INFLUENCE OF THE MEASUREMENT MEDIUM AND MATRIX MODIFIERS ON THE DETERMINATION OF SILICON IN WATERS BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

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ABSTRACT: An electrothermal atomic absorption (ETAAS) method has been developed for the direct determination of Si in natural waters. Measurements were carried out on previously alkalinized samples and using a mixture of Pd and Mg(NO₃)₂ as matrix modifier, with an ashing temperature of 1400 °C and an atomization temperature of 2400 °C. Transversally heated pyrolytically graphite tubes, equipped with L’vov platform and Zeeman effect correction, was employed in this study. A limit of detection of 2.6 µg/L Si was obtained and accuracy was evaluated by analyzing two Standard Reference Material at different concentration levels, a good agreement (≤5%) was obtained. This developed procedure was demonstrated of the need of using an alkaline medium for accurate Si determination by ETAAS. © JASEM

Silicon in natural waters is primarily derived from the weathering of silicates and aluminosilicates in the bedrock and soils of an area (Berner et al., 1996), but there is considerable complexity to the terrestrial cycle for silicon and there can be intense internal cycling within the biamass (Conley, 2002). Electrothermal atomic absorption spectrometry (ETAAS) and, specially the new generation of spectrometers equipped with transversally heated graphite furnaces and Zeeman effect background correction, provides a valuable tool for direct Si determination at trace levels (Frech et al., 1986 – Carnrick et al., 1993).

In our knowledge, there are only few published works on Si determination in waters by ETAAS (Matsusaki et al.,1996; Pohl et al.,1989; Lin et al.,1992; Ren et al., 1990; Fehse et al.,1984), probably due to the high temperature required for Si determination, which varies from 2600 °C (Lin et al.,1992 ) to 2800 °C (Ren et al., 1990) and 2900 °C (Matsusaki et al.,1996), the systematic need of using matrix modifiers, as cobalt nitrate plus boric acid (Matsusaki et al.,1996) or CaCO₃ (Lin et al.,1992 ), the required use of the standard-addition calibration method (Lin et al.,1992 ) and the lack of linearity reported for standards prepared in acidic medium (Pohl et al.,1989 ). Additionally, until now there is no serious discussion about the influence of the pH on ETAAS, Si determinations being proposed in the literature both in acidic and basic media, as appropriate for its determination .

The main purpose of this study was to critically evaluate the experimental conditions for Si determination in natural waters, studying the most convenient conditions, such as the best temperature program and the use of adequate matrix modifiers, but also evaluating the influence of the sample pH in order to guarantee an appropriate linearity and sensitivity of the calibration curves and an accurate determination of Si at mg/L concentration level.

MATERIALS AND METHODS

Apparatus: A Perkin-Elmer 4100Z1 (Uberlingen, Germany) atomic-absorption spectrometer with Zeeman effect background correction and transversely heated graphite atomizer, was used in this study. The instrument includes a THGA graphite furnace, an As-70 autosampler, a Perkin-Elmer silicon hollow cathode lamp and Digital Celebris 466 Computer and Epson LQ-570+ printer. Pyrolytically coated graphite tubes and L’vov-type graphite platforms were used for the determination of Si. The Autosampler was programmed to deliver 20 µL aliquots. The absorbance signals were measured as peak area during a 3 seconds sampling period. The furnace conditions are summarized in (Table 1).

Reagents and samples: All reagents used were of the highest purity available and at least of analytical reagent grade. High purity water, 18.2 (MΩ cm⁻¹) specific resistivity, was obtained with a MillQ system from Millipore (Saint-Quentin Yvelines, France). The calibration standards were prepared by dilution of a stock standard solution Sigma (St Louis, USA) of 980 mg/L. The chemical modifiers assayed were Mg(NO₃)₂, H₂O and Pd(NO₃)₂, both from Merck (Darmstadt, Germany).
Ultrapure HNO$_3$, 65\% (w/w) from Fluka (Buchs, Switzerland) and NaOH from Scharlau (Barcelona, Spain), were employed to provide the pH medium of samples and standards.

High purity, 99.995\% argon C-45 was supplied by Carburos Metalicos (Barcelona, Spain) and employed as carrier gas in the ETAAS determination.

Two certified reference waters were selected SPS-SW1 was used for low concentration and SRM 1640 was chosen for high concentration.

**Table 1. Instrumental conditions and furnace program for the ETAAS determination of Si in water.**

<table>
<thead>
<tr>
<th>Step</th>
<th>Temperature °C</th>
<th>Ramp Time (s)</th>
<th>Hold Time (s)</th>
<th>Argon flow (mL min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying</td>
<td>110</td>
<td>1</td>
<td>20</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>5</td>
<td>30</td>
<td>250</td>
</tr>
<tr>
<td>Ashing</td>
<td>1400</td>
<td>10</td>
<td>20</td>
<td>250</td>
</tr>
<tr>
<td>Atomization</td>
<td>2400</td>
<td>0</td>
<td>5</td>
<td>50</td>
</tr>
<tr>
<td>Cleaning</td>
<td>2600</td>
<td>1</td>
<td>2</td>
<td>250</td>
</tr>
</tbody>
</table>

Wave length 251.6 nm
Slit width 0.2 nm
Source Hollow cathode lamp, 15 mA
Read time 3 s
Signal mode Peak Area
Sample volume 20 µL

*Procedure of ETAAS determination of Si: 0.25 to 5 ml of sample, as a function of their Si concentration, were diluted to a final volume of 25 mL. To 9.5 mL of this solution it was added 0.5 mL of NaOH 10\% (w/v), 16 µL of the basic sample solution and 4 µL of a mixed solution containing 2000 mg/L of Pd and 2000 mg/L of Mg(NO$_3$)$_2$ were introduced in a pyrolytically coated graphite tube, equipped with a L’vov platform, and then the tube submitted to the thermal program indicated in (Table 1).

Peak area absorbance measurements, obtained for samples using a 3 seconds integration time, were interpolated in an external calibration prepared from alkaline solutions of Si containing from 50 to 400 µg/L, measured in the presence of the same amount of matrix modifier and in the same conditions than samples.

**RESULTS AND DISCUSSION**

To evaluate the heating conditions for Si determination by ETAAS in both, acidic and basic, media, it was employed Pd as modifier, due to the general use of this reagent in ETAAS and in Si determination of different types of samples. This modifier was used in the preliminary studies to avoid incorrect interpretation of phenomena observed in the two media under study, as a lack of linearity of calibration curves in standard and sample measurements, which could be due to the absence of an appropriate environment for ashing and atomization.

**Study of the heating program:** 200 µg/L solutions of Si, in the presence of 400 mg/L Pd as modifier, in both, acidic HNO$_3$ 1\% (v/v), and alkaline NaOH 0.5\% (w/v), were dried in two steps at 110 °C and 130 °C respectively, using 1 and 5 seconds heating ramps and a hold time of 20 and 30 seconds respectively, and then they were ashed at different temperatures from 500 to 1800 °C for an atomization fixed temperature of 2400 °C. Using the best ashing temperature, which corresponds to 1400 °C, solutions of Si were atomized at increasing temperatures, from 2000 to 2600 °C.

An ashing value of 1400 °C was selected in both studied media. This temperature is comparable with that previously reported in some studies using Mg(NO$_3$)$_2$ modifier (Hauptkorn et al., 1994) and without modifier in acidic media (Ren et al., 1990) but lower than that reported for the use of a mixture of Ca(NO$_3$)$_2$ and boric acid modifier at neutral pH (Lin et al., 1994) and in the presence of NiCl$_2$ in acidic medium (Kobayashi et al., 1997, 1995) or CaCO$_3$ (Lin et al., 1992) and higher than the 1300 °C recommended for determination of trace silicon in aluminium oxide treated with NH$_4$F and HCl (Zhao et al., 1997).

Regarding the atomization step, a compromise value of 2400 °C for atomization was selected in acidic and alkaline medium. This atomization temperature is higher than that reported in the presence of Mg(NO$_3$)$_2$ (Hauptkorn et al., 1994) but lower than that found using Ca(NO$_3$)$_2$ and boric acid (Lin et al., 1994) and...
CaCO$_3$ (Lin et al., 1992), which correspond to 2600 ºC, or using Co(NO$_3$)$_2$ plus boric acid (Matsusaki et al., 1996), which use, 2900 ºC, or using NiCl$_2$ (Kobayashi et al., 1997, 1995), which requires an atomization temperature of 3000 ºC.

A final cleaning step was employed, in all cases, to remove the remaining Si from the tube walls.

An argon flow of 250 mL min$^{-1}$ was employed during the drying ashing and cleaning steps. However for the atomization the argon flow was reduced to 50 mL min$^{-1}$ in order to provide as higher as possible residence time of the Si atomic vapour in the measurement zone without tube damage. The complete stop of the argon flow during the measurement steps was avoided in order to ensure the best conservation of graphite tubes.

An integration measurement time of 3 seconds was selected to obtain sensitive and repetitive peak area absorbance values.

**Influence of matrix modifiers:** Figure 1. show the absorbance peak area values found for a concentration of 200 µg/L Si measured in acidic and in basic medium, both, in the absence and in the presence of Pd, or a mixture of Pd and Mg(NO$_3$)$_2$ modifiers. As it can be seen, the signals obtained in acid medium are consistently low than those found in alkaline medium, thus evidencing the influence of pH medium on the ETAAS signals of Si.

On the other hand, the use of Pd or mixture of Pd and Mg(NO$_3$)$_2$ clearly increase the absorbance of Si by a factor of 3 in HNO$_3$ medium and by a factor of the order than 4 in NaOH medium.

From the aforementioned studies it can be concluded that in all cases it is necessary the use of matrix modifiers for obtaining of sensitive and well defined absorbance peaks of Si in spite of the medium employed. The mixture of Pd and Mg(NO$_3$)$_2$, for acidic and alkaline solutions, are very convenient matrix modifiers and, as can be seen in the (figure 2 and figure 3) not only the size, but also the shape of the absorbance signals, as enhanced by the use of modifiers in both, acidic and basic medium.

![Figure 1](image1.png)

**Fig 1.** Influence of matrix modifiers on the 200 µg/L Si absorbance signals obtained in acid and basic medium.

![Figure 2](image2.png)

**Fig 2.** Influence of matrix modifiers on the size and the shape of 200 µg/L Si absorbance signals obtained in acid medium. A$_1$ Absorbance background obtained without modifier. A$_2$ Absorbance peak obtained with presence of 400 mg/L Pd plus 400 mg/L Mg(NO$_3$)$_2$. 

Mamoune El Himri, Abdelouahad El Himri, Agustín Pastor, Miguel De La Guardia
Analytical figures of merit of ETAAS Si determination: Table 2, shows the expressions of typical calibration lines obtained for Si, from 50 to 400 µg/L, for both acidic and alkaline media and in the presence of Pd and a mixture of Pd and Mg(NO$_3$)$_2$. From those expressions, it can be concluded that the use of Mg(NO$_3$)$_2$ in HNO$_3$ solutions does not provides an additional signal enhancement of Si, being the limit of detection 4.8 and 5 in the presence of Pd and Pd plus Mg(NO$_3$)$_2$ respectively. On the other hand, the sensitivity values obtained in NaOH were a 25% higher than those found in acid medium and limit of detection values were of the order of 2.6 µg/L which is two times better than that found in acidic medium.

From the aforementioned results, it can be concluded that ETAAS Si determination in waters can be carried out directly, with a good degree of sensitivity, in 0.5% (w/v) NaOH using Pd and Mg(NO$_3$)$_2$ as modifiers.

### Table 2. Comparison of analytical features obtained for ETAAS determination of Si in acidic and basic media, using Pd and a mixture Pd and Mg(NO$_3$)$_2$ as modifiers.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Modifier</th>
<th>Calibration equation</th>
<th>Correlation Coefficient</th>
<th>LOD$^b$ (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid medium</td>
<td>Pd</td>
<td>$A = (4.74 \pm 0.09) \times 10^{-4}C + (1.7 \pm 0.3) \times 10^{-2}$</td>
<td>$R^2 = 0.9979$</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>Pd + Mg</td>
<td>$A = (4.89 \pm 0.17) \times 10^{-4}C + (1.51 \pm 0.5) \times 10^{-2}$</td>
<td>$R^2 = 0.9976$</td>
<td>5</td>
</tr>
<tr>
<td>Basic medium</td>
<td>Pd</td>
<td>$A = (6.71 \pm 0.06) \times 10^{-4}C + (0.53 \pm 0.09) \times 10^{-2}$</td>
<td>$R^2 = 0.9997$</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>Pd + Mg</td>
<td>$A = (7.01 \pm 0.05) \times 10^{-4}C + (1.04 \pm 0.08) \times 10^{-2}$</td>
<td>$R^2 = 0.9998$</td>
<td>2.7</td>
</tr>
</tbody>
</table>

$^a$ C expressed in µg/L  
$^b$ Limit of detection established from 3*S blanc/slope.

### Table 3. Comparison of results obtained in control waters by ETAAS and Colorimetric reference procedure for Silicon determination

<table>
<thead>
<tr>
<th>Sample</th>
<th>ETAAS/NaOH (µg/L)</th>
<th>Colorimetry (µg/L)</th>
<th>Certified Value (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRM 1640</td>
<td>4720 ± 150</td>
<td>4770 ± 300</td>
<td>4730 ± 120</td>
</tr>
<tr>
<td>SPS-SW1</td>
<td>985 ± 15</td>
<td>1020 ± 75</td>
<td>1000 ± 10</td>
</tr>
</tbody>
</table>

Accuracy studies: The accuracy was evaluated by measuring two waters reference material SPS-SW1 and SRM 1640 containing respectively 1000 and 4730 µg/L$^{-1}$ of Silicon. The table 3 shows the results obtained by ETAAS developed method are in a good agreement with the certified value.

Conclusions: Studies carried out demonstrate for the first time that for the correct ETAAS determination of Si in natural waters it is absolutely necessary to...
work on alkaline media. The data found in acidic HNO₃ media was less sensitive than those found in 0.5% (w/v) NaOH.

The use of Pd and specially mixture of Pd and Mg(NO₃)₂ are necessary, as matrix modifiers, to obtain, sensitive results of Si determination by ETAAS. The methodology developed provides a low limit of detection of 2.6 µg/L.

REFERENCES


