Technol Rep Yamaguchi Univ 5(5) : 305-311, 1996

Determination of Silicon by Atomic Absorption Spectrometry Using a Graphite Furnace Coated with Tungsten Carbide

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(Received July 15, 1996)

Abstract

Silicon was determined by atomic absorption spectrometry with a coated graphite furnace. Pyrolytic graphite tube was coated with tungsten carbide. A mixture of strontium nitrate, ammonium tungstate and EDTA ammonium salt was then added to a sample solution as a matrix modifier. Using a coated tube with tungsten and this matrix modifier, the determination of silicon was successful with high sensitivity and better reproducibility. No interference from metal nitrates and chlorides was observed. In spite of addition of EDTA ammonium salt, the sulfate interference was serious.

The determination of silicon by use of conventional atomic absorption spectrometry (AAS) with a graphite furnace has been difficult, because a vaporization loss of silicon oxide and a formation of refractory carbides with the carbon of the graphite tube before atomization1)-4). These behavior cause a remarkable reduction in both the sensitivity and reproducibility; also memory peaks arise due to the atomization of residual silicon carbide during previous determination.

Several approaches have appeared in the literature to resolve these problems. Some methods involve pre-coating the wall of the graphite tube with elements that tend to form more thermodynamically stable carbides than silicon carbide; these coating extend the tube lifetime. Coating with such elements as tantalum5)-7) and zirconium8) have been reported. Others have attempted to prevent the vaporization loss of analyte before atomization by adding a suitable matrix modifier. Several matrix modifiers such as salts of calcium9)-11), magnesium12), nickel13), tungsten14), molybdenum10), lanthanum11) and niobium3) have been proposed.

The behavior of boron in the graphite furnace during preatomization stage has been similar to that of silicon and this behavior of boron has been more remarkable. Therefore, boron has been well known as one of the unamenable elements used for conventional AAS with a graphite furnace. In a recent work15), we determined the boron with higher sensitivity by AAS with a doubly coated graphite furnace with titanium and tungsten carbides. Birova et al.16) determined silicon in metallic niobium by AAS with a graphite furnace with tungsten carbide lining, but they did not investigated the use of a matrix modifier. In this work, we found that using a coated

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graphite tube with tungsten carbide and a matrix modifier the determination of silicon was performed with higher sensitivity and better reproducibility. The effect of coating a graphite tube with tungsten carbide and the addition of a mixture of strontium nitrate, ammonium tungstate and EDTA ammonium salt as a matrix modifier are described.

Experimental

Apparatus and reagents

A Hitachi Model GA-2B graphite-furnace atomizer was used with a Hitachi Model 180-30 atomic absorption spectrometer. A tube type coated graphite cell was used in an argon atmosphere. The signal was recorded with a Hitachi Model D-2500 chromato-integrator. A Hitachi silicon hollow-cathode lamp was used as a radiation source. A deuterium-arc background correction was used throughout. Samples were deposited by using a Hitachi autosampler.

All of the solutions were prepared from analytical reagent-grade chemicals and deionized-distilled water, and then stored in polyethylene bottles. A commercially available silicon standard solution (sodium silicate solution, Ishizu Seiyaku, Ltd., Japan) with a silicon concentration of 1000 mg l^{-1} was diluted with deionized-distilled water to a working solution of 20 mg l^{-1}.

Tube coating procedure

The coating of pyrolytic graphite tubes with tungsten carbide was treated in the following manner. The tubes were immersed in ammonium tungstate solution (2800 mg l^{-1}) under reduced pressure. A vacuum was applied until no more gas bubbles were observed to evolve from the graphite. After removal from the tungstate solution the tubes were dried at room temperature for 1 h and at 100 ℃ for 3 h. The tubes were then placed in an atomizer and heated for 30 s at 100 ℃, at a heating rate of 20 ℃ s^{-1} to 1100 ℃ and for 7.5 s at 2900 ℃. This heating procedure in the atomizer must be repeated 3 times. This coating procedure should be repeated 3 times in order to obtain quantitative results.

Procedure of sample analysis

A 10-μl sample solution was deposited in the center of a coated graphite tube with metal carbide by an autosampler; it was then dried, ashed and atomized. Argon was used as a sheath gas at a flow rate of 2.0 l min^{-1} and carrier gas (internal gas) at 0.1 l min^{-1}. The durations and temperatures were 30 s at 100 ℃ for drying, 30 s at 1100 ℃ for ashing and 7.5 s at 2900℃ for atomization. The absorbance signals during the atomization step were recorded at 251.6 nm (0.4 nm band width); the peak height were taken as the analytical signals. The graphite tube was fired at the attainable maximum temperature (about 3000℃) for 3 s after measuring each sample, so as to clear any residue from the tube surface.

Results and Discussion

Effect of matrix modifier

It should be stressed that the absorbance values of silicon were considerably low when the determination of silicon was carried out without any matrix modifier. Here, the effects of alkaline earth metals, nickel and cobalt nitrates on the atomic absorption of analyte using the coated tube with tungsten were investigated for a salt concentration of 0.01 mol l^{-1}. Strontium nitrate gave the most effective enhancement of the sensitivity for the analytical signal. The effect of the concentration of this strontium salt was also investigated. A maximum enhancement effect was obtained with between concentration of 1×10^{-4} and 1×10^{-2} mol l^{-1}.

When ammonium tungstate which was used as a coating agent was added in the sample solution, the analytical sensitivity of silicon was not enhanced, but the reproducibility of analytical signals was improved and the life time of tube was also extended. The added ammonium tungstate may reinforce the coating of inner surface of graphite tube. Tungsten has been demonstrated to be useful as a matrix modifier for silicon by Parajon and Sanz-Medel[14)]. Therefore, ammonium tungstate was also added together with strontium nitrate. In this case, in order to prevent the precipitation of strontium tungstate, EDTA ammonium salt was added. The effect of the concentration of this ammonium tungstate on the analytical signal of silicon in the presence of 0.001 mol l^{-1} strontium nitrate was investigated. Between concentration of 280 and 1120 mg l^{-1} ammonium tungstate, the atomic absorption of silicon was not varied. The effect of the concentration of EDTA ammonium salt in the presence of 0.001 mol l^{-1} strontium nitrate and 280 mg l^{-1} ammonium tungstate on the atomic absorption of silicon was also investigated. When the concentration of EDTA was less than 0.01 mol l^{-1}, the analytical signal of silicon was not varied. Above this concentration, the analytical signals were slightly suppressed.

In the determination of boron[15)], the addition of organic reducing agent has enhanced the analytical sensitivity. However, in the determination of silicon by use of tungsten coated graphite tube, this effect was not observed.

As a result, it is concluded that a mixture of 0.001 mol l^{-1} strontium nitrate, 0.01 mol l^{-1} EDTA ammonium salt and 280 mg l^{-1} ammonium tungstate is the best condition as a matrix modifier to enhance the analytical sensitivity of silicon and to improve the reproducibility of analytical signals.

Effect of ashing temperature

Using a tungsten coated tube and this matrix modifier, the effect of varying the ashing temperature on the atomic absorption signal of silicon was investigated. As shown in Fig. 1, the maximum absorbance was observed at 1100 ℃. Thus, 1100 ℃ of ashing temperature was applied.

Calibration curve

Using a tungsten coated tube and an uncoated tube (pyrolytic graphite tube), the calibration curves of silicon were found to be linear up to at least 1.0 mg l^{-1} as shown in Fig. 2. Using a coated tube with tungsten and this matrix modifier, the detection

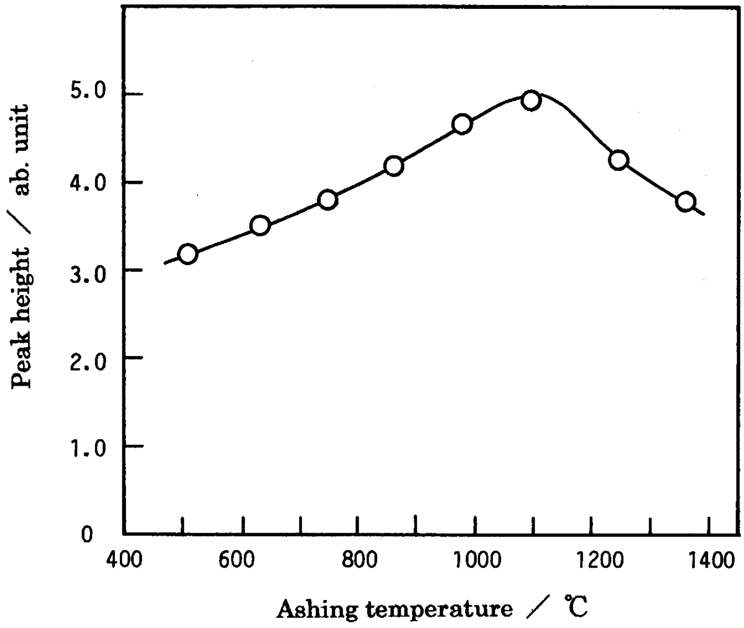

Fig. 1 Effect of ashing temperature on the atomic absorption of silicon(1.0 mg l^{-1}). Ashing time: 30 s.

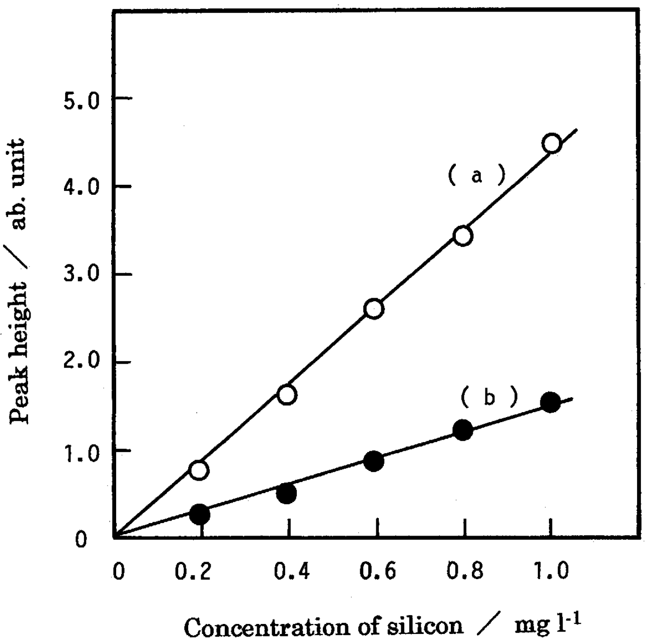

Fig. 2 Calibration curves for silicon in the presence of 0.001 mol l^{-1} $Sr(NO_3)_2$ and 0.01 mol l^{-1} $EDTA(NH_4)_4$ by the use of (a) a coated tube with tungsten and (b) an uncoated tube. Using a coated tube, 280 mg l^{-1} $(NH_4)_2WO_4$ is added.

limit (3σ of the blank) and relative standard deviation were estimated to be 0.009 mg l^{-1} and 1.4 % for 0.5 mg l^{-1} silicon determination, respectively. The sensitivity of atomic absorption of analyte using a coated tube was estimated to be about 3-times higher than that using an uncoated tube. When the uncoated tube was used, ammonium tungstate was not added and the memory effect was observed. Accordingly, in this case, after measuring each sample, the furnace was fired without sample in order to remove the residual silicon carbide formed during the previous measuring.

Effect of pH

The effect of pH of the sample solution on the atomic absorption signal of silicon was investigated. The pH was adjusted with nitric acid and sodium hydroxide. As shown in Fig.3, no variation in absorbance of silicon was observed between pH 2 and 12. Such a wide pH range is very advantageous for practical application of this method.

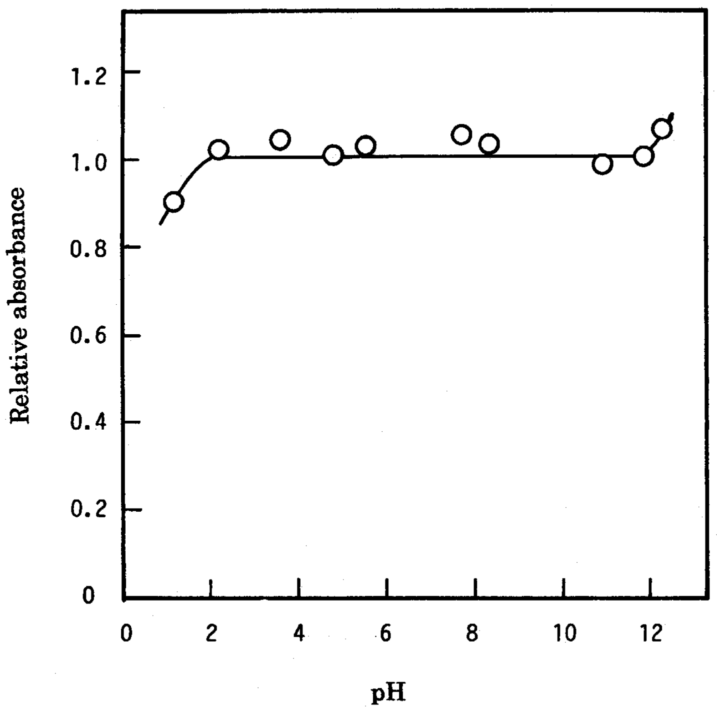

Fig. 3 Effect of pH on the atomic absorption of silicon(0.6 mg l^{-1}). The absorption of each test solution is normalized by that at pH 4.8.

Effect of coexisting salts

The effect of coexisting nitrates and chlorides of sodium, potassium, magnesium, calcium, aluminum, zinc, cobalt, nickel and copper on the atomic absorption of silicon were investigated by using a coated tube with tungsten. When the concentrations of nitrates and chlorides were less than 0.01 mol l^{-1}, the degree of interference was negligible except for aluminum salt. Above this concentration, the analytical signals

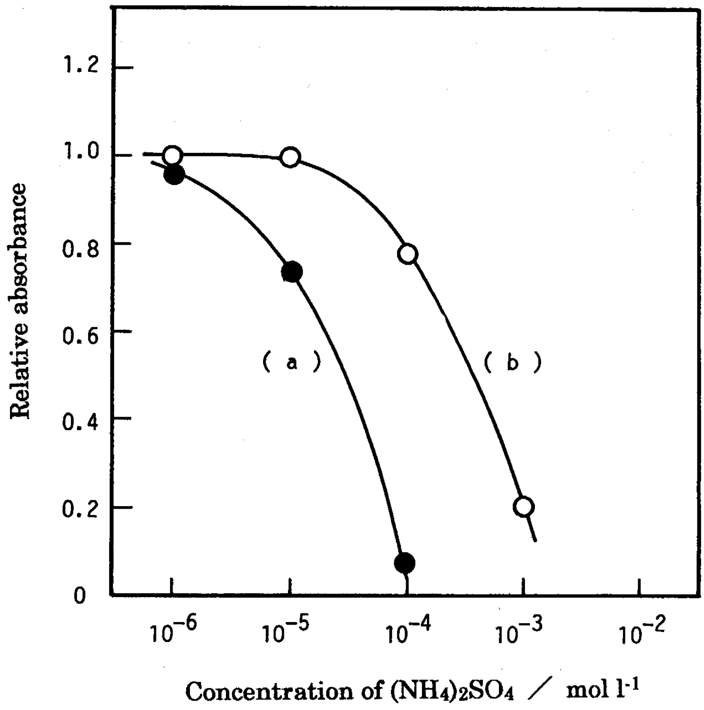

Fig. 4 Effect of ammonium sulfate on the atomic absorption of silicon(1.0 mg l^{-1}) in the presence of (a) 0.001 mol l^{-1} $Sr(NO_3)_2$, 0.01 mol l^{-1} $EDTA(NH_4)_4$ and 0.01 mol l^{-1} NH_3 and (b) 0.001 mol l^{-1} $Co(NO_3)_2$ and 0.01 mol l^{-1} HNO_3. All test solutions contain 280 mg l^{-1} $(NH_4)_2WO_4$. The absorbance of each test solution is normalized by that of the respective solution containing no sulfate.

were slightly suppressed. In the presence of aluminum salt, above its concentration of 0.001 mol l^{-1}, the analytical signals were slightly suppressed.

On the contrary, in spite of adding EDTA, interference from the coexisting sulfate was serious. The results obtained with the ammonium sulfate are shown in Fig.4. Instead of strontium nitrate cobalt nitrate was used as an additive, the sulfate interference was slightly suppressed, but its interference was much severer than that in the case of using a coated tube with titanium carbide(17). The result obtained with other sulfates were similar to that of ammonium sulfate. This kind of sulfate interference may be interpreted in terms of the formation of volatile silicon sulfide(3) in the furnace during preatomization stage, followed by a thermal decomposition of coexisting sulfate. Using a coated tube with titanium carbide(17), in the absence of EDTA, the interference from sulfate have been similarly serious. However, this interference could be removed by the addition of EDTA ammonium salt. Accordingly, when the sample contains the sulfate, the use of a coated tube with titanium is recommended.

Determination of silicon in the actual sample

The proposed method was applied to the determination of a trace amount of silicon in tap water, sodium hydroxide and sodium carbonate. The chemicals was accurately weighed and dissolved in water. After an aliquot of the tap water or the sample

Table 1 Analytical results of silicon in actual samples

Sample	Si found*
Tap water	2.69 ± 0.14 (mg l^{-1})
Sodium hydroxide A	$(1.05 \pm 0.14) \times 10^{-2}$ (%)
Sodium hydroxide B	$(1.36 \pm 0.12) \times 10^{-2}$ (%)
Sodium carbonate	$(5.97 \pm 0.46) \times 10^{-3}$ (%)

*Mean and standard deviation

solution was diluted to 25 ml with 0.001 mol l^{-1} strontium nitrate, 0.01 mol l^{-1} EDTA ammonium salt and 280 mg l^{-1} ammonium tungstate, the atomic absorption signal of silicon was measured. The results are presented in Table 1. Hence the use of a graphite furnace coated with tungsten carbide and a mixture of strontium nitrate, EDTA ammonium salt and ammonium tungstate as a matrix modifier was confirmed to be a suitable method for determining trace amounts of silicon in actual samples by AAS without requiring preliminary separation.

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