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 $Mg(NO_3)_2$ as matrix modifier, with an ashing temperature of 1400 ºC and an atomization temperature of 2400 ºC. Transversally heated pyrolitically 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 ºC (Lin et al.,1992) to 2800 ºC (Ren et al., 1990) and 2900 ºC (Matsusaki et al.,1996), the systematic need of using matrix modifiers, as cobalt nitrate plus boric acid (Matsusaki et al.,1996) or $CaCO_3$ (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
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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 appropriates 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 $Mg(NO_3)_2$, $6H_2O$ and $Pd(NO_3)_2$, both from Merck (Darmstadt, Germany).

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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.

Step	Temperature °C	Ramp Time (s)	Hold Time (s)	Argon flow (mL min^{-1})
Drying	110	1	20	250
	130	5	30	250
Ashing	1400	10	20	250
Atomization	2400	0	5	50
Cleaning	2600	1	2	250

Wavelength	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 ºC and 130 ºC 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 ºC for an atomization fixed temperature of 2400 ºC. Using the best ashing temperature, which corresponds to 1400 ºC, solutions of Si were atomized at increasing temperatures, from 2000 to 2600 ºC.

An ashing value of 1400 ºC 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 ºC recommended for determination of trace silicon in aluminium oxide treated with NH_4F and HCl (Zhao et al., 1997).
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Regarding the atomization step, a compromise value of 2400 ºC 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.
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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.
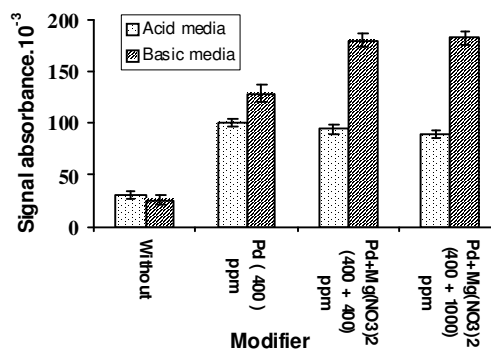

Fig 1. Influence of matrix modifiers on the 200 µg/L Si absorbance signals obtained in acid and basic medium.
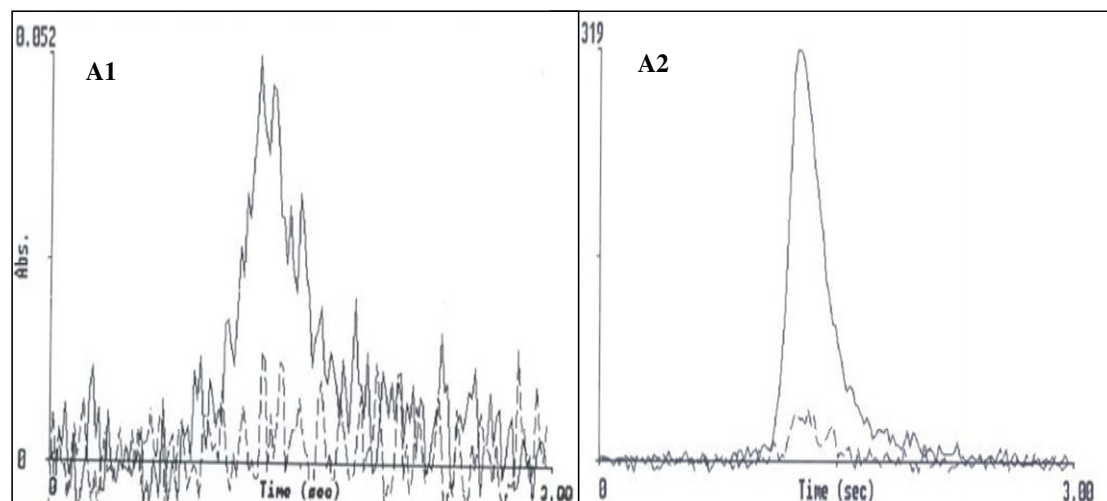

Fig 2. Influence of matrix modifiers on the size and the shape of 200 µg/L Si absorbance signals obtained in acid medium. **A$_1$** Absorbance background obtained without modifier. **A$_2$** Absorbance peak obtained with presence of 400 mg/L Pd plus 400 mg/L Mg(NO$_3$)$_2$
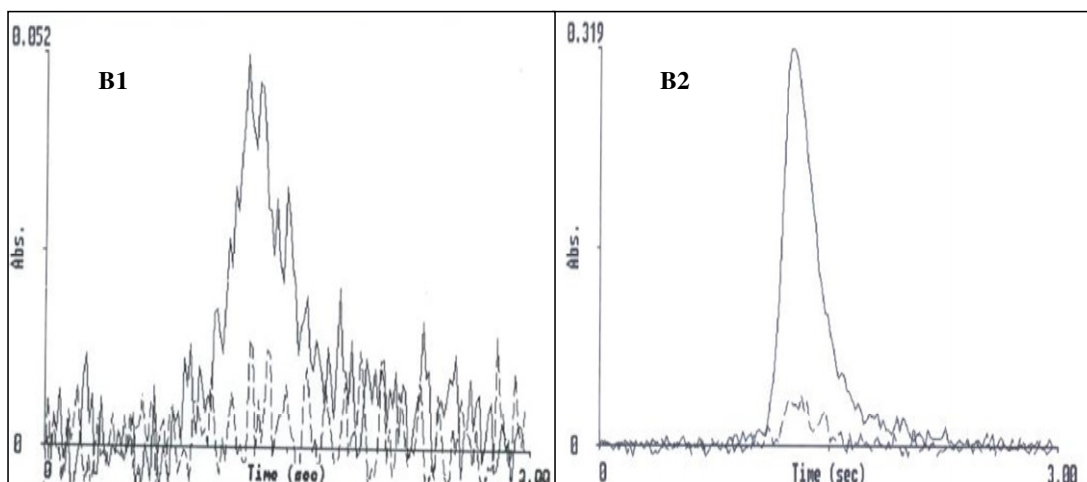
Fig 3. Influence of matrix modifiers on the size and the shape of 200 µg/L Si absorbance signals obtained in and basic medium. **B₁** Absorbance background obtained in basic medium without modifier. **B₂** Absorbance peak obtained in basic medium with presence of 400 mg/L Pd plus 400 mg/L Mg(NO₃)₂.

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(NO₃)₂. From those expressions, it can be concluded that the use of Mg(NO₃)₂ in HNO₃ 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(NO₃)₂ respectively. On the other hand, the sensitivity values
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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(NO₃)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(NO₃)₂ as modifiers.

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

[a] C expresed 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

Sample	ETAAS/NaOH (µg/L)	Colorimetry (µg/L)	Certified Value (µg/L)
SRM 1640	4720 ± 150	4770 ± 300	4730 ± 120
SPS-SW1	985 ± 15	1020 ± 75	1000 ± 10

Accuracy studies : The accuracy was evaluated by measuring two waters reference material SPS-SW1 and SRM 1640 containing respectively 1000 and 4730 µgL⁻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

Mamoune El Himri, Abdelouahad El Himri, Agustín Pastor , Miguel De La Guardia

work on alkaline media. The data found in acidic HNO_3 media was less sensitive than those found in 0.5% (w/v) NaOH.

The use of Pd and specially mixture of Pd and $Mg(NO_3)_2$ 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.

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Mamoune El Himri, Abdelouahad El Himri, Agustín Pastor , Miguel De La Guardia