

A modified method for biogenic silica determination

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Abstract We describe a modified method for the determination of biogenic silica (BSi) in lacustrine sediment samples with BSi concentrations $>0.5\%$ SiO_2 (detection limit). To speed up the leaching procedure (48 samples per day), we suggest the use of Teflon autoclaves that can be left unattended (no stirring of the solution) for 3 h at 100°C in an oven. We suggest a volume correction by Na measurement to account for volume errors during pipetting off a hot solution. We also propose to carry out a correction for minerogenic silica by the simultaneous determination of Al in the leachate. Analytical precision and accuracy of the proposed method are 2.4% (relative standard deviation) and 70–110% recovery (relative to the mean of four international reference sediment samples), respectively. Additionally, we demonstrate that pre-treatment of the samples with H_2O_2 and/or HCl prior to alkaline leaching is not necessary for all samples. Due to the great

diversity of lacustrine and marine sediments, however, the pre-treatment procedure should be tailored for samples from different sites.

Keywords Biogenic silica · NaOH-extraction · ICP-OES · Teflon autoclaves

Introduction

The determination of biogenic silica (BSi) in sediments is an important method used frequently to estimate historic changes in primary productivity of lakes or oceans. Compared to more laborious methods, such as separation and counting of individual siliceous organisms (diatoms, chrysophytes, radiolarians, sponge spicules, etc.), chemical leaching is faster and can be easily automated. Current methods of BSi determination, however, are still relatively time consuming (10–20 samples per day) or not applicable when BSi-concentrations in the sediments are low. Here we propose a faster, more reliable analytical BSi method to apply in multi-proxy studies of sediment cores.

Description of currently used BSi analytical procedures

Essentially three methodological approaches are applied for BSi-analysis. They are: (1) X-ray

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diffraction, (2) infrared spectroscopy, and (3) wet chemical extraction.

- (1) X-ray diffraction is the fastest way to obtain analytical results because it is usually automated (auto sampler) and does not require chemical pre-treatment. Semi-quantitative results are obtained by either measuring the height or area of the amorphous opal-bulge in the diffraction pattern (Eisma and Gaast 1971) or by determining the peak intensity of the tridymite peak in the diffraction patterns after conversion of amorphous BSi through thermal treatment of the samples (Goldberg 1958). X-ray diffraction methods, however, are not very accurate and are only applicable when BSi concentrations are >10%.
- (2) Infrared spectroscopy takes advantage of the absorption of the specific wavelength of the SiO₂ group and yields good results even for low BSi concentrations (Chester and Elderfield 1968). It can also be automated, however, it requires an IR-spectrometer, which may not be available in every laboratory.
- (3) Wet chemical extraction is the most widely used method for BSi determination, because it just requires chemicals and instruments that are available in most analytical laboratories. Various laboratories use different methods of wet chemical extraction and subsequent measurement, which makes it difficult to compare inter-laboratory results (Conley 1998).

In this paper we suggest a method to speed up the chemical extraction procedure. We also propose a more reliable correction of the analytical results and we show that the determination of low BSi concentrations is also possible.

The wet chemical extraction procedure is based on the assumption that biogenic silica can be leached selectively from sediment samples by treatment with an alkaline solution. Commonly, hot solutions of NaOH or Na₂CO₃ in different concentrations are used for this purpose. Because lacustrine and marine sediments are usually a mixture of four main components (biogenic silica, organic remains, carbonates and silicate minerals), varying amounts of the other sediment components in addition to BSi may be dissolved during treatment with a hot alkaline solution. Solution of silicates (e.g., clay minerals)

will occur and will confound BSi results. Accurate estimation of BSi requires correction for the mineral component within the sample. This correction of the ‘apparent’ BSi content of a sample can be accomplished in two ways (Fig. 1):

Continuous monitoring of the dissolution progress (*timed dissolution method*)

Correction based on analysis of Al, which originates from the leached (clay) minerals (*single-step, wet-alkaline leach method*).

The first method was developed by DeMaster (1981) and improved by applying a continuous flow technique developed by Müller and Schneider (1993). With this technique, the amount of minerogenic silica that is extracted from the sample is determined by monitoring the extraction process and by graphic extrapolation of the linear portion of the extraction curve back to the abscissa (Fig. 1). Recent studies suggest that this way of correction for ‘apparent’ BSi may over-estimate true total BSi content (Kamatani and Oku 2000).

The second method (Eggimann et al. 1980; Mortlock and Froehlich 1989) corrects for the leached minerogenic silica by determining Al within the leachate, assuming that all Al originates from the dissolution of siliceous minerals in a sample. The largest

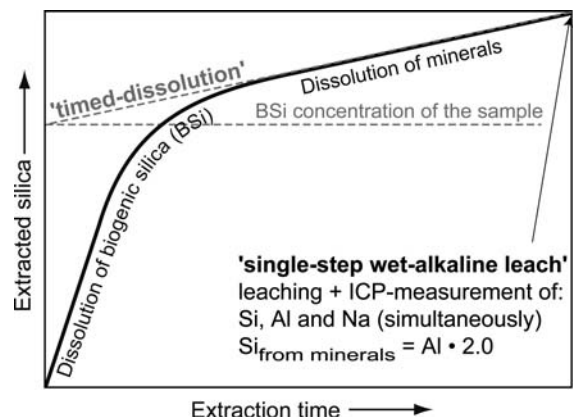


Fig. 1 Schematic illustration of the two possible correction methods for ‘apparent’ Si released from minerals or other non-biogenic sediment compounds. In the ‘timed dissolution’ method the linear part of the dissolution curve is extrapolated back to the y-axis to obtain BSi-values. In the ‘single-step wet-alkaline leach’ method Si, Al and Na concentrations are simultaneously measured by ICP-OES after complete dissolution of BSi. Mineral dissolution is accounted for by Al-determination and correction assuming an Al:Si ratio of 1:2 for BSi calculation

uncertainty of the latter method derives from the fact that an Al:Si ratio must be assumed for the mineral fraction of the sample. Depending on the minerals in the sample, this ratio may vary from 1:1 (e.g., kaolinite) to 1:2 (e.g., montmorillonite) or even 1:3 (nontronite), which may change the correction factor to be applied. Although presumably a wide range of Al:Si ratios is encountered in lacustrine sediments (e.g. Koning et al. 2002) for most sediments, however, it is the best first-order approximation to use a mean Al:Si ratio of 1:2, because montmorillonite is a common mineral in many catchments and also represents the mineral that is most easily dissolved during the leaching process (Müller and Schneider 1993). A correct value for this ratio becomes more important when samples with very low BSi content are analyzed. In such cases an additional determination of the mineral composition of the sample (e.g., by X-ray diffraction analysis or by SEM-EDX techniques) can be used to determine the appropriate Al:Si ratio. A very time consuming method for estimating a sample-specific Al:Si ratio would be to leach a BSi-free sample (e.g., a small quantity of sample where siliceous organisms have been removed by manual selection under a binocular microscope) for 3 h and determine the Al:Si ratio in this leachate of purely minerogenic matter. This would then be regarded as representative for a whole batch of samples with comparable mineralogical composition. The best way to tackle the problem of varying Al:Si ratios is to monitor changing Al-concentrations during the leaching procedure as well. A respective method was described by Koning et al. (2002) and it is probably the most accurate way to determine BSi-values in samples with very low BSi-concentrations. As it is a laborious method it may, however, not easily be applied to large series of samples.

Description of BSi determination with ICP

Our method basically follows that of Carter and Colman (1994) which is based on Mortlock and Froehlich (1989). For the non-carbonaceous, relatively organic-poor sediments that we analyzed the following modifications were implemented:

1. No pre-treatment of the samples with H_2O_2 and HCl

2. Leaching in Teflon autoclaves in an oven at 100°C without stirring and not in plastic test tubes in a water bath
3. No centrifuging after NaOH-leaching
4. Volume correction by Na determination in the solution.

These modifications simplify and speed up the leaching process in such a way that, depending on laboratory capacities (oven, autoclaves), 48 or more samples can be leached in 8 h.

Depending on the BSi-concentration, between 10 and 50 mg of freeze dried, homogenized sediment were weighed directly into Teflon autoclaves. After adding 10 ml of 1M NaOH (Titrisol, Aldrich, Switzerland) and 1 min of ultrasonic treatment (ultrasonic bath), leaching was done at 100°C in an oven using an autoclave system (Heinrichs et al. 1986). After 3 h without stirring the samples, all BSi was extracted, even from the samples with high BSi-content (Fig. 2). Complete leaching was checked by SEM examination of the residual particles for absence of biogenic material (scales of diatoms, chrysophytes, spicules etc.). A sub-sample of 5 ml from the hot solution was added to ca. 30 ml of de-ionized water in 50 ml PE-flasks and neutralized with HNO_3 to pH = 6. After cooling to 20°C the volume of the solution was adjusted to 50 ml. Subsequently, concentrations of Si, Al and Na were determined simultaneously with an inductively-coupled-plasma atomic emission spectroscope (ICP-OES; Co.: Spectro) at Eawag (Dübendorf).

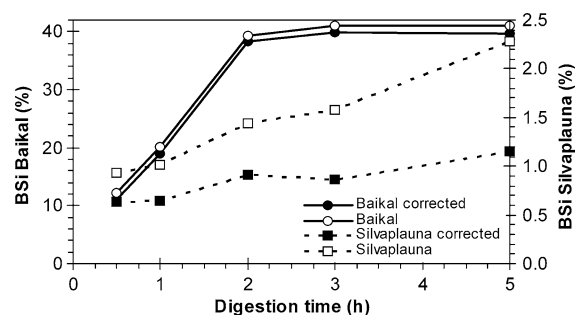


Fig. 2 Variation of extracted BSi from samples with high BSi-content (Lake Baikal sediments, left axis) and low BSi-content (Lej da Silvaplana sediments, right axis) at different extraction times. The raw data are shown in comparison to data that was corrected for 'apparent' BSi (Al-content) and volume inaccuracy (i.e., Na content)

To test for completeness of BSi dissolution, sediment sample sets representing two different sedimentary environments and lithologic types were leached under varying conditions, i.e., different temperatures and duration of leaching, different leaching agents, etc. One set of sediment samples came from Lake Baikal, Russia and is characterized by high BSi contents of up to 40 wt% ((w/w)%). These sediments represented a mixture of diatoms and spicules (~ 40 (w/w)%), fine grained terrigenous minerals (~ 50 (w/w)%), and organic material (~ 10 (w/w)%). The second set of samples included sediments with low BSi content (<1.4 (w/w)%) from Lej da Silvaplauna, Switzerland. These sediments originate from a high-alpine, proglacial lake, and mainly consist of detrital minerals (glacial rock flour ~ 96 (w/w)%), organic material (~ 2 (w/w)%), and small amounts of BSi (1.4 (w/w)%). In addition reference material that was used in an inter-laboratory comparison exercise (Conley 1998) was analyzed for comparison (Table 1). The method was then applied to a sediment profile of 77 samples from Lej da Segl (a proglacial lake adjacent to Lej da Silvaplauna) in the Upper Engadine, Switzerland. Unless otherwise noted, sediment BSi concentrations are given as wt% SiO₂ in a given dry mass of sample.

Discussion of analytical results of the modified BSi method

The concentrations of international reference materials were determined to test the analytical accuracy of the “Single step leach” BSi method (Table 1). All values are within the given ranges, i.e., 70–110% recovery, with respect to the mean concentrations specified in Conley 1998. In addition, BSi concentrations of an

internal reference sediment from Lake Baikal (BK 93–15) were measured to test the analytical precision. For eight replicates, a mean value of 41.8% and an absolute standard deviation (SD) of 1.01% (relative SD: 2.4%) were determined. Our results are in good agreement with values obtained on the same reference sample by the “timed dissolution” method (Müller and Schneider 1993; Table 2). Concentrations determined with the latter method, however, are systematically higher by $\sim 9\%$ than those measured by the “single step leach” method (Table 2). This supports the findings of Kamatani and Oku (2000), who argue that the “timed dissolution” method tends to overestimate the total BSi content of a sample because the dissolution of ‘apparent’ BSi (e.g., from clay minerals) during the starting phase of the leaching procedure (first few minutes) is not taken into account. This result, and the fact that the BSi content of the analyzed international reference material (Table 1) could also be determined within the given range (Conley 1998), gives us confidence that the proposed simplification of the single-step alkaline-leach method yields robust results. From blank measurements, a detection limit of 0.5% SiO₂ was determined.

Our experiments showed that leaching in Teflon autoclaves (Heinrichs et al. 1986) works best because the flat bottom of the Teflon beakers ensured that all of the sediment material was exposed to the dissolving agent during the entire leaching time. Therefore, no shaking of the samples during the 3 h leaching procedure was necessary. In addition, loss of 1 M NaOH during leaching was negligible because autoclaves were tightly sealed. Use of Teflon autoclaves simplifies and speeds up the leaching procedure significantly. Our lab is equipped with a conventional drying oven and the above mentioned autoclave system (Heinrichs et al. 1986) with 24 vessels.

Table 1 BSi concentrations of reference material as analyzed in this study compared to the mean values determined in an inter-laboratory comparison exercise (Conley 1998)

Sample ID	Sample name	Conley 1998		This study	
		BSi	SD	BSi	SD
Blass et al. 2005	Still pond	2.82	± 1.17	1.95	± 0.28
Carter and Colman 1994	Lewis Lake	44.3	± 9.38	46.92	± 0.30
Chester and Elderfield 1968	R-64	6.49	± 2.09	6.19	± 0.48
Conley 1998	Yellowstone Lake	38.2	± 9.48	41.51	± 0.75

SD: standard deviation

Table 2 Mean BSi concentrations (% SiO₂) of the internal reference sediment from Lake Baikal (BK 93–15) determined with the “timed dissolution” method and with the modified “Single-step leach” method described in this paper

Method	BSi (%)	SD	n
“Timed dissolution”	45.9	±0.95	8
“Single-step leach”	41.8	±1.01	8
Difference (absolute)	4.1		
Difference (relative)	8.9		

SD: standard deviation

Routine analysis proved that 48 or more samples can be leached in 8 h.

As there was no need to shake the samples during the 3 h leaching period, subsequent centrifugation of samples was not necessary. Therefore, 5 ml of the hot supernatant solution could be transferred directly with a pipette to PE-flasks filled with de-ionized water. It proved to be beneficial to take an aliquot from the hot solution, because cooling promotes Silica polymerization especially in samples with high BSi-concentrations which might lead to erroneously low results. The error in volume measurement, introduced by taking the hot solution, was corrected for later by using Na as an “internal standard” since it could be determined simultaneously to Si and Al by ICP-OES. Because exactly 10 ml of 1 M NaOH were added for the leaching procedure, the initial Na concentration could be calculated. Na concentrations were measured in the volume-calibrated solution with ICP-OES, so the dilution factor could be calculated. This allowed a correction for the volume (5 ml) that was taken from the hot leachate. Considering the final BSi-concentrations this correction usually was in the range of ~2% or less. Because of the high Na concentration in the sodium hydroxide, Na originating from dissolution of minerals was considered negligible.

Mortlock and Froehlich (1989) suggest removal of organic matter and carbonates by H₂O₂/HCl pre-treatment, which otherwise might result in an under-estimation of BSi, because opal might be covered by organic and calcareous components, and therefore be less susceptible to complete dissolution. We found the opposite in our samples, i.e., lower BSi concentrations in samples that were treated with H₂O₂ and/or with HCl prior to NaOH-leaching (Fig. 3). Either

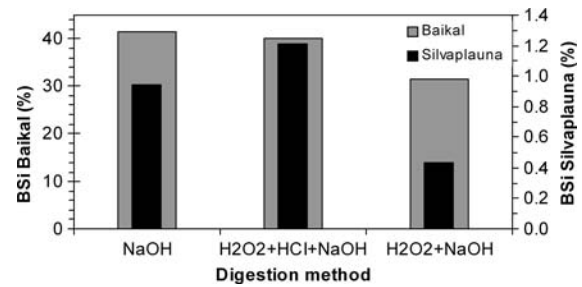


Fig. 3 Comparison of BSi concentrations in samples without pre-treatment to samples with peroxide (H₂O₂) and peroxide + HCl (H₂O₂ + HCl) pre-treatment prior to NaOH leaching

BSi was lost during the pre-treatment procedure or pre-treatment influences reactions during BSi-leaching and determination. In the case of H₂O₂ treatment without HCl, BSi concentrations in the H₂O₂ solution are remarkably high (up to 4%) and consequently, BSi concentrations after the subsequent alkaline leaching were significantly reduced. For this reason, we did not apply any pre-treatment to the samples. Pre-treatment, however, is required for calcareous samples, in which some BSi may be trapped within calcite crystals. For instance, diatoms often act as nuclei during bio-induced calcite precipitation (Sturm et al. 1982). In those cases pre-treatment of samples with HCl is recommended. This shows the necessity of optimizing the analytical techniques for any group of samples from lacustrine or marine environments.

As an illustration for the application of the described method to analyze BSi, sediments were chosen from a high alpine proglacial lake, Lej da Segl (Upper Engadine, Switzerland; Fig. 4). In the minerogenic sediments of this lake, BSi concentrations were rather low, between 1 and 8%. Nevertheless, BSi concentrations display a relatively smooth curve (Fig. 4) without high-frequency fluctuations but with a clear minimum between AD 1500 and AD 1850. These low BSi-values occur during the late Little Ice Age period (Fig. 4) and suggest reduced bio-production and/or increased dilution by lithoclastic input at this time (Blass et al. 2005).

Conclusions

Four general conclusions can be drawn from the experiments conducted during this study:

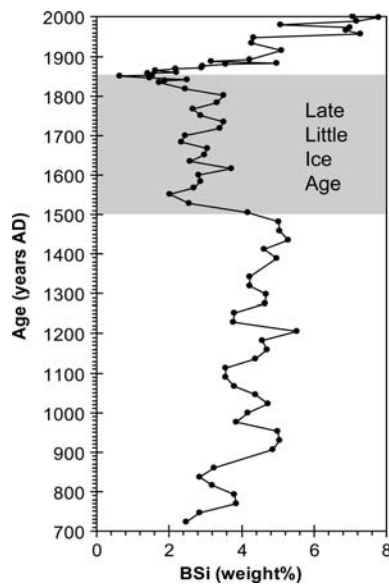


Fig. 4 BSi concentrations in a sediment core of Lej da Segl (Upper Engadine, Switzerland). A reduction in BSi concentration is observed during the late ‘Little Ice Age’ (shaded in grey), pointing to either reduced primary production or stronger dilution by allochthonous lithoclastics (redrawn from Blass et al. 2005)

1. Procedures of sample pre-treatment should be chosen depending on the sediment type. Pre-treatment with H_2O_2 may confound BSi results in some cases.
2. Digestion of samples can be done in Teflon autoclaves at 100°C for 3 h without intermittent shaking of the samples.
3. Errors in volume determination, due to high temperature during sub-sampling of the solution are in the range of 2% and can be corrected for by simultaneous measurement of Na concentrations as an internal standard.
4. Correction of measured BSi-concentrations by simultaneous measurement of Al-concentrations is not only fast, but accurate. The approach does not suffer from the overestimation of total BSi that was described for the “timed dissolution” method. This is especially important for samples with low BSi concentrations.

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