

A KINETIC SEQUENTIAL INJECTION ANALYSIS METHOD FOR SILICATE DETERMINATION IN WATER SAMPLES CONTAINING PHOSPHATES

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ABSTRACT

This manuscript describes the adaptation of Sequential Injection Analysis (SIA) for the determination of silica in boiler feed water containing phosphates as a routine method being adopted to a Petrochemical industry in Saudi Arabia (Ibn Zahr). The method is based on the reaction of ammonium molybdate with silica to form an intensely yellow complex (ammonium molybdosilicates) which is reduced to blue complex monitored spectrophotometrically at 813 nm. A comparison was made on the effectiveness of triammonium citrate and oxalic acid to eliminate phosphate by rendering it innocuous. Interference study of phosphate on this method was also studied. The sensitivity of the method was enhanced by sandwiching the reagents in the holding coil between two samples of 100 μ L volume each and dispensing to the detector at a flow rate of 10 μ L/s. The Reagent and samples were stacked into four distinct zones in a 190 cm long holding coil. Another 190 cm long reaction coil was used to ensure more uniform mixing of samples and reagent by radial dispersion. The sensitivity was further enhanced by heating the holding coil at 60 C in a thermostated water bath. To maximize zone penetration while minimizing dilution of the sample the reaction mixture was delayed at the holding coil for 3.53 mins (fixed time kinetic method). The effect of delay time, flow rate, temperature and volume of analyte and reagents on the sensitivity of this method was also studied. The linear working range is 0.5 ppm to 50 ppm. The detection limit is 0.5 ppm with a sample through put of 10 samples/hour. The method was validated by comparison with (APHA) batch spectrophotometric method. The results were found to be in agreement with these methods thus indicating accuracy. The method described has good reproducibility, rapid and suitable for online and in situ determination.

Keywords: Silica, Sequential Injection, Delay time

INTRODUCTION

The determination of silica in water samples is very important in the industry because silica deposits on stream turbine blades at high pressure and temperature. This lowers the efficiency of heat transfer, leading to costly down time for cleaning and may result to total failure of the boiler system. Phosphates is usually added to the boiler feed water to ensure that it's in the alkaline range, this serves as an anticorrosion measure [1]. Phosphates react similarly with reagents used for silica determination to give the same colored product; this poses a serious interference problem for the colorimetric determination of silica in the presence of phosphate. This interference problem is especially challenging when analyzing very low concentration of silica. For the proposed SIA method, triammonium citrate was used to discriminate silica from phosphates by chelating phosphates from the molybdate complex [2]. Oxalic acid has also been used to eliminate phosphate interference, it was reported that the concentration of oxalic acid greatly determines its selectivity for phosphates or silica. Oxalate concentration of the order of 10% (w/v) prevents phosphate interference, while lower concentration of 0.25% (w/v) avoids the formation of molybdosilicic acid [3]. Mixing of sample and three different reagents in the holding coil of the SIA manifold is usually challenging as four distinct zones are formed in the holding coil. Galhardo and Masini used an

auxiliary reaction coil for effective mixing of silicates samples and reagents for the determination of phosphates and silicates by SIA; they suggested that 3 holding coils are necessary for SIA with 3 reagents [4]. For this proposed SIA method two holding coil, delay time, sandwiching of reagents with silica samples and flow reversal were used to promote mixing of silica samples with reagents in the holding coil. The correlation coefficient obtained for silica determination without sandwich of samples and reagents was less than 0.900, this value increased to 0.999 on applying sandwich of sample and reagent, suggesting improved accuracy of the SIA method. Delay time has the advantage of promoting zone penetration while minimizing dispersion and hence increasing the sensitivity of the method.

Several flow/sequential injection methods have been reported for the determination of silica. A spectrophotometric method for the simultaneous determination of silica and phosphates using molybdenum chemistry by sequential injection has been reported [4]. Silica in sea water has been determined by flow injection as silicic acid, based on the formation of beta silicomolybdic acid reduced with tin(II) chloride to form an intense colored molybdenum blue[5]. Li, et al proposed a Flow injection method for the simultaneous determination of silicates and phosphates in boiler water at power plants based on a series flow cell by using flow injection spectrophotometry[1]. Grudpan et al used stopped flow injection for the simultaneous determination

of phosphate and silicates using molybdenum blue [6]. Yaqoob et al determined silica in fresh water using flow injection with luminal chemiluminescence detection [7].

Most industries use the conventional batch spectrophotometric method for the analysis of silica. Silicate analysis by the conventional batch spectrophotometric method is tedious, consumes more reagents, waste time and highly prone to errors because of the difference in time absorption measurements are taken for each samples. All these errors are minimized by using sequential injection which uses a flow program, ensuring accurate reproducible conditions for each sample analyzed.

The proposed SIA method is based on the reaction of silica with ammonium molybdate to give a yellow complex. Phosphate interference is destroyed by use of triammonium citrate and subsequent reduction with a mixture of sodium sulphite/1-amino-2-naphthol-4 sulphonic acid to give the blue complex which is monitored spectrophotometrically at 813 nm. A comparison of the effectiveness of oxalic acid and triammonium citrate to destroy phosphate interference was made, the effect of delay time, sample volume, reagents volume, flow rate, temperature and phosphate interference were also studied.

2. Experimental

All reagents were prepared from analytical grade chemicals. Distilled water used was deionised and then degassed. All reagents were prepared and stored in polythene vessels.

2.1 Preparation of reagents and standard sample solutions.

1. Silica stock solution: 0.3530g of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ was dissolved in distilled water and diluted to one Liter to give 100ppm of SiO_2 . Series of standards for the experiments were prepared from the stock solution.
2. Ammonium molybdate solution: 10 g ammonium molybdate tetra hydrate were dissolved in a 100 ml of distilled water. Heated slightly in water a bath until clear solution was obtained
3. Hydrochloric acid (6M), 1+1, 25 ml of concentrated hydrochloric acid was taken and diluted to 50 ml standard flask
4. Ammonium molybdate reagent: 100 ml of ammonium molybdate solution was mixed with 50 ml of 1+1 HCl solution.
5. Triammonium citrate reagent: 10 g of triammonium citrate was dissolved in distilled water and diluted to 100 ml in a standard flask
6. Reducing Agents
Solution A: 10 g sodium bisulphate (NaHSO_3) was dissolved in 70 ml water.
Solution B: 0.8 g of NaHSO_3 and 0.16g 1-amino-2-naphthol-4-sulphonic acid were dissolved in 20 ml distilled water.
Solutions A and solution B were mixed and the total was made up to 100 ml in a volumetric flask, filtered and stored in air tight polyethylene container.

2.2. Apparatus

The manifold used in this method consists of SIA combined with a fiber optic spectrometer. The SIA system is the *FIALab 3500* (Medina, WA USA). It is composed of a syringe pump, a multi-position valve, a Z-

flow cell with SMA fiber optic connectors as well as pump tubing and PC. The *Syringe Pump* is 24,000 steps with an optical encoder feedback and 1.5 seconds to 20 minutes per stroke of 2.5 ml size. It is > 99% accuracy at full stroke. The volume capacity of syringe is 2500 μl . The *Multi-Position Valve* has eight ports with a standard pressure of 250 psi (gas)/600 psi (liquid); zero dead volume; chemically inert; port selection is usually done using the software program. The *Z-Flow Cell* is 10 mm path length plexiglass compatible with standard SMA terminated fiber optics was used. *Pump Tubing* of 0.30" ID Teflon type supplied by Upchurch Scientific, Inc. (Oak Harbor, WA, USA) was used for connecting the different units; and making both the holding coil (190 cm long) and the reaction coil (190 cm long).

The fiber optic spectrometer is composed of a light source, 200 micron fiber optic connectors and a detector. The light source is *LS-1 Tungsten Halogen* (Ocean Optics, USA) optimized for VIS-NIR (360nm-2 μm) wavelength range. The detector is *USB2000 Spectrometer* (Ocean Optics, USA) adapted to 200-1100nm wavelength range. The SIA manifold is illustrated below.

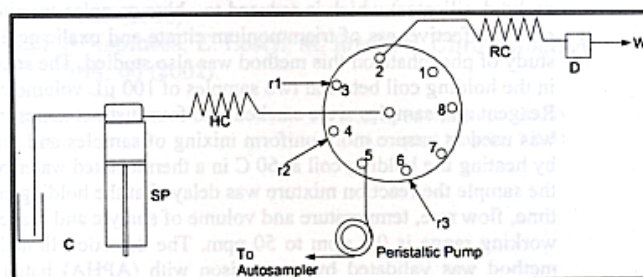


Fig1. SIA manifold

C = carrier (distilled water), SP = syringe pump, HC = Holding coil, r1 = Ammonium molybdate reagent, r2 = triammonium citrate, r3 = sodium sulphite/aminonaphthol reducing agent, P = peristaltic pump, RC = reaction coil, D = detector, W = waste

2.3. Software Packages

FIALab for Windows version 5.0 from FIALab® (Medina, WA USA) was utilized for programming, controlling the SIA manifold and data acquisition.

2.4. Method and Procedure

The following steps are the protocol applied for analysis of Silica in water:

- i. Working solutions of ammonium molybdate/HCl solution, triammonium citrate, sodium sulphite/1-amino-2-naphthol-4-sulphonic acid and samples containing silica were linked to the selector valve through ports 3, 4, 6, and 5, respectively and also water as a carrier was linked to the syringe at the in-position valve.
- ii. The auto sampler probe was directed to sample vial, the peristaltic pump switched on, rotated clockwise at 70% for 40 s to propel sample and flush sample tubing.
- iii. The syringe was filled with 2500 μl of the carrier by directing the two-way valve to the (in-position) mode with flow rate of 100 $\mu\text{l s}^{-1}$.
- iv. Tubes were loaded with their respective reagents by performing aspiration runs and directing the two-way valve to the (out-position) mode with flow rate of 50 $\mu\text{l s}^{-1}$.

- v. With a $100 \mu\text{L s}^{-1}$ flow rate, the syringe was emptied and step II was repeated.
- vi. The following volumes were sequentially aspirated and delayed in the holding coil: $100 \mu\text{L}$ volume of sample, $40 \mu\text{L}$ ammonium molybdate/ HCl solution delayed for 60 s, $40 \mu\text{L}$ of triammonium citrate delayed for 30 s, $40 \mu\text{L}$ sulphite/1-amino-2-naphthol-4-acid solution delayed for 60 s and another $100 \mu\text{L}$ of sample delayed finally for 120s.
- vii. With a flow rate adjusted at $10 \mu\text{L s}^{-1}$, a $2000 \mu\text{L}$ volume was dispensed to the Z-flow cell passing through the reaction coil and, simultaneously, the reference and absorbance scan were performed by the spectrometer at 813 nm wavelength and the maximum value of the monitored peak was recorded as absorbance.

3. Results and discussion

3.1 Optimization of Parameters

The method for the determination of silica in the presence of phosphate by Sequential injection was optimized using the uni-variate method approach. The parameters optimized were delay time, flow rate to detector, volume of sample, volume of reagents and temperature. A standard solution containing 10 ppm silica was used for all optimization procedure.

3.1.1 Delay Time

This method makes use of the delay time to ensure zone penetration in the holding coil while at the same time promoting chemistry between samples and reagents. Higher Delay time ensures more intensely colored products formation; this subsequently enhances the sensitivity of the method. The delay time was varied between 1.83 mins to 6.50 mins. The optimum delay time was observed at 3.53 mins. One would expect the absorbance to keep increasing after optimum time is reached. This was found not to be the case due to dispersion taking place in the holding coil which increases with time.

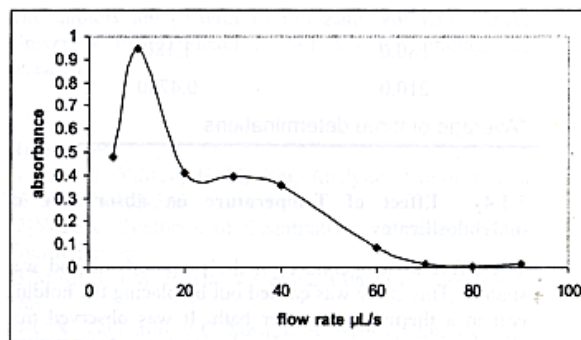
Table 1 Effect of delay time on the absorbance of molybdosilicate

Delay time (min)	Absorbance*
1.83	0.528
2.17	0.542
2.50	0.770
2.83	0.823
3.53	0.826
4.17	0.759
4.83	0.783
5.50	0.799
6.50	0.615

*Average of three determinations

3.1.2 Flow rate

The flow rate to detector is very important. Low flow rate ensures that the colored products spends more time in the flow cell and absorbance is well measured, It also provides more time for the colored complex to be formed en route to the detector. The optimum flow rate for the proposed SIA method was observed to $10 \mu\text{L/s}$. There was a drop in absorbance at higher flow rate because of high speed of the colored molybdosilicates product through the flow cell and hence very low sensitivity.



* Average of three determinations.

Fig 2 Plot of absorbance versus flow rate

3.1.3 Sample Volume / Combined Reagent Volume

The effect of sample volume and combined reagent volume was studied. The sample volume was varied between 40 to $320 \mu\text{L}$ while the combined reagent volume was varied 30 to $210 \mu\text{L}$. Increasing the volume of sample from $40 \mu\text{L}$ to $200 \mu\text{L}$ increases the sensitivity of this method. More sample volume means more analyte and hence a higher absorbance reading. Above $200 \mu\text{L}$, absorbance decreases due to high sample to reagent volume ratio and increased dispersion. Above $120 \mu\text{L}$ of combined reagent volume, absorbance started to decrease due to the low sample to reagent volume ratio and increased dispersion. The optimum sample volume and combine reagent volume for the proposed SIA method were $200 \mu\text{L}$ and $120 \mu\text{L}$.

Table 2 Effect of sample volume on the absorbance of molybdosilicates

Sample volume (μL)	Absorbance*
40.00	0.4840
80.00	0.6790
120.0	0.6380
160.0	1.540
200.0	1.600
240.0	1.450
280.0	1.220
320.0	1.020

*Average of three determinations

Table 3 Effect of combined reagents volume on the absorbance of molybdosilicates

Reagent volume (μL)	Absorbance*
30.00	0.6440
60.00	0.6740
90.00	1.500
120.0	1.600
150.0	1.340
180.0	1.180
210.0	0.4780

*Average of three determinations

3.1.4 Effect of Temperature on absorbance of molybdosilicates

The effect of temperature on the proposed method was studied. This study was carried out by placing the holding coil in a thermostated water bath. It was observed that absorbance values increased with increase in temperature. Higher temperature speeds up the formation of the blue molybdosilicates complex and hence increases the intensity of the blue colored complex formed. The optimum temperature was 60 C. Above the optimum value, there was a decreased absorbance value probably due to dissociation of the blue colored molybdosilicate blue complex.

Table 4 Effect of temperature on absorbance of molybdosilicates

Temperature (°C)	Absorbance*
20.0	0.567
40.0	0.570
50.0	0.628
60.0	0.675
70.0	0.630

*Average of three determinations

3.1.5 Interference study of phosphate on silica determination and comparison of effectiveness of triammonium citrate and oxalic acid to destroy phosphate interference.

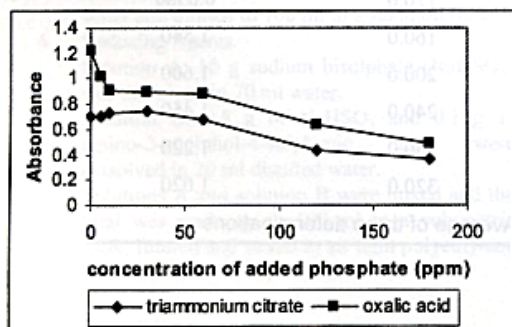


Fig. 3 Comparative study of effectiveness of oxalic and triammonium citrate to destroy phosphate interference
*average of 3 determinations

The interference of added phosphate on this method was studied; a comparison was also made between oxalic acid and triammonium citrate ability to destroy phosphate interference. The concentration of added phosphate was varied between 0, 5, 10,30,60,120,to180 ppm. It was observed that phosphate interference becomes significant at concentrations higher than 60 ppm of phosphates for both oxalic acid and triammonium citrate phosphate destroying reagents. This indicates that either reagent can be used for destroying phosphate interference at a concentration lower than 60 ppm of phosphates. There was a sharp decrease in absorbance values for the first 2 points for oxalic acid plot indicating that at concentration less than 10 ppm of phosphate, triammonium citrate is a more stable phosphate destroying agent than oxalic acid. The concentration of phosphate usually present in the water samples are in the range of 2 to 21 ppm. The higher absorbance values of oxalic acid plot over triammonium citrate plot suggests higher sensitivity with use of oxalic acid as phosphate destroying reagent because the formation of molybdosilicates blue complex is favored in an acidic medium. However, triammonium citrate has been used for the proposed SIA method because it was more stable to changes in the acidity of the medium compared to oxalic acid.

4.1 Method evaluation

4.1.1 Calibration Curve

The linearity of the proposed SIA method for silica determination was studied under optimum conditions described above. The correlation coefficient was 0.9999. The method is linear between 0.5 to 50 ppm. The detection limit was 0.5 ppm. The equation for absorbance measurement was $A = 0.220 + 0.009x$

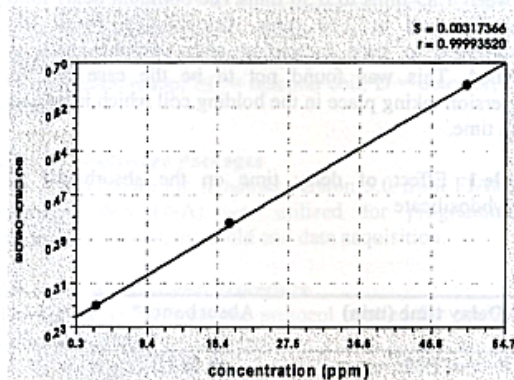


Fig 4 Calibration Curve obtained for silica determination

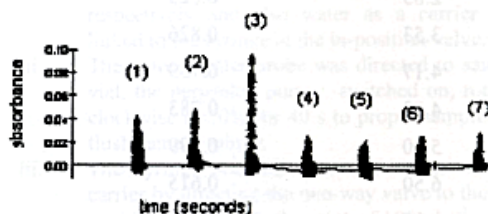


Fig.5 Absorbance versus run time for silica determination with (1) 2 ppm (2) 5 ppm (3) 10 ppm standards, (4) (5) and (6) (7) were obtained from water samples. Results are in duplicates. The concentration of phosphate present in water samples (4) (5) (6) (7) are

usually in the range of 2 to 21 ppm.

4.1.2 Comparisons of results with APHA standard method

The results obtained using the proposed method was compared with standard method of water analysis for silica by American public health association (APHA). The results were found to be in agreement. The calculated t-value was 0.1799 which is less than 2.776 (95% confidence level). The proposed SIA method was found to be more accurate than APHA method at higher concentrations of silica in water.

Table 5 Comparisons of results with APHA standard method

Added (ppm)	Found (SIA method) (ppm)	Found (APHA) (ppm)
3.00	2.91 ± 0.15	2.55 ± 0.07
20.00	20.14 ± 0.24	17.80 ± 0.14
50.00	49.95 ± 0.09	42.90 ± 0.42

*Average of three determinations

5. Conclusion

The proposed SIA method is simple, sensitive, accurate, cost saving, reproducible and avoids the need for dilution of high concentration of silica samples. The sensitivity and linear range of the proposed method is greatly enhanced by delay time and use of 190 cm long tubing for each holding and reaction coil. Sensitivity of this method was further enhanced by placing holding coil in a thermostated water bath.

Triammonium citrate phosphate destroying agent was observed to be more stable to changes in pH and more effective at destroying phosphate interference at low concentration of phosphate.

This method is being employed for the routine determination of Silica in a petrochemical company (Ibn Zahr).

The proposed SIA method was found to be in good

agreement with APHA batch spectrophotometric method (t-value 0.1799). This method is far more precise and accurate than the batch APHA standard method in recording absorbance measurements at fixed time as long as the reaction chemistry involved is time dependent, thus rendering the present methods more favorable for routine analysis.

Acknowledgement

The authors are grateful to Ibn Zahr and King Fahad University of Petroleum & Minerals for funding this research.

References

- [1] Y.-S. Li, Y. Muo, H.-M. Xei, *Analytica Chimica Acta* 455 (2002) 315-325
- [2] Vogel's "Textbook of Quantitative Inorganic analysis Fourth edition
- [3] M. Miro, J.M. Estela, V. Cerda, *Talanta* 60 (2003) 867-886
- [4] C.X. Galhardo, J.C Masini, *Analytica Chimica Acta* 417 (2000) 191-200
- [5] J. Floch, S. Blain, D. Birot, P. Treguer, *Analytica Chimica Acta* 377 (1998) 157-166
- [6] K. Grunpan, P. Ampan, Y. Udnan, S. Jayasvati, S. Lapanantnoppakhun, J. Jakmunee G.D Christian, J. Ruzicka, *Talanta* 58 (2002) 1319-1326
- [7] M. Yaqoob, A. Nabi, P.J Worsfold, *Analytica Chimica Acta* 519 (2004) 137-142
- [8] C.E. Lenchan, N.W. Barnett, S.W. Lewis, *The Analyst* 127 (2002) 997-1020
- [9] M.S. Sultan, *J. Flow Injection* 19 (2002) 109-114
- [10] F. Mas, J.M. Estela, V. Cerda, *Analytica Chimica Acta* 239 (1990), 151-155
- [11] Y. Nurusawa, *Analytica Chimica Acta* 204 (1988) 53-62
- [12] R. Kuroda, I. Ida, H. Kimura, *Talanta* 32 (1985) 353-357
- [13] American Public Health Association, Standard methods for the examination of water and waste water, 19th edition, Water Environment Federation, American Water Works Association.

(Received May 2, 2005)
(Accepted June 3, 2005)