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Determination of Silicon in Some Metallurgical Materials by Atomic Absorption Spectrophotometry*

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Atomic absorption spectrophotometric determination of silicon in some metallurgical samples after dissolution of the samples with hydrofluoric acid was studied using a nitrous oxide-acetylene flame. A sample solution was sprayed into a nitrous oxide-acetylene flame and silicon absorption was measured at 251.6 nm. Under the optimum operating conditions a sensitivity of 0.56 p.p.m. for silicon at signal-to-noise ratio of 2 was obtained in aqueous solution. The linear calibration graph was obtained over the concentration range of 0–100 p.p.m. of silicon with a mean relative standard deviation of 2.3%. Many of diverse elements and acids interfered with the silicon absorption and, therefore, the calibration graph for silicon must be made with the standard solutions matched with the sample solutions. The present method was applied to the determination of silicon in some metallurgical materials with satisfactory results. Furthermore, the effect of water-miscible organic solvents on the silicon absorption and the solvent extraction of silicon as silicomolybdic acid into methyl isobutyl ketone were investigated in an attempt to increase the sensitivity for silicon by atomic absorption spectrophotometry. It was found that miscible and immiscible organic solvents enhanced the silicon absorption about 2-fold.

1. Introduction

The determination of silicon by atomic absorption spectrophotometry has been made by using a nitrous oxide-acetylene flame^{1,2)}. Bowman and Willis³⁾ investigated the application of the nitrous oxide-acetylene flame, and determined silicon in bauxite by atomic absorption spectrophotometry after a borate-carbonate fusion for dissolution of samples, and Capacho-Delgado and Manning⁴⁾ have determined silicon in cements using a fusion technique. Price and Roos⁵⁾ described the determination of silicon in steel, cast iron, aluminum alloys and cement, without precipitation of silica or an alkali fusion. Campbell⁶⁾ reported the determination of silicon in aluminum alloys after treatment with sodium hydroxide and hydrogen peroxide, and found that the addition of organic solvents has little effect on the atomic absorption of silicon.

In this paper, the determination of silicon in aluminum metals and alloys, cast iron, stainless steels and nickel alloy by atomic absorption spectrophotometry are described. The present paper also describes the effect of water-miscible organic solvents on the silicon absorption and the solvent extraction of silicomolybdic acid into methyl isobutyl

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ketone in order to increase the analytical sensitivity for silicon by atomic absorption spectrophotometry.

2. Experimental

Apparatus A Hitachi Model 207 atomic absorption spectrophotometer equipped with a nitrous oxide burner was used for all measurements. Other accessories included a Westinghouse high spectral output silicon hollow-cathode lamp and a Hitachi QPD₅₄ chart recorder.

Reagents A silicon standard solution (Si 1000 p.p.m.) was prepared by dissolving 0.214 g of pure silicon dioxide (Wakō Pure Chemical Ind. Ltd.) in a polyethylene bottle with 5 ml of hydrofluoric acid, leaving it at room temperature for about 2 hours until the oxide was completely dissolved, and adding 50 ml of saturated boric acid solution and 45 ml of distilled water with a pipette. Various other concentrations were made by diluting aliquot of the stock solution. For comparison, another silicon standard solution was prepared by dissolving reagent-grade sodium silicate with distilled water and standardized against the above-mentioned silicon standard solution by atomic absorption spectrophotometry.

Ammonium molybdate solution (10 w/v %) was prepared by dissolving 10.0 g of ammonium molybdate tetrahydrate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, in distilled water and diluting exactly to 100 ml.

All other solutions were made with analytical-reagent grade chemicals and distilled water. All acids used were of analytical-reagent grade.

3. Results and Discussion

Operating conditions The optimum operating conditions listed in Table 1 were established with a 100 p.p.m. solution of silicon. The atomic absorption by silicon was measured at different burner heights under various flame conditions in an attempt to obtain the optimum flame conditions for silicon. The flame profiles of silicon in various

Table 1. Operating conditions for the determination of silicon.

| | |
|------------------------|---|
| Wavelength | 251.6 nm |
| Slit-width | 0.16 mm |
| Bandpass | 1.8 nm |
| Lamp current | 10 mA |
| Nitrous oxide pressure | 1.8 kg/cm ² |
| flow rate | 6.0 l/min. |
| Acetylene pressure | 0.8 kg/cm ² |
| flow rate | 5.0 l/min. |
| Burner height | Lower light beam lies 1 mm above the burner head |
| Burner slot | 0.45 mm x 50 mm |

flame conditions were showed in Fig. 1. Under these conditions the sample feed rate was about 5 ml per minute and the analytical sensitivity was 0.56 p.p.m. at signal-to-noise ratio of 2. The linear calibration graph was obtained over the range of 0-100 p.p.m. of silicon.

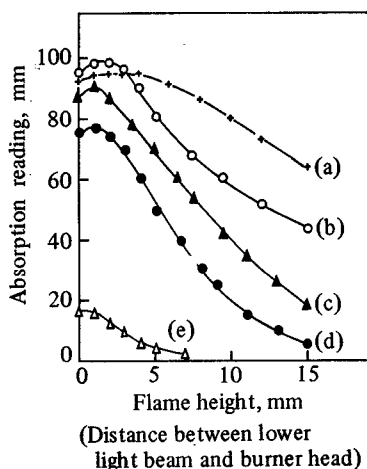


Fig. 1. Flame profile of silicon in a nitrous oxide-acetylene flame
 Si: 100 p.p.m.; Nitrous oxide flow rate: 6.0 l/min; Acetylene flow rate, l/min
 (a)-5.40, (b)-5.20, (c)-5.00, (d)-4.85, (e)-4.70 (Abs. sens.: 1.23)

Dissolution of silicon in glassware with hydrofluoric acid Silicon in the materials not decomposed with the acids normally used is converted to acid-soluble silicates by fusion or heating with alkali. Hydrofluoric acid is not usually applied for the decomposition of samples in which silicon is to be determined, because fear of losing silicon as volatile silicon tetrafluoride. Langmyhr and Graff⁷⁾ described the method in which the materials containing silicon were decomposed with hydrofluoric acid to determine silicon colorimetrically. This decomposition can be carried out at a relatively higher temperature, e.g. 100°C.

Hydrofluoric acid attacked a glassware to dissolve significant amounts of silicon, but the presence of boric acid suppressed the dissolution of silicon^{8,9)} as shown in Fig. 2. Therefore, boric acid was added to the hydrofluoric acid solution of samples when a glassware had to be used in the present study.

Effect of acids The effect of acids normally used in the dissolution of various samples was examined over the concentration range of 0-2.0 N. The results obtained are shown in Fig. 3. Both sulfuric and phosphoric acids interfered by reducing the silicon sensitivity, whereas acetic acid enhanced the silicon absorption. On the other hand, hydrofluoric, nitric, hydrochloric and perchloric acids showed little effect on silicon absorption. The effect of hydrofluoric acid was studied using a silicon standard solution prepared from sodium silicate.

Effect of diverse elements It has been already reported that both aluminum and iron, either separately or in combination, enhanced the atomic absorption of silicon^{5,10)},

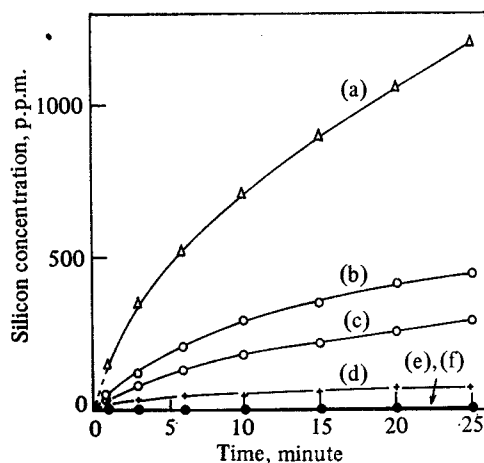


Fig. 2. Dissolution of silicon glassware by 5 ml of hydrofluoric acid diluted to 100 ml, in the presence of boric acid
Saturated boric acid solution added, ml
(a)-0, (b)-10, (c)-20, (d)-30, (e)-40, (f)-50
(Abs. sens.: 1.23)

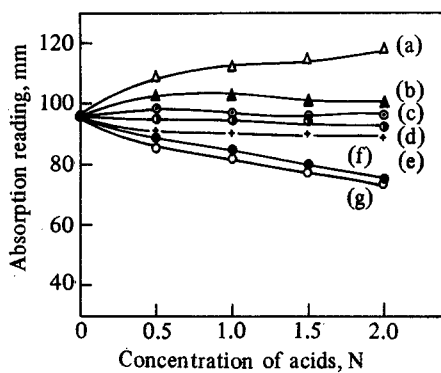


Fig. 3. Effect of acids on silicon absorption
Si: 100 p.p.m.
(a)-Acetic acid, (b)-Hydrochloric acid,
(c)-Hydrofluoric acid, (d)-Nitric acid,
(e)-Perchloric acid, (f)-Sulfuric acid,
(g)-Phosphoric acid, (Abs. sens.: 1.23)

while phosphate depressed it⁵⁾. Campbell⁶⁾, also, reported that aluminum enhanced the silicon absorption.

The examination of the effect of various foreign elements in a nitrous oxide-acetylene flame showed that most elements affected the silicon absorption. The elements examined and their effect are shown in Table 2. In this experiment the concentration of silicon was 100 p.p.m. and that of interferent 2000 p.p.m. Bismuth, cobalt indium, iron, mercury, molybdenum, tellurium, tin and titanium, caused an enhancement in silicon absorption and beryllium, calcium, cesium, magnesium, potassium, strontium, thallium

Table 2. Effect of diverse elements on the atomic absorption of silicon (Concentration of elements added, 2000 p.p.m.; silicon added, 100 p.p.m.)

| Element | Absorption reading (mm) | Recovery of Si (%) | Element | Absorption reading (mm) | Recovery of Si (%) |
|-----------------|-------------------------|--------------------|-----------------|-------------------------|--------------------|
| None | 95 | 100 | Mn ^b | 96 | 101 |
| Al ^a | 92 | 97 | Mo ^d | 107 | 113 |
| Ag ^b | 97 | 102 | Na ^a | 92 | 97 |
| Ba ^a | 98 | 103 | Ni ^c | 98 | 103 |
| Be ^c | 90 | 95 | Pb ^b | 97 | 102 |
| Bi ^b | 105 | 110 | Pd ^a | 98 | 103 |
| Ca ^b | 89 | 94 | Rb ^a | 94 | 99 |
| Cd ^c | 97 | 102 | Sb ^a | 95 | 100 |
| Co ^b | 100 | 105 | Se ^e | 96 | 101 |
| Cr ^a | 96 | 101 | Sn ^a | 100 | 105 |
| Cs ^a | 89 | 94 | Sr ^b | 90 | 95 |
| Cu ^c | 95 | 100 | Te ^e | 114 | 120 |
| Fe ^a | 103 | 108 | Ti ^a | 108 | 114 |
| Hg ^a | 100 | 105 | Tl ^a | 90 | 95 |
| In ^a | 101 | 106 | V ^d | 89 | 94 |
| K ^a | 21 | 22 | We ^e | 98 | 103 |
| La ^a | 94 | 99 | Y ^b | 95 | 100 |
| Lj ^a | 95 | 100 | Zn ^b | 99 | 104 |
| Mg ^b | 85 | 89 | Zr ^b | 95 | 100 |

a: Added as chloride.

b: Added as nitrate.

c: Added as sulfate.

d: Added as ammonium molybdate or vanadate, respectively.

e: Added as sodium selenite, tellurite or tungstate, respectively.

and vanadium, showed a depressing effect. The depressing effect of potassium was remarkable and, therefore, studied in detail with other compounds. The results are shown in Table 3. Though the effect was somewhat dependent on the counter anions, the depression is probably caused by the formation of potassium hexafluorosilicate, which is hardly soluble in water¹¹⁾. This explanation is also supported by the fact that the depressing effect of potassium was not observed in the case of the silicon solution prepared from sodium silicate.

For the purpose of the application of the present method to the determination of silicon in some materials containing silicon, the effect of iron, aluminum, cobalt, chromium and nickel was examined in the concentration range of 0-20000 p.p.m. on 100 p.p.m. of silicon. Large amounts of iron, cobalt and aluminum affect the silicon absorption, as shown in Fig. 4 and, therefore, the matched standard solutions must be used for the preparation of calibration graphs for the determination of silicon in the samples, the major constituent of which is one of these elements.

Table 3. Effect of potassium on the silicon absorption
(Concentration of potassium added, 2000 p.p.m.; silicon added, 100 p.p.m.)

| Potassium compound | Absorption reading (mm) | Recovery of Si (%) | Potassium compound | Absorption reading (mm) | Recovery of Si (%) |
|--------------------|-------------------------|--------------------|--------------------|-------------------------|--------------------|
| None | 98 | 100.0 | Nitrate | 17 | 17.3 |
| Tartrate | 36 | 36.7 | Cyanide | 17 | 17.3 |
| Iodide | 33 | 33.7 | Iodate | 15 | 15.3 |
| Thiosulfate | 26 | 26.5 | Bromide | 15 | 15.3 |
| Sulfate | 22 | 23.0 | Oxalate | 15 | 15.3 |
| Chloride | 20 | 20.4 | Carbonate | 15 | 15.3 |

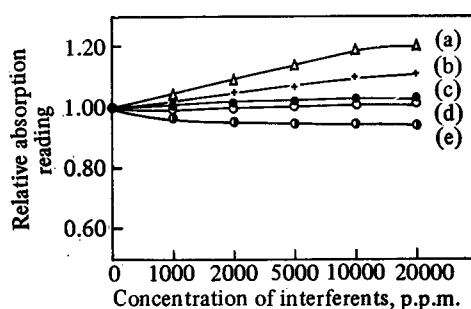


Fig. 4. Effect of diverse elements on silicon absorption
Si: 100 p.p.m.
(a)-Iron, (b)-Cobalt, (c)-Nickel,
(d)-Chromium, (e)-Aluminum
(Abs. sens.: 1.23)

Effect of water-miscible organic solvents As organic solvents are well known to enhance the absorption of many elements in atomic absorption spectrophotometry¹²⁻¹⁵, the effect of thirteen available water-miscible organic solvents, methanol, ethanol, propyl alcohol, isopropyl alcohol, butyl alcohol, isobutyl alcohol, acetone, 1,4-dioxane, ethyl methyl ketone, diethylene glycol diethyl ether, diethylene glycol monoethyl ether, diethylene glycol monomethyl ether and diethylene glycol monobutyl ether, on the silicon absorption was studied. The standard solution of silicon with various solvent compositions (% by volume) were prepared for each solvent and the absorption of these solutions were measured in a nitrous oxide-acetylene flame. By comparing the results with that of a standard solution of silicon, enhancements in sensitivity were obtained. Fig. 5 shows that propyl alcohol and acetone gave higher absorption readings with an increase of solvent concentration. It was, however, observed that the presence of acetone in the silicon aqueous solution gave a large memory effect on silicon absorption. Absorption readings were generally greater than that of the aqueous silicon solution. This result is different from that by Campbell⁶ who showed that the addition of organic solvents has silicon absorption. The observed enhancement may be attributed to the fact that organic

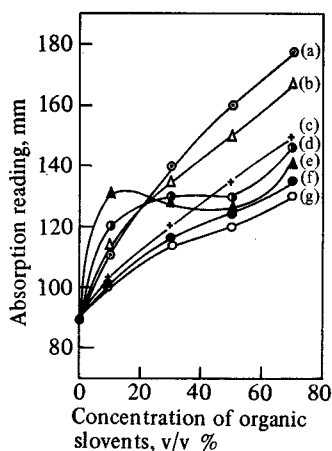


Fig. 5

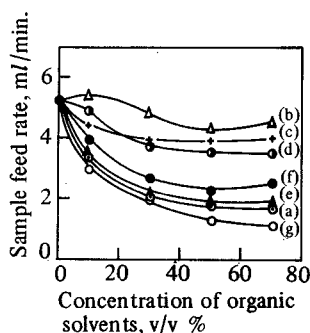


Fig. 6

Fig. 5. Effect of water-miscible organic solvents on silicon absorption Si: 100 p.p.m. (Abs. sens.: 1.23)

Fig. 6. Effect of water-miscible organic solvents on sample feed rate (a)-Propyl alcohol, (b)-Acetone, (c)-1,4-Dioxane, (d)-Methanol, (e)-Isopropyl alcohol (f)-Ethanol, (g)-Diethylene glycol diethyl ether

little effect on solvents act as a fuel when sprayed into the flame, and also to the finer drop-size in the spray. On the other hand, Allan¹⁵⁾ showed that with organic solvents a greater volume of solution reaches the flame per unit time than with water. The present experiment (Fig. 6), however, showed that a sample feed rate (ml per minute) is smaller than with water alone. This observation is in agreement with that by Willis¹⁶⁾, who pointed out that the particle size in the flame plays a major role in determining the atomization efficiency.

The extraction of silicon as silicomolybdic acid into methyl isobutyl ketone

Silicon is usually determined colorimetrically using its reaction with molybdate in acidic solution with subsequent reduction of the resultant heteropoly acid to "molybdenum blue". Kirkbright, Smith and West¹⁷⁾ reported the procedure for the subsequential determination of silicon in a nitrous oxide-acetylene flame. Furthermore, the indirect atomic absorption methods for determination of silicon based on heteropoly chemistry of molybdate have been reported^{18,19)}. Although the indirect atomic absorption spectrophotometry at the wavelength of molybdenum spectral line is more sensitive than the direct determination of silicon, this technique is very difficult in the extraction procedure, in which the amount of molybdenum in excess in organic phase affects on molybdenum absorption by giving higher results for silicon.

In the present study, the silicon absorption was measured in a nitrous oxide-acetylene flame by spraying the methyl isobutyl ketone extract containing silicomolybdic acid. This experiment was made using a silicon standard solution prepared from sodium silicate.

The influence of co-extracting elements, *e.g.* arsenic, germanium and phosphorus, on the extraction procedure and the elimination of interferences were also investigated. Preliminary experiment revealed that the extraction of silicomolybdic acid with methyl isobutyl ketone was quantitative in the pH range of 0.4–0.7. The pH of a silicon standard solution, therefore, was adjusted to 0.4–0.7 with dilute nitric acid solution, and transferred to a 100-ml separatory funnel together with 10% ammonium molybdate solution; the solution was diluted to a final volume of 50 ml with distilled water. A 10-ml portion of methyl isobutyl ketone was added to the separatory funnel and the content was shaken thoroughly for about 3 min. After about 10 min for separation of the layers, the methyl isobutyl ketone extract was dehydrated with anhydrous sodium sulfate. By spraying the extract into a nitrous oxide-acetylene flame, the silicon absorption was measured. The acetylene flow rate was adjusted to 4.5 liters per minute to give a rose-red inner cone about 2.5–3.0 cm in height above the burner head when methyl isobutyl ketone was sprayed into the flame; other instrumental parameters were the same as shown in Table 1. It was confirmed that shaking for 3 min was sufficient for quantitative separation in a single extraction. Other immiscible organic solvents for the extraction than methyl isobutyl ketone, *e.g.* butyl alcohol, amyl alcohol, ethyl acetate and isobutyl acetate, were investigated. Methyl isobutyl ketone was the best. Under this extraction condition the analytical sensitivity for silicon was 0.30 p.p.m. at signal-to-noise ratio of 2. And the linear calibration graph was obtained over the range of 0–60 p.p.m. of silicon in the organic phase.

The effect of foreign elements listed in Table 2 was examined. In this investigation the amount of silicon was 600 μg and that of foreign elements 5000 μg . Most of the elements did not interfere with the silicon absorption. The effect of arsenic, germanium and phosphorus, which are known to form the central atoms of heteropoly acids in which molybdate is the co-ordinating group, was also examined. All of these elements were found to interfere slightly with the determination of silicon. This is caused by the extraction of arsenomolybdic, germanomolybdic or phosphomolybdic acids into methyl isobutyl ketone accompanying with silicomolybdic acid. It has been reported that citric acid efficiently destroys both arsenomolybdic and phosphomolybdic acids, but does not affect silicomolybdic acid²⁰. This suggests that a selective method for the determination of silicon can be developed without separation of arsenic and phosphorus. Chalmers and Sinclair²¹ investigated the effect of complexing agents on selective formation of heteropoly acids, and found that silicomolybdic acid was slowly decomposed with various compounds, *e.g.* tartaric acid. In the present work, the effect of tartaric acid, manitol, citric acid and oxalic acid were investigated from the view-point of eliminating the interferences from arsenic, germanium and phosphorus in the determination of silicon. The results obtained are shown in Table 4. It is seen from the Table that tartaric acid can be used for phosphorus, manitol for arsenic, and oxalic acid for germanium, respectively. This phenomena may be explained in terms of substitution reaction, for example:

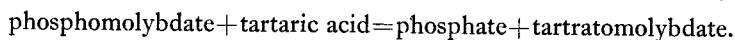


Table 4. Influence of complexing agents on selective formation of silicomolybdic acid in the presence of arsenic, germanium or phosphorus.

| Complexing agent* | Recovery** of silicon (%) | | |
|-------------------|---|---|--|
| | In the presence of arsenic 5000 μg | In the presence of germanium 5000 μg | In the presence of phosphorus 5000 μg |
| None | 90 | 95 | 88 |
| Tartaric acid | 105 | 110 | 99 |
| Manitol | 102 | 107 | 85 |
| Oxalic acid | 95 | 101 | 80 |
| Citric acid | 105 | 107 | 83 |

* A 10-ml portion of each solution was added. Their concentrations were as follows: tartaric acid, 10%, manitol, 9%, citric acid, 8% and oxalic acid, 6%.

** Recovery is expressed as the ratio of absorption reading in each solution to that obtained for silicon alone. The amount of silicon in each solution was 600 μg .

Application to the determination of silicon in some metallurgical materials

Based on the above-mentioned observations, the following procedure for the determination of silicon in some metallurgical materials was developed. The decomposition of the samples, *e.g.* aluminum metals and alloys, cast iron, stainless steels and nickel alloy, followed the JIS method^{22,23}, and finally dissolution of silicon in the solution was made with hydrofluoric acid.

Aluminum metals and alloys—Dissolve 0.200 g of the sample in 15 ml of mixed acid A* or 20 ml of mixed acid B** with heating on a hot plate for about 20 min. Cool and transfer to a 100-ml polyethylene beaker, add 5 ml of hydrofluoric acid and heat on a water bath until the residue is completely dissolved. Cool and add 50 ml of saturated boric acid solution. Transfer the solution to a 100-ml volumetric flask and dilute to a final volume of 100 ml with distilled water.

Cast iron—Dissolve 0.200 g of the sample in 10 ml of nitric acid (1+1) or aqua regia with heating on a hot plate for about 30 min. Cool and add 10 ml of concentrated perchloric acid. Heat the solution for about 15 min. Cool and further treat it in the same manner as described in aluminum metals and alloys.

Stainless steels—Dissolve 0.200 g of the sample in 10 ml of hydrochloric acid (2+1) with heating on a hot plate for about 30 min. Cool and add 10 ml of concentrated perchloric acid. Heat the solution until the color of the solution changes to orange due to dichromate ion and further treat it in the same manner as described in aluminum metals and alloys.

* Mixed acid A is a mixture of sulfuric, nitric and hydrochloric acids, and distilled water in a ratio of 3:3:3:10 by volume.

** Mixed acid B is a mixture of nitric and hydrochloric acids, and distilled water in a ratio of 1:1:2 by volume.

The sample solutions obtained in the above-mentioned procedure were diluted to an appropriate volume with distilled water according to the silicon content. Results of the determination of silicon in three aluminum metals, eight aluminum alloys, a cast iron, two stainless steels and a nickel alloy by the proposed method are shown in Tables 5 and 6. The results were obtained by using the calibration graphs for silicon, which were made with the standard solutions matched with the sample solutions, because other

Table 5. Results of the determination of silicon in aluminum metals and aluminum alloys by atomic absorption spectrophotometry.

| Sample No. | Atomic absorption method | | Certificate value (%) |
|-----------------------|--------------------------|-------------------|-----------------------|
| | a (%) | b (%) | |
| Aluminum metal | | | |
| HK-1 | 0.56 | 0.51 | 0.524 |
| HK-3 | 0.64 | 0.65 | 0.652 |
| No. 3 | 0.31 | 0.34 | 0.35 |
| Aluminum alloy | | | |
| No. 387 (1) | 26.5 ₈ | 27.0 ₀ | 26.33 |
| No. 387 (2) | 26.6 ₆ | 26.5 ₀ | 26.50 |
| No. 387 (3) | 26.2 ₀ | 26.9 ₀ | 26.21 |
| No. 388 (1) | 28.1 ₀ | 28.3 ₀ | 28.48 |
| No. 388 (2) | 26.6 ₀ | 26.7 ₀ | 26.57 |
| No. 397 (1) | 27.7 ₀ | 27.5 ₄ | 27.24 |
| No. 397 (2) | 27.1 ₀ | 27.1 ₈ | 27.03 |
| No. 425 | 23.8 ₀ | 23.1 ₁ | 23.54 |

a: The sample was decomposed with mixed acid A.

b: The sample was decomposed with mixed acid B.

Table 6. Results of the determination of silicon in cast irons, stainless steels and nickel alloy by atomic absorption spectrophotometry.

| Sample No. | Atomic absorption method (%) | | Certificate value (%) |
|------------------------|------------------------------|-------------------|-----------------------|
| | | | |
| Cast iron | | | |
| GK-10 | 1.34 ^a | 1.28 ^a | 1.229 |
| | 1.31 ^b | 1.26 ^b | |
| Stainless steel | | | |
| GK-4 | 0.57 | 0.55 | 0.517 |
| GK-9 | 0.74 | 0.76 | 0.745 |
| Nickel alloy | | | |
| B.C.S. No. 310 | 0.82 | 0.85 | 0.84 |

a: The sample was decomposed with nitric acid (1 + 1).

b: The sample was decomposed with aqua regia.

elements and acids interfered with the silicon absorption. The results obtained are satisfactory and the method is considerably simpler and shorter than the gravimetric or colorimetric methods.

Acknowledgment

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