instrumental sensitivity for B [cps/(mg/L)]	$\approx 70*10^3$	$\approx 1*10^3$
Detector type	CCD, simultaneous	PMT, sequential
Calibration solutions	Matrix matched from EG-Si and $B(OH)_3$	
Rinse solution between samples	$HF/HNO_3/H_2O$ = 20/50/430 (v/v/v) initially and ≈ 5% (v/v) HNO_3 later	≈ 5% (v/v) HNO_3
Sample uptake time [sec]	90	40
Readings per measurement	3	5
Total integration time [sec]	102	15
Rinse time [sec]	120	10
HPLC-HR-ICP-MS parameters		
Isotopes monitored	^{10}B, ^{11}B, ^{28}Si, ^{56}Fe, ^{63}Cu, ^{66}Zn, ^{103}Rh	
Internal standard	5 µg/L Rh in 1% (v/v) HNO_3 added via t-piece before nebulizer	
Mass resolution settings	low ($m/\Delta m \approx 300$): ^{10}B, ^{11}B, ^{103}Rh medium ($m/\Delta m \approx 4000$): ^{10}B, ^{11}B, ^{28}Si, ^{56}Fe, ^{63}Cu, ^{66}Zn, ^{103}Rh	
Nebulizer and spray chamber type	Meinhard and Scott type	
Torch	standard	
Cones	Ni, standard	
Mobile phase	H_2O (A), 1 mol/L formic acid (B)	
Gradient	0-1 min: 0-1% B, 1-3 min: 1-10% B, 3-5 min: 10-100% B	
Flow rate [mL/min]	0.8	
Column temperature [°C]	30	
Injection volume [µL]	100	
Fraction collection interval [sec]	12	

Digestion procedure for MG-Si

The digestion of Si was performed in open vessels using HNO_3 and HF, resulting in a vigorous exothermic reaction. HF is a contact poison, leading to severe acid burns in case of skin contact. All work involving HF was conducted in a working fume hood using suitable, protective gloves, sleeves and goggles. Dissolution of Si using HNO_3 and HF leads to formation of nitrous gases. 1 g (1.0000 ± 0.0005 g) MG-Si was weighed directly into a 100 mL PP measuring cylinder. 5 mL of water and 5 mL of 65% HNO_3 were added to the sample. 48% HF was added in portions of 4 times 0.5 mL and 7 times 1 mL. During HF addition the measuring cylinder was kept inside a water bath for cooling the strong, exothermic dissolution reaction. After each HF addition the measuring cylinders were swirled to blend the reagents. Breaks of up to approximately 3 minutes were introduced between each addition of HF in order not to provoke a too strong reaction. After the final HF addition the temperature of the water bath was set to 60°C and samples were left for 2 hours before dilution to 50 mL measurement volume and immediate B quantification by ICP-OES.

Results and discussion

Problem definition and transient signal measurement by ICP-OES

Over a period of approximately 3 months 310 MG-Si samples were measured for B concentrations by ICP-OES after open vessel digestion using instrument 1 and instrument 2 in parallel. All parallel measurements were performed from the same sample digest, on the same day and against the same set of calibration standards. Results were consistently biased towards higher results for instrument 1. Subsequent investigations of transient B signal profiles using both ICP-OES showed, that of parameters summarized in table 1 uptake, integration and rinse time, the rinse solution used between sample measurements as well as the sample type; i.e. calibration or real sample solution; were influencing the measurement result. Although the same behaviour was observed for both ICP-OES, transient signal profiles are only shown for instrument 1 due to the convenience of its data export options (figure 1).

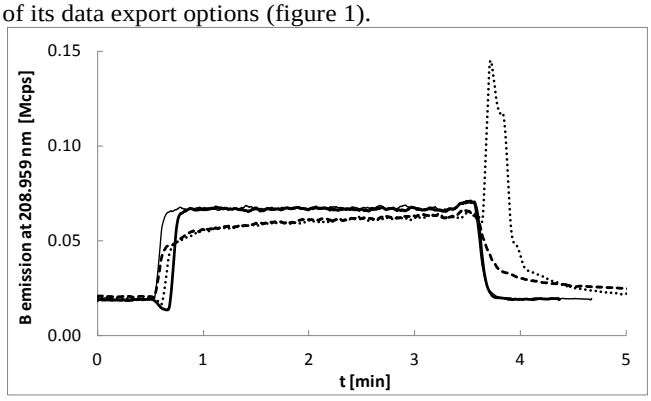

Figure 1. Transient B signal profiles of B in a 1 mg/L calibration solution and a digest of MG-Si sample *Elkem 2*. (—) 1 mg/L B calibration solution, rinsed with dilute HNO_3. (—) 1 mg/L B calibration solution, rinsed with dilute HNO_3/HF blend. (···) *Elkem 2*, rinsed with dilute HNO_3. (---) *Elkem 2*, rinsed with dilute HNO_3/HF blend.

As illustrated in figure 1 the B signal of a calibration solution is stable over time and does not show delayed wash-out, irrespective of the rinse solution used. The same was observed for EG-Si digests spiked with $B(OH)_3$ before and after digestion, which yielded identical signals irrespective of the point of spike addition. In contrast the B signal of the MG-Si sample *Elkem 2* increased steadily over time by approximately 16% between minutes 1 and 3.5 during sample introduction. It is obvious that longer uptake and integration times will result in comparably higher estimates of the B concentration in real samples. In addition the real sample wash-out with dilute HNO_3 resulted in a distinct B spike with a maximum at approximately minute 3.7. The addition of HF to the rinse solution prevented formation of this B spike during the wash-out and required a longer rinse time to reach the baseline again. Even after 9 minutes of continuous rinsing with a dilute blend of HNO_3 and HF the B signal for sample *Elkem 2* was still approximately 2400 cps above the baseline level before sample introduction. Using dilute HNO_3 the baseline for *Elkem 2* is reached after approximately 5.5 minutes. The B memory effect; or rather B fractionation; observed for real samples in this experiment was interpreted as chemical differences between real sample and calibration solutions or EG-Si digests spiked with $B(OH)_3$.

In another set of experiments this B fractionation was confirmed for an entire set of MG-Si samples consisting of 4 materials sourced from 3 of Elkem's Si smelters in Norway, 8 materials from Bluestar's production in China, the silicon standard reference material NIST 57b from the USA and the silicon standard reference material IPT134 from Brazil. For sample *Elkem 2* the height of the B spike during sample wash out with dilute HNO_3 reproduced with a relative standard deviation of 4.7% for 5 sample injections. Water as well as a 1 g/L mannitol solution in water, which as a B complexing agent could improve the behavior of B in the sample introduction system, did not result in any differences compared to dilute HNO_3 as rinsing agent.[19, 20] In a further attempt to improve B signal stability and wash-out it was found that B recovery for MG-Si samples was reduced by 10 to 30% in digests containing 0.005% to 0.05% (v/v) TX-100 in contrast to EG-Si digests spiked with $B(OH)_3$ or calibration standards, which both yielded quantitative recoveries independent of the added TX-100 concentration.[21] Moreover the addition of TX-100 to real sample digests changed the appearance of solutions from being clear to white opaque. This was not observed for calibration solutions and digests of EG-Si spiked with $B(OH)_3$. It can be debated whether this behaviour is related exclusively to B chemical differences in the different sample types or an interaction between TX-100 and other components not present in calibration solutions or EG-Si digests. On the other hand this observation could theoretically be related to an interaction between the hydrophilic part of TX-100 and an unknown B species in real samples, rendering the resulting product less soluble and thereby reducing B recovery from real samples.

Several modifications of the sample digestion procedure were tried to eliminate the observed chemical differences. These were inverse dissolution of real samples; i.e. the addition of HNO_3 increments to measure cylinders containing sample material and HF; use of more HNO_3 for sample digestion, addition of H_2SO_4 to sample digests and application of microwave assisted digestion protocols in combination with varying amounts of HNO_3, HF and HCl added to the samples. None of these changed the transient B signal stability or wash-out of MG-Si digests during ICP-OES measurement.

HPLC-HR-ICP-MS boron speciation investigations

Speciation of HNO_3/HF digests from *Elkem 1*, *Elkem 2* and several other MG-Si materials revealed that B is present as at least two different chemical species (figure 2). While the first

peak eluting at 2.2 minutes is boric acid ($B(OH)_3$) or its equivalent in solution, the chemical species of the second peak eluting at 6.2 minutes is unknown (figure 2A). The first eluting B species was not considered to be the reason behind the B fractionation observed during ICP-OES measurements, since it is the compound $B(OH)_3$ used for preparing the calibration standards where no signal instability and B fractionation were observed. B does not form stable BF_4^- complexes during digestion despite the presence of a large surplus of HF. Different B compounds, including $B(OH)_3$, $NaBF_4$ and $Na_2B_4O_7$, added to sample digests did exclusively result in an increase of the first B peak.

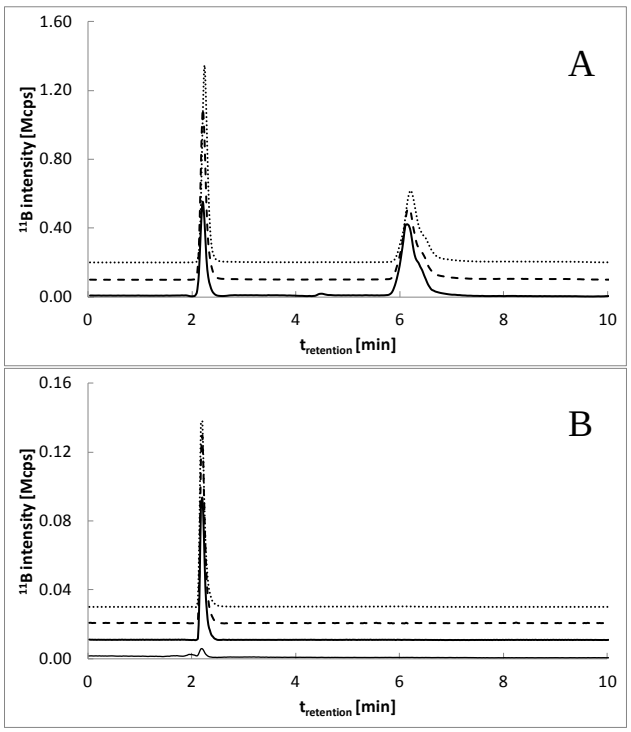

Figure 2. HPLC-HR-ICP-MS chromatograms of different B compounds added to an MG-Si digest prepared from *Elkem 2* (A) and an EG-Si digest (B). (—) un-spiked *Elkem 2* in (A) and EG-Si spiked with $Na_2B_4O_7$ in (B). (---) Sample spiked with $B(OH)_3$. (···) Sample spiked with $NaBF_4$. (—) EG-Si digestion blank in (B). Traces were off-set for clarity.

The unknown B species eluting at 6.2 minutes contributes with approximately 56 ± 3% (1 SD, n = 6) to the total integrated peak area of *Elkem 2*. It was found that the unknown B compound was not affected by long term storage of sample digests over a period of approximately 2 months. Electron spray ionization-mass spectrometry (ESI-MS), nuclear magnetic resonance (NMR), x-ray diffraction (XRD), x-ray photo electron spectroscopy (XPS) and electron paramagnetic resonance (EPR) experiments did not aid identification of the unknown B species due to a lack of instrumental sensitivity and in the case of ESI-MS potentially also the inability of the compound to form cationic or anionic species during soft ionization. Addition of isotopically labelled $^{10}B(OH)_3$ to an EG-Si and MG-Si sample before digestion showed that the unknown B compound was most likely not formed during the digestion procedure (figure 3). Figure 3A illustrates the typical elution peak and accompanying tail observed for chromatograms of $B(OH)_3$ in EG-Si digests, irrespective of the point of spike addition. We speculate that this is related to the partial formation and hydrolyzation of $B(OH)_xF_y$ on the column. The increase in the observed $^{10}B/^{11}B$ isotope ratio at 6.6 minutes might in addition be over amplified by unstable chromatographic baselines. Considering the size of the peak related to the unknown B species in MG-Si with an elution time of 6.2 minutes we considered this observation of limited practical relevance and did not investigate this further. Figures 3B and 3C respectively show chromatographic separations of an un-spiked and a spiked sample of *Elkem 2*, to which the $^{10}B(OH)_3$ spike was added before sample dissolution. For the un-spiked MG-Si sample the $^{10}B/^{11}B$ isotopic ratio remains nearly constant and close to the natural range over the chromatographic run, whereas for the spiked MG-Si sample only the first peak and its accompanying tail show increased $^{10}B/^{11}B$ ratios. Beginning with the elution of the second peak a natural $^{10}B/^{11}B$ ratio is reached, suggesting that $^{10}B(OH)_3$ added before sample dissolution is not involved in formation of the unknown B compound and thus not implementing the digestion procedure as its source under given experimental constraints.

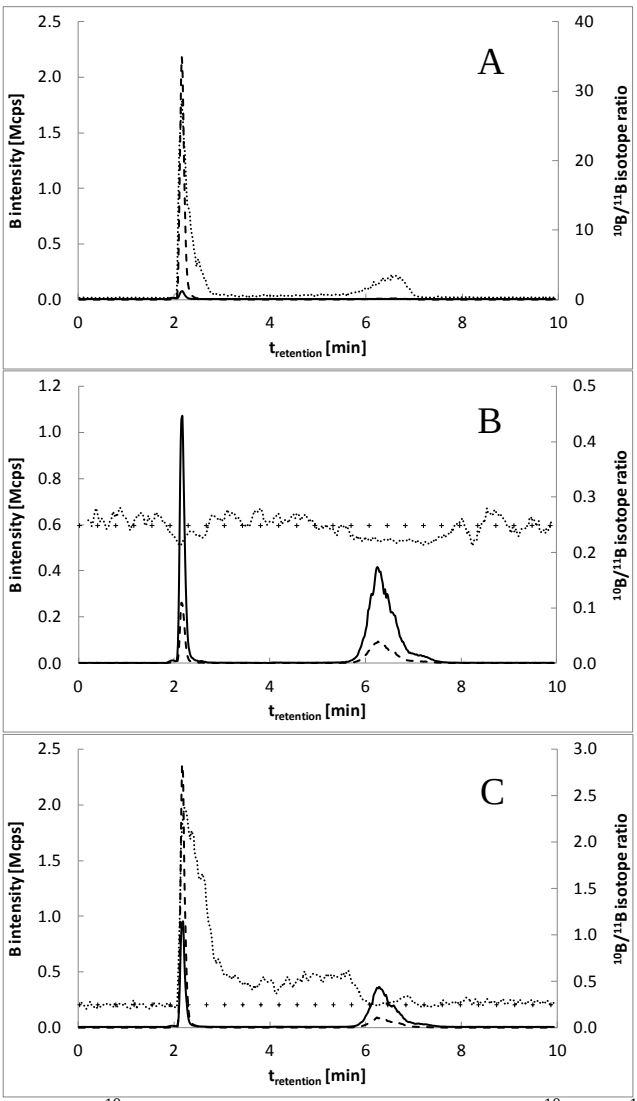

Figure 3. $^{10}B(OH)_3$ spiking experiments illustrating ^{10}B and ^{11}B traces as well as transient raw $^{10}B/^{11}B$ isotopic ratios for digests of spiked EG-Si (A), un-spiked *Elkem 2* (B) and spiked *Elkem 2*

(C). (—) ^{11}B intensity, (---) ^{10}B intensity, (⋯) measured $^{10}B/^{11}B$ isotope ratio and (+++) natural $^{10}B/^{11}B$ isotope ratio.

In further investigations HPLC fractions of MG-Si digests were collected and those corresponding to the unknown B compound eluting at 6.2 minutes were re-chromatographed using HPLC-HR-ICP-MS. Since most of the Si matrix was removed this way, the parallel determination of Si and other elements was possible. Of the respective isotopes listed in table 1, only ^{28}Si co-eluted with the unknown B compound. The atomic B/Si ratio in the unknown compound was estimated to be 1/10, which indicates a B-Si-cluster resistant to digestion with HNO_3 and HF. Attempts to selectively precipitate the Si present in the digest using NH_3 led to the loss of the unknown compound due to co-precipitation, but not to the loss of $B(OH)_3$ in solution, again pointing to the possibility of the unknown compound being a B-Si-cluster.

Further tests revealed that the unknown B compound in sample digests can be effectively oxidized using H_2O_2 in open vessels but not, for example, aqua regia even when using closed microwave assisted digestion under harsh conditions. The effect of H_2O_2 on the speciation of B in a digest of sample *Elkem 2* at several points after addition of H_2O_2 with a volumetric sample/H_2O_2 ratio of 9/1 was tested. According to our findings the unknown B compound is quantitatively converted within less than 20 minutes to $B(OH)_3$ in solution after H_2O_2 addition (table 2).

Table 2 Influence of incubation time with H_2O_2 on B recoveries from digests of *Elkem 2*. Reproducibilities of results are given as 1 standard deviation of 3 experiments.

Incubation time with 5 mL H_2O_2 2 hours after final HNO_3 addition	B in Si [mg/kg], measured as $B(OH)_3$	B in Si [mg/kg], measured as unknown B compound	B in Si [mg/kg], total	Average fraction of $B(OH)_3$ [%]
0 minutes (untreated)	17.7 ± 0.2	27.6 ± 0.4	45.3 ± 0.1	39
20 minutes	44.4 ± 0.9	0	44.4 ± 0.9	100
24 hours	45.0 ± 1.9	0	45.0 ± 1.9	100

Sample preparation method development for ICP-OES

Based on initial HPLC experimental results, MG-Si sample preparation methods involving the addition of H_2O_2 at different points during digestion were tested with the aim of converting the unknown compound to $B(OH)_3$. The best results were achieved using the digestion method as described above and adding 5 ml H_2O_2 after either complete sample dissolution in the measure cylinder or during sample dilution with water before measurement. This way no major changes during sample handling were required and the compound was converted quantitatively to $B(OH)_3$. It was observed that the addition of H_2O_2 before complete sample dissolution inhibited digestion. The amount of H_2O_2 added was not optimized during these initial experiments.

The new sample preparation procedure was tested and validated for ICP-OES at Elkem's central laboratory in Kristiansand. Analogue to experiments described in figure 1, the transient B signal stabilities and wash-out behaviors of typical samples prepared, using the modified digestion protocol, were measured by ICP-OES and compared to samples not treated with H_2O_2 as well as calibration solutions. Addition of H_2O_2 to real sample digests immediately led to the elimination of previously observed differences between real samples and calibration solutions. B baseline readings for samples treated with H_2O_2 were reached within less than 1 min without the previously observed spike following instrument rinsing with dilute HNO_3. The conversion time of the unknown compound to $B(OH)_3$ perceived in these experiments was below the time required for sample introduction to the ICP-OES, which was approximately 2 minutes. Also, following the addition of TX-100 to real samples, solutions remained clear.

The amount of H_2O_2 required for conversion of the unknown B compound was optimized using a high B MG-Si sample sourced from Elkem's production with a bulk B concentration of approximately 85 µg/g, determined after H_2O_2 treatment. A set of digests was prepared, different increments of H_2O_2 from 0.25 to 5 mL H_2O_2 were added before dilution to final volume and transient B signal stabilities as well as wash-out behaviour with dilute HNO_3 were monitored. These measurements showed that 0.25 mL of 30 % H_2O_2 sufficed to dependably convert the unknown B compound into $B(OH)_3$, therefore avoiding signal instability over time and B fractionation in the sample introduction system of the ICP-OES. We found that the measured B concentration was constant for the investigated range of H_2O_2 volumes added. The effect of H_2O_2 addition to digests on B quantification by ICP-OES was evaluated using a set of 5 MG-Si samples. Measurements were performed on both ICP-OES (table 1). Corresponding results are summarized in table 3 and illustrated in figure 5.

Table 3 Summarized B quantification results for ICP-OES measurements of MG-Si samples obtained with and without H_2O_2 addition to sample digests.

Sample	No H_2O_2 added		H_2O_2 added	
	Instrument 1	Instrument 2	Instrument 1	Instrument 2
	B in MG-Si [µg/g]†			
Sample 1	10.9 ± 0.9 (n = 4)	11 ± 1 (n = 4)	13.4 ± 0.2 (n = 4)	12.7 ± 0.8 (n = 4)
Sample 2	35.6 ± 0.8 (n = 4)	34 ± 1 (n = 4)	42.2 ± 0.6 (n = 4)	41 ± 2 (n = 4)
Sample 3	37.8 ± 0.8 (n = 4)	35 ± 2 (n = 4)	45 ± 1 (n = 4)	43 ± 2 (n = 4)
Elkem 1	22 ± 4 (n = 36)‡	20 ± 2 (n = 36)‡	26 ± 1 (n = 16)	26 ± 1 (n = 16)
Elkem 2	47 ± 7 (n = 36)‡	41 ± 3 (n = 36)‡	52 ± 2 (n = 14)	53 ± 2 (n = 14)
Simple linear regression parameters	r^2 = 0.940, slope = 0.82, intercept = 2.32		r^2 = 0.997, slope = 1.01, intercept = -0.66	

† Results are given with ± 1 SD

‡ Data partly taken from initial instrument validation before the effect of H_2O_2 was known and investigated

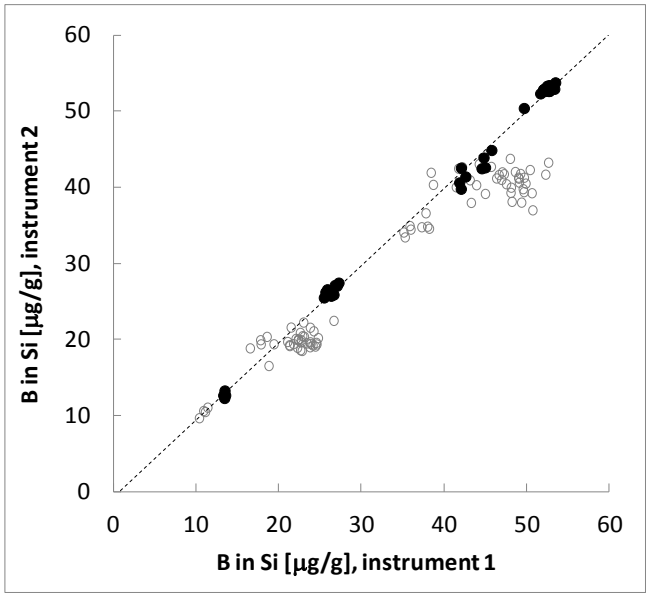

Figure 5. Individual ICP-OES B quantification results from table 3 obtained with and without H_2O_2 addition to sample digests. Data recorded with (●) and without (○) H_2O_2 added to samples. Dashed line represents a simple, linear regression through data obtained with H_2O_2 added to samples (regression parameters in table 3).

Results obtained from measurements of samples not treated with H_2O_2 shown in figure 5 are on average biased by 9 ± 5% (1 SD, n = 5 sample materials) towards higher results obtained with instrument 1. For samples *Elkem 1* and *Elkem 2*, which have been measured most frequently over a period of approximately 3 months without addition of H_2O_2 on both instruments, the bias is on average 14 ± 11% (1 SD, n = 72 measurements). Following the addition of H_2O_2 the bias between the different instruments is reduced to 0 ± 1% (1 SD, n = 30 measurements) for these materials. Corresponding *Elkem 1* and *Elkem 2* measurements involving H_2O_2 cover a time period of approximately 8 months. For *Elkem 1* and *Elkem 2* data in table 3, measurement reproducibility improved approximately by a factor 3 to 5 when adding H_2O_2 to sample digests, depending on instrument and sample material. The bigger gains are observed for instrument 1 due to the longer integration time and higher instrumental sensitivity. However, as a result of H_2O_2 addition the average measured B concentration; calculated from average results of instruments 1 and 2; increased by 21 ± 2% (1 SD, n = 5 sample materials) under given experimental constraints.

Comparison of ICP-OES results to other instrumental techniques

For cross validation of ICP-OES based B measurements employing the modified sample digestion protocol a set of 3 MG-Si samples was sent to different laboratories for external analysis. Instrumental methods included were secondary ion mass spectrometry (SIMS), prompt gamma activation analysis (PGAA), glow discharge mass spectrometry (GDMS) and HR-ICP-MS. *Elkem 1*, *Elkem 2* and a random production sample from one of Elkem's Si smelters with a B bulk concentration of approximately 35 µg/g were selected. Portions of crushed samples were claimed and split into aliquots of 3-6 g before packing into polyethylene zip lock bags and dispatch to external laboratories. A randomly selected aliquot of each sample material was subjected to ICP-OES analysis at Elkem's central laboratory using instrument 1. ICP-OES results following the modified sample preparation protocol agreed within 2 quoted uncertainties with PGAA measurements. For ICP-OES results uncertainties are assumed as standard deviations and a relative standard deviation of approximately 2% was obtained for each of the 3 samples from 3 readings in a single measurement. Uncertainties for PGAA were approximately 3% (coverage factor k=1). HR-ICP-MS analyses, following sample preparation without the use of H_2O_2, resulted consistently in approximately 20 ± 4% (1 SD, n = 3) higher B concentrations in comparison to ICP-OES, with quoted uncertainties of 20%. SIMS on average gave 31 ± 7% (1 SD, n = 3) lower results in comparison to ICP-OES. GDMS did not produce satisfactory results either. Since B quantification with PGAA exclusively utilizes the isotope ^{10}B and a natural B isotopic composition has to be assumed for calculation of the total B content, the $^{10}B/^{11}B$ isotope ratios of two of the samples provided were checked using quadrupole ICP-MS.[22] Mass bias was corrected externally against NIST 951 $B(OH)_3$ using sample standard bracketing and a linear law.[23] $^{10}B/^{11}B$ isotope ratios of 0.248 ± 0.006 and 0.244 ± 0.005 (1SD, n=8 replicates) for *Elkem 1* and *Elkem 2* respectively were found, which is in good agreement with natural B isotopic abundances given by the IUPAC.[24, 25]

To validate the revised sample preparation protocol further an additional set of 9 samples, consisting of 4 sub samples each of *Elkem 1* and *Elkem 2* from different containers and one sample of NIST 57b marked as unknown, was submitted for PGAA analysis. Again the same samples were also measured at Elkem's central laboratory by ICP-OES. In some cases multiple analyses of different digests, partly involving both ICP-OES as well as different analysts were performed. Analyte recovery from real samples was used as a means of quality control. Results are summarized in table 4.

Table 4 Comparison of PGAA and ICP-OES results for B in MG-Si using H_2O_2 for ICP-OES sample preparation.

Sample material	Sub sample	ICP-OES results†	PGAA results†	PGAA deviation from ICP-OES
		B in MG-Si [µg/g]		[%]
Elkem 1	A	27.0 ± 0.5 (n = 4)	28.0 ± 1.2	3.7
	B	26.5 ± 1.4 (n = 5)	28.0 ± 1.3	5.7
	C	26.7 ± 1.4 (n = 4)	27.0 ± 1.0	1.1
	D	26.8 ± 1.1 (n = 10)	28.5 ± 1.8	6.3
	E	26.2 ± 0.5 (n = 5)	27.5 ± 1.2	5.0
Average		*26.6 ± 0.6 (2 SD)*	*27.8 ± 1.1 (2 SD)*	*4 ± 2 (1 SD)*
Elkem 2	A	53.6 ± 3.9 (n = 1)	55.0 ± 2.4	2.6
	B	53.4 ± 4.0 (n = 1)	56.0 ± 2.9	4.9
	C	53.1 ± 0.9 (n = 6)	57.0 ± 3.2	7.3

	D	53.7 ± 2.3 (n = 6)	56.0 ± 3.1	4.3
	E	53.8 ± 1.0 (n = 12)	57.1 ± 3.3	6.1
Average		*53.3 ± 0.6 (2 SD)*	*56.2 ± 1.7 (2 SD)*	*5 ± 2 (1 SD)*
NIST 57b	n/a	14.2 ± 0.6 (n= 4)	15 ± 0.7	5.6

Additional NIST 57b B concentration values[§], [μg/g]	
12.5 ± 2.1	Reference B concentration in certificate
14.3 ± 0.2	B concentration obtained using PGAA
10.6 ± 0.4	B concentration obtained using ICP-OES

† ICP-OES results are given with ± 2 SD. PGAA results are given with combined measurement uncertainty (Uc, k=2)

§ Taken from NIST 57b certificate and literature. Quoted with Uc (k=2) [18]

All ICP-OES results agree within two quoted uncertainties with PGAA results, but only four do so within one quoted uncertainty. It is conspicuous that PGAA generally yields B concentrations 5 ± 2% (1 SD, n = 9) above ICP-OES, apparently independent of the herein investigated B concentrations. One hypothesis offering an explanation is the loss of volatile B species from sample solutions prepared for ICP-OES, which was not confirmed in this work. Virtually B free EG-Si samples spiked with B before and after digestion to B concentrations corresponding to approximately 3 to 100 μg/g in Si yielded recoveries of 101 ± 1 % (1SD, n = 10), without discernible differences with respect to the point of spike addition and speed of sample dissolution. Sample heterogeneity on the other hand should give deviations both ways between ICP-OES and PGAA. Incomplete oxidation of the unknown B compound and hence reduced analyte recovery related to B fractionation in the ICP-OES sample introduction system could also not be detected in this work.

It has been shown numerous times that PGAA is a powerful tool for estimation of B concentrations at the trace level.[26, 27] The two basic approaches for obtaining elemental concentrations by PGAA are either relative or absolute, with varying sources of uncertainties to be considered in each case. In both cases however, determination of the peak area, baseline correction, interference contribution to the analyte signal, detector efficiency and self absorption effects have to be accounted for.[28, 29] In general PGAA spectra are highly complex and B has been described as a very special case, since more than one hundred peaks of other, interfering elements can occur in the relevant energy range of the measured γ-emission spectrum.[30] A corresponding routine for interference correction and B peak fitting has been reported in literature.[31] Still, results of the international pilot study P33, initiated by the Consultative Committee on the Quantity of Material (CCQM) in the year 2003 and dedicated to the quantification of B in Si by neutron activation and other analytical methods, have not been officially released.[32] Eventually we also want to mention variation of the B isotopic composition as a source of uncertainty in PGAA measurements.[22] This is very rarely mentioned in literature but has potential to contribute significantly to PGGA measurement uncertainty, given the large natural variation of the ^{10}B mole fraction in nature, which is well above 7% from its lowest to its highest extreme.[24, 25] Even if all preceding corrections associated with PGAA are highly accurate, a deviation between true and assumed $^{10}B/^{11}B$ isotope ratio may result in systematic under or over reporting of measured B concentrations. The B concentration found by PGAA for NIST 57b in this study is approximately 5 % higher than PGAA data quoted by Sieber et al, whereas our ICP-OES results obtained with the revised sample preparation protocol are in excellent agreement with Sieber's data.[18] It has to be mentioned though, that ICP-OES as well as PGAA results for NIST 57b reported in this study are based on a limited number of observations.

Conclusions

For the first time it has been demonstrated that there are different molecular species of B present in acidic digests of MG-Si prepared with HNO_3 and HF. One of them was identified as $B(OH)_3$. The second and unknown B compound is stable to acidic digestion but sensitive to oxidation with H_2O_2 after sample dissolution. The molecular structure of this compound was not identified. Preliminary experiments indicate that it could be a B-Si cluster or polymer with a B/Si stoichiometry of approximately 1/10. HPLC-HR-ICP-MS experiments involving isotopically enriched $^{10}B(OH)_3$ did not yield formation of this compound during Si dissolution under given experimental constraints; i.e. addition of $^{10}B(OH)_3$ to solid EG-Si and MG-Si samples before dissolution.

It was also shown that this unknown B compound fractionates in the PTFE/PFA ICP-OES sample introduction system, causing signal instability, significant underreporting of B concentrations and necessitating prolonged wash-out times. Addition of H_2O_2 to sample digests led to stable B signals and improved measurement reproducibility. Generally samples prepared using the modified digestion protocol yielded significantly higher B concentrations than estimated using sample digestion without addition of H_2O_2. The exact increase in measured B concentrations will depend on timing of sample uptake and data acquisition as well as rinsing agent and wash-out time used. To the best of our knowledge the use of H_2O_2 for sample preparation is not an approach commonly followed for dissolution of any Si sample types. Preliminary investigations suggest that the findings documented in here are relevant not only for MG-Si, but also for ferro-silicon (FeSi) alloys as well as purer grades of Si, such as for example high purity, p-type Si wafer material.

We believe that our findings may prove a valuable contribution to the provision of MG-Si and other Si standard reference materials certified for their B concentrations. For standard reference material NIST 57b for example, only a reference value for the B concentration is available, presumably due to the fact that measurements from PGAA and another method, probably ICP-OES, were significantly biased. Nonetheless, more effort is required to ascertain the accuracy of B concentrations measured by any of the methods applied herein.

Future efforts will also require identification of the molecular structure of the unknown B compound, clarification of whether it is already present in solid Si and its implications for Si refining as well as final, electronic material properties.

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Notes and references

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