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DETERMINATION OF SILICON BY  
MEASUREMENT OF THE ABSORBANCE  
OF THE N-AMYL ALCOHOL EXTRACT  
OF  $\alpha$ -SILICOMOLYBDIC ACID  
(APPLICATION TO HIGH-PURITY  
COPPER METAL AND BRASSES)

ELSIE M. DONALDSON  
AND  
W. R. INMAN

MINERAL SCIENCES DIVISION

SEPTEMBER 1965

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DETERMINATION OF SILICON BY MEASUREMENT OF THE  
ABSORBANCE OF THE N-AMYL ALCOHOL EXTRACT  
OF  $\alpha$ -SILICOMOLYBDIC ACID  
(APPLICATION TO HIGH-PURITY COPPER METAL AND BRASSES)

by

Elsie M. Donaldson\* and W.R. Inman\*\*

ABSTRACT

A procedure involving n-amyl alcohol extraction of  $\alpha$ -silicomolybdic acid and spectrophotometric measurement of the extract (at 350 m $\mu$ ) has been applied to the determination of trace amounts of silicon in high-purity copper metal and brasses. Interference from phosphorus and arsenic is eliminated by the selective destruction of their heteropoly complexes in a 3N sulphuric acid medium prior to the extraction of the silicon complex.

RÉSUMÉ

On a appliqué au dosage de traces de silicium dans le cuivre métal très pur et dans les laitons un procédé qui comporte l'extraction à l'alcool n-amylique de l'acide  $\alpha$ -silicomolybdique et la mesure spectrophotométrique de l'extrait (à 350 m $\mu$ ). L'interférence causée par le phosphore et l'arsenic est éliminée par la destruction sélective de leurs complexes hétéropolaires en milieu sulfurique 3N avant de procéder à l'extraction du complexe de silicium.

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## INTRODUCTION

Recently, the Mines Branch laboratories were engaged in collaborative work with the National Bureau of Standards on the analysis of brasses and bronzes for use as spectrographic standards. Because part of this project involved the determination of trace amounts of silicon in brasses, the present investigation was undertaken to assess existing methods for determining silicon in copper-base materials and, if necessary, to modify and adapt these methods to the samples under consideration.

Most of the spectrophotometric methods for determining silicon in copper-base materials are based on the formation of yellow  $\beta$ -silicomolybdic acid or its reduction product "molybdenum blue". However, this method is not suitable for the accurate determination of small quantities of silicon in brasses unless provision is made for the removal of copper. Copper salts decrease the intensity of the colour of the yellow  $\beta$ -silicomolybdic acid<sup>(1)</sup>, presumably by hastening the conversion of the  $\beta$ -form to  $\alpha$ -silicomolybdic acid<sup>(2)</sup>. Copper also interferes in the spectrophotometric determination of both the reduced and unreduced forms of the  $\beta$ -acid because of the background colour exhibited by its solutions<sup>(3, 4)</sup>.

It is known that silicomolybdic acid can be extracted into various organic solvents<sup>(5)</sup> and several investigators<sup>(6 - 8)</sup> have utilized this separation technique for determining silicon in copper-base materials. These methods involve single<sup>(7, 8)</sup> or multiple stage<sup>(6)</sup> extractions of silicomolybdic acid and the subsequent determination of silicon by spectrophotometric measurement of the blue complex produced in the organic phase by reduction with a suitable reducing agent<sup>(6, 8)</sup>, or in the aqueous phase after back-extraction of the yellow complex into an aqueous medium<sup>(7)</sup>. Although these methods are probably quite adequate for the determination of small amounts of silicon in brasses, it was considered that a simpler and less time-consuming procedure would result if absorbance measurements were made directly on the organic phase after a single-stage extraction of silicomolybdic acid with a suitable organic solvent.

This report describes the successful application of a single-stage extraction procedure, in which  $\alpha$ -silicomolybdic acid is extracted into n-amyl alcohol and absorbance measurements made directly on the extract, to the determination of small amounts of silicon in brasses. The method is also applicable to high-purity copper metal.

## APPARATUS AND REAGENTS

Apparatus

Spectrophotometer:	Beckman Model DU.
pH meter:	Leeds and Northrup, equipped with a miniature pH electrode assembly.
Centrifuge:	Clinical type.
Teflon beaker covers.	

ReagentsStandard Silicon Solution

Fuse 213.9 mg of pure silicon dioxide with 2 g of Specpure sodium carbonate in a covered platinum crucible, cool, and transfer the crucible and contents to a 400-ml plastic or Teflon beaker containing approximately 200 ml of water. Heat gently to dissolve the melt, cool, dilute to exactly 500 ml with water, and store in a plastic bottle. Dilute 10 ml of this stock solution to 200 ml with water and store in a plastic bottle. (1 ml of this diluted solution = 10  $\mu$ g of silicon.)

Ammonium Molybdate, 8% Solution

Dissolve 40 g of ammonium molybdate  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$  in water, dilute to 500 ml, and store in a plastic bottle.

Boric Acid, 5% Solution

Dissolve 50 g of boric acid in approximately 800 ml of hot water, cool, dilute to 1 litre, and store in a plastic bottle.

Silica-free Ammonia Solution

Bubble ammonia gas into cooled, distilled water in a plastic bottle until the solution is saturated.

### Sulphuric Acid, 40% Solution

Add 200 ml of concentrated sulphuric acid to approximately 250 ml of water, cool, dilute to 500 ml, and store in a plastic bottle.

### Sulphuric Acid, 8% Solution

Add 40 ml of concentrated sulphuric acid to approximately 400 ml of water, cool, dilute to 500 ml, and store in a plastic bottle.

### N-amyl Alcohol

Analytical reagent, obtained from Mallinckrodt Chemical Works.

## PROCEDURE

### Calibration Curve

Add 4 ml of 8% sulphuric acid solution to each of six 100-ml plastic beakers (Note 1, p.4). Then, by burette, add to the last five beakers 1, 2.5, 5, 7.5 and 10 ml, respectively, of standard silicon solution (i.e., 1 ml = 10  $\mu$ g Si). The first beaker contains the blank. Add to each of the resulting solutions 20 ml of 5% boric acid solution and 5 ml of 8% ammonium molybdate solution and dilute to approximately 40 ml with water. Then, using a pH meter, adjust the pH of each solution to  $2.0 \pm 0.2$  with silica-free ammonia solution and dilute to approximately 50 ml with water. Cover the beakers with Teflon covers, heat in a steam bath for 30 minutes, then cool in water for 20 to 30 minutes to approximately room temperature. Transfer each solution to a 100-ml volumetric flask, dilute to volume with water, mix and immediately transfer the resulting solution back into the plastic beaker (to minimize contact with glass). Pipette a 20-ml aliquot of each solution into 60-ml separatory funnels containing 5 ml of 40% sulphuric acid solution, stopper, and immediately mix well. Add to each funnel exactly 10 ml of n-amyl alcohol and shake for 2 minutes. Allow 5 minutes for the layers to separate, then drain off and discard the lower aqueous layer. Wash each extract with 10 ml of 8% sulphuric acid solution by shaking for 1 minute. After the layers have separated, again discard the lower aqueous phase. Drain the n-amyl alcohol extracts into 15-ml centrifuge tubes and centrifuge for 30 seconds. Determine the absorbance of each extract against n-amyl alcohol as the reference solution, using 2-cm cells at a wavelength of 350 m $\mu$ .



Correct the absorbance value obtained for each extract of  $\alpha$ -silicomolybdic acid by subtracting that obtained for the blank. Plot micrograms of silicon vs absorbance.

Procedure for High-purity Copper and Brass Samples (containing up to 0.15% each of arsenic and phosphorus and 0.10% of iron)

In the following procedure, a reagent blank is carried along with the samples (Note 2, p.4):

Transfer a 1-g sample to a 100-ml plastic beaker (Note 1, p.4), add 5 ml of water and 4 ml of 1:1 sulphuric acid solution, cover with a Teflon cover, and add 2 ml of concentrated nitric acid. Place the beaker in a steam bath and heat gently for 1 hour to ensure complete dissolution of the sample and to remove oxides of nitrogen. Then cool to room temperature, add 2 ml of 1:3 hydrofluoric acid (of low fluosilicic acid content), and place in a water bath (60 - 70°C) for 30 minutes. Cool, add 20 ml of 5% boric acid solution, let stand for 15 minutes, then add 5 ml of 8% ammonium molybdate solution. Neutralize a portion of the excess acid by adding several ml of silica-free ammonia solution (to minimize the length of time the sample is in contact with the glass pH electrode), then proceed with the pH adjustment and subsequent formation of  $\alpha$ -silicomolybdic acid as described for the Calibration Curve in this report. Transfer the resulting solution to a 100-ml volumetric flask, dilute to volume, and immediately transfer back into the plastic beaker. Then transfer a suitable aliquot (10 - 20 ml) of both sample and blank solutions, depending on the silicon content of the sample, to 60-ml separatory funnels containing 5 ml of 40% sulphuric acid solution and analyse the solution for silicon by the procedure given under Calibration Curve. When 20-ml aliquots of sample solution are taken,

$$1 \mu\text{g of silicon} = 0.0005\%.$$

Notes

1. Plastic beakers which have been employed for the determination of silicon in samples containing phosphorus should be soaked for some time (preferably overnight) in 1:3 ammonia solution, followed by an acid rinse and finally by a distilled water rinse prior to use. Low results will be obtained for silicon, especially in samples containing phosphorus, if this precaution is not taken, because of the "seeding effect" described by Morrison and Wilson<sup>(9)</sup>, which results in precipitation of part of the phosphomolybdic acid.
2. It is recommended that two reagent blanks be carried along with the samples because of the relative ease with which solutions may become contaminated by silicon-bearing dust in the air.

## EXPERIMENTAL

### Extraction of Silicomolybdic Acid

Butyl (6, 8, 10-17) and amyl (7, 18-20) alcohols have been used for the extraction of silicomolybdic acid. N-amyl alcohol was chosen as the extractant in the present work because of its relatively low solubility in water and because Wadelin and Mellon<sup>(5)</sup> have shown that a n-amyl alcohol solution of silicomolybdic acid has a greater extinction coefficient (at 350 m $\mu$ ) than corresponding solutions of silicomolybdic acid in many other solvents.

Preliminary experiments with test solutions containing boric acid showed that up to 40  $\mu$ g of silicon (as either  $\alpha$ - or  $\beta$ -silicomolybdic acid) contained in 25 ml of approximately 3N sulphuric acid solution can be extracted quantitatively in a single stage into 10 ml of n-amyl alcohol. The extraction of larger amounts was not attempted, because of the high absorbance of the resulting extract when 1-cm cells are used for the spectrophotometric measurement. The absorbance of the extracts of both  $\alpha$ - and  $\beta$ -silicomolybdic acids remains relatively constant for at least 3 hours after extraction. The effect of longer time intervals was not investigated.

### Effect of Different Acid Media on the Extraction of Molybdic Acid

Molybdic acid is appreciably soluble in some organic solvents and such solutions absorb in the ultraviolet region<sup>(5)</sup>. This absorbance would contribute to a high reagent blank in the present work; therefore, tests were carried out to determine whether extraction from different mineral acid media would affect the quantity of molybdic acid extracted into n-amyl alcohol. Because Miyamoto<sup>(7)</sup> recommends extraction of  $\beta$ -silicomolybdic acid from a 3N sulphuric acid medium, separate test solutions were prepared containing 5 ml of 2% ammonium molybdate solution and sufficient amounts each of concentrated hydrochloric, nitric or sulphuric acids to give an approximate concentration of 3N on dilution to 100 ml with water. A 20-ml aliquot of each solution was extracted with 10 ml of n-amyl alcohol and the absorbance of each extract was measured over the wave length range 300 to 400 m $\mu$  against n-amyl alcohol as the reference solution.

The results of these tests showed that considerably less molybdic acid is extracted from sulphuric acid media than from hydrochloric or nitric acid media; consequently, all succeeding experiments were conducted in sulphuric acid media.

### Absorption Spectra of n-Amyl Alcohol Extracts of $\alpha$ - and $\beta$ -Silicomolybdic Acids

In 1952 Strickland<sup>(2)</sup> published a series of papers dealing with the mechanism of formation and reduction of silicomolybdic acid. He proved that at least two forms of silicomolybdic acid exist, both having the same formula and both yellow in colour, but having different absorption spectra. The stable form, which is formed at low acid concentrations, was designated  $\alpha$ -silicomolybdic acid. The other form,  $\beta$ -silicomolybdic acid, is formed at higher acid concentrations but is slowly and irreversibly transformed to the  $\alpha$ -acid in about 25 to 30 hours. This transformation is hastened in the presence of excess neutral electrolyte, by heating and by an increase in pH above 2.5. Although Strickland's findings indicate that the stable  $\alpha$ -silicomolybdic acid is the better form to use for the photometric determination of silicon, many investigators still use the  $\beta$ -form because of its greater sensitivity in the visual region of the spectrum. In the present work preliminary investigations were carried out with both forms, in order to determine which would be most suitable for the determination of small amounts of silicon in brasses.

To determine a suitable wave length for the measurement of the absorbance of the n-amyl alcohol extracts of both  $\alpha$ - and  $\beta$ -silicomolybdic acids, spectral transmittance measurements were carried out as follows:

A test solution containing predominantly  $\beta$ -silicomolybdic acid was prepared essentially by the method of Miyamoto<sup>(7)</sup>, i.e., a solution containing sulphuric acid, boric acid and silicon was adjusted to pH 1.0 with silica-free ammonia solution, diluted to 50 ml with water, then 5 ml of 8% ammonium molybdate solution were added, and after a 10-minute time interval the resulting solution of  $\beta$ -silicomolybdic acid was diluted to 100 ml with water. (The pH of the solution at the point of formation of the  $\beta$ -acid was approximately 1.45.) A 20-ml aliquot of this solution was immediately acidified with sulphuric acid so that the resulting concentration was approximately 3N, then quickly extracted with 10 ml of n-amyl alcohol. The absorption spectrum of the extract and that of a corresponding reagent blank solution were determined against n-amyl alcohol as the reference solution, using 1-cm cells.

A test solution containing  $\alpha$ -silicomolybdic acid was prepared approximately by the method of Bell and Machlan<sup>(8)</sup>, i.e., a solution containing the same quantities of sulphuric acid, boric acid, silicon and ammonium molybdate as described above was adjusted to pH 1.8 with silica-free ammonia solution, diluted to 50 ml with water, covered and heated on a steam bath for 30 minutes, cooled to room temperature, and then diluted to 100 ml with water. Twenty-ml aliquots of the resulting solution of  $\alpha$ -silicomolybdic acid and a corresponding reagent blank solution were acidified with sulphuric acid, extracted with n-amyl alcohol, and measured as described above for the  $\beta$ -acid.

The absorption spectra of these solutions are given in Figures 1, 2 and 3. The isobestic point shown in Figure 3 (i.e., point at which the two forms have the same absorbance) occurs at 336.5 m $\mu$ , which agrees fairly well with the points obtained by Strickland<sup>(2)</sup> (335m $\mu$ ) and Ringbom et al.<sup>(21)</sup> (340 m $\mu$ ) from measurements made in aqueous media. Figure 3 also shows that the absorbance index of the  $\beta$ -form, which is generally considered to be more sensitive than the  $\alpha$ -form, is greater only at wave lengths above the isobestic point. Because of the magnitude of the reagent blanks (shown in Figures 1 and 2) below 350 m $\mu$ , this wave length was chosen for all further measurements of both the  $\alpha$ - and  $\beta$ - silicomolybdc acids.

#### Effect of Ammonium Molybdate Concentration on the Formation of $\alpha$ - and $\beta$ -Silicomolybdc Acids

Because the formation of  $\alpha$ -silicomolybdc acid (as described in the previous section) is the result of heating the  $\beta$ -acid at 100°C, the concentration of ammonium molybdate required for the quantitative formation of the  $\beta$ -acid in solutions containing a given quantity of silicon would, of necessity, be the same for the  $\alpha$ -acid. Experiments showed that at least 2 ml of 8% ammonium molybdate solution are required for the complete formation of the  $\beta$ -acid and, consequently, for the  $\alpha$ -acid, in solutions containing 200  $\mu$ g of silicon. An intermediate concentration (5 ml of 8% solution) was chosen for all further experimental work.

#### Stability of $\alpha$ - and $\beta$ -Silicomolybdc Acids in 3N Sulphuric Acid Media

According to Strickland<sup>(2)</sup>,  $\beta$ -silicomolybdate solutions are much more rapidly decomposed by strong acid than are solutions of the  $\alpha$ -compound. Jean<sup>(22)</sup> investigated the stability of  $\alpha$ - and  $\beta$ -silicomolybdc acids in 2N sulphuric acid media and showed that the  $\alpha$ -acid is relatively stable over a period of 4 hours but that the absorbance of the  $\beta$ -acid decreases considerably because of its transformation to the  $\alpha$ -form. The results of tests (Table 1) carried out to determine the effect of time on the stability of the  $\alpha$ - and  $\beta$ -acids under the present experimental conditions corroborate Jean's results and show the rate of transformation of the  $\beta$ -acid to the  $\alpha$ -acid in 3N sulphuric acid media, i.e., the  $\beta$ -acid is almost completely converted to the  $\alpha$ -form in 2 hours. On the basis of these results the stable  $\alpha$ -acid was chosen for the present investigation.

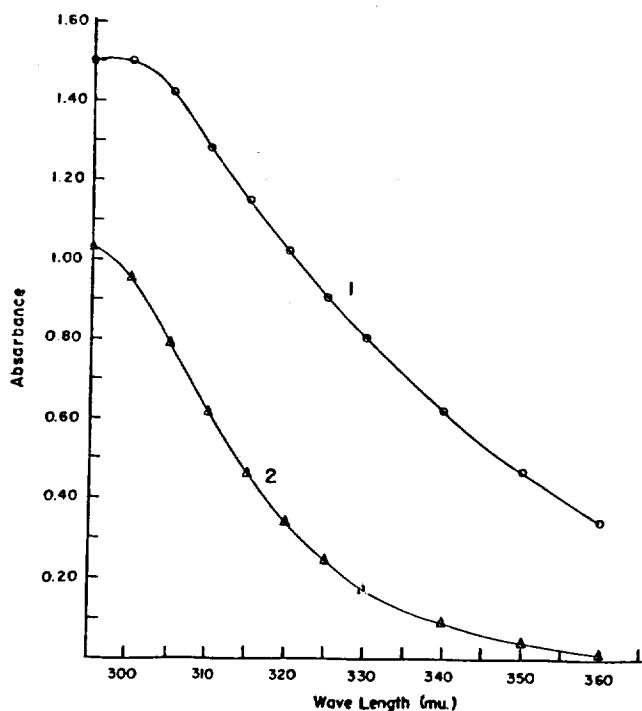


Figure 1 - Absorption spectra of the n-amyl alcohol extracts of  $\beta$ -silicomolybdic acid and a corresponding reagent blank (vs n-amyl alcohol).  
1)  $\beta$ -silicomolybdic acid (12.5  $\mu\text{g}$  Si)  
2) reagent blank

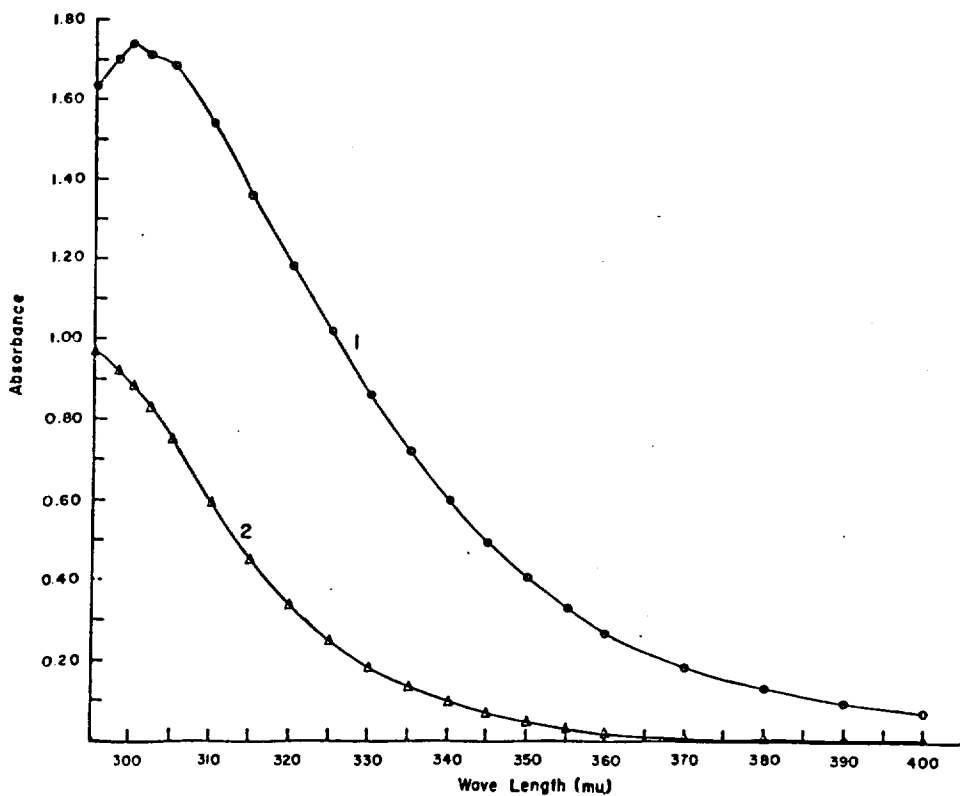


Figure 2 - Absorption spectra of the n-amyl alcohol extracts of  $\alpha$ -silicomolybdic acid and a corresponding reagent blank (vs n-amyl alcohol).  
1)  $\alpha$ -silicomolybdic acid (12.5  $\mu\text{g}$  Si)  
2) reagent blank

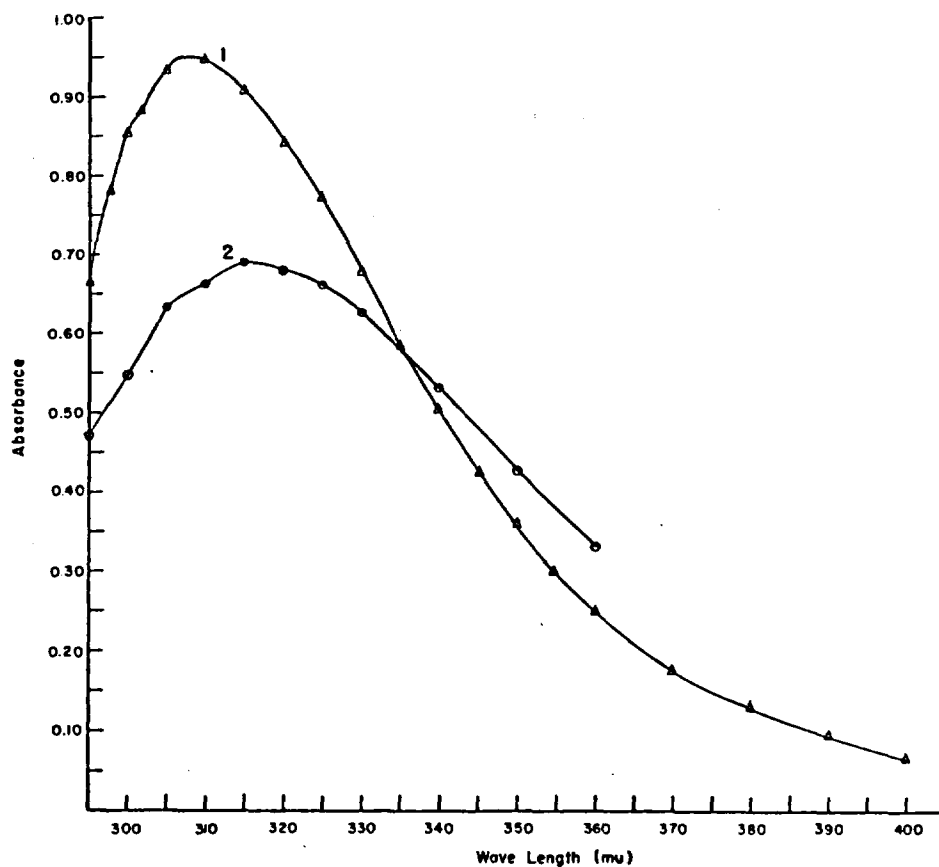


Figure 3 - Absorption spectra of the n-amyl alcohol extracts of  $\alpha$ - and  $\beta$ - silicomolybdic acids (vs reagent blanks).

- 1)  $\alpha$ -silicomolybdic acid (12.5  $\mu\text{g}$  Si)
- 2)  $\beta$ -silicomolybdic acid (12.5  $\mu\text{g}$  Si)

TABLE 1

Effect of Time on the Stability of  $\alpha$ - and  $\beta$ -Silicomolybdic Acids in 3N Sulphuric Acid Media

Time	Absorbance of 25 $\mu\text{g}$ of Si** Prepared as the $\alpha$ -acid	Absorbance of 25 $\mu\text{g}$ of Si** Prepared as the $\beta$ -acid
1 minute	0.690	0.858
15 minutes	0.692	0.825
30 "	0.693	0.790
1 hour	0.691	0.730
2 hours	0.687	0.707
3 "	0.682	-----
4 "	0.672	-----

\*\* 1-cm cells used for absorbance measurements.

Effect of Heating Time on the Formation of  $\alpha$ -Silicomolybdic Acid

Literature references to methods for determining silicon as  $\alpha$ -silicomolybdic acid show considerable variations (i.e., approximately 5 minutes to 3 hours) in the heating time required for complete conversion of the  $\beta$ -acid to the  $\alpha$ -acid (13, 21, 19, 8, 22, 11). However Strickland<sup>(2)</sup> and Andersson<sup>(11)</sup> state that the rate of conversion is dependent, to some extent, on the excess of molybdate and the concentration of silicon present in solution. Tests carried out to determine the heating time required under the present experimental conditions showed that the conversion is complete in approximately 30 minutes.

Effect of Sulphuric Acid Concentration on the Extraction of  $\alpha$ -Silicomolybdic Acid in the Presence of Phosphorus and Arsenic

Brass samples generally contain small amounts of phosphorus and arsenic which interfere in the spectrophotometric determination of silicon by being partially or completely transformed to their respective heteropoly acid complexes under the experimental conditions required for the formation of silicomolybdic acid. Many investigators, including Miyamoto<sup>(7)</sup> and Bell and Machlan<sup>(8)</sup>, have utilized oxalates, citrates and tartrates, which are known to form complexes with molybdate, to bleach the interfering colour of the phospho- and arseno-molybdates. However Strickland<sup>(2)</sup> has stated that these compounds slowly bleach the colour of silicomolybdate

solutions at room temperature, and, later, DeSesa and Rogers<sup>(23)</sup> corroborated this statement and showed the magnitude of this bleaching effect on solutions of the  $\beta$ -acid.

According to Jean<sup>(22)</sup>, phospho- and arseno-molybdic acids are destroyed in 2 to 4N acid media; consequently this technique was investigated in the present work. Tests were carried out to determine the concentration of sulphuric acid which would allow complete extraction of  $\alpha$ -silicomolybdic acid, but would result in complete destruction of the phospho- and arseno-molybdic acids.

The results of these tests (Table 2) showed that  $\alpha$ -silicomolybdic acid is completely extracted from approximately 1.4 to 4.3N sulphuric acid media, but a concentration of at least 2.2N is required for essentially complete destruction of up to 500  $\mu$ g of phosphorus and arsenic as their respective heteropoly acid complexes. A concentration of approximately 3N was considered to be optimum.

#### Effect of Diverse Ions

Tungsten, vanadium, niobium, tantalum, titanium, zirconium, cerium, phosphorus, arsenic, germanium, iron, aluminum, chromium and cobalt are known to form heteropoly complexes (22, 24, 11). However, with the exception of phosphorus, arsenic, iron and aluminum, the possible interference effects of the remainder of these ions were not investigated in the present work because they did not occur as impurities or alloying elements in the brass samples under consideration.

Although tests (described in the previous section) showed that the presence of 500  $\mu$ g of phosphorus<sup>V</sup> or arsenic<sup>V</sup> in the aliquot taken for extraction does not interfere in the determination of silicon by the proposed method, the presence of 500  $\mu$ g of both yields erratic results for silicon. Further tests conducted with solutions containing phosphorus, arsenic, iron and aluminum showed that up to at least 300  $\mu$ g each of phosphorus<sup>V</sup> and arsenic<sup>V</sup>, 200  $\mu$ g of iron<sup>III</sup> and 6 mg of aluminum<sup>III</sup> can be tolerated in the aliquot taken for extraction, without affecting the silicon result.



TABLE 2

Effect of Sulphuric Acid Concentration on the Extraction of  
 $\alpha$ -Silicomolybdic Acid in the Presence of Phosphorus and Arsenic

Concentrated Sulphuric Acid Present (ml)	Approximate Normality of Solution	Absorbance of Extract (1-cm cell)		
		I Si Present, 25 $\mu$ g	II Si Present, 25 $\mu$ g P <sup>V</sup> Present, 500 $\mu$ g	III Si Present, 25 $\mu$ g As <sup>V</sup> Present, 500 $\mu$ g
0.25*	0.3	0.533	-----	-----
0.50*	0.7	0.659	-----	-----
0.75*	1.1	0.687	-----	-----
1.00	1.4	0.697	1.302	-----
1.25	1.8	-----	0.825	0.790
1.50	2.2	0.705	0.722	-----
2.00	2.9	0.706	0.699	0.710
2.50	3.6	0.706	0.707	0.704
3.00	4.3	0.714**	0.691	-----
				0.698

\* Organic phase slow in separating.

\*\* Extract turbid.

Application to Synthetic Copper and Brass Samples  
and to National Bureau of Standards Brass Samples

Preliminary experiments to determine the applicability of n-amyl alcohol extraction of  $\alpha$ -silicomolybdic acid and photometric measurement of the extract to the determination of small amounts of silicon in brasses were carried out with a series of synthetic copper samples, prepared as described under "Procedure", and to which phosphorus, arsenic, iron and aluminum had been added. In these tests, high absorbance values were obtained for the reagent blanks because of increased extraction of molybdic acid in the presence of the nitrate, fluoride and ammonium salts resulting from the sample dissolution and solution preparation, prior to the formation and extraction of  $\alpha$ -silicomolybdic acid. Attempts to reduce the excess molybdic acid in the extracts by washing with water or 1% sulphuric acid solution resulted in a loss of silicon. However, when the extracts from the above tests were washed with 10 ml of 8% sulphuric acid solution (approximately 3N) the absorbance of the reagent blank was reduced considerably and complete recovery of the added silicon was obtained (Table 3).

The accuracy of the proposed method was tested further by applying it to the analysis of a series of synthetic brass samples and to the National Bureau of Standards brass samples under consideration. The results of these analyses are given in Tables 3 and 4.

#### DISCUSSION

Table 3 shows that the results obtained by the proposed method for synthetic copper and brass samples agree favourably with the total calculated percentage of silicon present. Table 4 shows that the results obtained for the brass samples submitted by the National Bureau of Standards are in excellent agreement with the analytical results obtained by R. K. Bell of the National Bureau of Standards laboratories.

TABLE 3

The Determination of Silicon in Synthetic  
Copper and Brass Samples

Sample	Total Si Present, %	Si Found, %
Cu + 0.0010% Si (+0.15% P, 0.15% As, 0.10% Fe and 3.0% Al)	0.0014	0.0014
Cu + 0.0040% Si (as above)	0.0044	0.0043
Cu + 0.0080% Si (as above)	0.0084	0.0085
Aluminum Brass + 0.0010% Si (containing 2.80% Al, 0.068% Fe, 0.024% Pb and 0.125% P)	0.0031	0.0033
Aluminum Brass + 0.0030% Si (as above)	0.0051	0.0052
Aluminum Brass + 0.0060% Si (as above)	0.0081	0.0078

Triplicate determinations of silicon in the above copper metal and aluminum brass by the proposed method gave average results of 0.0004 and 0.0021%, respectively.

TABLE 4  
The Determination of Silicon in NBS Spectrographic  
 Brass Standard Samples

	Approximate Uncert- ified Value for Si, %*	Si Found, %**
NBS-C1100 Cartridge Brass (0.106% Pb, 0.072% Fe, 0.055% Sn, 0.052% Ni, approx. 0.003% Mn, approx. 0.01% P)°	0.01 (0.0098)	0.0094
NBS-C1101 Cartridge Brass (0.05% Pb, 0.037% Fe, 0.016% Sn, 0.013% Ni, approx. 0.006% Mn, approx. 0.002% P)°	0.005 (0.0047)	0.0049
NBS-1101 Cartridge Brass (as for C-1101)°	0.005 (0.0047)	0.0046
NBS-C1102 Cartridge Brass (0.020% Pb, 0.011% Fe, 0.006% Sn, 0.005% Ni, approx, 0.004% Mn, approx 0.006% P) °	0.002 (0.0016)	0.0017
NBS-1102 Cartridge Brass (as for C1102)°	0.002 (0.0016)	0.0017
NBS-C1118 Aluminum Brass (2.80% Al, 0.068% Fe, 0.024% Pb, 0.125% P) °°	(0.0021)	0.0021
NBS-C1119 Aluminum Brass (2.14% Al, 0.033% Fe, 0.051% Pb, 0.070% P) °°	(0.0016)	0.0015
NBS-C1120 Aluminum Brass (1.46% Al, 0.015% Fe, 0.105% Pb, 0.018% P)°°	(0.0011)	0.0011

\* From National Bureau of Standards Miscellaneous Publication 260-2, October 15, 1964. Figures in parentheses are analytical results obtained by R.K. Bell, Standard Reference Materials Section, National Bureau of Standards, Washington, D.C.; private communication.

\*\* The results given for silicon are the average of triplicate determinations by the proposed method.

° Cartridge brass standards also contain small amounts of aluminum, antimony, arsenic, beryllium, bismuth, cadmium, silver and tellurium.

°° Aluminum brass standards also contain small amounts of silver, arsenic and antimony.

In the proposed method, the dissolution of high-purity copper and brass samples is accomplished with nitric, sulphuric and hydrofluoric acids, according to the methods described by Bell and Machlan<sup>(8)</sup> and Miyamoto<sup>(7)</sup>. Several methods are given in the literature for the spectrophotometric determination of silicon in copper-base materials in which the samples are decomposed with nitric acid or mixtures of hydrochloric and nitric and sulphuric and nitric acids. However, these methods do not take into consideration the possible presence of refractory silicides which would not be decomposed with these acids, and also the possible formation of colloidal or polymerized silicic acid which does not react with ammonium molybdate<sup>(1)</sup>. Hydrofluoric acid is necessary to obtain solution of these silicides<sup>(1)</sup> and it also assists in preserving the silicon in the monomeric or "reactive" form<sup>(25)</sup>.

According to Strickland<sup>(2)</sup>, an absorbance-temperature gradient exists for  $\alpha$ -silicomolybdic acid, which was determined by Ringbom et al.<sup>(21)</sup> to be approximately 0.39% per degree centigrade. However, the error resulting from this gradient in the determination of silicon by the proposed method is relatively insignificant because the quantities of silicon dealt with are small, and also because the solutions of  $\alpha$ -silicomolybdic acid are cooled to approximately room temperature prior to extraction of the silicon complex.

The proposed method is suitable for samples containing up to 0.02% of silicon.

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