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SEQUENTIAL INJECTION ANALYSIS (SIA) FOR IBN ZAHR WATER QUALITY CONTROL

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ABSTRACT

This manuscript describes the adaptation of Sequential Injection Analysis (SIA) for the determination of silica, iron, ammonia, and phosphates, in water as a routine method being used by the quality control unit of a Petrochemical industry in Saudi Arabia (Ibn Zahr). The results obtained from the adopted SIA methods were found to be in agreement with results obtained from batch spectrophotometric APHA Standard methods (American Public Health Association).SIA has the additional advantage of reducing cost by minimizing time, amount of reagent consumed, man power required and improved accuracy of analysis due to computer aided analysis procedure.

Keywords: Sequential injection, quality control

1. INTRODUCTION

The determination of silica, ammonia, phosphates and iron in water samples is very important in the industry because water is used for a variety of purposes which include feed water for boilers, manufacturing processes and a host of other industrial uses. Most industries use the conventional batch spectrophotometric method for the analysis of these water quality parameters, these batch methods are tedious, reagent consuming, time wasting and highly prone to errors because of the difference in time absorption measurements are taken for each samples. All these errors are minimized by sequential injection analysis which uses a computer aided flow program, ensuring accurate reproducible conditions for each sample analyzed. Several flow injection/sequential injection methods for silica, iron, ammonia and phosphate determination in water have been reported [2-16]. Phosphate and silica in water are very important water quality parameters for boiler feed water determination. Silica in boiler feed water is known to 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 [6]. Accurate and reproducible determination of phosphates and Silica in boiler feed water is highly imperative. Adopting SIA method for phosphates and silica ensured their accurate determination. Ammonia is used extensively as a raw material or by product in a nearby fertilizer plant. Ammonia, determination in water is also very important because it can induce corrosion of pipes and other metal structures. Hydrated iron is known to dissociate with the loss of an H^+ (proton) which increases acidity and also induces corrosion. Delay time, sandwich of samples and reagents, length of holding coil tubings, heating holding coil in a thermostated water bath, has been used to improve the sensitivity of the adapted SIA methods.

2. Experimental

2.1 Reagents and discussion

The reagents and solution for the adapted SIA methods were prepared using analar grade chemicals according to the method procedure. Distilled water used was double distilled and deionised.Silica determination was carried out using plastic wares.

2.1.1 Preparation of reagents for ammonia determination

The procedure was adapted from the FIAlab method for the determination of ammonia.
Reagent r1:Sample carrier stream Hypochloride was prepared by pippeting 10 ml of 5.25% sodium hypochloride solution into a one Liter volumetric flask (common household bleach),4.8 g of sodium hydroxide pellets was weighed, dissolved in the same volumetric flask and made up to mark with distilled water.
Reagent r2:75g of sodium salicylate, 0.4 g sodium nitroferricyanide (III) dihydrate, 4.8 g of sodium hydroxide pellets, 0.4 ml Brij 35 surfactant were all weighed and dissolved in one liter volumetric flask.
Carrier:distilled deionised water

2.1.2 Preparation of reagents for the determination of phosphate

This procedure was adapted from FIAlab method.
Reagent r1: 8 g of ammonium molybdate tetra-hydrate,0.2 g antimony potassium tartrate half hydrate were dissolved in a one liter volumetric flask.

Reagent r2: 2 ml of acetone and 60 g ascorbic acid were dissolved in a one liter volumetric flask.
Carrier: Reagent r2

2.1.3 Preparation of reagents for the determination of silica

All reagents were prepared in plastic wares.
Reagent r1
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.
Hydrochloric acid (6M), 1+1: 25 ml of concentrated hydrochloric acid was taken and diluted to 50 ml in a standard flask. 100 ml of ammonium molybdate solution was mixed with 50 ml of 1+1 HCl solution.
Reagent r2:Triammonium citrate reagent: 10 g of triammonium citrate was dissolved in distilled water and diluted to 100 ml in a standard flask.
Reagent r3
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 mark in a volumetric flask, filtered and stored in air tight polyethylene container.

2.1.4 Preparation of reagents for the determination of iron

Reagent r1
10% solution of Hydroxylamine Hydrochloride was prepared by dissolving 10g in 100ml distilled deionised water.
Reagent r2
The chromogenic reagent was prepared by dissolving 0.5g of 1,10 Phenanthroline in 100ml of 0.05M HCl in a 100ml standard volumetric flask, 1M sodium acetate is prepared and then mixed with 1,10 phenanthroline in the ratio of 4:1 by volume;this is to ensure that the pH of the iron II/phenanthroline stacked zones in the holding coil was maintained at 3.5 to 4.5 in order to ensure rapid color development.
Carrier was prepared from 0.1M sodium acetate/ 0.1M acetic acid solution.
Stock solution of iron (III) were prepared by dissolving 0.702g of ferrous ammonium Sulphate hexahydrate $(Fe(NH_4)_2(SO_4)_2).6H_2O$ with 0.05M HCl solution in a 1000ml standard flask.

2.2 Apparatus

The manifold used for these methods (Fig.1) 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 *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).

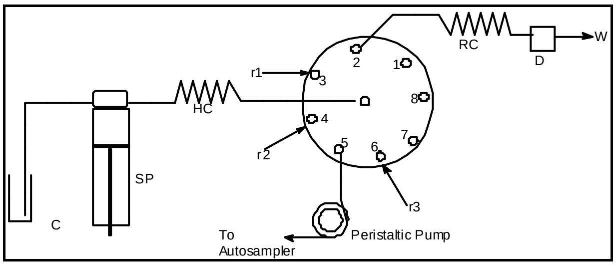

Fig. 1 SIA manifold: C = Carrier, SP = syringe pump, HC = holding coil, r1, r2, r3 = reagents, RC = reaction coil, D = spectrophotometer, W= waste

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-2µm) wavelength range. The detector is *USB2000 Spectrometer* (Ocean Optics, USA) adapted to 200-1100nm wavelength range.

2.1. Software Packages

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

3.0 Results and Discussion

3.1. Determination of silica

The method is based on the reaction of ammonium molybdate with silica to form an intensely yellow complex (ammonium molybdosilicates), triammonium citrate was used to destroy phosphate interference and the final product is reduced to blue complex monitored spectrophotometrically at 813 nm. The analysis was carried out with the aid of a computer flow program.The following volumes of samples and reagent were aspirated into the holding coil:100 µL sample, 40 µL ammonium molybdate/ HCl delayed for 60 s, 40 µL of triammonium citrate delayed for 30 s, 40 µL sulphite/1-amino-2-naphthol-4-acid solution delayed for 60 s and another 100 µL of sample aspirated and delayed finally for 120s. With a flow rate adjusted at 10 µl s^{-1}, a 2000 µl 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; the maximum value of the monitored peak was recorded as absorbance. Absorbance versus time run obtained is shown in Fig. 2.

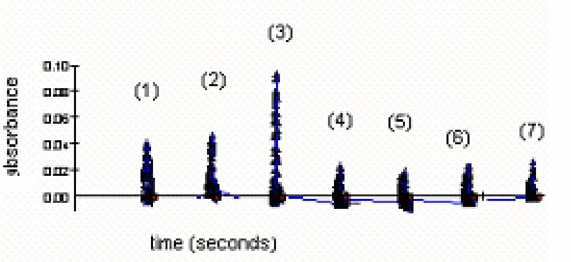

Fig. 2 Absorbance versus run time for silica determination with (1) 2 ppm (2) 5 ppm (3) 10 ppm standards, (4) (5) and (6) (7) were obtained from water samples. Results are in duplicates

The linear working range is 0.5 ppm to 50 ppm, the correlation coefficient obtained is 0.999. The detection limit is 0.5 ppm with a sample through put of 10 samples/hour. The equation for absorbance measurement was A = 0.220 + 0.009x. 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 calculated t-value (Table 1) was 0.1799 which is less than 2.776 (95% confidence level). The sensitivity can further be enhanced by heating the holding coil at 60°C in a thermostated waterbath. The method described has good reproducibility, rapid and suitable for online and in situ determination of silica.

Table 1: Comparison of results obtained with SIA method and batch spectrophotometric method (APHA) for the determination of silica in water

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		

3.2 Determination of phosphate

The first step of the reaction protocol involves the formation of molybdophosphate which is reduced by ascorbic acid catalyzed by antimony (Sb) to form a blue complex. This method was adapted from the FIALab flow injection method for the determination of phosphate. A computer flow program was used for carrying out the analysis. 100 µL of sample, 100 µL of reagent r1, 120 µL of reagent r2 and 10 µL of distilled water were aspirated into the holding coil, delayed for 100 s and then propelled by flow reversal to the reaction coil. The coloured complex formed in the holding coil was dispensed to the detector with a flow rate of 10 µL/s. An additional flow reversal (10 µL of distilled water) was incorporated into the flow program to increase the flow reversals and hence maximize zone penetration in the holding coil. A peristaltic pump was used to propel sample from auto sampler into the sample tubing. A reference spectrophotometer scan time of 3 seconds was incorporated into the Program to zero the baseline. Analysis was done in duplicates. The correlation coefficient obtained using water as carrier was 0.955, this was greatly improved to 0.999 on using ascorbic acid (r2) as carrier. Suggesting improved sensitivity of the method with use of ascorbic acid as the carrier. Absorbance versus time run for phosphate is shown in Fig, 3. Indicating excellent linearity for 2, 7 and 20 ppm with the following calibration equation: $A = 0.052 + 0.0085x$; $r = 0.999$ with a sample throughput of 12 samples per hour.

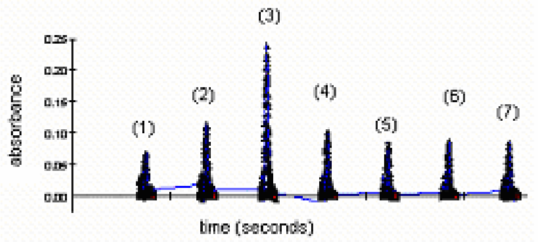

Fig. 3 Absorbance versus run time for phosphate determination with (1) 2 ppm (2) 7 ppm (3) 20 ppm standards,(4) (5) and (6) (7) were obtained from water samples, results are in duplicates.

The calculated t-test value (Table 2) was 0.465 which is less than 2.131 (95% confidence level), indicating agreement with ammonium metavanadate batch spectrophotometric (APHA) method (420 nm).Below is table 2 where comparison was made between APHA method and SIA method for the determination of phosphate.

Table 2: Comparison of results obtained with SIA method and batch spectrophotometric method (APHA) for the determination of phosphates in water.

Sample code	Concentration (ppm) Determined by SIA method	Concentration (ppm) Determined by APHA method
BW1	9.181 ± 0.484	11.604 ± 0.419
BW2	5.739 ± 0.185	5.453 ± 0.146
BW3	3.106 ± 1.007	2.363± 0.136
BW4	6.078 ± 0.434	7.461 ± 0.064
BW12	6.277 ± 0.126	7.190 ± 0.153
BW13	6.198 ± 0.002	4.291 ± 0.029
BW12T	21.730 ± 0.011	21.557 ± 0.104
BW13T	9.860 ± 0.059	10.048 ± 0.362
*Average of two determinations BW stand for boiler water		

3.3 Determination of total iron in water

This method involves the filtration of sample with Whatman filter paper (no 42) to eliminate interference from solids particles present in water samples which can block the tubing and damage the instrument. This was followed by reduction of iron (III) to iron (II) with hydroxylamine hydrochloride. The iron (II) solution is reacted with 1, 10 phenanthroline and the red complex formed determined spectrophotometrically at 510 nm. A computer flow program was used for carrying out the analysis procedure, the following reagents and sample volume were aspirated into the holding coil, 100 µL of sample, 20 µL of hydroxylamine hydrochloride solution delayed for 10 s, 100 µL 1,10 phenanthroline solution delayed for 60 s and finally another 100 µL of sample aspirated and delayed for a total time of 240 s.The iron complex formed in holding coil was dispensed to the detector at a flow rate of 10 µL/s. Although the reaction for the complexation of iron(II) is slow (Fig. 4), nevertheless the precision of determination was very high due to the fact that SIA measurements are always taken at a fixed time.

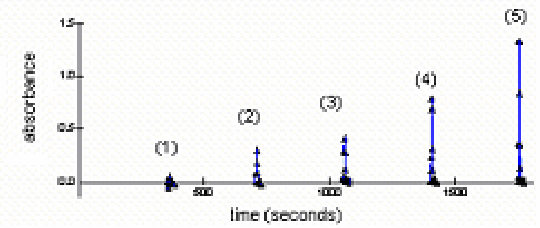

Fig.4 Absorbance versus run time for iron standards with concentration of (1) 0.5 ppm (2) 5 ppm (3)10 ppm (4)30 ppm (5) 50 ppm.

This gives an accuracy that would not be attained with ordinary conventional methods thus rendering the present SIA method much more precise and accurate. The sensitivity of iron determination was greatly enhanced by delay of sample reagents in holding coil and use of 0.1M sodium acetate/ 0.1M acetic acid solution as carrier to ensure that the pH of the iron II/phenanthroline stacked zones in the holding coil was maintained at 3.5 to 4.5 to ensure rapid color development. The sampling frequency is 10 samples/hour; the linear range is 0.5

ppm to 50 ppm, with a detection limit of 0.4ppm. The correlation coefficient of calibration curve obtained for the adapted SIA method for determination of iron was 0.9949. The linear equation obtained for the calibration was A = 0.128 + 0.024x.

3.4 Determination of Ammonia in water

This method involves reaction of hypochlorite with ammonium ion in water to give the monochloroamine which reacts with salicylate to give a blue colored complex (indophenol) which is monitored spectrophotometrically at 770 nm. Absorbance versus time run for ammonia is shown in Fig. 5 indicating excellent linearity for 0.5, 10, 20 and 30 ppm with the following calibration equation: A = 0.0303 + 0.0336x with r = 0.9998.

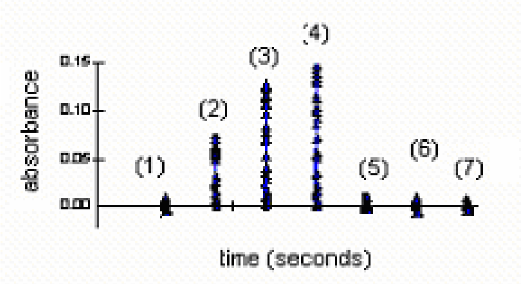

Fig 5 Absorbance versus run time for ammonia determination with (1) 0.5 ppm (2)10 ppm (3) 20 ppm (4)30 ppm standards, (5) (6) (7) were obtained from water samples (triplicates).

4.0 Conclusion

The adapted SIA methods are simple, sensitive, accurate, cost saving, reproducible time saving and avoid the need for dilution of high concentration of samples. The sensitivity and linear range of the adapted methods have been greatly enhanced by delay time, placing holding coil in a thermostated water bath for silica and ammonia determination and use of reagent as carrier for phosphate determination. The methods were all in agreement with standard methods by APHA.

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