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## MOLYBDENUM BLUE METHOD DETERMINATION OF SILICON IN AMORPHOUS SILICA

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**Abstract:** The determination of Silicon (Silica) in materials using the Molybdenum blue reaction was studied. The UV-Visible spectrophotometer scanning for the silicon molybdenum blue reaction was studied between a wavelength of 400nm and 800nm. The instrumental analytical procedure applied consists of four basic parts: the sample pretreatment, the instrument adjustment, the calibration and measurement and the calculations. The instrument was optimized using standard solution of  $KMnO_4$  with conventional calibration method applied. The performance characteristics of the spectrophotometer at a wavelength of maximum absorption ( $\lambda_{max}$ ) of  $825 \pm 5nm$  for the silicon-molybdenum blue analysis are observed. The procedure was applied to amorphous silica produced from glass sand and the findings were observed to correspond with existing standard.

**Keywords:** Molybdenum blue reaction, Performance characteristic, Instrument optimization, Silicon

### INTRODUCTION

Silicon analysis is of great importance in environmental and industrial monitoring application. Its presence in material is usually estimated by calorimetric (spectrophotometric) method. The overall high concentration and strong tendency to form stable silicides with many element makes silicon a very important material (as impurity) in high purity materials. For similar reason, its determination at trace levels have been documented to be difficult [6].

A very sensitive method in which silicomolybdic acid is formed and then reduced to molybdenum blue is now used for the determination of silicon in trace amounts in materials e.g. sea water, potable water, biological samples and other materials. Several procedures have been published for the determination of silicon in different materials using the molybdenum blue method as reported in literature [1,3,8,11,12]. The variations can be seen in the sample dissolution, conditions of the silicomolybdic complex formation and reduction, reducing agents and other reagents.

The molybdenum Blue Silicon method in conjunction with a UV-visible spectrophotometer is a standard analytical method [7] with Association of Analytical Chemist (AOAC) approval [12]. It is easy, especially after reducing the yellow molybdic acid to the blue thus forming a stable complex that allows for sample analysis and direct determination.

Methods suitable for detailed description in an analytical procedure are either non-instrumental or makes use of instruments that are easily adjustable. Methods for the determination of trace amounts of analyte, lack the necessary sensitivity that must be replaced by relative methods of analysis. This typically involves the measurement

of a physical property that through comparison with known reference solution is then converted to a value for the concentration of the component to be determined in the sample [12].

UV-Visible spectrophotometer is a good example of a relative method of analysis. It requires an instrumental adjustment (optimization) that can be easily described and is usually not very critical consequently; the measured absorbance is nearly independent of the instrument used. Remaining minor variations between different instruments can usually be accounted for in the calibration graph prepared from reference solutions [12].

### MOLYBDENUM BLUE METHOD

The acidification of solutions having molybdate ion and silicate form a yellow crystalline precipitate known as molybdosilicate (silicomolybdic acid) [1,9,11]. When there is selective reduction, using reducing agents such as hydrazinum sulphate, 1-amino-2-naphthol-4-sulphonic acid [11] and others, a blue color is produced due to Molybdenum Blue of uncertain composition.

The intensity of the blue color is proportional to the amount of silicate initially incorporated into the heteropoly acid. This is the basis for the use of the Molybdenum blue method in quantitative and qualitative analytical technique [8].

This is peculiar to hetero atoms whose ion forms heteropoly acids such as tungstate, Phosphate, germanate and arsenate. These heteropoly acids may be present as interferences and must be suppressed by introducing masking agents such as oxalic acid, citric acid and tartaric acid [3, 6].

This work presents the determination of the silicon in the amorphous silica produced from glass sand and characterized by a metallurgical

microscope, XRD & EDXRF [10]. Considering the fact that, a standard analytical method is needed for the determination, it was subjected to the silica-molybdenum blue reaction using ascorbic acid as the reducing agent and analyzed using the UV-Visible spectrophotometer. The UV-Visible spectrophotometer was optimized using  $KMnO_4$  as a standard carried out with the normal calibration method [2].

**MATERIALS AND METHOD**

**Safety**

The Material Safety Data Sheet (MSDS) for the detailed information and safety precautions for all the chemical reagents used in addition to the appropriate safety sections in the instrument manual was reviewed and applied.

**Reagents**

Silicon Standard Solution was used in Atomic Absorption Spectrophotometer (AAS) Standard. Acidified Molybdate Solution of Analytical grade was formed by diluting Ammonium Molybdate  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  in HCl. This solution was prepared fresh each day. Ascorbic acid, Oxalic acid solution (5%  $m/v$ ), Glycerin solution (1%  $v/v$ ). All the reagents used are of an analytical grade. The sand used in this work is the glass sand sourced from Igbokoda, Ondo State, Nigeria. Amorphous silica was produced from this sand by fluxing the acid-washed sand with NaOH at an elevated temperature in furnace specifically designed and developed for this work, which produced a yield of 82.5%.

**Apparatus/Instrument**

UV-Visible spectrophotometer, 1cm quartz cell and a wavelength range of 190 – 1100nm.

**Procedure**

All reagents having silicon was stored in a polyethylene container. Also all glassware was treated with acid to avoid introduction of silicon and all reagents were prepared using silicon-free deionized water.

**Blank solution:** The blank solution was prepared by pipetting 1ml of acidified ammonium molybdate solution, 5ml of oxalic acid solution. 1ml of ascorbic acid, 1ml of 1% ( $v/v$ ) glycerin and made up to mark with silicon-free deionized water.

**Standard working solutions:** silicon molybdenum blue mixtures containing 0.1, 0.2, 0.4, 0.6, 0.8, 1.0  $mgdm^{-3}$  of the standard silicon stock solution was made by dilution method after pipetting appropriate aliquot of the stock for a 5  $mgdm^{-3}$  concentration and reacting with other reagents as in the blank.

**Scanning of the spectrophotometer with silico-molybdenum reaction [Determination of  $\lambda_{max}$ ]**

6ml standard silicon stock solution was measured. 3ml of acidified ammonium molybdate (yellowish in color) was added. After 5mins, oxalic acid, ascorbic acid, and glycerin solutions were sequentially mixed in a predetermined order and proportion. The mixture was made up to 100ml mark with deionized water and immediately transferred into a polyethylene container and left for 20mins for blue color development.

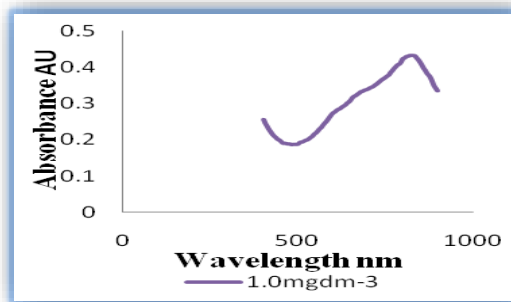


Figure 1: Spectrum of Molybdenum Blue reaction at  $825 \pm 5nm$ . The mixture was introduced into 1cm quartz cuvette of the spectrophotometer and scanned between 400 – 800nm wavelength. The blank solution was used to establish a baseline in the instrument. A fit of absorbance against wavelength gave the spectrum of the reaction as shown in Figure 1.

**Spectrophotometric determination of silicon in amorphous silica using molybdenum blue reaction**

0.1000g of the silica was weighed accurately into a porcelain crucible in a fume hood. 1ml of water and 2mls of hydrofluoric acid (HF) was introduced into the sample drop-wise. The mixture was gently swirled until dissolved in accordance to Vogel [8].

3ml of acidified ammonium molybdate was added to the dissolved sample. After 5mins, 5ml oxalic acid, 1ml of 0.04m ascorbic acid and 1ml of 1% glycerin solutions were added one after the other. The mixture was made up to 100ml mark with deionized water and immediately transferred into a polyethylene container and left for 20mins for blue color development.

The absorbance of the sample was measured at  $\approx 825 \pm 5nm$  against a reagent blank sample. The corresponding silicon concentration of the amorphous silica sample was deduced from the calibration curve by interpolation and the percentage silicon was calculated.

**RESULT AND DISCUSSION**

The absorption spectrum for the molybdenum blue reaction showed maximum absorption ( $\lambda_{max}$ ) at  $825 \pm 5nm$ . The scanning of the instrument gave standard results as shown in Table 1.

Table 1. Normal Calibration Data for Standard results at  $825 \pm 5nm$

Absorbance (AU)	Concentration ( $mgdm^{-3}$ )
0.000	0.0
0.027	0.1
0.141	0.2
0.201	0.4
0.258	0.6
0.350	0.8
0.433	1.0
0.520	1.2
0.606	1.4
0.693	1.6
0.866	2.0
0.930	4.0
0.970	6.0

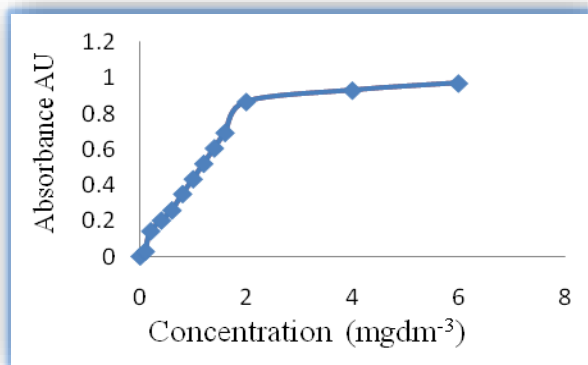


Figure 2. Graphically illustrates of the normal calibration data for standard results at  $825 \pm 5\text{nm}$

Microscopic analysis of the silica showed a resolved 2-D imaging at a magnification of 200x of a particle size of 1.5 $\mu\text{m}$  agglomerates on drying (Figure 3a). X-ray diffraction pattern showed diffraction maxima  $25^\circ$  and base width between  $22^\circ$  and  $30^\circ$  ( $2\theta$ ) and the quantitative analysis of the elemental composition (Figure 3b) was done by using Energy Dispersive X-ray florescence model [XR–100CR] following a standard technique [10].



Figure 3(a): Optical Micrograph of the particles of silica gel at magnifications of 200X viewed using metallurgical microscope (AP2000 MTI). The micrographs showed that the particle sizes are on a micro particle scale of about 1.5 $\mu\text{m}$ . The shape of the particle was found to be uniform and agglomerated.

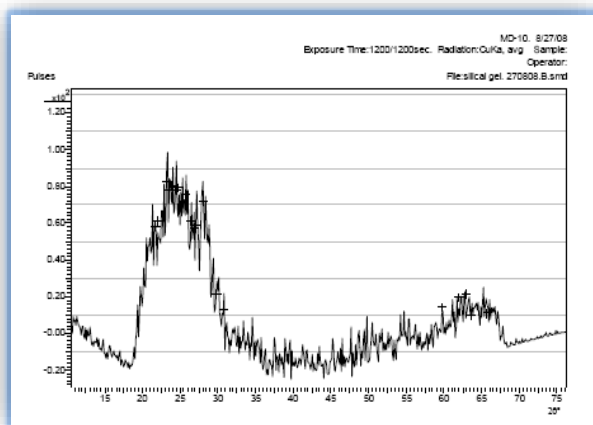


Figure 3(b): XRD diffractogram (MD 10) of amorphous silica

A linear correlation was obtained between concentration and absorbance giving a linear range of 0.00 – 2.00  $\text{mgdm}^{-3}$  was observed from the plot in Figure 2 above. The slope of the calibration curve was determined to give the sensitivity of the instrument for silicon determination as  $0.438\text{AU mg}^{-1}\text{dm}$ , with a molar absorptivity of  $3.540 \times 10^7 \text{AU mol}^{-1}\text{dm}^3\text{cm}^{-1}$ . The detection limit is calculated by analyzing a  $0.4 \text{mgdm}^{-3}$  standard and reagent blank 8 times. Using 3 times the standard deviations  $D_L = (n, 3s.d)$  confident limit, giving a detection limit of  $0.002 \text{mgdm}^{-3}$ . The concentrations of the standards were chosen such that their absorbance bracketed the absorbance of the sample. By interpolation, the concentration of the sample with absorbance 0.427 AU and 0.219 AU gave  $0.99\text{mgdm}^{-3}$  and  $0.49\text{mgdm}^{-3}$  respectively.

The wavelength of maximum absorption (as shown in Figure 1) was taken as  $825 \pm 5\text{nm}$ . This was because the absorption peaks for the reaction appeared for some reaction mainly between 820 – 830nm and average was taken. It was also observed that with different Ammonium molybdate  $(\text{NH}_4)_6\text{MO}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  having different assays, different points of maximum absorption can be obtained e.g. Fisher product gave 815nm and AVIS chemical gave  $825 \pm 5 \text{nm}$ . This corresponds to reported range in literature. It changes color and throws down precipitate after 1 or 2days and so must be prepared fresh before use daily.

Preparations of the standard solution of the molybdenum blue are better done by dilution method. This is due to variations in the absorbance which could be caused by pH considerations and colloidal formations when direct preparations are made.

### CONCLUSION

After thorough investigation in this work, it was observed and concluded that the UV-Visible spectrophotometer determination of silicon using the molybdenum blue reaction provides a standard method of confirming the presence of silicon in materials.

This work will therefore provide more literature for silicon determination and given a good understanding and behavior of the Ammonium molybdate produced by different sources.

### REFERENCES

- [1] Adeeyinwo C. E and Adesina K. (2002), "Performance characteristic of visible spectrophotometer in Analyzing silicon" *Journal of Applied Sciences* 5(4), p 3139 – 3147.
- [2] Adeeyinwo, C. E., Okorie, N. N. and Idowu, G. O. (2003), "Basic Calibration of UV/visible spectrophotometer" *International Journal of Science and Technology*, vol 2 No. 3, pp. 247-252.
- [3] Armstrong F. A. J (1951), "The determination of silicate in sea water" *Journals of Marine Biological Association of the United Kingdom*. Vol 30 No 1 pg 149 – 160.
- [4] Dyck et al (2000), "Spectrometric determination of silicon in food and biological samples and interlaboratory trial" *Journal Anal. Spectrom*, Vol. 15, pp. 735- 741.
- [5] Hioki A., Lam J.W., and McLaren, J.W. (1997), "On-line determination of dissolved silica in seawater by ion exclusion chromatography in combination with inductively coupled plasma mass spectrometry" *Anal Chemistry*, volume 69 issue 1, pp 21 – 24.

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- [6] Hornung M. and Krivan V (1997), "Determination of silicon in biological tissue by electrothermal Atomic Absorption Spectrometry using slurry sampling of original and pre-ashed samples" *Journal of Analytical Atomic Spectrometry* Vol. 12, pp 1123-1130.
- [7] Lim P. G. (2005), "Total silica Analysis using a double beam Atomic Absorption Spectrophotometer" *Proceedings World Geothermal Congress, Anataly, Turkey*, pp. 24-29.
- [8] Jeffery G.H., Basset J., Menham J., Denney R.C. (1909): *Vogel's Textbook of quantitative chemical analysis. 5<sup>th</sup> Edition Revised. Published by Bath Press, Avon, Great Britain. Pp 309-342.*
- [9] Mondal J. K. and Kundun D (2009), "Spectrometric determination of trace silica in water after enrichment on polyurethane foam and complexation with Rhodamine B" *EJAC, Eurasian J. Anal chemistry. 4(1)* pg 46 – 52.
- [10] Okorie N.N. (2012) "validation of uv-visible spectrophotometric method for the analysis of prepared amorphous silica using developed method" *A thesis submitted for masters programme at Federal University of Technology, Akure.*
- [11] Rajkovic D (1997), "Spectrophotometric determination of traces of silicon as molybdenum blue in uranium dioxide" *Freseuius' Journal of Analytical Chemistry, vol. 225, No 3, pp 190 – 194.*
- [12] Van dalen H. P. J and Galam Leo De (1981), "Formulation of Analytical procedures involving flame Atomic - Absorption Spectrometry" *Analyst, Vol 106 pp 695 – 701.*



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