

COPRECIPITATION OF TRACE AMOUNTS OF SILICON WITH ALUMINUM HYDROXIDE AND THE DETERMINATION BY FLAME ATOMIC ABSORPTION SPECTROMETRY**Ardeshir Shokrollahi* and Masoud Gohari**

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A simple preconcentration method of silicon based on coprecipitation with aluminum hydroxide prior to its flame atomic absorption (FAAS) determination was established. The recovery values of analyte ion was higher than 95%. The parameters including types of hydroxide ion source for precipitation, acid type for dissolution step, amount of aluminum ion as collector, pH, temperature, standing and centrifuge time, and sample volume were optimized for the quantitative recovery of the analyte. The influences of matrix ions were also examined. The relative standard deviation was found to be 3.2%. The limit of detection was calculated as (0.1 mg L⁻¹). The preconcentration factor is 100 for (200 mL) solution. The proposed method was successfully applied for the determination of silicon in some water and alloy samples.

Keywords: coprecipitation; silicon; aluminum hydroxide; atomic absorption spectrometry.

INTRODUCTION

Silicon (Si) is the most abundant element (27.2%) present in the earth's crust following oxygen (45.5%).¹ It is best known as the material from which transistors and integrated circuits are made, although the quantities consumed are small compared to metallurgical uses.² Most of the silicon in aqueous systems and oceans is available in the form of H₄SiO₄, which makes it an important compound in environmental silicon-chemistry and biology. In the surface layers of oceans silicon concentrations are (0.030 mg L⁻¹), whereas deeper water layers may contain 2 mg L⁻¹ silicon. Rivers generally contain (4 mg L⁻¹) silicon.³

Silicon is also an essential element in biology. Various sea sponges as well as microorganisms like diatoms need silicon in order to have structure. It is much more important to the metabolism of plants, whereas only tiny traces of silicon appear to be required by animals.⁴ The human body contains a total amount of 1 g of silicon, which decreases at a later age. Organisms mainly require silicon for bone development, whereas the element is found mostly in skin and connective tissue.⁵ Silicon is able to counterbalance high aluminum concentrations by formation of hydroxyaluminosilicate,⁶ hence, a silicon deficit may enhance the toxic effects of aluminum ions. An interaction between aluminum and silicon was also discussed in its relation to Alzheimer's and Parkinson's diseases.⁷ In rats silicon deficiency leads to deleterious effects on osteogenesis.⁸ Recently the most recent findings on biological effects of silicon on animals and human beings have been reviewed.⁹

A variety of methods have been used for silicon determination including Colorimetry,¹⁰ Spectrophotometry,¹¹ Atomic absorption spectrometry (AAS),¹² Flame photometry and atomic fluorescence spectroscopy (AFS),¹³ X-Ray Fluorescence (XRF) and Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS),¹⁴ inductively coupled plasma atomic emission spectrometry (ICP-AES),¹⁵ spark source mass spectroscopy (SSMS),¹⁶ inductively coupled plasma-high resolution isotope dilution mass spectrometry (ICP-HRIDMS),¹⁷ dynamic reaction cell inductively coupled plasma mass spectrometry (DRC-ICP-MS),¹⁸ neutron activation analysis (NAA),¹⁹ proton induced gamma-ray emission (PIGE),²⁰

voltametry,²¹ FT-Raman,²² chromatographic separation,^{23,24} flow injection chemiluminescence (FI-CL),²⁵ flow injection spectrophotometry,²⁶ flow injection-fluorometry,²⁷ and Stopped-flow injection.²⁸

Due to lower analyte levels than the quantitation limits of instrumental techniques and interferences effect, separation and preconcentration technique such as cloud point and solid phase extraction are used prior to determination.²⁹⁻³³ There are few researches connected with silicon preconcentration due to metalloid properties of silicon, nevertheless techniques such as ion exchange,³⁴ liquid extraction,³⁵ and polarography extraction³⁶ have been reported for this purpose. Fluoride generation is also an efficient method for increasing silicon sensitivity in atomic spectrometry.³⁷

Coprecipitation has also been widely used for the preconcentration of trace amounts of analyte³⁸⁻⁴² due to some advantages including simplicity, rapidity and obeying green chemistry rules. According to the literature survey, coprecipitation of silicon with CaCO₃⁴³ and Al(OH)₃⁴⁴ have been reported in geology and polymer literature but no analytical research has been performed for preconcentration of silicon through coprecipitation. Reaction of silicon with aluminum hydroxide to form insoluble aluminosilicate is favored in the presented research; hence this paper describes fundamental condition for the coprecipitation of trace amounts of silicon with aluminum hydroxide as a means of preconcentration prior to FAAS silicon determination.

EXPERIMENTAL**Instrument**

All determination was performed by using a Perkin-Elmer Atomic Absorption Spectrophotometer Model 460 equipped with Si Hollow cathode lamp and nitrous oxide burner head. Lamp current was adjusted to 40 mA. The wavelength and slit were 251.6 nm and 0.2 nm respectively. The fuel to oxidant ratio was adjusted to form a reducing (rich, red) flame. The pH values of the solutions were measured by a Metrohm 620 pH meter equipped with Metrohm combined glass electrode. A Sartorius model TE214S microbalance was used for weighing the chemicals. An Orum Tadjhiz centrifuge model T4.50 was used to accelerate the phase separation process.

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Reagent and solution

All chemicals used in this work, were of analytical-reagent grade. Distilled and deionized water was used throughout. A stock solution of (1000 mg L^{-1}) Si was prepared from fusing (0.2139 g) of silicon dioxide (Merck) with (2.0000 g) of sodium carbonate (Merck) in a platinum crucible at $1000 \text{ }^\circ\text{C}$ follow dissolving the melt with deionized water, transferring to a 100 mL polyethylene volumetric flask, and diluting to volume with deionized water. A solution of 1.0% (w/v) Al^{3+} ion was prepared by dissolving (8.9492 g) $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Merck) in distilled deionized water and diluting to (100 mL). A solution of 10% (w/v) KOH was prepared by dissolving (10 g) KOH (Merck) in distilled deionized water and diluted to a (100 mL) polyethylene flask.

HCl 37% (Merck) was used for dissolution step. A solution of 10% (w/v) Na_2CO_3 or NaOH was prepared by dissolving (10 g) Na_2CO_3 (Merck) or NaOH (Merck) in distilled deionized water and diluting to a (100 mL) polyethylene flask separately. Ammonia solution 10% (v/v) was prepared by transferring (40 mL) 25% Ammonia (Merck) to a (100 mL) polyethylene flask and diluting to the mark.

Procedure

For all optimization, a centrifuge tube containing (50 mL) of an aqueous solution (2 mg L^{-1}) Si, (400 mg L^{-1}) Al^{3+} ion as a collector with adjusting pH at 7 by KOH 10% , was centrifuged at 4000 rpm and room temperature for 5 min . The supernatant was removed and the precipitate was dissolved with a few drops of concentrated HCl. Then it was completed to (2 mL) with deionized water. The analyte in the final solution was determined by flame atomic absorption spectrometry.

Preparation of real samples

The water samples were filtered through a Millipore cellulose membrane of pore $0.45 \mu\text{m}$. The samples were stored in polyethylene bottle. (20 mL) of these samples were analyzed in procedure given in the procedure section.

For alloy sample (DIN 2.4879) (0.1 g) of sample was transferred to a 100 mL platinum crucible. Then (20 mL) of concentrated HCl was added and the crucible was placed on a hot plate and heated to dissolve all components. After cooling, the solution was filtered and transferred to a (250 mL) polyethylene volumetric flask and diluted to mark with deionized water. (20 mL) of the sample was analyzed according to the procedure given in the procedure section.

RESULT AND DISCUSSION

Effect of hydroxide ion source on precipitation

The coagulation step is a very important factor to achieve a quick coprecipitation and the easy separation of the coprecipitate part from supernatant with simple separation procedure. High recovery of analyte and good reproducibility are also connected to coprecipitation condition, therefore initial method development studies was performed with different bases such as ammonia (NH_3), soda ash (Na_2CO_3), caustic soda (NaOH) and caustic potash (KOH). The recovery of analyte was 90.8 , 91.5 , 100.3 , and 99.6 after using NH_3 , Na_2CO_3 , NaOH and KOH, as hydroxide ion source respectively. According to the results, NaOH and KOH are suitable hydroxide ion sources for this coprecipitation procedure. Since NaOH is hygroscopic and difficult to handle, KOH was selected as a hydroxide ion source for the following steps.

Effect of type of solvent

HCl and HNO_3 were used for dissolution step. Higher recovery was found by using HCl, therefore, all further works were performed using HCl for dissolution of precipitate. It must be noted that dissolution and dilution of silicon content matrices with acid, followed by AAS determination is routine in the geology laboratories and is reported in the literature.⁴⁵

Effect of pH

The influence of pH of the sample solution on the recovery of silicon was separately investigated in the pH range of 4.0 - 10.0 by adjusting pH value of the solution with addition of different value of KOH solution. As shown in (Figure 1), silicon was quantitatively coprecipitated in the pH range of 7.0 - 9.0 . The decrease in signal at $\text{pH} > 9.0$ is due to the dissolution of precipitate as an $\text{Al}(\text{OH})_4^-$ in high alkaline solution. In order to achieve high efficiency and good selectivity, the pH of approximately 7 was selected for all subsequent coprecipitation works.

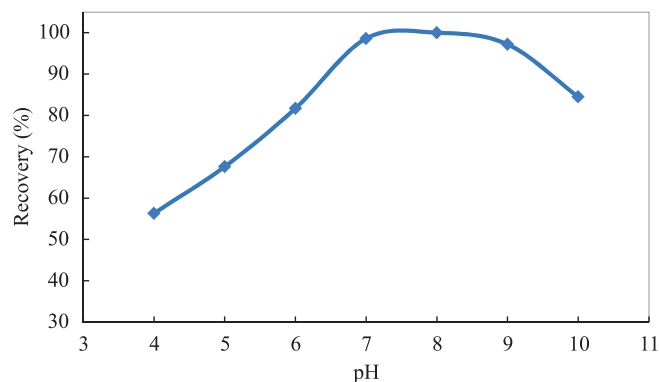


Figure 1. Effect of pH on the recovery of analyte

Effect of amount of Al^{3+} ion

The amount of collector is very important and must be optimized. Sufficient amount of collector must be added to the sample solution to ensure perfect coprecipitation of analyte, in contrast the amount of collector must be small to limit final volume. For this purpose the influence of amount of aluminum as collector on the recovery of silicon was investigated in the range of (5 - 30 mg). The results are depicted in (Figure 2). Acceptable recovery value was obtained in the range of (15 - 25 mg) aluminum. In lower amounts, the collection is incomplete and in higher value of collector, the amount of precipitate is large, consequently large volumes of acid must be added

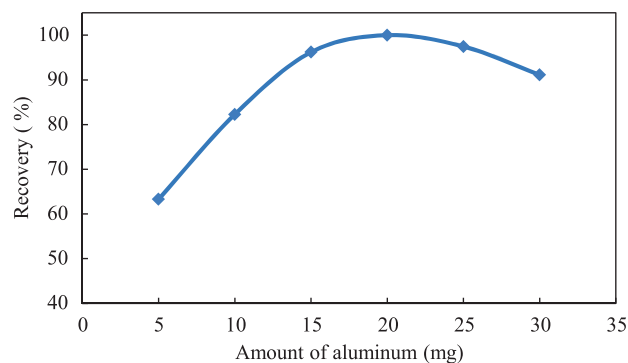


Figure 2. Effect of amount of aluminum on the recovery of analyte

to dissolve the precipitate. All further works were performed with (20 mg) of aluminum.

Effect of standing time, temperature and centrifuge time

Standing time, which is important for the quality of coprecipitation, was checked at different times in the range of 0-6 h. The result was depicted in (Figure 3). Quantitative recovery was found only after formation of precipitate and further contact time did not lead to better recovery. For standing time above 3 h, solubility of precipitate in acid medium decreased and a viscous fluid was formed after acid addition.

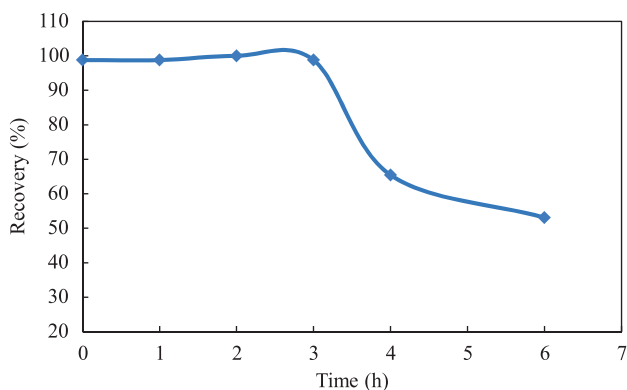


Figure 3. Effect of contact time on the recovery of analyte ($T=25\text{ }^{\circ}\text{C}$)

Effect of temperature on coprecipitation was also examined in the range of 25-70 $^{\circ}\text{C}$. As depicted in (Figure 4) quantitative recovery was obtained at room temperature. Viscous solution was formed after dissolution of precipitates which had been formed in high temperature similar to the case of high standing time. Low aspiration efficiency of viscous solution and low atomization efficiency in FAAS were the reasons of decreasing absorption signal of analyte in the case of high temperature and long standing time.

Centrifuge time was also optimized working with 1-15 min time period of the centrifugation at 4000 rpm. The required centrifugation time for the successful coprecipitation with quantitative recovery of the analyte was determined to be at least 2 min but in order to obtain more compact precipitate, time of 5 min was chosen for all subsequent coprecipitation works.

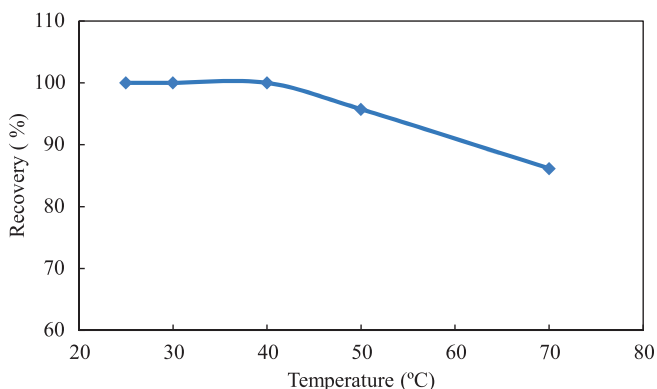


Figure 4. Effect of temperature on the recovery of analyte

Effect of sample volume

The effect of the sample volume on the coprecipitation efficiency of the analyte was also examined in the sample volume range of (10-500 mL). The precipitate was successfully dissolved in (0.5 mL) of concentrated HCl. The final volume was completed to (1.0-5.0 mL)

by deionized double distilled water. The preconcentration factor is calculated by the ratio of the highest sample volume (200 mL) and the lowest final volume (2 mL), therefore preconcentration factor was calculated as 100.

Interference studies

In order to assess the possible analytical applications of the presented coprecipitation procedure, the effect of some foreign ions that ordinarily exist in various real samples was examined at the optimized condition. The recovery of analyte was generally higher than 95%. Tolerable limit was defined as the highest amount of foreign ions that produce an error not exceeding 5% in the determination of analyte by the coprecipitation method. The results are summarized in Table 1. Low tolerable level of Mn^{2+} is due to formation of MnO_2 which causes a problem as insoluble material in FAAS sample aspiration. The tolerable levels of other metal ions are suitable for separation and preconcentration of silicon in real samples.

Table 1. Effect of diverse ions on the silicon recovery

Ion	Concentration (mg L^{-1})
NH_4^+ , Li^+ , Na^+ , K^+ , Ca^{2+} , Sr^{2+} , B^{3+} (as H_3BO_3), Cl^- , NO_3^- , I^-	5000*
Br^- , SO_4^{2-}	1000
Mg^{2+} , Ba^{2+} , Pb^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Fe^{3+} , Cr^{3+} , Al^{3+} , Ti^{4+} (dissolved TiO_2), Zr^{4+} , F^- , $\text{Cr}_2\text{O}_7^{2-}$, MoO_4^{2-} , PO_4^{3-}	100
Mn^{2+}	10

*One time rinse of precipitate with lukewarm distilled water was done.

Analytical performance

Calibration graph was pictured by Abs vs. concentration after coprecipitation of (50 mL) of standard solutions under optimum experimental condition. Dynamic range was obtained in the range of 0.2-8.0 mg L^{-1} . The equation of calibration graph was $y=0.037x+0.001$ with correlation coefficient of 0.9995. The detection limit (LOD) was calculated under optimal experimental conditions. The LOD, based on three times the standard deviation of the blank ($k=3$, $N=12$) was (0.1 mg L^{-1}). The precision of the method was evaluated under the optimum conditions. For this purpose, the procedure was repeated 10 times with solution containing (100 μg) of silicon. The relative standard deviation was 3.2%. Sample throughput was also found to be 12 samples h^{-1} .

Application to real samples

In order to estimate the accuracy of the presented coprecipitation procedure, different amounts of silicon were spiked in two different water samples given in Table 2. The resulting solutions were submitted to the presented procedure given in procedure section. The recovery values were generally higher than 95%. A good agreement was obtained between the added and measured analyte amounts. The accuracy was also tested with silicomolybdate colorimetric method¹⁰ as independent analysis. Further good agreement was also obtained between colorimetric and presented method. These results confirm the validity of the proposed method, denoting that the presented method could be applied successfully for the separation and preconcentration of trace amounts of silicon in water samples.

The coprecipitation procedure presented was also applied to a Ni-Cr alloy (DIN 2.4879) sample.⁴⁶ (20 mL) of prepared sample as explained in the preparation of real samples section was used for silicon determination with the presented procedure. In order to limit

Table 2. Silicon determination in water samples (n=4)

Sample	Added (mg L ⁻¹)	Found (mg L ⁻¹)	Recovery (%)	Colorimetry (mg L ⁻¹)
Tap water*	0.0	2.9±0.1	-	2.9±0.1
	2.0	5.0±0.2	102.0	
	3.0	5.8±0.2	98.3	
	4.0	6.9±0.2	100.0	
Well water	0.0	6.2±0.2	-	6.1±0.1
	1.0	7.2±0.2	100.0	
	2.0	8.3±0.2	101.2	
	3.0	9.3±0.3	101.0	

*Tap water and well water of Ahmad Abad, Shiraz, Iran.

final volume, separation of foreign ions (Ni²⁺, Cr³⁺, and Fe³⁺) by hydroxide formation in pH 7 prior to coprecipitation procedure can be done. We found that Si never coprecipitates with foreign ions and the results are the same as when this separation step is skipped. As shown in Table 3, the recovery of spiked sample is good and there is satisfactory agreement between the results and data obtained by spark atomic emission spectroscopy analysis, suggesting that the coprecipitation procedure is suitable for the sample type examined.

Table 3. Silicon determination in Ni-Cr alloy sample (n=4)

Sample	Added (mg L ⁻¹)	Found (mg L ⁻¹)	Recovery (%)	Value in alloy (%)	Spark AES (%)
Alloy	0.0	3.2±0.1	-	0.80±0.03	0.81±0.05
	1.0	4.1±0.1	97.6		
	2.0	5.1±0.2	98.0		
	3.0	6.3±0.2	101.6		

CONCLUSION

Because of low sensitivity of determination of silicon by flame atomic absorption spectrometry, a preconcentration step prior to determination is needed for most samples such as natural water samples. The proposed coprecipitation method is simple, fast, room temperature, efficient and inexpensive for silicon determination in water, alloy and the other samples. This technique can be recommended for routine analysis of silicon in environmental and industrial samples. Under the optimum experimental conditions, quantitative recovery was achieved with a preconcentration factor of 100. For comparison, merit numbers of the presented method have been compared with some previous methods for Si determination. As shown in the Table

Table 4. Comparison of presented method for Si determination with some previous methods

Method	LOD (mg L ⁻¹)	RSD (%)	Dynamic range (mg L ⁻¹)	Ref
Flame photometry	5.00	2.02	25-500	14
AFS	0.55	1.8	2-100	14
Spectrophotometry	0.0076	-	0.01-0.1	12
Polarography	-	4	0.56- 8.4	37
Chromatography	0.250	1.15	0.25-10	24
ET-AAS	0.052	4.4	0.8-7.1	13
FI-Spectrophotometry	-	1.2	0.05-22	27
FI-fluorometry	0.00006	1.04	0.0001-0.005	28
FI- CL	0.00035	1.0-3.8	0.00035-0.140	26
Fluoride generation ICP-AES	0.98	2.32	Up to 100	38
Presented method	0.1	3.2	0.2-8.0	-

4, the limit of detection of the presented method is much better than flame photometry, AFS, chromatography and is comparable with fluoride generation ICP-AES. The RSD of the presented method is also better than polarography, ET-AAS, and FI-CL. The dynamic range of the proposed method is broader than flame photometry, spectrophotometry, and polarography.

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