INFLUENCE OF TEMPERATURE ON THE PHOTOMETRIC DETERMINATION OF SILICON BY THE MOLYBDENUM BLUE METHODS*

By G. V. L. N. Murty, F.A.Sc., K. S. R. Krishnaiah and M. S. Raju

(*Department of Chemical Laboratories, The Tata Iron and Steel Co. Ltd., Jamshedpur*)

Received October 21, 1965

Abstract

Some systematic studies have been carried out on the influence of temperature on the photometric determination of silicon by the molybdenum blue procedure. It has been shown that temperature exerts a distinct influence on the colour intensities involved in the different procedures and the extent of this influence depends largely on the nature of the acid medium and the reducing agent employed. Ascorbic acid has been successfully employed to overcome the influence of temperature.

Our thanks are due to the management of the Tata Iron and Steel Company for permitting the publication of this paper.

A survey of the available literature reveals that the effect of temperature on the photometric determination of silicon is not thoroughly examined. Thompson and Houlton,[1] Stumm[2] and Hill[3] observed practically no effect of temperature up to 30° C. on the intensity of the yellow silicomolybdate. Straub and Grabowski[4a] and Sanders and Cramer[4b] showed that the photometric molybdenum blue method tolerates wide variations in temperature and observed no change in colour intensity at 24 $\pm$ 5° C. Milton[5] and Greenfield[6] studied the effect of temperature on the formation of molybdenum blue colour, using stannous chloride as the reducing agent and pointed out a gradual decrease in the intensity of the colour at higher temperatures. The influence of the higher temperatures prevailing in tropics on the formation and reduction of silicomolybdate complex was also observed in our laboratories (Murty and Sen[7, 8] and Murty[9]).

* Some of the salient features of this paper appeared as a note in *Current Science*.[16]

In the present investigations the influence of temperature has been studied up to 45° C., since in tropical countries the room temperatures sometimes go as high as 45° C. in summer months. The following procedures have been applied to pure silicate solutions. Spekker photoelectric absorptiometer has been employed for measuring colour intensities.

Procedure I.—Vaughan's procedure for the determination of silicon in aluminium alloys.[10]

Procedure II.—Protsenko's procedure for the determination of silica in blast furnace slags.[11]

Procedure III.—Sherrington's procedure for the determination of silicon in steels.[12]

In all cases zero silicon blank was considered.

Influence of Temperature and Time Intervals on the above Procedures

A number of experiments were conducted to make an assessment of the influence of various temperatures and time intervals on the colour intensities at different concentrations of silicon. The results are presented in Tables I, II and III.

(*a*) *Influence of temperature.*—An examination of these tables shows:

(i) At various temperatures and concentrations investigated, the intrinsic values of the colour intensities in the three procedures follow the order Procedure I > Procedure III > Procedure II.

(ii) At temperature 30° C. and above there is a distinct decrease in the intensities of the colour in case of all the procedures, though to different extents. This effect progressively increases with increase in the temperature.

(iii) At any particular temperature above 30° C. the influence of temperature on the various procedures follows the order Procedure I > Procedure II > Procedure III.

(*b*) *Influence of time intervals.*—Time intervals after the addition of reducing agent do not exert any influence on the colour intensities involved at 20° C. At temperature 30° C. and above, the colour intensities show a gradual decrease with increase of time intervals, the rate of decrease being higher, the higher the temperature. Even at some of these higher temperatures, the effect does not show itself right from the beginning but only after certain time intervals. Further increase of time beyond these limits tends to make the influence more pronounced. This time interval is progressively shortened with increase of temperature. Such effect of time is considerable in Procedure I and least in Procedure III.

It is thus clear that temperature and time intervals have distinct influence on the colour intensities involved in all the procedures examined, though to different extents. The methods employed for the development of colour in the procedures under consideration differ in essence only in the choice of the reducing agent and the medium in which the silicomolybdate is subjected to reduction. Procedures I and II have sulphuric acid in common as the medium with two differing reducing agents, *viz.*, stannous chloride and ferrous ammonium sulphate. A comparison of the results obtained in these cases shows that the use of stannous chloride as reducing agent leads to a more pronounced effect. On the other hand, Procedures II and III have the reducing agent, *viz.*, ferrous ammonium sulphate in common. Different media, *viz.*, sulphuric and oxalic acids have been employed. In Procedure III where oxalic acid is used the effect of time and temperature is considerably less significant.

It is thus evident that the extent of the influence of temperature on the procedures is governed by both the factors, namely the reducing agent as well as the medium. By choosing a proper medium for reduction and appropriate reducing agent it may be possible to evolve a satisfactory procedure applicable to various temperatures likely to be encountered in tropics. With this end in view some exploratory work was carried out employing the remaining combinations of reducing agents and media. This did not show much promise.

As an alternative reducing agent ascorbic acid[13-15] has shown considerable promise and hence it has been tried in an exhaustive manner. The results obtained at two temperatures (20° C. and 45° C.) and two time intervals (15 and 45 minutes) only are presented in Table IV.

It can be readily seen from Table IV that even though ascorbic acid gives slightly lower colour intensities as compared with stannous chloride, it results in the striking advantage of freedom from influence of temperature.

Based on an incidental observation that the initial acid concentration exerts considerable influence in Procedure III, this aspect has been well examined employing various reducing agents. It has been found that slight changes in the initial acid concentration do not influence the results when ascorbic acid is used as a reducing agent.

TABLE I

Photometric determination of silicon: Effect of temperature—Procedure I

Kodak filter No. 8 (680 mμ), Water setting ·120, Cell: 1 cm.

Silicon content / Temp.	Drum difference: 15 minutes					20 minutes					30 minutes					45 minutes				
	20°C.	30°C.	35°C.	40°C.	45°C.	20°C.	30°C.	35°C.	40°C.	45°C.	20°C.	30°C.	35°C.	40°C.	45°C.	20°C.	30°C.	35°C.	40°C.	45°C.
200 μg.	79·7	78·0	76·7	73·2	66·0	79·5	77·7	75·1	69·7	63·5	79·3	74·7	73·0	66·5	59·4	78·8	72·6	69·2	62·5	56·2
100 μg.	38·5	35·7	35·6	33·2	30·0	38·5	35·5	35·0	32·2	29·4	37·8	34·5	33·2	31·0	27·0	37·4	33·1	31·0	28·5	25·4
40 μg.	15·0	12·7	12·7	11·7	11·0	15·0	12·5	12·7	11·2	10·6	15·0	12·4	11·9	10·7	9·2	15·0	11·8	10·9	9·7	8·4
20 μg.	7·0	5·7	5·7	5·7	4·7	7·0	5·7	5·7	5·0	4·4	6·9	5·4	5·2	5·0	3·4	7·0	5·4	4·6	4·4	3·2

All temperatures are ± 1° C.

TABLE II

Photometric determination of silicon: Effect of temperature—Procedure II

Kodak Filter No. 8 (680 mμ), Water setting 120, Cell: 1 cm.

Silicon content / Temp.	Drum difference: 15 minutes					20 minutes					30 minutes					45 minutes				
	20°C.	30°C.	35°C.	40°C.	45°C.	20°C.	30°C.	35°C.	40°C.	45°C.	20°C.	30°C.	35°C.	40°C.	45°C.	20°C.	30°C.	35°C.	40°C.	45°C.
200 μg.	50·1	49·0	47·8	42·5	40·5	50·3	49·0	47·8	42·5	40·5	50·3	49·0	47·8	42·5	40·5	50·3	48·8	47·8	42·5	40·4
100 μg.	25·1	24·2	23·7	21·5	20·0	25·1	24·0	23·7	21·5	20·0	25·1	24·0	23·7	21·5	20·0	25·1	24·0	23·7	21·5	20·0
40 μg.	8·1	7·9	7·7	7·4	6·9	8·1	7·9	7·7	7·4	6·9	8·1	7·9	7·7	7·4	6·9	8·1	7·9	7·7	7·4	6·9
20 μg.	4·5	4·5	4·3	4·0	3·8	4·5	4·5	4·3	4·0	3·8	4·5	4·5	4·3	4·0	3·8	4·5	4·5	4·3	4·0	3·8

All temperatures are ± 1 C.°

TABLE III

Photometric determination of silicon: Effect of temperature—Procedure III

Kodak Filter No. 8 (680 mμ), Water setting 120, Cell: 1 cm.

Silicon content / Temp.	Drum difference																			
	15 minutes					20 minutes					30 minutes					45 minutes				
	20°C.	30°C.	35°C.	40°C.	45°C.	20°C.	30°C.	35°C.	40°C.	45°C.	20°C.	30°C.	35°C.	40°C.	45°C.	20°C.	30°C.	35°C.	40°C.	45°C.
200 μg.	63·1	62·8	61·6	61·1	60·2	62·9	62·8	61·6	61·3	60·0	62·7	62·0	60·8	60·2	59·3	62·2	61·8	59·7	58·8	58·2
100 μg.	28·9	28·9	28·5	28·1	27·8	28·9	28·8	28·5	28·1	27·7	28·6	28·8	28·0	27·3	27·8	28·2	27·5	27·5	27·3	27·8
40 μg.	9·3	9·3	9·3	9·0	9·0	9·3	9·3	9·0	9·0	8·9	9·2	9·2	8·8	9·0	8·7	9·1	9·1	9·1	8·8	9·0
20 μg.	5·3	4·8	5·2	4·7	5·0	5·2	5·0	5·1	4·7	5·0	5·1	4·9	4·7	4·5	5·0	5·0	4·9	4·5	4·5	5·0

All temperatures are ± 1° C.

TABLE IV

Photometric determination of silicon: Effect of temperature

Reducing agent: Ascorbic acid. Kodak Filter No. 8 (680 mμ), Water setting 120, Cell: 1 cm.

Silicon content / Temp.	Drum difference											
	Procedure I				Procedure II				Procedure III			
	15 mts.		45 mts.		15 mts.		45 mts.		15 mts.		45 mts.	
	20°C.	45°C.	20°C.	45°C.	20°C.	45°C.	20°C.	45°C.	20°C.	45°C.	20°C.	45°C.
200 μg.	58·8	59·0	59·4	59·0	58·3	58·2	58·0	58·4	58·0	57·5	58·5	57·5
100 μg.	27·2	27·5	27·7	27·7	27·3	27·2	27·3	27·4	27·0	27·0	27·5	27·2
40 μg.	10·5	10·0	10·4	9·8	9·8	9·7	9·9	9·9	8·6	9·0	9·0	9·0
20 μg.	5·5	5·3	5·7	5·2	4·8	4·7	4·8	4·9	5·2	5·0	5·5	5·1

All temperatures are ± 1° C.

The main features of our findings may, therefore, be stated as follows:

(i) The use of stannous chloride as reducing agent results in increasing colour intensities involved. It also results in a marked influence of temperature and time on the colour intensities in Procedures I and II. In case of Procedure III there is a considerable reduction in the influence of temperature and time, though slightly lower colour intensities have been obtained. It is, however, imperative that the initial acid concentration should be rigidly controlled.

(ii) When ferrous ammonium sulphate is used as a reducing agent the colour intensities are of much lower order and are also appreciably influenced by temperature and time intervals in Procedures I and II. This influence is very much reduced in case of procedure III and practically disappears at lower silicon concentrations (less than 40 μg.). This, therefore, lends itself for successful adoption, provided the silicon concentrations are kept sufficiently low and the initial acid concentration is properly maintained.

(iii) Judging from the influence of temperature, both stannous chloride and ferrous ammonium sulphate seem to be unsatisfactory as reducing agents in the different media employed in the investigation. However, the oxalic acid medium affords a distinct advantage over the sulphuric acid medium.

(iv) The use of ascorbic acid as a reducing agent has resulted in some important observations and there is practically no influence of temperature and time intervals on the colour intensities in all the procedures under consideration.

Acknowledgements

Our thanks are due to the management of the Tata Iron and Steel Company for permitting the publication of this paper.

References

1. Thompson, T. G. and Houlton, H. G. — *Ind. Eng. Chem. Anal. Ed.*, 1933, **5**, 417.
2. Stumm, J. T. .. *Proc. Am. Soc. Testing Materials*, 1944, **44**, 749.
3. Hill, U. T. .. *Anal. Chem.*, 1949, **21**, 589.

4a. Straub, F. G. and Grabowski, H. A. — *Ind. Eng. Chem. Anal. Ed.*, 1944, **16**, 574.

4b. Sanders, W. F. and Cramer, C. H. — *Anal. Chem.*, 1957, **29**, 1139,

5. Milton, R. F. .. *Analyst*, 1951, **76**, 431.
6. Greenfield, S. .. *Ibid*, 1959, **84**, 380.

7. Murty, G. V. L. N. and Sen, N. C. *Curr. Sci.*, 1948, **17**, 363.

8. ——— .. *Metallurgia*, 1952, **45**, 53.

9. Murty, G. V. L. N. .. *Ibid.*, 1958, **58**, 52.

10. Vaughan, E. J. .. "Further Advances in the use of Spekker Photoelectric, Absorptiometer in *Metallurgical Analysis Monograph*, Institute of Chemistry, 1942, pp. 11, 12 and 13.

Metallurgical Analysis by Means of Spekker Photoelectric Absorptiometer, by Haywood, F. W. and Wood, A. A. R., Adam Hilger Ltd., London, 1944, p. 103.

11. Protsenko, P. T. .. *Zavodskaya Laboratoriya*, 1957, **23**, 911.

12. Gentry, C. H. R. and Sherrington, L. G. *J. Soc. Chem. Ind.*, 1946, **65**, 90.

13. Gibson, M. .. *Harwell Atomic Energy Research Establishment Report*, 1950, *C/R* 521.

14. Boulin, R. .. *Compt. rend. Congr. intern. Chim. Ind.*, 1959, **1**, 142–6.

15. Baczyk, S. .. *Chem. Anal. (Warsaw)*, 1960, **5**, 3–11.

16. Murty, G. V. L. N., Krishnaiah, K. S. R. and Raju, M. S. *Curr. Sci.* 1965, **34**, 561.